

⁴¹Ca measurements on the 1 MV AMS facility at the Centro Nacional de Aceleradores (CNA, Spain)



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ABSTRACT

We present a detailed study of the performance parameters for ⁴¹Ca measurements at the 1 MV AMS system at the Centro Nacional de Aceleradores (CNA) in Seville.

Mixing CaF₂ with Ag, we get stable (⁴⁰CaF₃)⁻ currents between 50 and 100 nA. Transmission of the 2+ state in the He stripper is 41%, while optical transmission in the HE sector is typically higher than 95%. At low energies we cannot separate ⁴¹Ca from the isobar ⁴¹K at the detector, but the interference is reduced by using (⁴¹CaF₃)⁻ ions. The remaining contribution is corrected by measurement of the other stable isotope of potassium, ³⁹K, to estimate this interference (K-correction). After this correction, we reach a ⁴¹Ca/⁴⁰Ca background level between 5×10^{-12} and 8×10^{-12} , making possible measurements of ⁴¹Ca/⁴⁰Ca ratios higher than 4×10^{-11} .

Intercomparisons with the 0.6 MV AMS system at ETH Zurich show a quite good correlation.

1. Introduction

The main interest of ⁴¹Ca accelerator mass spectrometry (AMS) measurements comes from its use as a tracer of the calcium metabolism [1–3]. The most recent value of its half-life, $(9.94 \pm 0.15) \times 10^4$ years [4], makes ⁴¹Ca a perfect candidate for this. A much lower radioactive dose is received (below natural background) and it allows larger tracing time in comparison to the short-lived isotopes ⁴⁵Ca and ⁴⁷Ca, and it has a negligible natural abundance in comparison with stable isotopes of calcium.

The main interference in ⁴¹Ca measurements is its stable isobar, ⁴¹K (with a natural isotopic abundance of 6.73%). In the past, CaH₂ and extraction of (CaH₃)⁻ were used to reduce the presence of ⁴¹K in the beam. Since (KH₃)⁻ ion is not stable, the only ⁴¹K contribution would come from the extraction of (⁴¹K¹H²H)⁻. The ⁴¹K/⁴⁰Ca interference is on the order of 10^{-13} [5], leading to a final ⁴¹Ca/⁴⁰Ca background $< 10^{-15}$ thanks to the discrimination in the detector. However, the chemical preparation of CaH₂ and its handling are problematic, because of its hygroscopic character, making it not suitable for large-scale applications.

In contrast, CaF₂ sample material can be easily prepared followed by an extraction of (CaF₃)⁻, but the ⁴¹K/⁴⁰Ca interference is increased to 10^{-12} – 10^{-11} , and currents are lower [6]. For biomedical applications of ⁴¹Ca, which do not require very low background, and usually a large number of samples have to be handled, the use of CaF₂ instead of CaH₂ means a great advantage. Because of that, simple ⁴¹Ca radiochemical procedures for CaF₂ production were established for biological samples [7–9].

At larger accelerator AMS facilities (terminal voltage ≥ 5 MV) this ⁴¹K interference can be discriminated on different ways. For instance, at these energies, ⁴¹Ca and ⁴¹K signals in a multinode ionization chambers can be distinguished, and final ⁴¹Ca/⁴⁰Ca background levels in the order of 10^{-15} can be achieved [10]. Even in 3 MV systems, the use of silicon nitride detector windows is enough to provide a very good identification of both isobars, reaching ⁴¹Ca/⁴⁰Ca background levels on the order of 10^{-14} [11].

Since biomedical studies can be designed so that ⁴¹Ca/⁴⁰Ca ratios are higher than 10^{-10} , compact AMS facilities (terminal voltages ≤ 1 MV) are able to make this kind of ⁴¹Ca measurements without

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relatively large background, even when no ^{41}K - ^{41}Ca separation on the detector signal can be reached [12]. The trace amount of potassium may differ from one sample to another, and may depend on the chemical preparation, so treating $^{41}\text{K}/^{40}\text{Ca}$ contribution as part of the background would be incorrect. However, since ^{41}K and ^{39}K are both natural isotopes of potassium, measuring $^{39}\text{K}/^{40}\text{Ca}$ together with $^{41}\text{Ca}/^{40}\text{Ca}$ let us correct the interference due to ^{41}K [13]. The $^{41}\text{K}/^{39}\text{K}$ measured ratio is not exactly the natural one because of the slightly different transmissions in the stripper and the high energy (HE) sector depending on the mass. This experimental ratio can be easily measured in blanks, and then applied sequentially during the data analysis (K-correction).

The first compact AMS system reported to measure ^{41}Ca had been the 0.6 MV AMS system at ETH Zurich [12,13]. Most of the systems used to measure ^{41}Ca use terminal voltages ≥ 3 MV, and there is no robust published information of the performance for systems operating with voltages between 0.6 MV and 3 MV. The possibility of 1 MV AMS systems for ^{41}Ca has been discussed in previous bibliography [14,15], but no studies of their optimal conditions have been published. Moreover, all these studies were performed using argon as stripper gas. Helium has been proved to provide much higher transmissions for ^{41}Ca , among others, at low energies [16], and no studies about the performance of He stripping at 1 MV had been performed. In order to be able to optimize this kind of systems for routine measurements of ^{41}Ca , a detailed characterization is needed. In addition, the K-correction has to be implemented to get reliable results.

During the last years, we have optimized the performance parameters of the 1 MV compact AMS system at the CNA for ^{41}Ca . In the first section of this paper we present the main results of the optimization experiments for important performance parameters: ion source output, He stripper transmission, detector signal identification, background level and HE sector transmission. In the second section, we present the results of an intercomparison with the 0.6 MV AMS system at ETH Zurich. In order to do that, we measured two different standards from the ETH in-house set [17], and 40 biomedical samples previously measured at the 0.6 MV AMS system.

2. Performance of the 1 MV AMS system at CNA for ^{41}Ca

2.1. Experimental system and measurement technique

A detailed description of the 1 MV AMS system SARA (Spanish Accelerator for Radionuclide Analysis) can be found in previous publications [18,19]. However, in the last years, several changes have been made in the system. The most important are the upgrade to the new SO-110B ion source [20], the change of the stripping gas from Ar to He, and the substitution of the original detector with a miniaturized gas ionization chamber provided by the ETH Laboratory of Ion Beam Physics [21].

In Fig. 1, a schematic view of the setup for ^{41}Ca is shown. In the ion source, negative ions are produced by Cs sputtering with an energy of 35 keV. After focusing with an Einzel lens, the molecular ions ($^{40}\text{Ca}^{19}\text{F}_3^-$), ($^{41}\text{M}^{19}\text{F}_3^-$), and ($^{39}\text{K}^{19}\text{F}_3^-$), are selected sequentially with an 90° bouncer magnet and injected into the tandem accelerator (^{41}M denotes ions of mass 41, i.e. ^{41}Ca and ^{41}K). The presence of an electrostatic lens (Q-Snout) in front of the low-energy acceleration tube allows focusing the beam in the stripper channel tube independently of the extraction energy from the ion source.

The quadrupole triplet (Q-pole) after the high-energy acceleration tube allows focusing the beam in the same point in the high energy sector independently of the charge state. This additional focusing from the Q-pole is more important for ^{41}Ca measurements than for other radionuclides. The focusing of the high energy acceleration tube depends on the effective charge state $\frac{M_0}{M}q$, where M_0 is the mass of the negative molecular ion selected in the LE side and M the mass of the positive ion selected in the HE side [22,23]. Therefore, the optics of the

$^{41}\text{Ca}^{2+}$ beam would be equivalent to that of charge state 5+ because of the high mass difference with the initial negative ion, with a mass of 98 u. In contrast, compact AMS systems (such as the 0.6 MV AMS system TANDY at ETH Zurich) are usually designed for charge states 1+, 2+ and 3+.

The 90° analyzing magnet and the 120° electrostatic deflector (ESA) perform the selection of charge state, mass and energy; this system is designed to provide an achromatic transport to the beam. ^{41}Ca and ^{39}K are finally measured with the two anode gas ionization chamber, using isobutane as counting gas.

The sequential injection of ^{39}K and ^{41}M in the detector is done by using different voltages at the accelerator terminal and the electrostatic deflector, as it is done in plutonium measurements [24]. ^{40}Ca is measured in the movable Faraday cup (FC-3) with the same terminal voltage as the one used to inject ^{39}K (around 970 kV).

2.2. Extraction of $(\text{CaF}_3)^-$ from CaF_2 with the SO-110B ion source

First tests of ^{41}Ca with the 1 MV system were done mixing the CaF_2 material with Nb powder in a CaF_2 :Nb mass ratio of 1:3. Typical currents of $(^{40}\text{CaF}_3)^-$ were lower than 50 nA. In order to improve this, a test was performed with different blank targets, mixing CaF_2 with Nb or Ag and in 4 different mass ratios: 1:1, 1:2, 1:4 and 1:9.

Results, which are presented in Fig. 2, show a high increase of the current when Ag is used instead of Nb, and it also appears to be more stable. Optimal behavior is reached when the CaF_2 :Ag mass ratio is 1:4, with stable $(^{40}\text{CaF}_3)^-$ currents higher than 75 nA. This mass ratio is the one closer to the density relationship between Ag and CaF_2 , which is 3.3, meaning similar volumes of fluoride and silver. If we suppose that ionization efficiency is linearly dependent on the silver amount, this configuration with the same volume of CaF_2 and Ag would be that one with the highest total ion extraction yield.

2.3. He stripper performance for calcium at 1 MV

Preliminary tests of calcium measurements with the 1 MV AMS system were performed before the stripper gas was changed to He. In those tests with Ar, transmission for $^{40}\text{Ca}^{3+}$ was only 6% [20]. After changing the stripper gas to He, transmission for $^{40}\text{Ca}^{3+}$ increased to 28%.

However, using charge state 3+ would not allow us to measure ^{39}K because of the m/q interference of $^{13}\text{C}^+$. Since transmission for 4+ state is too low at the available energies, state 2+ has to be used, so special care with possible molecular interferences has to be taken. Transmission of $^{40}\text{Ca}^{2+}$ at 972 kV terminal voltage (stripping energy of 415 keV) for different He gas pressures is presented in Fig. 3. Measurement was performed with a blank sample. Since pressure is only measured at the center of the stripper channel, we use a simple calculation to estimate He mass thickness ρ_A : assuming a triangular distribution of the gas pressure in the stripper channel, we use the half of the average measured pressure and a temperature of 294.14 K to calculate the stripper gas density. This approximation is not trustworthy at low pressures, so only data with mass thicknesses above $0.015 \mu\text{g}\cdot\text{cm}^{-2}$ is used to get the fitting curve.

In order to get the charge state fraction, we have applied the fitting found in Ref. [25]. This fitting gets the parameters Φ_{2+} , σ_p and σ_m for a transmission curve $T(\rho_A) = \Phi_{2+} [1 - \exp(-\sigma_p \rho_A)] (1 - \sigma_m \rho_A)$. The factor $[1 - \exp(-\sigma_p \rho_A)]$ represents the production of Ca^{2+} ions; $(1 - \sigma_m \rho_A)$, the losses because of scattering. $\Phi_{2+} = 53\%$ is the 2+ charge state fraction for a stripping energy of 415 keV, very close to the one for 223 keV, which is a 60% [16].

Fig. 3 also shows the dependence between $^{41}\text{M}/^{40}\text{Ca}$ ratio and He mass thickness in a blank sample. Exponential fitting lets us estimate the molecular destruction cross section as $255 \text{cm}^2 \cdot \mu\text{g}^{-1}$. A maximum transmission of 45% is found for stripper pressures around 0.015 mbar, meaning a mass thickness of $0.03\text{--}0.04 \mu\text{g}\cdot\text{cm}^{-2}$; nevertheless, since

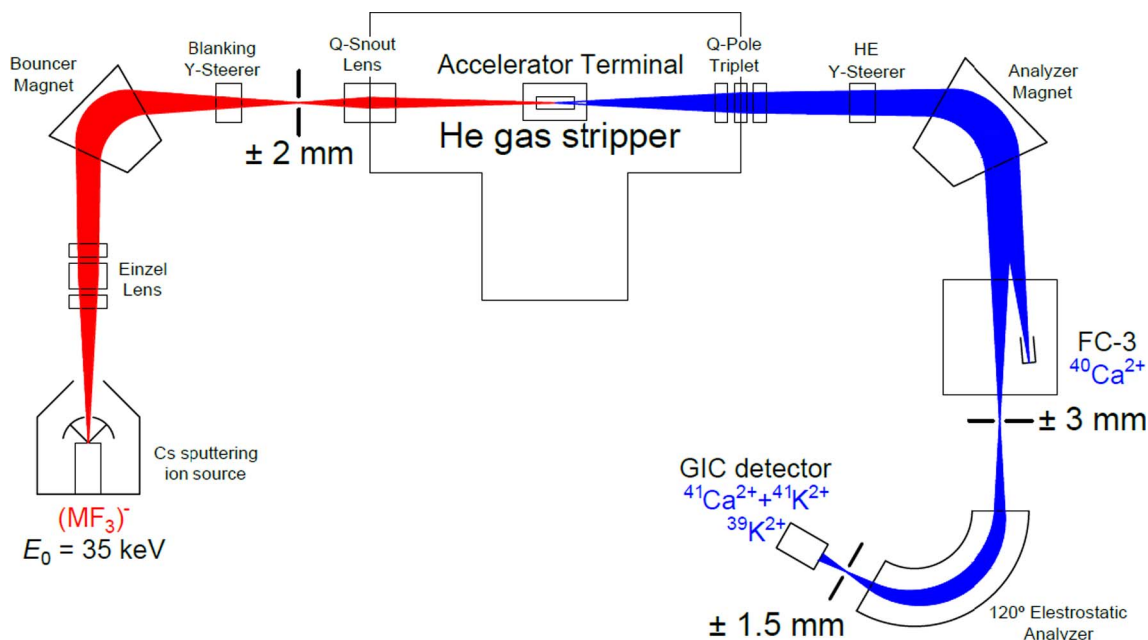


Fig. 1. Schematic view of the experimental setup for ^{41}Ca measurements on the 1 MV AMS system. M refers to both, K and Ca.

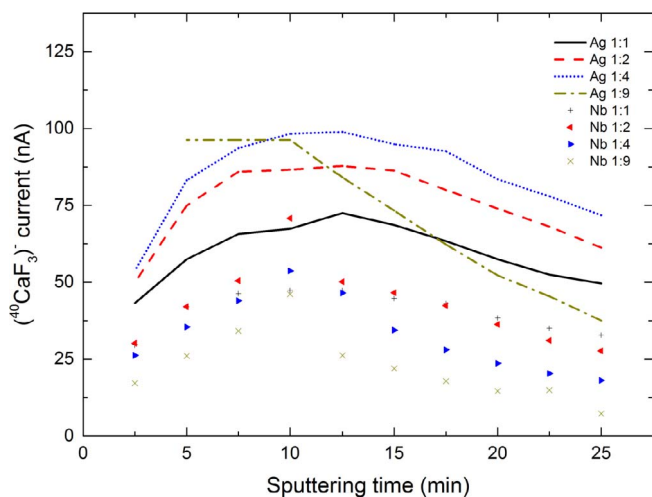


Fig. 2. $(\text{CaF}_3)^-$ current from different blanks with different mixes of CaF_2 with Ag or Nb.

molecular background at that pressure is still important, a higher stripper pressure is needed to ensure the molecular $^{41}\text{M}/^{40}\text{Ca}$ background destruction. A He pressure of 0.03 mbar (around $0.075 \mu\text{g}\cdot\text{cm}^{-2}$) is used during measurements to destroy these molecules. Transmission is 41% at this pressure, which means that 22% of the total Ca^{2+} ions produced are lost.

2.4. $^{41}\text{M}^{2+}$ and $^{39}\text{K}^{2+}$ detection with the compact ΔE -E GIC

Because of the same mass-charge ratio, $^{82}\text{Se}^{4+}$ ions reach the detector together with $^{41}\text{M}^{2+}$ ions, and $^{78}\text{Se}^{4+}$ with $^{39}\text{K}^{2+}$. These ions are injected into the accelerator as $(^{82}\text{Se}^{16}\text{O})^-$ and $(^{78}\text{Se}^{18}\text{O})^-$, respectively. Gas pressures necessary to stop $^{41}\text{Ca}^{2+}$ ions are not enough to stop $^{82}\text{Se}^{4+}$ ions, with twice the energy of that one of $^{41}\text{Ca}^{2+}$, not losing its total energy. Because of that, the 2 dimensional spectrum, which can be seen in the left part of Fig. 4, does not show the $^{82}\text{Se}^{4+}$ peak with defined energy, because of the different energies lost depending on the trajectory of the ion inside the detector. Using a pressure enough to stop

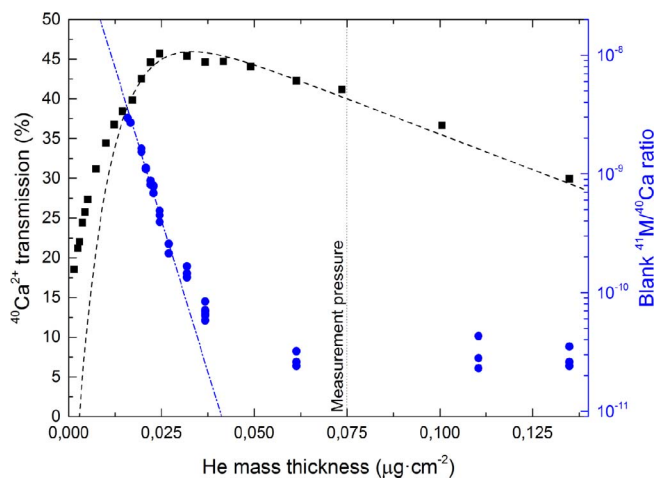


Fig. 3. Ca^{2+} transmission from a blank sample in the He stripper for a terminal voltage of 972 kV (black squares) and $^{41}\text{M}/^{40}\text{Ca}$ background dependence with the stripper pressure (blue circles). This fit only involves mass thicknesses above $0.015 \mu\text{g}\cdot\text{cm}^{-2}$. The exponential fitting of the $^{41}\text{M}/^{40}\text{Ca}$ background only involves mass thicknesses below $0.027 \mu\text{g}\cdot\text{cm}^{-2}$ in order to estimate the molecular destruction cross section.

$^{82}\text{Se}^{4+}$ ions in the second anode would not let $^{41}\text{Ca}^{2+}$ ions reach this second anode.

Since ^{41}K and ^{41}Ca signals cannot be distinguished, there is no advantage in using both anodes. Because of this, during measurements gas pressure is set to stop both ions in the first anode, taking only the signal of the first anode. In this 1-dimensional spectrum, shown in the right part of Fig. 4, $^{82}\text{Se}^{4+}$ peak has a well-defined energy of twice the energy of $^{41}\text{Ca}^{2+}$, as expected.

Fig. 5 shows the linear regression of the $^{41}\text{M}/^{40}\text{Ca}$ and $^{39}\text{K}/^{40}\text{Ca}$ ratios for blank samples in one of our measurements. The slope $^{41}\text{K}/^{39}\text{K}$ of the linear regression differs from one measurement to another because of the little changes on the tuning of the system. However, the linear regression is always robust, with R^2 values around 0.9, and those slopes are always close to the natural $^{41}\text{K}/^{39}\text{K} = 0.0721$. For this linear regression, different runs from the same sample are taken separately, showing a strong variability with time of both, $^{41}\text{M}/^{40}\text{Ca}$ and $^{39}\text{K}/^{40}\text{Ca}$ ratios.

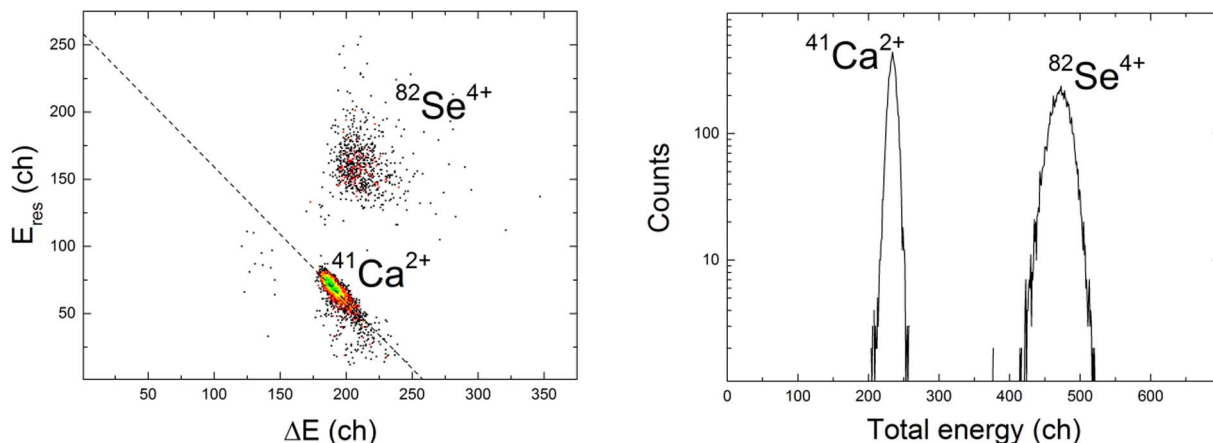


Fig. 4. GIC spectra from a standard sample ($^{41}\text{Ca}/^{40}\text{Ca} \approx 10^{-8}$). Left picture shows the 2-dimensional spectrum when $^{41}\text{Ca}^{2+}$ ions are stopped in the second anode; right one, the one-dimensional spectrum when both ions, $^{41}\text{Ca}^{2+}$ and $^{82}\text{Se}^{4+}$, are stopped in the first anode.

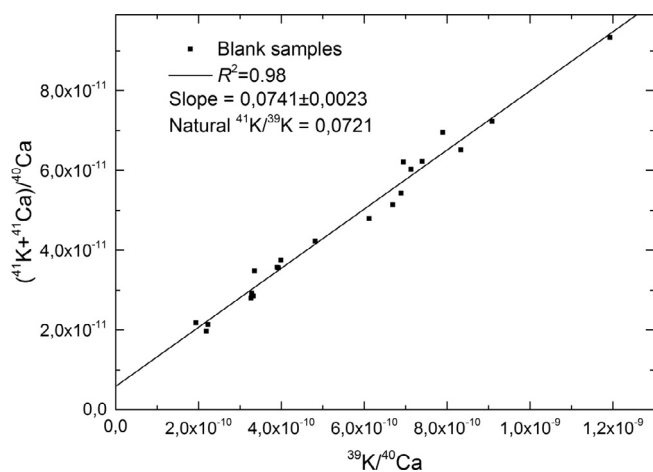


Fig. 5. Linear correlation between measured $^{39}\text{K}/^{40}\text{Ca}$ and $^{41}\text{M}/^{40}\text{Ca}$ in 7 different blank samples at the 1 MV AMS system. Due to the time evolution of the potassium rates, different runs of the same sample are also represented separately.

2.5. Background levels

A first estimation of the $^{41}\text{Ca}/^{40}\text{Ca}$ background is given by the Y-intercept of the linear regression done to get the measured $^{41}\text{K}/^{39}\text{K}$ ratio for the K-correction. We have done tests with two different blank materials: commercial calcium fluoride washed with Milli-Q water, and commercial calcium carbonate washed before adding HF to form calcium fluoride.

It can be seen in Fig. 5 that this background is on the order of 10^{-12} . The background value finally applied for blank correction is calculated as the average of the $^{41}\text{Ca}/^{40}\text{Ca}$ ratios, after the K-correction, of the different blank samples. Typical values of the $^{41}\text{Ca}/^{40}\text{Ca}$ background in measurements with the 1 MV AMS system are between 5×10^{-12} and 8×10^{-12} . This value is similar to the one typically obtained with the 0.6 MV system at ETH [13]. No difference in this background level has been observed when using different original materials.

2.6. ERM-AE701 standards

For ^{41}Ca measurements, we use the AE701 standards from the Institute for Reference Materials and Measurements (IRMM) of the European Commission's Joint Research Centre [26]. Most measurements involve samples with $^{41}\text{Ca}/^{40}\text{Ca}$ ratios between 10^{-10} and 10^{-8} , so we use three from the 8 different standards: AE701/3, AE701/4 and AE701/5, with approximate nominal $^{41}\text{Ca}/^{40}\text{Ca}$ ratios, respectively, of

Table 1
Blank corrected $^{41}\text{Ca}/^{40}\text{Ca}$ ratios from ERM-AE701.

Standard	$^{41}\text{Ca}/^{40}\text{Ca}$ nominal ratio	$^{41}\text{Ca}/^{40}\text{Ca}$ measured ratio	Experimental/nominal relation (%)
AE701/3	1.0181×10^{-8}	$(0.988 \pm 0.019) \times 10^{-8}$	97.0
AE701/4	1.0479×10^{-9}	$(1.029 \pm 0.049) \times 10^{-9}$	98.2
AE701/5	1.0520×10^{-10}	$(1.000 \pm 0.013) \times 10^{-10}$	95.1

10^{-8} , 10^{-9} and 10^{-10} .

Table 1 shows the average blank corrected $^{41}\text{Ca}/^{40}\text{Ca}$ ratios, of 2 cathodes from each of these 3 standards used during one of our measurements after K-correction and background correction. The experimental/nominal relation changes a little from one measurement to another, but it is typically higher than 90% (correction factor < 1.1). Even when standards are measured in a decreasing order in $^{41}\text{Ca}/^{40}\text{Ca}$ ratio, no higher experimental/nominal relation is observed in lower $^{41}\text{Ca}/^{40}\text{Ca}$ ratio standards, meaning not important cross contamination in the ion source not considered by the blank correction.

3. Intercomparison measurements with ETH Zürich 0.6 MV system

3.1. Measurement of ETH ^{41}Ca in-house standards

Looking for tests of reliability of our measurements, we measured 2 different standards from the in-house set from the ETH Laboratory of Ion Beam Physics [13,17]. These are the B10 and B8 standards, with nominal $^{41}\text{Ca}/^{40}\text{Ca}$ ratios of 4.200×10^{-10} and 4.000×10^{-8} , respectively.

From each of the standards, we pressed 3 cathodes. The $\text{CaF}_2:\text{Ag}$ mass ratio was 1:10, so it was not the optimal one for measurements at the 1 MV system system (see Section 2.2). Results are shown in Table 2, although one of the B10 cathodes is not shown since it didn't pass the discard criterions used during data analysis: that $^{40}\text{Ca}^{2+}$ current must

Table 2
 $^{41}\text{Ca}/^{40}\text{Ca}$ ratios from ETH standards measured at the 1 MV system (SARA).

ETH standard	$^{41}\text{Ca}/^{40}\text{Ca}$ nominal ratio	Sample	$^{41}\text{Ca}/^{40}\text{Ca}$ ratio at SARA
B10	$(4.200 \pm 0.042) \times 10^{-10}$	ETH-B10a	$(4.20 \pm 0.33) \times 10^{-10}$
		ETH-B10c	$(4.43 \pm 0.23) \times 10^{-10}$
		ETH-B8a	$(4.06 \pm 0.18) \times 10^{-8}$
B8	$(4.000 \pm 0.040) \times 10^{-8}$	ETH-B8b	$(4.06 \pm 0.18) \times 10^{-8}$
		ETH-B8c	$(4.17 \pm 0.20) \times 10^{-8}$

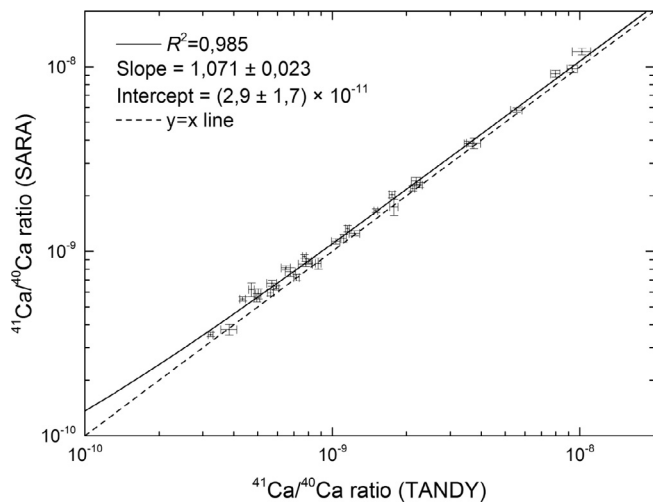


Fig. 6. Final $^{41}\text{Ca}/^{40}\text{Ca}$ ratio measurements of biomedical samples with the 0.6 MV system at ETH Zurich (TANDY) and the 1 MV system at CNA Seville (SARA).

be higher than 20 nA and $^{39}\text{K}/^{40}\text{Ca}$ lower than 1.25×10^{-9} . Our measurements does not differ from nominal values more than a 5.5%, but seem to be systematically higher.

3.2. Measurement of biomedical samples

In order to study the performance of the ^{41}Ca measurements at the 1 MV system with samples for biomedical studies, we measured a total of 40 samples from 7 different subjects which were previously measured in the 0.6 MV AMS system TANDY at ETH Zurich. These samples are part of the measurements carried out by the ETH Laboratory of Ion Beam Physics in Zurich for the NutriTrace group at the National University of Singapore. Sample preparation is based on previous published methods [7,27]. The first calcium separation was done by oxalate precipitation, while final CaF_2 precipitation was performed by adding HF. At ETH Zurich, samples were mixed with silver in a weight ratio of 1:9; at CNA Seville, in a weight ratio of 1:4.

6 of the 40 samples did not pass one of the discard criterions for any of the different runs of the measurement: runs with $^{39}\text{K}/^{40}\text{Ca}$ ratios higher than 1.25×10^{-9} are discarded to ensure that $^{41}\text{K}/^{40}\text{Ca}$ interference is not higher than 10^{-10} . The $^{41}\text{Ca}/^{40}\text{Ca}$ ratios measured with TANDY and SARA for other 34 samples are presented in Fig. 6. The agreement between the two measurements is quite good, even though $^{41}\text{Ca}/^{40}\text{Ca}$ ratios in the 1 MV system are higher by a 7%, while uncertainties for both systems are around 4%. Since the difference is independent of the $^{41}\text{Ca}/^{40}\text{Ca}$ ratio, it might originate from the different standards used in both labs. In any case, this small difference is consistent with the difference observed in the measurement in the Section 3.1, and the time evolution for each subject is conserved, which is the most important factor in biomedical studies [12,28].

4. Conclusions and prospects

An optimized set-up of the 1 MV AMS system at CNA for ^{41}Ca measurements has been established. Our system has good capabilities for measurements in the $^{41}\text{Ca}/^{40}\text{Ca}$ range of 10^{-10} – 10^{-8} and possibilities of measuring $^{41}\text{Ca}/^{40}\text{Ca}$ ratios down to 4×10^{-11} , but with higher uncertainties.

Since the $^{40}\text{Ca}^{2+}$ transmission in the He stripper of the 1 MV system at CNA is a little lower than that one in the 0.6 MV system at ETH, but optical transmission in the HE sector is higher, overall transmission is almost the same for both systems: $\sim 40\%$. $^{41}\text{Ca}/^{40}\text{Ca}$ background level is close to 5×10^{-12} thanks to the measurement of ^{39}K to estimate the ^{41}K interference. Mixing calcium fluoride with Ag in a weight ratio of

1:4 instead of using Nb improves importantly ion source output. Optical transmission through the HE sector is typically higher than 95% thanks to the quadrupole triplet at the exit of the accelerator.

Intercomparisons with the 0.6 MV system at ETH show that $^{41}\text{Ca}/^{40}\text{Ca}$ ratios measured in our system are reliable. Our measurements of the ETH in-house standards do not differ from the nominal values even when the relative content of silver is much higher than the optimal one at the 1 MV system. The intercomparison with biomedical samples proves the capability of perform those kind of measurements at the 1 MV system, unless there is a slight difference of a 7% between these measurements and those at ETH.

The 1 MV system at CNA is already being used to perform ^{41}Ca measurements on concrete samples from the primary shield of decommissioning nuclear power plants.

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