

PACS: 81.20.Ym, 71.55.Ak, 64.70.D-,F-

REFINING ANCIENT LEAD BY VACUUM DISTILLATION

V.D. Virich¹, Yu.V. Gorbenko¹, G.P. Kovtun¹, S.S. Nagorny², T.S. Potina¹,
D.A. Solopikhin¹, A.P. Shcherban¹¹National Science Center "Kharkov Institute of Physics and Technology"
Kharkiv, Ukraine²INFN – Gran Sasso Scientific Institute, I-67100 L'Aquila, ItalyE-mail: shcherban@kipt.kharkov.ua

Received November 3, 2016

A complex method for refining lead by distillation in vacuum has been described. A brief comparative description of different methods of lead refining was submitted. Analysis of different methods showed that to increase the efficiency of lead deep cleaning the development of complex refining processes is required. The computational studies of the behavior of impurity elements in the ancient lead are performed. The ideal coefficients of impurities separation α_i are calculated at lead distillation temperatures. The range of volatile and nonvolatile impurities was detected by magnitude α_i in lead. Performed computational studies of the impurity elements behavior in lead formed the basis for developing an integrated method of deep refining of ancient lead. To implement this approach the special distillation device was developed, and the procedure of deep purification of lead was described. The results of the study of the deep refining ancient lead have been demonstrated. The cleaning high efficiency of the proposed approach, combined with high performance and yield of the suitable product, was shown. A pilot batch of ancient lead containing base metal > 99.998 wt. % suitable for growing high quality scintillation crystals $PbWO_4$ and $PbMoO_4$ has been produced.

KEYWORDS: ancient lead, deep refining, separation coefficients, vacuum distillation, low-background scintillation crystals

РАФІНУВАННЯ АНТИЧНОГО СВИНЦЮ ДИСТИЛЯЦІЄЮ У ВАКУУМІ

В.Д. Вірич¹, Ю.В. Горбенко¹, Г.П. Ковтун¹, С. С. Нагорний², Т.С. Потина¹,
Д.О. Солоніхін¹, О.П. Щербань¹¹Національний Науковий Центр "Харківський фізико-технічний інститут", м. Харків, Україна²INFN - Gran Sasso Scientific Institute, I-67100 L'Aquila, Italy

Описано комплексний метод рафінування свинцю дистиляцією у вакуумі. Дана коротка порівняльна характеристика різних методів рафінування свинцю. Аналіз різних методів показав, що для підвищення ефективності глибокого очищення свинцю необхідне відпрацювання комплексних процесів рафінування. Виконано розрахункові дослідження закономірності поведінки домішкових елементів в античному свинці. Розраховані ідеальні коефіцієнти поділу домішок α_i при температурах дистиляції свинцю. За величиною α_i в свинці виявлено спектр легколетких і труднолетких домішок. Виконані розрахункові дослідження поведінки домішкових елементів в свинці лягли в основу розробки комплексного методу глибокого рафінування античного свинцю. Для реалізації такого підходу розроблено спеціальний дистиляційний пристрій і описана процедура глибокого рафінування свинцю. Наведено результати дослідження глибокого рафінування античного свинцю. Показано високу ефективність очищення запропонованого підходу в поєднанні з високою продуктивністю і виходом придатного продукту. Отримано дослідну партію античного свинцю з вмістом основного металу > 99,998 мас. %, придатного для вирощування якісних скінтіляційних кристалів $PbWO_4$ і $PbMoO_4$.

КЛЮЧОВІ СЛОВА: античний свинець, глибоке очищення, коефіцієнти розподілу, вакуумна дистиляція, низько-фонові скінтіляційні кристали

РАФИНИРОВАНИЕ АНТИЧНОГО СВИНЦА ДИСТИЛЛЯЦИЕЙ В ВАКУУМЕ

В.Д. Вирич¹, Ю.В. Горбенко¹, Г.П. Ковтун¹, С. С. Нагорный², Т.С. Потина¹,
Д.А. Солонихин¹, А.П. Щербань¹¹Национальный Научный Центр "Харьковский физико-технический институт", г. Харьков, Украина;²INFN – Gran Sasso Scientific Institute, I-67100 L'Aquila, Italy

Описан комплексный метод рафинирования свинца дистиляцией в вакууме. Дана краткая сравнительная характеристика различных методов рафинирования свинца. Анализ различных методов показал, что для повышения эффективности глубокой очистки свинца необходима разработка комплексных процессов рафинирования. Выполнены расчетные исследования закономерности поведения примесных элементов в античном свинце. Рассчитаны идеальные коэффициенты разделения примесей α_i при температурах дистиляции свинца. По величине α_i в свинце выявлен спектр легколетучих и труднолетучих примесей. Выполненные расчетные исследования поведения примесных элементов в свинце легли в основу разработки комплексного метода глубокого рафинирования античного свинца. Для реализации такого подхода разработано специальное дистиляционное устройство и описана процедура глубокого рафинирования свинца. Приведены результаты исследования глубокого рафинирования античного свинца. Показана высокая эффективность очистки предложенного подхода в сочетании с высокой производительностью и выходом годного продукта. Получена опытная партия античного свинца с содержанием основного металла > 99,998 мас. %, пригодного для выращивания качественных скінтіляційних кристаллов $PbWO_4$ и $PbMoO_4$.

КЛЮЧЕВЫЕ СЛОВА: античный свинец, глубокая очистка, коэффициенты разделения, вакуумная дистиляция, низкофоновые скінтіляційні кристаллы

Lead is an excellent material for passive protection in low-background experiments as well as for the production of lead tungstate and molybdate crystals for use as optical waveguides in low-background experiments for registration of rare nuclear decays [1]. Molybdates and tungstates of lead are also the promising scintillators for use at cryogenic temperatures [2]. However, the conventional lead containing a radioactive isotope ^{210}Pb the activity of which can be tens or even thousands of Bq/kg, which is unacceptable to create the low-background scintillation devices. Период полураспада ^{210}Pb составляет 22,3 года. Therefore, a radioactivity of lead, smelted hundreds and thousands of years ago, can be very low [3-5].

Besides a purity of the radioactive scintillation detectors the strict requirements are imposed to content of stable of chemical elements, in particular, to the content of transition metals (Fe, V, Cr, Mn, Ni, Co, etc.) leading to a reduction of optical and scintillation properties of crystals. Their content should not exceed $\sim (0.1...1)$ ppm [6].

The developed methods of refining must have high performance, high cleaning efficiency (> 100 fold), high yield of suitable product ($> 95\%$) and minimal ($< 1\%$) unrecoverable losses of the refined metal.

One method for deep refining of metal is a distillation in vacuum [7, 8]. An interest in the distillation is due to the fact that this method allows to achieve a high degree of purification of metals with a high yield of good product, and it is environmentally friendly. However, a simple distillation does not provide the required degree of deep cleaning of lead with removal of certain impurities. A comprehensive approach to distillation purification of lead is more effective one.

The aim of this work was to study the regularities of behavior of impurity elements in lead during distillation purification, as well as the study of the complex process of deep refining ancient lead in combination with vacuum distillation.

EXPERIMENTAL METHODS FOR REFINING LEAD

Producing high purity lead requires multi-step processes that combine different methods of deep cleaning.

Electrolytic methods [9] allow to get a lead with total content of metal impurities of 1...100 ppm, however, to produce a metal with impurities concentration which meets to modern demands, it is subjected to further purification. In addition, when electrochemical methods of cleaning lead are used, the emission of harmful gases and vapors inevitably occurred, so careful precautions are needed.

The heating under vacuum at the temperatures of 750...1250 K is an effective method to remove the separate impurities (As, Te, Zn) from lead. However, the weak removal of contaminants such as Bi, Mg and Sb is observed at vacuum heating [10].

The zone re-crystallization can also be used for deep cleaning of lead. Refinement of lead by zone melting has been widely discussed, wherein the behavior of Sn, Cu, Ag, Au, Mg, Na, Bi, Sb was studied quantitatively and that of Co, Ni, Fe, Ge, Cd, As – qualitatively. Sn, Sb, Bi, Mg as well as Na with distribution coefficient close to one ($K \sim 1$) [11] are the impurities which difficult to remove at zone recrystallization of lead. The disadvantage of this method is the low yield (60...70%) of suitable product.

An effective way of lead refining is the method of distillation under a vacuum. The method involves manufacturing to produce a high-purity grades of lead [12].

Computational analysis of impurities behavior in lead

Theoretical basis of the distillation method of refining metals are presented in [13-15]. The distillation method for refining is based on the difference in the compositions of shared liquid mixture and steam formed therefrom. This difference is estimated by the value of relative volatility α of separable component (as applied to the refining process by distillation this value is called the separation coefficient).

In the case of ideal dilute solution, where the activity coefficients of main and impurity elements $\gamma_A = \gamma_B = 1$, the ideal separation coefficient α_i for the molecular evaporation is defined as

$$\alpha_i = \frac{p_A^0 \sqrt{M_B}}{p_B^0 \sqrt{M_A}}, \quad (1)$$

where p_A^0 , p_B^0 are the vapor pressure of pure main and impurity components A and B; M_A and M_B – the molecular weight of A and B, respectively.

Using expression (1), the ideal separation coefficients of impurities α_i , the values of which are given in Table 1 below, were calculated at temperatures of lead distillation.

By a magnitude α_i the impurities in lead can be separated into volatile (Zn, Te, Mg, Sr, Tl, Bi, Ca, Li at al.) with $\alpha_i \sim 10^{-2}...10^{-5}$, and nonvolatile (Mn, Ag, Al, Ni, Co, Cu, Sn, Si, Cr, Fe, U at al) with $\alpha_i \sim 10^2...10^9$. For most of impurity elements the values of α_i are significantly different from 1, which suggests an efficient cleaning of lead. Vapor pressure values of the elements at given temperatures were taken from paper [16].

Listed in Table 1 the values of α_i are used to calculate the efficiency of purification of the melt (x_p/x_0) vs the mass change (G_p/G_0) at 1100 K and dependence of the degree of purification of condensate (x_k/x_0) vs fraction of distillation (G_k/G_0) at 1200 K. The parameters are as follows: x_0 , x_p and x_k - initial and final content of impurities in the melt and in

the condensate of component A, weight %; G_0 , G_p and G_K - the initial and final mass of melt and condensate. Such calculations for separate impurities are given in [17]. Calculations indicate that for impurities with $\alpha_i < 10^{-2}$ the removal of volatile impurities from lead by distillation them from the melt will be effective procedure which accompanied by a loss of base metal $< 5\%$. Removal of low-volatile impurities by distillation of lead into condensate will be effective one with the yield of suitable condensate of more than 95% already at $\alpha_i > 5 \cdot 10^1$. These data were taken into account when creating the distillation device and for the choice of mode of lead distillation process.

Table 1

Calculated values of the ideal coefficients of impurities separation α_i at molecular distillation of lead under vacuum

	T=1100 K	T=1200 K	T=1300 K
Na	$7.2 \cdot 10^{-5}$	-	-
Mg	$6.4 \cdot 10^{-4}$	$1.0 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$
Zn	$1.5 \cdot 10^{-4}$	-	-
Li	$4 \cdot 10^{-3}$	$5.3 \cdot 10^{-3}$	$6.7 \cdot 10^{-3}$
Tl	$8.5 \cdot 10^{-2}$	$9.8 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$
Te	$8.2 \cdot 10^{-2}$	$3.5 \cdot 10^{-1}$	-
Bi	$6.3 \cdot 10^{-2}$	$7.4 \cdot 10^{-2}$	$8.8 \cdot 10^{-2}$
Ca	$4.4 \cdot 10^{-2}$	$3.4 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$
Sr	$1.2 \cdot 10^{-2}$	$1.4 \cdot 10^{-2}$	$2.4 \cdot 10^{-2}$
Ba	$1.2 \cdot 10^{-1}$	$1.5 \cdot 10^{-1}$	$1.8 \cdot 10^{-1}$
Pb	1	1	1
In	$3.8 \cdot 10^1$	$2.5 \cdot 10^1$	$1.8 \cdot 10^1$
Sb	$5.9 \cdot 10^1$	$3.6 \cdot 10^1$	$2.5 \cdot 10^1$
Mn	$1.4 \cdot 10^2$	$6.3 \cdot 10^1$	$3.3 \cdot 10^2$
Ga	$5.3 \cdot 10^2$	$2.6 \cdot 10^2$	$1.4 \cdot 10^2$
Ag	$6.3 \cdot 10^2$	$2.6 \cdot 10^2$	$1.4 \cdot 10^2$
Al	$4.4 \cdot 10^3$	$1.6 \cdot 10^3$	$6.7 \cdot 10^2$
Ni	$1.2 \cdot 10^4$	$3.1 \cdot 10^3$	$6.1 \cdot 10^2$
Be	$1.6 \cdot 10^4$	$4.4 \cdot 10^3$	$1.6 \cdot 10^3$
Co	$3.8 \cdot 10^4$	$9 \cdot 10^3$	$2.7 \cdot 10^3$
Sn	$4.9 \cdot 10^4$	$1.7 \cdot 10^4$	$7.4 \cdot 10^3$
Sc	$5.6 \cdot 10^4$	$1.4 \cdot 10^4$	$4.6 \cdot 10^3$
Cu	$1.2 \cdot 10^5$	$3 \cdot 10^4$	$9.8 \cdot 10^3$
Nd	$2.7 \cdot 10^5$	$7.8 \cdot 10^4$	$3.4 \cdot 10^4$
U, V, Tl, La, Fe, Si, Au, Ge, Cr	$> 10^5$	$> 10^5$	$> 10^5$

Initial lead

The subject of study was the ancient lead. The sunken 36-meter ship, which went from Spain to Italy, was discovered by archaeologists at the bottom of the Mediterranean Sea near the island of Sardinia in 1988. The more than 1,500 ingots of lead with weight of about ~ 33 kg each (Fig. 1) were on board among the transported cargo. The ship with the lead located on it, which spent about two thousand years on the seabed at a depth of 30 m, was perfectly shielded from exposure of cosmic rays.



Fig. 1. The ingots of archaeological lead with stamps (photo INFN / Cagliari Archeological Superintendence).

Distillation device and a procedure of deep refining of lead

The main stages of the complex process of lead refining were as follows. The first stage – filtration of lead combined with heating to remove surface contaminants and various impurities as well as gas-forming impurities. The second stage – re-condensation of metal into superheated liquid phase to remove the low-volatile and volatile impurity elements.

The special distillation device was developed for the implementation of complex method of deep refining [18, 19]. The apparatus for the distillation was produced of high-pure dense graphite of MPG-7 grade with a minimum content of impurities, having a chemical inertness with respect to lead. Fig. 2 shows a scheme of a distillation device for refining lead.

A feature of lead is that it belongs to a low-melting metals ($T_{\text{melt}} = 600.5 \text{ K}$) and has a low vapor pressure at the melting temperature ($4.3 \times 10^{-7} \text{ Pa}$) [16]. Earlier studies on vacuum distillation of other fusible metals (Cd, Zn, Te, etc.) show that acceptable rates of evaporation in the processes of distillation correspond to pressures of the vapor at a level (27...80) Pa, that for lead corresponds to the melt temperature 1200...1250 K [16]. These features were taken into account when developing the new approach to the process of lead refining.

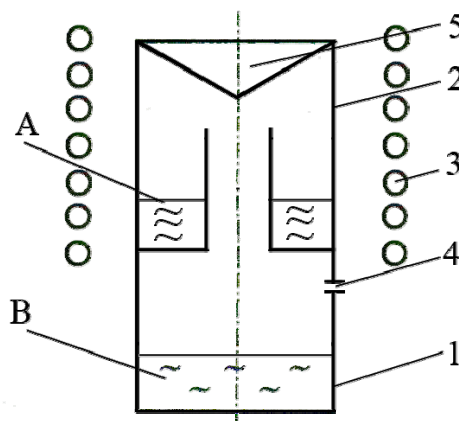


Fig. 2. Scheme of the distillation device for refining lead: A - initial lead; B - refined metal; 1 - condenser 2 - crucible 3 - heater, 4 - hole (aperture) 5 - steam deflector.

The operation of the device for lead refining by vacuum distillation consists as follows. The initial lead was pre-warmed and subjected filtration under vacuum. Then, the filtered lead weighing about 1.5 kg was placed in the crucible 2, the device chamber was evacuated and supported under a pressures of not more than 10^{-1} Pa during refining. Lead melt was heated up to 1220 K, then it was evaporated and collected in the condenser 1 at a temperature about 1120 K in the form of refined metal B. The removal of low-volatile impurities (Cu, Fe, Si, Ni, Co, V, Cr, Au, Ag, Al, Tl, Sb, Sn, Mn, etc.), remaining in a lead residue in the crucible 2, was occurring during evaporation of lead to 95% of the initial charge. Volatile impurities, that partly transferred into the condenser together with lead during its condensation, were removed through a hole 4 in the condenser due to the exposure of purified condensate during the refining process (~ 5 hours) at a temperature ($T_{\text{cond.}} \approx 0.8T_{\text{evapor.}}$). The lead was subjected to a double distillation according to the described procedure. After each distillation process, the residue in the crucible was about 30...50 g. The Fig. 3 shows a photo of refined lead after distillation.



Fig. 3. The distillates of the refined ancient lead by the weight of ~ 1 kg each.

RESULTS AND DISCUSSION

Content of impurities in lead samples was determined by laser mass spectrometry of high resolution with double focusing according to Mattauhu Duke MS-3101 with registration on the film, to measure optical density of which the microphotometer registering IFO-451 was used.

The main advantages of mass spectrometers having ion source and laser dual focus are on the one hand, the high absolute and relative sensitivity, and on the other hand, the possibility of simultaneous registration with subsequent quantitative determination of almost all elements (from lithium to uranium). Random error of the analysis results is characterized by the value of relative standard deviation 0.15...0.30.

Analysis of impurity elements in the initial ancient and refined lead was performed for 72 elements. The content of the main impurity elements in the initial and refined lead is shown in Table. 2. Moreover, the table indicates only the impurity elements, the content of which in the initial lead was at a level exceeding the limit of sensitivity of the laser mass spectrometer. The concentration of other impurities in the refined lead was below the detection limit of the method of laser mass spectrometry: for Rb, Y, Zr, Nb, Ru, Pt, Au $< 1 \cdot 10^{-2}$ ppm; for Sc, In, Te $< 1 \cdot 10^{-1}$ ppm; for Se, Pd < 1 ppm.

The purity of the initial lead on the sum of impurities is about ~ 99.7 wt. %. It should be noted that the main impurity elements in the initial lead are Cu, Ag, Sn, Sb, and their multiplicity of distillation removal is the value from ~ 100 to 600. The purity of lead after refining with taking into account these and the other impurities is > 99.998 wt. %.

A number of impurities (Na, K, Ca, S, As) there are also in the initial lead, and the removal efficiency of this elements is low - 1.5...2.5. Such situation for sodium can be explained by the fact that its content is at the sensitivity limit of the method definition, and calcium, sulfur and arsenic is apparently transferred to the refined metal in the form of stable compounds. Nevertheless, the proposed lead refining procedure (heating, filtration and a double distillation) provide a high (more than 100 fold) the efficiency of metal purification.

Table 2

The content of the main impurity elements in ancient lead before and after refining by distillation under vacuum

Element	before refining	after refining
	content, ppm	
Na	0.05	0.05
Mg	0.08	< 0.03
Al	0.12	0.009
Si	0.044	< 0.04
S	0.76	0.4
K	0.1	0.045
Ca	0.2	0.16
Mn	0.12	< 0.07
Fe	0.1	< 0.08
Ni	0.37	< 0.1
Zn	< 0.2	< 0.2
Cu	23	< 0.05
As	1.6	0.8
Ag	300	< 0.5
Cd	< 0.8	< 0.8
Sn	1800	7.7
Sb	560	6.3

The authors of this work have produced earlier a pilot batch of the Greek archaeological lead with an upper limit for a wide range of elements at the level 0.1...0.6 ppm [17, 18]. On the basis of obtained high purity Greek lead the high-quality scintillation single crystal of tungstate lead $PbWO_4$ was grown. The crystal was successfully used as an optical fiber in a low-background experiment to search for double beta decay ^{106}Cd with the help of scintillator $^{106}CdWO_4$ in an underground laboratory in Gran Sasso, Italy [20].

Thus, proposed in this paper the complex method of lead refining allow to produce a final product of more than 2 orders of magnitude purer compared with the initial metal. The obtained so ancient lead is supposed to use for the growth of scintillation crystal of tungstate and molybdate of lead.

CONCLUSIONS

The computational studies of the behavior of impurity elements in the ancient lead were carried out. Ideal coefficients of impurities separation (α_i) were determined at the temperatures of distillation and condensation of lead, on the basis of these coefficients the range of low-volatile and volatile impurities was identified during refining of lead by distillation under a vacuum.

A complex method of refining in combination with vacuum distillation was proposed and investigated in the work for the deep cleaning of ancient lead. To implement such method, the special distillation device has been developed and tested. The purification efficiency of the proposed method is better by more than two orders of magnitude relative to the initial purity.

The pilot batch (~ 2.5 kg) of ancient lead of a purity > 99.998 wt % suitable for the growing scintillation crystals $PbWO_4$ and $PbMoO_4$ was fabricated.

REFERENCES

1. Danevich F.A. et al. Application of PbWO_4 crystal scintillators in experiment to search for 2β decay of ^{116}Cd // Nuclear Instruments and Methods in Physics Research. A. – 2006. – Vol. 556. – P. 259 – 265.
2. Danevich F.A. et al. Feasibility study of PbWO_4 and PbMoO_4 crystal scintillators for cryogenic rare events experiments // Nuclear Instruments and Methods in Physics Research A. – 1991. – Vol. 622. – P. 608 – 613.
3. Alessandrello A., Cattadori C., Fiorentini G. et al. Measurements on Radioactivity of Ancient roman Lead to be Used as Shield in Searches for Rare Events // Nucl. Instrum. Methods. – 1991. – Sect. B. – Vol. 61. – No. 1. – P. 106 – 117.
4. Alessandrello A., Allegretti F., Brofferio C. et al. Measurements of Low Radioactive Contaminations in Lead Using Bolometric Detectors // Nucl. Instrum. Methods. – 1993. – Sect. B. – Vol. 83. – No. 4. – P. 539 – 544.
5. Danevich F.A., Kim S.K., Kim H.J. et al. Ancient Greek lead findings in Ukraine // Nucl. Instrum. Methods. – 2009. – Sect. A. – Vol. 603. – No. 3. – P. 328 – 332.
6. Kovtun G.P., Boiko R.S., Danevich F.A. et al. Proizvodstvo i svojstva nizkofonovykh scintillyatorov vol'framatov kadmiya i svinca dlya poiska dvojnogo beta-raspada [Development and properties of cadmium and lead tungstate low-background scintillators for double beta decay experiments] // Yaderna fizyka ta energetyka [Nuclear physics and atomic energy]. – 2014. – Vol. 15. – No. 1. – P. 92 – 100. (In Russian)
7. Ivanov V.E., Papirova I.I., Tihinskij G.F., Amonenko V.M.. Chistye i sverhchistye metally [Pure and very pure metals] // M.: Metallurgiya, 1965. – 170 p. (In Russian)
8. Pazuhin V.A., Fisher A.Ya. Razdelenie i rafinirovaniye metallov v vakuume [Separation and refining of metals in vacuum]. – M.: Metallurgiya, 1969. – 204 p. (In Russian)
9. Kozin L.F., Morachevskij A.G. Fiziko-himiya i metallurgiya vysokochistogo svinca [Physical chemistry and metallurgy of high purity lead]. – M.: Metallurgiya, 1991. – 223 p. (In Russian)
10. Aleksandrov B.N., Udovikov V.I. Povedenie primesej v svince pri vakuumnom progreve, distillyacii i zonnnoj plavke [Behavior of impurities in lead at warming, distillation and zone melting up the vacuum]. Fizika kondensirovannogo sostoyaniya [Condensed matter physics] // Har'kov: FTINT AN USSR, 1973. – No. 25. (In Russian)
11. Aleksandrov B.N., D'yakov I.G. Zonnaya ochistka alyuminiya i svinca [Zone-refining of aluminum and lead] // Fizika metallov i metallovedenie [The Physics of Metals and Metallography], 1962. – Vol. 14. – No. 2. – 267 p. (In Russian)
12. Esyutin V.S., Nurgaliev D.N. Vakuum-distillyacionnaya ochistka svinca ot primesej v apparate nepreryvnogo dejstviya [Vacuum-distillation lead purification from impurities in the unit of continuous action] // Cvetnye metally. – 1975. – No. 12. – P. 28-30. (In Russian)
13. Devyatyh G.G., Elliev YU.E. Vvedenie v teoriyu glubokoj ochistki veshchestv [Introduction to the theory of deep cleaning substances]. – Metallurgiya, 1973. – 320 p. (In Russian)
14. Belyaev A.I. Fiziko-himicheskie osnovy ochistki metallov i poluprovodnikovyykh materialov. – M.: Metallurgiya, 1973. – 320 p. (In Russian)
15. Devyatyh G.G., Elliev YU.E. Glubokaya ochistka veshchestv [Deep cleaning substances]. – M.: Vysshaya shkola, 1974. – 180 p. (In Russian)
16. Nesmeyanov A.N. Davlenie para himicheskikh ehlementov [The vapor pressure of the chemical elements]. – M.: Izd-vo AN SSSR [Publisher of the USSR Academy of Sciences], 1961. – 396 p. (In Russian)
17. Boiko R.S., Virich V.D., Danevich F.A. et al. Ultrapurification of Archaeological Lead // Inorganic Materials. - 2011. - Vol. 47. – No. 6. – P. 645 – 648.
18. Kovtun G.P., Shcherban' A.P., Solopikhin D.A. et al. Purification of Cadmium and Lead for Low Background Scintillators. Proc. 1st Int. Workshop Radiopure Scintillators for EURECA (RPScint'2008). – Kyiv, 2009. – P. 59 – 63.
19. Patent № 94547, C2. Ukraine. Ustrojstvo dlya rafinirovaniya metallov distillyaciej v vakuume [An apparatus for refining metals by distillation in vacuum]. Shcherban' A.P., Kovtun G.P., Solopihin D.O. Byul. – No. 9. – 2011. (In Russian)
20. Tretyak V.I. et al. First results of the experiment to search for 2β decay of ^{106}Cd with $^{106}\text{CdWO}_4$ crystal scintillator in coincidence with four crystals HPGe detector // EPJ Web of Conference 65 (2014) 01004.