MDPI

Review

Material Screening with Mass Spectrometry

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Abstract: Inductively coupled plasma mass spectrometry is a powerful analytical technique. Because of its sensitivity, accuracy, multielement capability, high throughput, rapid analysis times and low detection limits, it is able to determine simultaneously long-lived radionuclides at trace and ultra-trace levels as well as isotope ratios. It has been increasingly applied in the framework of rare events experiments like those investigating the nature of dark matter and neutrinos, where the screening and selection of extremely radiopure materials for the experimental apparatus is crucial. Here, the inductively coupled plasma mass spectrometry (ICP-MS) measurements of the chemical purity of a Cs_2HfCl_6 crystal scintillator used to study α decay of naturally occurring Hf isotopes and its own raw materials are reported. Moreover, in the framework of the GERDA/LEGEND experiment, an overview of the ICP-MS results to monitor the recycling process of enriched germanium scraps is shown. Significant outcomes, such as low detection limits despite the small amount of sample to analyze and fast ICP-MS results, have been achieved in response to the challenges required by modern low background experiments.

Keywords: inductively coupled plasma mass spectrometry (ICP-MS); ultra-trace analysis; isobaric interferences; crystals; radio-purity; Hf α-decay; [76]Ge purification

1. Introduction

Naturally occurring low-level radioactivity measurements play an essential role during the setting up of nuclear physics experiments searching for rare events like neutrino-less double-beta decay, neutrino interactions and investigations about the nature of dark matter. The rare event processes are so-called because they have a low probability of happening or the particles involved have an extremely low interaction cross-section with the matter. All these experiments have in common the need for ultrapure materials to build extremely high sensitivity detectors often represented by crystals [1].

Some of the inorganic crystals are intrinsic scintillators in which the luminescence is produced by a part of the crystal lattice itself. However, other crystals require the addition of doping ions (e.g., thallium or cerium), which are responsible for producing the scintillation light [2–6].

In 1948, NaI(Tl) scintillation crystals came into use and provided better conditions for γ-ray detection even if the history of the scintillating materials used for radiation detection goes back to work by Röntgen and his discovery of X-rays in 1895. Over the years, numerous useful scintillators have been discovered and developed. Scintillation detection has been extended to many other inorganic crystals (e.g., CsI(Tl), $CdWO_4$). In the early 1960s, Freck and Wakefield reported the use of germanium crystals as detectors to measure ionizing radiation, but only 10 years later, high purity Ge detectors will revolutionize the nuclear sector because of their best energy resolution. Over the past few decades, the great interest in rare event searches has involved a broadening of the scintillators' fields of application. Relevant technological developments have been achieved with many improvements in terms of performance of detector materials, photomultipliers, electronic components, computing and data transmission. Several examples of the development of

new scintillators as components of modern detector systems have been reported in the literature.

Among the experiments located in the underground laboratories of Gran Sasso National Laboratories (LNGS) investigating the nature of the neutrino or the nature of dark matter, some examples must be highlighted within this framework: the cesium hafnium chloride (Cs_2HfCl_6) crystal scintillator used to investigate rare naturally occurring α decays of ^{174}Hf isotope [7] (extensively discussed in Section 2) or the high purity enriched Zn^{82}Se crystals for the study of the neutrino-less double-β-decay of ^{82}Se and the determination of the two-neutrino double-β-decay half-life of ^{82}Se in the framework of LUCIFER project and CUPID-0 experiment respectively [1,8]. Neutrino-less double-β-decay of the isotope ^{130}Te has been investigated by the cryogenic underground observatory for rare events (CUORE) experiment in which the detector consists of an array of 988 TeO_2 crystal bolometers operated at cryogenic temperatures.

Moreover, scintillating NaI(Tl) crystals are widely used as dark matter (DM) detectors: for instance, 25 highly radiopure NaI(Tl) detectors are successfully used by DAMA/LIBRA experiment to investigate the presence of DM particles in the galactic halo by exploiting the DM annual modulation signature. In addition, these detectors are suitable for various other rare process studies like searches for solar axions and cluster decay, possible processes of Pauli exclusion principle violation in ^{127}I and ^{23}Na isotopes and electron stability [9,10]. This is due to several characteristics such as i.e., high light response and duty-cycle (experimental live-time), appropriate signal-to-noise discrimination near the energy threshold, high stability and reproducibility of measurements, possibility to realize crystals with large masses, scalability and segmentation of the setup to increase sensitivity [9–11].

The germanium detector array (GERDA) experiment searches for neutrino-less double-beta ($0\nu\beta\beta$) decay of ^{76}Ge using an array of isotopically enriched high purity germanium (HPGe) detectors. The latter, made from high-purity (99.9999%) Ge material, are enriched in the ^{76}Ge isotope from the natural abundance of 7.8% to more than 85%. The Ge detectors are both the source and detector for the $0\nu\beta\beta$ decay. Moreover, the detector modules developed for the cryogenic rare event search using superconducting thermometers (CRESST) experiment, a search for WIMP dark matter particles via their elastic scattering off nuclei, are based on scintillating $CaWO_4$ crystals as absorbers.

In the framework of low-energy, ranging from few keV to MeV, and low background experiments as those previously mentioned, the choice of the isotopes as the interaction target and the chemical and radio-purity of the different components of the detectors together with surrounding materials is a prerequisite to guarantee a successful outcome.

Chemical purity is a key factor during crystal growth because the higher the contamination, the more difficult the crystallization [12]. Furthermore, low concentration of transition metals and other elements like Mg, K, Mn, Bi, Sn, Mg, Al and Cu is a general requirement of the initial raw materials in order to obtain high-quality scintillating crystals, as reported by Cardenas et al. [13]. Contaminants may distort the crystal lattice affecting, thus, the crystal features: the lack of homogeneity characterized by the presence of bulk defects like bubbles and metallic inclusions or veils and cracks may drastically affect the optical quality, light output, energy resolution, charge propagation and bolometric properties of such crystals [1].

Besides a high crystal perfection in order to allow for a high sensitivity detector, a low concentration of radioactive impurities, typically below 10^{-13} g·g^{-1}, is needed; thus, the use of radiopure materials with the lowest internal background is mandatory. Intrinsic contamination of the different materials employed coming from the impurity of raw materials or contamination during production processes as well as the exposure to cosmic rays must be assessed right from the start in order to reduce as much as possible detector background maximizing at the same time the signal-to-background ratio. This means a detailed screening of all materials to be used in the experimental setup, from the reagents and tools used for the synthesis of crystal powder to the finished crystal together with its handling, storage and transport before mounting in the experimental setup, not

to mention each component of the final apparatus. Last, but not least, a great variation in radiopurity between different batches of the same raw material must be taken into account in selecting materials. This involves a large number of measurements to be done for each reagent and the final component involved.

The contamination may come from long-lived, naturally occurring isotopes, such as ^{238}U, ^{232}Th, ^{40}K and their daughters and from cosmogenic activation of the detector materials and surroundings. The main sources of background interfering with the signals of the extremely rare events included cosmic rays, especially muons from the Earth's atmosphere, gamma rays and neutrons from (α, n) reactions or ^{238}U spontaneous fission due to primordial radionuclides such as ^{232}Th, ^{238}U coming from the experimental environment such as laboratory walls or produced by surface and bulk contamination of the detector construction and shielding materials [14]. In particular, the background resulting from ^{238}U, ^{232}Th decay products include the noble gas radon able to diffuse out of materials, thus interfering with the radioactive equilibrium of the decay chains [15].

Besides cosmic rays and radon isotopes, whose effects are usually negligible in deep underground facilities using a radon-free cleanroom for all the steps involved in the setup of the experiment or suitable filters fitting for this purpose, the main contribution to the background is represented by the radioactive contamination of the different components and chemicals employed in each step due to primordial radionuclides like ^{238}U, ^{232}Th and ^{40}K and their decay products. For nuclear physics searches, an extremely low radioactive contamination is required, so sensitivities ranging from parts per trillion (10^{-12} g·g^{-1} or ppt) to parts per quadrillion (10^{-15} g·g^{-1} or ppq) levels are necessary to detect any trace of radioactivity typically below 10^{-13} g·g^{-1}.

Whatever the nature of such rare events, detectors able to discriminate the weak and rare signals over the dominating background caused by natural radioactivity and cosmic rays are required. Since the energy range of the expected signals for rare events experiments is similar to those of the decay of radioactive nuclides or other possible nuclear reactions, these latter phenomena may cause background interfering with the signals of concern. For this reason, severe suppression of potential backgrounds is required. An extensive screening and material selection process must be conduct since radiopurity requirements are stringent.

For these reasons, analytical methods characterized by high sensitivity, low detection limit, high sample throughput and short analysis time are the best candidates to detect ultra-trace amounts of such radionuclides. The most frequently analytical techniques applied to measure the natural radioactivity and, therefore, to select highly radiopure materials for the experimental apparatus are ultra-low background γ-ray spectrometry with high purity germanium detectors (γ-HPGe), inductively coupled plasma mass spectrometry (ICP-MS), accelerator mass spectrometry (AMS) and neutron activation analysis (NAA). These different and complementary radioassay techniques are usually applied within the rare events nuclear physics experiments depending on the decay products, impurities and the matrix of each component involved.

Each one has its own advantages and disadvantages for a given application. From a laboratory perspective focused on radiopurity screening of materials, the most significant advantage of ICP-MS is its multi-elemental capability, in contrast to AMS and NAA, where only one radionuclide can be measured at a time.

Furthermore, an ICP-MS analysis requires small amounts of sample (few grams or less) and short times compared to γ-spectrometry, even if different sample preparation steps are necessary to dissolve the sample and to separate the elements of interest from the sample matrix, thus involving possible sample contaminations (time-consuming sample preparation). On the contrary, the nondestructive γ-spectrometry is able to determine the amount of different radioactive nuclides checking also for secular equilibrium with a detection limit of about 1 µBq/kg (^{232}Th: 0.2×10^{-12} g·g^{-1}, ^{238}U: 0.08×10^{-12} g·g^{-1}) achieved only using long measurement times and large amounts of sample.

AMS is based on the direct counting of atoms. It is characterized by a high isotope sensitivity and selectivity for extreme ultra-trace analysis of both radionuclides and stable nuclides (e.g., ^{14}C, ^{10}Be, ^{26}Al, ^{36}Cl, ^{41}Ca, ^{59}Ni, ^{129}I, Th, U and Pu). The analysis requires smaller samples (mg and even sub-mg amounts) and shorter measuring times (less than 1 h) to be performed compared to other radioanalytical techniques, but the experimental equipment is more complicated and expensive due to higher purchase and maintenance costs required by a particle accelerator [16].

NAA is another powerful analytical technique able to perform a qualitative and quantitative analysis of long-lived primordial radionuclides at trace level by irradiating samples in a nuclear reactor. During irradiation, the naturally occurring stable isotopes of which the sample is made are converted into radioactive isotopes by neutron capture and subsequently, they decay according to their characteristic half-lives, emitting γ-rays with specific energies. As already explained for AMS, since NAA requires a nuclear reactor, other analytical techniques are preferred, for instance, ICP-MS, for which also stand-alone equipment is available. Moreover, since low detection limits are required to detect primordial radionuclides in detector construction materials, pre-and/or post-irradiation chemical treatments are required, thus, making NAA less attractive [14].

1.1. ICP-MS Analytical Technique

Since its first development in the early 1980s, ICP-MS quickly became the leading analytical technique for fast and sensitive, trace and ultra-trace multi-elemental analysis. In addition, ICP-MS can be used to obtain precise isotope ratios of long-lived natural and artificial radionuclides in different materials. Due to the high precision and accuracy, excellent sensitivity, low detection limits, high throughput, small sample volume required, wide linear dynamic detection range, ICP-MS is widely used for quite different applications in areas ranging from environmental monitoring, health and food safety, high-purity materials screening (e.g., metals, alloys, semiconductors and insulators for microelectronics), geo and cosmochemistry, archeometry, forensic and pharmaceutical analysis [17,18].

Over the years, continuous improvements in computer hardware and software, sample introduction, plasma efficiency, ion transmission, detector performance and automation increased its utility, sensitivity and resolution. Although quadrupole-based ICP-MS equipped with collision/reaction cell is the most used worldwide, at the same time, the development of high-resolution mass spectrometers (H-ICP-MS) has been necessary to overcome limitations due to spectral interferences (isobaric overlap, polyatomic ion interferences and double-charged ions).

The isobaric interferences are due to the direct overlap of isotopes having the same nominal mass coming from different elements (e.g., ^{114}Sn and ^{114}Cd, ^{148}Nd and ^{148}Sm, ^{160}Gd and ^{160}Dy). Low-resolution instruments cannot distinguish between the isotopes, but this type of interference can be overcome by choosing a non-interfered isotope in case of multi-isotopic elements or using mathematical corrections.

Polyatomic ions, mainly argides, hydrides, carbides, nitrides and oxides, are molecular species naturally formed in the argon plasma due to precursors in the argon gas, in solvents and acids used during sample preparation or in the sample matrix. Typical polyatomic interferences are those interfering with monoisotopic elements like ^{40}Ar^{35}Cl$^+$ on ^{75}As$^+$ and ^{40}Ar^{63}Cu$^+$ on ^{103}Rh$^+$, ^{238}U^{1}H$^+$ on ^{239}Pu$^+$. Other examples of polyatomic interferences and the affected isotopes are reported as follows: ^{40}Ca^{16}O or ^{40}Ar^{16}O$^+$ on ^{56}Fe, ^{138}Ba^{16}O$^+$ on ^{154}Sm and ^{154}Gd, ^{38}ArH and ^{23}Na^{16}O on ^{39}K. The lanthanide element isotopes are especially prone to molecular oxide formation. The use of H-ICP-MS acting on mass resolution (e.g., for the mass spectrometric separation of ^{187}ReO$_3^+$ from ^{235}U$^+$ ions, a mass resolution m/Δm = 3000 is required), cold plasma for selected elements with low ionization potential such as K, Na, Ca or Sr as reported by Nisi et al. [19], reaction/collision cells, just to name a few approaches have resulted in reduction and, in some cases, complete elimination of many polyatomic interferences.

Doubly charged ions (e.g., $^{184}W^{2+}$ on $^{92}Mo^+$, $^{138}Ba^{2+}$ on ^{69}Ga, $^{140}Ce^{2+}$ on ^{70}Ge, $^{232}Th^{2+}$ on ^{116}Sn, $^{238}U^{2+}$ on ^{119}Sn) are common for elements having a low second ionization potential such as the alkaline earth, rare earth elements and, for instance, Th and U. Moreover, the greater the concentration of the element the higher the formation of M^{2+} interferences. Doubly charged ions were found to depend significantly on the inductively coupled plasma operating conditions and generally increase with increasing carrier gas flow rates. They also increase by about an order of magnitude when a desolvated aerosol is introduced to the ICP [20].

Moreover, nonspectral interferences or matrix effects resulting in suppression or enhancement in analyte signal may occur during sample introduction, in the plasma during atomization, ionization and excitation as well as in mass spectrometry, during extraction, focusing and transport of ions from the plasma to the detector. They can be reduced by using an internal standard or a purification step of the sample solution. A total dissolved solids (TDS) content in the sample of <0.2% (2 g/L) is usually recommended in ICP-MS to reduce sample-specific matrix effects and a potential nebulizer clogging.

There are many ways to reduce interferences, among them also a proper tuning of the plasma and torch conditions, especially for oxides and doubly charged species, or a reduction of the sample argon gas flow rate to reduce oxides, the use of an internal standard, a standard addition method, an appropriate sample introduction system or simply a dilution of the sample is frequently used.

By using an H-ICP-MS operating in the high-resolution mode ($m/\Delta m = 10{,}000$), most target elements may be resolved from polyatomic interferences, but the enhanced mass resolution results in a reduced ion transmission and, therefore, in a loss of sensitivity (typically a signal intensity reduction of about one order of magnitude occurs).

In addition, dedicated and effective purification methods based on liquid–liquid extraction, selective precipitation, solid-phase chromatographic extraction have been developed in order to quantify the concentration of impurities as well as U, Th and K to ppt levels or below in different types of samples. For instance, Nisi et al. [19] developed a procedure for Th and U separation and preconcentration from Te and TeO_2 by means of UTEVA resins in the framework of the CUORE neutrino-less double-beta decay experiment, La Ferriere et al. [21] reported an improved cleanliness procedure combined with anion exchange separation for the trace determination of Th and U in copper and lead shielding materials in support of the Majorana demonstrator experiment reaching sub-ppt sensitivity, Miyamoto et al. [22] developed an automatic sequential separation of U, Th, Pb and lanthanides using an anion exchange column and pressurized gas. The use of TRU resin has been reported by Kaizer et al. [23] for the determination of Th and U in selenium, aluminum and copper materials in the context of SuperNEMO experiment and AMS development.

Each step concerning sample treatments such as sample dissolution (dry ashing, wet digestion or closed-vessel acid digestion using microwave oven systems) and matrix separation, if required, must be performed in a cleanroom taking all the precautions needed to avoid any potential source of contamination.

Even if the so strict radiopurity requirements pose a considerable challenge on the materials selection and analysis in the framework of rare events experiments, ICP-MS, with its high sensitivity and high throughput, has become a key analytical technique well-suited to determine a wide range of minor, trace and ultra-trace elements.

1.2. Materials and Instrumentation

The need for reliable and accurate radiopurity measurements at ultra-trace levels requires ultra-pure reagents, inert and clean equipment as well as cleanroom in order to avoid any further contamination during all stages of sample preparation and analysis.

Highly purified HNO_3 was prepared by double-distillation of trace analysis grade acid ($HNO_3 \geq 69\%$, VWR Chemicals, Mississauga, ON, Canada) using a sub-boiling distillation system (Milestone, Bergamo, Italy). Single element 1000 mgL^{-1} stock standard solutions and multielement standard solution of trace analysis grade were purchased from Sigma-

Aldrich. All aqueous solutions were prepared with ultra-pure water (UP H_2O, 18.2 MΩ*cm resistivity) obtained from a Milli-Q IQ Element water system (Millipore, Burlington, MA, USA). Argon 5.0 of 99.999% purity was supplied by Air Liquide (Milano, Italy).

All analytical steps were performed in an ISO6 cleanroom at Gran Sasso National Laboratory (LNGS), and all the apparatus intended to come into direct contact with the sample and glassware were washed with 5% HNO_3 aqueous solution and then rinsed with ultra-pure water. Measurements were carried out using a single quadrupole inductively coupled plasma mass spectrometer (ICP-MS, 7500a, Agilent, Santa Clara, CA, USA) and a high-resolution double-focusing magnetic sector field inductively coupled plasma mass spectrometer (HR-ICP-MS, Finnigan Element 2, Thermo Fisher Scientific, Bremen, Germany).

2. Results and Discussion

2.1. Contribute of ICP-MS to Search for α Decay of ^{174}Hf Using Cs_2HfCl_6 Scintillator Crystal

A solid scintillator crystal of Cs_2HfCl_6 (CHC) was studied in order to measure the half-life ($T_{1/2}$) of the α decay of ^{174}Hf. Previously this measurement was performed more than fifty years ago [24], and the result was $T_{1/2} = 2.0 \pm 0.4 \times 10^{15}$ year in spite of the theoretical prediction of $T_{1/2}$ from 3×10^{16} year to 7×10^{16} year [25–27]. The expected counting rate for this kind of experiment is in the order of few events per day, so the internal background should be as low as possible in order to achieve a better value of signal-to-noise ratio. In this framework, the materials used as a detector or to set up the experiment need to be accurately selected and characterized in terms of their chemical purity and radioactivity content.

This application is very interesting because the collaboration managed all phases of the experiment, starting from the purchasing of the raw materials, through their purification by means of cleaning processes properly developed to the crystal growth in ultra-clean conditions. At all times, ICP-MS played a fundamental role because of its fast and very sensitive measurements despite having a small amount of sample. The mass spectrometry analysis gives information about long-lived radionuclides; then, in the crucial steps of the production process and during the characterization of the final crystal, it needs to be supported by complementary radiometric techniques to have complete information about the secular equilibrium of the whole decay chains.

First of all, ICP-MS was used in this experiment to measure the chemical purity of the raw materials: CsCl beads (99.998%) and $HfCl_4$ powders (99.8%), the highest purity grades available on the market, were selected [13]. The concentration of the transition metals must be lower than 1 ppm to ensure a high-quality scintillating crystal, while the rare earth elements needed to be checked due to their naturally high affinity to the hafnium. Moreover, the content of long-lived radionuclides such as K, Th and U to guarantee a low internal background of the final crystal was determined.

More than 40 elements and 100 isotopes were monitored by ICP-MS (Element 2) through the whole crystal production process. About ten milligrams of powdered raw materials and CHC crystal were dissolved in an ultrapure nitric acid solution (10% *v/v* in ultrapure water) and then properly diluted before ICP-MS analysis. The uncertainties mainly depend on the semiquantitative method applied to calculate the concentration of each element. The concerned method is based on a single level multielement standard solution covering the whole mass range (i.e., Li, Y, Ce and Tl at 10^{-8} g·g^{-1}), and this implies an error equal to ±30% of the given result. The upper limits were computed with a 68% confidence level. The measured concentrations of the most relevant elements are listed in the following table (Table 1).

Table 1. Some elements monitored by inductively coupled plasma mass spectrometry (ICP-MS). The values are expressed in 10^{-9} g·g^{-1}. The uncertainty is $\pm 30\%$ of the given result.

Element [1]	CsCl	HfCl$_4$ (Initial)	HfCl$_4$ (Purified)	CHC Crystal
	(10^{-9} g·g^{-1})	(10^{-9} g·g^{-1})	(10^{-9} g·g^{-1})	(10^{-9} g·g^{-1})
Al (MR)	1000	30,000	3000	2000
K (H)	2400	1400	<500	<2000
Mn (MR)	100	43	12	<20
Fe (MR)	600	3300	1200	<500
Sn	<10	50	10	<10
La	8.7	2600	550	130
Lu	<10	<500	<500	<300
Ta	<3	<8000	<8000	<4000
Ir	<2	<4000	<4000	<2000
Pt	<40	<100,000	<100,000	<40,000
Bi	<3	<2000	<2000	<1000
Th	<0.5	<1	<1	<0.5
U	<0.5	3200	270	<0.5

[1] All samples are acquired in low-resolution mode unless stated otherwise (MR = medium-resolution mode, H = high-resolution mode).

The initial CsCl reagent was sufficiently pure for both chemical and radioactive contamination, while the HfCl$_3$ needed to be purified by applying the adequately studied process of static sublimation [13]. The effectiveness of this proposed purification procedure, with regard to some dangerous elements such as Al, K, Mn, Fe, Sn, La and overall U, can be appreciated by comparing the values reported on the third and fourth columns of Table 1. Moreover, the well-known segregation effect, related to the crystal growth by the Bridgman technique, significantly improved the purity of the final CHC crystal reducing the U concentration below the detection limit [13].

As it can be seen from the data, the detection limits for some elements heavier than Hf are highly correlated to the sample matrix since they are affected by isobaric interferences due to polyatomic species containing hafnium isotopes. The most relevant ones are shown in Table 2.

Table 2. Drawbacks affecting the ICP-MS measurement.

Element	Isotope	Abundance	Interferences	Mass Resolution [1]
	(amu)	(%)		
Al	27	100	^{11}B^{16}O, ^{12}C^{15}N	1450
K	39	93.26	^{38}Ar^{1}H	5540
Mn	55	100	^{37}Cl^{16}O^{1}H, ^{40}Ar^{15}N	2250
Fe	56	91.75	^{40}Ar^{16}O	2500
Lu	175	97.41	^{174}Hf^{1}H, ^{174}Hf Tail	
Ta	181	99.99	^{180}Hf^{1}H, ^{180}Hf Tail	
Ir	191	37.3	^{174}Hf^{16}O^{1}H	10,850
	193	62.7	^{177}Hf^{16}O	8140
Pt	190	0.014	^{174}Hf^{16}O	7600
	194	32.97	^{178}Hf^{16}O	8048
	195	33.83	^{179}Hf^{16}O	8090
	196	25.24	^{180}Hf^{16}O	8375
	198	7.16		
Bi	209	100	^{174}Hf^{35}Cl	2920

[1] Resolution values needed to solve the isobaric interferences. The Element 2 can work at three resolution modes: low (m/Δm = 300), medium (m/Δm = 4000) and high (m/Δm =10,000).

The issues encountered for ICP-MS measurement of Al, K, Mn and Fe are widely studied since they are based on Ar, O and N, usually present in the torch. The other polyatomic species listed in Table 2 are generated by the huge amount of Hf isotopes, and they need to be looked at more specifically. In particular, the signals of Lu and Ta,

which are monoisotopic elements, are adjacent to the Hf ones. Therefore, the background in their respective regions of interest is high due to the "abundance sensitivity effect", peak spread and temporary formation of hafnium hydrides species. This results in an important worsening of the limit of detection. A similar situation has occurred for Ir and Pt since almost all their isotopes are heavily interfered with by hafnium oxides, as well as for Bi because its mass region is masked by hafnium chloride.

Many of these interferences may be overcome acting on the mass resolving power of the mass spectrometer, but when the relative intensity of the interfering signal is huge, like the hafnium oxides versus Pt isotopes, the peaks cannot be completely separated.

2.1.1. Study of the Secular Equilibrium: ICP-MS and γ-ray Spectrometry Data Joining

As already widely explained in this work, mass spectrometry and radiometric measurements are fully complementary then the radio-purity of the samples monitored applying different approaches is worth to be discussed. A relevant case study is reported in the following paragraph.

In Table 3, the activities of ^{235}U and those of the nuclides belonging to the ^{238}U chain, measured by γ-ray spectrometry, are compared to those of the ^{238}U, directly computed by its concentration determined via ICP-MS.

Table 3. Activities measured by γ-ray spectrometry and ICP-MS.

Chain Nuclide		CsCl	HfCl$_4$ (Raw)	HfCl$_4$ (Purified)	CHC Crystal [2]
		(Bq/kg)	(Bq/kg)	(Bq/kg)	(mBq/kg)
^{235}U	^{235}U	<0.53	(1.4 ± 0.8)	<2.7	<26
^{238}U	^{234}Th	<22	<58	(130 ± 30)	<8.6
	^{234m}Pa	<19	(50 ± 20)	<140	<3.7
	^{226}Ra	<0.54	<0.86	<4.5	<12
	^{238}U [1]	<0.006	40 ± 10	3 ± 1	<6

[1] Values evaluated on the basis of ICP-MS determinations. [2] For CHC crystal, better detection limits were achieved because of the higher amount of sample analyzed (7 g) and the longer data acquisition time applied (2848 hs).

Under secular equilibrium conditions, ^{226}Ra is the most sensitive radionuclide for the ^{238}U chain activity measurement using γ-spectrometry. The comparison of the data about its activity and that calculated on the basis of ICP-MS measurement points out a major disagreement of almost two orders of magnitude for the HfCl$_3$ (raw) sample. On the other side, the activity of ^{234m}Pa is comparable to that of ^{238}U since it is closer to the ^{238}U than ^{226}Ra in the decay chain. In this case, the different chemical behavior of these nuclides, belonging to the same decay chain, may lead to the break of the secular equilibrium during the material production or purification processes.

For instance, the most common salts of Ra are more soluble in water than those of Th and U, its precursors; for this reason, Ra can be removed quite easily, causing disequilibrium.

Looking at the data set in Table 3, an additional interesting consideration can be done: assuming that the contamination of U in the sample presents natural isotope abundance, the activity of ^{238}U can be estimated based on the ^{235}U one even if they belong to two different decay chains (30 ± 15 Bq/kg).

2.1.2. Total α Activity Measurement of CHC Crystal

The growing scientific interest in the CHC crystal and the rare α decay of naturally occurring Hf isotopes have led several groups around the world to work on this topic. Recently, a study of the total α activity of the CHC crystal was carried out in the detector set up at the Subterranean Low-Level Assay (STELLA) facility of the LNGS. A total of 2848 hs of data taking using the "source = detector" approach have shown a candidate signal in the region of interest of ^{174}Hf (553 ± 23 total α events). Further ICP-MS investigations were performed in order to determine the abundance of other radionuclides, potentially

interfering in the same energy region. The expected counts evaluated on the basis of the concentrations measured via ICP-MS are reported in Table 4.

Table 4. Expected signals of interfering nuclides in the ^{174}Hf α decay energy region.

Nuclide	Half-Life Time	Concentration	Expected Signal
	(Year)	(10^{-9} g·g^{-1})	(counts)
^{144}Nd	2.29×10^{15}	<2.4	<0.007
^{147}Sm	1.060×10^{11}	0.6 (1)	36 (6)
^{148}Sm	7×10^{15}	0.4 (1)	$3.6\,(1) \times 10^{-4}$
^{152}Gd	1.08×10^{14}	<0.02	$<1 \times 10^{-3}$
^{186}Os	2.0×10^{15}	<0.25	$<6 \times 10^{-4}$
^{190}Pt	6.5×10^{11}	<0.02	<0.1
^{209}Bi	2×10^{19}	<2	$<4 \times 10^{-7}$

The ^{147}Sm resulted in the only dangerous nuclide due to its relatively short half-life time; in fact, it has given a significant contribute (36 $\pm$ 6 α events predicted) well discriminated by means of the good energy resolution of the detector (29 $\pm$ 5 α events measured) [7]. The half-life of ^{174}Hf was measured in $7.0 \pm 1.2 \times 10^{16}$ year that is in excellent agreement with the theoretical prediction of T$_{1/2}$ from 3×10^{16} year to 7×10^{16} year.

2.2. ICP-MS: The Right Tool for Monitoring the Recycling Process of Enriched Germanium Scraps

The chemical radiopurity is a key requirement for crystals to be used in detectors assembly of nuclear physics experiments such as those investigating the nature of the neutrino.

Germanium detectors manufactured from enriched ^{76}Ge, are particularly well-suited for the neutrino-less double beta decay ($0\nu\beta\beta$) searches thanks to a higher detection efficiency and energy resolution [28]. These types of detectors are used in nuclear physics experiments like GERDA, Majorana Demonstrator as well as LEGEND [29–33]. Several steps, like isotope enrichment, reduction of germanium dioxide to metal, zone refinement, chemical purification of scraps and manufacturing waste containing enriched germanium to be recovered and crystal growth, are necessary to convert bulk germanium into the enriched and ultra-pure material used in detectors for rare event experiments [33–35].

The isotope enrichment was performed by gas centrifuge enrichment process: this involves the fluorination of metallic ^{nat}Ge to the gaseous ^{nat}GeF$_4$, its enrichment passing through many centrifuges and its subsequent hydrolysis to ^{76}GeO$_2$ followed by drying and calcination steps to remove water and other impurities. An ICP-MS analysis for each ^{76}GeO$_2$ batch produced was performed in order to assess the effectiveness of the enrichment process and the chemical purity. Following the H$_2$ reduction of GeO$_2$ to metallic Ge, the ingot was zone-refined.

After multiple zone-refining passes, the purest central section was directly used for detector grade germanium crystal growth by the Czochralski method [35]. The ends of the ingot (head and tail, later called kerf), where the impurities accumulate, are cut off and subjected to a chemical purification performed at the LNGS, where a chemical plant has been designed and built to fit this purpose. The chemical purification process of the kerf includes chlorination (from metallic Ge to GeCl$_4$), fractional distillation, hydrolysis (from GeCl$_4$ to GeO$_2$*nH$_2$O), filtration and calcination (GeO$_2$ purified).

Moreover, it is necessary to store the material just purified underground as soon as the purification process gets completed in order to minimize its cosmogenic activation and, therefore, the production of undesired radionuclides like ^{68}Ge and ^{60}Co. This could represent an issue because while ^{60}Co can be removed during chemical purification and zone-refinement, this does not happen to the ^{68}Ge isotope, for which the only solution is to limit the exposure to cosmic radiation [33].

The chemical plant, installed at the LNGS to recycle the precious enriched germanium scraps collected during the crystal production process, has required a high sensitivity

instrument for quick monitoring of a large number of contaminants during the purification process. The ICP-MS, being a rapid, multi-elemental trace analysis technique, is the most suitable one for this kind of application. In Table 5, all samples to be analyzed with their own description are reported.

Table 5. Samples analyzed.

Sample	Description
Ge kerf	Starting material
$GeCl_4$ c	Sample after chlorination
$GeCl_4$ d	Sample after distillation
GeO_2 purified	Final product after purification

The Ge kerf is the starting metallic material to be purified, while $GeCl_4$ c is collected immediately after its conversion in the reactor at 400 °C by means of gaseous chlorine. The next step is the distillation that runs continually until the purity of the $GeCl_4$ d samples, periodically collected and immediately analyzed, does not meet the strict experimental requirements. The last measurement was carried out on GeO_2 obtained by hydrolysis of the purified $GeCl_4$ and subsequent calcination.

An overview of the most interesting contamination levels for each sample is reported in Table 6.

Table 6. Contamination levels for each sample reported as 10^{-9} g·g^{-1}. The uncertainty is ±30% of the given result.

Element [1]	Ge Kerf (10^{-9} g·g^{-1})	$GeCl_4$ c (10^{-9} g·g^{-1})	$GeCl_4$ d (10^{-9} g·g^{-1})	GeO_2 Purified (10^{-9} g·g^{-1})
Li	20	5	<5	<5
Be	<20	<5	<5	<5
B	90	85	<10	<10
Na	840,000	<1000	<1000	<500
Mg	18,000	700	230	190
Al (H)	<6000	<2000	<2000	<2000
K (H)	<16,000	<5000	<5000	<5000
Sc	<200	<200	<20	<10
V	250	180	100	<5
Cr	<200	<200	<100	<50
Mn	<50	45	<20	<10
Fe (MR)	<10,000	<5000	<5000	<5000
Co	<10	<10	<5	<5
Ni	2400	110	<100	<100
Cu	14,000	100	<100	<100
Zn	890	<50	<50	<50
Ga	6200	21,000	<10	<10
As (H)	<1000	<1000	<1000	<1000
Rb	55	<5	<5	<5
^{88}Sr	170	<10	<10	<10
Mo	<50	<50	<10	<10
Ag	<50	<50	<20	<5
Cd	<300	<300	130	<20
Cs	90	70	20	15
Ba	1600	<20	<20	<20
La	10	<5	<5	<5
Ce	30	<20	<20	<20
Pr	<5	<5	<5	<5
Sm	<10	< 5	< 5	<5
Eu	<5	<5	<5	<5
Tb	<5	<5	<5	<5

Table 6. *Cont.*

Element [1]	Ge Kerf (10^{-9} g·g^{-1})	GeCl$_4$ c (10^{-9} g·g^{-1})	GeCl$_4$ d (10^{-9} g·g^{-1})	GeO$_2$ Purified (10^{-9} g·g^{-1})
Dy	<5	<5	<5	<5
Ho	<2	<2	<2	<2
Er	<2	<2	<2	<2
Tm	<10	<5	<5	<5
Yb	<10	<5	<5	<5
Lu	<10	<5	<5	<5
Hf	<10	<5	<5	<5
W	<200	<50	<50	<50
Os	<10	<10	<10	<10
Pt	<100	<100	<50	<50
Au	<50	<50	<5	<5
Hg	<20	<20	<20	<20
Tl	<50	<50	15	<5
Pb	720	300	25	12
Bi	100	25	<5	<5
Th	<5	<2	<2	<2
U	<5	<2	<2	<2

[1] All samples are acquired in low-resolution mode unless stated otherwise (MR = medium-resolution mode, H = high-resolution mode).

Most of the elements reported in Table 6 were analyzed using a quadrupole mass spectrometer without an isobaric interference suppression system like collision or reaction cell. Despite an uncertainty equal to 30% of the given result, a semiquantitative analytical method was adopted since large numbers of elements must be screened to manage the purification plant. General drawbacks affecting the ICP-MS measurement and the determination of some common elements such as Al, K and Fe have been already discussed in different sections of this work. Here, it is worth mentioning some interferences specifically related to the nature of the samples measured in this application and the different strategies adopted to overcome them.

The most dangerous interferences during this assessment are shown in Table 7.

Table 7. Interferences observed during acquisition.

Element	Isotope (Amu) (amu)	Abundance (%)	Interferences	Mass Resolution [1]
Al	27	100	^{11}B^{16}O, ^{12}C^{15}N	1450
K	39	93.26	^{38}Ar^{1}H	5540
Cr	52	83.79	^{12}C^{40}Ar	2375
Fe	56	91.75	^{40}Ar^{16}O	2500
As	75	100	^{40}Ar^{35}Cl, ^{76}Ge tail	7770
Mo	95	15.84	^{76}Ge^{19}F	6800
Cd	111	12.80	^{76}Ge^{35}Cl	7960

[1] Calculated resolution values needed to solve the isobaric interferences. The Element 2 can work at three resolution modes: low (R = 300), medium (R = 4000) and high (R = 10,000).

Arsenic is affected by both the abundance sensitivity effect (tailing) due to ^{76}Ge, and the presence of ^{40}Ar^{35}Cl, especially with regard to the analysis of the GeCl$_4$ samples. Al and As are monoisotopic elements, while the isotopes of K and Fe are also affected by serious isobaric interferences; therefore, the use of a high-resolution mass spectrometer was mandatory to get out accurate determination for all of them. On the other hand, for those who concern Mo and Cd, the analysis was successful performed in low-resolution mode, acquiring the isotopes not affected by interferences.

An accurate characterization of the chemical plant designed for the recycling of the enriched germanium scraps was done thanks to the data reported in Table 6. The most valuable considerations are summarized below.

The Ge kerf material is not homogeneously, ranging from fine powder to metal scraps of about ten grams. The chemical contamination is likely very changeable, too, since, after the zone refining process, the impurities were distributed along the longitudinal axis of the ingot.

After homogenization and collection of a representative aliquot of the whole batch, the ICP-MS characterization was performed. A significant presence of several elements that may represent an issue for the crystal growth was detected.

The analysis of $GeCl_4$ c sample, produced in the reactor by chlorination, has shown a significant reduction of several contaminants such as Na, Mg, Ni Cu, Zn Rb, Sr and Ba due to the high selectivity of the chemical reaction, but on the other hand, gallium reacts with Cl_2 to produce $GaCl_3$ similarly to the germanium. Therefore, its concentration is of the same order of magnitude in Kerf and $GeCl_4$ $_C$ samples. However, the gallium and all the residual contamination were efficiently removed after the distillation step. Lastly, the measurement of the GeO_2 purified sample has excluded recontamination during hydrolysis and calcination steps.

Finally, a characterization of germanium isotope abundances was done both in starting material and final product after the purification process in order to assess the enrichment in ^{76}Ge required by the experiment. In Table 8, the isotope abundances referred to the same sample batch after and before the purification steps are shown.

Table 8. Isotope abundances.

Sample	$^{70}Ge/Ge$ (%)	$^{72}Ge/Ge$ (%)	$^{73}Ge/Ge$ (%)	$^{74}Ge/Ge$ (%)	$^{76}Ge/Ge$ (%)
Ge kerf	0.0004 ± 0.0001	0.0011 ± 0.0003	0.010 ± 0.01	7.2 ± 0.5	93.2 ± 0.8
GeO_2 purified	0.0006 ± 0.0002	0.0010 ± 0.0003	0.011 ± 0.03	7.1 ± 0.4	93.1 ± 0.8

A standard germanium solution of natural isotopic composition was used to correct instrumental mass bias. The isotopic characterization has shown that no change in isotope abundance during the purification process has occurred.

3. Conclusions

ICP-MS is one of the most sensitive analytical techniques for low-level long-lived radionuclide analysis. Over the years, it has been widely employed for the screening of materials to be used in the framework of rare event searches like those hosted in the underground laboratories of the LNGS investigating the nature of dark matter and neutrino. These low-level background experiments require highly radiopure detector materials in order to maximize the signal-to-background ratio, so an extensive chemical and radio-purity screening to evaluate the intrinsic contamination of the detector components and their related raw materials is required. In this paper, the chemical purity and the radioactive contamination of the Cs_2HfCl_6 crystal scintillator and its starting materials were reported: more than 40 elements and 100 isotopes were monitored through the whole crystal production process by exploiting ICP-MS multi-elemental capability, sensitivity, high throughput and quick analysis response. These key features of the ICP-MS have similarly been successful exploited to monitor the recycling process of the enriched germanium scraps for each step of the whole chemical purification process.

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