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PURIFICATION OF ARCHAEOLOGICAL LEAD

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The study of the complex method of deep purification of archaeological lead, developed at the NSC KIPT, is described. The obtained results on the refining and application of purified ancient lead are presented. Pilot batches of ancient Greek and Roman lead of purity >99.9996...99.998 wt.% were produced for growing perfect crystals of $^{arch}PbWO_4$ and $^{arch}PbMoO_4$, that are used as scintillation detectors for recording rare events in modern low-background experiments. The most interesting experiment is RES-NOVA aimed at detecting neutrinos from astrophysical sources such as supernova (SN) collapse using cryogenic detectors made on the basis of archeological lead ($^{arch}PbWO_4$). A method of oxidizing refinement of metals is proposed, which can be used for additional removal of chemical and radioactive impurities U, Th, ^{40}K from lead.

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INTRODUCTION

At present, there is growing interest in physics without accelerators with a very low frequency of events, for example, in experiments with solar and terrestrial neutrinos, double beta decay (ββ), the search for dark matter. Many open-ended questions in modern physics can be further resolved only by the methods capable to filter out the weak signal from background and noise. This is especially true for experiments based on the detection of ionizing particles. In this case, false counts owing to environmental radioactivity, internal contamination of the detector and shielding material, from the air environment (radon), from cosmic rays, or from neutrons can obscure the readings of the signals of interest.

In the early 1960s, Ge(Li) and Si(Li) crystals, and later high-purity Ge crystals, revolutionized the nuclear field due to their high energy resolution. The latest generation of detector technologies are cryogenic detectors, which developed in various laboratories around the world. They achieve even higher energy resolution, as they are able to register phonons, thermal fragments of an ionizing event. In many fields, the above detectors are used for studies with very low event rates. Therefore, these detectors require a low background.

The occurring everywhere presence of primary radionuclides in ores and other raw stock leads to a wide range of contamination of the final product. With some exceptions, the main radioactive impurities are usually ^{40}K, U, and Th with most of their daughter nuclides. To protect detectors against external gamma radiation the shielding materials are used. The number of materials suitable for reducing ambient γ-ray emission is very limited, especially when cost is taken into account. Without taking into account such exotic elements as tungsten or tantalum then the mercury, iron, copper, and lead are suitable shielding elements for one reason or another. Pb is the best shielding material because of its high atomic number, reasonable cost and mechanical properties. In addition, it has a low neutron cross section and a low probability of interaction with cosmic rays, including the formation of radionuclides by activation. Unfortunately, its own radioactivity, as a rule, is not insignificant.

The nature and origin of this contamination have been thoroughly studied by many authors. A consistent general result is that only ^{210}Pb with its daughter nuclides ^{210}Bi and ^{210}Po is responsible for lead's proper radioactivity. Due to the long half-life of ^{210}Pb (22.3 years), the content of these nuclides in lead can be much higher than expected from secular equilibrium [1]. The concentrations of ^{210}Pb reported in the literature range from the detection limit of the corresponding detector to 2500 $Bq \cdot kg^{-1}$ [2]. Johnson and Matthey companies [3] succeeded in producing expensive lead for use in the electronics industry with an activity lower by more than two orders of magnitude (0.4 $Bq \cdot kg^{-1}$) compared to normal commercial specimens.

An alternative to modern certified lead is ancient lead, which has undergone multiple decays, so ^{210}Pb is almost completely absent. The availability of such lead, however, is very limited, as "sources of supply" such as the cargo of sunken ships or the ballast of sailing ships are rare. However, an extremely large cargo of ancient Roman lead [4] and ancient Greek lead [5] was also discovered. The content of ^{210}Pb in Roman lead was measured by a bolometer and was found to be less than 20 $mBq \cdot kg^{-1}$ [6]. In ancient Greek lead, assuming secular equilibrium of the ^{238}U decay chain in lead, the activity of ^{210}Pb via ^{238}U can be limited to < (5…14) $mBq \cdot kg^{-1}$ before melting and, with a caveat, < (0.2…0.9) $mBq \cdot kg^{-1}$ after melting. The data presented show the lowest lead contamination with the isotope ^{210}Pb, ever reported. The archaeological lead, having such low radioactive contamination without additional purification, is used as a shielding material for detectors in low-background experiments.

However, the chemical purity of ancient lead [2, 4–6] with the base metal content of 99.0…99.8 wt.% is far different from the specifications for the raw compounds used to grow $PbWO_4$ and $PbMoO_4$ crystalline scintillators. In order to produce high-quality crystals, it is necessary to ensure the level of raw materials purity at least 99.995 wt.%.

The purpose of the work is to present the comprehensive method of deep purification developed at NSC KIPT and the results obtained for the refining and application of purified ancient lead in modern low-background experiments for the registration of rare events.

EXPERIMENT

Producing high-purity lead requires the use of multi-stage processes combining various methods of fine purification.

Electrolytic methods [7] make it possible producing lead with a total content of metal impurities in the amount of 1...100 ppm, however, to obtain metal with a concentration of impurities that meets modern requirements, an additional purification is necessary. In addition, it is inevitable the release of harmful gases and vapors in the electrochemical lead refining methods, so careful safety precautions are required.

To remove certain impurities (As, Te, Zn) from lead, it is effective heating it in a vacuum at the temperatures of 750…1250 K. However, during the vacuum heating, a weak removal of such impurities as Bi, Mg, and Sb is observed [8].

The zone recrystallization method is also used for lead purification. The refining of lead by zone melting have been devoted with many works where the behavior of Sn, Cu, Ag, Au, Mg, Na, Bi, Sb was studied quantitatively, and Co, Ni, Fe, Ge, Cd, As done qualitatively. Impurities which are difficult to remove during zone recrystallization of lead are Sn, Sb, Bi, Mg, as well as Na, what have a distribution coefficient near unity ($k \sim 1$) [9]. The drawback of the method is the low yield (60...70%) of a suitable product.

One of the effective techniques of refining metals, including lead, is the vacuum distillation method [10–12]. This method involves industrial production with obtaining highly pure grades of lead [13].

Therefore, for the fine cleaning of archaeological lead, we developed a complex refining method based on distillation. The peculiarity of lead is that it belongs to fusible metals (T_{melt} = 600.5 K) and it is characterized by low vapor pressure at the melting temperature ($4.3 \cdot 10^{-7}$ Pa) [14]. Calculations show that acceptable evaporation rates of fusible metals in distillation processes correspond to their vapor pressure at 27...80 Pa, which for lead corresponds to the melt temperature of 1200...1250 K. These data were initial ones for choosing the distillation process temperature, the value of which was chosen to be ~ 1220 K.

At this temperature, the calculations of the separation coefficients α_i of impurities in lead were performed, which are divided into easy-volatile with $\alpha_i < 1$ and heavy-volatile with $\alpha_i > 1$. In particular, according to the calculated data, it can be concluded that the closest easy-volatile impurities are barium and thallium, and the closest heavy-volatile impurity is manganese. According to this criterion, the efficiency of these impurities removal from lead by vacuum distillation would be low. For all other impurities, the calculated purification ratio is 100 or more times, which should correspond to a significant removal of these impurities. Calculations of the efficiency of Pb melt purification from easy-volatile impurities depending on the residue fraction, as well as the efficiency of condensate purification from heavy-volatile impurities depending on the fraction of distillation [15–17] were also made. The above features and calculations were the reason for the search for a new approach to the development of a distillation device for refining and the selection of lead distillation process modes.

Thus, a special device was developed for the refining of lead by a complex method which includes melting the metal and its filtration followed by distillation in a vacuum. The simplified diagram and operation of the device are described in detail in papers [15, 17–19].

The initial lead was subjected to preliminary filtration in a vacuum in a separate device that combines filtration and pouring of the metal into measuring ingots. Such a filtration procedure, on the one hand, leads to additional (3–5 times) removing metal impurities from Pb, and on the other hand, to the removal of oxidizing impurities, which leads to an increase in the productivity of refining processes.

Then the filtered lead was placed in a crucible, the chamber of the installation was evacuated to a vacuum and during refining the pressure was maintained in it at no more than 10^{-1} Pa. The lead melt was heated to 1220 K, at the same time it evaporates and condenses in the condenser in the form of refined metal (Figure,b).

When lead evaporates up to 95% of the initial loading, the heavy-volatile impurities (Cu, Fe, Si, Ni, Co, V, Cr, Au, Ag, Al, Tl, Sb, Bi, Li, Sn, Mn, etc.) which remain in the lead residue in the crucible are deleted from it. Easy-volatile impurities (Na, K, P, As, Se, Te, Cd, Zn, etc.) that enter in the condenser with lead during its condensation are removed from the condenser volume by evaporation during the refining process at the condensate temperature ($T_{cond} \approx 0.8\ T_{evap}$).

Archaeological Greek lead found at the bottom of the Black Sea near the southern coast of Crimea among the remains of a Greek ship of the first century BC was subjected to a fine cleaning process [5]. Comparison of the measurement data of the work [5] with the known ratios of lead isotopes $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ for various deposits of antiquity [20, 21], allowed us to assume that the revealed lead was extracted from the silver-lead ore deposit on Mount Lavrion forty kilometers southeast of Athens (Attica, Greece). Such lead was found in the amount of 0.2 t, which is now in Ukraine.

The object of research was also ancient Roman lead, discovered by archaeologists in 1988 at the bottom of the Mediterranean Sea near the Sardinia Island on a sunken 36-meter ship sailed from Spain to Italy. Among the cargo being transported on the ship, there were more than 1500 lead ingots weighing ~ 33 kg each (see Figure,a). The ship with lead which was on it, lay for about two thousand years at the bottom of the sea at the depth of 30 m, beautifully shielded from exposure to cosmic rays [22]. This valuable metal is available in Italy [23] at the Gran Sasso National Laboratory (about 4 t) and at the Archeology Department of the Ministry for Cultural Assets of Cagliari (about 33 t).

The elemental composition of lead before and after refining was monitored by inductively coupled plasma mass spectrometry (ICP-MS) at the Gran Sasso National

Laboratory (NLGS, Italy) and laser mass spectrometry (LMS) at the NSC KIPT of NASU.

RESULTS AND DISCUSSION

The results of the analysis of archaeological lead before and after refining are presented in the Table.

It should be noted that the main impurities in the initial Roman lead are the elements Cu, Ag, Sn, Sb, the removal efficiency of them is ~ 100–600 times (see Table). The purity of the initial lead by the total amount of impurities is 99.7 wt.%. The purity of lead after refining, taking into account these and other impurities, is > 99.998 wt.%.

The initial Roman lead also contains a number of impurities (Na, K, Ca, S, As), the removal efficiency of them is low – 1.5–2.5 times. This situation for sodium can be explained by the fact that its content is at the limit of sensibility of the determination method, and calcium, sulfur and arsenic are probably transferred to the refined metal in the form of stable compounds. Nevertheless, the proposed lead refining procedure (heating, filtration and double distillation) provides high (more than 100 times) efficiency of metal purification.

Figure shows photos of Roman archaeological lead bars with epigraphy [22] (a) and the resulting distillates of purified lead [24] (b).

For deep purification of archaeological Greek lead, the same approach was used as for Roman lead [17, 18, 25].

Content of major impurity elements (ppm) in ancient Roman and Greek lead before and after refining by vacuum distillation

Element	Roman lead		Greek lead	
	before refining	after refining	before refining	after refining
Na	0.05	0.05	–	–
Mg	0.08	< 0.03	< 1	< 5
Al	0.12	0.009	< 1	< 1
Si	0.044	< 0.04	1	0.08
S	0.76	0.4	–	–
K	0.1	0.045	0.5	0.3
Ca	0.2	0.16	< 5	< 5
Ti	–	–	< 0.5	< 0.5
Mn	0.12	< 0.07	< 0.05	< 0.05
Fe	0.1	< 0.08	< 0.09	< 0.09
Co	–	–	< 0.01	< 0.01
Ni	0.37	< 0.1	< 0.1	< 0.1
Cr	–	–	< 0.1	< 0.1
Zn	< 0.2	< 0.2	< 0.3	< 0.3
Cu	23	< 0.05	200	0.3
As	1.6	0.8	–	–
Ag	300	< 0.5	80	0.7
Cd	< 0.8	< 0.8	< 0.05	< 0.05
Sn	1800	7.7	–	–
Sb	560	6.3	230	< 0.6
^{arch}Pb, wt.%	> 99.7	> 99.998	> 99.94	> 99.9996

a

b

Roman lead bars (a) and purified lead distillates weighing ~ 1 kg each (b)

In ancient Greek Pb, according to the content of the main impurities in the initial material and their removal efficiency, a similar pattern to Roman lead is observed. The difference in the percentage composition of the initial lead is explained by the fact that Greek Pb was remelted with elements of the process of removing various contaminants and inclusions from it before distillation [5]. As follows from the Table, the purity of the initial Greek lead was > 99.94 wt.%, and after refining, that of lead is > 99.9996 wt.%. The main impurities in Greek lead are Cu, Sb, and Ag. After refining, their concentrations are significantly reduced by more than 10–500 times. The content of other impurities in purified lead is below the sensibility limit of the analysis methods: for Rb, Y, Zr, Nb, Ru, Pt, Au < $1 \cdot 10^{-2}$ ppm; for Sc, In, Te < 0.1 ppm; and for Se, Pd < 1ppm.

Thus, the above results demonstrate that the complex method of fine cleaning of archaeological lead by vacuum distillation developed at NSC KIPT makes it possible to obtain the final product of purified ancient lead by two orders of magnitude cleaner than the initial metal.

It should be emphasized that there is a possibility of additional purification of archaeological lead before the distillation process by removal of both chemical and radioactive elements U, Th, ^{40}K, using the method of oxidative refining of metals proposed in the patent [26].

The proposed method can be applied to reduce by 5–10 times the content of chemical and radioactive impurities in such metals as Au, Ag, In, Ga, Cu, Mn, Sn, Pb, Bi, etc. and in their alloys in the amount of 0.2 to 2.5 kg, depending on the needs for the refined material. At the same time, the yield of refined product is almost 100%.

The pilot batches of ancient Greek and Roman lead with the purity of >99.9996...99.998 wt.%, obtained by a complex method, are suitable for growing perfect scintillation crystals of $^{arch}PbWO_4$ and $^{arch}PbMoO_4$, and they are successfully used in many modern international experiments, that is confirmed by a number of scientific papers.

The authors of paper [27] conducted a study of the effectiveness of an $^{arch}PbMoO_4$ crystal made using additionally purified ancient Roman lead as a promising scintillation bolometer for searching for the neutrinoless double β-decay (0ν2β) of the ^{100}Mo isotope.

$^{arch}PbWO_4$ crystals found a successful application as light guides in a low-phonon experiment to search for double beta decay in ^{106}Cd using the $^{106}CdWO_4$ scintillator in the Gran Sasso underground laboratory [24, 28].

The large-mass $^{arch}PbWO_4$ crystal grown from purified ancient Greek Pb operates as a cryogenic particle detector. The detector demonstrated excellent energy resolution below 1% over a wide energy range within 2.6…7 MeV.

The measured internal impurities of the crystal were used to estimate the background in the Region of Interest (RoI) for the detection of SN. This detector allows you to reach a background level that is by 7–9 times lower than the background target of the newest RES-NOVA experiment [29, 30]. The RES-NOVA experiment is aimed for detecting neutrinos from astrophysical sources, such as SN collapse, using cryogenic detectors made on the base of archeological lead ($^{arch}PbWO_4$), via Coherent Elastic neutrino-Nucleus Scattering (CEνNS) [29].

The RES-NOVA neutrino telescope will be installed deep in the underground Gran Sasso Laboratory (LNGS), Italy, where cover rocks of 3600 m.w.e. (meter of water equivalent) provide 10^6-fold suppression of cosmic radiation compared to sea level. The main background source in $^{arch}PbWO_4$ crystals is expected to be Pb itself, particularly ^{210}Pb, the naturally occurring radionuclide of the ^{238}U decay chain. Commercial Pb with low background content cannot be used for the experiment due to the internal predominant concentration of ^{210}Pb. The potential of the promising research project RES-NOVA for the detection of supernova neutrinos had been explored in papers [29–32].

CONCLUSIONS

The results of the scientific research work performed at the NSC KIPT on the development of a purification method of ancient lead by filtration and vacuum distillation using a specially developed device for the implementation of this method are presented. A method of oxidizing refining of lead is proposed for additional purification from chemically active impurities, including radioactive U, Th, ^{40}K.

The results of research on obtaining pilot batches of ancient Greek and Roman lead of a purity >99.9996...99.998 wt.% for growing perfect crystals of $^{arch}PbWO_4$ and $^{arch}PbMoO_4$ as scintillation detectors for low-background experiments on the registration of rare events are presented.

The results of the application of $^{arch}PbMoO_4$ and $^{arch}PbWO_4$ scintillation crystals using purified archaeological Roman and Greek lead are given. Of particular interest is the newest RES-NOVA experiment aimed at detecting neutrinos from astrophysical sources, such as SN collapse, using cryogenic detectors made on the base of ancient lead ($^{arch}PbWO_4$), via Coherent Elastic neutrino Nucleus Scattering (CEνNS) as a detection channel.

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ОЧИСТКА АРХЕОЛОГІЧНОГО СВИНЦЮ

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Описано дослідження комплексного методу глибокої очистки археологічного свинцю, розробленого у ННЦ ХФТІ. Представлено одержані результати з рафінування і застосування очищеного стародавнього свинцю. Отримано дослідні партії античного грецького і римського свинцю чистотою >99.9996...99.998 мас.% для вирощування досконалих кристалів $^{apx}PbWO_4$ і $^{apx}PbMoO_4$, які використовують у якості сцинтиляційних детекторів для реєстрації рідкісних подій у сучасних низькофонових експериментах. Найбільш цікавий експеримент RES-NOVA спрямований на виявлення нейтрино від астрофізичних джерел, таких як колапс супернової (СН), за допомогою кріогенних детекторів, що виготовлені на основі археологічного свинцю ($^{apx}PbWO_4$). Запропоновано спосіб окислювального рафінування металів, який може бути використаний для додаткового очищення свинцю від хімічних і радіоактивних домішок U, Th, ^{40}K.