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Проведеними дослідженнями показано вплив методів аналізу на точність визначення проби золота дорогоцінних сплавів різного компонентного складу в системі пробірного контролю. Встановлено вплив лігатурного складу ювелірних сплавів на визначення проби. Зокрема експериментально підтверджено, що нікель у поєднанні з цинком як комплексний легуючий компонент суттєво змінює процес купелювання золотих сплавів. Це приводить до відхилення проби золотого сплаву, визначеної купелюванням у порівнянні з рентгенофлуоресцентним аналізом (РФА), у бік зменшення в межах від 0,10 до 0,15 %.

За допомогою РФА сплавів на основі золота з вмістом нікелю встановлено мікролегування модифікаторами й активно діючими розкислювачами (індій, паладій, платина і ін.). Встановлено, що модифікатори використовують як окремо, так і комплексно, але суттєво впливу на визначення проби вони не чинять.

Виявлено ряд систематичних і випадкових помилок в методиках, які впливають на результати визначень і відносяться до техніки виконання підготовчих операцій, а також операцій виконання аналізів. На підставі одержаних результатів розроблено постійний температурний режим та вдосконалено процедуру процесу купелювання золотих сплавів з вмістом нікелю з метою подальшого вдосконалення та метрологічної атестації методики.

Доведено, що використання методу РФА для контролю проби і вмісту компонентного складу сплаву сучасних ювелірних виробів та музейних цінностей (антикваріату) на основі золота є можливим не лише як методу скринінгу. Метод може замінити пробірний камінь (з очевидними перевагами) і бути альтернативою купелюванню. Застосування РФА для поточного контролю проби та вмісту сплаву ювелірних виробів доцільно збільшити до 30 % (проти 2 % відповідно до чинного законодавства). Його використання дозволить збільшити кількість аналізованих зразків без погіршення товарного вигляду ювелірних виробів замовника

Ключові слова: сплави золота, лігатурний склад, рентгенофлуоресцентний аналіз, метод купелювання (пробірний аналіз), пробірний контроль

INFLUENCE OF THE ALLOY COMPOSITION ON DETERMINING THE MILLESIMAL FINENESS OF GOLD BY X-RAY FLUORESCENT AND ASSAY ANALYSIS

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1. Introduction

The quality and value of a precious alloy is primarily determined by millesimal fineness of gold, regulated by the legislative base as the state standard and certifying

the content of weight units of the main precious metal in one thousand weight units of the alloy. However, as a century ago, the main objective of the assay control remains unchanged – the consumer should get a piece of jewelry, the value of which by the content and the kind of precious

metal is guaranteed by the state and is certified by the mark. In addition, to remove the technical barriers and to implement free trade, jewelry products on the European market should have the mark of the International Vienna Convention on control and branding of products from precious metals “Common Control Marks” – CCM [1]. They are recognized by all signatories no matter in which country testing and branding were performed. Thus, in the face of the trade globalization the problem of ensuring the quality and conformity of jewelry products with the national, the European or global standards is becoming increasingly important.

During accreditation and execution of works in accordance with the requirements of ISO 17025 regarding joining the International Vienna Convention, assay treasury enterprises should demonstrate high precision of determining millesimal fineness of gold in precious alloys.

Determining the millesimal fineness of gold jewelry alloys in the member countries of the International Convention is carried out using the method of cupellation (assay analysis) for ISO 11426:2007, which is the most accurate and ruining [1, 2]. The essence of the method lies in removal of non-precision alloying metals from the melted precious alloy by oxidation of lead at the temperature of 900 °C in the cupel (porous crucible), located in a muffle furnace. The composition of jewelry alloys based on gold with the content of zinc, nickel, palladium and copper has been improved for years. Introduction of a new composition of alloying components and impurities causes a change in the systems of condition, mechanisms of formation of a solid solution, product manufacturing technology, structure, and properties. In addition, it complicates a complex process of analysis for existence in it of the main component – gold.

Introduction of metals of the nickel and platinum group to precious alloys reduces the gold standard during cupellation. In addition, fluidity of the melt of liquation non-homogeneity in the cast condition, related to the violation of technology essentially influences determining the 585 millesimal fineness of gold of the alloys (of systems Au–Ag–Zn–Ni–Cu and Au–Ni–Zn–Cu).

The new non-destructive spectrometric methods have been actively applied in the practice of assay control for the last 10 years. Despite a number of advantages related to the use of the XFA (X-ray fluorescence analysis) in determining the millesimal fineness of an alloy, its results are difficult to analyze [1]. This applies to the cases when there is a coating or there are two different types of alloys (yellow and white gold; gold and silver), or the product after casting was subject to additional heat treatment (recrystallization annealing) of not high quality.

However, currently there is a lack of fundamental scientific research regarding the comparison of accuracy of millesimal fineness of white gold alloys with different component composition, determined by the X-ray fluorescence analysis and assay analysis, as well as the correlation between the indicators of the millesimal fineness.

Therefore, the studies of determining the impact factors on determining the millesimal fineness of gold of a precious alloy by the method of cupellation and XFA, establishing the correlation between them and further improvement of the technique of assay analysis should be considered relevant.

2. Literature review and problem statement

Determining the content of precious metal (millesimal fineness) in the alloy has its specificity, indicated in the regulatory-legislative base [5, 6].

Paper [7] deals with the problems of determining gold and the content of impurities in highly doped gold alloys. The main attention is paid to determining the content of gold and the review analysis of the methods based mainly on the emission spectroscopy. However, there is no assessment of the corresponding indirect methods of determining the content of gold.

Article [8] indicates the possibility of using spectrometry as an effective method for studying alloys of gold. According to the author, it is spectrometry that is a valuable additional component of the analytical strategy of chemistry of precious metals along with the method of cupellation. However, the correlation of the results of these methods was not performed in this paper and statistical dependences were not determined.

The quantitative chemical analysis of gold in alloys of precious metals, the use of reference material from a gold alloy to control stability of experimental parameters was described in paper [9]. The authors noted that the method of cupellation is most commonly used in the assay control. This is due not only to its convenience and availability of appropriate standardized procedure, but mainly due to a rather small error of measuring results obtained at cupellation. However, the comparative analysis of research results obtained by cupellation and by other methods was not performed.

Paper [10] describes the quantitative determining precious metals in alloys by the gravimetric method of cupellation and X-ray fluorescence analysis. However, only procedural features, advantages and disadvantages of each method were determined.

In article [11], considerable attention was paid to the use of XFA method for determining the content of gold in alloys as the most progressive technologies of research. Along with this, the impact of the component composition on the accuracy of determining millesimal fineness was not identified, there is no comparison of the results of the XFA with the results obtained by other methods and with specifications on the alloys themselves.

The issue of determining gold content (millesimal fineness) in modern alloys, in particular, gold-based white alloys, by the ruinous techniques remains not enough studied today. However, there are progressive enough developments, in particular [12], in which the authors propose the improved cupellation techniques due to the reconstruction of the furnace and development of a new slag separator with subsequent automation of this process. According to the authors, this will significantly reduce the duration of research and increase the accuracy of the obtained results.

The main problem regarding precise determining of the millesimal fineness of precious metal is selection of the representative sample of material for testing. Primarily, this refers to a wide range of new alloys containing nickel, zinc, gallium, palladium, zirconium, silicon, cadmium, magnesium, boron, etc. The specified metals affect the course of testing and the change in the magnitude of millesimal fineness when performing the assay analysis (cupellation). However, no studies that specify this influence were found as evidenced by paper [13].

In addition, the research in paper [11] indicates that precision of determining millesimal fineness with the help of the XRA method is significantly influenced by the harmonized structure of the alloy, which is noted in the research in [11]. The authors argue that the extension of the lines of the X-ray displays in the homogenized condition was recorded in the alloys. Besides, it is possible to conclude from the assessment of the artificially segregation state of the base of the peaks that the magnitude of extension of the lines of the homogenized samples can not be regulated by segregation, but is rather caused by micro doping of modern alloys.

In papers [14–16], the chemical composition of the studied objects was determined by the XFA method. It is worth noting that XFA has become a standard method in the archaeological science through its non-destructive nature. The method is widely used to study numismatic and antiquarian collections of archaeological findings. The data obtained with its use can be correlated with production processes, the origin of the raw materials and geographical distribution of historical mints to prove authenticity. In these works, the XFA was pointed out the method of screening, however, the mechanics of the process itself in expert studies was not explored.

It is interesting that in paper [16], the first analyses of samples obtained by the XRF method, were proved by the results of the plasma mass spectrometry.

Research [17] proves that homogeneity of the structure of the alloy of a sample is a necessary condition for precision of measurement with the help of the XFA method. The author notes that the substantial advantages of the method include its high rate and the fact that it operates in a non-destructive way. Thus, it is a perfect supplement to cupellation for the statistical quality control of samples. And the impact of heterogeneity on the result of the analysis should be reduced or eliminated by measuring in different positions. According to the authors, the XFA is clearly superior to cupellation because the latter involves melting of the whole part in order to obtain a representative result. However, the paper did not present any quantitative and qualitative results, only a comparative analysis of the essence of the methods.

The methods of cupellation and the XFA are compared in paper [18] at a much deeper level. The application of energy-dispersed X-ray fluorescent spectrometer for the detection of layers of cladding, such as rhodium and nickel, is discussed in the findings. The authors illustrate the usefulness of the XFA in analytical laboratories not only as a method of screening, which can replace the touchstone (with a number of obvious advantages over it). In addition, it is an alternative to cupellation for the analyses, which present the basic results and an additional method when it is necessary to determine the entire composition of a sample. However, the authors do not analyze the effect of alloying components on the accuracy of obtained results, they do not determine the correlation between the methods, as well as quantitative indicators characterizing it.

The above makes it possible to assert that there is a need for theoretical and practical substantiation of the requirements for the procedure of the ruinous methods of testing modern jewelry alloys based on gold. In particular, it enables determining the millesimal fitness in them with the minimal error using updated techniques and equipment.

There are also the grounds to believe that insufficient studying of the impact of the component composition of gold alloy on determining millesimal fineness by cupellation and

its correlation with the XFA causes the need for research in this direction.

3. The aim and objectives of the study

The aim of this research is to establish the impact of the component composition of precious alloys on determining precision of millesimal fineness of gold by the method of assay (cupellation) and X-ray fluorescence analysis. This work will ensure the establishment of the correlations between the precision of millesimal fineness of the sample, determined by the assay and X-ray fluorescence analysis. It will also give an opportunity to choose the method and techniques for testing gold-based white jewelry alloys with the content of alloying components, such as silver, zinc, nickel, palladium to address the specific needs of the assay control.

To achieve the set goal, the following tasks were solved:

- to determine the impact of the alloy composition of alloys based on modern and ancient gold on the accuracy of determining millesimal fineness (gold content) by the X-ray fluorescence analysis;
- to determine the impact of the alloy composition of jewelry alloys based on gold on the accuracy of determining millesimal fineness by the method of cupellation (assay analysis);
- to improve the technique of cupellation of alloys based on gold of the white color with the content of nickel and zinc for the assay control;
- to establish the correlation and statistical relationship between millesimal fineness of gold, determined by different methods of analysis.

4. Materials and methods for testing gold alloys with various alloying components

4.1. The studied materials and equipment involved in the experiment

The study of alloys was conducted on the samples of jewelry of white gold of 585 millesimal fineness containing silver, copper, zinc, nickel, palladium, indium by the cupellation method and the XFA method for comparison and correlation of results. The work was performed on the basis of the accredited laboratories of treasury enterprises of the assay control of Ukraine, the laboratory of Kyiv national university of trade and economy, laboratory of the National University of food technologies in accordance with the agreement on scientific cooperation. All modern samples of jewelry arrived for the assay control of Kyiv, Lviv, Odesa and Donetsk treasury enterprises of assay control in the period from 2008 to 2017 on request of economic entities. During sampling, the following requirements were met: the jewelry pieces were made by method of casting by the melted models; the items were made from alloys of white color gold of 585 millesimal fineness.

In addition, 42 archaeological jewelry items of the period from V century BC to II century AD were explored. The samples were provided by the Museum of historical treasures of the National historical museum of Ukraine to be explored using XRA and the raster electronic microscope in accordance with the Treaty of cooperation.

During the cupellation, two control samples – checks – were prepared on each sample of the alloy. Checks were

received from gold, silver, zinc, nickel and copper, according to the composition of the alloy. The weights of the batches of samples of jewelry alloys and gold for the checks were determined with the error that did not exceed 0.00002 g, of silver for quartation and of copper with the error of not more than 0.0002 g.

The XFA of the jewelry (samples) was performed on the spectrometer ElvaX (Ukraine) – the desktop laboratory energy-dispersive X-ray fluorescent spectrometer (EDXRF) of the company “Elvatech”. The spectrometer is a measuring device for express analysis of the elemental composition of substances that are in different aggregate states.

The base model of the spectrometer ElvaX can detect a significant part of elements from chlorine to uranium, recording the spectra at the radiator voltage of the order of magnitude of 40–49 kV. The standard time of set is 100 seconds. 10 seconds is enough for the approximate evaluation of the composition of alloys that do not contain light elements.

The qualitative composition of the jewelry alloy was determined by the spectrum, which was displayed on the monitor of the device (Fig. 1).

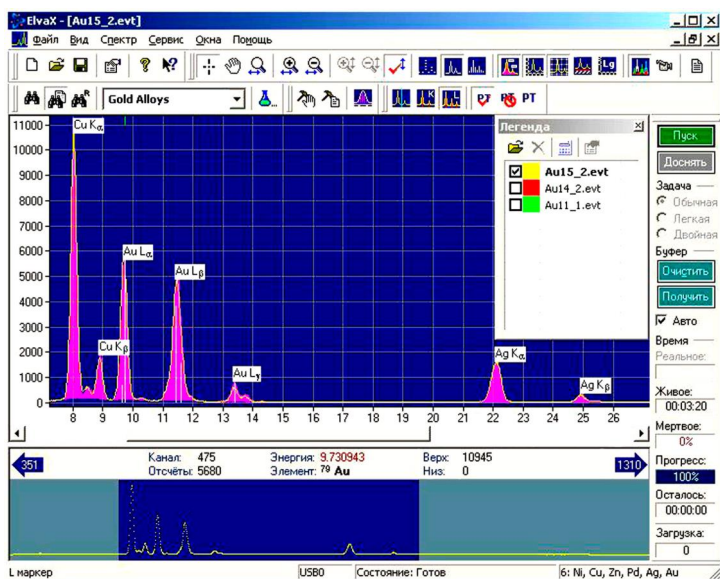
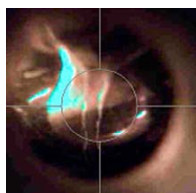


Fig. 1. Spectrum of the sample of gold alloy at a monitor screen

The alloys of unknown composition were identified using the set analytical parameters, as well as by comparison with the alloys of the known composition, comparing the spectrum.

ElvaX Software is a part of the ElvaX spectrometer and performs the functions of the controlling shell for registration of X-ray spectra with their subsequent processing for the analysis of substances (Fig. 2).



Atomic number	Element	Concentration, %
79	Au	58.592
29	Cu	33.174
47	Ag	7.383
30	Zn	0.851

Fig. 2. Visualization of the reference point of the method of X-ray fluorescence analysis of gold jewelry from alloy GoSiNm 585-70-1.5

The study of the microstructure of the samples was performed by the method of raster electronic microscopy on the microscope BS-340, equipped with the digital image analysis system with high resolution (4,096×4,096 pixels) at magnification in the range from 10 to 2×105. The micro-sections (dimensions 2×2) were prepared by polishing the surface layer of the sample. The sample and sequentially all its areas (microvolume) that were required for the research were irradiated by a finely focused electronic beam of the energy analyzer of X-ray spectra Link-860 (England). The conditions of the analysis were as follows: energy of excitation was 20 keV; calibration standard was Co; current on the standard – $5 \cdot 10^{-10}$ A; time of analysis was 200 sec. The program for quantitative analysis ZAF4/FLS was used. The maximum area of generation of X-ray radiation under the specified conditions is about 0.3 μm in the sample of pure gold, this value for silver is 0.8 μm .

The process of cupellation was carried out under oxidizing conditions in muffle furnaces of the companies “Fisher” (France), “Naborten” (Germany) with controlled oxidizing atmosphere. Each product was cut, the required weight of the studied part of the product was measured and rolled in the mills. The strips were finely cut, the batches from the studied alloy were made. The temperature of 1,000–1,020 °C was maintained in the furnace during the whole process, the temperature is maximum at the end of cupellation, when the ratio of lead to noble metals falls dramatically. The duration of the cupellation process was about 25 minutes. The gold and spirals were weighed according to GOST 17234-71 on assay scales with accuracy of 0.00001 grams.

4. 2. Procedure for determining the millesimal fineness of gold alloys by the assay and X-ray fluorescence analysis

The millesimal fineness in gold alloys with the content of different alloying impurities was established by the assay analysis (cupellation) [19]. Lead bags were applied for the batches of the studied alloys and checks. The amount of lead was calculated depending on the weight fraction of copper in the alloy. At the weight fraction of 1–5 %, the amount of lead was 2 g; at 5.01–10 %, it was 2.5; at 10.01–20 % < it was 3; at 20.01–30 %, it was 3.5; at 30.01–40 %, it was 4; at 40.01–50 %, it was 4.5; at more than 50 % – 5 g. The weight of the silver batch for quartation exceeds the weight of gold in the batch of the alloy or the check not less than by 2.3 times (but not more than by 3 times).

Completeness of the extraction of nickel from the alloy was ensured by the additional lead content in comparison with the traditional amount for gold alloys of yellow color and a change in the cupellation procedure.

For the gold alloys of white color, the divergence between the results of two parallel methods of determining did not exceed 0.06 %. If the divergence between the results of the parallel methods of determining exceeded the admissible value, the analysis was repeated. The divergence between the results of the analysis does not exceed the permissible divergence of 0.12 % at reliable probability of 0.95.

The component composition and impurities of the jewelry alloy were determined by X-ray fluorescence analysis.

Measurement with the use of the X-ray fluorescence analysis was conducted according to the methodology approved by the State array service of February, 18, 2008 [6].

The technique of measurements of weight fraction of different chemical elements in gold-based jewelry alloys on the spectrometer SER-01 involves the excitation of atoms of the sample during X-ray radiation. The intensity of the characteristic radiation was recorded by the spectrometer.

The spectrometer automatically processes the range of intensities of the characteristic radiation and calculates the weight fraction of the chemical elements in the sample by the grade characteristic of dependence of intensity on the content of chemical elements taking into consideration the matrix effects. The spectrometer is provided with the database on the content of current alloys in Ukraine, in this case, the program determines concentrations of chemical elements in the sample, the brand of the alloy, from which this sample was cast.

Control of convergence of results of determining the weight fraction of metals in the samples of jewelry alloys of gold, control of errors of the measurement of the weight portion of metals in the samples of jewelry alloys of gold was carried out in accordance with the current technique [6]. Two measurements of millesimal fineness – ω_1, ω_2 – were performed for each studied sample. In this case, the weight fraction of metal in jewelry gold alloys (ω), % was calculated from formula (1):

$$\omega = 0.5 (\omega_1 + \omega_2), \tag{1}$$

where ω_1, ω_2 are the results of determining the weight fraction of metal in jewelry gold alloys, %.

The result of the measurements and calculations was rounded up to decimal character after the point. The results of measurements and calculations of weight fraction of metal in jewelry alloys have the form:

$$(\omega \pm \Delta) \%, P=0.95; n=2,$$

where Δ is the boundaries of absolute error, %.

During determining the weight fraction of chemical elements, the boundaries of absolute error were established $\pm \Delta, \%$: gold – 0.3, silver – 0.3, palladium – 0.3, copper – 0.2, platinum – 0.3, zinc – 0.4, nickel – 0.4, cadmium – 0.2, indium – 0.3.

During each measurement, the convergence of the results of determining the weight fraction of metals in the samples of jewelry alloys was controlled, which was calculated provided that (2):

$$|\omega_1 - \omega_2| \leq 0.2. \tag{2}$$

Selection and preparation of samples were performed by the sampling procedure. The weight of the sample was from (0.20 ± 0.05) g to (12.0 ± 0.1) kg, the section for measurement was not less than 2 mm, the thickness of the sample was not less than 0.3 mm. All samples had an even smooth surface free from impurities or coatings. For gold-based jewelry alloys, the discrepancy between the results of two parallel methods of determining Millesimal fineness by the method of XFA did not exceed 0.06 %. Each sample was tested in different points. The total number of the points of research for each sample was from 2 to 10, depending on the structure, shape, and the type of alloy. During the analysis, the sample was oriented so that the grooves from polishing on its surface were parallel to the optical path of X-ray radiation.

5. Results of determining the millesimal fineness of gold in jewellery alloys with different content of alloying components

The content of the component composition of precious alloys based on white gold jewelry of 68 samples was determined by the method of X-ray fluorescence analysis (XFA) to evaluate their compliance with the requirements of the current regulatory and technical documentation. According to the design of a piece of jewelry, from 3 up to 5 control points were selected for each sample. The results testing the composition of the alloys are shown in Table 1.

Table 1

Results of testing precious metal alloys based of white gold of 585 millesimal fineness by XFA method, %

No. of sample	Millesimal fineness		Component composition of alloy, %						Meeting the standard
	claimed	fact	Au	Ag	Ni/Pd	Cu	Zn	the rest	
1	2	3	4	5	6	7	8	9	10
1	585	585	62.85	0.33	6.81	27.90	1.99	–	n/m *
2	585	500	58.30	–	8.96	25.69	7.67	Fe 0.05	n/m
3	585	585	59.67	1.25	9.12	25.12	4.78	–	n/m
4	585	500	58.30	–	8.96	25.69	7.67	Fe 0.05	n/m
5	585	585	59.39	1.06	7.98	26.36	5.13	Fe 0.04	n/m
6	585	585	59.49	0.27	9.76	26.04	4.35	–	n/m
7	585	585	59.39	1.06	7.98	26.36	5.13	Fe 0.04	n/m
8	585	585	60.10	0.36	8.08	25.73	5.71	–	n/m
9	585	585	60.34	1.60	4.83	28.37	4.87	–	n/m
10	585	585	58.48	1.06	8.01	12.40	7.72	–	n/m
11	585	585	58.60	0.99	8.33	24.27	7.77	–	n/m
12	585	585	58.82	1.00	8.13	24.12	7.78	–	n/m
13	585	500	54.95	0.20	9.28	28.39	7.14	–	n/m
14	585	500	58.55	0.45	9.12	25.65	6.17	–	n/m
15	585	585	64.37	2.83	7.52	22.49	2.77	–	n/m

Continuation of Table 1

1	2	3	4	5	6	7	8	9	10
16	585	585	64.59	3.76	4.14/0.04	27.39		In 0.03	n/m
17	585	585	64.37	2.83	7.52	22.49	2.77	–	n/m
18	585	375	37.93	2.26	14.5	38.79	6.50	–	n/m
19	585	500	57.18	3.62	8.05/0.02	23.72	7.35	–	n/m
20	585	500	57.10	4.96	6.96/0.05	24.52	6.30	Cd 0.02; Fe 0.04	n/m
21	585	585	61.01	0.13	7.82	25.57	5.35	–	n/m
22	585	585	59.32	–	4.59	31.02	2.93	–	n/m
23	585	500	57.95	–	8.54	26.42	7.03	–	n/m
24	585	585	61.01	0.13	7.82	25.57	5.35	–	n/m
25	585	585	59.62	0.12	8.77	28.69	2.73	–	n/m
26	585	500	58.36	–	7.92	25.19	8.52	Rd coating	n/m
27	585	585	59.29	0.81	8.51	25.58	5.69	Cd 0.06	n/m
28	585	500	58.30	0.68	7.89	25.23	7.82	Rd coating	n/m
29	585	585	60.40	0.85	8.08	27.60	2.91	Cd 0.14	n/m
30	585	585	–	33.92	11.8	46.60	7.63	–	n/m
31	585	500	58.16	–	9.43	26.34	5.98	–	n/m
32	585	585	59.93	3.85	7.85	25.02	3.34	–	n/m
33	585	585	60.64	6.84	4.20	25.57	2.48	Cd 0.21	n/m
34	585	585	59.45		9.79	24.55	6.19	–	n/m
35	585	585	60.80	10.52	5.57/1.35	19.66	2.02	–	n/m
36	585	585	60.63	1.44	7.05	26.81		–	n/m
37	585	500	54.13	2.11	9.71	29.80	3.77	Fe 0.11	n/m
38	585	585	59.17	0.24	8.23	26.76	5.58		n/m
39	585	500	52.89	9.05	7.60/0.25	24.83	4.68	Cd 0.65	n/m
40	585	585	58.86	1.41	5.95	29.49	4.21	–	n/m
41	585	585	59.54	3.98	–	34.86	1.56	–	n/m
42	585	500	55.05	24.75	–	12.58		Cd 0.04	n/m
43	585	500	55.01	30.90	/10.0	3.95		Fe 0.07	n/m
44	585	585	59.29	5.67	6.86/0.32	22.85	4.83	Cd 0.08	n/m
45	–	–	32.05	49.29	1.92/4.41	11.67	0.49	Cd 0.06	n/m
46	585	585	60.82	6.24	8.29	22.36	2.23	–	n/m
47	585	500	57.95	8.00	7.68	26.26		–	n/m
48	585	500	57.76	–	8.70	26.03	7.42	–	n/m
49	585	585	61.44	31.19	–/4.58	0.33	–	–	n/m
50	585	585	58.86	–	8.08	23.94	9.01	–	n/m
51	585	585	58.69	0.95	8.38	24.77	7.14	–	n/m
52	585	585	59.54	–	8.88	24.61	6.97	–	n/m
53	585	585	59.27	2.62	8.47	23.33	6.31		n/m
54	585	585	58.86	2.45	5.55/0.13	27.28	5.73	–	n/m
55	585	585	60.76	6.45	3.51/0.21	23.86	5.21	–	n/m
56	585	585	59.97	0.41	8.44	25.78	5.40	–	n/m
57	585	585	58.93	0.59	9.75/0.17	25.69	4.87	–	n/m
58	585	585	59.10	0.30	6.49	28.20	5.91	–	n/m
59	585	585	58.85	–	9.08	24.99	7.07	–	n/m
60	585	585	59.57	5.88	8.68	21.79	4.08	–	n/m
61	585	585	58.88	–	9.00	24.85	7.27	–	n/m
62	585	585	59.24	0.71	9.29	26.05	4.72	–	n/m
63	585	500	58.33	2.74	7.87	25.52	5.54	–	n/m
64	585	585	59.40	0.32	7.96	24.37	7.95	–	n/m
65	585	585	59.77	2.41	4.82	27.51	5.49	–	n/m
66	585	585	59.20	8.15	5.49	20.25	6.91	–	n/m
67	585	585	58.78	–	25.10	3.65	12.5	–	n/m
68	585	585	59.00	2.68	9.35	26.73	2.28	–	n/m

Note: * – n/m – does not meet the standard by the content of component composition

Analysis of the results of research into component composition of jewelry alloys based on white gold with the help of the XFA indicates a mismatch with the requirements of TU U 27.4-00201514-010:2005, GOST 30649-99 by the content of alloying components and millesimal fineness.

The content of the components in the researched gold-based alloys was within, %: Ag 0.12 – 33,92; Ni 1.92–25.10; Pd 0.02–10; Zn 1.56-12.5, the rest was Cu 12.40 – 46.60.

Eighteen samples of jewelry pieces that were claimed as having 585 millesimal fineness actually have a lower millesimal fineness, which was 26.5 %. Tests on the spectrometer actually revealed 500 and 375 millesimal fineness of gold instead of the claimed 585. A lower than 585 millesimal fineness of gold was found in the alloys that have a high fraction of nickel (Ni) from 6.98 to 14.5 % and of zinc (Zn) from 8.52 to 3.77 %.

The actual decrease in millesimal fineness of gold in the alloy up to 500 was noted for sample No. 43, which has a high content of palladium (Pd, 10 %) along with the maximum content of silver (31 %). The rest of the metals, which were defined as micro impurities and micro additives, specifically, iron, indium, cadmium, make up a small fraction (0.03–0.65 %) and were evaluated as acceptable. Their significant effect on changing the millesimal fineness gold was not recorded.

The elements of micro alloying were established: modifiers and active deoxidizing agents: indium, palladium, cadmium, etc., are used both separately and in a complex to form a uniform microstructure, improvement of plasticity, prevention of liquation sections.

Two samples – No. 26 and No. 28, covered with rhodium (Rd) have deviations from the claimed 585 millesimal fineness of gold downward to decreasing to 500.

Several tests by XFA were performed to establish the unknown composition of the alloy of jewelry archaeological treasures (products of the Scythian period). Each sample was studied at 10 control points and boundary indicators of the content of basic components of alloys, specifically, gold, silver, and copper (Table 2).

Table 2

Boundary indicators of content of main components of gold-based alloys of archaeological samples of jewelry (V century, BC – II century, A.D.), %

No. of sample	Millesimal fineness of gold	Weight fraction Au	Weight fraction Ag	Weight fraction Cu
69	300–399	30.0–42.0	53.0–67.7	2.5–3.0
70	400–499	42.5–51.5	48.0–50.0	2.5–3.6
71	500–599	44.0–45.5	44.0–45.5	2.5–3.5
72	600–699	62.0–71.1	23.2–34.7	2.5–3.0
73	700–799	74.3–81.5	16.6–25.8	0.6–3.6
74	800–899	82.7–91.9	10.1–16.8	0.7–4.3
75	900–1,000	93.1–98.2	1.0–5.0	0.2–3.8

To estimate the microstructure of the archaeological gold-based alloys, the microsections were explored on the electronic microscope. The samples were prepared according to standard metallographic technique of polishing, etching was carried out using different solutions of cyanide.

Analysis of the results of the study of the microstructure of archaeological gold indicates the heterogeneity of the phase state and zonal concentration of slag elements. The latter consist of phosphorus, silicon and others and are fixed on the surface of the sample (a probe microscope). The

zonal concentration is associated with their alloying by the copper minerals (malachite, chrysocol) and migration of slag elements on the boundary of deposits of silver grains during long storage in aggressive media (Fig. 1).

The content of gold in each group of samples is in a very wide range: from 300 to 1,000 particles, an insignificant content of copper was observed (0.2–4.3 %). The interval of gold within the group is 100 units.

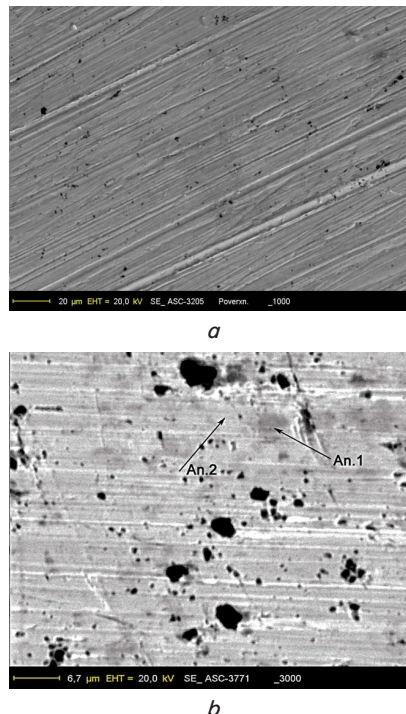


Fig. 3. Microstructure of the microsection of a jewelry fragment, IV century, B.C.: a – 1,000×20 μm; b – 3,000×6,7 μm; An1-An2 – visible liquation of silver and slag impurities

This gives grounds to assert that the data of the component composition of the archaeological samples are an important identifying feature of authenticity of the jewelry. The data of this test made it possible to generate the identification series of the composition of the alloys of gold items for different historical periods. Unlike the archaeological samples, modern jewelry pieces have a polished surface, a more uniformed microstructure, with minor liquation that is considered a rough technological defect (Fig. 2).

To compare precision of millesimal fineness of gold, determined by different methods, the jewelry pieces were tested by the method of cupellation. The samples and parts of the products, which by the results of XFA caused doubts, had a complex shape and another shade. A sample of the results of testing gold-based precious alloys with the content of nickel and zinc, obtained by the method of XFA and by cupellation, was shown in Table 3.

Analysis of the results of research into the samples of jewelry items (No. 52–68, Table 3) by the method of XFA with the content of nickel (from 3.51 to 25.10 %) and zinc (from 2.28 to 12.5 %) indicates a higher millesimal fineness of gold compared with the millesimal fineness of these alloys, obtained by the method of cupellation. In addition, cupellation revealed a decrease in the indicator of 585 millesimal fineness of the alloy regarding the specification to these alloys from 1.2 to 1.5 %.

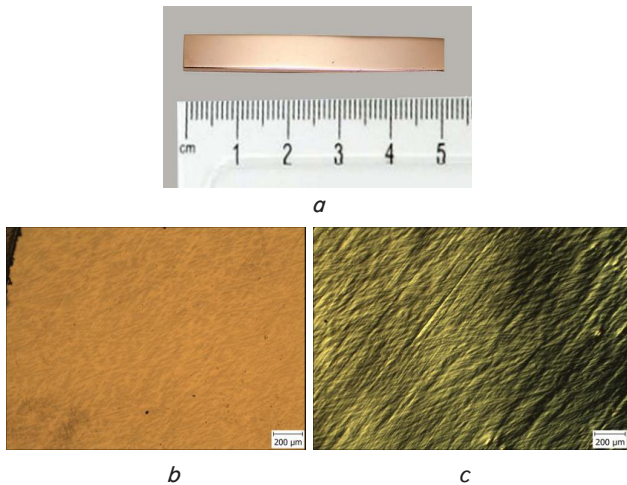


Fig. 4. Samples of modern alloys of gold of 585 millesimal fineness: *a* – quality of treatment of the surface of industrial samples; *b* – microstructure of sample 9 (1,000×200 μm); *c* – microstructure of sample 22 (1,000×200 μm)

Table 3

Results of testing alloys based on white gold of 585 millesimal fineness with the content of nickel and zinc by the XFA method and cupellation, %

No.	Alloy composition by the results of XFA						Content of Au at cupellation	Deviation of content of Au, +/- (gr. 7 – gr. 8)
	Ag	Cu	Zn	Ni	Pd	Au		
52	–	24.61	6.97	8.88	–	59.54	58.88	+0.66
53	2.62	23.33	6.31	8.47	–	59.27	58.74	+0.53
54	2.45	27.28	5.73	5.55	0.13	58.86	58.64	+0.22
55	6.45	23.86	5.21	3.51	0.21	60.76	60.50	+0.26
56	0.41	25.78	5.40	8.44	–	59.97	59.30	+0.67
57	0.59	25.69	4.87	9.75	0.17	58.93	58.62	+0.31
58	0.30	28.20	5.91	6.49	–	59.10	58.92	+0.18
59	–	24.99	7.07	9.08	–	58.85	58.66	+0.19
60	5.88	21.79	4.08	8.68	–	59.57	59.24	+0.33
61	–	24.85	7.27	9.00	–	58.88	58.77	+0.11
62	0.71	26.05	4.72	9.29	–	59.24	59.14	+0.10
63	2.74	25.52	5.54	7.87	–	58.33	57.78	+0.55
64	0.32	24.37	7.95	7.96	–	59.40	58.68	+0.72
65	2.41	27.51	5.49	4.82	–	59.77	58.62	+1.15
66	8.15	20.25	6.91	5.49	–	59.20	59.05	+0.15
67	–	3.65	12.5	25.10	–	58.78	57.83	+0.95
68	2.68	26.73	2.28	9.35	–	59.00	58.95	+0.05
Σaverage								+0.419

The millesimal fineness of the gold-based alloy, determined by different methods, corresponds to the claimed millesimal fineness of 585, except for samples 59, 63.

Deviation of millesimal fineness, specified by the XFA in comparison with cupellation, is in the range from +0.10 to +1.15 % towards increasing. The average discrepancy between the millesimal fineness of the obtained results is +0.419 % towards increasing of millesimal fineness of the XFA. Fig. 3 shows the dynamics of the changes in millesimal fineness of gold alloy of millesimal fineness 585 determined by cupellation and the X-ray fluorescence analysis.

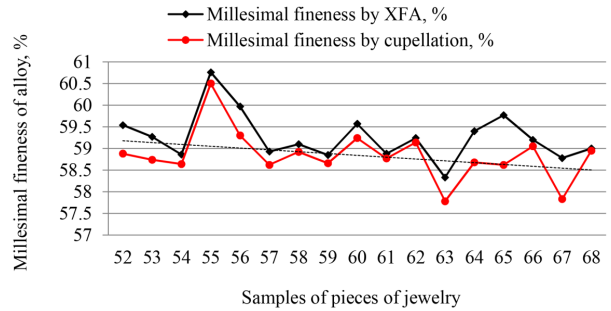


Fig. 5. Dynamics of a change of millesimal fineness of gold alloy 585 containing nickel and zinc, %: series 1 – millesimal fineness determined with the help of X-ray fluorescence analysis; series 2 – millesimal fineness determined by cupellation

A decrease in the indicator of millesimal fineness of gold, determined by the method of cupellation compared with the specification, was noticed in the alloys, containing a significant content of nickel and zinc, and a small content of silver. These components normally form a fluid structure, and nickel and palladium as transition metals have even unlimited solubility in gold. When the temperature is lowered, the phenomenon of decomposition of the state generates a gap in the areas of mixing in the two phases of solid solution: Au–Ni; Au–Pd, while systems Au–Pt, Au–Cu behave differently. That is why the probability of the active influence of nickel and palladium on determining millesimal fineness during the cupellation procedure.

The indicators of millesimal fineness of jewelry alloys, obtained by the XFA (method of fundamental parameters, %) and cupellation (%), are expressed by the equation of linear regression and R^2 , are shown in Fig. 4.

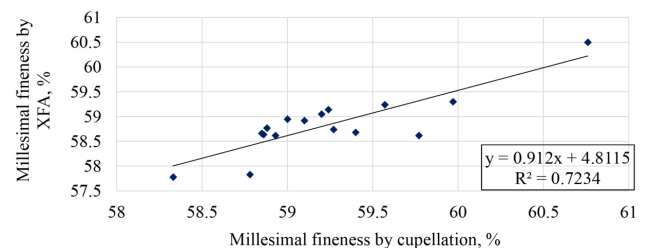


Fig. 6. Distribution of millesimal fineness of gold-based jewelry alloy with content of nickel and zinc of millesimal fineness 585, determined by X-ray fluorescence and assay analysis (cupellation)

The mean absolute error is 0.12 %, which is higher or lower than corresponding alloys in absolute value within the same composition. That is, between the results of the millesimal fineness, received by XFA and cupellation, there is a statistically significant relationship that has mean absolute error of 0.12 % by the ANOVA table at a 95 % level of probability.

Preliminary testing of 17 samples of jewelry based on white gold by the cupellation method, which revealed deviations from the specifications on millesimal fineness, were aimed at the optimization of current technique. The testing of alloy by the cupellation method revealed the gold particles on the cupel, which were not taken into consideration in the sample, resulting in an understatement of millesimal fineness. Nickel and zinc increase fluidity of gold alloy and

its filling the mold. This increases the probability of the loss of gold particles during melting due to nickel being captured by gold and their deposition on the cupel. Considering this, the process of cupellation was optimized.

The essence of optimization is as follows: the assay buttons, formed as a result of cupellation, were kept in the muffle oven for 2 minutes, crashed and annealed at the temperature of 800 °C for 3 minutes in the muffle furnace and rolled in the plates of the thickness of 0.10–0.15 mm. Then, the plates were annealed again under similar conditions and additionally shaped in bilateral spirals.

After the additional examination, the cupels were cleaned from the remnants of gold that were attached to the corresponding spirals. Further melting of spirals was carried out

after control weighing in hot nitrogen acid within 15 minutes until vapors of nitrogen oxides stop to be released. The collection of separated silver was carried out separately. Then golden spirals were fried in the muffle furnace at the temperature of 700–800 °C for about 5 minutes, cooled and weighed. The millesimal fineness was determined from the standard formula.

Calculation of millesimal fineness of jewelry alloys based on gold containing nickel and zinc by the new procedure of cupellation gave more realistic results, presented in Table 4.

The data on determining the millesimal fineness of jewelry alloy based on white gold by the cupellation method, shown in Table 4, indicate the possibility of decreasing millesimal fineness by the adjustment of heat treatment and its rigid control over time.

Table 4

Results of testing jewelry alloys based on white gold by the XFA and by the new cupellation procedure, %

No.	Alloy composition (RFA), %						Millesimal fineness of Au by cupellation, %	Deviation of millesimal fineness of Au, +/- (gr. 7 – gr. 8), %
	Ag	Cu	Zn	Ni	The rest	Au		
76	–	23.8	9.5	7.20	–	58.70	58.60	+0.10
77	0.02	25.44	7.57	7.96	Rh 0.05 Sn 0.03	58.97	58.54	+0.43
78	1.74	25.35	5.28	7.63	Sn 0.35	59.57	59.32	+0.25
79	1.74	25.35	5.28	7.63	Pd 0.28 Pt 0.28 Sn 0.08 Cd 0.07	59.57	59.47	+0.10
80	2.33	27.90	1.99	6.81	–	60.85	60.46	+0.39
81	–	25.69	7.67	8.96	Fe 0.05	58.30	58.13	+0.17
82	–	25.12	4.78	9.12	–	59.67	59.42	+0.25
83	–	25.69	7.67	8.96	Fe 0.05	58.30	58.13	+0.17
84	1.06	26.36	5.13	7.98	Fe 0.04	59.39	59.23	+0.16
85	0.27	26.04	4.35	9.76	–	59.49	59.31	+0.18
86	1.06	26.36	5.13	7.98	Fe 0.04	59.39	59.22	+0.17
87	0.36	25.73	5.71	8.08	–	60.10	59.87	+0.23
88	1.60	28.37	4.87	4.83	–	60.34	59.96	+0.38
89	2.83	22.49	2.77	7.52	–	64.37	63.96	+0.41
90	3.76	28.39	–	4.14	In 0.03	63.59	63.08	+0.51
91	–	4.59	4.59	4.59	–	59.32	59.20	+0.12
92	–	8.54	8.54	8.54	–	57.95	57.74	+0.21
93	26.68	1.310	–	–	Pd 14.70	57.32	57.23	+0.09
94	0.13	25.57	5.35	7.82	–	61.01	60.54	+0.47
95	31.19	0.331	–	–	Pd 4.58 In 2.44	61.44	61.31	+0.13
96	–	23.94	9.01	8.08	–	58.86	58.65	+0.21
97	6.24	8.29	8.29	8.29	–	60.82	60.64	+0.18
98	2.11	29.80	3.77	9.71	Cd 0.29 Fe 0.11	54.13	53.89	+0.24
99	24.75	12.58	–	–	Cd 0.04	55.05	54.69	+0.36
100	8.24	31.94	–	3.51	Pd 0.03 Pt 0.19 Sn 0.13	59.38	59.06	+0.32
101	3.26	22.78	7.80	7.26	–	58.90	58.34	+0.56
102	3.27	22.82	7.75	7.28	–	58.88	58.62	+0.26
							Σaverage	+0.261

Mean deviation by millesimal fineness of the alloys based on white gold, determined after optimization the cupellation technique in comparison with the method of XFA is $+0.261\%$, by the specification, it is 0.2% .

Fig. 5 shows the areas of gold content (millesimal fineness) in the alloys based on white gold of 585 millesimal fineness, obtained by the XFA and the cupellation method.

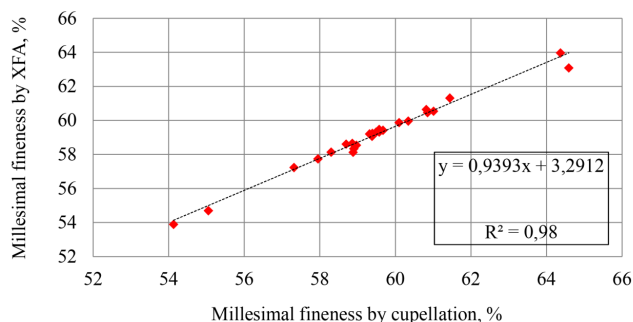


Fig. 7. Results of testing jewelry alloys based on white gold by X-ray fluorescence and assay analysis (optimized technique) and their statistical relationship

The totality of the data as for determining millesimal fineness by different methods is described by the equation of regression and R^2 . P is the values by ANOVA table that are lower than 0.05 , so it can be argued that there is a statistically significant relationship between the results, obtained by XFA and cupellation at the level of 95% . Mean absolute error is 0.16% .

Common advantages and disadvantages of both techniques are shown in Table 5.

Table 5

Effectiveness of application of the methods of assay control for gold alloys

Properties, characteristics of the method	XFA	Cupellation
Precision of millesimal fineness	–	+
Error	$1.0\% \text{ Au}$	$0.2\% \text{ Au}$
Application to the system Au-Ag-Cu	+	+
Application to the system Au-Ag-Cu-Pd-(Ni)	+	+
Simultaneous estimation of Au, Ag, Pd	+	–
Estimation of other precious metals: Pt, Rh, Ir	+	–
Estimation of content of other metals	+	–
Convenience and rate, automation of process	+	–
Non-destructive character	+	–

6. Discussion of results of studying the influence of composition of gold alloys on determining the precision of millesimal fineness of gold by the cupellation method and XFA

In the course of X-ray fluorescence, assay and microstructural analysis, the impact of component composition of the alloy based on white gold on determining the accuracy of millesimal fineness of gold was verified. The aim was to establish the relationship between the indicators of millesimal fineness, determined by XFA and cupellation. It was also possible to identify the parameters of testing processes (cupellation), the microstructure and composition of compo-

nents of gold-based alloys that affect determining millesimal fineness of gold. In addition, the influence of these characteristics on the establishment of authenticity and originality of ancient (archaeological) gold was assessed.

A variety of jewelry alloys of 585 millesimal fineness based on white gold and the sample of authentic archaeological gold were explored as the objects of research.

Analysis of the component composition of alloys based on white gold of 585 millesimal fineness, obtained by the method of XFA, makes it possible to state that gold, silver, zinc, nickel, palladium are basic in them; impurities include indium, iron, and cadmium. The most common systems that were established during the exploration of the gold-based alloys are: Au–Ni–Ag–Zn and Au–Pd–Ag–Zn; Cu is introduced only to guarantee stability and reliability of products in use. Organoleptic studies showed that doping gold with nickel gives the alloy its white cold shade with its content in the alloy from 6 to 25% . Palladium (Pd) makes yellow color of gold white with a warm tint in its content from 0.28 to 14.70% . The most common are compositions with silver (Pd 14.70 ; Ag 26.68%), with indium and silver (Pd 4.58 ; In 2.44 ; Ag 31.19); with nickel, silver, and platinum (Pd 0.28 , Pt 0.28).

Addition of such elements as Zn, Cd, and In ensures high-quality casting, better wetting and fluidity of the precious alloy. The dependence of zinc on a decrease in inter-phase tension improves the quality of the product surface. Zn decreases the probability of formation of dendritic structure of the surface, decreases roughness of the surface.

Mismatch of the studied alloys with the requirements of normative and technical documents by the content of the components can lead to the deterioration of consumer properties during the use, including corrosion resistance, mechanical strength, safety, wear resistance, etc.

The results of determining the gold content in alloys, obtained by the method of XFA, are characterized by consistently overestimated millesimal fineness compared with the specification, which is associated with a number of shortcomings of both the method itself and technological peculiarities of products manufacturing. During the organoleptic study it was found that the complexity of the shape of the product, lack of equal area for exposure, existence of soldering spots partially influenced the change of the components. A more significant effect was associated with the technological operations: polishing, coating the surface with other alloy and treatment with nitric acid. A significant influence on the change of the magnitude of millesimal fineness of gold of structural transformations of the alloy, associated with the formation of liquation, the method of receiving the shape, the casting technology, was observed. This is proved by a slight increase in millesimal fineness of gold in the surface areas of modern products, obtained by casting according to the melted out models.

Instead, in the samples of ancient gold, obtained by casting into the mold and stamping, a big divergence in the content of gold, silver, copper at various points (up to 10) was observed. It was characterized by the imperfection of the technological process, and as a result, the existence of significant liquation, essential variation of the content of major components in different parts of the alloy, proved by microscopic research.

Conducted research into determining millesimal fineness in the alloys based on white gold by the cupellation method revealed a number of errors in the techniques that

affect the results of determining. These errors relate to the technique of performing the preparation operations as well as operations of analyses that cause the understated millesimal fineness compared to the standard sample and are explained by the complicated processes of melting.

In the process of cupellation, lead oxide absorbs the main part of the precious alloy in the form of molten glass and diffuses into a porous crucible. Some losses of noble metals during cupellation occur as a result of their evaporation at high temperatures.

Losses of gold at cupellation are significantly influenced by the content of silver and the ratio between gold and silver in an alloy. Silver at cupellation protects against increased losses (the more silver, the smaller the losses).

Additives and impurities of copper, zinc, iron, tin, nickel, palladium in the lead alloy also increase losses of gold during cupellation.

Nickel in combination with zinc as a complex doping component ensures high fluidity and significantly affects the change in the process of testing (cupellation) of gold alloys.

This increases the probability of the loss of gold particles through its being captured by nickel and deposition on the cupel. And, as a result, it is expressed in deviation of millesimal fineness of gold alloy, determined by cupellation compared with XFA towards decreasing in the range from 0.10 to 0.15 %.

This can be explained by the fact that cupellation of gold alloy begins with melting a gold alloy, silver and lead. This results into selective dissolution of less noble metals. Cupellation ends in the formation of surface oxides of lead, their decomposition and absorption by the cupel.

Mass transportation, which is defined as volume diffusion from a volume layer to the surface layers of the alloy, is an important phenomenon because it leads to decomposition on the surface of most types of non-precious metals. This stream of atoms may be represented by the internal flow of lattice vacancies, created by decomposition of separate atomic objects on the surface of alloys. Usually gold alloys, located near the equiatomic composition, form a face-centered cubic (FCC) lattice, rather than face-centered tetragonal (FCT) one. However, there are two ordered crystallographic structures (AuCuI and AuCuII) above 683 K (410 °C).

When ordering of AuCuI dominates in the alloy, the location of the atoms passes from the FCC into the FCT, which leads to considerable stresses as a result of distortion of the crystalline lattice. These stresses lead to a decrease in resistance of material. The transition from a compact cubic structure to tetragonal allows fewer noble elements to migrate easily across the surface, which in this way increases the rate of volume diffusion.

In addition, electronic configuration of gold, formed under the influence of such effects as “reduction of lanthanides”, “relativist” and “aurophilic” affects its chemical reactivity and crystalline structure of the element and alloys on its basis. And, given that gold nanoparticles are less than 10 nm, the structure of FCC of gold is not stable due to the formation of decahedral, icosahedral forms or defects in the structures. Some features, such as electronegativity and the difference of atomic radii, restrict the range of formation of solid solutions of gold with other elements. Such systems as Au–Ni, Au–Cu, Au–Pt and Au–Pd form solid solutions at high temperatures, but their mutual solubility decreases as the temperature of drop formation increases.

Thus, the nickel particles quickly capture the gold particles and sediment it on the cold cupel, which lowers millesimal fineness of the precious alloy.

To avoid the losses of noble metals during cupellation, we optimized the method of assay analysis of alloys based of white gold, which excludes losses of gold partly or completely.

The results of determining the millesimal fineness of gold alloys with the content of nickel and zinc after testing by the improved technique of cupellation and researched the XFA suggest a significant decrease in the difference of indicators of millesimal fineness (+0.261 %). In addition, there is a greater difference in the indicators of millesimal fineness of gold alloys, determined by assay analysis and XFA that do not contain additives and micro additives at all. The difference in millesimal fineness of gold in these alloys ranges from +0.38 to +0.56 % towards increasing the millesimal fineness at the XFA. The exception is the sample with content of indium and without zinc. The difference in millesimal fineness of gold reaches +0.51 %. In addition, in the samples that do not contain nickel and zinc and contain additives of palladium and indium, the difference in the samples is minimal (+ 0.09–0.13).

Studying the millesimal fineness of gold alloys with content of silver, copper and alloying components from the group of platinum by XFA and cupellation indicate a greater correlation compared with the alloys with the content of nickel and zinc. This proves that determining the millesimal fineness of gold is influenced by the cupellation procedure and, in particular, by the fact of gold being captured by nickel and subsequent “freezing” of the cupels.

Comparison of the effectiveness of two methods of analysis – the golden cupellation and the XFA is an important argument in favor of applying one or another method in the field of jewelry alloys. The results of this comparison in the critical form are shown in Table 5. The studies found that cupellation as a universal method that has a destructive nature can be applied only to systems of Au–Ag–Cu. In case of studying alloys of white color with the content of nickel or palladium, the precision of determining millesimal fineness decreases by 1.5 %, so it is necessary to apply the optimized technique.

The conducted studies made it possible to argue that the component composition of a precious alloy affects the determining of millesimal fineness of gold.

7. Conclusions

1. It is proved that the use of the XFA method for the control of millesimal fineness and content of the component alloy of modern jewelry and museum valuables (antiques) based of gold is possible not only as the method of screening. The method can replace the touchstone (with obvious advantages), and be an alternative to cupellation. The study of the influence of different component composition on the accuracy of determining millesimal fineness of gold alloy is the subject of subsequent promising scientific research. The accuracy of the results of XFA is 1.2 of millesimal fineness for white gold alloys.

2. It was established that the millesimal fineness of gold alloys containing nickel, obtained by the method of cupellation, has the understated content of gold (millesimal fineness) from the standard sample or the specifications.

Deviation of millesimal fineness of gold alloy, determined by cupellation compared with XFA, is in the range from 0.10 to 0.15 % towards decreasing. The mean difference in the obtained results is +0.419 % towards overstatement of millesimal fineness by the results of the XFA. To eliminate this phenomenon, it is necessary to determine preliminarily the composition of the alloy by the XFA and qualitatively to remove palladium and nickel.

3. The causes of the influence of “freezing” of lead alloy on the loss of noble metals in cupellation were identified, which made it possible to develop the method that eliminates this effect. The procedure of the cupellation process was optimized by the strict control of the temperature mode of annealing and the time of exposure. It made it impossible to understate the millesimal fineness of the gold alloy. The mean divergence in the obtained results by the two methods is +0.261 % towards overstatement of millesimal fineness by the results of the XFA. The totality of the data on determining millesimal fineness by the XFA and by cupellation by the updated technique was described by the regression equation and R^2 . P is the value by the table ANOVA that is less than 0.05. That is why it can be argued that there is a statistically significant relationship between the results, obtained by the

XFA and cupellation, at the level of 95 %. The mean absolute error is 0.16 %.

4. The correlation dependence of the millesimal fineness of the alloy based on white gold (containing nickel and zinc), determined by the X-ray fluorescence and assay analysis, was established. The obtained regression dependences make it possible to calculate the exact millesimal fineness of gold in % by the actual indicators of millesimal fineness, obtained by the X-ray fluorescence analysis. This makes it possible to reduce the time to conduct the complex and laborious research into cupellation, which completely destroy the piece of jewelry and to adjust the indicator of millesimal fineness, obtained by the XFA.

5. The results of the study revealed a greater difference between the indicators of millesimal fineness of gold alloys determined by assay and X-ray fluorescence analysis in the system of Au–Ag–Cu–Ni–Zn. The difference in millesimal fineness of gold in these alloys ranges from +0.38 to +0.56 % towards increasing the millesimal fineness at the XFA. A smaller difference in the indicators of millesimal fineness, determined by the assay analysis and the XFA, for the gold alloys in the system of Au–Ag–Cu–Pd–In (+ 0.09–0.13 %) was established.

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Катодним темплатним методом були отримані тонкі плівки гідроксиду нікелю, які надалі випробувувались у різних розчинах. Розчини містили 0,1 М КОН та 0,1 М КОН з додаванням різної кількості K_2WO_4 : 0,1, 0,3 та 1 мМ. Випробування плівок показало, що наявність іонів вольфрамату може істотно впливати на електрохімічні та електрохромні характеристики плівок $Ni(OH)_2$. Вихідний зразок, який випробували у розчині 0,1 М КОН, показав відмінності у порівнянні з електрохімічними характеристиками зразків, що випробували у розчинах з 0,1 М КОН та K_2WO_4 . Відмінність полягала в значній різниці між величинами густин струмів катодного й анодного піків та наявність струмового плато на циклічній вольтамперограмі. При цьому вихідний зразок продемонстрував найвищу серед усіх абсолютну глибину затемнення 74 %. З іншої сторони вихідний зразок мав зростання величини абсолютної глибини затемнення, а потім поступове її зменшення.

У свою чергу зразки, що випробували у розчинах з вольфраматом, мали кращі електрохімічні характеристики – чіткі катодні та анодні піки, що мали більш близькі значення густин струмів. Динаміка зміни абсолютної глибини затемнення для всіх зразків у серії з додаванням вольфраматів мала постійне її збільшення. При цьому зразок випробуваний у розчині з 1 мМ вольфрамату мав найменше значення абсолютної глибини затемнення – 60 %. Для концентрацій вольфрамату 0,1 та 0,3 мМ абсолютна глибина затемнення складала в свою чергу 72 та 71 % для останнього циклу.

Зразки, що випробувувались у розчинах з вольфраматом, мали значно менший час освітлення – 40–50 с, у порівнянні з 360 с у зразка, який випробували у чистому розчині 0,1 М КОН.

Також був запропонований можливий механізм, що пояснює відмінності у поведінці різних зразків.

Ключові слова: електрохромізм, електроосадження, інтеркаляція, $Ni(OH)_2$, гідроксид нікелю, вольфрамат, WO_4^{2-} , полівініловий спирт

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A STUDY OF THE EFFECT OF TUNGSTATE IONS ON THE ELECTROCHROMIC PROPERTIES OF $Ni(OH)_2$ FILMS

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1. Introduction

Smart devices are a new class of devices that tend to be a combination of standard device and computer. Such combination allows for expansion of device's functionality.

Use of these devices opens a wide range of possibilities for rational use of time and energy resources [1, 2]. This becomes possible due to flexible operation schedule, including switching based sensor readouts or other information passed to the computer [3].