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Hands on mass spectrometry: ICP-MS analysis of enriched ^{82}Se samples for the LUCIFER experiment

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In the Gran Sasso Summer Institute 2014 Hands-On Experimental Underground Physics at LNGS I tried myself as an operator of an ICP-MS instrument. Two spectrometers were calibrated and used for an assay of contamination (by the elements which are important for the crystal growth and scintillation properties of the detectors) and isotopic composition of the LUCIFER ^{82}Se samples. Obtained results are consistent with expectations based on previous studies.

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1. Introduction

LUCIFER is an upcoming experiment for the search of neutrinoless double beta decay ($0\nu\beta\beta$) of ^{82}Se with the help of ZnSe scintillating bolometers [1]. Operated at extremely low temperatures (≈10 mK) such devices need high purity crystals with a very good crystal perfection and a low level of intrinsic radioactivity. Moreover, in the case of $0\nu\beta\beta$ application the nuclide of interest is required in sufficient amount, i.e. isotope enriched materials should be employed.

The simplified production scheme of crystals for the LUCIFER experiment is as follows: 1) raw Se refinement → 2) SeF_6 synthesis → 3) SeF_6 enrichment → 4) Se conversion → 5) Se beads production → 6) ^{82}Se enrichment → 7) purification → 8) ZnSe synthesis → 9) ZnSe crystal growth → 10) mechanical processing → 11) recovery and recycling → 12) package and shipment. The purity of Zn and Se used for the synthesis of ZnSe and crystal growth is particularly important. Point defects due to impurities may act as traps both for the phonons involved in the development and propagation of bolometric signal and for the free carriers involved in the scintillation process. The purity issue is more difficult in the case of the enriched selenium given the complexity of its production process. Special care is taken in order to reduce the contamination with impurities defined as critical for the scintillation performance of ZnSe crystals (Fe, Cr, V, Ni, As, Cu, Mo, Si, and S).

Two samples of the enriched ^{82}Se material (after step 7 in the production chain) were sent to the LNGS Chemistry Service and Chemical Plant for the ICP-MS analysis of the contamination by the elements which are important for the crystal growth and scintillation properties of the detectors. Besides that the isotopic composition of the enriched samples is to be compared with the natural selenium.

2. Instrumentation

Inductively coupled plasma mass spectrometry (ICP-MS) has a leading place among all the inorganic mass spectrometric techniques [2]. An inductively coupled plasma is a plasma that is ionized by inductively heating the gas with an electromagnetic coil, and contains a sufficient concentration of ions and electrons to make the gas electrically conductive. It has a wide range of application: medical, forensic, environmental research, industrial and biological monitoring, geochemistry etc.

For our purposes we used THERMO ELEMENT2 and Agilent 7500a ICP-MS devices located in a cleanroom (ISO6, class 1000). Sample introduction was done with CETAC ASX-520 AutoSampler. Both instruments used liquid samples, which were prepared in advance by dissolving received solid material (balls ∼2 mm in diameter) in 1 mL of 70% HNO_3 in ultrasonic bath at 70 °C for an hour and then diluting them with ultrapure water up to the values given in Table 1.

The operator prepares the solutions, sets up the necessary sequence in the computer software, starts the program and within several (tens of) minutes the following stages should be automatically passed to get a spectrum: sample introduction (liquid solution uptake with a help of peristaltic pump); vaporization in nebulizer of the sample mixed with argon gas; spray chamber selects droplets of size less than ∼10 microns; atomization and ionization in the plasma torch; ion acceleration and focusing; mass separation in a double focusing alalyzer (combination of magnetic

Sample	Label	Mass, mg	Total dilution
1	Selenium82 Conv. 31	65	1846
2	Selenium82 Conv. 36	99	1818

Table 1: Labels, masses and total dilution of the two studied samples. Both samples were dissolved in 1 mL of 70% HNO_3 and diluted with ultrapure water.

and electric sector fields) for THERMO ELEMENT2 or quadrupole for Agilent 7500a; energy focusing; ion detection with a secondary electron multiplier.

The plasma is generated in a quartz glass torch by inductive coupling to a radiofrequency (RF ∼27 MHz) power source. The load coil, located at one end of the torch, is hollow and internally cooled by water. The RF magnetic field causes motion of free electrons within the Ar gas, causing intense heating (up to ∼10000 K). The plasma temperature is selected to maximise ionisation efficiency for the elements with a high first ionisation energy, while minimising second ionisation (double charging) for elements that have a low second ionisation energy. Ionisation is caused by collisions between free electrons and Ar gas atoms.

Making the plasma from argon, instead of other gases, has several advantages. First, argon is abundant (in the atmosphere, as a result of the radioactive decay of potassium) and therefore cheaper than other noble gases. Argon also has a higher first ionization potential than all other elements except He, F, and Ne. Because of this high ionization energy, the recombination of argon is energetically more favorable than the recombination of the sample atom. This ensures that the sample remains ionized so that the mass spectrometer can detect it.

A fraction of the formed ions passes through a ∼1 mm hole (sampler cone) and then a ∼0.4 mm hole (skimmer cone). Their purpose is to allow a vacuum that is required by the mass spectrometer. The pressure in the torch is ∼1 bar, between the cones $\sim 10^{-3}$ bar and behind the cones $\sim 10^{-7}$ bar. Argon acts here as a carrier a cooling gas. The mass range of ELEMENT2 is 2 – 260 a.m.u. and dynamic range is $>10^9$. It has high ionization yields (>90%) for almost all elements. For ELEMENT2 the resolution R = m/Δm, where Δm = FW(5%)M, is constant in the whole mass range, while for quadrupole machine it is a function of mass.

ICP-MS has great speed, precision, and sensitivity. However, compared with other types of mass spectrometry, such as TIMS and Glow Discharge, ICP-MS introduces a lot of interfering species: argon from the plasma, component gasses of air that leak through the cone orifices, and contamination from glassware and the cones.

THERMO ELEMENT2 has three resolutions to choose from. Low resolution (R = 300) is used for the analysis of non-interfered isotopes. In this mode the ELEMENT2 sensitivity is the highest of all commercially available ICP-MS instruments. Additionally, the flat top peak shape is an advantage for high precision isotope ratio measurements. Medium resolution (R = 4000) guarantees interference-free analysis for most elements in the majority of sample matrices. For example, transition elements are routinely measured in medium resolution due to the formation of many interfering polyatomic species in the mass range 24 – 70 a.m.u. High resolution (R = 10000) is used for the analysis of elements in the most challenging sample matrices. The main advantage of high mass resolution as a technique to remove spectral interferences is that it is not just limited to a particular type of interference. For example with high resolution of ELEMENT2 iron at m/z = 56

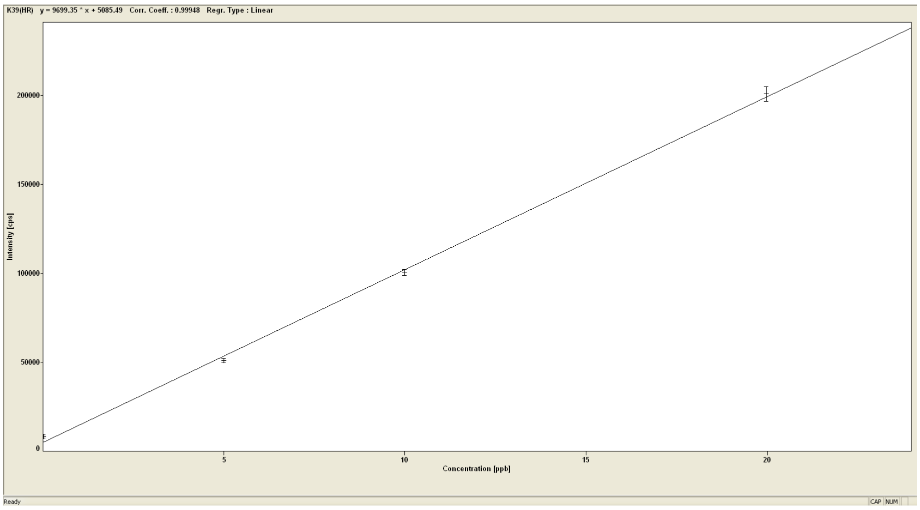

Figure 1: Calibration curve for ^{39}K obtained on THERMO ELEMENT2 at high resolution (R=10000).

is easily separated in a simple matrix from ^{40}Ar^{16}O as well as in more complex matrices from, for example, ^{40}Ca^{16}O.

3. Calibration

We used tune-up solution containing 1 μg/L of B, Ba, Co, Fe, Ga, In, K, Li, Lu, Na, Rh, Sc, Tl, U and Y dissolved in a 5% HNO$_3$ to make a calibration of ELEMENT2. For the Agilent 7500a we used tune-up agilent containing 1 ppb of natural Li, Y, Ce, Tl. The calibration curve, linking counting rate (cps) with concentration (ppb), for ^{39}K at high resolution (R = 10000) obtained on ELEMENT2 is shown in Figure 1.

4. Measured contamination and enrichment of the samples

The measured contamination and enrichment of the samples is given in Table 2 and Table 3, respectively. Numbers in the Table 2 were obtained on THERMO ELEMENT2, while the ones in Table 3 – on Agilent 7500a. Uncertainties of the contamination values are $\sim$30% due to a high purity of material and the presence of background (measured with a blank solution).

5. Summary

In the Gran Sasso Summer Institute 2014 Hands-On Experimental Underground Physics at LNGS I tried myself as an operator of an ICP-MS instrument. The spectrometers were calibrated and used for the measurement of contamination by certain elements and isotopic composition of the LUCIFER ^{82}Se samples. Obtained results are consistent with expectations based on previous studies. This technique (together with HPGe measurements) is an integral part of any low-background experiment. I believe I will definitely find an application to acquired knowledge in my future work.

Isotope	n_1, ppb	n_2, ppb
^{24}Mg (LR)	< 90	< 90
^{55}Mn (LR)	< 20	< 20
^{59}Co (LR)	< 20	< 20
^{63}Cu (LR)	< 27	18
^{110}Cd (LR)	< 20	< 20
^{182}W (LR)	33	18
^{206}Pb (LR)	< 40	< 40
^{209}Bi (LR)	< 1	< 1
^{232}Th (LR)	< 1	< 1
^{238}U (LR)	< 2	< 2
^{23}Na (LR)	< 1000	3300
^{121}Sb (LR)	< 2	< 2
^{202}Hg (LR)	< 2	< 3
^{125}Te (LR)	3300	5400
^{95}Mo (LR)	24	14
^{152}Sm (LR)	< 2	< 2
^{27}Al (MR)	< 1800	< 1800
^{44}Ca (MR)	< 7000	< 7000
^{52}Cr (MR)	< 20	< 20
^{56}Fe (MR)	< 500	< 500
^{28}Si (MR)	14000	< 10000
^{51}V (MR)	< 90	< 90
^{32}S (MR)	185000	180000
^{58}Ni (MR)	< 100	< 100
^{75}As (MR)	< 90	< 50
^{59}Co (MR)	< 10	< 10
^{39}K (HR)	< 1800	< 1800

Table 2: Contamination of the samples measured with THERMO ELEMENT2. The concentrations of the isotopes of interest in ppb (10^{-9} g/g) are refered to solid samples. n_1 – for sample 1; n_2 – for sample 2. LR – low resolution (R=300), MR – medium resolution (R=4000), HR – high resolution (R=10000). Uncertainties are about 30%.

Se isotope	Ref. Nat., %	Exp. Nat., %	Exp. Enr., %
74	0.89	0.72 ± 0.02	< 0.001
76	9.37	8.66 ± 0.26	< 0.08
77	7.63	6.74 ± 0.20	< 0.004
78	23.77	23.31 ± 0.70	< 0.02
80	49.61	50.94 ± 1.53	4.8 ± 1.4
82	8.72	9.63 ± 0.29	95.1 ± 2.9

Table 3: Experimental and reference values of the isotopic composition of enriched and natural selenium samples. Results were obtained on Agilent 7500a.

References

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