Analytical control of jewelry alloys in Assay Offices of Russia

Dr. Lysyakova V. I., Director of Moscow Assay Office

Russian hallmarking supervision was introduced by Russian tsar Peter The Great as a common state system more than 300 years ago, in 1700.

Applying of marks after assay of articles (items) in gold and silver alloys was adopted from practices of some European towns.

At present, hallmarking supervision on the territory of Russian Federation (RF) is carried out by Russian state Hallmarking Chamber, which is a part of the Ministry of Finance. It consists of 18 territorial inspections (Assay Offices) and their 7 branches.

Assay Offices are located throughout Russia. The most western Assay Office are in Kaliningrad, on Baltic Sea, the most eastern ones are in Chabarovsk and Vladivostok, on Japanese Sea.

The largest Assay Offices are to be found in Moscow and St. Petersburg. The Moscow Assay Office has occupied a building in the center of Moscow for more than 100 years. After the recent reconstruction, the total aria exceeded 3000 m^2. The staff consists of 120 people. More then a half of them are engaged in reception, touchstone department, assaying and marking. The rest are in management and general supporting duties.

Around 18-20 millions items are hallmarked in Moscow Assay Office annually. More then 70 % of those are made of gold alloys. Items made of Pt and Pd constitute less than 0.2 % and the rest are silver items.

The daily flow varies with the time of year. It increases significantly before Christmas holidays, 8th March (Women's day) and before large jewelry exhibitions (fairs).

The main tasks of Assay Offices are to control whether the content of precious metals meets the standards established in Russia and to apply the state mark.

The following table presents the standards for fineness of precious metal alloys for alloys of Pt, Au, Ag and Pd, which are established in RF.

Pt	**Au**	**Ag**	**Pd**
950	999	999	850
900	958	960	500
850	750	925	
	585	875	
	500	830	
	375	800	

This list is longer than the one set by the ISO 9202.

All new items made of precious metals must be submitted to one of Assay Offices for an assay. They are hallmarked only if all parts, including solder, are up to one of the standards laid down by the law. If the article doesn't meet the announced standard, it can be hallmarked by the closest lower fineness (upon agreement with the customer) or returned to the maker for re-melting.

The process of assay and hallmarking of items articles submitted to an Assay Office consists of several steps:

Parcels arrive to the reception office and articles are accepted by weight or by count in the presence of maker's representative. Items can be submitted in any form – from part-finished Russian-manufactured product to imported jewelry ready for sale.

Customer fills out standard forms containing all necessary information about the parcel (the type of an article, it's weight and precious metals involved). This information is entered in Assay Office's computer and passed for the preparation of an invoice.

The charges vary according to the weight of an article, the precious metal involved and the customer (it is more expensive for private citizen than for manufactures). Russian Assay Offices are budget organizations and the money received for the assays and marking go to RF budget.

Articles are accepted from private citizens only if they have the manufacturer's sign. If articles brought for sale are made abroad, they are accepted for hallmarking only with customs declarations.

Touchstone testing

Accepted articles with standard forms are transferred to touchstone department. Forms contain information on statistical sampling for control analysis.
Special program allows to control flows of articles from manufactures and to follow the sampling normatives for control analysis.

Normatives for sampling the articles for destructive analysis are established by internal instruction. For example, for golden articles no less than one article is analyzed from 0,5-1 kg of batch (depends on the level of trust for manufacturer).

Articles chosen from batches are submitted to chemical laboratory. The rest of the articles are analyzed by touchstone method. So, for batches of identical articles a combination of statistical sampling for destructive analysis and numerous touchstone tests are used.

Touchstone technique is simple, but requires significant work experience.

The sample to be analyzed along with a comparative sample (so-called needles)

With a known composition is placed on a stone. Special reagents are applied on to streaks and comparison of touch behavior and solvent reactions allow to determine the precious metal content.

Comparative samples have to be adequate to analyzed alloys, because various alloy elements have different influence on color of the alloy and their solvent reaction.

To provide a reliable result, this method requires a number of comparative alloys. The analytical accuracy depends on the operator experience and varies between 0,5-2 %

All articles in gold, platinum and palladium are checked using touchstone analysis.

All silver articles are checked if there are less then 100 articles in the batch. If there are more then 100 articles in the batch at least 30% of the articles are checked.

Silver articles with precious metal plating are not checked by touchstone method, but are hallmarked according to the result of the control analysis.
All articles, the fineness of which is doubted after touchstone analysis, are transferred to the chemical laboratory for extra analysis in addition to statistical sampling.

Assaying

The items arrive to the chemical laboratory for analysis from the touchstone department.

For analysis of golden articles, fire assay or cupellation method is used as in every European Assay Offices. The method is based on a processes of refining gold known from old times. The best human inventions live long, and this is exactly what happened to cupellation method. The main idea of the method stayed the same, only technical support changed. Nowadays, no other method allows to

determine the gold content with such precision. Accuracy of gold determination is 0,05 % if electronic balances capable of weighing up to 0,01 mg along with specially designed thermostatically controlled electric furnaces are used.

In our lab, we use balances produced by companies Mettler and Sartorius and special furnaces with controlled air flow produced by a Russian company Termit.

Sampling for fire assay requires removing 100 – 250 mg of representative material from the article. That's why we seldom use triangular steel scraper for this purpose, because surfaces of article may be enriched by plating or chemical attack. To take a sample for analysis the article is destroyed (cut).

The procedure of analysis involves weighing the samples, which are normally in the range of 125 to 250 mg and wrapping them in lead foil with addition of pure silver (The ratio of gold to silver is 1: 2,5).

This and other lead-wrapped samples, along with check samples, are placed in magnesite cupels which stand in furnace at about 1000°C. After about 15 minutes, the base metals associated with the gold are extracted into the molten lead, oxidized by oxygen of air and absorbed into the cupel leaving silver bead, containing all the original gold.

This bead is rolled into a thin strip, coiled into a spiral and immersed in nitric acid to eliminate *the* silver.

After annealing, the residual golden coil is weighed. Relating this to the original weight allows us to calculate the gold content.

The check samples are considered an essential part of the assay because they provide independent evidence of its accuracy.

Check samples are synthetic alloys composed from pure metals. They have to be adequate to the analyzed samples. This is important because the value of the check correction depends on alloy composition.

This method is described in standard ISO 11426 and in the Russian standard. The Russian standard, besides instructions for gold determination, contains instructions for silver determination by means of cupellation method. The method requires cupellation of extra samples without adding silver. Total gold and silver content in the sample is determined according to the weight of the received bead. Silver content is determined according to the difference.

Atomic absorption analysis is used for complete determination of jewelry alloys composition. However, we use this method to determine the content of the main components (besides gold), since the analysis of traces is beyond our goals.

Silver in silver jewelry alloys is determined by applying volumetric method using ammonium thiocyanate (Volhard) or potentiometric titration with sodium chloride solution. The sample is dissolved in dilute nitric acid. The silver content is determined by titration with standard solution with visual or potentiometric indication of the end point. . Accuracy of silver determination is 0,1 %.

Platinum and palladium in their alloys are determined gravimetrically. The samples are dissolved in aqua regia. Palladium is precipitated with dimethylglyoxime, platinum is reduced by mercury (1) chloride. The accuracy of platinum and palladium determination is about 0,3 %.

The important task of jewelry alloy control is entrusted to the chemical laboratories (labs) of the Assay Offices. Buyers and manufacturers of jewelry are interested in liability of analysis results, in

other words, in laboratory's competence. Competence of a chemical laboratory is determined in the process of its accreditation by special organizations. Requirements for accredited laboratories correspond to ISO 17025. If results of accreditation are positive, laboratories receive certificates of accreditation confirming laboratory's competence.

The important criteria for lab accreditation include availability of premises and safe work conditions; availability of qualified personnel, equipment and reagents, standard samples, standardized or validated analysis methods, etc. Every laboratory must have a quality control system for quantitative chemical analysis, including both internal and external control of analysis results. The Hallmarking Chamber carries out external control. Besides, Assay Office laboratories take part in the international system for precision control of results of jewelry alloy analysis "Labtest", organized by Prague Assay Office.

As for now, 3 laboratories of the Russian State Hallmarking Chamber received accreditation certificates from the Russian organization for accreditation.

Hallmarking

After the analysis is completed and all forms are filled out, the article batch is sent to the marking department.

In Russian Assay Offices 3 methods of marks application are used:

- Mechanical
- Electrical spark method
- Laser.

More then 80% of articles are hallmarked with the mechanical method.

When a hallmark is applied with the use of electrical spark, the item is an anode and the hallmark-bearing electrode is a cathode. At the moment of electrical spark anode's material is evaporated and a hallmark is left, repeating the image of the cathode. The advantage of this method is the ability to hallmark hollow articles, articles with jewels, enamel, ets.

Laser hallmarking is based on application of laser ray impact on metals through a mask with required image. Laser method has the same advantage as the electrical spark method.

A mark with an image of a sickle and a hammer on a 5-pointed star background was used In Russia from 1965 to 1994. In 1994, a new state mark was established with an image of a woman head facing right. This image is placed into frames of different geometrical forms with a three-digit number that shows the content of the basic precious metal in 1000 parts of alloy and Assay Office's code – letters of Russian alphabet.

Hallmarks are classified into basic marks and additional marks. Additional marks are placed on the parts that can be easily separated from an article.

All articles made of precious metal must have a maker's mark. State mark is applied to the right from the maker's mark.

All marked articles pass internal control to ensure that marks have been correctly applied and that the article was not damaged.

Marked articles are sent to the reception office and returned to the customer.

X-ray fluorescence spectrometer

The workload in Assay Offices increases constantly, so does the variety and nomenclature of samples. The staff of the AO has to overcome the difficulties resulting from that.

First, non-traditional alloys that need to be analyzed cause the difficulties. During the Soviet period, we have been a closed country and have worked with a limited number of jewelry alloys regulated by branch standards. All those alloys were provided with comparative samples for touchstone testing (needles). Nowadays, many imported items need to be analyzed and marked. Besides, Russian factories and workshops buy lots of foreign alloys of unknown composition. The AO has many needles with the composition similar to a variety of modern alloys. However, it is difficult sometimes to choose the right needle based on a very limited knowledge of the alloy composition of the tested item.

Second, our state standards for fire assay methods require that the necessity of making a check adequate to the analyzed alloy. If the composition is totally unknown, it has to be determined first.

The work of analytical department of assay offices is not limited by determination of fineness of articles made of precious metal. Objects of analysis include ligatures, solders, electrolytes, tailings, sections, different alloys of technical purpose and other materials that contain precious metals and come for expertise from law-enforcement bodies and revision department of assay office.

The objects of analysis are characterized by great variety in terms of number of determined elements and the range of their contents. Experienced analysts familiar with traditional methods of "wet chemistry" solve many problems. However, during the past years, problems and tasks of assay laboratories became more complicated and the necessity of implementation of modern, non-destructive, express, multi-element methods of analysis into the practice of analytical control became evident.

In 2000, in accordance with the request from the Russian State Hallmarking Chamber was developed a new X-ray spectrometer MetExpert GOLD. The spectrometer had to satisfy the following requirements:

1. Determination of precious metals and main components of jewelry alloys and solders (Au, Ag, Pt, Pd, Rh, Ir , Cu, Zn, Ni, In, Sn, Pb, Cd) in concentration range 0,5–100 % with analytical accuracy not higher then 0,5 % abs.;

- Analysis must be executed without standard samples;
- Express analysis;
- Local analysis;
- Possibility of analysis of any other alloys;
- Simple operation, not requiring high operator's experience.

All these requirements have been met by the creator of X-ray spectrometer MetExpert GOLD.

We have used this spectrometer for two years and were pleased with the quality of the instrument.

The spectrometer is specially adapted for analysis of alloys containing precious metals and jewelry items made of them.

The diameter of the primary X-ray beam used for the local analysis is about 1 mm.

Small items can be conveniently positioned in a pullout sample holder. A special device for aiming allows to select easily the site for analysis, thus enabling the analysis of multi-fragment jewelry items.

The spectrometer has an option of being equipped with a special chamber that permits positioning of both small and larger items. The dimensions of the chamber are: width – 400 mm, depth – 400 mm, height – 350 mm.
The chamber enables an easy and accurate aiming into desired point.

Detachable recorder that can be distanced from the spectrometer for1,5 m, allows the analysis of large objects like antique items, icon frames, etc.

This is express analysis, and the exposition is set by the operator.

Recommendation for choice of exposition:

1. For the most accurate analysis like with validation of techniques, accuracy control, etc., recommended exposition is 60-100 seconds.
2. For routine analysis of jewelry alloys shorter exposition of about 30 seconds can be used.
3. For fast article sorting exposition can be reduced to 10 seconds.
4. For cases, when it's necessary to identify or determine low contents of elements, exposition is 100 - 200 seconds.

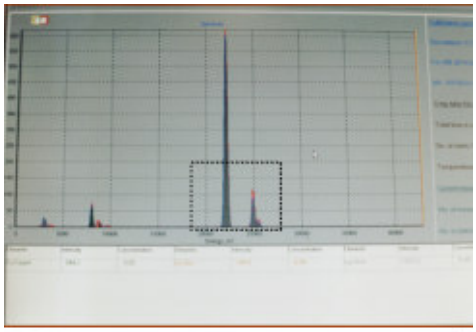
The MetExpert Gold spectrometer uses the method of Fundamental parameters which doesn't require the use of standard samples and plotting the calibration curve.

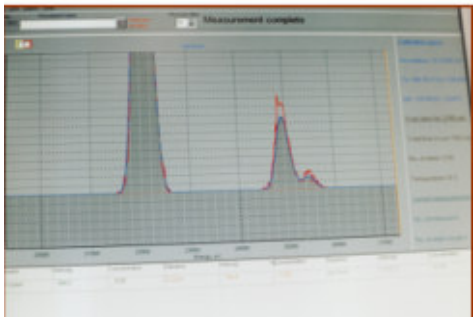
After mathematical processing the spectrum of analyzed alloy in which
the peaks corresponding to different elements are in different colors and the table with analysis results are displayed.

The software included in MetExpert Gold spectrometer package allows to process the spectra mathematically with the use of three programs: "Jewelry alloys", "All elements", and "Selected elements" The program for processing can be chosen by activation of icon [Mode] with a mouse. When a "Jewelry alloys" Mode is chosen, the program identifies and selects for processing only the data for elements that are the components of jewelry alloys and solder. When "All elements" Mode is chosen, all spectrum lines (all elements – from Ca to Am) are identified and processed.

The use of "Jewelry alloys" mode is recommended when jewelry alloys and articles are analyzed, thus providing more accurate results.

"All elements" mode is a method of choice in the following cases:
- analysis of objects of unknown nature;
- analysis of articles with installations when installed material has to be identified. This is the case of qualitative analysis!





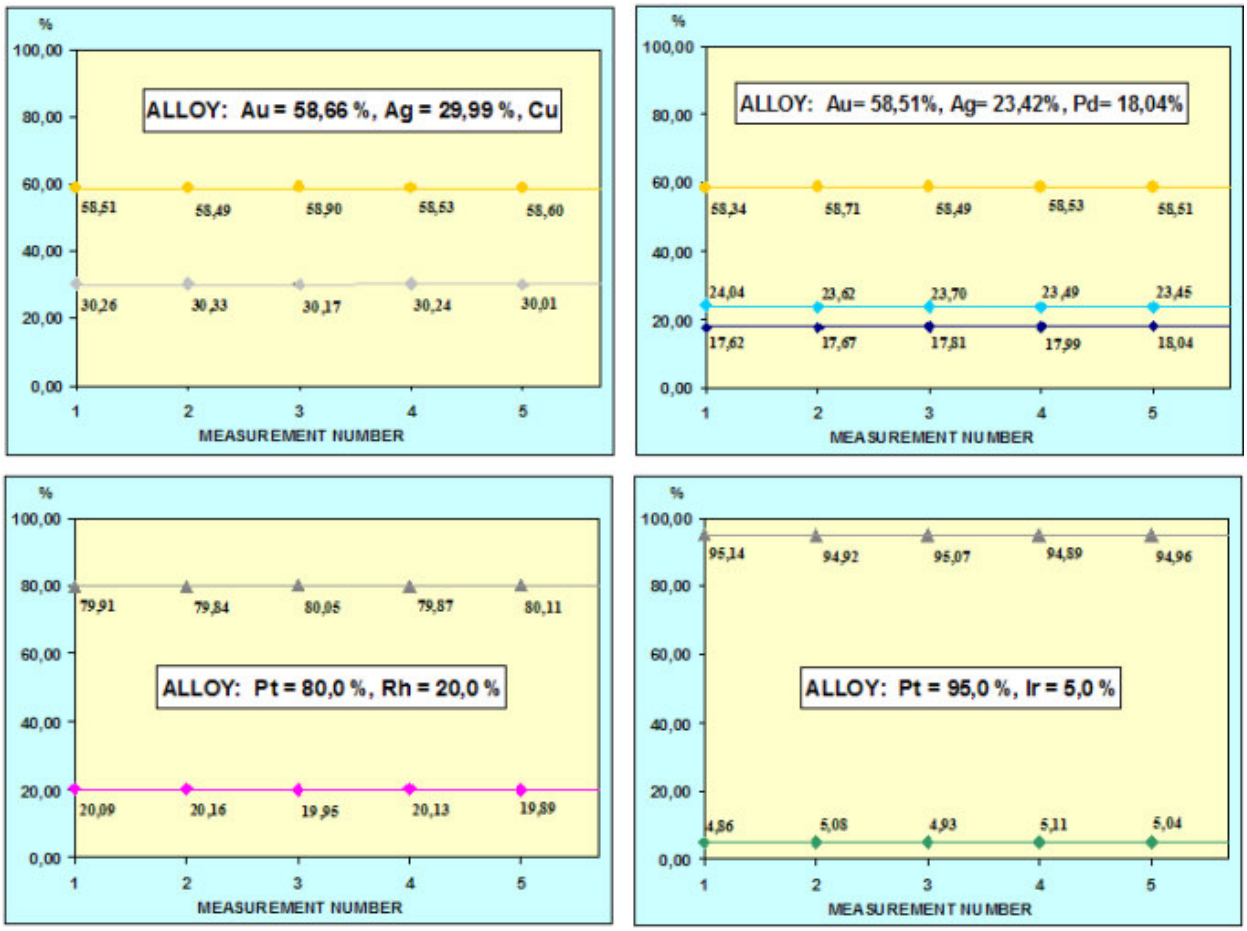
Program "Selected elements" allows to choose the list of elements to be determined and is used for analysis of alloys with known composition.

To check the correctness of identification, different areas on the spectrum have to be examined with magnification. The red (contouring) line shows the real collected spectrum. The blue line represents the calculated (model) spectrum. This is the spectrum that is used for calculations and determination of the composition of analyzed material. The peaks corresponding to different elements are in different colors. Evidently, in an ideal case, the real and the model spectra (red and blue lines) have to be close. All the peaks present in the spectrum have to be identified (colored) and the intensity of the identified peaks should be above the background. If any of the listed criteria is not met, the correctness of the results should be questioned.

Information on analysis accuracy received earlier is not actual today because the work was done on the spectrometer with a lower energy resolution and old version of software.

We are planning a new validation of analysis technic in accordance with ISO 5725. From our work experience with the spectrometer we know, that the difference between the received result and accepted reference value does not exceed 0,5 % for single determination and for the average from 2-3-determinations is 0,2 – 0,3 %.

The tables, shown in annex, demonstrate analysis results for gold and platinum base alloy and illustrate repeatability and accuracy of analysis.



For correct use of analysis results it's necessary to remember that X-ray spectroscopy is a method of surface analysis.

X-ray fluorescence spectrometer is designed for the chemical analysis of object's surfaces on an area determined by the diameter of the primary X-ray beam. The deepness of X-ray penetration into the object depends on the conditions of excitation and on the properties of analyzed matter. In the case of jewelry alloys, the X-ray beam penetration is no longer than 40-50 μ. Thus, the signal is formed in a relatively small volume of the material and the item needs to be uniform for extrapolation of the results of the analysis for entire item. Uniformness of the item implies its homogeneity and absence of surface coating.

During X-ray fluorescence analysis of objects with coating, the primary X-ray beam passes the coating and excites the fluorescence of both the coating, under layer and the major material of the object. The emission of the surface layers has a significant impact on the spectrum and the impact increases with the thickness of the coating. Naturally, the results cannot be interpreted as the real quantitative composition of the alloy of the object.

An oxide film formation on the surface is another source of errors during surface analysis. Before analyzing old objects, the surface has to be scrubbed with an abrasive rubber and wiped with alcohol.

I'd like to show you several printouts of spectras and results of analysis of different alloys to illustrate analytical possibilities of the spectrometer.

The X-ray spectrometer MetExpert Gold significantly helps us in everyday work. We use this instrument to solve the following problems:

1. Determining compositions of jewelry alloys and choosing needles for touchstone testing;

2. Determining compositions of jewelry alloys for composing check for the cupellation method;

3. Determining compositions of ligatures-import alloys for making jewelry alloys. They contain all components except gold;

4. In some cases the method of XRA substitutes the method of touchstone testing and even chemical analysis. For example, articles made of alloys Pt-Ru, Pt-Co, not provided with adequate needle, come to the Assay Office for hallmarking. The gravimetrical method is destructive and long-lasting, it’s accuracy is comparable with the accuracy of X-ray analysis.

5. The use of the spectrometer allows to reduce the amount of determination with the use of chemical methods. We make a decision about returning articles without hallmark if the article's fineness is less than the announced standard and the difference exceeds the value of analysis accuracy. This usually happens with articles of small manufactures who work with customer's materials.

6. Analysis of different alloys of technical purpose and other materials that contain precious metals and come for expertise from law-enforcement bodies and revision department of assay office. Usually these materials have unpredictable composition. They are secondary raw materials, scrap of precious metals and before quantitive analysis sorting and identification is required.

For example, in one of such orders, there were about 2 kg of different fragments of metals, white and gray, of different sizes. We have done this expertise using the X-ray spectrometer MetExpert Gold. There were fragments of pure Pt and Ag, of different silver-base alloys, Pd-Ir alloy, thermo-couple scrap and others. Without the spectrometer MetExpert Gold it would have been very difficult to analyze those materials.

7. Museum department of Moscow Assay Office has portable model of X-ray spectrometer MetExpert Gold, which is placed in a case, It’s weight is about 12 kg. A lot of expertise is done in different museums using this instrument. The analysis accuracy of this model is the same.

All these examples show how useful is the X-ray spectrometer in our everyday work.

At present the Russian state Hallmarking Chamber ordered for making 16 X-ray spectrometers MetExpert Gold for all Assay Offices of Russia.