Appendix 9. Protocols (CIP 0 - CIP 6)

Mining and Metallurgical Company "Norilsk Nickel"
Institute of Criminalistics of the Russian Federal Security Service
State Research Institute for Rare Metals

Complex Procedure

for identification of the Nature and the Source of Origin of Precious Metal Containing Products of Mining and Metallurgical Operations

Moscow, 2006

1. The purpose and the scope of the Complex Procedure

The present Complex Procedure is aimed at identifying the nature and the source of origin of materials produced from ores containing precious metals as well as their mixtures and mixes with other materials.
The Complex Procedure employs a combination of analytical methods to determine the following:

- elemental composition of a substance, including contaminants;
- phase composition of a substance;
- elemental composition (and morphology) of individual microparticles in a substance thus allowing a semi-quantitative determination of the substance in terms of a limited number of microparticle groups where the groups are considered to represent individual phases.

The information obtained by these methods is compared to the corresponding information in the Reference Data Base (hereinafter - RDB) in order to assess the nature and source of origin of an analyzed substance.
Systematized information on precious metal-containing products produced at different process lines of metallurgical operations, and periods of time is included in the RDB. The RDB containing information on 70 types of products was started in 2003 and continues to be updated. Information on each product produced by Norilsk Nickel is summarized in a corresponding databank and “Product Data Sheet”. Databanks and “Product Data Sheets” are continuously updated as new types of products appear or as additional results of analyses of products become available.

Target materials of this procedure are:

- precious metal- (PGMs, gold and silver) containing products and intermediates of mining and metallurgical operations, withdrawn from illegal circulation; their mixtures and the mixes with other materials;
- microresidues left on the surface of evidence material and other objects that are assumed to have been in contact with the stolen materials, (e.g. dust, dirt on the floor, furniture, clothing, tools, packing, car covers and other parts of a cars’ interior, etc.), as well as microresidues on bodies, in the hair or under nails of a crime suspect. Methods for sample collection and handling of microresidues are described in detail in the scientific literature[1,2] and are therefore not included in the protocols.

[1] “Criminalistics”: Textbook. Chief Editor N.P. Yablokov; 3rd edition – M., “Youth” (“Junost”), 2005. P. 257.
[2] Khrustalev V.N. “Conceptual Fundamentals of Criminalistic Analysis of Substances, Materials and Products thereof”. Author’s abstract of dissertation/thesis made by J.D., M. – 2004. P.p. 41-43.

Criminalistic examination of such materials pursues the following objectives:

- identification of the confiscated material as a certain type of product;
- provenance of the material (company, shop, process line).

2. The procedure for determining the nature and the source of origin of a substance

In order to identify the nature and the source of origin of a substance as a product of any operating unit or of a particular plant, it is necessary to compare the results of the study of the sample with the information contained in the RDB. An overview of the analytical methods and their corresponding protocols within the Complex Procedure is given in Figure 1.

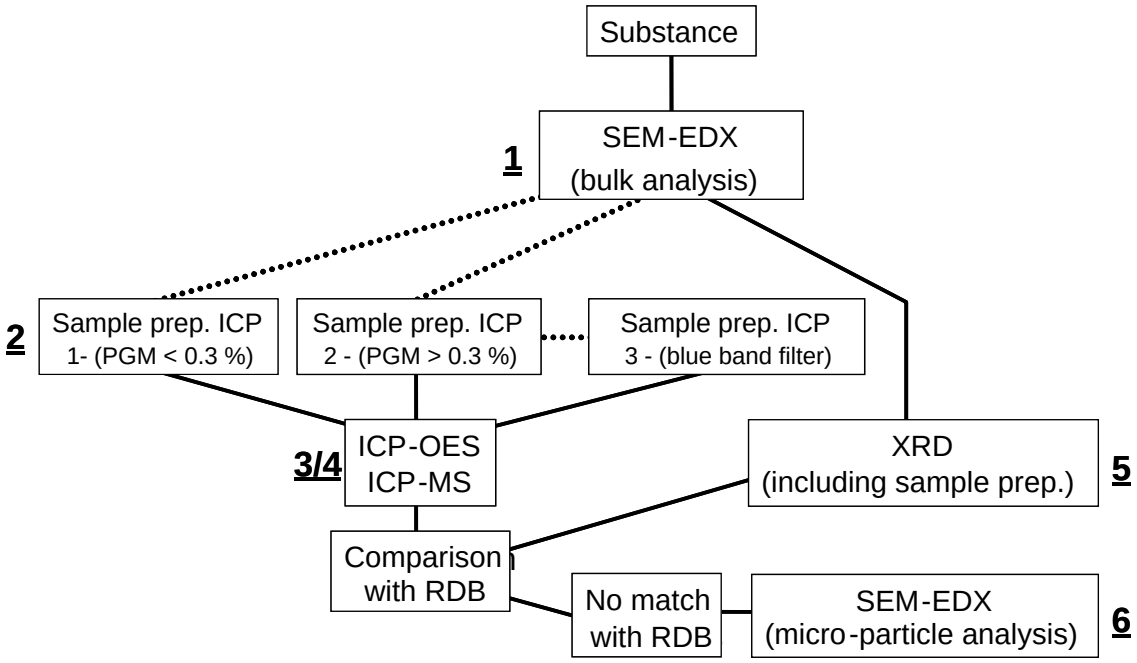

Figure 1 Overview of the Complex Procedure, consisting of 6 analytical methods which are described in this document. The numbers refer to the protocol numbers.

At the first stage of the study, the bulk elemental composition of the substance is determined by Scanning Electron Microscopy with X-Ray Spectral Microanalysis (SEM-EDX) in accordance with **Protocol 1** of the Complex Procedure. The results are used in the preliminary identification of the substance, and for the determination of the sample preparation method (**Protocol 2**) for the ICP-MS and ICP-OES analyses.

The next stage includes the determination of the elemental composition by Inductively Coupled Plasma Optical Emission Spectrometry (**Protocol 3**) and Inductively Coupled Plasma Mass-Spectrometry (**Protocol 4**) and the study of the phase composition by X-Ray Diffractometry (**Protocol 5**). Selection of which of the methods 3 or 4 to use depends on the

elements that are to be determined and their concentrations **(See Paragraph 2 in Protocols 3 and 4)**. The results of each study are compared with the data in the RDB. In the case of a full match of the sample characteristics with one of the RDB products (i.e. when all diagnostic features overlap), a conclusion as to the type of this product and its source of origin can be made.

If the features of the sample analyzed by the aforementioned methods do not match any of the product types represented in the RDB, than the hypothesis that the sample is a mix of products is examined. For this purpose it is necessary to examine the elemental composition and morphology of individual particles of the sample using SEM-EDX (**Protocol 6**). If the features of some particles match the features of particles belonging to any product or products from the RDB, this product or a mixture of products may be present in the material under analysis. The assumption that the substance is a mixture can be further verified by comparing all previously identified features of this sample with the features of the pattern mixture of the appropriate types of products represented in the RDB (superposition method). A conclusion is made upon the results of this comparison. If no particles with the features typical of ore products containing precious metals are found, it can be concluded that such products are not present in the analyzed sample.

Application of the complete Complex Procedure is possible only if the mass of the sample is greater than 10 g. Smaller samples may in some cases result in failure to identify the full range of features as specified in the Complex Procedure. If the mass of a sample is less than 1g, then that sample can be examined only by SEM-EDX (Protocol 6).

The Complex Procedure includes the following analytical protocols:

1. **Determination of the bulk elemental composition of precious metal-containing products by scanning electron microscopy with X-ray microanalysis**
2. **Wet acid digestion of PGM containing products for ICP-OES and ICP-MS analysis**
3. **Determination of the elemental composition of precious metal-containing products by ICP-OES**
4. **Determination of the elemental composition of precious metal-containing products by ICP-MS**
5. **Determination of the phase composition of precious metal-containing products by XRD**
6. **Determination of the elemental composition of micro particles of precious metal-containing products by scanning electron microscopy with X-ray microanalysis**

Determination of the bulk elemental composition of precious metal-containing products by scanning electron microscopy with X-ray microanalysis

Author:

Quality manager:

Authorisation:

Date :

This procedure is applicable as of November 1st 2006

0 Update and review summary

0.1 Updates

#	Section	Nature of Amendment	Date	Authorisation

0.2 Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

CONTENT

1 Title

Determination of the bulk elemental composition of precious metal-containing products by scanning electron microscopy with X-ray microanalysis.

2 Scope

The method is intended for the quantitative determination of the bulk element composition of dispersed materials. This method enables the determination of the quantitative content of elements in the following concentrations ranges:

- from 5 to 100 wt. % for elements from oxygen to fluorine;
- from 0.2 to 100 wt. % for elements from sodium to uranium

3 Safety and environment

The general analysis and safety requirements prescribed by national and local laws and regulations in force at the enterprise must be followed.

4 Definitions

Accuracy (trueness): closeness of the agreement between the mean value achieved from the series of analysis results and the adopted true value.

Error (of measurement): deviation of the analysis result from the true value.

Reference Material (RM): material or substance for which the property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement, or for assigning values to materials.

Calibration function: functional relationship relating the measured signal intensity to the analyte quantity.

Detection limit: lowest content of analyte, which could be detected with 95% probability using this particular method.

Probe (subsample): portion of the tested material that is removed for testing, following the procedures described in the protocol to assure its representativeness.

5 Principle

The method is based on the interaction between a scanning electron beam with sample material. During the interaction of the electron beam with sample material, secondary electrons and X-ray emission are generated along with a variety of other signals.

Secondary electrons are emitted from the atoms occupying the surface of the sample directly exposed to the electron beam. Collection and display of these secondary electrons forms a readily interpretable image of the surface. The contrast of the image is determined by and displays the sample morphology.

The X-ray emission depends on the elemental composition of the analyzed material. Energy measurement of the characteristic X-ray emission permits the determination of qualitative elemental composition. Measurement of the intensity of a characteristic line is used to calculate quantitatively the concentration of the associated element. Calculations of the elements' concentrations are made with the use of physical models of interaction between the

electron probe and sample material.

6 Reagents and Materials

- Technical, particle free, distilled ethyl alcohol (96%).

7 Apparatus and Equipment

- Scanning Electron Microscope with Energy Dispersive Microanalyzer providing the determination of elements from boron to uranium with spectral resolution better than 135 eV for the Kα line of Mn at a count rate of 1000 counts per second;
- Ultrasonic disperser with frequency of 20-33 KHz;
- Adjustable volume pipette of 200-1000 μL;
- Sample mounts (stubs, studs) for scanning electron microscope;
- Disposable carbon conductive double sided adhesive tapes for scanning electron microscope sample mounts;
- Set of reference materials for EDS calibration;
- Optical binocular microscope with magnification from 20 to 100 times.

8 Sample preparation

Separate a probe (subsample) weighing 0.5 g from the powder sample by repeated quartering and place it into a disposable 1.5 mL plastic test tube. Add 1 mL of ethyl alcohol and mix the contents using the ultrasonic disperser for 5 minutes.

During this ultrasonic mixing, take 0.2 mL of the suspension by a micropipette and place it on the scanning microscope sample mount covered with a conducting carbon film.

Dry the sample stage with the suspension on it at ambient temperature. Use an optical binocular microscope (20-100 times total magnification) to control the process of suspension transfer on the sample mount. The dried sediment must form a thick layer of micro particles that does not crumble. If micro particles form crumbly aggregates, the process of sample preparation should be repeated using a newly prepared sample mount.

9 Calibration

Prior to beginning an analysis, verification of the operational condition of the scanning electron microscope with the X-ray microanalyzer must be established. This includes presence of system peaks, accuracy of magnification, and determination of spectral energy calibration and resolution. Energy calibration of the Energy Dispersive Microanalyzer is performed every 2 hours of equipment work using a “Set of reference materials for X-ray microanalysis” in accordance with the Operating Manual.

10 Quality control

Appropriate control of the analytical results is executed in accordance with ISO 5725 requirements using natural minerals as Reference Materials. Recommended minerals as reference materials are: Wollastonite, Zircon, and Rhodonite.

Quantitative analysis accuracy is considered satisfactory when the following conditions are

met:

$$\frac{|C - C_K|}{C_K} \leq 0{,}05 \ , \qquad (1)$$

Where,

- C_k is the accepted value of the element mass concentration (more than 1%) in the reference mineral
- C is the measured average (n=5) element mass concentration in the reference mineral

If condition (1) is not achieved, the microanalyzer must be recalibrated (see paragraph 9).

11 Procedure

Prepare the scanning electron microscope and energy dispersive microanalyzer according to their Operation Manuals. Specific values of instrument operating parameters will depend upon the specific model of instrument used.

Examples of measurement parameters, provided for reference, are as follows:

- Accelerating potential: 20 KV;
- Field of vision: 2.0 x 2.0 mm;
- Spectrum integral intensity: ≥ 300000 counts;
- Spectral resolution ≤ 135 eV for Mn-Kα;
- Element range: from Oxygen to Uranium;
- Concentration range: from 0.2 to 100 wt. %.

The integral (bulk) elemental composition of a substance is defined by measuring the integral X-ray spectrum emitted by the collection of micro particles on the sample stage in the field of vision of the electron microscope. The field of vision is chosen so that the maximum possible number of micro particles are in full view at a time. The number of micro particles must exceed 1000 particles.

The bulk elemental composition is based on the average of 5 measurements for which the fields of vision are not overlapping.

12 Calculation

At the first stage of processing of each obtained spectra, qualitative element analysis is conducted on the basis of the location of characteristic lines. If characteristic lines overlap, a best estimate of the elements presents in the micro particle is checked with the help of an element composition calculation (using the software of the analyzer). An element is considered present if the value of its calculated concentration is greater than the detection limit.

Quantitative content of the detected elements is calculated using software supplied with the analyzer. For each element detected in the examined substance, the range of concentrations determined in the five analyses is calculated.

The results on the bulk element composition are used for preliminary identification of the

sample material and the choice of analytical methods for its further analysis (including sample preparation methods – see Step 2) the CIP-0 Protocol.

13 Reporting procedures including expression of results

Analysis results are recorded in a form required by the examining laboratory's reporting protocol. In addition to the analysis results, the protocol also must include:

- date of the testing,
- information about the expert (a profession acquired after graduation from the University, expert profession, period of service as an expert, post taken),
- incoming sample data (source of the sample's origin, who, when and in what way sampling has been executed),
- data about the number of executed measurements on the basis of which analysis results were obtained.

14 Normative references and manuals

ISO 5725–1 through ISO5725-6 Accuracy (trueness and precision) of measurement methods and results. Part 1/Cor1:1998, Part 2/Cor1:2002, Part 3/Cor1: 2001, Part 4:1994, Part 5/Cor1:2005, Part 6/Cor1:2001.

ISO/IEC 17025:2005 General Requirement for the Competence of Testing and Calibration Laboratories.

The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics: 1998 (EURACHEM).

15 Method performance

Relative error is better than 15% for elements from sodium to uranium and 30% for elements from oxygen to fluorine, except in cases where there are peak overlaps for which accurate corrections cannot be made.

For spectrums with 300000 counts total intensity the detection limits are:

- from oxygen to fluorine - 5 percent by weight;
- from sodium to uranium - 0.2 percent by weight.

Wet acid digestion of PGM containing products for ICP-OES and ICP-MS analysis

Author:

Quality manager:

Authorisation:

Date :

0 Update and review summary

0.3 Updates

#	Section	Nature of Amendment	Date	Authorisation

0.2 Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

CONTENTS

1 Title

Wet acid digestion of PGM containing products for ICP-OES and ICP-MS analysis.

2 Scope

This procedure is intended for full acid digestion of PGM-containing ore concentrates, semi products of their pyro- and hydro- metallurgical processing and also final (commodity) concentrates for subsequent ICP-OES and ICP-MS analysis.

3 Safety and Environment

The general analysis and safety requirements prescribed by national and local laws and regulations in force at the enterprise must be followed.

4 Definitions

"Tsar's vodka": freshly prepared 3:1 (v:v) mixture of concentrated HCl and HNO_3.

Probe (subsample): portion of the tested material that is removed for testing, following the procedures described in the protocol to assure its representativeness.

5 Principle

The method is based on dissolution of the examined sample's probe in inorganic acids. If the sample has not dissolved completely, the sediment is melted together with barium peroxide or sodium peroxide and the resulting fusion product is dissolved using inorganic acids.

6 Reagents and Materials

- De-ionized water of specific resistance 18 MOm·cm;
- Analytical grade Nitric acid;
- Analytical grade Hydrochloric acid (concentrated);
- Analytical grade Hydrochloric acid diluted 0,3 vol.%, 10 vol.%, 15 vol.%, 20 vol.%;
- "Tsar's vodka";
- Analytical grade Sulfuric acid 10 vol.%;
- Analytical grade Hydrofluoric acid (concentrated);
- Analytical grade Barium peroxide;
- Analytical grade Sodium peroxide;
- Analytical grade Sodium sulfate;
- Reference Materials having a composition similar to the samples being tested.

7 Apparatus and Equipment

- Analytical balance with precision equal to or better than 0,001g;
- Electric oven with closed coil
- Muffle furnace providing heating temperature up to 1000˚C.
- Drying oven with temperature regulation providing maintenance of the required temperature up to 150˚C;
- Adjustable pipettes with 1, 2, 5 and 10 ml marks;

- 100, 250 ml volumetric flasks;
- Graduated beakers volume 50, 100 ml;
- Glass beakers volume 100, 250, 300, 600 ml;
- Conical glass funnels # 5;
- 50-100 ml Teflon beakers with lids;
- Glass-carbon bowls (Teflon beakers) volume 200 ml;
- Watch glass;
- Agate mortar and pestle;
- Corundum crucibles;
- "Blue band" de-ashed paper filters;
- Equipment for crushing homogenization of probes (ball crusher or disk mill fitted with tungsten carbide components).

8 Sample preparation

Using the quartering method, select a probe having a mass of 100 g from the received sample. If the mass of the sample is less than 500 g, the probe mass should be 10 g.

If the mass of the probe is not more than 10 g, it is sent to the examination in full.

Select a probe from a Reference Material to be prepared along with the test samples. Select one or more Reference Materials that are similar to the composition of the test samples as determined in Protocol CIP 1. The available Reference Materials appropriate for use with the RDB are given in Table 1.

Table 1.

Reference Materials for use with the RDB. N refers to Transpolar Branch of OAO GMK Norilsk Nickel and K refers to Kolskaya GMK.

Sample Code (Passport Number)	Sample Identification
N18	Nickel Sludge
N19	Copper Sludge
N20	KP-1 Grade Concentrate
N21	KP-2 Grade Concentrate
K11	Nickel Sludge
K16	Copper Sludge
K22	Platinum-Palladium Concentrate
K25	Dried Copper Sludge

Dry the probes for samples and Reference Materials at 105°C to constant weights and homogenize them by means of crushing (abrasion) in an agate mortar or with the help of a mill.

9 Calibration

Not required

10 Quality Control

The completeness of sample dissolution is judged by the following methods:

- Visually by the absence of sediment;
- Dilution of appropriate reference materials;
- Batch variation method.

If using the batch variation method, one should prepare four additional batches 1/5 the size indicated in paragraph 11. The compositions of these additional probes are measured in accordance with Protocols 3 and 4. The measurements results of these additional diminished probes must coincide with the measurement results of the regular probes, within the limits of error, calculated by the t-criteria (Δ=3, 18*MSD, where MSD - mean-square deviation).

11 Procedure

Method 1[1] - Samples with low precious metals content (less than 0.3 percent by mass).

Select 4 batches of samples 1.00 g each, by repeated quartering from the powder sample, and place each one into a Teflon beaker (glass-carbon bowls). Wet each sample with 1 ml of deionized water and add 50 ml of 'tsar vodka' during 0.5-1 hour while heated up to slow boiling. Cool the solutions and add 10 ml of hydrofluoric acid. Let the solutions stand for 2 hours at room temperature. Steam the resulting solutions at a temperature of 60-70˚C to the condition of wet salts. Then, add 15 ml of "tsar vodka" and 5 ml of hydrofluoric acid and again steam the solutions to the condition of wet salts. Repeat treatment by the "tsar vodka", then add 10 ml of concentrated hydrochloric acid and steam the solution to the condition of wet salts. Finally, add 10 ml of concentrated hydrochloric acid and 30-40 ml of deionized water and boil the solution for 5-10 min.

The completeness of sample dissolution is judged visually by the absence of sediment.

If there is no sediment, pour the resulting solution into a 100 ml volumetric flask, add 10 vol.% solution of the hydrochloric acid to reach the mark, and then mix the contents.

If sediment is present, see **Additional method.**

Method 2[1] - Samples with high precious metals content (above 0.3 percent by mass)

Select 4 subsamples weighing 0.50g each by repeated quartering from powder sample, and place them into separate Teflon beakers (glass-carbon bowls). Wet each sample with 1 ml of de-ionized water and then add 16 ml of the "tsar vodka". Let the resulting solutions sit for 30 min at room temperature and then for 1.5-2 hours under heating up to a temperature of 60-70˚C. Add 3 ml of hydrofluoric acid and steam to the condition of wet salt and add 10-15 ml of concentrated hydrochloric acid and again steam to the condition of wet salt. Repeat the HF

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[1] For determination of Arsenic, Selenium and Tellurium the following method of probe preparation is used.

Place probe batch of 0,2 g weight in the 300 cm^3 beaker, then add 30 cm^3 of nitric acid and 1-2 cm^3 of Bromine. Place the beaker covered with a watch glass in an exhaust hood for 1 hour for sulfur oxidation. Then, warm the beaker on an electric hotplate for 20-30 minutes for bromine evaporation. After that cool and wash off beaker walls with water. Heat the beaker until dissolution is complete, cool the solution, pour it into the volumetric flask (100-250 ml), and add deionized water to the mark. Let insoluble sediment settle and then filter solution through the 'blue band' filter.

and HCl additions two more times. Dissolve the wet salts by heating to the temperature of 60-70˚C in 50 ml of concentrated hydrochloric acid. Pour the solution into a 100 ml measuring flask, increasing its volume with the 20% hydrochloric acid to reach the mark, and mix well.

The completeness of sample dissolution is judged visually by the absence of sediment.

If sediment is present, see **Additional method.** (See below)

Additional method [2]– If residue is present

For either Method 1 or Method 2, if the probes did not dissolved completely, filter the solutions with the residues through the dual 'blue band' paper filters in to 600 ml beakers. Wash filters with sediments 3-4 times with hot 20 vol.% solution of hydrochloric acid and 3-4 times with hot deionized water. Preserve the filter with sediment. Evaporate the filtrate to a volume of 10-20 ml, then add 20 ml of hydrochloric acid and cool (Filtrate 1).

Place the filter with residue into a corundum crucible and place it in an oven. Raise the temperature gradually to 600-650˚C to dry, ash and calcine the material. Hold the temperature for a period of 30-40 minutes. Cool the crucible and mix its contents with barium peroxide (mass proportion 1:10) and place in a separate corundum crucible for further melting in a muffle furnace. Place crucibles with mixes in a warm (≤ 200˚C) muffle furnace and slowly heat up to 900°C over 2 hours. Cool the crucibles with fusion products at room temperature. Place the crucibles in 250cm^3 beakers, pour 100ml of 15 vol.% hydrochloric acid over the contents, cover the beakers with watch glasses, and dissolve the fusion[3]. After dissolution of the fusion is finished, extract each crucible from the solution with the help of a glass rod and wash with 15 vol.% hydrochloric acid and then water. Heat each solution to the point of full chemical decomposition of barium peroxide and than add to Filtrate 1.

Evaporate the combined Filtrate 1 to wet salts. Add 20 ml of analytical grade hydrochloric acid and add water up to 100 ml. Heat until boiling and add drop by drop 1-2 ml of hot (10 vol.%) sulfuric acid and then add also by drops a solution of sodium sulfate until obtaining a transparent solution upon addition of the last drop. Cool the solution, filter it through the 'blue band' filter and wash the sediment 5-6 times with the 0,3 vol.% hydrochloric acid. Evaporate the filtrate to a volume of 20-30 ml. Pour it into a 100 ml volumetric flask and bring to the mark with 10 vol.% hydrochloric acid. Mix the contents of the volumetric flask well.

Note: If barium peroxide is not available, sodium peroxide could be used for dissolving of the sediment.

12 Calculation

Not required

13 Reporting procedures including expression of results

Solution results are recorded in a form required by the examining laboratory's reporting protocol. It must be recorded in the report in what form the sample was received (in form of powder, or bar, or cake and etc.), how it was fined, whether any residue was left after dilution, and what actions was taken in order to dissolve this residue.

14 Literature and manuals

[2] In order to determine Barium (Sodium) and Sulfur, an additional probe must be picked up from the solution before using **additional method.**

[3] If dark residues are present on the filter, the filter must be ashed and the smelting procedure repeated.

Not required

15 Method performance

Not required

Determination of the elemental composition of precious metal-containing products by ICP-OES

Author:

Quality manager:

Authorisation:

Date :

Update and review summary

0.1 Updates

#	Section	Nature of Amendment	Date	Authorisation

0.2 Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

CONTENTS

1 Title

Determination of the elemental composition of precious metal-containing products by ICP-OES.

2 Scope

This procedure is intended for determining sodium, aluminum, magnesium, sulphur, phosphorus, potassium, calcium, chromium, manganese, iron, cobalt, arsenic concentrations in the range of $1 \cdot 10^{-4}$ to 100 weight % in the tested material; as well as titanium, nickel, copper, selenium, molybdenum, ruthenium, rhodium, palladium, silver, tin, antimony, tellurium, barium, tungsten, platinum, gold and lead concentrations in the range of $1 \cdot 10^{-2}$ to 100 weight %, using the method of optical emission spectroscopy with inductively coupled plasma.

3 Safety and Environment

The general analysis and safety requirements prescribed by national and local laws and regulations in force at the enterprise must be followed.

4 Definitions

ICP-OES: - method of inductively coupled plasma optical emission spectroscopy.

Error (regarding a single analysis result): difference between a test result and the accepted reference value.

Error index "Δ": limits of the error associated with a test results determined under reproducibility conditions with the stipulated probability.

Precision: closeness of agreement between independent test results obtained under stipulated conditions.

Standard Deviation: measure of how values are dispersed about a mean in a distribution of values.

Repeatability: precision under repeatability conditions, i.e. conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time.

Repeatability Standard Deviation: standard deviation of test results obtained under repeatability conditions.

*Repeatability Limit "r"***:** value less than or equal to which the absolute difference between two test results obtained under repeatability conditions may be expected to be with a probability of 95%.

Reproducibility: precision under reproducibility conditions, i.e. conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

Reproducibility Standard Deviation: standard deviation of test results obtained under reproducibility conditions.

Reproducibility Limit "R": value less than or equal to which the absolute difference between two test results obtained under reproducibility conditions may be expected to be with a probability of 95%.

Reference Material (RM): material or substance of the subject for analytical testing

sufficiently homogeneous regarding one or several reliably determined characteristics to be used for the measurement method assessment.

Calibration function: functional relationship relating the measured signal intensity to the analyte quantity.

5 Principle

The method is based on measuring the intensity of the spectral line caused by stimulation of identifying element's atoms in an inductively coupled plasma. During these measurements, solution of the sample under analysis is sprayed into the plasma. Quantification of an element's concentration is made by comparison of the intensity of its spectral line with those of a series of calibration standard solutions.

6 Reagents and Materials

- 99.996% Gaseous argon;
- Ultra pure water, >18MΩ·cm;
- Ultra pure hydrochloric acid, 15 vol.%;
- Standard solutions of the elements to be analyzed with mass concentration 1000 µg/ml.

7 Apparatus and Equipment

- Inductively Coupled Plasma Optical Emission Spectrophotometer with computer controlled operating and data handling system.
- Adjustable pipettes with 200-1000 µl and 1.0-5.0 ml marks;
- 25 ml and 250 ml volumetric flasks;

8 Sample preparation

Executed in accordance with CIP protocol # 2.

9 Calibration

Prepare calibration solutions by dilution of the standard solutions with mass concentration 1000 µg/ml on the day of use. Concentrations of the determined elements are listed in Table 1.

Table 1
Mass concentration of the test elements in calibration solutions

Calibration solution No.	Mass concentration of each element, µg/ml
0- calibration blank	0
1	10
2	1,0
3	0,10

Preparation of calibration solution No. 1:

Pipet 2.5 ml of the standard solution (mass concentration of 1000µg/ml) of each of the test elements into a 250 ml volumetric flask. Then, add the diluted hydrochloric acid solution (15 vol%) to fill the flask to the mark.

Preparation of calibration solution No. 2:

Pipet 2.5 ml of calibration solution No. 1 into a 25 ml volumetric flask. Then, add the diluted hydrochloric acid solution (15 vol%) to fill the flask to the mark.

Preparation of calibration solution No. 3:

Pipet 2.5 ml of calibration solution No. 2 into a 25 ml plastic test-tube. Then, add the diluted hydrochloric acid solution (15 vol%) to fill the tube to the mark.

'Çalibration blank'

The diluted hydrochloric acid (15 vol%) which was used for preparation of calibration solutions is the 'calibration blank'.

Calibrate the spectrometer using solutions No. 1, 2, 3 and 'calibration blank'. Measure the 'calibration blank' first and then the calibration solutions in decreasing order of their numbers. From the intensity of the test elements' emission lines, subtract the intensity of the 'calibration blank'. For each element, acquire 3 scans and calculate an average intensity value from these measurements.

Construct a calibration curve for each analytical wavelength within the following axes: average intensity (after subtracting the 'calibration blank') vs. mass proportion of the tested element in the calibration sample. Regression factors are automatically calculated and saved in the computer memory until the next calibration.

Calibration curves should be linear and have a linear correlation coefficient of at least 0.999. If calibration curves do not satisfy this condition, the spectrometer calibration must be repeated.

10 Quality Control

Quality Control of analysis results should be conducted in accordance with the regulations of the ISO 5725 with the use of Reference Materials, close to the tested samples in their chemical composition. Also, the difference between test results and corresponding value of the Reference Material must be smaller than the Error index "Δ".

If unacceptable results are obtained, the ICP's operating conditions and the spectrometer alignment must be checked and the calibration must be repeated. If the repeated calibration does not provide a smaller difference between the test result and the corresponding value of the Reference material, most likely the sample preparation was not done correctly. The samples must be digested again according to Protocol CIP 2.

Stability control of the Calibration Curves is conducted after measurement of each 10 samples.

Calibration solutions are used for the stability control of the Calibration Curves. The mass concentration of determined elements in the Calibration solutions should be in the range of the measured mass concentrations.

Calibration is considered stable when the following condition is fulfilled:

$$\frac{|C - C_K \cdot|}{C_K} \leq 0{,}05 \ , \qquad (1)$$

Where:

C_k – is the value of the element mass concentration of the Calibration solution, µg/ml;

C – is the measured value of the element mass concentration, µg/ml.

If condition (1) is not achieved, the spectrometer must be calibrated again.

Suitability evaluation of duplicate results on the same subsample is carried out in the following manner.

The arithmetic mean of two measurements executed on the same subsample is accepted as the final result of the analysis when the difference between them is within limits of the *Repeatability Limit "r_2"*

If the absolute deviation between the results of two measurements exceeds "r_2" one must obtain two more measurement results.

If in this case the difference between the biggest and the smallest values of 4 measurements is equal or less than the critical range $CR_{0,95,n=4}$ (calculated for the confidence level value of P=95%) than as the ultimate result one should record the arithmetic mean of the 4 measurements.

If the difference between the biggest and the smallest meanings of four measurement results is bigger than the critical range for four measurements, then the median value for four measurements should be recorded as the ultimate result, which is calculated in accordance with the following formula.

$$\overline{X} = med\{X_1 < X_2 < X_3 < X_4\} = \frac{X_2 + X_3}{2}, \qquad (2)$$

Where,

X_2 – the second smallest result;

X_3 – the third smallest result.

Deviation between the results of the initial and repeatable analysis must not exceed the *Reproducibility Limit R.*

11 Procedure

11.1 Procedure on determination of the element composition.

Prepare the spectrometer as described in its Operation Manual.

For an Optima 3000 (Perkin Elmer, USA), the following working parameters are given as guidelines of typical operating conditions. Daily operating conditions will vary slightly from these values in order to optimize instrumental response:

- ICP generator working frequency: 40 MHz
- Output capacity: 1,3 KWt
- Plasma forming argon flux: 15 l/min.
- Transporting argon flux: 0,8 l/min.
- Cooling argon flux: 0,5 l/min.
- Observation height: 15 mm;
- Sample feed rate: 0,85 ml/min.

The wavelengths of lines recommended[1] for this analysis are shown in Table 2.

Table 2
Recommended wavelengths of spectral lines

Test element	Wavelength, nm	Test element	Wavelength, nm	Test element	Wavelength, nm
Aluminum	396,150	Lead	220,353	Ruthenium	240,272
Antimony	217,579	Magnesium	279,553	Selenium	196,026
Arsenic	188,979 193,759	Manganese	260,568	Silver	338,289 328,068
Barium	455,403	Molybdenum	202,030	Sodium	589,592
Calcium	396,847	Nickel	231,604	Sulphur	180,669
Chromium	205,560	Palladium	340,462	Tellurium	214,283
Cobalt	228,616	Phosphorus	178,221 185,943 213,618	Tin	189,927
Copper	324,756	Platinum	265,946	Titanium	334,905
Gold	242,795	Potassium	766,485	Tungsten	207,912
Iron	238,204	Rhodium	343,489		

In the process of measurements, mutual influence of elements should be taken into consideration and if necessary a correction procedure should be applied.

Spectrometer calibration is done in accordance with § 9 of this Protocol.

During the analysis, inject blank solutions and solutions of tested samples in the spectrometer and measure the intensities of analytical lines of the determined elements. Subtract the intensity of the blank from each measured line. Obtain three measurements for each solution and calculate the mean value of the measured intensities for each analytical line. Use the corresponding calibration curve, to determine the mass concentration of each element in each tested subsample and record the values obtained.

11.2 Procedure for identification of the source of a sample of unknown origin.

The procedure for interpretation of the results of the ICP-OES measurements depends to some extent upon the type of sample being tested and the forensic question to be answered. The most straightforward application is comparison of the element concentrations determined in a sample of questioned origin with the compositions of products in the RDB. A decision that the composition of the substance being tested corresponds to the composition of one specific product in the RDB can be made if the concentration of each element in the unknown substance measured using this protocol (taking into account the error index of the method) is within the variability range of the concentrations of that element in that product.

[1] If analyst uses a different wavelength it should be specified in the analysis report.

In the case that the elemental composition coincides with the composition of a product in the RDB it is necessary to specify this conclusion in the analysis report.

In accordance with Protocol 0, the identification of an unknown substance can be considered complete if a correspondence with a product in the RDB is determined on the basis of elemental (Protocols 3,4) and phase (Protocol 5) composition.

The element concentrations determined using this protocol may also be used to answer other questions of forensic significance. The concentrations of elements, particularly the distribution of PGMs may be compared to world-wide databases to provide information concerning possible regions of origin for a sample. Some level of deconvolution of mixtures may be possible using the results of this protocol, when the composition of end members is known or can be estimated. Specific procedures for these and other similar interpretive evaluations cannot be provided in this analytical protocol, because they depend upon the specific case evaluations needed. The purpose of this protocol is to provide an analytical method that produces element concentrations of known accuracy and precision that can be utilized for answering a variety of questions of forensic interest.

12 Calculations

Weight % of the determined element is calculated using the following formula:

$$X = \frac{C \cdot V}{M} \cdot 10^{-4}, \quad (5)$$

Where,

C – mass concentration of the element determined using the calibration curve in µg/ml;

V – final volume of the sample solution including all dilutions if operator had done them) in ml;

M – weight of the subsample in g;

As the final result of an analysis of a sample, the arithmetic mean of two measurements or the median of four measurements are given. Whether the arithmetic mean or the median values are given depends on the quality of the measurements and the procedure for this is specified in § 10.

13 Reporting procedures including expression of results

Analysis results are recorded in a form required by the examining laboratory's reporting protocol. In addition to the analysis results, the report must also include:

- date of the testing,
- information about the expert(a profession acquired after graduation from the University, expert profession, period of service as an expert, post taken),
- incoming sample information (source of the sample's origin, who, when and in what way sampling was executed),
- the results of comparison of unknown substance composition with RDB (Does unknown sample composition match with composition of any product from RDB? With what specified product does it match?).

The number of significant figures in the analysis result (element concentration) should correspond to the number of significant figures according to the *Error index*.

14 Normative references

ISO 5725–1 through ISO5725-6 Accuracy (trueness and precision) of measurement methods and results. Part 1/Cor1:1998, Part 2/Cor1:2002, Part 3/Cor1: 2001, Part 4:1994, Part 5/Cor1:2005, Part 6/Cor1:2001.

The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics: 1998 (EURACHEM).

ISO/IEC 17025:2005 General Requirement for the Competence of Testing and Calibration Laboratories).

15 Method performance

Method performance is demonstrated by the calculation of the Accuracy, Repeatability and Reproducibility indexes according to the formulas from ISO 5725, and statistic correlations adjusted in the process of "Mastering CIP in Research Analytical Centre OSC 'Gipronikel Institute"[2]. Performance characteristics shown in Tables 3, 4 and 5 were obtained using certified reference samples and are taken from the report on "Mastering CIP in Research Analytical Centre OSC 'Gipronikel Institute"[2]. Comparison between the reference and measured values show no significant bias and therefore in the calculations the bias was neglected.

$\Delta = 1{,}96\sigma_R$;

$r_2 = Q(P,2)\sigma_r = 2{,}77\sigma_r$;

$CR_{0,95,n=4} = Q(P,4)\sigma_r = 3{,}63\sigma_r$;

$R = Q(P,2)\sigma_R = 2{,}77\sigma_R$;

$\sigma_R = 1{,}4\sigma_r$

Where:

Δ - Error index;

σ_r - Repeatability Standard Deviation;

σ_R – Reproducibility Standard Deviation;

r_2 – Repeatability Limit;

R – Reproducibility Limit;

$CR_{0,95,n=4}$ – critical range for four multiple determinations.

Metrological characteristics for precious metals are given in tables 3, 4 and for the rest of the elements – in table 5 (top values are listed).

2 Report on Scientific Research "Mastering CIP in Research Analitical Centre OSC 'GIPRONIKEL Institute', its development and improvement" Saint Petersburg. – 'GIPRONIKEL Institute', 2006.

Table 3

Error index "Δ" for precious metals, mass % . (P=0,95)

Content range	Ag	Au	Pt	Pd	Rh	Ru
from 0,0100 to 0,0200	0,0015	0,0015	0,0015	0,0015	0,0020	0,0020
from 0,0200 to 0,0500	0,0028	0,003	0,004	0,004	0,0035	0,005
from 0,050 to 0,100	0,006	0,007	0,007	0,007	0,008	0,010
from 0,100 to 0,200	0,012	0,015	0,015	0,015	0,020	0,024
from 0,200 to 0,500	0,028	0,020	0,025	0,025	0,030	0,034
from 0,50 to 1,00	0,04	0,04	0,04	0,04	0,05	0,07
from 1,00 to 2,00	0,09	0,09	0,06	0,06	0,07	0,09
from 2,00 to 5,00	0,21	0,17	0,13	0,13	0,14	0,20
from 5,00 to 10,00	0,30	0,22	0,21	0,21	0,22	0,28
from 10,0 to 20,0	0,4	0,3	0,4	0,4	0,4	0,6
from 20,0 to 50,0	1,0	0,7	0,7	0,7	0,7	1,3

Table 4.
Values of the repeatability limit r_2, critical range of repeated measurements $CR_{0,95,n=4}$, reproducibility limits R for precious metals (P=0.95).

	Mass, %			
		r_2	$CR_{0,95}$ (4)	R
Ag	from 0,0100 to 0,0200	0,0015	0,0020	0,0021
	from 0,0200 to 0,0500	0,0028	0,0036	0,0039
	from 0,050 to 0,100	0,006	0,008	0,008
	from0,100 to 0,200	0,012	0,016	0,017
	from 0,200 to 0,500	0,028	0,036	0,039
	from 0,50 to 1,00	0,04	0,05	0,06
	from 1,00 to 2,00	0,09	0,12	0,12
	from 2,00 to 5,00	0,21	0,27	0,29
	from 5,00 to 10,00	0,30	0,39	0,40
	from 10,0 to 20,0	0,4	0,5	0,6
	from 20,0 to 50,0	1,0	1,3	1,4
Au	from 0,0100 to 0,0200	0,0015	0,0020	0,0021
	from 0,0200 to 0,0500	0,003	0,005	0,005
	from 0,050 to 0,100	0,007	0,009	0,010
	from0,100 to 0,200	0,015	0,020	0,021

	Mass, %			
		r_2	$CR_{0,95}$ (4)	R
	from 0,200 to 0,500	0,020	0,026	0,028
	from 0,50 to 1,00	0,04	0,05	0,06
	from 1,00 to 2,00	0,09	0,12	0,13
	from 2,00 to 5,00	0,17	0,22	0,24
	from 5,00 to 10,00	0,22	0,29	0,31
	from 10,0 to 20,0	0,3	0,4	0,4
	from 20,0 to 50,0	0,7	0,9	1,0
Pt	from 0,0100 to 0,0200	0,0015	0,0020	0,0021
	from 0,0200 to 0,0500	0,004	0,005	0,005
	from 0,050 to 0,100	0,007	0,009	0,010
	from0,100 to 0,200	0,015	0,020	0,021
	from 0,200 to 0,500	0,025	0,032	0,034
	from 0,50 to 1,00	0,04	0,05	0,05
	from 1,00 to 2,00	0,06	0,08	0,08
	from 2,00 to 5,00	0,14	0,18	0,19
	from 5,00 to 10,00	0,21	0,27	0,30
	from 10,0 to 20,0	0,4	0,6	0,5
	from 20,0 to 50,0	0,7	0,9	1,0
Pd	from 0,0100 to 0,0200	0,0015	0,0015	0,0021
	from 0,0200 to 0,0500	0,004	0,004	0,005
	from 0,050 to 0,100	0,007	0,007	0,010
	from0,100 to 0,200	0,015	0,015	0,021
	from 0,200 to 0,500	0,025	0,025	0,034
	from 0,50 to 1,00	0,04	0,04	0,05
	from 1,00 to 2,00	0,06	0,06	0,08
	from 2,00 to 5,00	0,14	0,13	0,19
	from 5,00 to 10,00	0,21	0,21	0,30
	from 10,0 to 20,0	0,4	0,4	0,5
	from 20,0 to 50,0	0,7	0,7	1,0
Rh	from 0,0100 to 0,0200	0,0020	0,0026	0,0028
	from 0,0200 to 0,0500	0,0035	0,005	0,005
	from 0,050 to 0,100	0,008	0,011	0,011
	from0,100 to 0,200	0,020	0,026	0,028
	from 0,200 to 0,500	0,030	0,04	0,042
	from 0,50 to 1,00	0,05	0,07	0,07
	from 1,00 to 2,00	0,07	0,09	0,10

	Mass, %			
		r_2	$CR_{0,95}$ (4)	R
	from 2,00 to 5,00	0,14	0,19	0,20
	from 5,00 to 10,00	0,22	0,29	0,31
	from 10,0 to 20,0	0,14	0,6	0,5
	from 20,0 to 50,0	0,7	0,9	1,0
Ru	from 0,0100 to 0,0200	0,0020	0,0027	0,0029
	from 0,0200 to 0,0500	0,005	0,006	0,007
	from 0,050 to 0,100	0,010	0,013	0,014
	from0,100 to 0,200	0,012	0,027	0,033
	from 0,200 to 0,500	0,034	0,044	0,048
	from 0,50 to 1,00	0,07	0,10	0,10
	from 1,00 to 2,00	0,09	0,11	0,12
	from 2,00 to 5,00	0,20	0,27	0,29
	from 5,00 to 10,00	0,28	0,37	0,40
	from 10,0 to 20,0	0,6	0,7	0,8
	from 20,0 to 50,0	1,3	1,7	1,9

Table 5

Values of error index "Δ" (P= 0,95), repeatability limit r_2, critical range of repeated measurements $CR_{0,95,n=4}$, reproducibility limits R for base metals and contaminant elements (sodium, aluminum, magnesium, sulfur, phosphorus, potassium, calcium, chromium, manganese, iron, cobalt, arsenic, titanium, nickel, copper, selenium, molybdenum, tin, antimony, tellurium, barium, tungsten and lead).

Mass, %				
	± Δ	r_2	$CR_{0,95}$ (4)	R
from0,010 to 0,020	0,005	0,005	0,006	0,006
from 0,020 to 0,050	0,010	0,010	0,013	0,014
from0,050 to 0,100	0,020	0,021	0,028	0,028
from 0,100 to 0,200	0,030	0,031	0,041	0,042
from 0,20 to 0,50	0,04	0,042	0,055	0,056
from 0,50 to 1,00	0,05	0,07	0,09	0,10
from1,00 to 2,00	0,15	0,16	0,21	0,21
from 2,00 to 5,00	0,15	0,20	0,26	0,28
from 5,0 to 10,0	0,30	0,30	0,39	0,40
from 10,0 to 20,0	0,4	0,4	0,5	0,7
from 20,0 to 50,0	0,8	0,8	1,0	1,0
from 50,0	1,4	1,4	1,8	1,8

Determination of the elemental composition of precious metal-containing products by ICP-MS

Author:

Quality manager:

Authorisation:

Date :

0 Update and review summary

0.1 Updates

#	Section	Nature of Amendment	Date	Authorisation

0.2 Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

CONTENTS

1 Title

Determination of the elemental composition of precious metal-containing products by ICP-MS.

2 Scope

This procedure is intended for determining titanium, nickel, copper, selenium, molybdenum, ruthenium, rhodium, palladium, silver, tin, antimony, tellurium, barium, tungsten, iridium, platinum, gold and lead concentrations in the range from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-2}$ weight %, using the method of mass spectroscopy with inductively coupled plasma.

3 Safety and Environment

The general analysis and safety requirements prescribed by national and local laws and regulations in force at the enterprise must be followed.

4 Definitions

ICP-MS: - method of mass spectroscopy with inductively coupled plasma.

Error (regarding a single analysis result): difference between a test result and the accepted reference value.

Error index "Δ": limits of the error associated with a test results determined under reproducibility conditions with the stipulated probability.

Precision: closeness of agreement between independent test results obtained under stipulated conditions.'

Standard Deviation: measure of how values are dispersed about a mean in a distribution of values.

Repeatability: precision under repeatability conditions, i.e. conditions where independent test results are obtained with the same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time.'

Repeatability Standard Deviation: standard deviation of test results obtained under repeatability conditions.

*Repeatability Limit "r"***:** value less than or equal to which the absolute difference between two test results obtained under repeatability conditions may be expected to be with 95% probability.'

Reproducibility: precision under reproducibility conditions, i.e. conditions where test results are obtained with the same method on identical test items in different laboratories with different operators using different equipment.

Reproducibility Standard Deviation: standard deviation of test results obtained under reproducibility conditions.

Reproducibility Limit "R": value less than or equal to which the absolute difference between two test results obtained under reproducibility conditions may be expected to be with 95% probability.

Reference Material (RM): material or substance of the subject for analytical testing sufficiently homogeneous regarding one or several reliably determined characteristics to be used for the measurement method assessment.

Calibration function: functional relationship relating the measured signal intensity to the analyte quantity.

5 Principle

The method is based on ionization of the tested substance in the inductively coupled plasma and detection of the generated ions using a mass spectrometry method.

Inductively coupled plasma (ICP) – an argon plasma of high temperature created by a high frequency alternating electric field with the help of an external inductor. A solution for analysis is injected into the plasma in the form of an aerosol. During this process, recombination of argon ions with atoms formed from elements contained in the solution generates free ions. These ions are fed into the mass spectrometer with the help of a special interface.

In the mass spectrometer, the ions are separated on the basis of their mass-to-charge ratio and counted by an ion detector. The measured signal received by the detector is proportional to the concentration of isotopes of the determined elements.

6 Reagents and Materials

- 99.996% Gaseous argon.
- De-ionized water of specific resistance 18 MOm·cm.
- Ultra-purity grade hydrochloric acid, 15 vol.% solution.
- Standard solutions of the elements to be analyzed with mass concentration of 1000 µg/ml.

7 Apparatus and Equipment

- Inductively Coupled Plasma Mass Spectrometer with computer controlled operating and data handling system.
- Adjustable pipette with graduation marks at 1.0-5.0 ml.
- 25 ml volumetric flasks.

8 Sample preparation.

Executed in accordance with Protocol CIP 2.

9 Calibration

Prepare calibration solutions by dilution of the standard samples of mass concentration 1000 µg/ml on the day of use. Concentrations of the determined elements are listed in Table 1.

Table 1

Mass concentration of the determined elements in calibration solutions

Calibration solution No.	Element mass concentration, µg/ml
0 – 'calibration blank'	0
3	0,10
4	0,010
5	0,0010

Preparation of calibration solution No. 3:

Pipet 2.5 ml of calibration solution No. 2 (see Protocol 3) into a 25 ml volumetric flask. Then, add the diluted hydrochloric acid solution (15 vol.%) to fill the flask to the mark.

Preparation of calibration solution No. 4:

Pipet 2.5 ml of calibration solution No. 3 into a 25 ml volumetric flask. Then, add the diluted hydrochloric acid solution (15 vol.%) to fill the flask to the mark.

Preparation of calibration solution No. 5:

Pipet 2.5 ml of calibration solution No. 4 into a 25 ml volumetric flask. Then, add the diluted hydrochloric acid solution (15vol.%) to fill the flask to the mark.

The same diluted hydrochloric acid (15 vol.%) which was used for preparation of the calibration solutions is used as a **'calibration blank'**.

Calibrate the spectrometer using solutions No. 3, 4, 5 and 'calibration blank'. Measure the 'calibration blank' first and then the calibration solutions in decreasing order of their numbers. Measure the intensity recorded at the test elements' mass, and subtract the intensity of the corresponding mass for 'calibration blank'.

Plot a calibration curve for each measured mass within the following axes: intensity (deducting the 'calibration blank') vs. mass proportion of the tested element in the calibration sample. Regression factors are automatically calculated by least-squares method and saved in the computer memory until the next calibration.

Calibration curves should be linear and have a linear correlation coefficient of at least 0.999. If calibration curves do not satisfy this condition, spectrometer calibration must be repeated.

10 Quality control

Quality control of analysis results must be conducted in accordance with the regulations of the ISO 5725 with the use of Reference Materials, close to the tested samples in their chemical composition. Also, the difference between test results and data of the Reference Materials must be smaller than the Error index "Δ".

If unacceptable results are obtained, the cause of this condition must be found and corrective action taken. This may include realignment of the mass spectrometer or adjustment of the ICP operating conditions and must be followed by recalibration. If the repeated calibration does not provide acceptable quality conditions, a conclusion could be made that sample preparation was done incorrectly. In this case, the sample preparation procedure must be repeated in accordance with Protocol # 2.

Stability control of the Calibration Curves is also conducted after observation of 10 samples.

Calibration solutions are used for the stability control of the Calibration Curves. Mass concentration of determined elements in the Calibration solutions should be in the range of the measured mass concentrations.

Calibration Curves could be considered stable if the following condition is fulfilled:

$$\frac{|C - C_K|}{C_K} \leq 0{,}05 \ , \qquad (1)$$

Where:

- C_k – is the value of the element mass concentration of the Calibration solution, mg/ml.
- C – is the measured value of the element mass concentration, mg/ml.

If condition (1) is not achieved, the spectrometer should be recalibrated.

Suitability evaluation of two multiple determinations is executed in the following manner.

The arithmetic mean of the results of two determinations executed on two single subsamples is accepted as the final result of the analysis, if the difference between them is within limits of the *Repeatability Limit "r_2"*

If the absolute deviation between the results of two measurements exceeds "r_2", one must obtain two more measurement results.

If, in this case, the difference between the biggest and the smallest values of 4 measurements is equal to or less than the critical range $CR_{0,95,n=4}$ (calculated for the confidence level value of P=95%), then as the ultimate result one should record the arithmetic mean of the measurement results.

If the difference between the biggest and the smallest meanings of four measurement results is bigger than the critical range for four measurements, then the median value for four measurements should be recorded as the ultimate result, which is calculated in accordance with the following formula.

$$\overline{X} = med\{X_1 < X_2 < X_3 < X_4\} = \frac{X_2 + X_3}{2}, \qquad (2)$$

Where,

X_2 – second the smallest result;

X_3 – third the smallest result.

Deviation between the results of the initial and repeatable analysis must not exceed Reproducibility Limit R.

11 Procedure

11.1 Procedure on determination of the element composition.

Prepare the mass-spectrometer according to its Operation Manual.

For Inductively Coupled Plasma Mass Spectrometer Elan 6000 (Perkin Elmer, USA) the following working parameters are given as guidelines of typical operating

conditions. Daily operating conditions will vary slightly from these values in order to optimize instrumental response:

- ICP generator working frequency: 40 MHz;
- output capacity: 1,1 KW;
- plasma forming argon flux: 15 L/min.;
- transporting argon flux 0,8 L/min.;
- cooling argon flux: 0,5 L/min.;
- measurement exposure for one isotope: 1 sec.;
- number of parallel measurements: 6.

The list of recommended isotopes is shown in Table 2[1].

In the process of measurements, mutual influence of elements should be taken into consideration and a procedure for their correction should be applied.

Spectrometer calibration is done in accordance with § 9 of this Protocol.

In the process of measurements, blank solutions and solutions of tested samples are injected in the apparatus and intensities of analytical lines of the determined elements are measured (deducting the intensity of the blank). Using the calibration curve, mass concentration of the element in the tested subsample is determined and this result is recorded (printed or written down from the screen).

Table 2

The list of recommended isotopes

Element	Mass/charge ratio, T	Element	Mass/charge ratio, T
Ti	47	**Sn**	120
Ni	60	**Sb**	121
Cu	63 or 65	**Te**	126
Se	82	**Ba**	137 or 138
Mo	95	**W**	184
Ru	99	**Ir**	193
Rh	103	**Pt**	195
Pd	105	**Au**	197
Ag	107	**Pb**	Σ 206, 207, 208

11.2 Procedure for identification of the source of a sample of unknown orgin.

The procedure for interpretation of the results of the ICP-OES measurements depends to some extent upon the type of sample being tested and the forensic question to be answered. The most straightforward application is comparison of the element

[1] If operator is using different isotops, he/she has to give a list of isotopes used in the report on executed analysis.

concentrations determined in a sample of questioned origin with the compositions of products in the RDB. A decision that the composition of the substance being tested corresponds to the composition of one specific product in the RDB can be made if the concentrations of each element in the unknown substance measured using this protocol (taking into account the error index of the method) is within the variability range of the concentration of that element in that product.

In the case that the elemental composition coincides with the composition of a product in the RDB it is necessary to specify this conclusion in the analysis report.

In accordance with Protocol 0, the identification of an unknown substance can be considered complete if a correspondence with a product in the RDB is determined on the basis of elemental (Protocols 3,4) and phase (Protocol 5) composition.

The element concentrations determined using this protocol may also be used to answer other questions of forensic significance. The concentrations of elements, particularly the distribution of PGMs may be compared to world-wide databases to provide information concerning possible regions of origin for a sample. Some level of deconvolution of mixtures may be possible using the results of this protocol, when the composition of end members is known or can be estimated. Specific procedures for these and other similar interpretive evaluations cannot be provided in this analytical protocol, because they depend upon the specific case evaluations needed. The purpose of this protocol is to provide an analytical method that produces element concentrations of known accuracy and precision that can be utilized for answering a variety of questions of forensic interest.

12 Calculations

Weight % of the determined element is calculated using the following formula:

$$X = \frac{C \cdot V}{M} \cdot 10^{-4}, \quad (5)$$

Where,

C – mass concentration of the element determined using the calibration curve in µg/ml;

V – final volume of the sample solution (including all dilutions if operator had done them) in ml;

M – weight of the subsample in g.

For the final result of the testing, the arithmetic mean of two results or median of four results of multiple determinations made from single subsamples depending on the fulfillment of the conditions as specified in § 10 is reported.

13 Reporting procedures including expression of results

Analysis results are recorded required by the examining laboratory's reporting protocol. In addition to the analysis results, the protocol must also include:

- date of the testing,
- information about expert(a profession acquired after graduation from the University, expert profession, period of service as an expert, post taken),

- incoming sample information (source of the sample's origin, who, when and in what way sampling has been executed),
- the results of comparison of unknown substance composition with RDB (Does unknown sample composition match with composition of any product from RDB? With what specified product does it match?).

The number of significant figures in the analysis result (element concentration) should correspond to the number of significant figures according to the *Error index*.

14 Normative references

The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics: 1998 (EURACHEM).

ISO 5725–1 through ISO5725-6 Accuracy (trueness and precision) of measurement methods and results. Part 1/Cor1:1998, Part 2/Cor1:2002, Part 3/Cor1: 2001, Part 4:1994, Part 5/Cor1:2005, Part 6/Cor1:2001.

ISO/IEC 17025:2006 General Requirement for the Competence of Testing and Calibration Laboratories).

15 Method performance

Method performance is demonstrated by the calculation of the Accuracy, Repeatability and Reproducibility indexes according to formulas from ISO 5725, and statistic correlations adjusted in the process of the Procedure development[1] and are shown in Tables 3, 4, and 5.

Calculations were based on assumption that not excluded systematic error of the analysis is negligible.

$\Delta = 1{,}96\sigma_R$;

$r_2 = Q(P,2)\sigma_r = 2{,}77\sigma_r$;

$CR_{0,95,n=4} = Q(P,4)\sigma_r = 3{,}63\sigma_r$;

$R = Q(P,2)\sigma_R = 2{,}77\sigma_R$;

Where:

Δ - Error index;

σ_r - Repeatability Standard Deviation;

σ_R – Reproducibility Standard Deviation;

r_2 – Repeatability Limit;

R – Reproducibility Limit;

$CR_{0,95,n=4}$ – critical range for four multiple determinations.

[1] Report on Scientific Research "Development and improvement of the RDB for OSC MMC "Norilsk Nickel" containing platinum group metals" Moscow – "Forensic Institute FSS of Russia", 2006, 43◦c.

Metrological characteristics for noble metals are given in tables 3, 4 and for the rest of the elements – in table 5 (top values are listed).

Table 3

Error index "Δ" for precious metals, mass. % (P=0.95)

	Ag	Au	Pt	Pd	Rh	Ir	Ru
0.00010 — 0.00020	0.00003	0.000029	0.00003	0.00003	0.00003	0.000020	0.000020
0.00020 — 0.00050	0.00007	0.00007	0.00007	0.00007	0.00006	0.00005	0.00005
0.00050 — 0.00100	0.00015	0.00010	0.00015	0.00015	0.00008	0.00015	0.00015
0.0010 — 0.0020	0.00021	0.00015	0.0003	0.0003	0.00015	0.00029	0.00029
0.0020 — 0.0050	0.0005	0.0003	0.0004	0.0004	0.0004	0.0005	0.0005
0.0050 — 0.0100	0.0010	0.0007	0.0007	0.0007	0.0007	0.0010	0.0010

Table 4

Values of repeatability limit r_2, critical range of repeated measurements $CR_{0,95,n=4}$, reproducibility limit R for precious metals (P= 0,95)

An.	Mass. %			
		r_2	$CR_{0.95}$ (4)	R
Ag	0.00010 — 0.00020	0.00003	0.000039	0.00004
	0.00020 — 0.00050	0.00007	0.00009	0.00010
	0.00050 — 0.00100	0.00015	0.00020	0.00021
	0.0010 — 0.0020	0.00021	0.00027	0.00029
	0.0020 — 0.0050	0.0005	0.0007	0.0007
	0.0050 — 0.0100	0.0010	0.0013	0.0015
Au	0.00010 — 0.00020	0.000029	0.00004	0.00004
	0.00020 — 0.00050	0.00007	0.00009	0.00010
	0.00050 — 0.00100	0.00010	0.00013	0.00014
	0.0010 — 0.0020	0.00015	0.00020	0.00021
	0.0020 — 0.0050	0.0003	0.0004	0.0005
	0.0050 — 0.0100	0.0007	0.0009	0.0010
Pt	0.00010 — 0.00020	0.00003	0.00004	0.00004
	0.00020 — 0.00050	0.00007	0.00009	0.00010
	0.00050 — 0.00100	0.00015	0.00020	0.00021
	0.0010 — 0.0020	0.0003	0.0004	0.0004
	0.0020 — 0.0050	0.0004	0.0005	0.0005
	0.0050 — 0.0100	0.0007	0.0009	0.0010
Pd	0.00010 — 0.00020	0.00003	0.00003	0.00004
	0.00020 — 0.00050	0.00007	0.00007	0.00010
	0.00050 — 0.00100	0.00015	0.00015	0.00021
	0.0010 — 0.0020	0.0003	0.0003	0.0004
	0.0020 — 0.0050	0.0004	0.0004	0.0005
	0.0050 — 0.0100	0.0007	0.0007	0.0010
Rh	0.00010 — 0.00020	0.00003	0.00003	0.00004
	0.00020 — 0.00050	0.00006	0.00007	0.00008
	0.00050 — 0.00100	0.00008	0.00011	0.00012
	0.0010 — 0.0020	0.00015	0.00019	0.00021
	0.0020 — 0.0050	0.0004	0.0005	0.0005
	0.0050 — 0.0100	0.0007	0.0009	0.0010
Ir	0.00010 — 0.00020	0.000020	0.000027	0.000029
	0.00020 — 0.00050	0.00005	0.00006	0.00007
	0.00050 — 0.00100	0.00015	0.00021	0.00020
	0.0010 — 0.0020	0.00030	0.00042	0.00039
	0.0020 — 0.0050	0.0005	0.0006	0.0007
	0.0050 — 0.0100	0.0010	0.0013	0.0014
Ru	0.00010 — 0.00020	0.000020	0.000027	0.000029
	0.00020 — 0.00050	0.00005	0.00006	0.00007
	0.00050 — 0.00100	0.00015	0.00021	0.00020
	0.0010 — 0.0020	0.00030	0.00042	0.00039
	0.0020 — 0.0050	0.0005	0.0006	0.0007
	0.0050 — 0.0100	0.0010	0.0013	0.0014

Table 5

Values of error index "Δ" (P= 0,95), repeatability limit r_2, critical range of repeated measurements $CR_{0,95,n=4}$, reproducibility limit R for base metals and contaminants (titanium, nickel, copper, selenium, molybdenum, tin, antimony, tellurium, barium, tungsten and lead)

	Mass. %			
	± Δ	r_2	$CR_{0,95}$ (4)	R
0.00010 — 0.00020	0.00003	0.00003	0.00003	0.00004
0.00020 — 0.00050	0.00007	0.00006	0.00007	0.00008
0.00050 — 0.00100	0.00010	0.00008	0.00011	0.00012
0.0010 — 0.0020	0.00021	0.00015	0.00019	0.00021
0.0020 — 0.0050	0.0005	0.0004	0.0005	0.0005
0.0050 — 0.0100	0.0010	0.0007	0.0009	0.0010

Determination of the phase composition of precious metal-containing products by XRD

Author:

Quality manager:

Authorisation:

Date :

0 Update and review summary

0.1 Updates

#	Section	Nature of Amendment	Date	Authorisation

0.2 Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

CONTENTS

1 Title

Determination of the phase composition of precious metal-containing products by XRD.

2 Scope

This procedure is intended for determining the phase composition of substances, their composition features and the source of origin of test samples using the method of X-Ray Diffractometry.

3 Safety and Environment

The general analysis and safety requirements prescribed by national and local laws and regulations in force at the enterprise must be followed.

4 Definitions

Accuracy (trueness): closeness of the agreement between the mean value achieved from the series of analysis results and the adopted true value.

Reference Material (RM): material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials.'

Calibration Curve: graphical representation of measuring signal as a function of quantity of analyte.'

Detection Limit: lowest content of analyte that could be detected with the help of this particular method with 95% probability.

5 Principle

This method is based on the diffraction of X-rays by the test material's crystal lattice. Using an X-ray diffraction spectrum, or diffractogram (location and intensity of spectral lines), one can determine the inter-plane distances in the lattices of test materials. By comparing them to reference values for various crystalline substances, the components of the samples under study can be identified.

This method allows determinination of the phase composition of the substances and establishment of the differences between samples under analysis with the help of diffractogram appearance.

6 Reagents and Materials

- Technical distilled ethyl alcohol (96%).

7 Apparatus and Equipment

- X-Ray Diffractometer with computer controlled operating and data handling system.
- A toolset for preparing flat powder samples:
  - Corundum or agate mortar and pestle;
  - Polished glass plate to press the sample into the measuring cuvette;
  - Blade to remove the surplus sample material from the cuvette surface.

- ICDD computer database of reference spectra and search system.

8 Sample preparation

Place the sample into a mortar and grind it into a homogenous paste, adding some alcohol. Place the paste in the cuvette and press it with a polished glass plate. The sample top surface and the working surface of the cuvette must be on the same level. Cut off the surplus sample material with a blade. The surface area of the sample shall be not less than $1cm^2$.

9 Apparatus calibration

Apparatus calibration must be conducted daily before start of work and also after every goniometer adjustment. Use a finely ground and annealed powdered sample of α-quartz as a standard material for apparatus calibration. For calibration, scan the goniometer over the angle range from 15 to 100° (2Θ). Record the angular positions of the analytical lines, their intensities and half widths. Maximum allowed deviation of the angular positions of the X-ray diffraction lines from their true values is ± 0.05 2Θ. If this condition is not fulfilled, goniometer adjustment must be made and the calibration must be repeated.

10 Quality Control

Quality Control is realized by parallel measurements of two probes under the conditions of repeatability. Complete qualitative matching of all lines in the two diffractograms (± 0.05 2Θ) should de fulfilled, i.e. number and aspect angles of the X-ray diffraction lines should coincide. Relative intensity of any three reference diffraction lines should differ not more than 10%. If these conditions are not fulfilled, preparation of two probes and scanning are repeated. If after a second attempt, results are still unsatisfactory, operational examination of the apparatus should be conducted and a fault cleared.

11 Procedure

Analyze two replicate probes of each sample prepared in accordance with paragraph 8. Align the diffractometer according to its Operation Manual.

Perform the scanning while the sample is rotating. The rotation speed shall correspond to the scanning speed so that a full revolution is made with scanning step not exceeding 0.02˚ (2Θ)

For the X'Pert-MPD (Philips, Holland) typical measurement parameters are as follows:

- Radiation: Co-Kα;
- Tube voltage: 40KV
- Anode current: 45mA
- Primary beam: 1st slot width – 10 mm, 2nd slot width – 1 mm
- Secondary beam: slot width – 0.25 mm, detector slot width - 0.1 mm
- Scan range: 15 - 100˚ (2Θ)

- Scanning speed: 0.01˚ (2Θ)/sec.
- Sample rotation speed: 1 rev./sec.

12 Calculation

Phase composition determination

The phase composition of a substance is determined by comparing the diffractograms of the analyzed substance with the reference diffractograms in ICDD database (using the system of automatic data processing and search). In this case, each diffraction peak is defined by angular position (2Θ˚) or by interplanar spacing (measured in Angstroms units) and by relative intensity, normalized under intensity of the most intense diffraction peak.

Fingerprinting method used in the analysis of a substance.

In general, identification of the substance is done in accordance with the previous paragraph and is based on the analysis of its characteristic features revealed by the whole set of methods applied.

The "fingerprinting" method can be used by direct superposition of the diffractogram of the substance under study over diffractograms contained in RDB. If the main peaks of the known substances from the RDB are not present in the substance under investigation, then no known products of the RDB are present in the sample within the method's detection limit of 1-3% weight.

If a part of the diffractogram of the analyzed substance matches a product in the RDB (within the limits of variability of the phase composition typical for the relative type of products), it is likely that this type of product is present in the sample tested.

In other cases the fingerprinting method can be used for comparing the diffractogram of the test substance with model diffractograms of mixed substances, if the diffractometer is supplied with the corresponding software.

13 Reporting procedures including expression of results

Analysis results are recorded in a form required by the examining laboratory's reporting protocol. In addition to the analysis results, the report must also include:

- date of the testing;

- information about expert (a profession acquired after graduation from the University, expert profession, period of service as an expert, post taken);

- incoming sample information (source of the sample's origin, who, when and in what way sampling was executed).

14 Normative references and manuals

ICDD – The International Centre for Diffraction Data.

15 Method performance

The Complex Analytical Procedure XRD is not used as a quantitative method. Therefore, indices of Accuracy, Repeatability and Reproducibility are not applicable. For this method, the performance is determined by the status of the XRD, as mentioned in paragraph 9 “Apparatus calibration”.

The detection limit for crystalline phases is 1 to 3 %.

Determination of the elemental composition of microparticles of precious metal-containing products by scanning electron microscopy with X-ray microanalysis

Author:

Quality manager:

Authorisation:

Date :

Update and review summary

0.1 Updates

#	Section	Nature of Amendment	Date	Authorisation

0.2 Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

CONTENTS

1 Title

Determination of the elemental composition of microparticles of precious metal-containing products by scanning electron microscopy with X-ray microanalysis

2 Scope

This method is intended to identify the combination of microparticles of a product under testing by means of comparison of the microparticles' elemental composition with data stored in the database.

3 Safety and Environment

The general analysis and safety requirements prescribed by national and local laws and regulations in force at the enterprise must be followed.

4 Definitions

Accuracy (trueness): closeness of the agreement between the mean value achieved from the series of analysis results to the adopted real value.

Analysis results error: deviation of the analysis result from the true value.

Reference Material (RM): material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement, or for assigning values to materials.

Calibration function: functional relationship relating the measured signal intensity to the analyte quantity.

Detection limit: lowest content of analyte, which could be detected as being present with 95% probability using this particular method.

Microparticle: particles with an average diameter less than 100 µm.

5 Principle

5.1 Basic physics of the method

The method is based on the interaction between a scanning electron beam and a sample material. During the interaction of the electron beam with sample material, secondary electrons and X-ray emission are generated along with a variety of other signals.

Secondary electrons are emitted from the atoms occupying the surface of the sample directly exposed to the electron beam. Collection and display of these secondary electrons forms a readily interpretable image of the surface. The contrast of the image is determined by and displays the sample morphology.

The X-ray emission depends on the elemental composition of the analyzed material. Energy measurement of the characteristic X-ray emission permits the determination of the qualitative element composition. Measurement of the intensity of a characteristic line is used to calculate quantitatively the concentration of the associated element. Calculations of the elements' concentrations are made with the use of physical models of interaction between the electron probe and sample material.

The diameter of the excitation area of the discriminating X-ray emission varies in the range from 1µm to 9µm, depending on the average atomic number of the substance under testing.

5.2 Principle of microparticles combination identification.

The identification of a product by its microparticle content is carried out by the comparison of the microparticles' elemental compositions present in a product with data stored in the database (RDB).

Each product is represented in the database in the form of microparticle compositions grouped in several types. Each type is characterized by a definite set of elements and recorded in the form of a conventional formula, e.g.:

$$\mathbf{Pt_{48-68}–Pd_{7-19}–Ru_{2-11}–Rh_{0,6-4}–As_{0-1}–Se_{3-6}–Si_{0-1}–S_{2-7}–O_{2-8}–Ni_{1-7}–Cu_{0,5-3}}$$

Elements in this formula are ranged by their decreasing informational importance for classification and identification. The indices reflect either intervals of elements concentrations (in mass %) or range of relative integral intensities of analytical lines (in rel. %). Both formulas are reported in the database

In the evaluation of the information importance of the chemical elements the following considerations are taken into account:

- concentration of an element in the microparticle composition;
- whether this element is typical for the microparticles that form the material of a certain product;
- element 'specificity' – (for instance, such rare elements as Platinum, Palladium, Tellurium, Selenium, etc. are much more informative than widely occurring elements like Silicon, Aluminum, Oxygen, Iron).

By using the above criteria and measuring no less than 1000 microparticles, the number and relative content of microparticle types in a product are determined and stored in the RDB. Regularly through time, the products are measured and these data are again stored in the RDB. In this way, possible variation of the products through time is monitored.

6 Reagents and Materials

- Technical, particle free distilled ethyl alcohol (96%).

7 Apparatus and Equipment

- Scanning Electron Microscope with Energy Dispersive Microanalyzer providing the identification of elements within the range from boron to uranium and with spectral resolution not worse than 135 eV for Mn-Kα at a count rate of 1000 counts per second;
- Ultrasonic disperser with frequency (20-33) KHz;
- Adjustable dosing pipettes of (5-40) μL and of (200-1000) μL;
- Sample mounts (stubs, studs)for scanning electron microscope;
- Disposable carbon conductive double sided adhesive tapes for scanning microscope sample mounts;
- Set of reference materials for EDS calibration;
- Optical binocular microscope with magnification from 20 to 100 times.

8 Sample preparation

Separate a probe weighing 0.5 g from the powder sample by repeated quartering and place it into a disposable 1.5 mL plastic test tube. Add 1 mL of ethyl alcohol and mix the contents using the ultrasonic disperser for 5 min.

During this ultrasonic mixing, transfer 0.2 mL of the suspension into a clean test tube. Add ethyl alcohol to make a total volume of 1 mL and again ultrasonically mix the contents of this tube. Then during this mixing, transfer 10-20 µL of the alcohol suspension using a micropipette to a scanning electron microscope sample stub covered with a conductive carbon film. The microparticles must form a monolayer on the sample holder. Use an optical microscope to control the process of suspension transfer to the sample stub. If the particles do not form a monolayer, it is necessary to repeat the process of probe preparation on a newly prepared sample stub.

If the mass of the available sample is less than 0.5g, the amount of alcohol can be decreased pro rata, providing that particles form a monolayer on the scanning microscope sample stub.

Dry the sample holders with the monolayer of microparticles at room temperature and then place them in the electron microscope chamber.

9 Calibration

Prior to beginning an analysis, verification of the operational condition of the scanning electron microscope with the X-ray microanalyzer must be established. This includes presence of system peaks, accuracy of magnification, and determination of spectral energy calibration and resolution. Energy calibration of the Energy Dispersive Microanalyzer is performed every 2 hours of equipment work using a “Set of reference materials for X-ray microanalysis” and in accordance with the Operating Manual.

10 Quality Control

Appropriateness controls of the analytical results are executed in accordance with ISO 5725 requirements and using natural minerals as Reference Materials. Recommended minerals as reference material are: Wollastonite, Zircon, and Rhodonite.

Quantitative analysis accuracy is considered satisfactory when the following conditions are met:

$$\frac{|C - C_K|}{C_K} \leq 0{,}05 \ , \qquad (1)$$

Where,

- Ck is the standardized value of the element mass concentration (more than 1%) in the reference mineral,
- C is the measured average (n=5) element mass concentration in the reference mineral.

If condition (1) is not achieved, the microanalyzer must be recalibrated (see paragraph 9).

11 Procedure

11.1 Procedure on determination of the element composition and morphology of microparticles.

Prepare the scanning electron microscope and energy dispersive microanalyzer according to their Operation Manuals.

Suggested measurement parameters are as follows:

- Accelerating potential: 20 KV
- Field of vision: 50 – 300 μm
- Spectrum integral intensity: ≥ 300000 counts
- Spectral resolution ≤ 135 eV for Mn-Kα
- Elements determined: from Oxygen to Uranium
- Range of Concentrations determined: from 0.2 to 100%

Arbitrarily select the investigated area on the sample stage with a size corresponding to a field of vision 100x100 μm. Microparticles should form a monolayer on the sample stage surface. During measurements, the electron beam should be focused on the center of a microparticle. Examine all microparticles of size larger than 0.5 μm in the field of vision individually.

Then move to another field of vision, which does not overlap with the previously examined. Continue this operation until 1000 microparticles have been examined.

The morphology of the microparticles in the examined sample should also be recorded. Obtain images of the most typical and unusual microparticles. Record the correspondence of element composition with morphology of the microparticles.

11.2 Procedure on identification of microparticles composition.

When analyzing an unknown substance the elemental composition of each of a minimum of 1000 microparticles must be determined.

In the electronic version of the RDB, the match between the elemental composition of an analyzed microparticle in the unknown substance and the microparticle elemental compositions present in the RDB is automatically made on basis of its qualitative composition. When only a hard copy of the database is available, the comparison of the elemental composition of analyzed microparticles to the elemental composition of a certain type of microparticles present in the RDB is done as follows:

- Visually compare the qualitative composition of an analyzed microparticle with the range of qualitative compositions of all the types of microparticles present in the hard copy of the RDB. If the composition of the examined microparticle fits with a particular type of microparticle present in the RDB, it is assumed that the examined particle belongs to this particular type of microparticle.
- In the second step, compare the quantitative composition of the examined microparticle with the compositional range given in the RDB for the particular type of microparticle. When the composition of the examined microparticle is within the compositional range limits given in the RDB for this particular type of microparticle, it is concluded that the examined microparticle belongs to this particular type of microparticle.

Comparison of the elemental composition of each of the examined microparticles in the examined unknown substance with the compositional ranges of the stored types of microparticles will give one of the following three possible results:

- The examined microparticle corresponds to a type of microparticle only present in one particular product. The examined microparticle is related to this particular product.
- The examined microparticle corresponds to a type of microparticle present in different products. The examined microparticle is referred to all of these products.
- The examined microparticle does not correspond with the microparticle compositions present in the RDB. The examined microparticle is referred as unclassified.

With the above two steps we can conclude that Norilsk Nickel precious metal containing products are present in the examined unknown substance when:

- All types of microparticles forming one specific product in the RDB are present in the examined unknown substance.
- The relative weight of these different types of microparticles differs no more than the product variability given in the RDB.

If the measured microparticle compositions do not fulfill the above criteria, it is concluded that no products specified in the RDB are present in the examined unknown sample.

12 Calculation

At the first stage of processing of each obtained spectra, qualitative element analysis is conducted on the basis of the energy of characteristic lines. If characteristic lines overlap, a best estimate of the elements presents in the microparticle is checked with the help of element composition calculation (using the standard software of the analyzer). An element is considered present if the value of its calculated concentration is above the detection limit for that element.

Quantitative proportions of the detected elements are calculated using well-accepted software supplied with the analyzer. For each type of microparticle in the examined unknown substance, the range of its measured proportion is given (see paragraph 5.2).

13 Reporting procedures including expression of results

Analysis results are recorded in a form required by the examining laboratory's reporting protocol. In addition to the analysis results, the report also must include:

- date of the testing,
- information about expert (a profession acquired after graduation from the University, expert profession, period of service as an expert, post taken),
- incoming sample information (source of the sample's origin, who, when and in what way sampling has been executed).

14 Normative references and manuals

- ISO 5725–1 through ISO5725-6 Accuracy (trueness and precision) of measurement methods and results. Part 1/Cor1:1998, Part 2/Cor1:2002, Part 3/Cor1: 2001, Part 4:1994, Part 5/Cor1:2005, Part 6/Cor1:2001.
- ISO/IEC 17025:2006 General Requirement for the Competence of Testing and Calibration Laboratories).
- The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics: (Manual CITA/EURACHEM), 1998.

15 Method performance

Relative error does not exceed 15% for elements from sodium to uranium and 30% for elements from oxygen to fluorine, except in cases where there are peak overlaps for which correction cannot be made.

For spectra with 300000 counts integral intensity the element detection limits are:

- from oxygen to fluorine - 5 percent by weight;
- from sodium to uranium - 0.2 percent by weight.

Appendix 9. Protocols (CIP 0 - CIP 6)