

Розглянуто випробування жовтих та білих ювелірних сплавів на основі золота із вмістом міді, срібла, цинку, паладію, на пробірному камені за допомогою різних хімічних реактивів та РФА. Вдосконалено процедуру оцінювання відповідності проби дорогоцінних сплавів на основі золота різного компонентного складу з використанням результатів випробування натурів сплавів на пробірному камені.

Встановлено, що величина проби золота дорогоцінних сплавів системи ЗлСрЦМ, визначена під дією реактиву «хлорне золото» на пробірному камені, залежить від прояву контрастності якісної реакції від стандартного зразка (пробірної голки).

Під дією реактиву на сплавах «жовтого» золота утворюються хлористі сполуки зі сріблом і міддю, відновлюючись при цьому до металевого порошку чорно-бурого кольору. Мідь у цьому випадку розчиняється, а золото разом зі сріблом утворює на смужці інтенсивний осад, який залежить від лігатурного складу сплаву. Встановлено, що чим нижча проба сплаву, що випробовується, тим більша кількість «хлорного золота» розкладається, тим більше утворюється осаду хлориду срібла і відновлюється чистого золота з реактиву, а, отже, тим темніший отримуємо осад.

Доведено, що випробування дорогоцінних сплавів червоного кольору системи ЗлСрЦМ585 з вмістом цинку (більше 2 %), галію, індію реактивом на основі біхромату калію та хлориду міді є не ефективними.

Результати аналізу вказують на завищену пробу золота у порівнянні зі стандартною пробірною голкою.

Для усунення цього явища рекомендовано попередньо визначити склад сплаву методом РФА та розробити алгоритм випробування відповідно до вмісту сплаву іншими реактивами.

Визначено, що проба золота, встановлена на пробірному камені для сплавів системи ЗлСрЦМ585 (вміст цинку більше 2 %) більш контрастно проявляється під дією кислотних реактивів і залежить від компонентного складу сплаву.

Доведено, що на сплав «білого» золота, до складу якого входить паладій та срібло (ЗлСрПд585), кислотний реактив для золота 585 проби не діє.

Випробування сплаву «білого» золота (ЗлСрПд585) кислотним реактивом для золота 750 проби дає темний осад синюватого відтінку.

Встановлено більш контрастну дію на сплави «білого» і «жовтого» золота 750 проби кислотного реактиву для сплавів золота 750 проби

Ключові слова: сплави золота, пробірний камінь, «хлорне золото», біхромат калію, сульфат міді, пробірний контроль

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IMPROVING A PROCEDURE FOR DETERMINING THE ASSAY OF GOLD IN A PRECIOUS ALLOY OF DIFFERENT COMPOSITION USING A TOUCHSTONE

T. Artyukh

Doctor of Technical Sciences, Professor*

E-mail: Artyukhtn@gmail.com

G. Kupalova

Doctor of Economic Sciences,

Professor, Head of Department*

E-mail: prof.galina@gmail.com

V. Bazylevych

Doctor of Economic Sciences, Professor

Department of Economic Theory, Macro- and

Microeconomics**

E-mail: v_bazil@ukr.net

I. Hryhorenko

PhD, Associate Professor***

E-mail: soniki04@ukr.net

A. Ternova

PhD, Associate Professor***

E-mail: kaftov_tas@ukr.net

*Department of Environmental Management and Entrepreneurship**

**Taras Shevchenko National University of Kyiv Volodymyrska str., 60, Kyiv, Ukraine, 01033

***Department of Commodity Science, Expertise and Commercial Business

Vinnitsia Institute of Trade and Economics of Kyiv National University of Trade and Economics

Soborna str., 87, Vinnitsia, Ukraine, 21050

1. Introduction

At the present stage of economic development, more and more attention is paid to the issues of business social responsibility, consumer protection, environmental protection, compliance with the positive business practices that will not tolerate corruption, cheating, and fraud. Today, not only

business, but other structures as well, including state institutions, state control and supervision, public and independent commercial organizations, must influence the sustained development of society.

Consumers who are interested in ethical problems in the production of jewelry products force companies to change. The ethical production by a company implies the use of

precious alloys of known origin, working with which meets the environmental and social standards of value, reliability, and safety.

Since the State Assay service of Ukraine was eliminated in 2011, the responsibility of manufacturers, as well as the state-owned enterprises of assay control, has increased in terms of quality, value, and safety of jewelry items that are based on alloys from precious metals. According to the Law of Ukraine “On protection of consumer rights”, retail enterprises are required to provide qualified, comprehensible, reliable, and timely information about jewelry, its quantity, quality, and safety. They should prove it based on documents or by applying the appropriate means of identification [1]. Therefore, all the players in the jewelry market today are interested in the fabrication and selling high-quality and safe jewelry items. That makes the state-owned enterprises of assay control improve testing procedures for alloys based on precious metals.

Since February 2016, following the amendments to the law on standardization, the compulsory application of regulations has been replaced by the voluntary. Main normative-legal documents that regulate the quality and safety of jewelry are: The Law of Ukraine [2], DSTU 3527-97 [3], and Rules of trade [4]. In accordance with these regulations, the requirements to jewelry include:

- the presence of a mark of assay indicating the assay in line with the State standard, which defines the value of the alloy, and shows the number of units of the basic precious metal in the alloy [3];
- for the case when it is impossible to put a mark of assay (or the product is not subject to marking), the items should include documents issued by the bodies of assay control, confirming the proper value of the products;
- the presence of the marking label that confirms the value of a jewelry item based on product and trade characteristics, its compliance with marking with the indication of a normative (technical) document based on which it was made.

Modern jewelry industry manufactures precious jewelry alloys based on gold by adding various alloying components such as copper, zinc, palladium, cobalt, cadmium, lead, platinum, ruthenium, nickel, silver, indium, iridium, manganese, gallium. The EU countries implemented Directive 94/27/EC of the European Parliament and the EU Council (“Nickel directive”).

The directive bans direct contact between the skin and such harmful elements as nickel, cadmium, aluminum, tin, indium, lead, which cause allergies and a series of bad diseases [5]. It limits the level of leaching nickel to a threshold value of up to 0.5 µg per 1 cm² per week. Similar legislative initiatives to the white gold with a nickel content were implemented in Japan and China. The United States introduced the mandatory labeling of jewelry indicating the content of nickel and other components.

In addition to harmful effect on the human body, nickel, zinc, indium, and other chemical elements change the contrast of qualitative reaction when testing a gold alloy on a touchstone. It is difficult to test modern, “non-standard” alloys by using traditional reagents due to a weak or a low-contrast reaction. Introduction to the composition of alloying metals (nickel, zinc, cadmium, chromium, manganese, indium, silicon, cobalt) in the presence of silver and copper, in certain proportions, radically changes the mechanism and the color of corrosion products (their intensity). This leads to serious errors in determining the assay of gold on a

touchstone. Difference in determining the assay increases to 50 assays, instead of 2–5 for standard alloys. According to data from the World Council for gold, the accuracy in testing gold on a touchstone should be up to 1.5 %, while using the XFA method – 0.2±0.5 % [7].

The main task of the state-owned assay control enterprises is accurate determining of mass fraction of the basic metal in an item made from precious metals, establishing its compliance with one of the standards for assay and giving a mark of assay.

As defined by the International Convention on the control and branding of products made of precious metals (Vienna Convention as of November 15, 1972), the first step on the path of an item to marking is the input control.

Accordingly, it implies the application of the method of rubbing the touchstone and a non-destructive x-ray fluorescence analysis.

The method of testing the alloys of precious metals on a touchstone is the most widely used (90 %) and common at the state-owned enterprises of assay control, in a number of trade and consumer service establishments in Ukraine. It is an organoleptic method; accuracy of the obtained data largely depends on the tools used and experience of the expert. However, it does not warrant precise determination of qualitative and quantitative indicators for the ligature composition of precious metals [6].

This relates to that the jewelry industry of Ukraine has been, over the past 20 years, operating, for 60 %, with “non-standard” alloys based on gold. Therefore, the assay control inspection faces a series of problems that hinder the reliable determination of assay on a touchstone. First of all, it is the lack of means for identification – touch-needles to test non-standard alloys whose ligature composition is unknown.

In addition, the drawbacks of such tests are as follows: the low accuracy of assay determination in the presence of a thick coating layer, the shortcomings in current testing procedure. This is especially true for cases when the non-standard alloys are examined. However, it remains the basic one in most assay laboratories in Ukraine.

Therefore, it is necessary to improve the procedure of testing the alloys based on gold on a touchstone, whose composition includes chemical elements that produce insufficient contrast chemical reaction for the precise analysis of gold assay.

2. Literature review and problem statement

For several centuries people have used certain techniques and methods of analysis that had existed in ancient Egypt, and were known to Kievan Rus as early as IX–X centuries. A full description of the so-called “assay art”, a procedure for determining the composition of an alloy at the laboratories of mints houses was covered in [7]. The author, for the first time, detailed methods for determining the amount of silver, gold, and copper using touch-needles with known composition of a precious alloy.

Establishing the assay of a precious alloy by testing it on a touchstone stone has long historical and cultural traditions, as well as special features, defined by the normative-legal base [8, 9].

Paper [10] outlines common methods for studying gold alloys, including by testing on a touchstone. However, most attention is paid only to the description of the method using

classic chemical reagents for standard alloys based on precious metals, without specifying the characteristics of the method, its advantages or disadvantages.

Determining the assay and impurities in the highly-doped alloys based on gold by testing on a touchstone was used as a comparative method in [11] while applying a method of emission spectroscopy. However, the author does not provide a detailed assessment of the indirect methods for determining the content of gold, considering its colorimetric character.

Article [12] notes the significance and wide application of colorimetric methods, including the method of testing on a touchstone. The author notes that modern methods for analyzing gold alloys made it possible to improve the accuracy of results, however, they were not able to completely replace classical methods of analysis, specifically, testing on a touchstone. The article did not report a correlation analysis to modern methods: XFA, mass spectral, etc.

Paper [13] proved the importance of the method of testing on a touchstone in the field of social history and archeometallurgy. The European archaeological collections, which include hundreds of thousands of stone artifacts from the early Middle Ages, described as plates, were applied for the assay control. Traces of precious metals, preserved on a series of such artifacts, point to their application to test the content of a specific metal. The paper did not specify promising directions for improving a procedure of testing on a touchstone, nor the development of new chemical reagents.

The authors of work [14] indicate that the accuracy of analysis of alloys based on gold, when testing at a low-energy dispersive XFA-spectrometer, increased by 10 times compared with a conventional test on a touchstone. However, the results were based on studying the standard alloys and references. No study into the “unknown” component compositions based on precious alloys of different colors was carried out.

A comparative analysis of the accuracy of assay for standardized reference alloys based on gold, determined by the XFA method and by testing on a touchstone, was reported in [15]. It was shown that the accuracy of results, obtained by the XFA method, is much higher in comparison with colorimetric results. However, the issues that were not addressed included the “non-standard” alloys, the composition of a precious alloy, economics, etc.

Paper [16] notes that development of modern laboratory techniques and tools implies affordability and speed. Thus, it is necessary to improve express-methods, including testing on a touchstone. In this case, the authors indicated the possibility of losing accuracy of the results. They did not consider ways to improve the colorimetric research methods, only pointing to such a need.

In [17], authors point a series of advantages in using XFA at analytical laboratories as a method that can replace testing on a touchstone. However, they did not analyze the effect of alloying components on the accuracy of obtained results, did not define the intercorrelation between methods, nor other indicators that characterize it.

The authors of [18] reported interesting results of studying the structure and chemical composition of non-standard alloys AuAg and AuCu when the colorimetric methods were used as additional. However, the work is limited to the basic formulations of binary compositions.

Promising are the results of modern research that applied colorimetric methods as basic methods for establishing

the presence of gold in very small amounts or compounds of unknown composition in various sectors of the economy. In particular, [19] studied the adsorption of gold in chloride environments using a commercial sorbent (Lewatit TP 214 (L-214)) and the residue of biomass (rice hull (RH)). The primary reagent used by the authors was a solution of chloride. Paper [20] describes the synthesis of gold nanorods that are used in biotechnology and electronics. However, the work did not pay attention to the techniques themselves, did not describe features of chemical reagents and their behavior. Study [21] presented the colorimetric quantitative determining of two cephalosporins, cefoperazone (CFZ) and cefepime (CPM), which were designed and approved for use at clinical laboratories and the laboratories of quality control. The method is based on the use of regenerative properties of cephalosporins owing to dihydrothiazine of 7-aminocetaphosporanic acid and β -lactam ring for obtaining the nanoparticles of gold or silver from the respective solutions of metals. Paper [22] describes colorimetric determining of ascorbic acid based on triggering the aggregation of nanoparticles of gold.

The results of scientific studies point to the need to improve the procedures for colorimetric research into alloys based on gold with the use of more sensitive reagents, which are more promising, economical and fast, easy to use.

Thus, it can be argued that the use of colorimetric methods of analysis of precious alloys based on gold would make it possible to improve existing chemical toolset for assay control when testing on a touchstone. That would provide an opportunity to more accurately determine the content of gold assay considering new jewelry alloys, including those of white color, those containing nickel, zinc, indium, silicon, etc.

Thus, we have a reason to believe that there is a lack of understanding the behavior of modern precious alloys of different colors based on gold exposed to a variety of assay reagents. Therefore, it is necessary to explore the coloration processes in a chemical reagent with the mandatory development of an algorithm for testing precious alloys on a touchstone. That would make it possible to use them as a cheap alternative to test jewelry based on precious alloys of different complex shapes and variously treated surface where the application of XFA is unacceptable.

Taken in their totality, all the above studies became a prerequisite, which defined the creative-aspirational tasks of this research.

Development of new jewelry alloys based on gold is associated with the formation of a new component chemical composition, the structure that affects the precise analysis of an alloy. That complicates the process of determining the gold assay, the content of jewelry alloy during assay control and expert research. However, the improvement of existing methods for testing jewelry alloys based on gold with a different component composition, specifically on a touchstone, techniques for which have been already outdated, were neglected by modern publications.

3. The aim and objectives of the study

The aim of this study is to assess the conformity of a precious gold-based alloy with a different component composition in terms of purity (assay) by testing it on a touchstone using chemical reagents, to improve the standard research procedure based on it.

To accomplish the aim, the following tasks have been set:

- to define the impact of ligature composition of jewelry alloys based on gold on the accuracy of determining the assay (the content of gold) by testing on a touchstone using the reagent “chlorine gold”;
- to determine the impact of ligature composition of jewelry alloys based on gold on the accuracy of determining the assay by testing on a touchstone using a reagent based on potassium bichromate and chloride or copper sulphate;
- to determine the impact of ligature composition of jewelry alloys based on gold on the accuracy of determining the assay by testing on a touchstone using acid reagents;
- to improve the procedure for testing precious alloys based on gold with a different component composition on a touchstone.

4. Materials and methods to test gold alloys with various alloying components

4.1. The examined materials and equipment used in the experiment

We tested the standard yellow and white gold alloys containing silver, zinc, nickel (AuNiZnCu), (AuAgNiZnCu), assay 375, 500, 585, 750, jewelry gold alloys containing palladium. Representative samples of alloys (the examined objects) are given in Tables 1–4.

Sampling from the batch, as well as selective control at soldering joints of alloy products, were carried out in accordance with the industry standards of Ukraine on assay control.

4.2. Procedure for determining the purity of gold alloys on a touchstone and X-ray fluorescence analysis

The algorithm of research part of this work consists in the following:

- 1) determine the assay and content of jewelry alloys based on gold from the systems AuCu375, AuCu500, AuAgNiZn585, AuAgNiZn585, AuAgPd585 for samples of jewelry items and appropriate touch-needles by using XFA;
- 2) determine the assay and content of jewelry alloys based on gold from the systems AuCu375, AuCu500, AuAgNiZn585, AuAgNiZn585, AuAgPd585 for samples of jewelry items and appropriate touch-needles by testing on a touchstone using different reagents.

XFA refers to the non-destructive method of determining the qualitative and quantitative content of chemical elements in articles and is used as a preliminary analysis of jewelry alloys [6]. In the work, we applied the spectrometer ElvaX (Ukraine), which makes it possible to identify elements in the range from sodium (atomic number 11) to uranium (atomic number 92) (Fig. 1).



Fig. 1. X-ray fluorescence spectrometer ElvaX (Ukraine)

Table 1

Component composition of jewelry alloys based on gold (touch-needles)

No. of entry	Mark	Assay	Mass share of components, %			
			Au	Ag	Ni/Zn/Si	Cu/Pd
1	AuAgCu585-80	585	58.5–59.0	7.5–8.5	–	remaining/–
2	AuAgCu500-100	500	50.0–50.5	9.5–10.5	–	remaining/–
3	AuAgCu375-100	375	37.5–38.0	9.5–10.5	–	remaining/–
4	AuAgCu585-50	585	58.5–59.0	5.0–6.0	–	remaining/–
5	AuNiZnCu585-12,5-4,0	585	58.5–59.0	–	12.0–13.0/3.6–4.4/–	remaining/–
6	AuNiZnCu585-7,0-9,5	585	58.5–59.0	–	6.5–7.5/9.0–10.0/–	remaining/–
7	AuAgPd585-255-160	585	58.5–59.0	25.0–26.0	–	–/remaining
8	AuAgZnCu585-55-2,0	585	58.5–59.0	5.0–6.0	–/1.5–2.5/0.02–0.10	remaining/–
9	AuAgZnCu585-80-10,0	585	58.5–59.0	7.5–8.5	–/10.0/–	remaining/–

Table 2

Component composition of jewelry alloys based on gold (touch-needles)

No. of entry	Mark	Assay	Mass share of components, %			
			Au	Ag	Zn/Ni	Cu
23	AuAgCu375-20	375	38.0	2.0	–	remaining
24	AuAgCu 500	500	50.5	9.5	–	remaining
25	AuAgCu 585-80	585	58.5	8.5	–	remaining
26	AuAgCu 750-220	750	76.5	22.5	–	remaining
27	AuAgZnCu 585-55-2,0	585	59.0	6.0	2.0/–	remaining
28	AuAgZnCu 585-65-1,0	585	59.0	6.5	1.0/–	remaining
29	AuAgZnCu 585-80-1,0	585	58.5	8.0	1.0/–	remaining
30	AuAgZnCu 585-80-6,5	585	58.5	8.0	6.5/–	remaining
31	AuNiZnCu 585-125-40	585	58.5	–	4.0/12.5	remaining

The main functions of spectrometer are: registration of the spectra of x-ray fluorescence in the examined samples; determination of energy position and intensity of its lines; identification of the elemental composition of samples; determining the concentrations and relative content of elements in the examined sample. The spectrometer is controlled by software built on the following methods: fundamental parameters (focused on quantitative analysis of alloys) and regression (whose algorithm employs graded dependences, constructed in advance based on sets of standard samples).

Matrix absorption and effects of excitation are taken into consideration separately for each element in the composition. The method implies that all the chemical elements in a composition of the alloy's sample can be detected by a spectrometer. The sample must be homogeneous, have enough thickness to absorb the primary beam (minimum 200 μm) and a flat surface. The boundaries for the possible basic relative error of conversion characteristic (integral non-linearity) are not above ±0.05 %.

Using XFA, we calculated the atomic percentage of each metal in the alloy. The mass content of a precious metal in the alloy is the equivalent of the assay.

By applying a database on alloys, which is included in the software, we defined the content of components and the mark of an alloy for each examined sample. An example of the X-ray fluorescence spectrum for sample No. 11 – a gold alloy of yellow color (photograph from screen) is shown in Fig. 2.

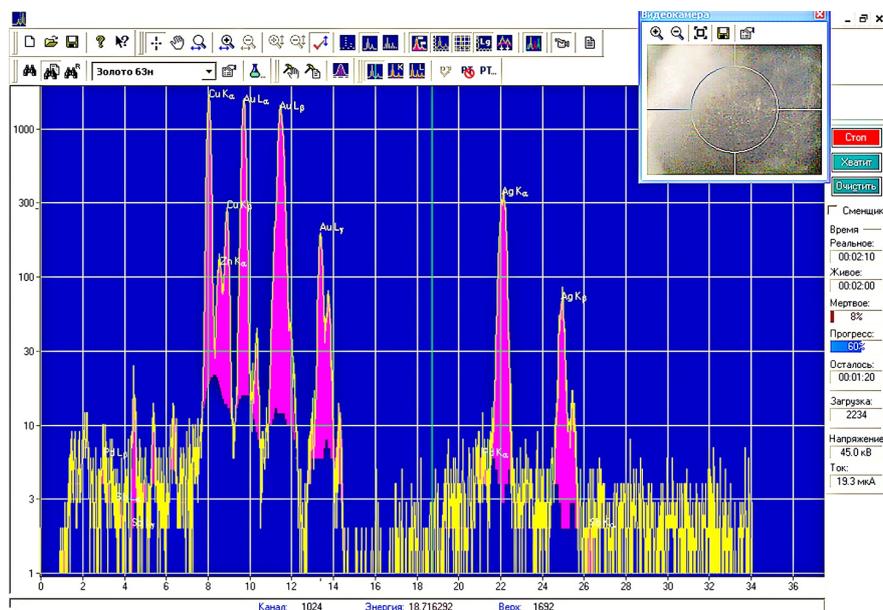


Fig. 2. Spectrum of X-ray fluorescence for sample No. 11 – a gold alloy of yellow color (photograph from screen)

For each examined sample, we performed two measurements of the assay and recorded the corresponding measuring results – ω₁, ω₂. In this case, the mass fraction of a metal in jewelry alloys (ω), %, was calculated from formula (1):

$$\omega = 0,5 (\omega_1 + \omega_2), \tag{1}$$

where ω₁, ω₂ are the results from determining the mass share of a metal in the jewelry alloys of gold, %.

The results of measurements and calculations of mass share of a metal in jewelry alloys are presented in the form:

(ω±Δ) %, P=0.95; n=2, where Δ is the limit of absolute error, % (Table 3).

Table 3

Limit of absolute error for the determined elements

No. of entry	Determined element	Measurement range, mass share (ω), %	Limits of absolute error Δ, %; (P=0.95; n=2)
1	Gold	From 20.0 to 99.0 incl.	0.3
2	Silver	From 0.5 to 35.0 incl.	0.3
3	Palladium	From 1.0 to 15.0 incl.	0.3
4	Copper	From 0.5 to 43.5 incl.	0.2
5	Platinum	From 1.0 to 9.0 incl.	0.3
6	Zinc	From 1.0 to 12.5 incl.	0.4
7	Nickel	From 2.5 to 15.0 incl.	0.4
8	Halium	From 0.5 to 1.5 incl.	0.3
9	Cadmium	From 0.1 to 2.5 incl.	0.2

During measurements, we controlled convergence between the results from determining the mass share of metals in the samples of jewelry alloys, calculated under condition (2):

$$|\omega_1 - \omega_2| \leq 0,2. \tag{2}$$

The method of testing on a touchstone is based on chemical reactions between reagents and a gold-based alloy, applied onto a touchstone. In addition, one visually compares the intensity of coloration of the sediments formed where the alloy was rubbed with the coloration of the sediment where a touch-needle was used (GSTU 47-083-02.8-2018) [9]. The intensity of coloration of the sediment formed where the examined alloy was rubbed, when compared with the coloration of the sediment where a touch-needle was used, makes it possible to draw conclusions on the assay. The assay evaluation procedure is as follows: if the sediments are identical in intensity, then the alloy and the touch-needle have the same assay. If the sediment of the alloy is darker than that at the strip of the touch-needle, the alloy's assay is lower than that of the touch-needle. If the sediment is lighter – the alloy's assay is higher than that of the touch-needle. This method for controlling the quality of gold products makes it possible to define the assay of gold of up to 0.5 % (5 assays).

The testing procedure is as follows: one rubs the examined alloy against the prepared surface of a touchstone, adjacent to it is the touch-needle rubbed, of appropriate assay and chemical composition (Fig. 3).

Tests on a touchstone of jewelry alloys based on gold (samples and touch-needles) involved a variety of reagents given in Table 4.

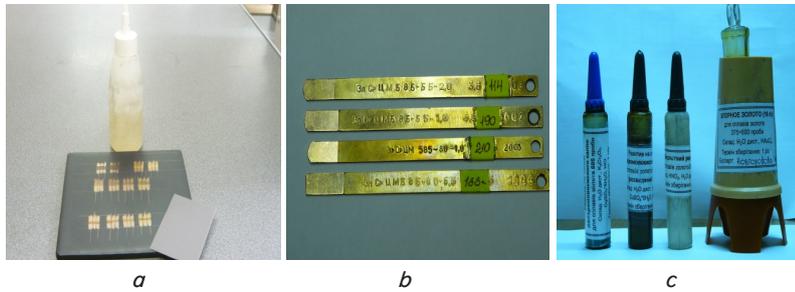


Fig. 3. Preparing a touchstone for operation: *a* – application of rubbed material onto the touchstone; *b* – a set of touch-needles; *c* – a set of assay reagents for testing alloys based on gold

5. Results of determining the purity (assay) of gold in the jewelry precious alloys based on gold on a touchstone

In order to assess the conformity of the composition of the alloy to the passport or specifications, at the first stage of research we preliminary analyzed the alloys of jewelry items for the content of the main component (gold) and component composition by XFA.

The results from testing a component composition and the assay of jewelry precious alloys based on gold in the studied samples using XFA method at the spectrometer “ElvaX” are given in Tables 5, 6.

The sample was 2 % of the volume of the batch that arrived to the state enterprise for assay control. The results of studying the component composition of standard alloys, identified by XFA, meet the well-defined content of components in accordance with acting norms. When using XFA for precious alloys based on gold, we acquired the x-ray spectra shown in Fig. 2 (sample No. 11). All the spectral peaks were computed, indicated by their uniform coloration.

Sample No. 11 is a jewelry women’s decoration (earrings), made from a precious gold-based alloy, of red color, the insert is emerald. The earring consists of two main parts – the main (front) and a fastening. The structural parts of the earring are: a base, an earring fixture, a hook, a pin, which were examined separately using XFA. Since the tested sample was claimed to be made of a single brand of alloy, we conducted two measurements of each element.

The results from calculating the content of the precious gold-based alloy for sample No. 11, defined by XFA, are given in Table 7. An example of determining a component composition of the alloy for sample No. 11 indicates the content of 58.8 % of gold, 5.29 % of silver, 2.14 % of zinc, the rest (33.77 %) is copper.

Table 4

Assay reagents to test precious alloys based on gold on a touchstone

No. of entry	Reagent title	Application for alloys based on gold
1	Chlorine gold (solutions: 6.0 g/dm ³ ; 9.0 g/dm ³ ; 18.0 g/dm ³)	Alloys of «yellow» and «white» gold. not exceeding assay 585
2	Reagent based on potassium bichromate and chloride or copper sulphate	Alloys of assays 375; 500; 585; 750 («yellow» and «white» gold) with different ligature
3	Acidic reagents (based on nitric acid of different concentration)	For alloys of gold, assay 375; 500; for alloys of gold, assay 585, whose ligature matches a standard touch-needle No. 14 (AuAgCu 583-34-383); for alloys of gold, assay 750 («yellow» and «white» gold); for alloys of gold, assay 958

The reagent “chlorine gold” was used for alloys based on gold, assay 585. The reagent based on potassium bichromate and chloride or copper sulphate was used for all alloys based on gold; acid reagents were used for alloys of gold, assay 375, 500, 585, 750.

Table 5

Results from testing the samples of jewelry items, fabricated based on gold of red color, using XFA method

No. of sample	Item title	Component composition of alloy, %			
		Au	Ag	Cu	Zn
10	Ring	59.83	6.42	32.34	1.70
11	Wedding ring	58.80	5.29	33.70	2.14
12	Wedding ring	58.68	28.05	13.27	–
13	Wedding ring	58.93	7.97	33.10	–
14	Earrings	58.70	8.00	32.10	–

Table 6

Results from testing the samples of jewelry items, fabricated based on gold of red and white color, using XFA method

No. of entry	Jewelry item title	Mass share of component, %					Alloy mark	Color
		Au	Ag/Pd	Si/Ga	Zn/In	Cu		
15	Decoration	58.88	5.29/–	0.02/–	2.14/–	33.70	AuAgZnCu 585-55-2,0	Red
16	Wedding ring	58.60	6.10/–	–	0.96/–	34.34	AuAgZnCu 585-65-1,0	Red
17	Earrings	58.84	7.61/–	–	1.12/–	32.43	AuAgZnCu585-80-1,0	Red
18	Ring	58.62	7.85/–	–	6.87/–	26.66	AuAgZnCu 585-80-6,5	Red
19	Ring	58.9	6.00/–	–	0.04/0.04	34.65	AuAgInCu 585-55-0,3	Red
20	Earrings	59.0	5.00/–	–/0.4	1.74/–	33.54	AuAgZnGaCu585-50-1,5-1,0	Red
21	Earrings	59.8	6.40/–	–	1.27/–	32.34	AuAgZnCu585-65-1,0	Red
22	Ring	59.0	25.5/16.5	–	–	–	AuAgPd 585-255-160	White

Table 7

Results of the qualitative identification of a precious gold-based alloy for 4-components of jewelry item No. 11, defined by XFA

Chemical element		Content of components in the item's parts, %			
No.	Title	Base	Earring fixture	Hook	Pin
29	Cu	33.70	33.70	33.69	32.44
30	Zn	2.14	2.14	2.15	–
46	Pd	–	–	–	–
47	Ag	5.29	5.29	5.29	8.59
50	Sn	0.04	0.02	–	0.01
51	Sb	–	–	–	–
79	Au	58.88	58.88	58.87	58.94

Data for the calculation of mass share of gold in the precious alloy at the base of sample No. 11, defined by XFA, are given in Table 8.

Table 8

Results of measuring the mass share of metal in the base of sample No. 11

No.	Determined element	Mass share ω_1 , %	Mass share ω_2 , %
79	Au	58.88	58.87
47	Ag	5.29	5.28
29	Cu	33.70	33.71
30	Zn	2.14	2.13

Control over convergence of results from determining the mass share of metals in the obtained results satisfies the condition: $|\omega_1 + \omega_2| \leq 0.2$. Next, we calculated mass fractions for each element, the result is given in Table 9.

$$\omega(\text{Au}) = 0,5(\omega_1 + \omega_2) = 0,5(58,88 + 58,87) = 58,88;$$

$$\omega(\text{Ag}) = 0,5(\omega_1 + \omega_2) = 0,5(5,29 + 5,28) = 5,29;$$

$$\omega(\text{Cu}) = 0,5(\omega_1 + \omega_2) = 0,5(33,70 + 33,71) = 33,70;$$

$$\omega(\text{Zn}) = 0,5(\omega_1 + \omega_2) = 0,5(2,14 + 2,13) = 2,14.$$

Table 9

Results from measuring the mass share of chemical elements in the alloy based on gold, sample No. 11, by XFA

No.	Title of the mass fraction of element	Mass share of element ω , %
79	Au	58.88 ± 0.3 %. $P=0.95$; $n=2$;
47	Ag	5.29 ± 0.3 %. $P=0.95$; $n=2$
29	Cu	33.70 ± 0.2 %. $P=0.95$; $n=2$
30	Zn	2.14 ± 0.4 %. $P=0.95$; $n=2$

The obtained mass shares of components in gold alloy No. 11 allow us to argue that in terms of qualitative and quantitative indicators it meets the approved norms and their content in line with TU U 27.4-00201514-010:2005 [23]. Since this piece of jewelry is composed of two different parts, the conformity of the composition of the alloy to the assay was analyzed separately for the fastener, specifically the hook and earring fixture. This sample, according to the

claimed alloy, contains elements such as gold, silver, zinc, and copper. The result of our study and calculations is the derived mass fraction of a component (element) for each component in the alloy, given in Table 10.

Table 10

Results of evaluating the conformity of the measured mass share of a metal in sample No. 11

Photograph of sample No. 11	Component	TU U 27.4-00201514-010:2005	Actually derived mass share of component, %	
		Mass share of component, %	Fixture	Hook
	Au	58.5–59.0	58.88	58.87
	Ag	5.0–6.0	5.29	5.29
	Zn	1.5–2.5	2.14	2.15
	Cu	remaining	33.70	33.69

Conformity of the content of the alloy AuAgZnCu 585-55-2.0 in sample No. 11 to standard in line with TU U 27.4-00201514-010:2005, according to the protocol of the study, is 98.9 %. Based on the proposed plan of research, we used XFA method to measure the mass fractions of components ω_1 , ω_2 for samples 10–21 (Tables 5, 6), to calculate for each element of the alloy ω , and chose the alloy's mark. During each measurement, control over the convergence of results from determining a mass fraction was satisfactory.

Based on the results of RFA for jewelry samples, we compiled a program of study for testing on a touchstone according to the available content of the component composition of a gold alloy (or a mark), which in each case was determined individually.

At the second stage of the study, we tested the selected touch-needles by applying the chemical reagent “chlorine gold” to where a touch-needle was used on a touchstone. Results of studying a color change in the sediment are given in Table 11 and Fig. 4.

It was established that the character and color of sediment formation at strips (rubbed) made by standard touch-needles of gold alloys depend on the ligature alloy that forms under the influence of the solution “chlorine gold”.

The research found that on the strips made by needle (AuAgCu585-50) with a low content of silver (5 %) and with a high content of copper – larger than 35 % – the reagent “chlorine gold” forms a light-red sediment (Fig. 4, b). The strip made by the needle AuNiZnCu585-12,5-4.0 demonstrates a light brown sediment with a mustard tint – indicating a larger presence of nickel content in the alloy (12.5 %) and a smaller content of zinc (4.0 %) (Fig. 4, e). The trace from a touch-needle made from the standard alloy AuNiZnCu585-6.0-9.0 demonstrates the sediment from the reagent of light brown color with a reddish tinge, which indicates a lower content of nickel – 6 % and a larger content of zinc – 9.0 % (Fig. 4, h). The strip made by a touch-needle from the alloy AuAg-Pd585-255-160 demonstrates a light trace, which is a characteristic feature of palladium content (Fig. 4, c).

Such an alloy can in practice be easily confused with alloy of assay 750, which is why we additionally tested it by acid reagent for assay 750. The strip made by a touch-needle from the alloy AuAgZnCu585-55-2.0 demonstrates a trace

left by the reagent of a light brownish-orange tint, indicating the presence of zinc in the alloy (Fig. 4, *f*). The touch-needle from the alloy AuAgZnCu585-80-10.0 leaves a still lighter brownish-orange tint, indicating the presence of a considerable amount of zinc in the alloy (10.0 %) (Fig. 4, *i*).

Characteristic color reaction of the jewelry gold-based alloy (rubbed by standard touch-needles) to the reagent “chlorine gold” and on a touchstone

No. of entry	Touch-needle of standard composition		Sediment color
	Mark	Content of composition	
1	AuAgCu585-80	Gold, assay 585, silver, copper	Light-brown
2	AuAgCu500	Gold, assay 500, silver, copper	Dark-brown
3	AuAgCu375	Gold, assay 375, silver, copper	Dark-brown, grey-brown: the sample «shines»
4	AuAgCu585-50	Gold, assay 585, low content of silver (5 %), high content of copper ≥ 35 %	Light-red
5	AuNiZnCu585-12,5-4,0	Gold, assay 585, with a larger content of nickel (12.5 %) and a lower content of zinc (4 %)	Light-yellow, brownish tint
6	AuNiZnCu585-7,0-9,5	Gold, assay 585, with a lower content of nickel (7 %) and a larger content of zinc (9.5 %)	Golden-yellow
7	AuAgPd585-255-160	Gold, assay 585, containing palladium	Light trace
8	AuAgZnCu585-55-2,0	Gold, assay 585, presence of zinc	Light-yellow
9	AuAgZnCu585-80-10,0	Gold, assay 585, with a large content of zinc in the alloy (10 %)	Light, bright yellow

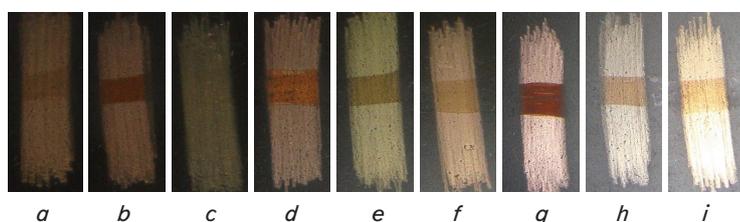


Fig. 4. Characteristic color reaction to the reagent “chlorine gold” by the materials rubbed on a touchstone with standard touch-needles based on gold alloys of different marks: *a* – AuAgCu585-80; *b* – AuAgCu585-50; *c* – AuAgPd585-255-160; *d* – AuAgCu500; *e* – AuNiZnCu585-12,5-4,0; *f* – AuAgZnCu585-55-2,0; *g* – AuAgCu375; *h* – AuNiZnCu585-6,0-9,0; *i* – AuAgZnCu585-80-10,0

Our research that involved touch-needles has revealed that for the case of a significant content of silver in a gold-based alloy the reagent “chlorine gold” forms sediments of brown shades of varying intensity. Coloration of these sediments increases with an increase in the content of copper and a decrease in the intensity of the tint by increasing the content of silver and zinc.

In other words, when testing the gold alloys that contain zinc, the reaction with traditional reagents is not contrast enough.

At the next stage, for the evaluation of conformity of the component composition of the alloy from the system AuAgCu585 and to determine the assay, we tested samples of jewelry items using the reagent “chlorine gold”, and a reagent based on potassium bichromate and copper sulphate.

A representative sample of objects and the results of testing the content of alloys by using XFA are given in Table 5.

Fig. 5 shows results from testing the alloys in jewelry items (samples No. 12 and No. 13) using the reagent “chlorine gold”.

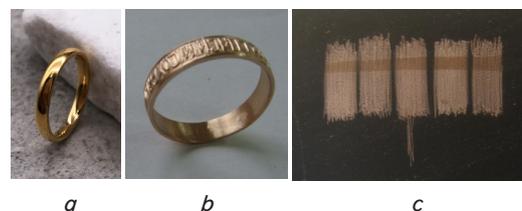


Fig. 5. Results from testing the alloys in jewelry items using the reagent “chlorine gold”: *a* – sample No. 12; *b* – sample No. 13; *c* – reaction to the rubbed material: left – sample No. 12, right – No. 13, center – touch-needle

Under the action of the reagent “chlorine gold” we have established different intensity of a brown color on the strips from samples No. 12 and No. 13. Thus, the sediment to the left from the touch-needle, which is located in the center, has a light brown color (No. 12), and the sediment on the strip to the right of the touch-needle (sample No. 13) is of a red-brown color. This indicates the likelihood of different magnitude of the assay.

To exclude the lower assay of gold in the studied samples, compared to that claimed, we compared the results with the study conducted by using XFA (Table 5). The obtained data indicate that in the first sample (No. 12) the content of gold is 58.68 %, copper – 13.27 %, silver – 28.05 %, in the second sample (No. 13), respectively, 58.93; 33.10, and 7.97 %. That is, the alloy that wedding ring No. 13 was made from contains almost 3 times more copper, which affects the discoloration of the sediment when testing by “chlorine gold” – it acquires a redder shade.

Therefore, testing on a touchstone the rubbed materials from samples using the reagent “chlorine gold” indicates that the assay of the investigated items (wedding rings) matches the stated assay 585. However, the contrast of the reagent’s manifestation is different and it is associated with a different content of copper. Therefore, the results from studying the samples confirm the patterns of color change, identified on touch-needles.

While testing on a touchstone the alloys based on gold of red color that contains silver, copper, zinc, assay 585, using the reagent “chlorine gold”, we discovered certain patterns. For the case of a significant content (5 %) of silver in a gold-based alloy, the reagent “chlorine gold” forms sediments of brown shades of different intensity: from dark-straw (brown, grey-brown) to light golden. The intensity of the sediment

coloration increases with increasing copper content ($\geq 33\%$) and decreases with increasing content of zinc (from 2 to 10 %). At a significant content of silver in an alloy, the reagent “chlorine gold” forms brown spots of different shades, whose coloration increases with increasing copper content and reducing the content of silver. The strips of alloys with a palladium content of the composition AuNiZnCu demonstrate that the reagent forms a yellow-golden sediment; the lighter the color of the sediment, the higher the alloy’s assay. The reagent “chlorine gold” affects the alloys of gold, assay 585, of the composition AuAgPd, by forming a light trace.

When testing the gold alloys with a zinc content above 2 %, we obtain a less contrast reaction. This indicates that zinc reduces the saturation of the sediment, therefore, control over purity of the assay must employ other reagents as well.

Next, we tested alloys of mark AuAgCu585-80 (sample No. 14) under the effect of a reagent based on potassium bichromate and copper sulphate. The reagent dissolved all components of the alloy except gold. After removing the excess reagent, the surface of strips demonstrates gold in the form of a sponge and the mixtures of insoluble salts of silver of red-brown color of varying intensity, indicating a different content of the alloy’s components (Fig. 6).

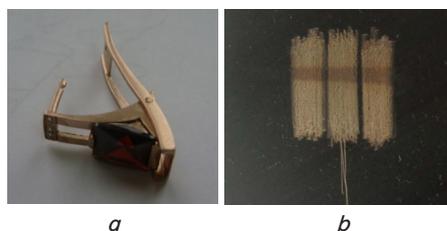


Fig. 6. Results from testing a gold alloy of sample No. 14: *a* – earring, sample No. 14, claimed assay 585, the alloy’s composition AuAgCu585-80; *b* – reaction from the reagent of potassium bichromate and copper sulphate: left and right – material rubbed from the alloy on a touchstone, center – rubbed with a touch-needle

The next stage of our work was to test the samples of articles made from alloys of gold from the system AuAgZnCu containing zinc (samples No. 15–21). These include a decoration – AuAgZnCu 585-55-2.0 (sample No. 15); a wedding ring – AuAgZnCu 585-65-1.0 (sample No. 16); an earring – AuAgZnCu-585-80-1.0 (sample No. 17); a ring – AuAgZnCu 585-80-6.5 (sample No. 18) (Fig. 7). Mass fraction of the components is given in Table 6.



Fig. 7. Samples of articles made of precious metals based on gold containing zinc, submitted for testing (samples No. 15–18)

An analysis of the component composition of samples, established by XFA, has made it possible to define the touch-needles, which are used to test golden articles made from gold alloys from the system AuAgZnCu, assay 585 (Fig. 4).

When testing on a touchstone, we investigated all parts that make up the article. The decoration consists of two

parts (a needle and the main part), so we rubbed two items. The wedding ring was tested where there is no solder. The earring was rubbed twice – at the main (front) side and the fixture; the ring – at caste and outer part.

The coloration of sediments on the strips from touch-needles, obtained under the action of the reagent “chlorine gold”, is significantly darker than the sediment left by the examined alloys. This indicates that all the examined alloys match the assay 585, but have different component composition (Fig. 8).

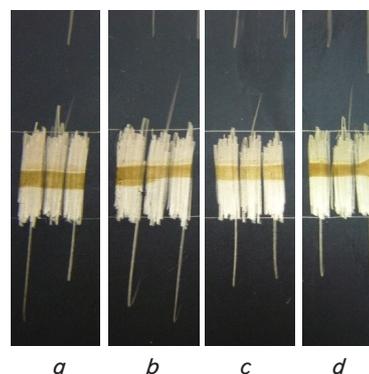


Fig. 8. Change in the intensity of the sediment coloration on the rubbed material from the examined samples and touch-needles under the action of the reagent “chlorine gold”: *a* – sample No. 15; *b* – sample No. 16; *c* – sample No. 17; *d* – sample No. 18

Therefore, when testing, by using the reagent “chlorine gold”, the alloys from the system AuAgZnCu, assay 585, whose ligature, in addition to silver and copper, contains zinc, the sediment coloration acquires a different shade, depending on the content of the latter. In particular, the more zinc in the alloy, the lighter (less saturated) the sediment on the rubbed material: from light straw to golden (Fig. 8). The presence of zinc in an alloy greatly complicates testing on a touchstone – it overestimates the assay for the examined articles.

Thus, to more accurately determine the purity of gold when testing gold alloys from the system AuAgZnCu, assay 585, it is not appropriate to use only the reagent “chlorine gold”, since the reaction is not contrast enough.

At the next stage, samples No. 15–18, containing zinc from 0.96 to 6.87 %, were tested with a reagent based on potassium bichromate and copper chloride. The strips left by gold alloys from the system AuAgZnCu 585 demonstrate, under the action of the specified reagent, a grey-brown sediment of different intensity (hue), (Fig. 9).

To determine the conformity of the examined samples of the articles to the claimed assay 585, we visually compared the intensity of the coloration of the sediment that forms on the strip of the investigated alloy with the coloration of the sediment from a touch-needle.

Fig. 10 schematically shows a change in the saturation of sediment coloration for the examined samples No. 19–21, containing zinc in the amount from 0.94 to 1.74 %, on a touchstone under the action of solution of potassium bichromate and copper chloride.

To obtain the means of identification – reference samples for a change in the color of the sediment on the material rubbed from alloys, we tested standard touch-needles by the reagent based on potassium bichromate and copper chloride (Table 12).

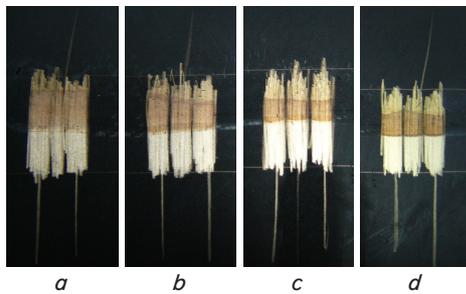


Fig. 9. Change in the intensity of the sediment coloration on the material rubbed from the examined samples and touchneedles under the action of the reagent “potassium bichromate and copper chloride”: *a* – sample No. 15; *b* – sample No. 16; *c* – sample No. 17; *d* – sample No. 18

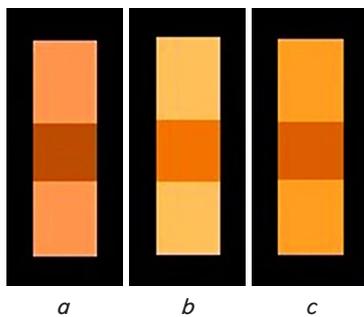


Fig. 10. Scheme of testing precious alloys based on gold of red color, assay 585, with a different content of zinc under the action of the reagent potassium bichromate and copper chloride: *a* – sample No. 19; *b* – sample No. 20; *c* – sample No. 21

Table 12

Change in the color of touchneedles from the system AuAgZnCu 585 with a different content of zinc under the influence of the reagent based on potassium bichromate and copper chloride

No. of entry	Effect of reagent based on potassium bichromate and copper chloride on a touchstone	
	Mark of alloy of touch-needle	Color of sediment formed under the action of reagent
27	AuAgZnCu 585-55-2,0	chestnut
28	AuAgZnCu 585-65-1,0	grey-brown
29	AuAgZnCu 585-80-1,0	light grey-brown
30	AuAgZnCu 585-80-6,5	intensive golden

The obtained sediment coloration of the strips from touchneedles are considerably darker than the sediments from the examined alloys. This indicates that all the examined alloys match the 585 assay. However, the probability of accepting the 585 assay for sample No. 20, which contains up to 1.74 % of zinc and 0.4 % of gallium, to be higher, is large; the quality response is contrast not enough that makes the process of testing more complicated.

When testing the above alloys on a touchstone using the reagent based on potassium bichromate and copper chloride, we revealed a certain pattern. Thus, increasing the content of zinc in red alloys, assay 585, from the system AuAgZnCu

leads to the creation of the lighter shade of the sediment that visually increases the alloy’s assay.

The next reagent for testing gold alloys from the system AuAgZnCu585 included acidic reagents. For clarity, and to compare the colors of the samples’ sediments, we tested the material rubbed with reference touchneedles from the system AuAgZnCu (Fig. 11). For the case of effect from an acidic reagent, for alloys of assay 500, on the material rubbed with a touch-needle of assay 375, a dark brown sediment was formed (Fig. 11, *a*). The material rubbed with a touch-needle of assay 500 demonstrated that the reagent exerted a very weak influence (Fig. 11, *b*). The action of the acid reagent on alloys of assay 750 on the material rubbed with a touch-needle of assay 585 leads to the formation of a black sediment (Fig. 11, *c*). The material rubbed with a reference needle of assay 750 demonstrated that the acidic reagent led to the formation of a barely noticeable sediment (Fig. 11, *d*).

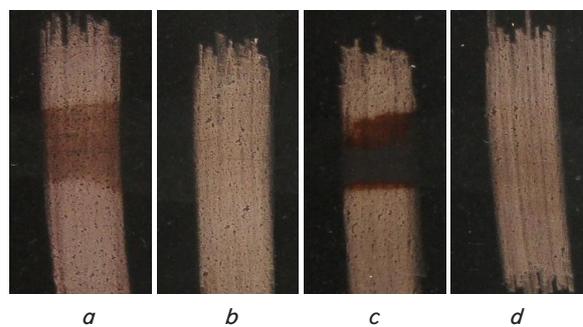


Fig. 11. Qualitative reaction from an acidic reagent on a touch-needle from the system AuAgZnCu: *a* – acidic reagent, assay 500, on gold alloy, assay 375; *b* – acidic reagent, assay 500, on gold alloy, assay 500; *c* – acidic reagent, assay 750, on gold alloy, assay 585; *d* – acidic reagent, assay 750, on gold alloy, assay 750

The most characteristic quality reaction was demonstrated by the action of the acidic reagent, assay 750, on the alloy of white gold, assay 585, containing silver and palladium in the amount of 25.5 and 16.5 %, respectively. The alloy of white gold, assay 585, demonstrated that the acidic reagent, for assay 750, acted with the formation of a bluish sediment (Fig. 12).



Fig. 12. The action of the acidic reagent, assay 750, on the alloy of white gold, assay 585, containing palladium and silver: *a* – sample 22; *b* – characteristic sediment on the alloy of “white gold”, assay 585

The alloys of “white” and “yellow” gold, assay 750, were tested using an acidic reagent for alloys of gold, assay 750; the formation of a barely noticeable tint was observed.

Consequently, the lower the content of gold in an alloy, the stronger the action of an acidic reagent; and this indi-

cates a lower assay of the alloy. An important feature is the time of the reagent's action on an alloy's strip – 2–3 seconds.

6. Discussion of results of studying the influence of ligature composition of an alloy on determining the assay on a touchstone

The composition of alloys based on gold from the system AuAgZnCu includes the following alloying elements: silver, copper, palladium, nickel, platinum, cadmium, zinc, indium. The components affect the formation of a solid solution, the mechanical and chemical properties of an alloy, its hardness, ductility, corrosion resistance, solubility, and the character identification on a touchstone. We have considered and analyzed in this paper four types of alloys from the system AuAgZnCu, assay 585, which are most commonly used, namely: AuAgZnCu 585-55-2.0; AuAgZnCu 585-65-1.0; AuAgZnCu 585-80-1.0; AuAgZnCu 585-80-6.5. We have constructed the following algorithm to test the alloys that consisted of such iterations:

- 1) determining the ligature composition of an alloy by using XFA;
- 2) determining the assay of an alloy by testing it on a touchstone.

To determine the qualitative and quantitative content of gold in jewelry alloys on a touchstone, we used the standard reagent “chlorine gold”, a solution based on potassium bichromate and copper chloride (“colored” reagent), acidic reagents.

The process of identification of alloys based on gold when testing on a touchstone was performed by comparing the color of the sediment formed under the action of a reagent on a reference needle and on the investigated alloy. The means of identification was the composition of jewelry alloys and touch-needles, determined by XFA method.

Results from studying the gold-based alloys on a touchstone have established that the material rubbed with standard touch-needles demonstrate, under the action of the reagent “chlorine gold”, a distinctive colored sediment: from light-brown to grey-brown. In this case, the lower the assay of gold and, consequently, the smaller the content of gold, the darker the grey-brown sediment (Table 11, Fig. 4).

The effect of the reagent on the strips (rubbed material) of alloys of “yellow” and “white” gold is that it forms, together with silver and copper from the solid solution of gold, chloride compounds, thereby reducing to a metallic powder of black and brown color. Copper in this case dissolves, and gold, together with silver, forms at the strip the more or less intense sediment, depending on the content of the ligature composition of the alloy. The amount of the reagent “chlorine gold”, which decomposes, depends on the assay of the examined precious alloy. Consequently, the lower the assay, the larger the silver chloride sediment, the more amount of pure gold is reduced from the reagent, and, consequently, the darker the sediment.

The strips of gold alloys, assay 585, demonstrate that the reagent “chlorine gold” leaves light brown spots. The content of silver, copper and zinc in a gold-based alloy when testing using the reagent “chlorine gold” influences the formation of the intensity of a brown spot. The intensity of coloration increases with increasing copper content and decreasing content of silver and zinc.

The strips from the alloys of gold, assay 585, with a significant content of copper, demonstrate that the reagent leaves a dark brown stain. The strips from the alloys of gold, assay 500, demonstrate that the action of the reagent “chlorine gold” leads to rapid formation of a dark brown (chestnut) sediment. The strips from the alloys of gold, assay 375, as well as lower assays, exhibit a quickly formed sediment of muddy-greenish-yellow hue. The strips from the alloys of “white” gold, assay 585, of the composition AuNiZnCu, demonstrate that the reagent creates a yellow-golden sediment; the lighter the sediment coloration, the higher the alloy's assay. The reagent “chlorine gold” has no effect on the alloys of “white” gold, assay 585, of the composition AuAgPd, and gold alloys from the system AuAgZnCu, assay 600 and above.

This is explained by that the reagent “chlorine gold” reacts with the ligature components of the alloy, which are in the state of solid solution with gold, applied onto a touchstone, releasing certain substances.

In this case, copper chloride and silver chloride, as well as the reduced powder of metallic gold from the reagent are formed according to the scheme:



Copper chloride remains in the solution, and the intensity of coloration of the mixture of sediments of silver chloride and gold powder depends on the ligature composition of an alloy. The lower the assay of the tested alloy, the greater amount of the reagent “chlorine gold” that decomposes, the larger the formed silver chloride sediment and the more pure gold is reduced from the reagent, and, consequently, the darker the sediment that is obtained.

However, the color of the sediment depends not only on the interaction between chlorine and silver, but for the most part on the ligature composition of a precious alloy, that is, on the content of Zn, Ni, In, Ga as part of a solid solution.

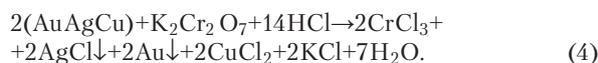
To establish the impact of concentration of alloying components that make up a precious gold-based alloy on determining the purity (assay) of gold, we performed tests using the reagent based on potassium bichromate and copper chloride (and sulphate) with the addition of hydrochloric acid. When testing the alloys (samples 15–22), we revealed the following pattern: with the increased content of zinc in the red alloys from the system AuAgZnCu, assay 585, the sediment color on the rubbed material acquires a lighter shade (light-golden). This visually overestimates the assay compared to alloys with a less content of zinc within a given assay.

Therefore, testing the precious gold-based alloys from the system AuAgZnCu, assay 585, containing more than 2 % of zinc, by using the reagent based on potassium bichromate and copper chloride, leads to an overstatement of the assay.

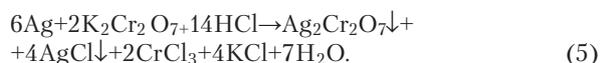
The action of reagent on a gold-based alloy with a content of zinc leads to dissolving all components in a solid solution of the alloy, except for gold. Upon removing the excess reagent, the surface of the strip exhibits gold in the form of a sponge and a mixture of insoluble salts of silver. For some alloys, this sediment is deposited with the equivalent amount of chromium chloride, thereby increasing the contrast of the reaction. The lower the assay of a gold alloy, the faster and the more actively the reagent affects the strip of an alloy, the darker the sediment.

Alloying components that are included in the solid solution of gold, including zinc, nickel, indium, influence the qualitative reaction, providing for its non-contrast appearance that indicates the overestimated purity of gold.

This fact is explained by that in general the processes that occur under the influence of this reagent on alloys AuAgCu can be represented as follows:



At the same time, the following reaction occurs:



If the reagent contains hydrochloric acid, it reacts with the alloy components, which are in the state of solid solution with gold, with the formation of sediments of silver chloride, silver bichromate, and sometimes – chromium chloride. Similar action is demonstrated by the reagent based on sulfuric acid. Silver sulfate forms instead of silver chloride at the same time. Upon removing the excess reagent, the surface of the strip with gold exhibits a sediment of salts of silver in the form of a sponge. When the course of the reaction yields the equivalent amount of chromium chloride, the reaction's contrast is enhanced.

The alloys whose ligatures includes zinc, nickel, indium, etc., and which are not affected by traditional reagents, react with copper chloride (assay reagent) to form, accordingly, chloride and copper.

For example,

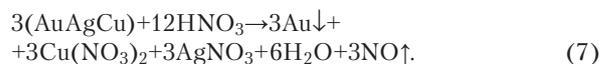


The presence of a large content of zinc (4 %) in a precious alloy based on gold leads to the formation of a greater quantity of zinc chloride, which produces a lighter color in the sediment on the rubbed materials and can bias the results of assay determination towards overestimation.

The alloys of gold with an assay above 600 should be tested on a touchstone using acidic reagents, which consist of diluted nitric acid with hydrochloric acid added by drops.

The action of acidic reagents on a solid gold solution leads to that nitric acid forms with silver and copper from the alloy the soluble nitric-acid salts. Pure gold is deposited in the form of a dark amorphous sediment of grey-brown color. Under the action of acidic reagents on the alloys of gold with an assay above 600 the released chlorine promotes the partial dissolution of amorphous sediment of gold and produces with silver the sediment of silver chloride (AgCl). The intensity of these reagents on the high- assay alloys is predetermined by the concentration of chlorine ion and depends on the amount of ligature in the alloy.

Under the action of acidic reagents on the rubbed material from a golden alloy, nitric acid forms with silver and copper, which are included in a solid solution of the golden alloy, the soluble nitric-acid salts. The strips from alloys of gold of respective assay, deposited on a touchstone, demonstrate that the corresponding acid reagents leave the sediments of greyish-brown shades. In this case, pure gold is deposited in the form of a dark brown amorphous sediment, that is, the reaction proceeds according to the following scheme:



When testing the samples of jewelry alloys based on gold, assay 585, which correspond to the standard touch-needles from the system AuAgZnCu (No. 1–13, 15 alloys 578/583) using the acidic reagent for the higher assay, the color reaction manifests itself very quickly and sharply, so you'd better off without it.

When testing the alloys of gold, assay 585, (touch-needles No. 1– 3, 15) and the alloy AuNiZnCu 585-125-40, it is better not to apply an acidic reagent due to a very rapid and drastic action of the reagent. The gold alloys of these compositions are appropriately tested either by the reagent “chlorine gold” or the corresponding reagent based on potassium bichromate and copper chloride (sulphate).

The alloy of “white” gold of mark AuAgPd 585-255-160, containing palladium, forms, when tested by an acidic reagent for gold, assay 750, a dark sediment of bluish hue (the strip of the alloy is exposed to this reagent for 2–3 s.). The acid reagent for the gold alloy, assay 585, produced no qualitative reaction.

It should be noted that using the acidic reagents for the alloys of gold with an assay above is accompanied by the formation of the intermediate product, gaseous chloride nitrosyl, which must be treated under the hood.

It is appropriate to test the gold alloys from the system AuAgZnCu 585-255-160 either by the reagent “chlorine gold” or the corresponding reagent based on potassium bichromate and copper chloride (sulphate).

7. Conclusions

1. It was established that determining the assay of gold in precious alloys from the system AuAgZnCu of red and white color on a touchstone using the reagent “chlorine gold” depends on the contrast manifestation of qualitative reaction against the level of a standard sample (touch-needle). The lower the assay of gold in the examined precious alloy, the greater the amount of the reagent “chlorine gold” that decomposes, the larger the amount of the formed silver chloride sediment and the larger the amount of pure gold reduced from the reagent, the darker the sediment. At a significant content of silver in a gold-based precious alloy the reagent “chlorine gold” forms brown spots of different shades – from light brown to grey-brown. The coloration of stains increases with an increasing copper content and a decrease in the content of silver and zinc. The reagent “chlorine gold” has no effect on alloys of gold from the system AuAgZnCu with an assay above 600 and on “white” gold, assay 585, of the composition AuAgPd, containing palladium. To prevent the overestimation of a gold alloy's assay, the assay control must preliminary determine the composition of the alloy by XFA, select touch-needles and other reagents.

2. It was established that testing the gold alloys from the system AuAgZnCu585 using a reagent based on potassium bichromate and copper chloride forms on a touchstone a sediment of grey-brown color of varying intensity: from chestnut to golden. It was determined that an increase in the content of zinc (above 2 %) in precious alloys based on gold of red color from the system AuAgZnCu585 influences creating a brighter tint of the sediment that visually overestimates the gold assay. It was proven that testing the

precious alloys of red color from the system AuAgZnCu585 containing zinc (above 2 %), gallium, indium, using the reagent based on potassium bichromate and copper chloride, is not effective. To eliminate such a phenomenon, one needs to preliminarily determine the composition of the alloy by XFA and employ other reagents for tests.

3. It was determined that the assay of gold, defined on a touchstone, for alloys from the system AuAgZnCu585 (the content of zinc above 2 %) manifests itself in a more contrast manner with a brown color under the action of acidic reagents, which depends on component composition of the alloy. The faster and the stronger the reagent, the lower the assay of the tested alloy relative to a touch-needle.

4. It is proven that the alloys of “white” gold, which include palladium and silver from the system AuAgPd, assay 585,

are tested by the acidic reagent for gold, assay 750, with the formation of a dark sediment of bluish tint. The acidic reagent for gold, assay 585, has no effect on this alloy.

The alloys of “white” and “yellow” gold from the system AuAgPd, assay 750, are tested by the acidic reagent for gold alloys, assay 750, with the formation of a light dark tint.

5. The practical significance of our research implies improving the testing procedure when examining the assay of “non-standard”, unknown alloys of precious metals based on gold. Specifically, for jewelry items made from special brands of steel and low-assay alloys that are used for the manufacture of jewelry items, personal jewelry, tableware, piercing services, etc. This research is of particular importance for the assay and customs control, voluntary certification, and testing when fraud and forgery may occur.

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Досліджено вплив різних комбінацій «мішень – сталева підкладка» на механічні та хімічні властивості захисних покриттів, отриманих за допомогою іонно-плазмової обробки. Широке застосування іонно-плазмових технологій для зміцнення виробів стримується недосконалістю обладнання, відсутністю достатніх теоретичних і експериментальних досліджень з контролю і регулювання фізичних властивостей і технічних параметрів процесу обробки. Зняття цих проблем можливе на підставі подальших досліджень і нових рішень в області технології зміцнення. Для досліджень в цьому напрямку використовувався експериментальна іонно-плазмова установка з програмним забезпеченням для регулювання і контролю енергії, дози, концентрації імплантованих іонів, тиску робочого газу, товщини покриття. Застосована ефективна методика підвищення якості робочої поверхні сталевого інструменту, яка дозволила здійснити масоперенос легуючих елементів поверхневою іонно-плазмовою обробкою. За рахунок регульованої низькотемпературної двохстадійної іонізації атомів азоту і легуючих елементів в реакційному обсязі відбувалося насичення кристалічної решітки заліза імплантованими іонами і утворення карбонітридних фаз легуючих елементів, відповідальних за підвищення твердості, зносо- і корозійної стійкості. Виявлено оптимальні параметри процесу імплантації ($U_p=25$ кВ, $I_p=35$ мА, $D=4,01 \cdot 10^{17}$ см⁻² за 1 год.), які дозволили досягти поліпшення поверхневих властивостей конструкційної вуглецевої, конструкційної легованої, інструментальної сталей. Встановлено взаємозв'язок між терміном служби виробів і властивостями отриманої після імплантації поверхні. Показано збільшення терміну служби виробів з покриттям TiN (в 1,5–3 рази), CrN (в 1,9–6 разів) і ZrN (в 3–12 разів) в порівнянні з виробами без покриття. Проведено аналіз і визначено найбільш ефективні варіанти комбінацій «мішень – сталева підкладка» для практичного застосування захисних покриттів. Оскільки застосування порівняно недорогих сталевих виробів з підвищеними характеристиками міцності має економічні вигоди для виробника і є однією з тенденцій сучасного виробництва

Ключові слова: іонна імплантація, захисне покриття, сталева підкладка, зносостійкість, термін служби

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ANALYSIS AND COMPARISON OF MECHANICAL AND CHEMICAL PROPERTIES OF PROTECTIVE COATINGS OBTAINED AT DIFFERENT COMBINATIONS OF "TARGET – SUBSTRATE"

L. Vasetskaya
PhD

Department of Machines and Apparatus of Chemical Production
Institute of Chemical Technologies of the Volodymyr Dahl East Ukrainian National University
Volodymyrska str., 31, Rubizhne, Ukraine, 93009
E-mail: VasLa@i.ua

1. Introduction

Wear-resistant steels and hard alloys are widely used in various sectors of the national economy. The stamps of such steels and alloys are distinguished by high resistance to surface abrasion and contact deprecation and are widely used in the automotive industry, metallurgy, the woodworking industry, medicine, electronics, etc. [1].

Ensuring the improvement of product quality is important to the consumer and contributes to the growth of the manufacturer prestige, but often leads to an increase in the

cost of products due to the complexity of technology production, as well as the associated energy and resource costs.

With the development and improvement of various technologies, it has become possible to obtain protective coatings that have good mechanical and chemical properties. However, the use of ion-plasma technology to harden the surface is hampered by imperfect equipment, the lack of sufficient theoretical and experimental research to control and regulate the physical properties and technical parameters of the process.

The use of coatings with high protective properties on the working surfaces of products from cheaper materials is