Appendix 10. TNO report

TNO Built Environment and Geosciences

Princetonlaan 6
P.O. Box 80015
3508 TA Utrecht
The Netherlands

T +31 30 256 42 56
F +31 30 256 44 75
info@nitg.tno.nl

TNO report

2007-U-R1163/C

Analytical verification and testing of the Complex Identification Procedure (CIP)

Date	November 2007
Author(s)	G. Klaver; H. Veld; P. van Gaans & B. van Os
Assignor	Russian Federal Centre of Forensic Science (RFCFS)
Project number	034.69322
Classification report	Confidential
Title	
Abstract	
Report text	
Appendices	
Number of pages	32 (incl. appendices)
Number of appendices	5

Contents

1 Introduction ... 5
1.1 Background ... 5
1.2 Objectives ... 5
1.3 Activities and deliverables ... 6

2 Document review ... 7
2.1 Description of the Complex Identification Procedure (CIP) ... 7
2.2 General comments on the CIP protocols ... 9

3 Analytical testing of the CIP ... 11
3.1 Bulk analysis by SEM-EDX ... 11
3.2 Determination of the phase composition by XRD ... 13
3.3 Wet acid digestion ... 14
3.4 Elemental composition by ICP-OES and ICP-MS ... 15
3.5 Identification of micro particles with SEM-XRSMA ... 20

4 The reference database (RDB) ... 27
4.1 Statistical evaluation of the chemical data of all products present in the RDB with Fuzy-c means clustering (FCM) by TNO ... 27
4.2 Statistical evaluation of the 33 products at risk using the chemical, X-Ray diffractograms and SEM-EDX phase data present in the RDB by BKA ... 28
4.3 Conclusions and recommendations ... 29

5 Conclusions and recommendations ... 31
5.1 Conclusions and recommendations from the desk audit and analyses ... 31
5.2 Conclusions and recommendations from the statistical evaluation of the RDB ... 31

1 Introduction

1.1 Background

Partially processed PGM (platinum group metal) materials from Russian producers are stolen on a large scale and illegally supplied to specialized PGM refineries worldwide for further processing. Similar problems occur in South Africa. South Africa and Russia cover together over 80% of the production of PGM-bearing intermediate products. In total the annual value of the thefts is estimated to be tens of millions of US dollars.

A number of leading Russian scientific research institutes have developed a combined method (using microscopy, ICP-AES, ICP-MS, XRD and SEM-XRMA) to characterize intermediate PGM materials from the mining process with such a high discrimination that it is claimed that samples taken out of one mine can be traced back to that mine. This "Complex Procedure for Identification of the Nature and the Source of Origin of Precious Metals Containing Products of Mining and Metallurgical Operations" is shortened to CIP (Complex Identification Procedure) for the purposes of the present project.

Russian law enforcement agencies instigated legal actions in Western Europe against companies suspected of dealing in stolen PGM materials. In order for the CIP expertise results to be accepted in court it was thought to be necessary to have the method validated analytically and forensically by a well respected independent international body. A project was initiated under the auspices of ENFSI (European Network of Forensic Science Institutes) to this end. This CIP project is supported by the Ministry of Justice of the Russian Federation and the IPA (International Platinum Association).

The project consists of the analytical verification and testing of the methods used according to guidelines by Eurachem (http://www.eurachem.ul.pt/guides/valid.pdf) as well as the forensic validation of the results obtained using these methods.

The overall objectives of this project are
1. to peer review the CIP in order for the CIP expertise results to be accepted in court
2. to provide advice on possible improvements

TNO has been contracted to perform the analytical verification and testing of the CIP. The current report, containing the results, will be an appendix to the final project report.

1.2 Objectives

The specific objectives for the current project were formulated as follows:

Confirmation of CIP fitness for purposes and tasks set forward on the basis of determination of a material's (substance's) characteristics and comparison thereof against the database in order to determine the origin of the product (the plant, the shop, the technological section).

For this purpose the following documents and materials were available:

1 CIP text
2 Passports of 69 products included in the data base (English contracted version)
3 Passport of Cu-slime (full version)
4 Two samples (represented in the data base) and the mixture of these two samples

1.3 Activities and deliverables

The forensic review board has formulated the following tasks and end-products for the TNO research:

1 Analysis of information contained in the passports of the 69 products with the purpose of confirmation of the individual identification characteristics of each product allowing for its differentiation from all of the other products included into the database.

2 Reproducing each method applied within the CIP framework by the TNO laboratory with use of the samples provided.

3 Reproduction of CIP is confirmed if all of the identification characteristics of the tested samples obtained as a result of its analysis fall into the range of the identification features of the related product from the database.

4 Standard deviations of replicate measurements are calculated for the quantitative element analysis methods (ICP-OES and ICP-MS) to indicate random errors. The standard deviations results should be similar to the corresponding CIP values.

5 Verification of the mixed sample identification procedure.

2 Document review

2.1 Description of the Complex Identification Procedure (CIP).

The original version of the CIP consists of one document describing the full procedure. In the course of the project this procedure has been subdivided into 6 protocols, referring to individual preparation and analytical techniques. These protocols will be discussed and reviewed in the following chapter.

On the basis of the available documents and the in-house analyses on the provided material all steps in the CIP are verified. Originally, the CIP consisted of a 15 page document. After a first review it was suggested to subdivide this document into protocols describing the preparation and analytical techniques. The current review refers to the protocols that are attached as an appendix to this report. The preparation of protocols has been a significant improvement of the CIP.
The CIP includes 4 different analytical techniques. These techniques are used to determine the following:

- Full elemental composition of a substance, including contaminants
- Phase composition of a substance
- Elemental composition and morphological structure of individual particles in a substance which allows the definition of groups of a limited number of particle types having certain elemental and morphological composition and constituting the substance.

The information of 69 products is included in the Reference Data Base (RDB) and the information obtained by an analysis conform the CIP is compared with the corresponding information in the RDB

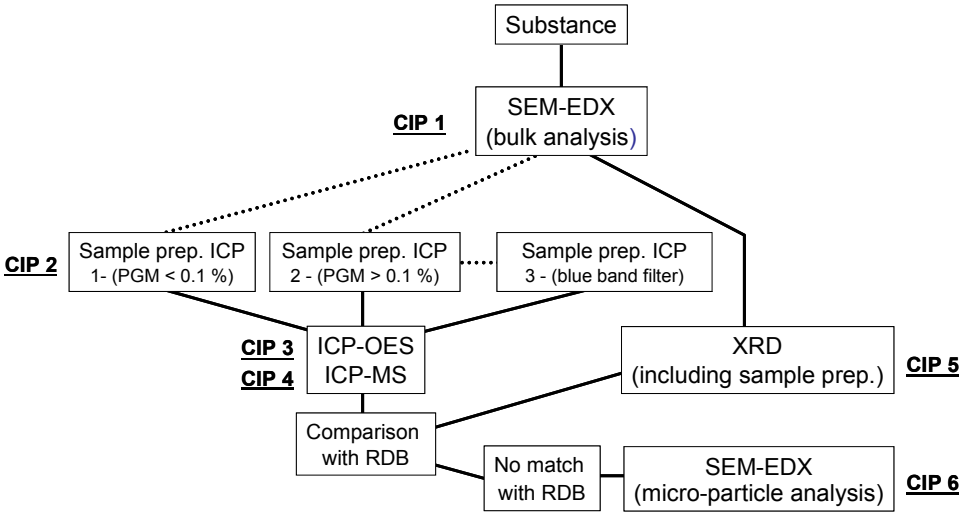


Figure 1 Analytical scheme as described in the Complex Identification Procedure, showing for which activity a protocol has been prepared.

The full CIP consists of 6 different protocols:

CIP-1 Determination of the integral elemental composition of precious metal-containing products by Scanning Electron Microscopy with X-Ray microanalysis

The analysis consists of at least 5 non-overlapping areas of the sample surface. These areas must contain at least 1000 particles.

Results are used for the primary analysis of a substance and determination of the methods for further study (method of sample preparation) within the framework of the Complex Procedure.

The bulk (integral) elemental composition of a substance is defined by taking measurements at not less than 5 non-overlapping areas of the samples' surface at the magnification rate ensuring the maximum possible amount of particles in view at a time, but not less than 1000 particles in one field of view.

Magnification for bulk elemental analysis in the aggregates - 20x

CIP-2 Wet acid digestion of PGM containing products for ICP-OES and ICP-MS analysis

CIP-2-Method-1: Samples with low precious metals content (< 0.1 wt. %)
3 sub samples (1g each), attack with HF, "tsar vodka" and HF, "tsar vodka" followed by HCL as described in protocol CIP-2 of the Complex Procedure

CIP-2-Method-2: Samples with high precious metals (> 0.1 wt. %)
3 sub samples (0.5g each), combination of attack with "tsar vodka" and 2 times HCL as described in protocol CIP-2 of Complex Procedure
Samples with high precious metal contents which do not dissolve completely in the "tsar vodka" + HCL attack are filtered, dried and ashed. Residue is melted with barium peroxide at 900 ^{0}C. The melt is leached with 10% HCL.

CIP-3 Determination of the elemental composition of precious metal-containing products by ICP-OES

The analyses are intended for determining sodium, aluminium, magnesium, sulphur, phosphorus, potassium, calcium, chromium, manganese, iron, cobalt, and arsenic in the concentrations 1.10^{-4} to 100 weight % and for titanium, nickel, copper, selenium, molybdenum, ruthenium, rhodium, palladium, silver, tin antimony, tellurium, barium, tungsten, iridium, platinum, gold and lead in the concentrations ranging from 1.10^{-2} to 100 weight %.

CIP-4 Determination of the elemental composition of precious metal-containing products by ICP-MS

The analyses are intended for determining titanium, nickel, copper, selenium, molybdenum, ruthenium, rhodium, palladium, silver, tin antimony, tellurium, barium, tungsten, iridium, platinum, gold and lead in the concentrations ranging from 1.10^{-2} to 1.10^{-2} weight %.

CIP-5 Determination of the phase composition of precious metal-containing products by XRD

The phase composition of the substance is determined by comparing the diffractograms of the analyzed substance with the reference diffractograms stored in the RDB.

CIP-6 Determination of the elemental composition of micro particles of precious metal-containing products by Scanning Electron Microscopy with X-Ray microanalysis.
The Scanning Electron Microscopy equipped with X-Ray microanalysis allows to:

- Identify the characteristics of individual particles of the sample substance (appearance, surface morphology, disparity, qualitative elemental composition)
- Determine the content of elements from oxygen to uranium with concentrations from 0.2 (5-for elements with the weight less than that of sodium) to 100 % weight.
- Present the aggregates of particles within a substance as a combination of a limited number of particle types with a certain elemental composition and morphology

2.2 General comments on the CIP protocols

Here only the general comments on the CIP protocols received 07-03-2007 are given. Detailed comments will be given directly to the Russian colleagues from the Mining and Metallurgical Company “Norilsk Nickel”, Institute of Criminalistics of the Russian Federal Security Service and the State Research Institute for Rare Metals. The general comments can be divided in:

- Absence of results on reference material
  In order to determine the recovery of the digestion methods and the overall accuracy of the ICP and ICP-MS determinations, results on certified reference samples have to be reported.

- Fine tuning of the protocols
  In the text of the protocols, analytical details are missing. Examples are the absence of the temperature and duration of the wet digestion, use of flasks but no description what kind of flasks, exact description of inter-element corrections, list of measured isotopes/masses etc.
  For an efficient implementation of the missing analytical details we recommend that specialists of the Russian Institutes and TNO discuss them in a joint meeting.

- The SEM-XRSMA protocol (CIP-6)
  The explanation of the qualitative and quantitative analysis has to be extended by some practical examples. Only after the short course of one day by the Russian scientists, the experienced TNO operator could execute the CIP-6 protocol. Availability of the RDB on micro particles would be very helpful in successfully running the CIP-6 protocol.

- Availability of the RDB for the phase composition of precious metal-containing products by XRD (CIP-5)
  The phase composition of a substance is determined by comparing diffractograms of the analyzed substance with the reference diffractograms in the ICDD

(International Centre for Diffraction Data) database. However in the CIP-5 protocol it preferred to use the “fingerprinting’ method in which the diffractograms of a substance are compared directly with the diffractograms contained in the RDB. To date the RDB is has not yet become available in an English translation.

3 Analytical testing of the CIP

The Complex Identification Procedure was tested by BKA and TNO by performing the CIP analyses on three different samples (N1, N2 and N3). The samples N1 and N2 are Norilsk Nickel certified reference samples for nickel and copper slimes, respectively. For sample N3 the task was to determine the relative proportion of N1 and N2.

It should be noted that the analyses were performed following the version of the Complex Identification Procedure dated 2005. At the time the analyses were carried out, the new protocols as reviewed in Chapter 2 and given in Appendix A were not available. The test results of BKA and TNO are discussed here on basis of the TNO results but when necessary comments or results given in the BKA report (S. Becker, 07-01-2007, Appendix B) are included.

3.1 Bulk analysis by SEM-EDX

The three samples N1, N2 and N3 were prepared for SEM-EDX analyses as described in the CIP 2005 protocol. Scanning electron microscopy (Philips XL-30 FEG REM) and X-ray microanalysis (Noran Vantage RMA system) were used for a semi-quantitative elemental analysis. The samples were measured at an accelerating voltage of 20 kV, 100 seconds counting time and a conductive coating was applied.

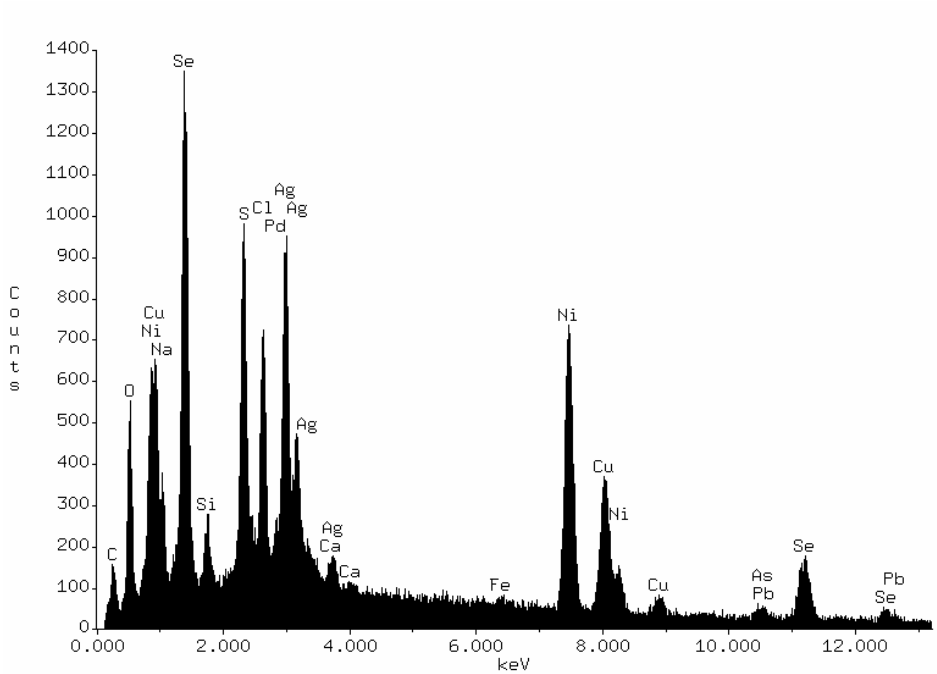
The EDX spectra and the semi-quantitative analyses of samples N1 (nickel slime), are given in Figures 2. In sample N1 the nickel concentration is higher than the copper concentration. The sample has in addition very high concentrations of silver (15.8 %), arsenic (1.3 %), selenium (18.6 %), palladium (0.7%) and lead (3.3 %). According to the scheme in Figure 1 the sample preparation for ICP-OES and ICP-MS has to be done according to CIP-2-method 2.

Contrary to sample N1 and as one should expect for a copper slime, the copper concentration in sample N2 is higher than the nickel concentration. Beside these two elements this sample has high arsenic (3.8 %) and chromium (0.5 %) contents. In the SEM screening no precious metals are found and therefore the sample preparation has to be done according to CIP-2-method 1 (fig. 1).
In sample N3 the nickel concentration is lower than the copper concentration. The sample has in addition very high concentrations of silver (7.7 %), arsenic (3 %) and selenium (8.7 %). According to the scheme in figure 1 the sample preparation for ICP-OES and ICP-MS has to be done according to CIP-2-method 2.

Table 1. Semi-quantitative results for Ni, Cu, Se and Ag for the samples N1, N2 and N3

Element	N1	N2	N3	(N1+N2)/2
Ni (wt %)	18.8	15.6	13.1	17.2
Cu (wt. %)	11.0	26.2	18.5	18.6
Se (wt. %)	18.6		8.7	9.3
Ag (wt.%)	15.8		7.7	7.9

Table 1 shows that the results for sample N3 are consistent with a 50-50 mixing of N1 and N2.



Accelerating Voltage: 20 KeV Take Off Angle: 35.1992°
Live Time: 100 seconds Dead Time: 23.782

Element	k-ratio (calc.)	ZAF	Atom %	Element Wt %	Wt % Err. (1-Sigma)
O -K	0.0380	4.485	43.64	17.06	+/- 0.50
Si-K	0.0053	2.155	1.67	1.14	+/- 0.05
S -K	0.0364	1.433	6.65	5.21	+/- 0.12
Cl-K	0.0228	1.397	3.68	3.19	+/- 0.21
Ag-L	0.1194	1.321	5.99	15.77	+/- 0.49
Ni-K	0.1862	1.008	13.09	18.78	+/- 0.40
Cu-K	0.1044	1.046	7.03	10.92	+/- 0.47
As-K	0.0112	1.134	0.70	1.27	+/- 0.79
Se-K	0.1599	1.162	9.63	18.57	+/- 0.74
Na-K	0.0092	4.120	6.78	3.81	+/- 0.19
Fe-K	0.0031	0.994	0.23	0.31	+/- 0.09
Pd-L	0.0050	1.381	0.26	0.68	+/- 0.46
Pb-L	0.0230	1.428	0.65	3.29	+/- 2.05
Total			100.00	100.00	

Figure 2 Bulk analysis of sample N1 by SEM-EDX. At the top the EDX spectrum and at the bottom the semi-quantitative results of sample N1 are given.

3.2 Determination of the phase composition by XRD

A qualitative determination of the crystalline compounds was performed with a Philips PW3020 X-ray diffractometer on N1, N2 and N3. The samples are recorded as 06AES661 (N1), 06AES662 (N2) and 06AES663. The following measuring conditions were applied:

Generator: Tension 40 kV, current 50 mA.
Divergence slit: Fixed ½°; Incident Beam: Soller slit: 0.04 rad; Antiscatter slit: Fixed ½°; Receiving slit: Fixed 0.2 mm; Diff. Beam Soller slit: 0.04 rad; Monochromator: Curved graphite.

A sample was prepared on a single-crystal sample holder on which a very thin layer of petroleum jelly was applied for good adhesion of the sample material.
X'Pert HighScore Plus and the ICDD PDF-2 database, release 2005 were used for identification. A recorded diagram is given in figure 3.

For the identification TNO made use of the reported presence of the following elements: Ni, Cu, O, S, Pb, and Ag.
For the interpretation of the diffraction data, BKA used the presence of the following elements (determined with XRF-EDX):
N1: **S, Cl, Ni, Cu, Se, Ag**, Si, Pd, As and Pb;
N2: **S, Cl, Ni, Cu, As**, Si, Se, Pb, Pd and Ag
N3: **S, Cl, Ni, Cu, As, Se, Ag**, Si, Se, Pb, Pd and Fe (main elements in bold).

Table 2 Overview of the components in the 3 samples as identified with XRD by TNO and BKA.

TNO XRD results								
Sample	NiO	Ag_2Se	NiS	AgCl	$Cu_7+2Cl_4(OH)10H_2O$	Na_2O	SiO_2	NaCl
N1	+	+			-	+/-	+/-	+/-
N2	+	-	+		+/-			
N3	+	+		+/-	-			
	+ = positive identification; +/- = possibly present; - = not identified							
BKA XRD results								
N1	$Ni_{1-x}Cu_xO$ – nickel copper oxide –major component							
	$PbSO_4$ – lead sulphate (Anglesit)							
	Ag_2Se – silver selenide (Naumannit)							
N2	$Ni_{1-x}Cu_xO$ – nickel copper oxide –major component							
	$(CuCl_2)_2*(Cu(OH)_2)_5 * H_2O$ – (Atacamite)							
	NiS – nickel sulfide (Digenit)							
N3	$Ni_{1-x}Cu_xO$ – nickel copper oxide–major component							
	$PbSO_4$ – lead sulphate (Anglesit)							
	Ag_2Se – silver selenide (Naumannit)							
	$(CuCl_2)_2*(Cu(OH)_2)_5 * H_2O$ – (Atacamite)							

A number of reflections remain unidentified in the recorded diffractograms because no match with the database could be found. In addition, several amorphous compounds are present in the samples. The amount of amorphous material was the highest in sample N2. BKA identified in addition to TNO one more phase in N1 and two more phases in

N3. In N2 the same phases were identified (Table 2). Identification of additional phases is possible when the chemical composition is better known or when the analyzing time is increased (Becker, 07-01-2007; Appendix B).

When the unknown sample is a pure Norilsk Nickel product it is better not to compare the recorded diffractograms with the ICDD PDF-2 database but with the diffractograms available in the RDB.

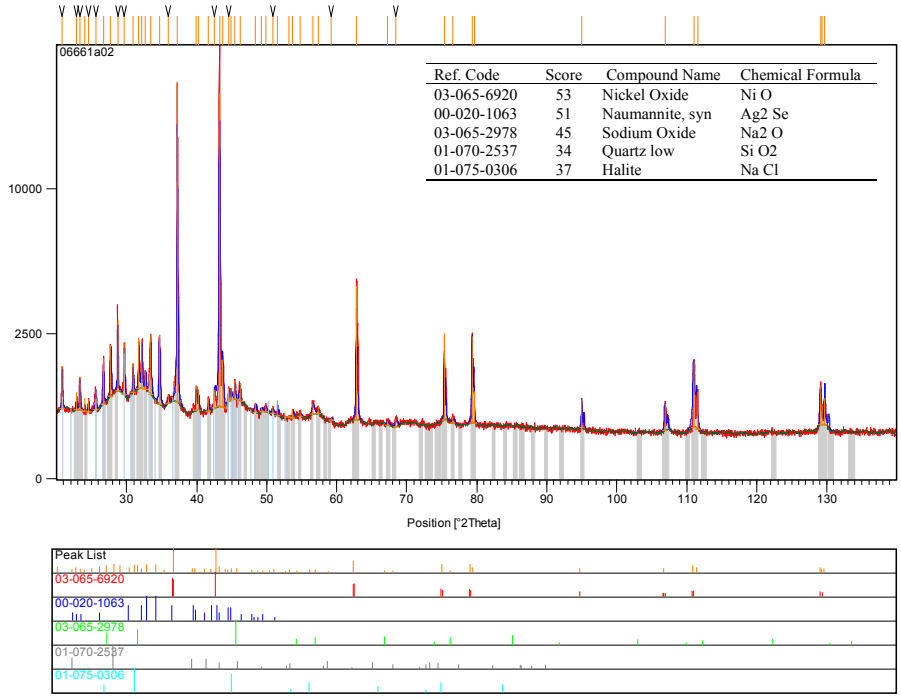


Figure 3 Diffractogram and identification of sample N1

3.3 Wet acid digestion

The wet acid digestion was performed according to the three methods given in the CIP protocol 2005. Method 1 (CIP-2-method 1, see Appendix A) consists of a combination of dissolutions in HF, HF and “tsar vodka”, followed by “tsar vodka” and finally HCl. In between the samples are evaporated. The dissolved sample is kept in solution in 10 % HCl. Method 2 (CIP-2-method 2, see Appendix A) consists of a combination of dissolutions in “tsar vodka” followed by twice HCl. In between the samples are evaporated. The dissolved sample is kept in solution in 10 % HCl.

Method 2 differs from method 1 that no HF is used and therefore silicates containing the elements zircon and hafnium will not completely dissolve. Figure 4 (see section 3.4.3) shows that when no HF is applied (method 2) some of the elements in sample N1 are less well digested than when HF is applied (method 1).

When the samples with digestion method 2 are not completely dissolved, the solutions are filtered. The filter with sediment is then dried and ashed. The sediment is melted with barium peroxide and leached with 10 % HCl. This solution is added to the solution

already obtained. With the CIP 2005 protocol the most experienced analyst of the TNO-Geolab could not perform this barium peroxide melting followed by leaching. With the correct description of the barium peroxide melting given in the CIP-2 –version 1.1 document, the barium peroxide melting could successfully be carried out.

3.4 Elemental composition by ICP-OES and ICP-MS

Digestion of the three samples was performed in triplicate following the description given in the CIP (2005). This resulted in a total of 9 solutions for the ICP-OES analyses for each method.

In the ICP-OES analysis the concentration of 25 elements and in the ICP-MS the concentration of 64 elements was determined. The results of both analytical techniques for two digestion methods as described in the CIP (method 1 and method 2) are given in Appendix C.
The results as given for each sample are the average of three analyses on the same solution.

3.4.1 ICP-OES

An overview of the ICP-OES parameters is given in Table 3. Calibration, identification, quantification and quality control were primarily performed according to the standard operating procedure of the TNO Geolab. This was done because some of the technical details were not described in the ICP-OES procedure in the CIP (see also Chapter 2). The results of the analyses are given in Appendix C.

Table 3 Overview of ICP-OES operating parameters

Type	SPECTRO CIROS^{CCD} ICP-Spectrometer with a radial plasma as ion source
Elements	Al, Ba, Be, Ca, Ce, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sr, Ti, V, Y, Zn and Zr
Argon Gas Tank Pressure	9 Bar
Nebulizer Gas Flow	0.8 L/min
Auxiliary Gas Flow	0.8 L/min
Coolant Flow	14 L/min
Plasma Power	1400 W
Pump step	1

3.4.2 ICP-MS

An overview of the ICP-MS parameters is given in Table 4. Calibration, identification, quantification and quality control were primarily performed according to the standard operating procedure of the TNO Geolab. This was done because some of the technical details were not described in the ICP-MS procedure in the CIP (see also Chapter 2).
The results of the analyses are given in Appendix C. It should be noted that the values for Se and Ag are not correct. This is due to an overload of the detector.

Table 4 Overview of ICP-MS operating parameters

Type	Agilent 7500a ICP-MS
Elements / masses	Lithium / 7; Beryllium / 9; Boron / 11; Sodium / 23; Magnesium / 26; Aluminium / 27; Phosphorus / 31; Potassium / 39; Calcium / 44; Scandium / 45; Titanium / 47; Vanadium / 51; Chromium / 52; Manganese / 55; Iron / 57; Cobalt / 59; Nickel / 60; Copper / 65; Zinc / 66; Gallium / 71; Arsenic / 75; Selenium / 82; Rubidium / 85; Strontium / 88; Yttrium / 89; Zirconium / 90; Niobium / 93; Molybdenum / 95; Silver / 107; Cadmium / 111; Tin / 120; Antimony / 121; Tellurium / 128; Caesium / 133; Barium / 137; Lanthanum / 139; Cerium / 140; Praseodymium / 141; Neodymium / 146; Samarium / 147; Europium / 151; Gadolinium / 157; Terbium / 159; Dysprosium / 163; Holmium / 165; Erbium / 166; Thulium / 169; Ytterbium / 172; Lutetium / 175; Hafnium / 178; Tantalum / 181; Platinum / 195; Mercury / 202; Thallium / 205; Lead / 208 Bismuth / 209; Thorium / 232; Uranium / 238
Precious Metals TNO's special task	Os, Ir, Ru, Rh, Pd, Pt and Au
Argon Gas Tank Pressure	517 kPaG
Carrier Gas Pressure	165 kPaG
Carrier Gas Flow	0.66 L/min
Makeup Gas Flow	0.36 L/min
Auxiliary Gas Flow	0.89 L/min
Plasma Gas Flow	15.02 L/min
PeriPump1	0.08 rps
Forward Power	1350 W
Reflected Power	0 W

3.4.3 *Comparison of the chemical composition of N1, N2 and N3*

In Figure 4 and 5 the chemical composition of samples N1, N2 and N3 are compared. Figure 4 is constructed by taking the ratio of N1/N2 and, subsequently sort the ratio's in a descending order. The elements relatively enriched in N1 plot on the left hand side of the figure; the elements on the right hand side are relatively higher in sample N2. The elements in the middle with a ratio close to 1 have similar concentrations in both samples. The application of this plot is that one can easily spot the elements that distinguish N1 from N2. This information can then be used for selecting "marker" elements, defined as the elements that are most useful to make a distinction between both samples. Sample N1 is enriched in REE and Zn-Se-Tl-Pb like sulphides, whereas the N2 sample has more metal oxy-anions like Mo, U, V and Cr, in combination with high P and B.

Also plotted in Figure 4 are the ratio's for the two digestion methods. It shows that there are no large discrepancies between both methods, except for the elements Zr, Hf, Th and Zn and Cd. The first three elements are probably present in a zircon phase, in which

the zircons from the N1 sample are much higher in Th than in the N2 samples. Because the ratio's in method 2 for Zr, Hf and Th are lower, it is expected that the N1 sample contains more zircon that is dissolved more completely with method 1 (use of HF) than with method 2 (Tsar Vodka only).

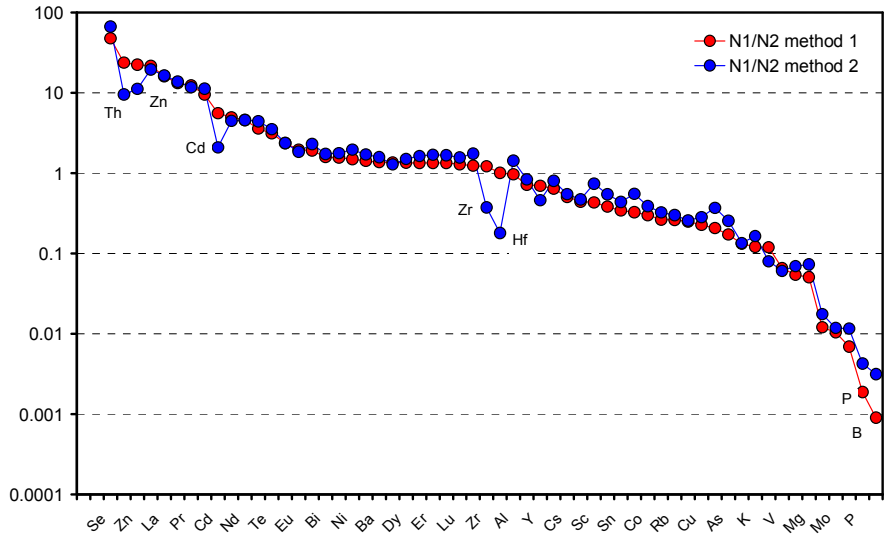


Figure 4 Comparison of the N1/N2 ratio for the two different digestion methods

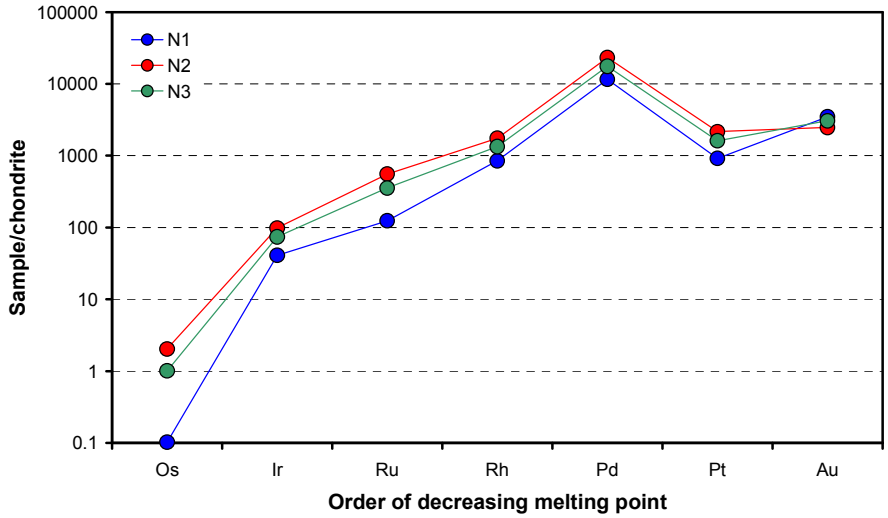


Figure 5 Comparison between N1, N2 and N3 after a chondrite normalisation on 7 elements with different melting points

Summarizing, the REE elements combined with Se, Zn, Cd, Tl and oxy-anion forming metals like V, Cr, Mo, V in combination with P and B show the largest variation when comparing sample N1 with N2.

In Figure 5 the PGE are plotted in the order of their decreasing melting point and normalized on the Canyon Diabolo chondrite values. Chondrite normalisation is carried out if one wants to compare enrichments or depletions of elements in relation with

processes after the formation of the Earth. It is assumed that the concentrations found in chondrites represent the primordial Earth. It can also be used for comparing ores or products of ores related to their origin. What can be seen in Figure 5 is that both samples N1 and N2 show a relative enrichment in Pd and are relatively depleted in osmo-iridium. For gold, sample N1, N2 and N3 show the same values. In addition, samples N3 falls nicely between N1 and N2, suggesting that N3 is a binary mixture of N1 and N2. Therefore, in order to distinguish such samples, marker elements can be a useful tool for distinguishing ore processed products. N2 is for Os about a factor 10 lower than N1, for Ir to Pt between a factor 3 and 5 and almost similar in gold. This suggests that N2 has been melted at a lower temperature than N1.

3.4.4 *Comparison of the TNO and BKA results for the N1 and N2 samples*

In Table 5 the results of TNO and BKA are compared. The results of BKA are given in Appendix B and consist of ICP-MS analyses only. The TNO results consist of ICP-OES and ICP-MS results. In this comparison the ICP-OES was calibrated according to the new CIP-3 protocol and not according to the standard ICP-OES 'rocktask' of TNO-Geolab. With this new calibration it was possible to analyze all elements according CIP-3 and CIP-4 with the ICP-OES. Sample N3 could not be analyzed with the new calibration as no sample material was left. The advantage of the ICP-OES is that for the major elements (>0,1%) the dilutions are much lower than for the ICP-MS (see also the BKA report in Appendix B). Moreover, the minor elements can still be measured whereas with the ICPMS only the trace elements need to measured. Exactly as is described in the CIP-protocols 2, 3 and 4.

Table 5 Comparison of the BKA and TNO results for the elements (Ti, Ni, Cu, Se, Mo, Pd, Ag, Sn, Sb, Te, Ba, W, Pt, Au and Pb) for samples N1 and N2. The method 1 and 2 are described in CIP-2. BKA: ICPMS results, TNO: ICPOES (all elements given in % and in brackets), rest are ICPMS results

Sample	**N1**	**N1**	**N1**	**N2**	**N2**	**N2**
Lab	**BKA**	**TNO**	**TNO**	**BKA**	**TNO**	**TNO**
Digestion method		**Method 1**	**Method 2**		**Method 1**	**Method 2**
Titanium (ppm)	566	103(235)	169(135)	1250	496(641)	457(673)
Nickel (%)	34.92	36.42	36.67	19.21	17.00	18.75
Copper (%)	6.01	5.78	5.75	21.87	18.69	20.48
Selenium (%)	8.48	7.39	8.67	0.16	0.09	0.07
Molybdenum (ppm)	27	11(11)	11(11)	1241	1052(958)	948(1080)
Palladium (%)	0.75	0.75	0.75	1.53	1.28	1.54
Silver (%)	7.18	7.23	8.01	0.28	0.24	0.27
Tin (%)	0.32	0.34	0.35	0.72	0.72	0.77
Antimony (ppm)	886	697(828)	749(780)	1197	1064(955)	930(748)
Tellurium (%)	0.60	0.59	0.59	0.17	0.15	0.15
Barium (ppm)	30	25(24)	22(22)	22	18(19)	14(19)
Tungsten (ppm))	0.01	0.21	0.27	0.13	0.12	0.12
Platinum (ppm)	1119	1099(947)	1099(947)	2461	2529(2312)	2325(2504)
Gold (ppm)	638	602(494)	591(581)	596	424(381)	389(481)
Lead (%)	2.31	2.40	2.35	0.16	0.17	0.16

As can be seen there is an excellent agreement between the BKA and TNO results. This indicates that applying the CIP protocols gives very reproducible results. Only the Ti

results of BKA are too high, but this is due to the large dilution which had to be applied in order to be able to analyze also the major elements with the ICP-MS.

3.5 Identification of micro particles with SEM-XRSMA

The method is based on the interaction between a scanning electron beam and the micro-particles in the sample material. The two signals that provide the greatest amount of information in SEM are the secondary electrons and X-rays.
Secondary electrons are emitted from the atoms occupying the top surface and produce a readily interpretable image of the surface. The contrast in the image is determined by the sample morphology.
The emitted X-ray has an energy characteristic and amount of the parent element. Detection and measurement of the energy permits qualitative elemental analysis. Measurement of characteristic line intensity permits quantitative elemental analysis.

3.5.1 Sample N1

In Figure 6 a SEM photo of the micro particles present in sample N1 is given. As can be seen from this photo the particles consist of well-formed cubic crystals and aggregates. In Figure 7 an EDX spectrum of the cubic crystals is given. They are nickel oxides with some minor amounts of Cu, Se and Ag. The second and most abundant particles are Se-Ag aggregates. A typical EDX spectrum is given in Figure 8. Much less abundant than the first two types are aggregates made out of lead sulphides (type 3 particles), see Figure 9. The percentage of each group was determined.

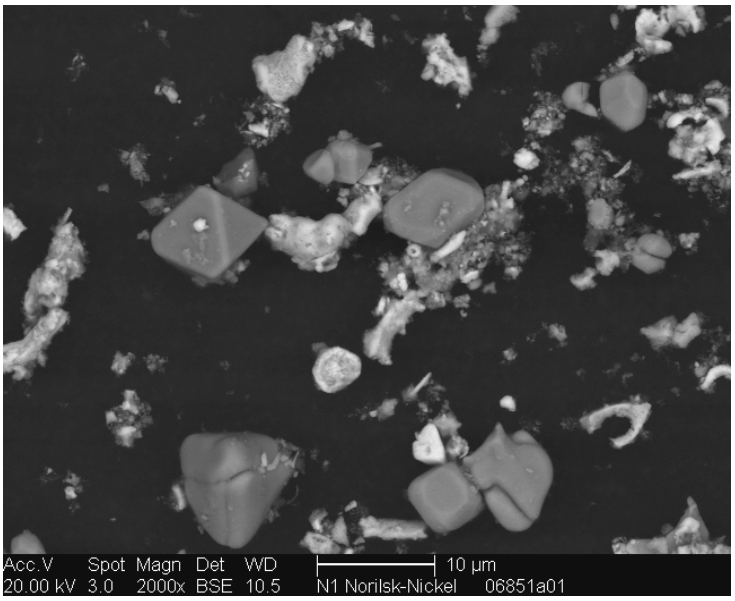


Figure 6 Particles present in sample N1. As can be seen the particles consist of well-formed cubic crystals and aggregates.

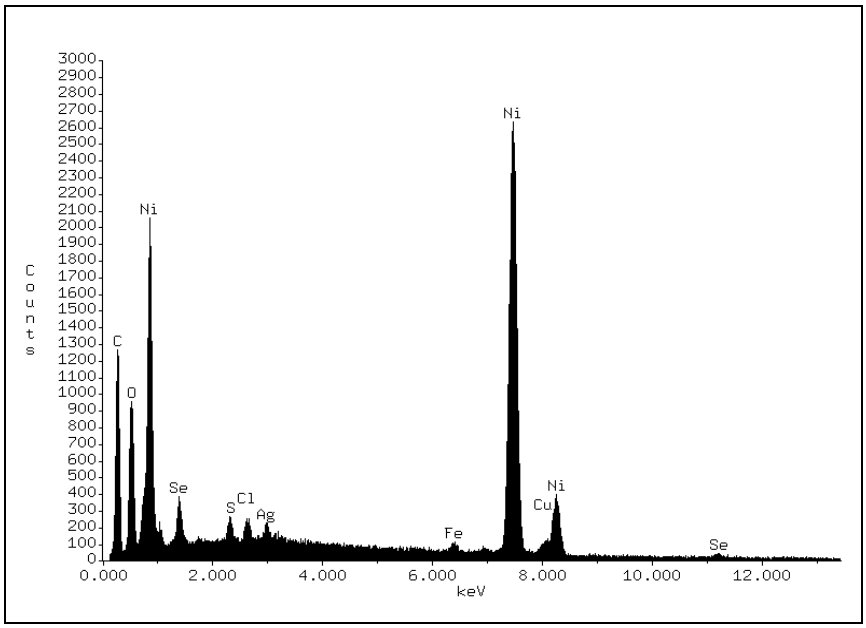


Figure 7 EDX spectrum of the cubic crystals, identified as particle type 1 (sample N1)

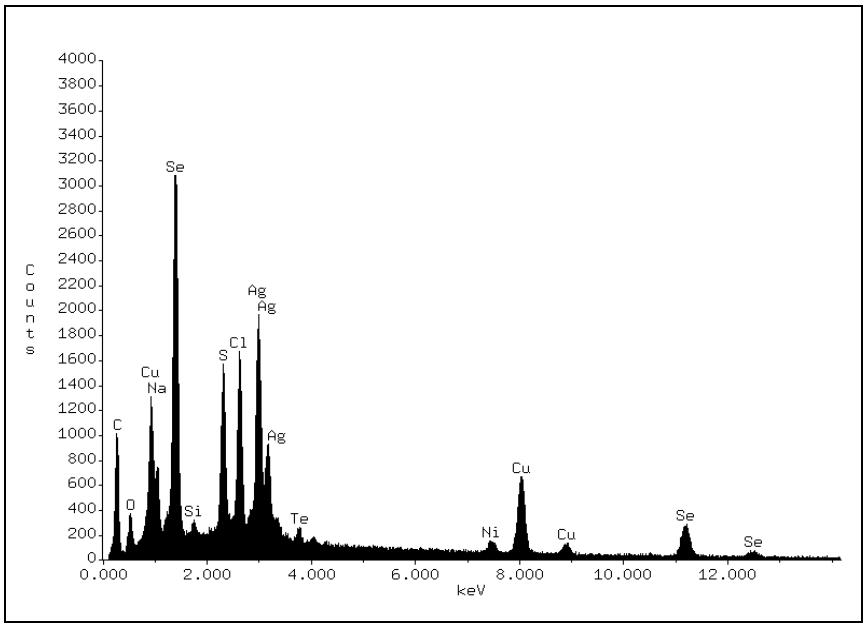


Figure 8 EDX spectrum of particle type 2 (sample N1)

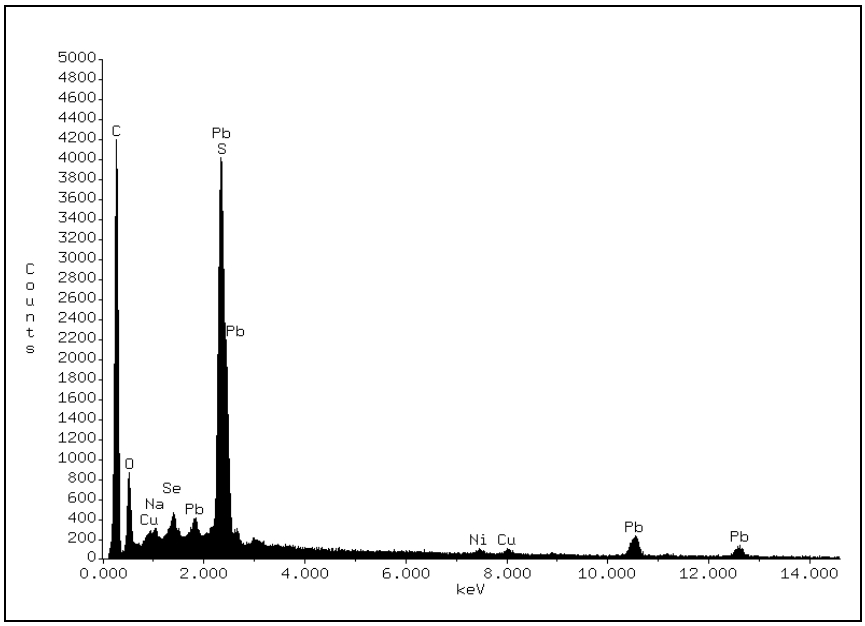


Figure 9 EDX spectrum of particle type 3 (sample N1)

3.5.2 *Sample N2*

In sample N2 only aggregates are found (Figure 10). The aggregates consist of Ni-Cu sulfides, Ni-Cu-As sulfides and Cu-Ni-As-Pd aggregates. In Figure 11 an EDX spectrum of a Ni-Cu sulfide is given and in Figure 12 an EDX spectrum of a Cu-Ni-As-Pd sulfide. After the analyses of more than 50 grains it is possible to identify some of the particles on base of their internal arrangement of grey and white areas in the Back Scatter Electron (BSE) mode.

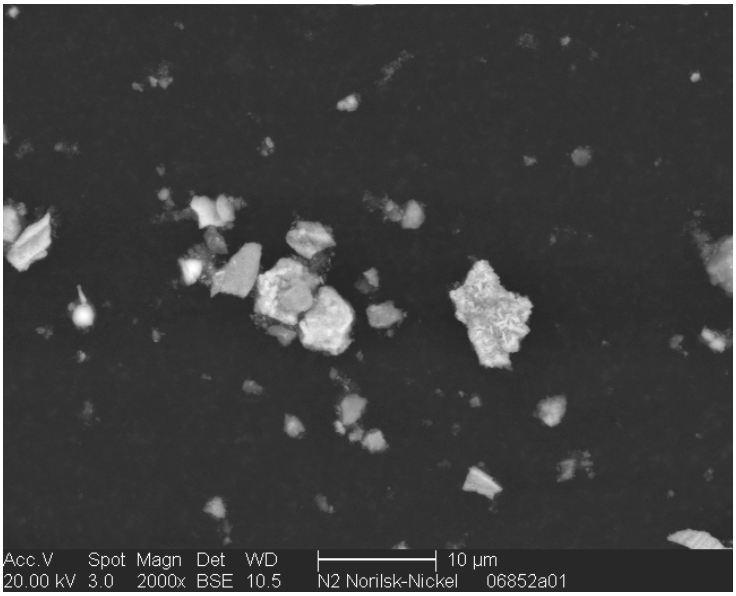


Figure 10 View of the aggregates as present in sample N2.

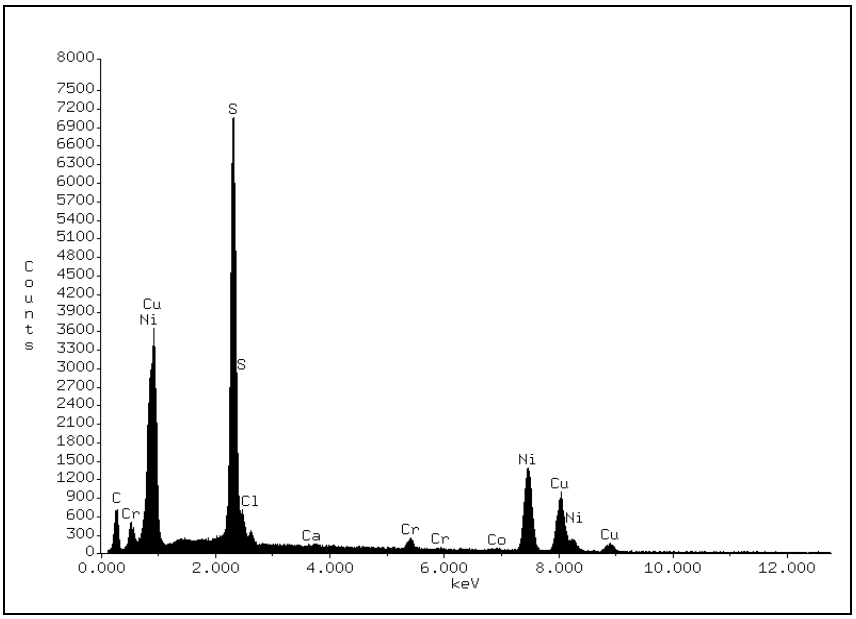


Figure 11 EDX spectrum of the Ni-Cu sulphide aggregates, identified as particle type 2, in sample N2

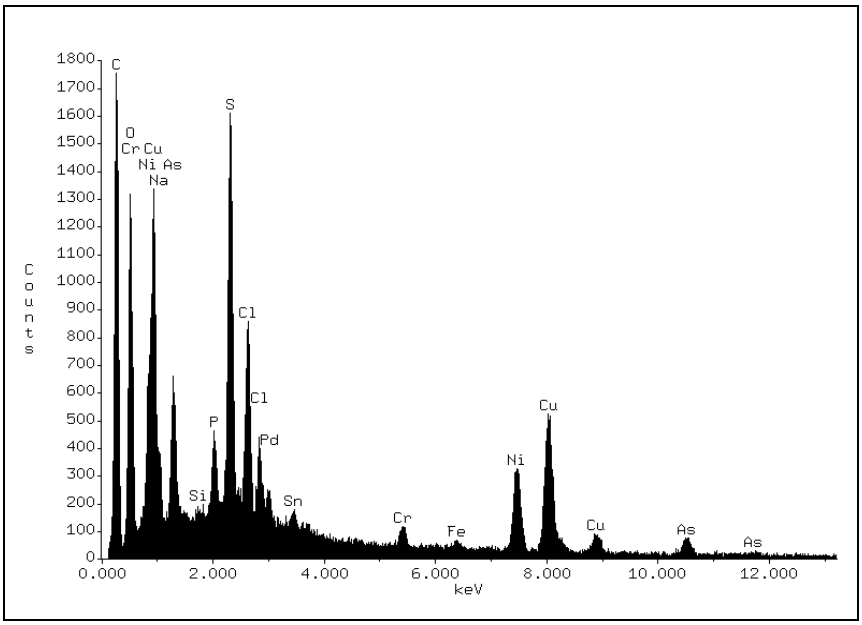


Figure 12 EDX spectrum of the Cu-Ni-As-Pd sulfide aggregates, identified as particle type 3, in sample N2

3.5.3 *Sample N3*

The SEM photo of sample N3 shows the presence of the cubic particles as has also been seen in sample N1 (Figure 13). The cubic crystals are again nickel oxides and their composition is similar as in sample N1. The aggregates consist mainly of Se-Ag aggregates found in N1 and the Cu-Ni and Cu-Ni-As-Pd aggregates found in N2. It was demonstrated by the Russian colleagues that on base of the analysis of a limited number of particles and the RDB that N3 is a mix of N1 and N2. However, in order to quantify the absolute contribution of sample N1 and N2 in N3 at least a thousands micro particles have to be determined. This was not done because no automatic measuring was available. It is recommended to automate the SEM-XRSMA procedure, which will give a more objective result.

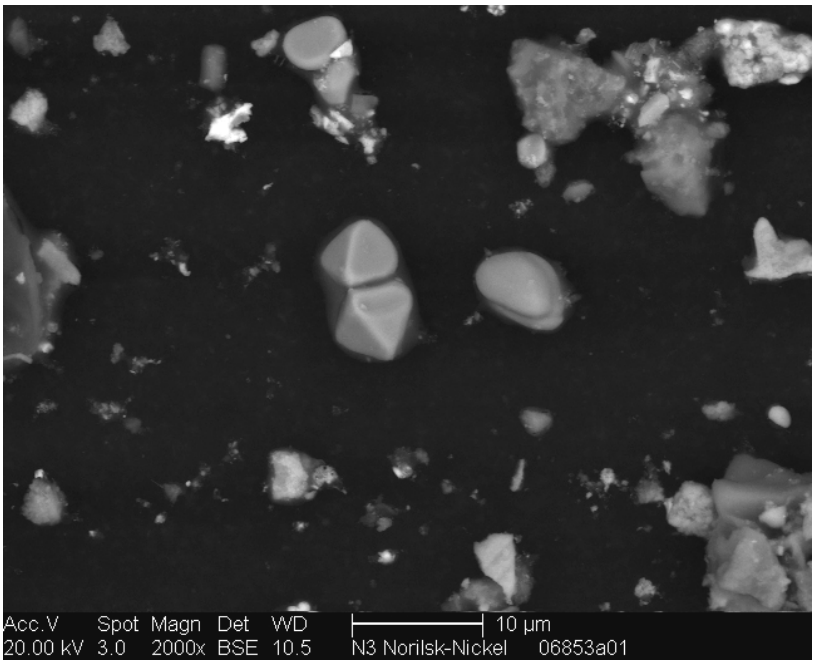


Figure 13 Photograph of sample N3, showing the cubic crystals

3.5.4 *Number of phases present in N1, N2 and N3*

BKA analysed about 100 particles in each sample. In Table xx the phases identified and encountered in each sample are given. Comparison of the type and number of particles each type present in N3 with the type and number of particles of each type present in N1 and N2 show clearly that N3 is a 50-50 mix of N1 and N2. Both BKA and TNO could only perform the analyses because they have experienced SEM technicians and mineralogists.

Table 6 Identification and quantification of the phases encountered in the samples N1, N2 and N3.

Sample	**N1**		**N2**		**N3**	
Phase	**Number**	**%**	**Number**	**%**	**Number**	**%**
Se-Ag	85	64.4	1	1	29	30.2
Cu-Ni			41	41	22	22.9
Cu-Ni-As			22	22	6	6.3
Cu-Ni-As-Pd			18	18	12	12.5
Cu-Ni-Pd			1	1		
Cu-Ni-Se-Ag	7	5.3				
Cu-Se					3	3.1
Cu-XX					5	5.2
Cu			10	10		
Ni-O	19	14.4	4	4	8	8.3
Ni-S			2	2	2	2.1
Pb	11	8.3			1	1.0
Sn	2	1.5				
Ca	2	1.5				
Unclassified	6	4.5	1	1	8	8.3
Total	132	100	100	100	96	100

4 The reference database (RDB)

Essentially the CIP consists of two basic parts: one is the detailed 5-stage analytical procedure for the substance to be assessed; the second is the comparison of the results of that analysis with the Reference Data Base (RDB). The RDB contains the results of about 60 known precious metal containing products obtained with the same analytical procedures.

For the CIP to be valid the overall measurement uncertainty (MU) of the analytical procedure must be fit-for-purpose. This is not only determined by the performance characteristics of the analytical procedure, but also by the given differentiation in the chemical and mineralogical characteristics of the (currently 61) different products within the RDB. The analytical performance has been described previously; here we focus on the fitness of discrimination and comparison procedures for the chemical data (ICP-MS and ICP-OES) of the RDB. The question to be answered here is if the analytical procedure in the CIP allows unambiguous identification of a test-specimen to one of the products in the RDB.

TNO has tested whether it was possible to discriminate all samples present in the RDB on basis of the chemistry given in the RDB. This was done with a Fuzy-c means clustering technique (FCM). The method and results are given in Appendix D. Here only the conclusions and recommendations of applying the Fuzy-C clustering method are given.
BKA did not make a statistical evaluation of the whole RDB but only of the products which were defined by Norisk Nickel as at-risk products. The at-risk products are K11/K12/K16/K18-25/N12-25/N27/N28/N30 and N35-39, in total 33 products. The aim of BKA was differentiation of all 33 Norilsk Nickel products. In order to achieve this goal BKA used beside the chemical data present in the RDB also the X-Ray diffractograms and the SEM-EDX phase analyses. The results of the BKA exercise are only available as a power point presentation (Appendix E). After a short description of the methods used the results of the BKA statistical evaluation will be given.

4.1 Statistical evaluation of the chemical data of all products present in the RDB with Fuzy-c means clustering (FCM) by TNO

The RDB evaluated contained 27 chemical attributes (elemental concentrations) for in total 173 observations on 61 products. Multiple observations were not available for all products, which implies that for these products no statistical uncertainty in their chemical characterization can be defined. Also, the similarity or dissimilarity of a test-specimen to these known products cannot be statistically ascertained. In order to have a robust comparison procedure, the RDB needs to be partitioned into groups of similar observations to which test-specimen can be compared.

Applying the FCM method to the chemical data present in the RDB lead to the following conclusions and recommendations:

- The first three stages of the analytical procedure are of sufficient accuracy and precision to narrow down the provenance of the test-specimen to groups of a few products, which can be further assessed in analytical stages 4 and 5.

- Based on the present chemical RDB, products cannot be uniquely separated from each other. With 15 clusters, groups of up to 10 products, but generally about 4 products, are discerned.
- The present RDB probably already allows differentiation into more than 15 clusters, which will lower the average number of products within a group, while still allowing adequate allocation of test-specimen.
- By adding additional analyses of all products to the RDB, separation will be improved, although overlap in compositional signature is still to be expected for some products.
- With additional analyses available for all products, each product can ideally be assigned to its own cluster. In that case a Discriminant Function Analyses (DFA) can be used to test the statistical significance of the separation.

The differentiation into 15 clusters is insufficient for an unambiguous allocation of the test-specimen N1, N2 and N3, but clearly narrows the focus for the next analytical stages of the procedure. Test-specimen 1 (product K16) is allocated with a low membership to cluster L that contains product N19 with a high membership, K16 with a low membership, and products K25 and K26 with a very low membership. Specimen 2 (product K11) is allocated to cluster M containing the products K11 and K12. The third specimen, which is a mixture of the two, is also allocated to cluster L.

4.2 Statistical evaluation of the 33 products at risk using the chemical, X-Ray diffractograms and SEM-EDX phase data present in the RDB by BKA

For the statistical evaluation the following methods were used:

- Grouping of the products on basis of the individual X-Ray diffractograms by an experienced X-Ray diffraction specialist. For this exercise only up to three X-Ray diffractograms per product were listed in the material datasheet of the examined RDB version.
- Statistical evaluation of the chemical data present for the 33 products present in the examined RDB version. Due to the partially small number of independent analyses per product the chemometric results should be treated with extreme caution. The statistical evaluation consists of:

  - Descriptive statistics using specific boxplots of the K and N series products. See for the results the power point presentation in appendix (xx).
  - Multivariate statistics consisting of cluster analysis, principal component analysis and discriminant function analyses. See for the results the power point presentation in Appendix E.

- The SEM-EDX results of the phases listed in the material datasheet of the examined RDB version.

With the cluster analysis and the X-Ray diffractograms the following result was achieved. ***A full separation of the 33 risk products is not possible.*** However, still a separation in more than 20 groups could be achieved. Degree of sub grouping based on X-Ray diffractograms and chemical analysis is the same.
Applying principal component analysis for groups where no full separation could be achieved was only partially successful. For instance for the group containing the products N20, N35, N37 and N39 only N37 could be separated by applying the

principle component analyses. This is no surprise because of the following description in the material sheet of N35: *"The diffractograms of leached secondary sludge N35, secondary sludge prior to leaching and washing (N37) and sludge following scrap washing (N39) are similar"*. With the SEM-EDX results the individual products in this group can be differentiated but only on basis of the presence or absence of minor phases. So the question is whether they should or should not be grouped together.

4.3 Conclusions and recommendations

- With chemistry only 15 (using all products) or 20 (using the 33 products at -risk) groups can be differentiated.
- By adding additional analyses of all products to the RDB, separation will be improved, although overlap in compositional signature is still to be expected for some products.
- With additional analyses available for all products, each product can ideally be assigned to its own cluster. In that case a Discriminant Function Analyses (DFA) can be used to test the statistical significance of the separation.
- Degree of sub grouping based on X-Ray diffractograms and chemical analysis is the same.
- With the SEM-EDX results, groups where no full separation could be achieved, the individual products in these groups can be differentiated. As this can only be done on basis of the presence or absence of minor phases, the question is raised whether or not we should group these products together.

5 Conclusions and recommendations

The Complex Identification Procedure describes the application of a number of analytical techniques for the identification of precious metal containing products. On the basis of the document review and the analyses the following conclusions and recommendations can be made:

5.1 Conclusions and recommendations from the desk audit and analyses

- On the basis of the desk audit and the analytical testing and verification it is concluded that the Complex Identification Procedure is fit for purpose.
- The individual protocols have been edited and revised by a team consisting of TNO and specialists from the involved Russian institutes. The versions to date have been included in the current report as an appendix.
- It is recommended not to compare the recorded XRD diffractograms with the ICDD PDF-2 database but with the diffractograms of the RDB (fingerprinting).
- For identification of unknown particles it is necessary to enquire the RDB in which all the Norilsk information is stored, e.g. chemical analyses, particle composition, and XRD diffractograms. To date this RDB is not yet available in an English version.
- Results of certified reference materials should be made available and included in the digestion, ICP-OES and ICP-MS protocols.
- The explanation of the qualitative and quantitative analysis as given in Protocol 6 (SEM-XRSMA) has to be illustrated with some practical examples.

5.2 Conclusions and recommendations from the statistical evaluation of the RDB

- The first three stages of the analytical procedure are of sufficient accuracy and precision to narrow down the provenance of the test-specimen to groups of a few products, which can be further assessed in analytical stages 4 and 5.
- Based on the present chemical RDB, products cannot be uniquely separated from each other. With 15 clusters, groups of up to 10 products, but generally about 4 products, are discerned.
- The present RDB probably already allows differentiation into more than 15 clusters, which will lower the average number of products within a group, while still allowing adequate allocation of test-specimen.
- By adding additional analyses of all products to the RDB, separation will be improved, although overlap in compositional signature is still to be expected for some products.
- With additional analyses available for all products, each product can ideally be assigned to its own cluster. In that case a Discriminant Function Analyses (DFA) can be used to test the statistical significance of the separation.
- One advantage of the FCM approach is that focus is on the relevance of the compositional differences (cluster centres), rather than just on statistical significance of threshold boundaries that may change with advances in analytical techniques.
- A second major advantage of FCM is in the fuzzy allocation of test specimen, which is allowed to be only partly similar to a cluster or intermediate between two or more clusters.

Complex Procedure

For Identification of the Nature and the Source of Origin of Precious Metal Containing Products of Mining and Metallurgical Operations

(CIP)

Mining and Metallurgical Company "Norilsk Nickel"

Institute of Criminalistics of the Russian Federal Security Service

State Research Institute for Rare Metals

Moscow, 2006

CONTENT

1 The purpose and the scope of the Complex Procedure 5

2 The procedure for determining the nature and the source of origin of a substance 6

3 CIP-1 Determination of the bulk elemental composition of precious metal-containing products by scanning electron microscopy with X-ray microanalysis ... 9

3.1 Update and review summary 10
3.2 Scope..... 11
3.3 Safety and environment 11
3.4 Definitions 11
3.5 Principle..... 11
3.6 Reagents and Materials..... 12
3.7 Apparatus and Equipment..... 12
3.8 Sample preparation 12
3.9 Calibration 12
3.10 Quality control 12
3.11 Procedure 13
3.12 Calculation..... 13
3.13 Reporting procedures including expression of results 14
3.14 Normative references and manuals..... 14
3.15 Method performance..... 14

4 CIP-2 Wet acid digestion of PGM containing products for ICP-OES and ICP-MS analysis..... 15

4.1 Update and review summary 16
4.2 Scope..... 17
4.3 Safety and Environment..... 17
4.4 Definitions 17
4.5 Principle..... 17
4.6 Reagents and Materials..... 17
4.7 Apparatus and Equipment..... 17
4.8 Sample preparation 18
4.9 Calibration 18
4.10 Quality Control 19
4.11 Procedure 19
4.12 Calculation..... 21
4.13 Reporting procedures including expression of results 21
4.14 Literature and manuals..... 21
4.15 Method performance..... 21

5 CIP-3 Determination of the elemental composition of precious metal-containing products by ICP-OES..... 23

1.1 Update and review summary 24
5.1 Scope..... 25
5.2 Safety and Environment..... 25
5.3 Definitions 25
5.4 Principle..... 26
5.5 Reagents and Materials..... 26

5.6 Apparatus and Equipment ... 26
5.7 Sample preparation ... 26
5.8 Calibration ... 26
5.9 Quality Control ... 27
5.10 Procedure ... 28
5.11 Calculations ... 30
5.12 Reporting procedures including expression of results ... 30
5.13 Normative references ... 31
5.14 Method performance ... 31

6 CIP-4 Determination of the elemental composition of precious metal-containing products by ICP-MS ... 37
1.2 Update and review summary ... 38
6.1 Scope ... 39
6.2 Safety and Environment ... 39
6.3 Definitions ... 39
6.4 Principle ... 40
6.5 Reagents and Materials ... 40
6.6 Apparatus and Equipment ... 40
6.7 Sample preparation. ... 40
6.8 Calibration ... 40
6.9 Quality control ... 41
6.10 Procedure ... 42
6.11 Calculations ... 44
6.12 Reporting procedures including expression of results ... 44
6.13 Normative references ... 45
6.14 Method performance ... 45

7 CIP 5 Determination of the phase composition of precious metal-containing products by XRD ... 51
1.3 Update and review summary ... 52
7.1 Scope ... 53
7.2 Safety and Environment ... 53
7.3 Definitions ... 53
7.4 Principle ... 53
7.5 Reagents and Materials ... 53
7.6 Apparatus and Equipment ... 53
7.7 Sample preparation ... 54
7.8 Apparatus calibration ... 54
7.9 Quality Control ... 54
7.10 Procedure ... 54
7.11 Calculation ... 55
7.12 Reporting procedures including expression of results ... 55
7.13 Normative references and manuals ... 55
7.14 Method performance ... 56

8 CIP 6 Determination of the elemental composition of micro particles of precious metal-containing products by scanning electron microscopy with X-ray microanalysis ... 57
1.4 Update and review summary ... 58
8.1 Scope ... 59

8.2 Safety and Environment 59
8.3 Definitions 59
8.4 Principle 59
8.5 Reagents and Materials 60
8.6 Apparatus and Equipment 60
8.7 Sample preparation 61
8.8 Calibration 61
8.9 Quality Control 61
8.10 Procedure 62
8.11 Calculation 63
8.12 Reporting procedures including expression of results 63
8.13 Normative references and manuals 64
8.14 Method performance 64

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 micro particles in a substance thus allowing a (semi)quantitative determination of the substance in terms of a limited number of micro particle groups where the groups are considered to represent individual phases.

The information obtained by these methods is compared with 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 repeated 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;
- micro residues 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 micro residues on bodies, in the hair or under nails of a crime suspect. Methods for sample collection and handling of micro residues are described in detail in the scientific literature[1,2] and are therefore not included in the protocols.

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).

[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.

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.

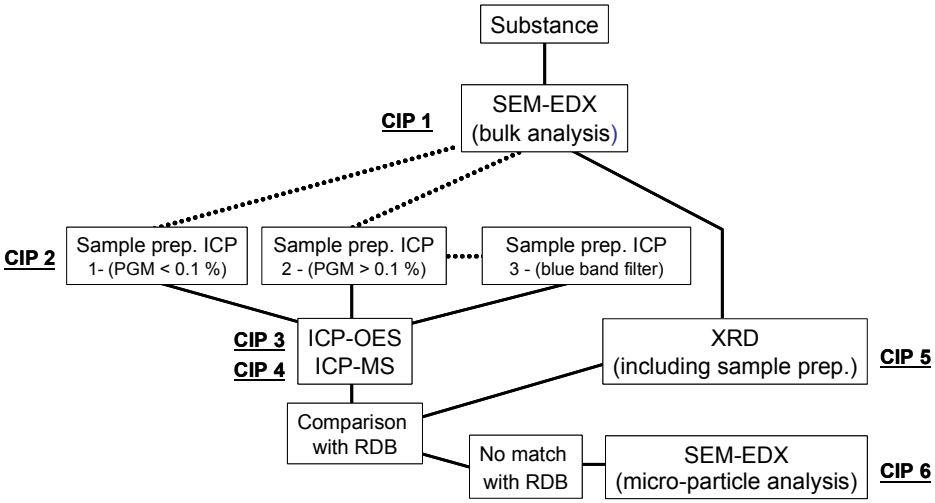


Figure 1 Overview of the Complex Procedure, consisting of 6 analytical methods which are described in this document. The numbers refer to the protocol numbers.

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 - CIP 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 CIP 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 CIP 3**) and Inductively Coupled Plasma Mass-Spectrometry (**Protocol CIP 4**) and the study of the phase composition by X-Ray Diffractometry (**Protocol CIP 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, then 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 CIP 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**

3 CIP-1 Determination of the bulk elemental composition of precious metal-containing products by scanning electron microscopy with X-ray microanalysis

Author:

Quality manager:

Authorisation:

Date :

3.1 Update and review summary

Updates

#	Section	Nature of Amendment	Date	Authorisation

Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

3.2 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

3.3 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.

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

3.5 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.

3.6 Reagents and Materials

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

3.7 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.

3.8 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.

3.9 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.

3.10 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 micro analyzer must be recalibrated (see paragraph 9).

3.11 Procedure

Prepare the scanning electron microscope and energy dispersive micro analyzer 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 ≤ 139 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 is 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.

3.12 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 Protocol CIP 2).

3.13 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 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.

3.14 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).

3.15 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.

4 CIP-2 Wet acid digestion of PGM containing products for ICP-OES and ICP-MS analysis

Author:

Quality manager:

Authorisation:

Date :

4.1 Update and review summary

Updates

#	Section	Nature of Amendment	Date	Authorisation

Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

4.2 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.

4.3 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.

4.4 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.

4.5 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.

4.6 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

4.7 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).

4.8 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.

4.9 Calibration

Not required

4.10 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).

4.11 Procedure

Method 1[3] - 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[3] - Samples with high precious metals content (above 0.3 percent by mass)

---

[3] 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.

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 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)

Addition method [4]– If residue is present

For either Method 1 or Method 2, if the probes did not dissolve completely, filter the solutions with the residues through the dual 'blue band' paper filters into 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[5]. 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.

---

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

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

4.12 Calculation

Not required

4.13 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.

4.14 Literature and manuals

Not required

4.15 Method performance

Not required

5 CIP-3 Determination of the elemental composition of precious metal-containing products by ICP-OES

Author:

Quality manager:

Authorisation:

Date :

1.1 Update and review summary

Updates

#	Section	Nature of Amendment	Date	Authorisation

Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

5.1 Scope

This procedure is intended for determining sodium, aluminum, magnesium, sulfur, 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.

5.2 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.

5.3 Definitions

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

An 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.

5.4 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.

5.5 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.

5.6 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;

5.7 Sample preparation

Executed in accordance with protocol CIP 2.

5.8 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 2.

Table 2 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.

'Calibration 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.

5.9 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 – 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%) then 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*.

5.10 Procedure

5.10.1 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[6] for this analysis are shown in Table 3.

Table 3 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	Manganese	260,568	Silver	338,289
	193,759				328,068
Barium	455,403	Molybdenum	202,030	Sodium	589,592
Calcium	396,847	Nickel	231,604	Sulfur	180,669
Chromium	205,560	Palladium	340,462	Tellurium	214,283
Cobalt	228,616	Phosphorus	178,221	Tin	189,927
			185,943		
			213,618		
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 paragraph 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.

5.10.2 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 concentrations of all elements in the unknown substance measured using this protocol (taking into account the error index of the method) is within the variability range of these elements' concentration in that product.

In the case that the elemental composition coincides with the composition of a product

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

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.

5.11 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 paragraph 10.

5.12 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*.

5.13 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).

5.14 Method performance

Method performance is demonstrated by the calculation of the Accuracy, Repeatability and Reproducibility indexes according to the formulas from ISO 5725–1÷5725–6-2002, and statistic correlations adjusted in the process of "Mastering CIP in Research Analytical Centre OSC 'Gipronikel Institute'[7]. 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 4, 5 and for the rest of the elements – in Table 6 (top values are listed).

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

Table 4 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 5 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
	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

	Mass, %			
		r_2	$CR_{0,95}$ (4)	R
	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
	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 6 Values of Error index "Δ", repeatability limit r_2, critical range of repeated measurements $CR_{0,95,n=4}$, reproducibility limits R for base metals and contaminant elements (P= 0,95

Mass, %				
	± Δ	r_2	$CR_{0,95}$ (4)	R
from 0,010 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

6 CIP-4 Determination of the elemental composition of precious metal-containing products by ICP-MS

Author:

Quality manager:

Authorisation:

Date :

1.2 Update and review summary

Updates

#	Section	Nature of Amendment	Date	Authorisation

Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

6.1 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.

6.2 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.

6.3 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"***:** the 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": the 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.

6.4 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.

6.5 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.

6.6 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.

6.7 Sample preparation.

Executed in accordance with Protocol CIP 2.

6.8 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 7.

Table 7 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.

6.9 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 CIP 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.

6.10 Procedure

6.10.1 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 8[8].

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 paragraph 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 sub sample is determined and this result is recorded (printed or written down from the screen).

Table 8 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

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

The procedure for interpretation of the results of the ICP-MS 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 with the composition of one specific product in the RDB can be made if the

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

concentrations of all elements in the unknown substance measured using this protocol (taking into account analysis' error index) are within the variability range of these elements' concentration 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.

6.11 Calculations

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

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

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 paragraph 10 is reported.

6.12 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*.

6.13 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).

6.14 Method performance

Method performance is demonstrated by the calculation of the Accuracy, Repeatability and Reproducibility indexes according to formulas from ISO 5725–1÷5725–6-2002, and statistic correlations adjusted in the process of the Procedure development[9] and are shown in Tables 9, 10, and 11.

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.

Metrological characteristics for noble metals are given in tables 9, 10 and for the rest of the elements – in Table 11 (top values are listed).

[9] 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.

Table 9 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 10 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 11 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

7 CIP 5 Determination of the phase composition of precious metal-containing products by XRD

Author:

Quality manager:

Authorisation:

Date :

1.3 Update and review summary

Updates

#	Section	Nature of Amendment	Date	Authorisation

Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

7.1 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.

7.2 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.

7.3 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.

7.4 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 determination of the phase composition of the substances and establishment of the differences between samples under analysis with the help of diffractogram appearance.

7.5 Reagents and Materials

- Technical distilled ethyl alcohol (96%).

7.6 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 (e.g. a blade of an office cutter);
- ICDD computer database of reference spectra and search system.

7.7 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.

7.8 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.

7.9 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.

7.10 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.

7.11 Calculation

7.11.1 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.

7.11.2 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.

7.12 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).

7.13 Normative references and manuals

ICDD – The International Centre for Diffraction Data.

7.14 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 %.

8 CIP 6 Determination of the elemental composition of micro particles of precious metal-containing products by scanning electron microscopy with X-ray microanalysis

Author:

Quality manager:

Authorisation:

Date :

}

1.4 Update and review summary

Updates

#	Section	Nature of Amendment	Date	Authorisation

Reviews

Review date	Outcome of Review	Next Review Date	Authorisation

}

8.1 Scope

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

8.2 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.

8.3 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.

Micro particle: particles with an average diameter less than 100 µm.

8.4 Principle

8.4.1 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.

8.4.2 Principle of micro particles combination identification.

The identification of a product by its micro particle content is carried out by the

}

comparison of the micro particles' elemental compositions present in a product with data stored in the database (RDB).

Each product is represented in the database in the form of micro particle 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 micro particle composition;
- whether this element is typical for the micro particles 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 micro particles, the number and relative content of micro particle 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.

8.5 Reagents and Materials

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

8.6 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 139 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.

}

8.7 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 micro particles 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 micro particles at room temperature and then place them in the electron microscope chamber.

8.8 Calibration

Prior to beginning an analysis, verification of the operational condition of the scanning electron microscope with the X-ray micro analyzer 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 Micro analyzer 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.

8.9 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 micro analyzer must be recalibrated (see Paragraph 9).

8.10 Procedure

8.10.1 Procedure on determination of the element composition and morphology of micro particles.

Prepare the scanning electron microscope and energy dispersive micro analyzer 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 ≤ 139 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. Micro particles should form a monolayer on the sample stage surface. During measurements, the electron beam should be focused on the centre of a micro particle. Examine all micro particles 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 micro particles have been examined.

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

8.10.2 Procedure on identification of micro particles composition.

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

In the electronic version of the RDB, the match between the elemental composition of an analyzed micro particle in the unknown substance and the micro particle 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 micro particles to the elemental composition of a certain type of micro particles present in the RDB is done as follows:

- Visually compare the qualitative composition of an analyzed micro particle with the range of qualitative compositions of all the types of micro particles present in the hard copy of the RDB. If the composition of the examined micro particle fits with a particular type of micro particle present in the RDB, it is assumed that the examined particle belongs to this particular type of micro particle.

}

- In the second step, compare the quantitative composition of the examined micro particle with the compositional range given in the RDB for the particular type of micro particle. When the composition of the examined micro particle is within the compositional range limits given in the RDB for this particular type of micro particle, it is concluded that the examined micro particle belongs to this particular type of micro particle.

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

- The examined micro particle corresponds to a type of micro particle only present in one particular product. The examined micro particle is related to this particular product.
- The examined micro particle corresponds to a type of micro particle present in different products. The examined micro particle is referred to all of these products.
- The examined micro particle does not correspond with the micro particle compositions present in the RDB. The examined micro particle 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 micro particles forming one specific product in the RDB are present in the examined unknown substance.
- The relative weight of these different types of micro particles differ no more than the product variability given in the RDB.

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

8.11 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 micro particle 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 micro particle in the examined unknown substance, the range of its measured proportion is given (see paragraph 8.4).

8.12 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).

8.13 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.

8.14 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 B — BKA Report

(see Appendix 11. Report by Becker et al on the BKA preliminary testing of the CIP entitled: “analysis round robin.”)

APPENDIX C – ICP-OES and ICP-MS results

ICP-OES – Method 1 digestion

Method 1	N1	RSD (%)	N2	RSD (%)	N3	RSD (%)
Li	1.7	5.4	0.7	3.4	1.2	3.9
Be	0.0	0.0	0.0	0.0	0.0	0.0
Na	22404.5	3.0	12888.6	1.2	18312.6	1.5
Mg	107.4	10.9	1306.5	1.7	799.5	3.8
Al	1116.6	9.1	790.3	2.8	967.6	4.8
P	2397.6	5.2	12723.7	2.6	7918.5	3.5
K	208.1	0.9	1032.8	0.6	658.8	2.5
Ca	3765.6	4.4	805.2	7.0	2380.1	1.4
Sc	0.0	0.0	0.0	0.0	0.0	0.0
Ti	144.4	7.9	540.0	3.3	375.3	2.8
V	10.0	4.7	19.5	2.5	15.0	2.7
Cr	896.0	4.9	5210.3	1.3	3180.8	2.1
Mn	0.0	0.0	33.2	2.3	17.0	3.7
Fe	3238.8	4.8	10934.7	1.5	7446.6	2.4
Co	2706.4	4.6	4041.3	1.6	3475.3	0.8
Ni	407401.0	4.5	221610.1	2.9	317840.6	1.0
Cu	63880.4	4.6	234754.9	2.9	154452.8	3.1
Zn	52.7	0.0	0.0	0.0	5.0	102.2
Sr	2.3	14.1	0.0	0.0	0.0	0.0
Y	0.0	0.0	0.0	0.0	0.0	0.0
Zr	6.2	8.4	5.4	6.8	6.2	8.1
Mo	0.0	0.0	1172.7	2.4	637.2	4.0
Ba	24.9	6.0	18.5	1.2	22.2	4.0
Ce	11.6	2.7	0.0	0.0	7.6	7.4
Pb	25299.3	4.5	1997.3	0.6	13735.3	3.2

ICP-OES – Method 2 digestion

Method 2	N1	RSD (%)	N2	RSD (%)	N3	RSD (%)
Li	1.9	1.4	0.8	17.2	1.4	2.0
Be	0.0	0.0	0.0	0.0	0.0	0.0
Na	22780.7	3.0	12202.7	5.0	18942.5	1.0
Mg	101.7	13.5	1249.3	8.1	640.7	3.0
Al	1633.9	3.0	1107.7	13.2	1422.6	1.1
P	2381.8	4.3	11855.6	8.3	7261.1	4.8
K	183.8	2.1	950.7	8.0	584.3	3.9
Ca	3885.7	2.9	881.7	25.6	2485.6	4.3
Sc						
Ti	234.5	2.7	607.1	7.7	457.6	1.3
V	10.5	1.4	19.9	8.6	15.3	2.1
Cr	928.0	1.8	5111.2	8.4	3009.8	3.8
Mn			39.7	6.5	17.9	4.0
Fe	3413.7	2.9	10707.6	7.0	7009.0	2.2
Co	2719.2	3.0	3837.4	7.2	3443.3	0.8
Ni	399597.2	2.8	200596.7	7.4	330677.6	1.6
Cu	61978.6	3.2	211340.9	7.5	140816.4	3.1
Zn	57.6	6.7			8.1	21.4
Sr						
Y			0.7	7.9		
Zr	8.4	3.2	19.6	2.6	15.3	0.6
Mo			1147.6	7.0	563.2	5.5
Ba	23.8	4.3	16.2	6.5	21.0	3.0
Ce	12.0	2.5	3.2	12.4	9.1	11.0
Pb	24920.9	2.9	1804.0	8.8	15436.1	4.2

ICP-MS – Method 1 digestion

Method 1	N1	RSD (%)	N2	RSD (%)	N3	RSD (%)
Pt	**937.9**	**3.3**	**2201.2**	**0.8**	**1647.1**	**2.3**
Pd	**6302.6**	**3.3**	**12665.2**	**0.7**	**9583.7**	**1.8**
Rh	**169.8**	**3.1**	**350.1**	**1.0**	**267.4**	**1.1**
Ru	**65.7**	**2.4**	**272.9**	**3.0**	**161.8**	**5.7**
Os	**0.1**	**13.4**	**1.0**	**2.8**	**0.5**	**4.9**
Ir	**22.1**	**2.9**	**53.1**	**1.4**	**39.9**	**2.5**
Re	0.4	5.8	8.5	2.0	5.0	3.7
Au	529.4	3.2	375.6	0.7	465.4	1.3
Li	1.0	14.9	0.5	3.8	1.0	4.9
Be	0.0	18.0	0.0	1.5	0.0	10.5
B	0.2	143.8	221.2	4.8	90.6	8.3
Na	14339.7	11.5	11543.1	2.4	16988.9	2.3
Mg	65.5	24.8	1288.0	0.6	752.8	2.9
Al	711.0	13.8	733.2	3.8	965.1	19.2
P	50.9	67.1	26926.8	3.4	15026.0	5.0
K	111.3	24.3	916.2	1.8	625.5	0.5
Ca	2743.6	6.6	761.9	7.5	2345.9	3.0
Sc	0.2	9.7	0.4	2.6	0.3	1.7
Ti	103.1	9.9	495.9	5.5	364.4	5.1
V	1.2	27.3	18.9	2.3	14.1	2.7
Cr	52.1	5.2	4303.5	2.3	2393.3	5.7
Mn	7.8	6.9	31.2	0.6	22.5	2.4
Fe	2818.5	6.5	10640.9	3.2	7634.7	3.7
Co	777.3	4.8	2586.7	3.1	1915.8	3.0
Ni	296333.9	5.8	197514.3	2.2	292326.3	0.6
Cu	47631.7	5.2	209248.2	2.2	142484.8	4.4
Zn	367.5	64.2	16.4	59.9	83.7	6.2
Ga	0.3	6.8	39.3	2.1	21.8	6.8
As	3518.5	5.3	20384.2	1.3	13743.8	3.7
Se*	16690.3	5.4	348.7	3.6	10028.3	0.7
Rb	0.3	5.3	1.3	1.9	1.0	3.3
Sr	31.0	7.0	6.2	7.1	20.1	2.9
Y	0.4	5.1	0.5	1.9	0.5	1.9
Zr	3.7	6.5	3.0	10.4	3.7	11.4
Nb	12.2	3.0	101.7	3.8	73.5	5.4
Mo	11.0	12.0	1052.2	1.2	600.8	4.0
Ag*	3598.3	1.7	4993.0	21.2	8700.6	47.3
Cd	3.0	113.3	0.5	1.6	0.7	18.8
Sn	2433.9	4.5	7066.7	1.3	4867.3	2.4
Sb	687.2	4.2	1063.5	1.8	913.2	1.5
Te	11700.1	4.7	3725.2	1.6	8093.9	1.5
Cs	0.0	4.7	0.1	3.0	0.0	5.7
Ba	24.8	5.1	18.0	1.3	20.9	4.5
La	5.5	5.2	0.3	5.9	2.9	3.4

Ce	10.7	3.8	0.5	4.2	5.6	4.5
Pr	0.9	4.9	0.1	4.7	0.5	3.3
Nd	2.3	4.9	0.5	0.9	1.4	2.0
Sm	0.2	2.8	0.2	2.7	0.3	18.6
Eu	0.0	6.6	0.0	2.4	0.0	4.9
Gd	0.1	4.7	0.1	1.6	0.1	2.6
Tb	0.0	4.8	0.0	3.0	0.0	2.5
Dy	0.1	2.9	0.1	4.9	0.1	0.3
Ho	0.0	4.5	0.0	1.0	0.0	3.1
Er	0.0	4.3	0.0	3.5	0.0	2.5
Tm	0.0	4.0	0.0	9.0	0.0	4.3
Yb	0.0	4.3	0.0	2.4	0.0	3.7
Lu	0.0	1.2	0.0	5.4	0.0	0.4
Hf	0.2	3.4	0.2	9.5	0.2	9.0
Ta	0.5	27.9	1.3	28.6	0.8	13.3
Hg	0.9	5.7	6.8	1.6	4.8	2.8
Tl	3.6	9.0	0.4	3.3	2.6	8.3
Pb	21555.0	4.7	1626.4	1.6	10597.9	4.1
Bi	166.2	4.2	104.5	2.0	125.9	1.1
Th	0.8	3.1	0.0	7.9	0.2	5.5
U	0.1	3.5	1.4	1.5	0.8	3.1

ICP-MS – Method 2 digestion

Method 2	N1	RSD (%)	N2	RSD (%)	N3	RSD (%)
Pt	**903.7**	**1.7**	**1983.8**	**7.0**	**1467.5**	**2.4**
Pd	**6086.6**	**2.8**	**11255.5**	**7.4**	**8821.8**	**1.8**
Rh	**157.8**	**2.5**	**315.8**	**6.5**	**242.3**	**1.8**
Ru	**69.0**	**5.6**	**252.0**	**9.5**	**145.0**	**4.9**
Os	**0.1**	**2.5**	**1.7**	**6.5**	**0.9**	**4.1**
Ir	**21.5**	**1.6**	**49.3**	**5.6**	**36.3**	**2.7**
Re	0.4	1.7	8.9	4.6	4.8	5.3
Au	516.3	2.7	339.9	6.8	460.8	1.2
Li	1.3	10.8	0.5	24.4	0.9	1.9
Be	0.0	10.5	0.0	14.7	0.0	9.0
B	0.7	31.7	217.0	6.2	124.8	9.2
Na	14957.6	10.4	8540.4	8.0	13104.4	3.4
Mg	63.7	18.3	866.6	10.3	435.3	5.2
Al	1087.5	12.1	757.2	17.9	950.9	1.4
P	82.8	43.7	19398.6	15.6	9159.1	7.1
K	111.9	20.6	677.2	9.0	367.9	2.5
Ca	2932.6	4.7	661.0	25.6	1759.7	1.9
Sc	0.2	0.7	0.3	10.6	0.3	2.2
Ti	169.7	5.2	457.1	9.3	335.2	3.5
V	1.0	19.1	16.8	12.5	11.9	5.8
Cr	63.4	3.2	3596.5	9.2	1772.8	7.0
Mn	8.4	10.7	32.4	9.7	19.1	4.2
Fe	2892.1	5.5	8881.8	11.1	5828.4	1.8
Co	779.4	4.4	1996.9	11.1	1379.5	2.9
Ni	277484.0	3.1	140974.8	10.0	218625.7	1.1
Cu	43182.6	3.3	151966.0	10.6	96331.6	5.1
Zn	138.3	3.5	12.3	45.4	76.2	3.0
Ga	0.4	4.8	31.3	9.8	15.4	5.9
As	3009.1	3.2	11775.7	9.3	7402.2	3.5
Se*	19042.2	2.9	285.1	10.9	10687.9	4.2
Rb	0.3	2.1	1.1	10.5	0.7	2.8
Sr	31.4	2.7	7.0	33.4	18.0	4.3
Y	0.4	2.2	1.0	10.7	0.7	3.0
Zr	5.6	2.0	14.9	5.4	10.8	1.6
Nb	17.2	2.9	213.8	4.4	142.0	5.3
Mo	11.2	2.7	947.5	8.9	458.6	6.4
Ag*	3537.6	13.8	4222.1	18.9	11062.6	7.3
Cd	1.0	34.7	0.5	12.5	1.0	63.1
Sn	2151.1	1.6	4896.8	6.6	3681.8	1.7
Sb	749.3	0.5	930.8	7.7	855.1	1.0
Te	10990.2	1.5	3097.5	9.8	7573.3	2.1
Cs	0.0	4.1	0.0	9.1	0.0	1.8
Ba	22.0	2.5	13.9	6.3	17.4	2.2
La	5.5	0.3	0.3	12.0	2.9	3.8

Ce	10.3	0.7	0.5	13.9	5.7	3.6
Pr	0.9	1.0	0.1	13.6	0.5	2.8
Nd	2.3	1.1	0.5	11.2	1.4	2.2
Sm	0.2	3.2	0.2	9.4	0.4	6.0
Eu	0.0	3.9	0.0	7.2	0.0	6.5
Gd	0.2	2.0	0.1	12.5	0.1	3.1
Tb	0.0	1.6	0.0	12.3	0.0	2.4
Dy	0.1	0.1	0.1	10.6	0.1	2.6
Ho	0.0	2.8	0.0	7.8	0.0	3.3
Er	0.1	1.7	0.0	6.8	0.0	3.0
Tm	0.0	0.5	0.0	8.2	0.0	4.8
Yb	0.1	3.4	0.0	9.2	0.0	2.1
Lu	0.0	3.0	0.0	9.5	0.0	2.1
Hf	0.2	2.5	1.2	8.1	0.8	2.9
Ta	5.4	17.9	9.8	25.9	9.0	18.1
Hg	1.2	3.4	8.9	10.2	5.1	6.4
Tl	4.1	6.0	0.4	6.8	2.8	5.7
Pb	21145.1	2.0	1526.6	8.5	12068.6	2.7
Bi	165.1	1.8	95.2	7.8	133.8	0.2
Th	0.9	2.0	0.1	8.1	0.4	4.1
U	0.1	3.3	1.4	6.8	0.7	5.7

APPENDIX D – Statistical evaluation RDB

METHOD VALIDATION FOR THE IDENTIFICATION AND DIFFERENTIATION OF PRECIOUS METAL CONTAINING PRODUCTS OF MINING AND METALLURGICAL OPERATIONS: CHEMICAL COMPARISON PROCEDURE

Introduction

During the meeting of members of the Forensic Review Board on 11-12 july at the Netherlands Forensic Institute (NFI) in the Hague, The Netherlands, it became clear that the theft of Precious Metal containing products (especially slime) is an international problem. In the recent past complex identification methods were developed for determinations of the nature and source of origin of these PGM-containing products. In order to gain international acceptance of these methods it is necessary that these methods are (forensically) validated under the guidance of ENSFI (Memo, 20 July, 2006).

The complex identification procedure (CIP) for precious metal containing products is described in a report of the Mining and Metallurgical Company "Norilsk Nickel", Institute of Criminalistics of the Russian Security Service and the State Research Institute for Rare Metals titled: ***Complex Analytical Procedure for the identification of the Nature and the Source of Origin of Precious Metal Containing Products of Mining and Metallurgical Operations (Moscow, 2005).***

A schematic overview of the procedure is shown in Figure 1. Essentially the procedure consists of two basic parts: one is the detailed 5-stage analytical procedure for the substance to be assessed, the second is the comparison of the results of that analysis with the Reference Data Base (RDB). The RDB contains the results of about 60 known precious metal containing products obtained with the same analytical procedures.

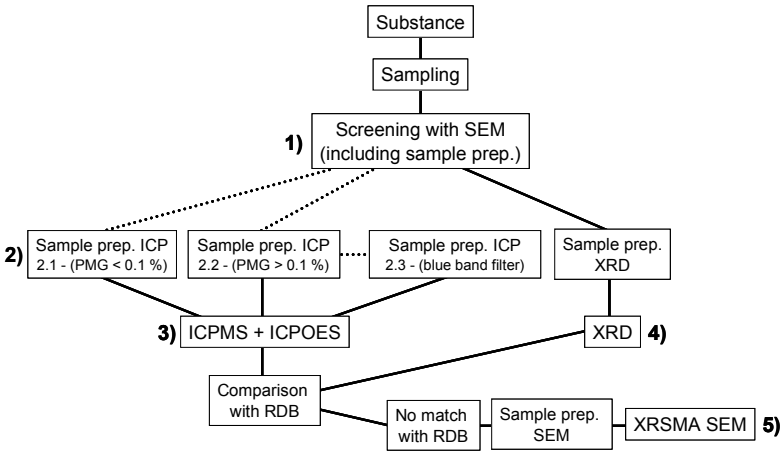


Figure 1 Schematic representation of the Complex Identification Procedure, showing the 5 consecutive analytical stages and the comparison with the Reference Data Base (RDB)

For the CIP to be valid the overall measurement uncertainty (MU) of the analytical procedure must be fit-for-purpose. This is not only determined by the performance characteristics of the analytical procedure, but also by the given differentiation in the chemical and mineralogical characteristics of the (currently 61) different products within the RDB. The analytical performance has been described previously, here we focus on the fitness of discrimination and comparison procedures for the chemical data (ICPMS and ICPOES) of the RDB. The question to be answered here is if the analytical procedure in the CIP allows unambiguous identification of a test-specimen to one of the products in the RDB.

Database partitioning

The RDB currently contains 27 chemical attributes (elemental concentrations) for in total 173 observations on 61 products. Multiple observations are not available for all products, which means that for these products no statistical uncertainty in their chemical characterization can be defined. Also, the similarity or dissimilarity of a test-specimen to these known products cannot be statistically ascertained. In order to have a robust comparison procedure, the RDB needs to be partitioned into groups of similar observations to which test-specimen can be compared.

Partitioning within a set of specimen can either be based on externally determined fixed threshold values for the attributes measured, or on a clustering of the available data. The first approach, that may be based on theoretical considerations, is robust, universally valid, and unambiguous. In practice, however, the threshold values chosen are often arbitrary and unnatural, with similar specimen falling in different groups and dissimilar specimen falling within the same group. Moreover, with more than three attributes the procedure becomes cumbersome. Either a strict hierarchy among single attribute thresholds, or a set of complex multivariate functions must be defined. Advantages of a data driven clustering approach are that coherent groups are recognized and maintained, and that there is no practical limit to the number of variables. Disadvantages are an inherent instability, as added observations may influence the grouping, and a less straightforward allocation of test-specimen.

Here we applied fuzzy *c*-means clustering (FCM) to partition the RDB, and to allocate the three test-specimen that were sent to TNO Built Environment and Geosiences, NFI, SKL and BKA for the current CIP validation. Based on their multivariate distance in attribute space, FCM groups specimen/observations of similar composition together. It thereby focusses on relevant variations in the density pattern of the multivariate datacloud, rather than on statistical significance alone. This makes the method robust to future changes (improvements) in analytical quality. The fuzzy nature of the method allows the distinction between specimen that are truly typical of a group and those that are less similar, as well as the recognition of samples of mixed character. This is especially useful for the allocation of test-specimen,

which could be mixtures of products. The similarity is expressed as a membership value ranging from 0, no similarity, to 1, identical to the cluster centre. The sum of the memberships of one data point to all clusters sums up to one.

The Fuzzy *c*-means algorithm (Table 1) was developed by Zadeh (1965), and first described for application in geosciences by Bezdek et al. (1984). Setting up the cluster model is an iterative procedure; once the cluster centra have been identified for a training set (here the RDB), additional samples can be allocated to the fuzzy clusters using the same algorithm. The optimal number of clusters can be determined using statistical criteria (F and H, see table 2; or scaled versions thereof), in combination with prior knowledge, and visual inspection of the clustering results in a non-linear, distance-congruent, 2-D representation of the data cloud (Sammon, 1970).

Table 1. Algorithms used in fuzzy *c*-means cluster analysis

In the case of C clusters for N cases analyzed for V variables (x) and a fuzzy exponent q then the cluster center (CC) of the ith cluster for the jth variable is:

$$CC_{ij} = \frac{\sum_{k=1}^{N} (u_{ki})^q * x_{kj}}{\sum_{k=1}^{N} (u_{ki})^q}$$

and the membership (u) for the kth case to the ith cluster:

$$u_{ki} = \frac{[(d_{ki})^2]^{-1/(q-1)}}{\sum_{i'=1}^{C} [(d_{ki'})^2]^{-1/(q-1)}}$$

where the standardized distance (d) of the kth case to the ith cluster (with s_j as the standard deviation of the jth variable) is given by:

$$(d_{ki})^2 = \sum_{j=1}^{V} [(x_{kj} - CC_{ij})/s_j]^2$$

Table 2. Classification entropy *H* and partition coefficient *F* functions and their limiting values

$H = -\sum_{k=1}^{N} \sum_{i=1}^{C} [u_{ki} * \log (u_{ki})/N]$	$0 \le H \le \log (C)$
$F = \sum_{k=1}^{N} \sum_{i=1}^{C} [(u_{ki})^2/N]$	$1/C \le F \le 1$

Results

Results of the FCM show an optimum of four clusters (Figure 2), which apparently represents the overall pattern in the RDB. A local suboptimum is found for 15 clusters, which seems more appropriate for the present purposes. Ideally, each product in the RDB would be reflected in an equivalent cluster centre, for now we will make a first appraisal how well de products are classified into 15 clusters.

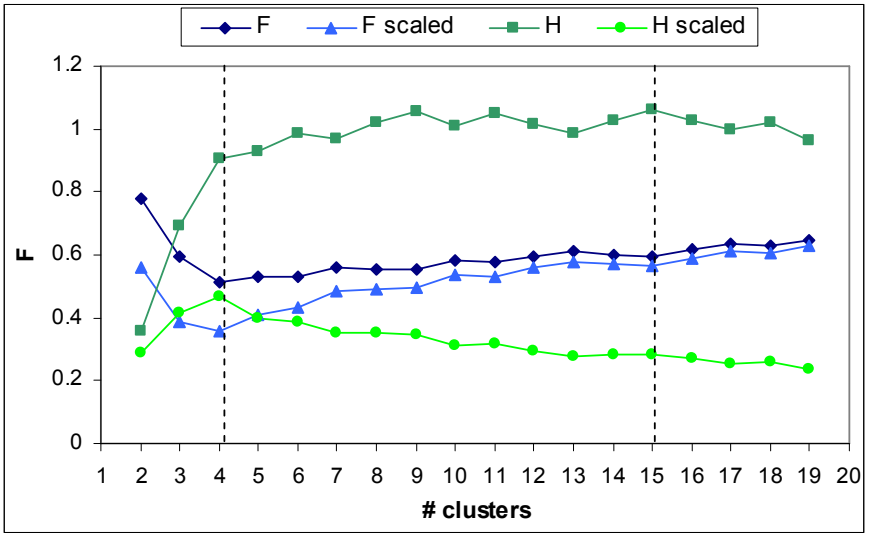


Figure 2 Clustering statistics F and H as a function of the number of clusters

Table 3 shows the clustering results for 4 and 15 clusters for the first 14 products in the RDB, while Table 4 summarizes the grouping of the RDB products to the clusters, as well as the allocation of the three test-specimen. Figures 3a and 3b show the 2-D non-linear configuration of the data clusters.

Table 3. Clustering results (membership values) for 4 and 15 clusters for the first 14 products in the RDB. Memberships less than 1/c, with c the number of clusters, are not shown.

	4 clusters					15 clusters														
	C1	C2	C3	C4		A	B	C	D	E	F	G	H	J	K	L	M	N	P	Q
K01-1			0.27	0.70														0.71		0.12
K02-1			0.30	0.67														0.79		0.08
K03-1				0.89																1.00
K04-1			0.58												0.07			0.64		
K05-01				0.86											0.08				0.11	0.62
K06-1				0.83																0.99
K07-1				0.85																1.00
K08-1				0.86																1.00
K09-1				0.83																0.99
K10-1				0.83																0.98
K11-1		0.35	0.41														0.86			
K11-2			0.64														0.98			
K11-3			0.63												0.10		0.74			
K11-4			0.71												0.07		0.86			
K12-1		0.32	0.44														0.85			
K12-2		0.34	0.46														0.91			
K12-3		0.28	0.51														0.96			
K12-4			0.60														0.97			
K13-1			0.58	0.38										0.07	0.22		0.20	0.34		
K14-1		0.33	0.26							0.09	0.08		0.09	0.09	0.07		0.10		0.07	

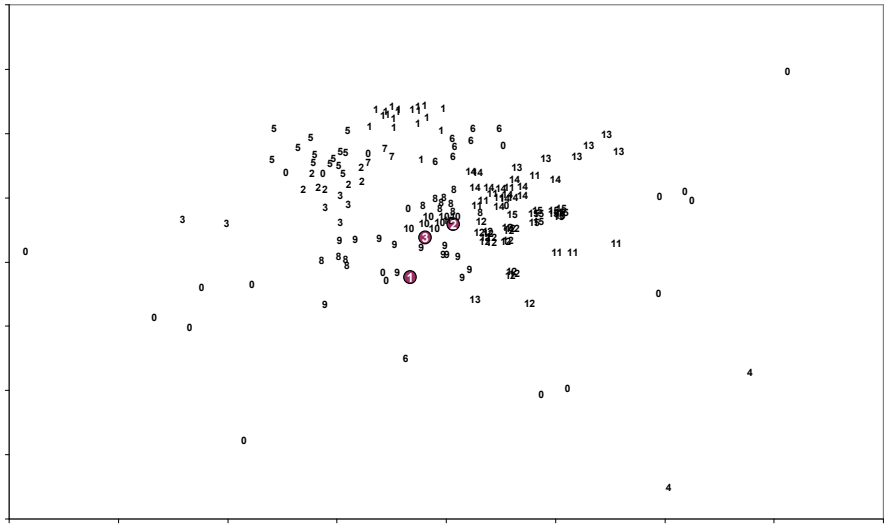
Table 4 Clustering results for 4 and 15 clusters. X: membership allocation to cluster is consistenlyt high for all n analyses, x: membership allocation is low or varied, o: membership allocation is very low but, in case of n>1, consistent.

		4 clusters				15 clusters														
	n	C1	C2	C3	C4	A	B	C	D	E	F	G	H	J	K	L	M	N	P	Q
N20	8	X				X														
N35	4	X				X														
N37	4	X				X														
N39	4	X				X														
N21	8	X					x	x	o											
N25	6	X					x	X												
N28	1	X					X													
N36	4	X					X		x											
K19	4		X							X										
K29	1		X							X										
K20	4		X								X									
K22	4		X							x	X									
N31	1		x	x							x									
K27	1		x																	
N32	1		x																	
K14	1		x	x																
K16	4		x	x												x				
K23	4		x	x																
K24	3		x	x											o					
K25	3		x	x												o				
K26	1		x	x												o				
K13	1			X											o		o	x		
K21	3			x	x															
N06	1		x	x	x															
N10	1		x	x	x															
N30	2		x	x	x															
N33	1		x	x	x										o					
N11	1		x	x								X								
N26	1		x	x								X								
N22	7		x	x	o								X							
N03	1			x	x									x						
N04	1		x	x	x									x						
N05	1		x	x	x									x						
N23	7			o	x									X	o					o
K18	3			X											X					
N38	4			X											X					
K28	1			x											X					
N34	1			x											X					
N19	7			X												X				
K11	4			X													X			
K12	4			X													X			
K04	1			X														X		
N14	2			X														X		
N18	7			X														X		
K15	1			x														X		
N13	2			x	x													X		
K01	1				X													X		
K02	1				X													X		
N12	2				X													X		
N24	7				X														X	o
N27	7				X									o					X	
K03	1				X															X
K05	1				X															X
K06	1				X															X
K07	1				X															X
K08	1				X															X
K09	1				X															X
K10	1				X															X
N15	2				X															X
N16	2				X															X
N17	3				X															X
TN01	1															x				
TN02	1			X													X			
TN03	1			X												x				

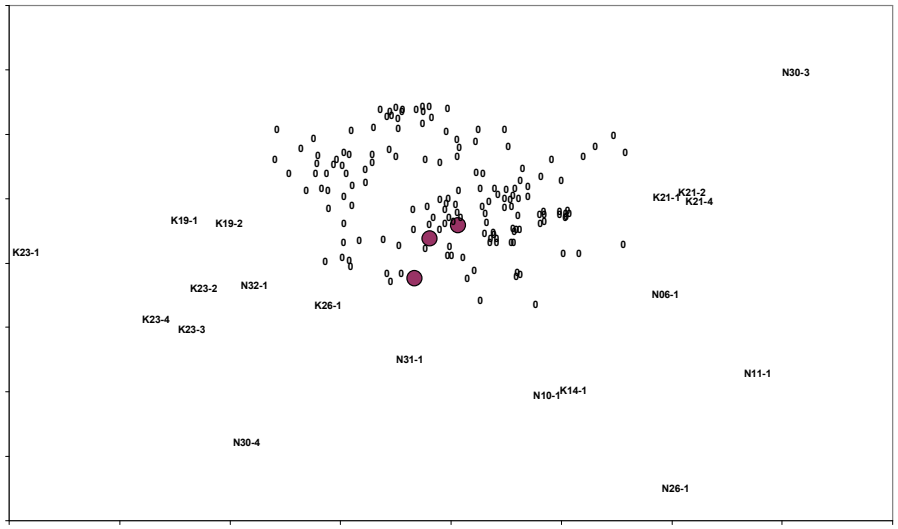
Most of the products are clearly allocated to one cluster. With 15 clusters, only products N19 and N22 are (almost) uniquely allocated to their own cluster. These are both products for which 7 individual analyses are present within the database. Products K16, K25, and K26 show a weak association to the N19-cluster as well. Products N24 and N27 are combined into one cluster (P), but show consistent low memberships to different secondary clusters, indicating that these products might be separable with a higher number of clusters. The third block in Table 3 lists a number of products that are not clearly allocated to one or two clusters. This group includes both products with relatively extreme, but in case of n>1 rather varying, composition (K14, K21, K23, N06, N10, N30, N31, N32), but also products of more intermediate composition (K13, K16, K24, K25, K26, K27, N33).

The differentiation into 15 clusters is insufficient for an unambiguous allocation of the test-specimen, but clearly narrows the focus for the next

analytical stages of the procedure. Test-specimen 1 (product K16) is allocated with a low membership to cluster L that contains product N19 with a high membership, K16 with a low membership, and products K25 and K26 with a very low membership. Specimen 2 (product K11) is allocated to cluster M containing the products K11 and K12. The third specimen, which is a mixture of the two, is also allocated to cluster L.



3a



3b

Figure 3 2-D non-linear representations of the RDB data

a) Differentiation of the 15 clusters and position of the three test-specimen (red dots), 1=A, 5=B, 2=C, 7=D, 3=E, 6=F, 4=G, 13=H, 11=J, 8=K, 9=L, 10=M, 12=N, 14=P, 15=Q; the zero cluster represents observations that are not allocated predominantly to one cluster

b) Identification of products with relatively extreme compositions

Conclusions and recommendations

- The first three stages of the analytical procedure are of sufficient accuracy and precision to narrow down the provenance of the test-specimen to groups of a few products, which can be further assessed in analytical stages 4 and 5.
- Based on the present chemical RDB, products cannot be uniquely separated from each other. With 15 clusters, groups of up to 10 products, but generally about 4 products, are discerned.
- The present RDB probably already allows differentiation into more than 15 clusters, which will lower the average number of products within a group, while still allowing adequate allocation of test-specimen.
- By adding additional analyses of all products to the RDB, separation will be improved, although overlap in compositional signature is still to be expected for some products.
- With additional analyses available for all products, each product can ideally be assigned to its own cluster. In that case a Discriminant Function Analyses (DFA) can be used to test the statistical significance of the separation.
- One advantage of the FCM approach is that focus is on the relevance of the compositional differences (cluster centres), rather than just on statistical significance of threshold boundaries that may change with advances in analytical techniques.
- A second major advantage of FCM is in the fuzzy allocation of test specimen, which are allowed to be only partly similar to a cluster or intermediate between two or more clusters.

References

C.J. Bezdek, R. Ehrlich and W. Full, (1984) FCM: the fuzzy *c*-means clustering algorithm, *Comput. Geosci.* **10**:191–203.

Sammon, J. W. (1970) An optimal discriminant plane. *IEEE Trans. Comput.* **C13**:826-829.

L.A. Zadeh, (1965) Fuzzy sets, *Int. Control* **8**:338–353.

Appendix E – BKA Statistical evaluation of RDB

Bundeskriminalamt

CIP: Statistical evaluation of RDB

v2.0

S. Becker
Bundeskriminalamt
Forensic Science Institute
Germany

April 2007

Bundeskriminalamt

CIP:
Statistical evaluation of RDB

1.) RDB data set:

a) Complete set of 67 materials : K1-K29 = 29

N1-N39 without N29 = 38

= 67

b) Products defined by NN as at risk products:

K11/K12/K16/K18-K25 = 11

N12-N25 N27/N28, N30, N35-N39 = 22

= 33

CIP:
Statistical evaluation of RDB

Aim:

Differentiation of all 33 NorilskNickel (NN) at risk products.

CIP:
Statistical evaluation of RDB

Evaluation of X-Ray diffractograms

For the evaluation of the X-Ray diffractograms only a small number of diffractograms per product could be taken into account – only up to three X-Ray diffractograms per product are listed in the material data sheet.

CIP:
Statistical evaluation of RDB

Statistical evaluation of elemental concentrations:

All 33 NorilskNickel (NN) at risk products were taken into account. The number of independent analyses per product varied throughout the dataset (n = 2 up to n = 8). In total 145 analyses were taken into account.

Due to the partially small number of independent analyses per product the chemometric results should be treated with extreme caution.

Differentiation of NN at risk products

Descriptive statistics

Multivariate statistics

Cluster analysis, PCA, (discriminant analysis /LDA)

Differentiation of NN at risk products

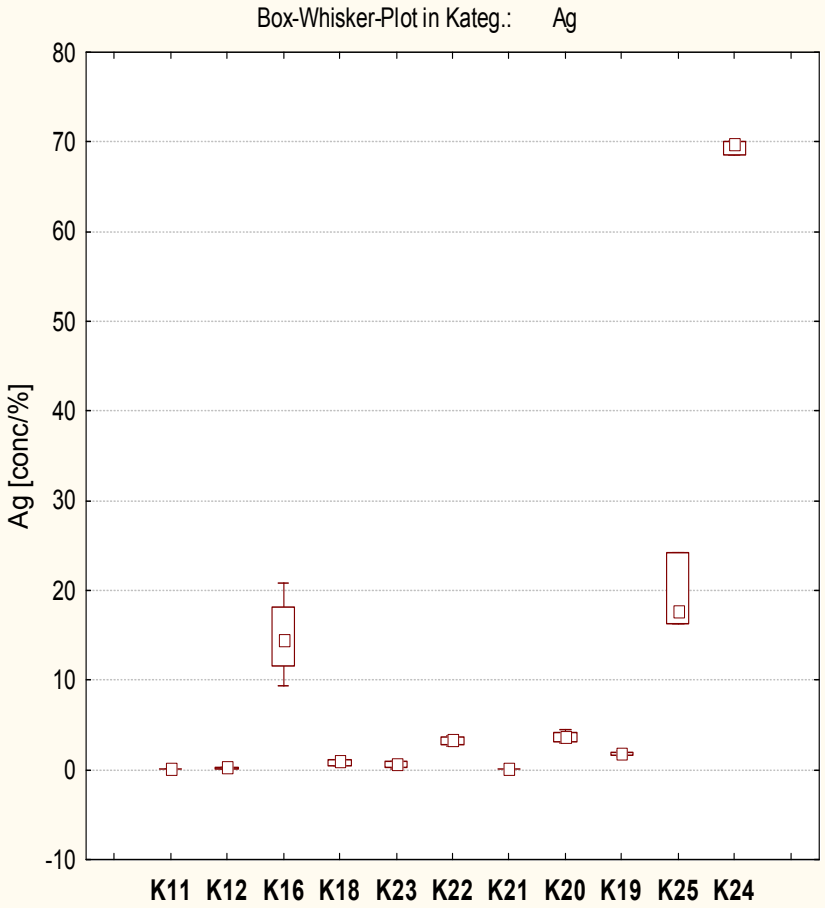
Step 1:

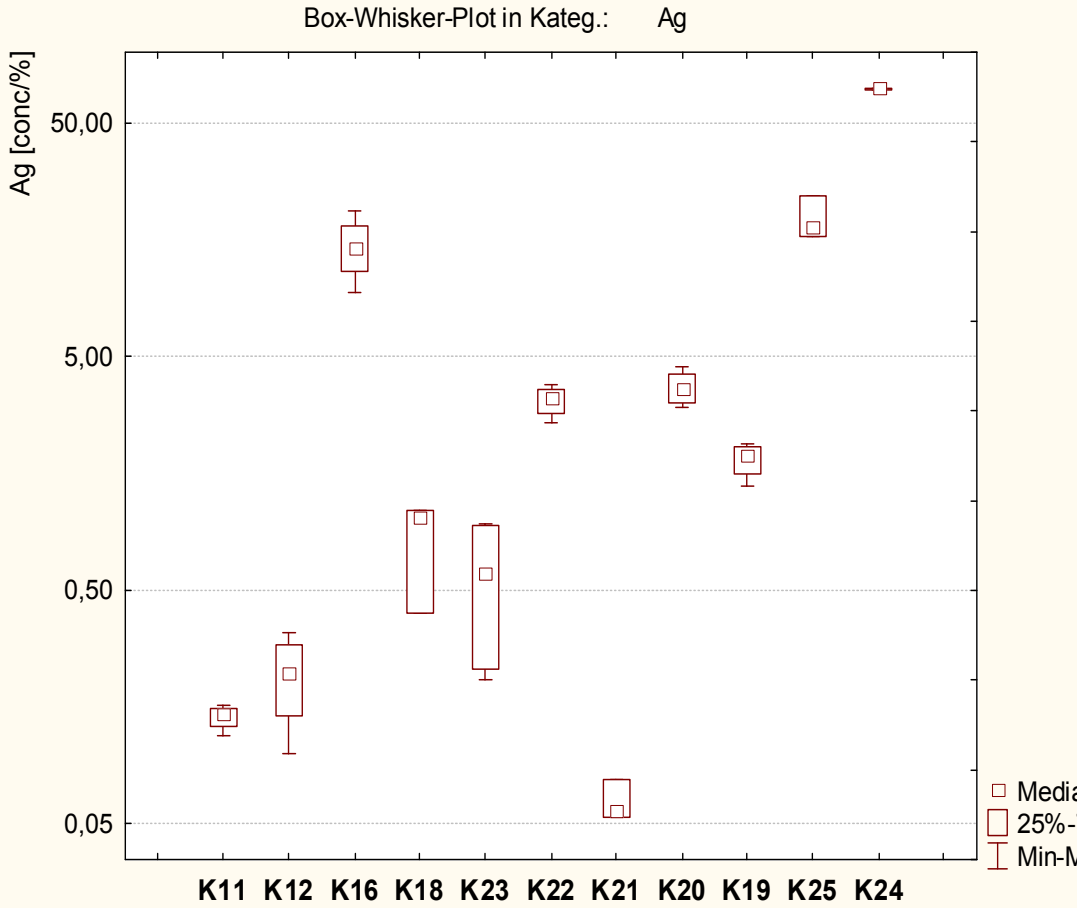
Descriptive statistics

Bundeskriminalamt

Differentiation of NN at risk products

Descriptive statistics Ag; K-series

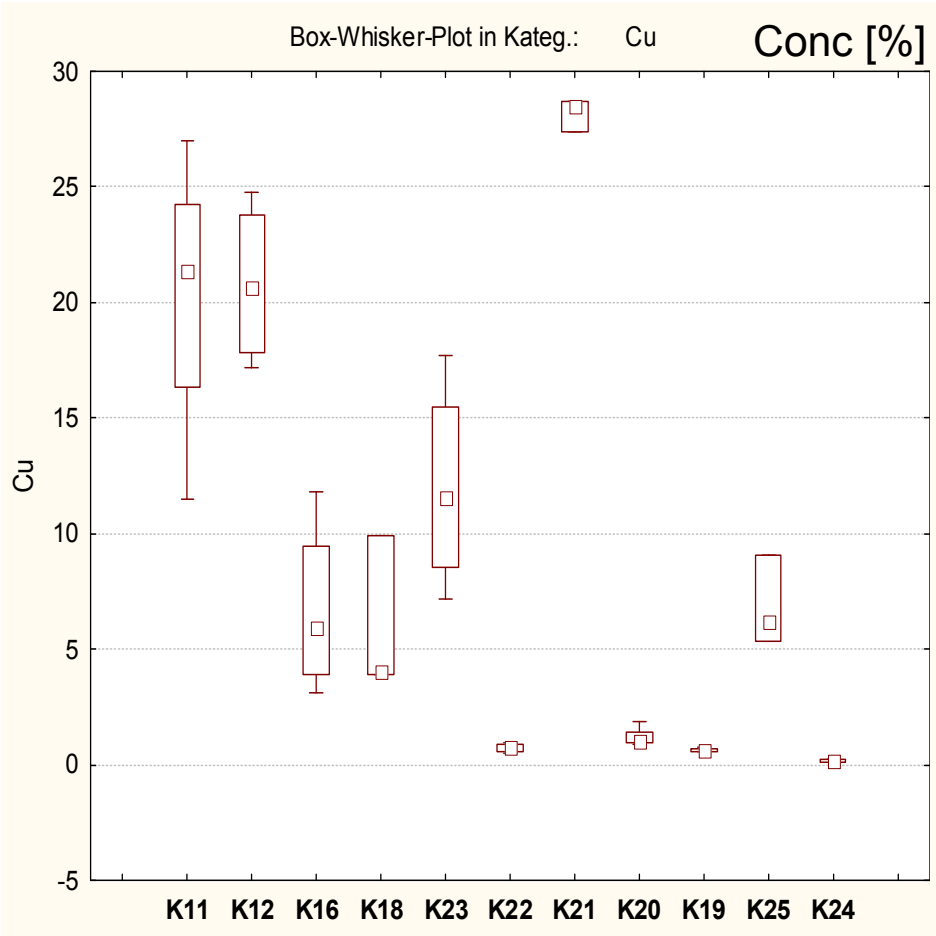


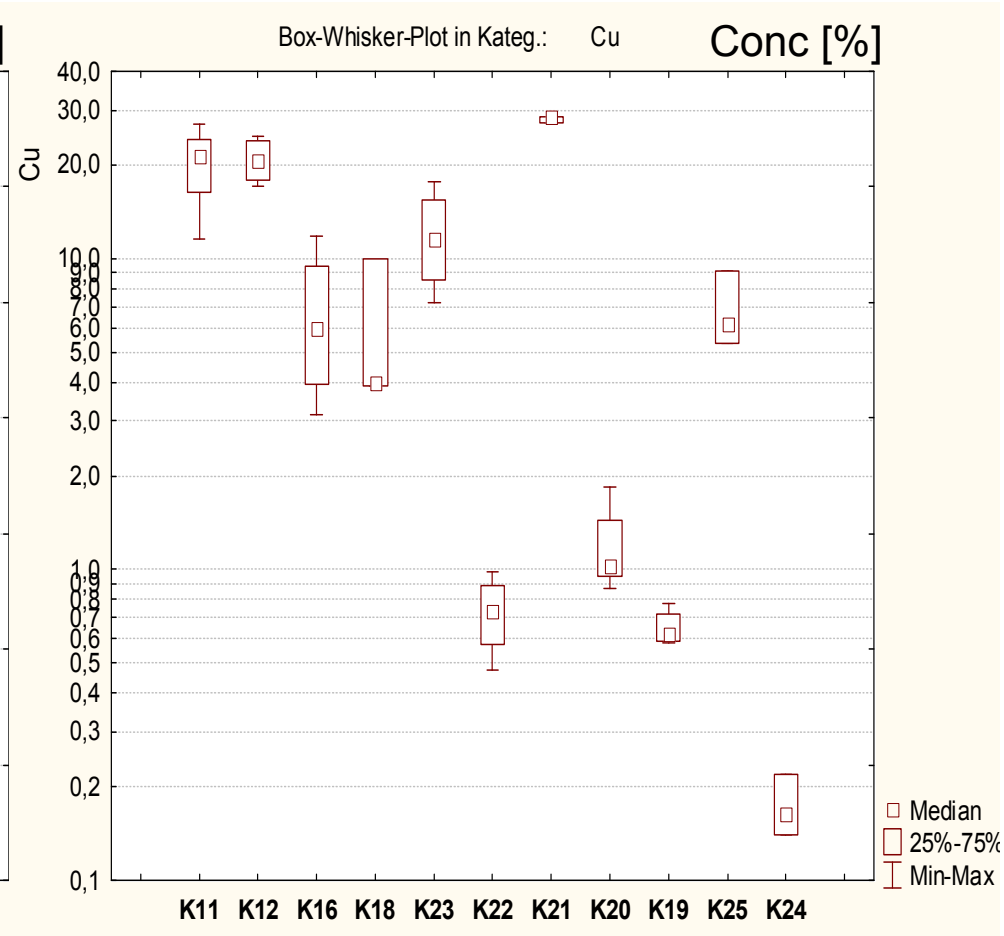


Bundeskriminalamt

Differentiation of NN at risk products

Descriptive statistics Cu; K-series

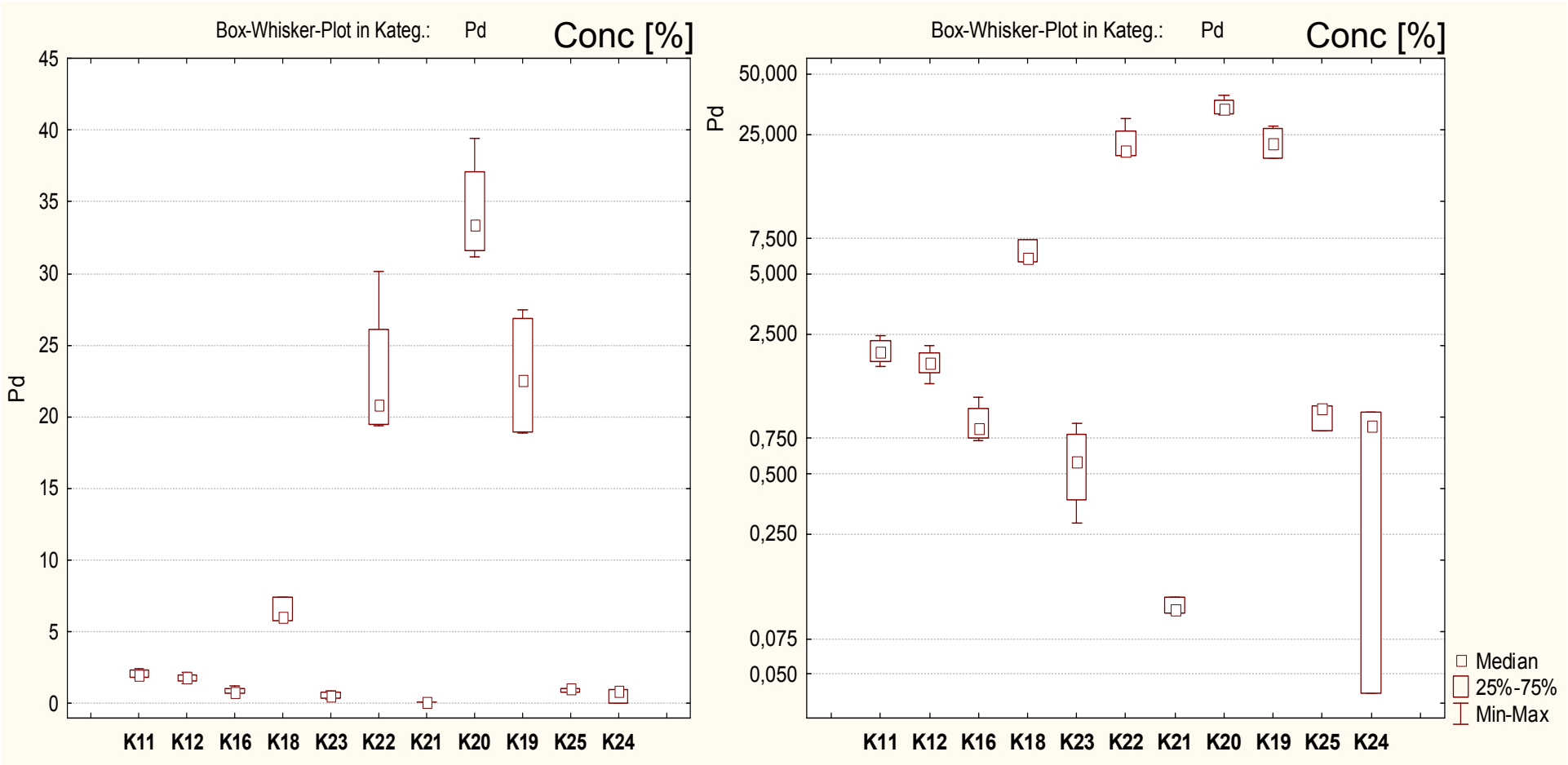




Bundeskriminalamt

Differentiation of NN at risk products

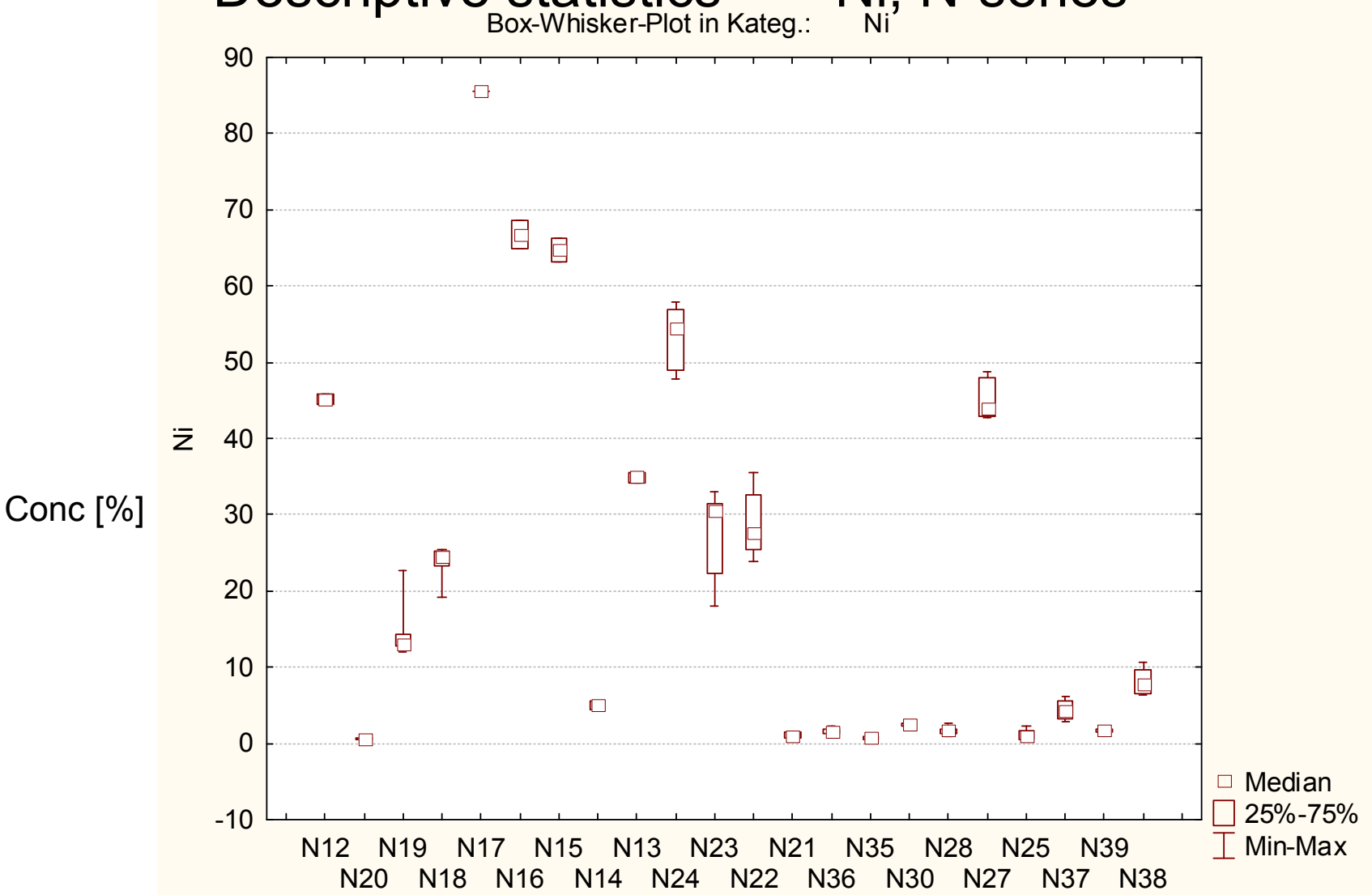
Descriptive statistics Pd; K-series



Bundeskriminalamt

Differentiation of NN at risk products

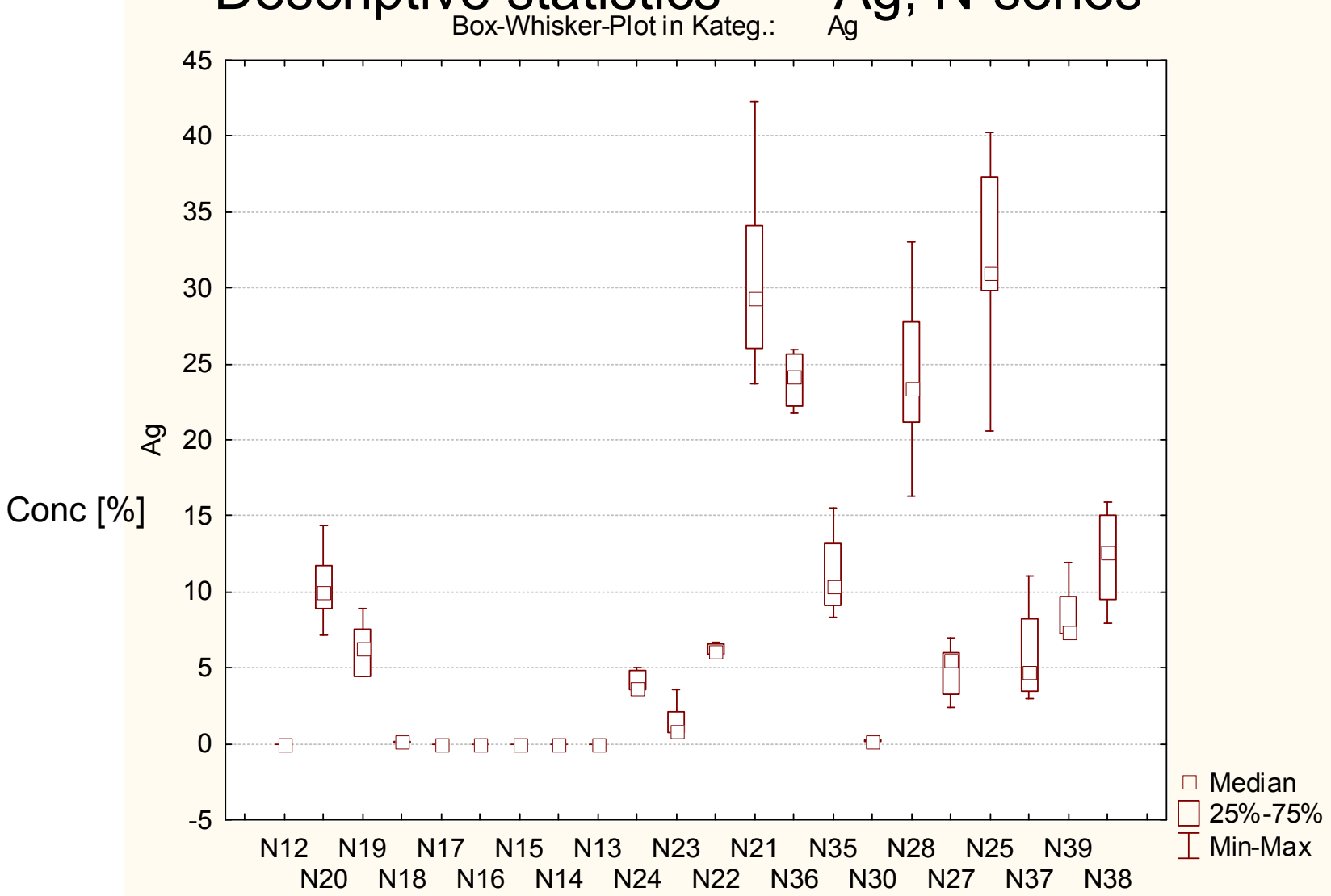
Descriptive statistics Ni; N-series



Bundeskriminalamt

Differentiation of NN at risk products

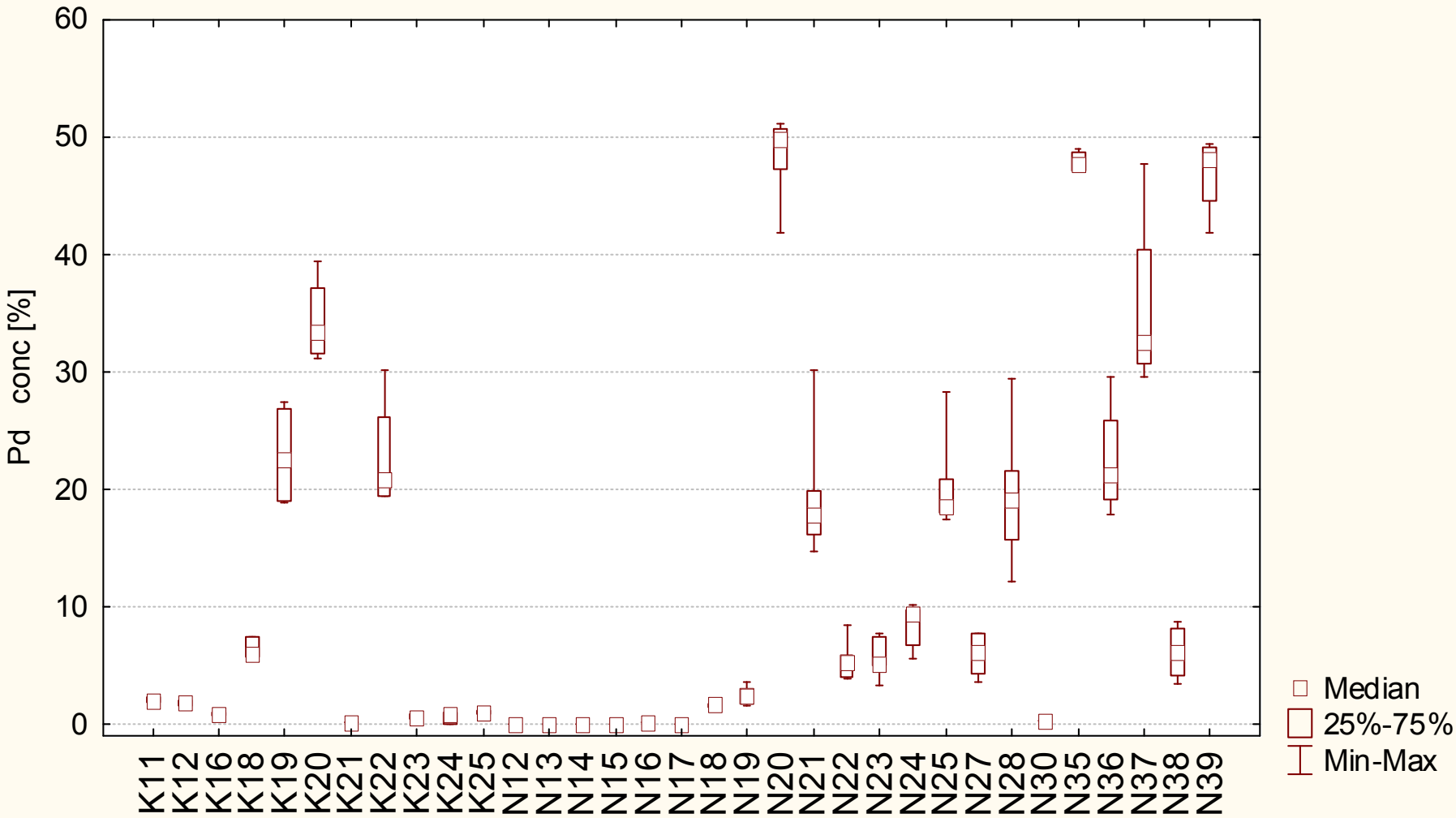
Descriptive statistics Ag; N-series



Bundeskriminalamt

Differentiation of NN at risk products

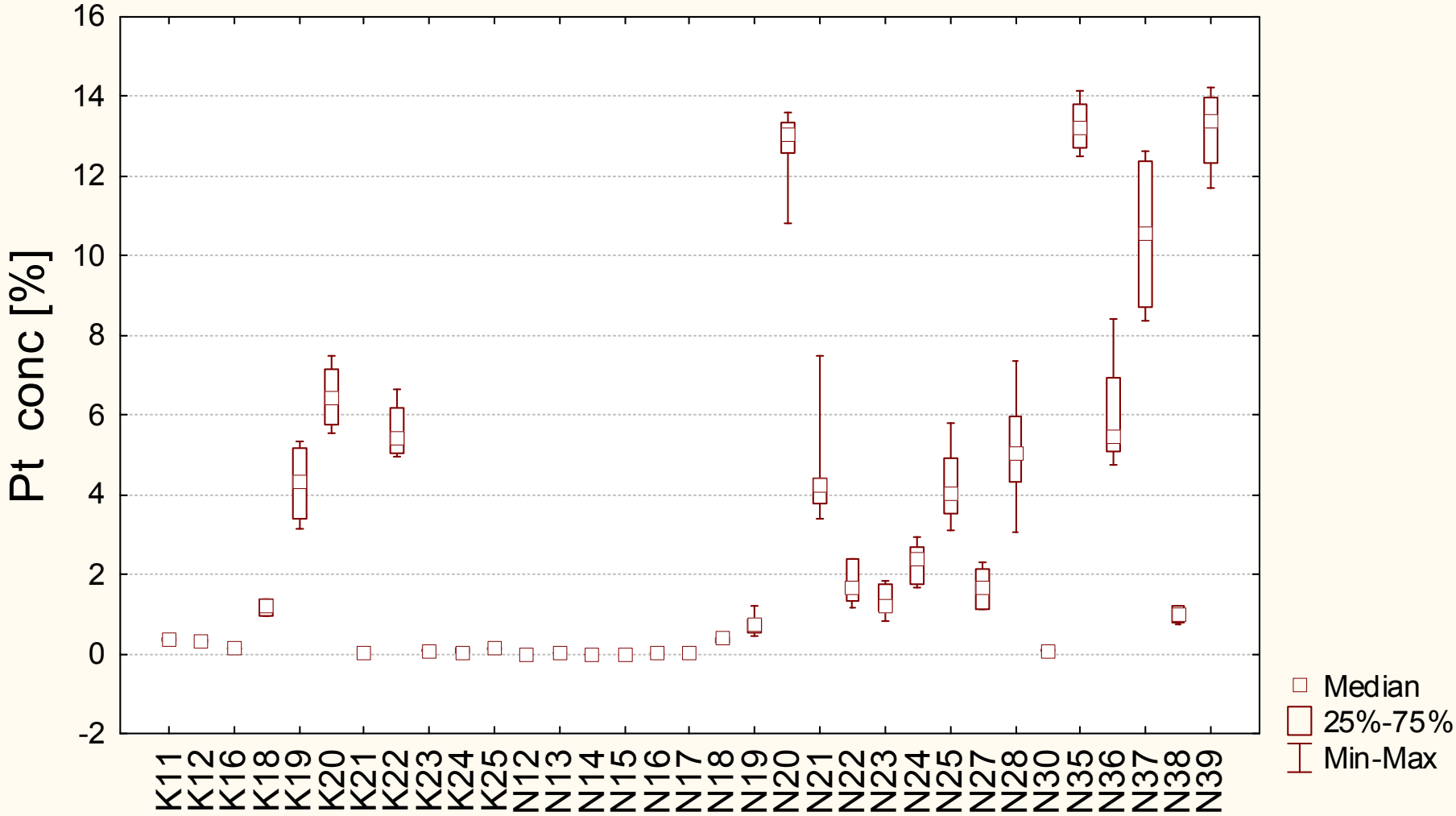
Descriptive statistics Pd; N & K-series



Bundeskriminalamt

Differentiation of NN at risk products

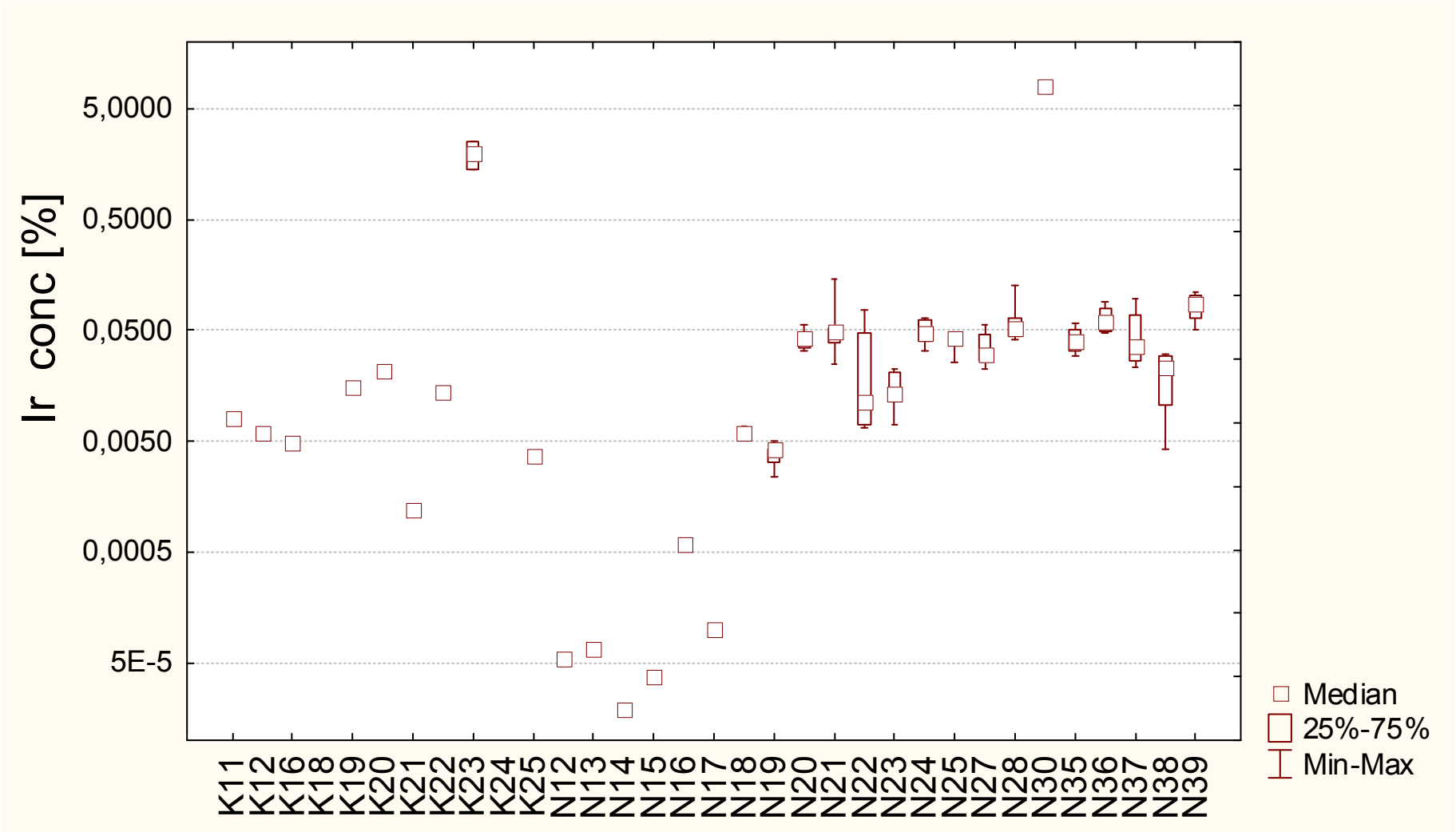
Descriptive statistics Pt; N & K-series



Bundeskriminalamt

Differentiation of NN at risk products

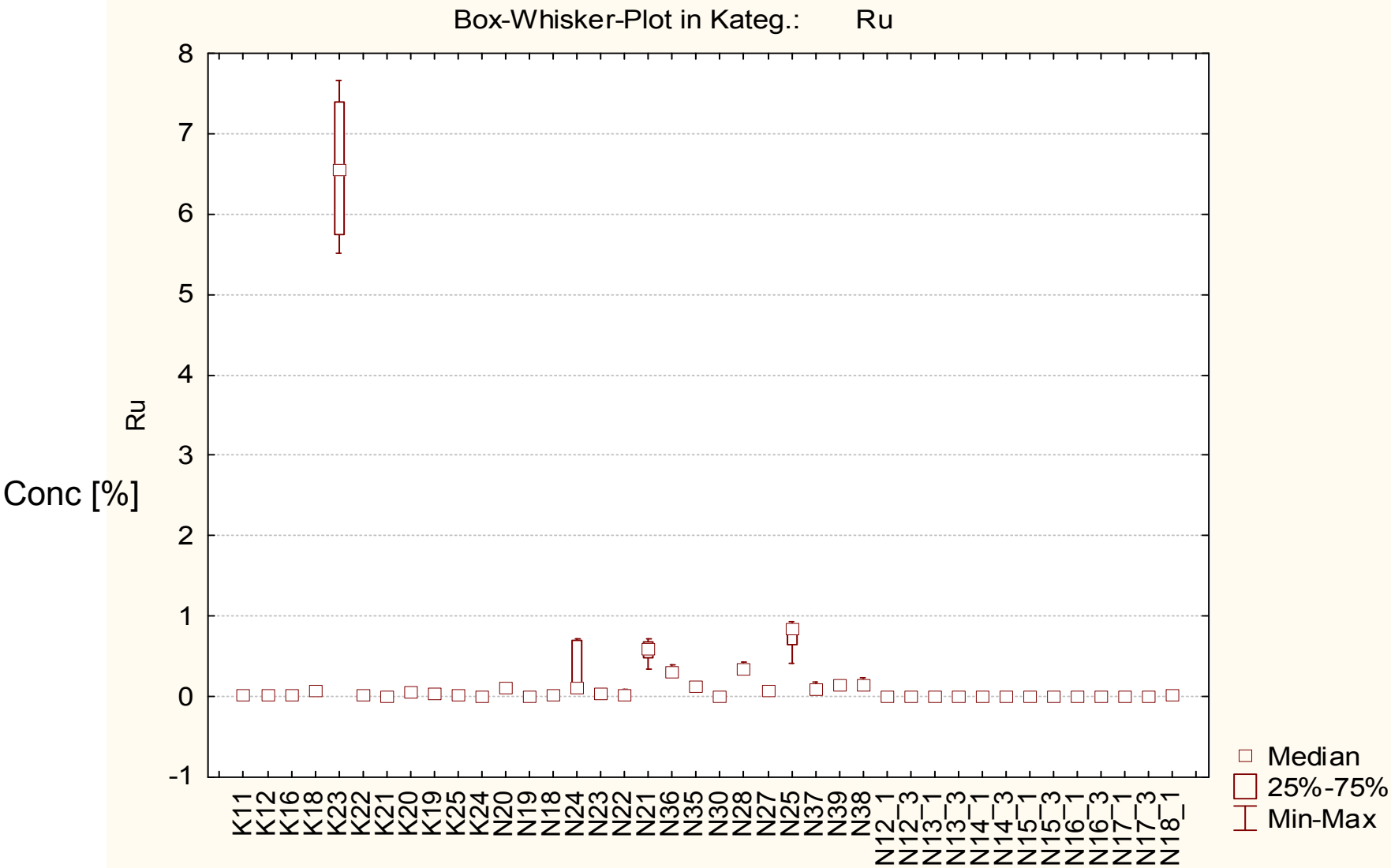
Descriptive statistics Ir; K & N-series



Bundeskriminalamt

Differentiation of NN at risk products

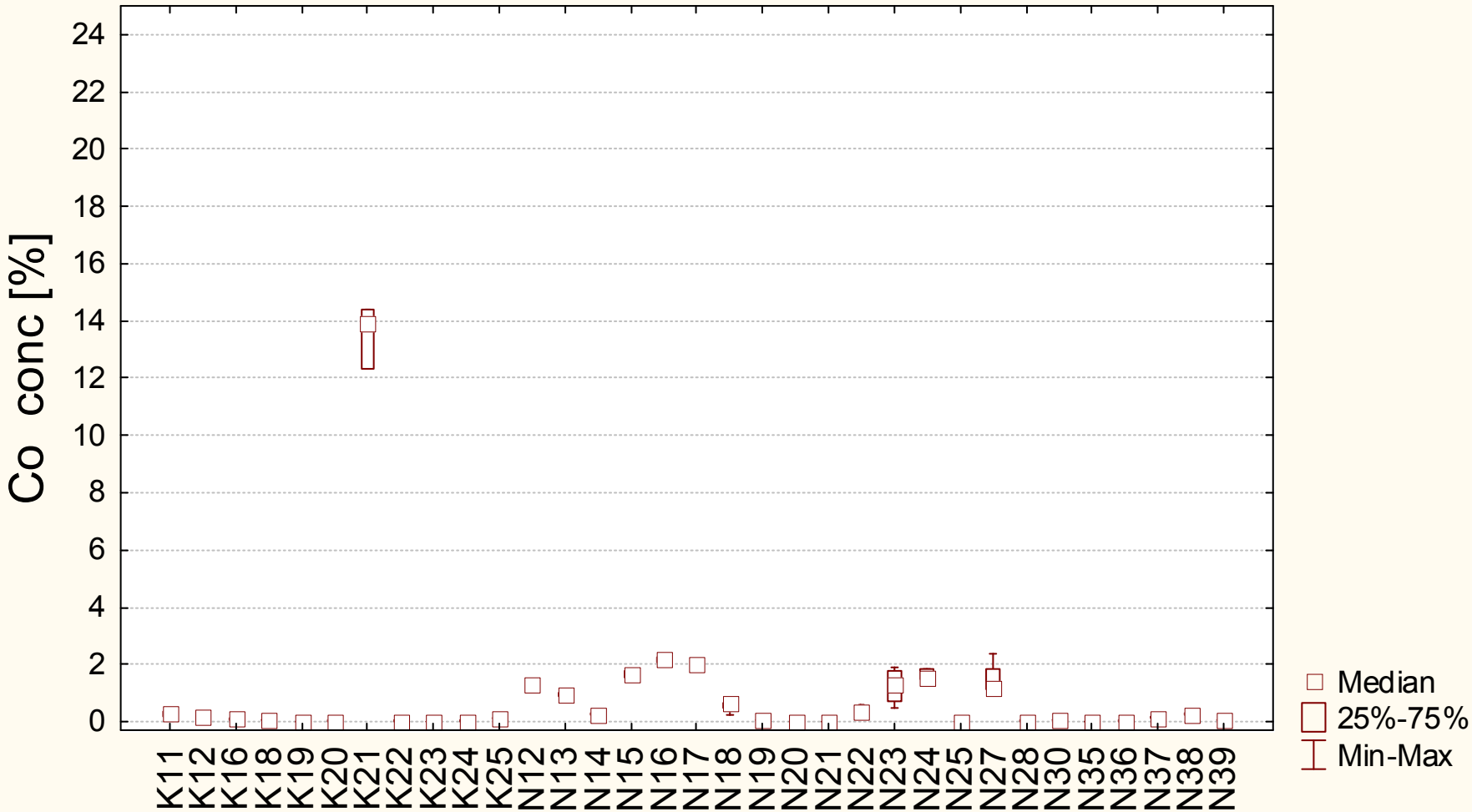
Descriptive statistics Ru; K & N-series



Bundeskriminalamt

Differentiation of NN at risk products

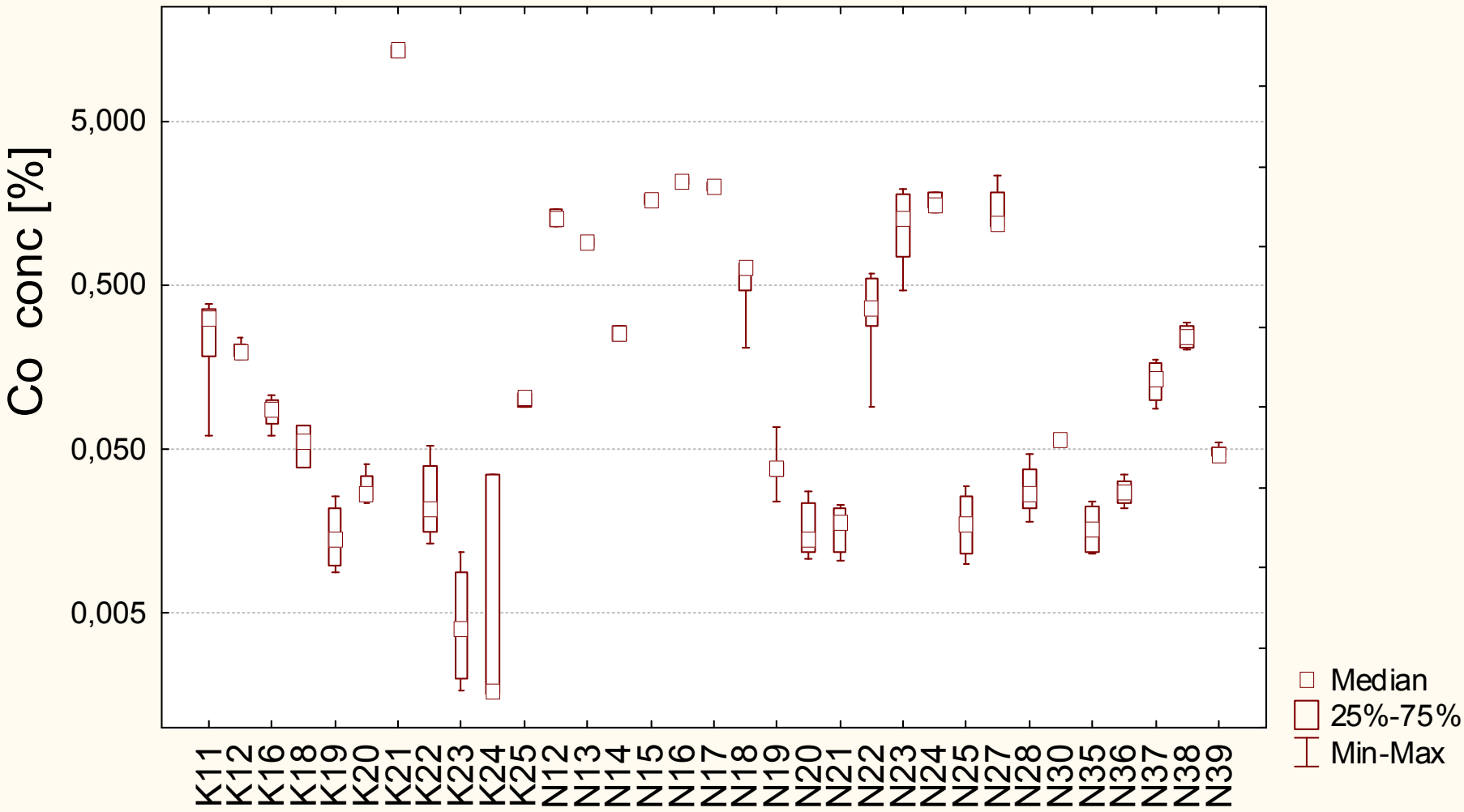
Descriptive statistics Co; K & N-series



Bundeskriminalamt

Differentiation of NN at risk products

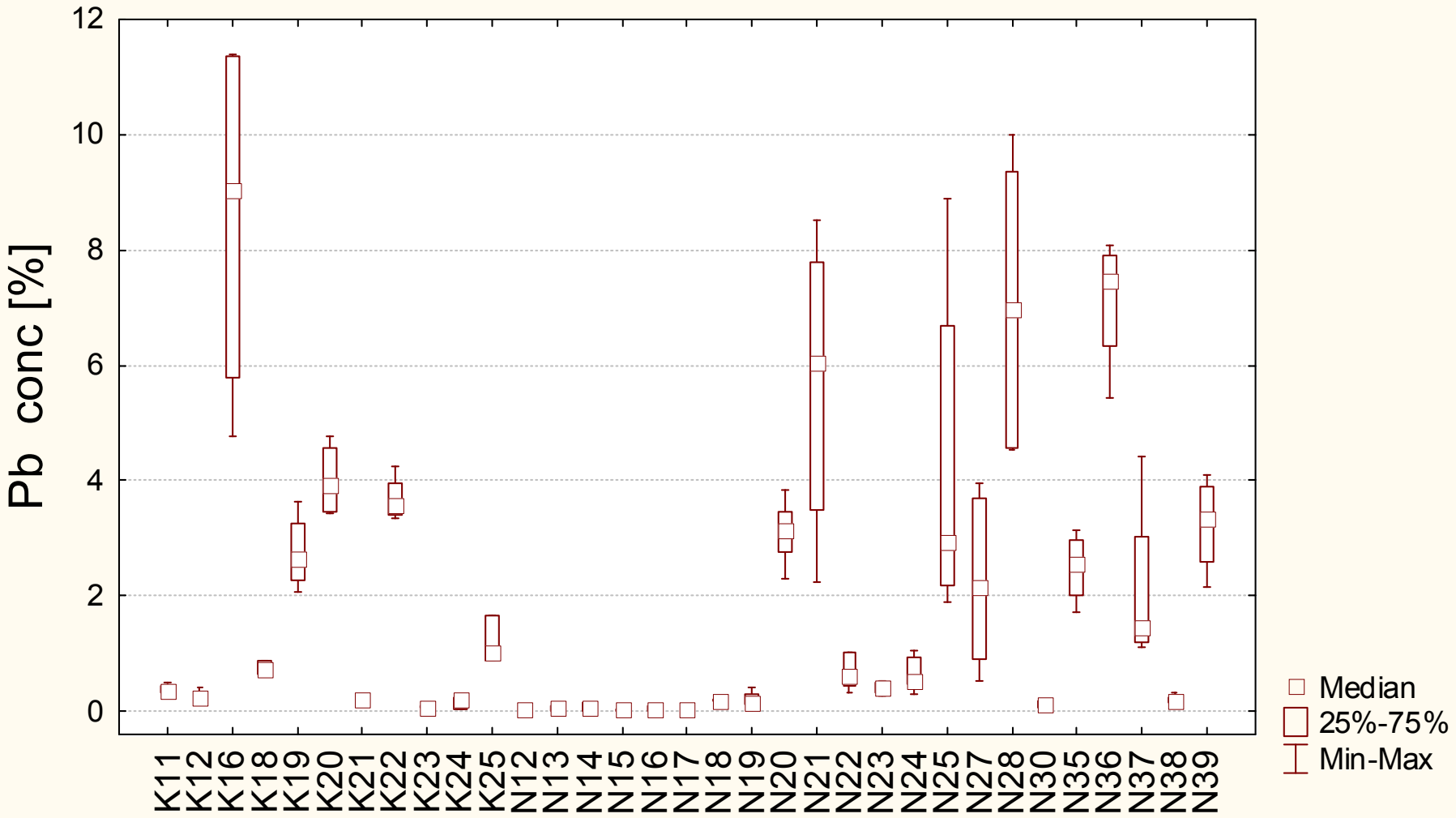
Descriptive statistics Co; K & N-series



Bundeskriminalamt

Differentiation of NN at risk products

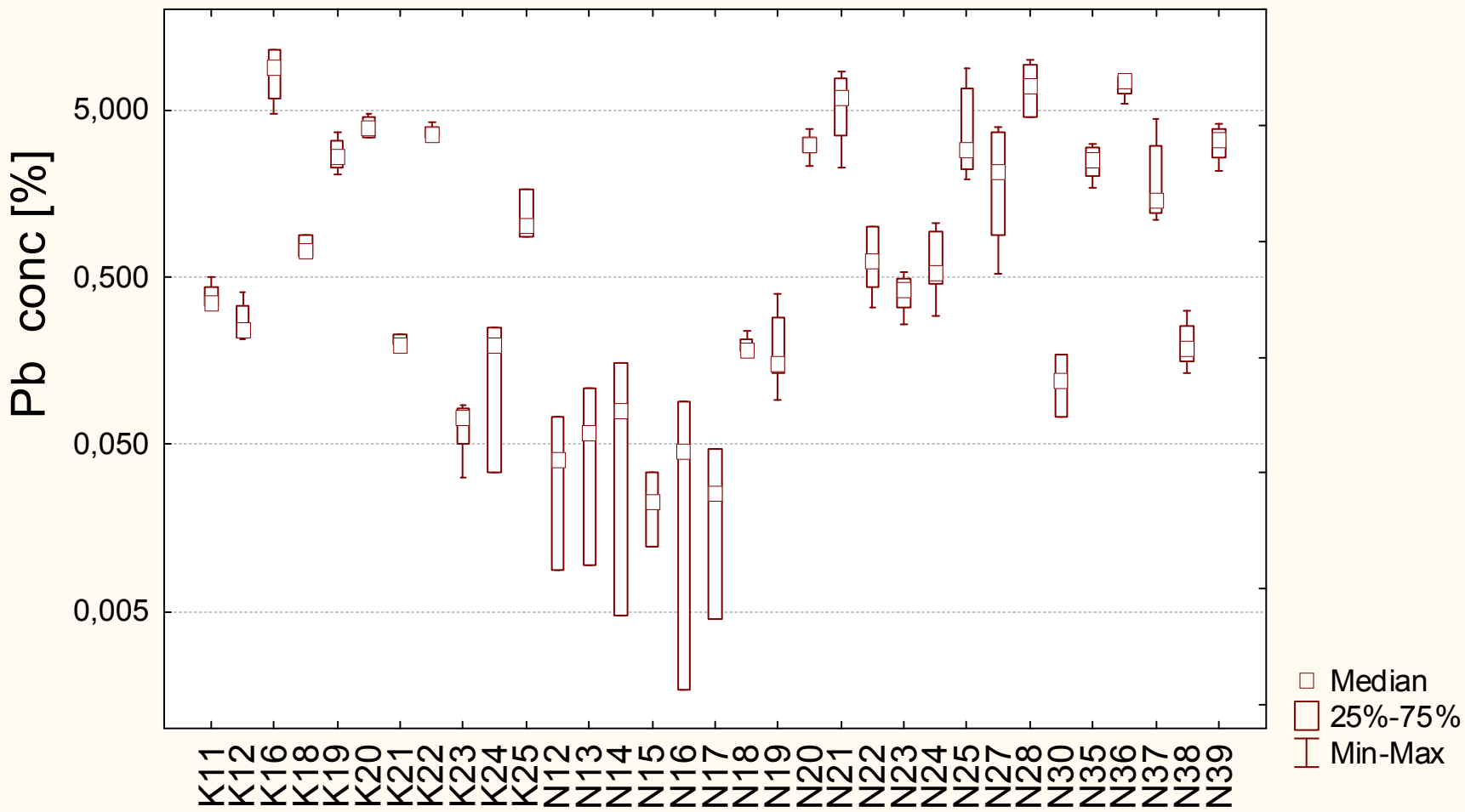
Descriptive statistics Pb; K & N-series



Bundeskriminalamt

Differentiation of NN at risk products

Descriptive statistics Co; K & N-series



Differentiation of NN at risk products

Step 2:

Multivariate statistics

Differentiation of NN at risk products

Multivariate statistics

Cluster analysis:

- Software used for calculation: Statistica v7.1 (Stat Soft Inc.)
- Data treatment: Before calculation all data fields with values below detection limit (such as < 0,001) were replaced by a value of zero.
- All calculations for cluster analysis applying Euclidian distance and single linkage.

Differentiation of NN at risk products

Cluster analysis

Varied parameters:

1.) Number of elemental concentrations:

all elements: 27 elements; Ir and W were omitted due to incomplete data

or

only 9 elements

Ni, Cu, Au, Ag, Pd, Pt, Rh, Ru, Pb

2.) Not normalised and normalised data.

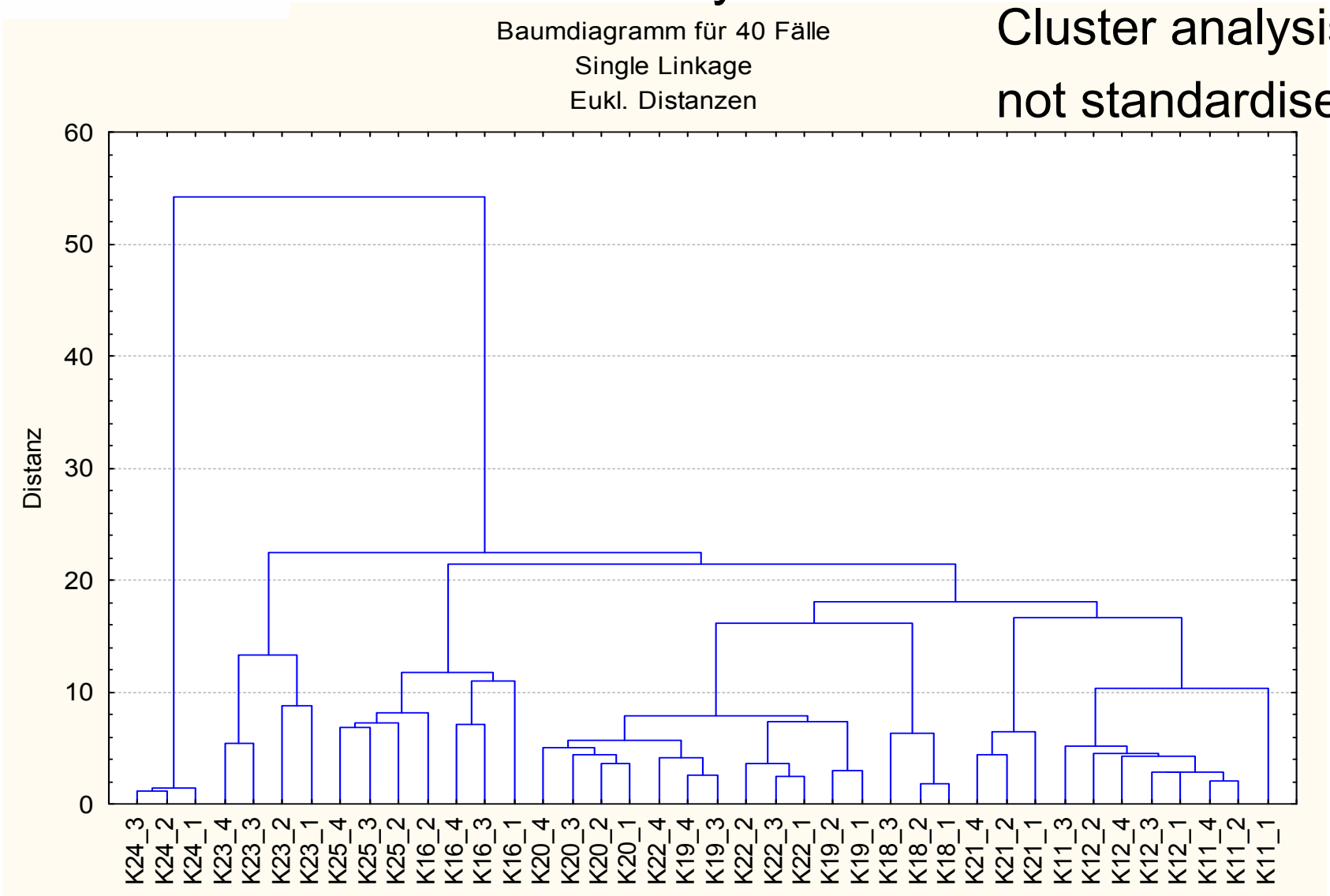
Bundeskriminalamt

Differentiation of NN at risk products

only K-series

Cluster analysis

not standardised

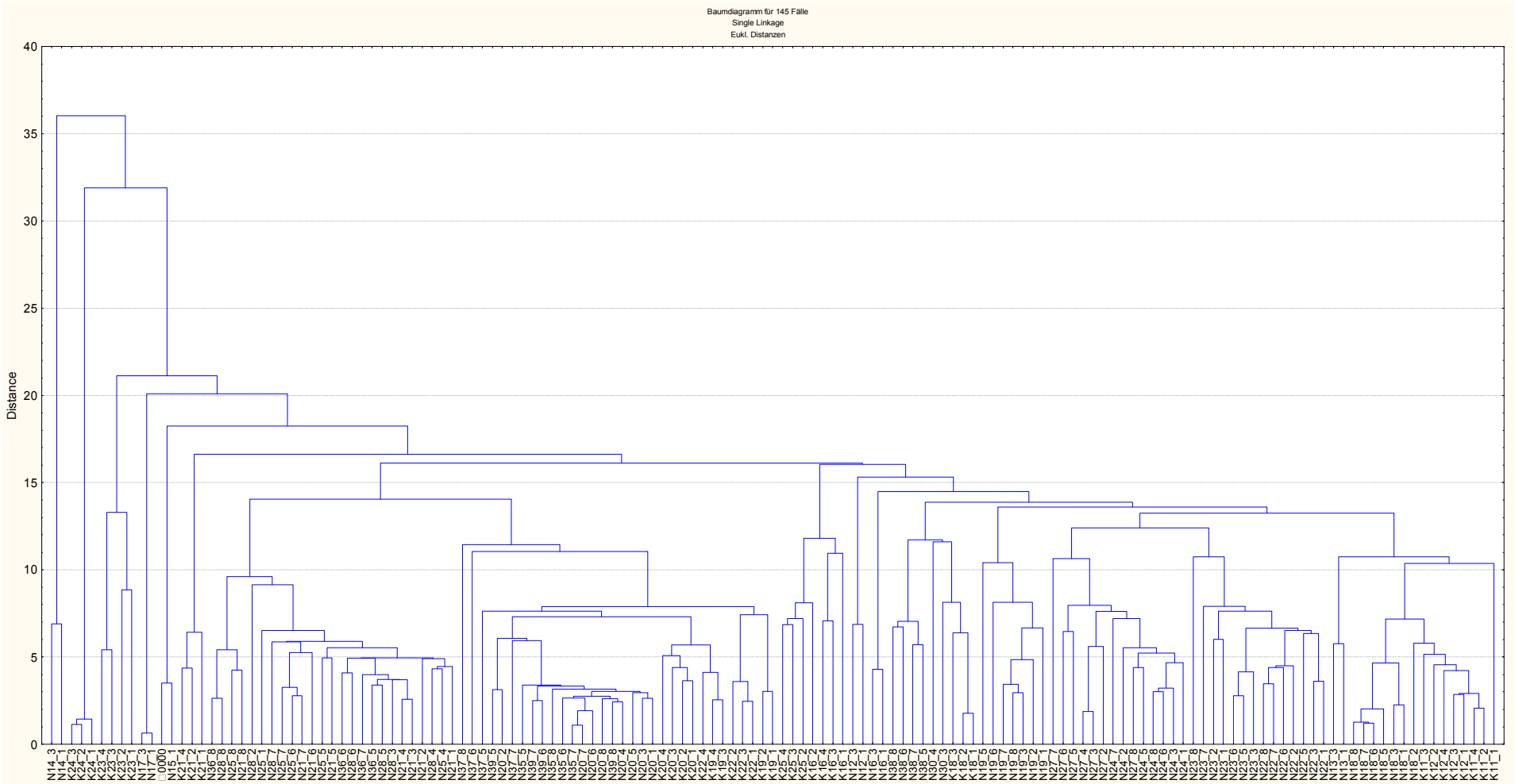


Bundeskriminalamt

Differentiation of NN at risk products

Cluster analysis

- K & N series; 27 elements; data not standardised



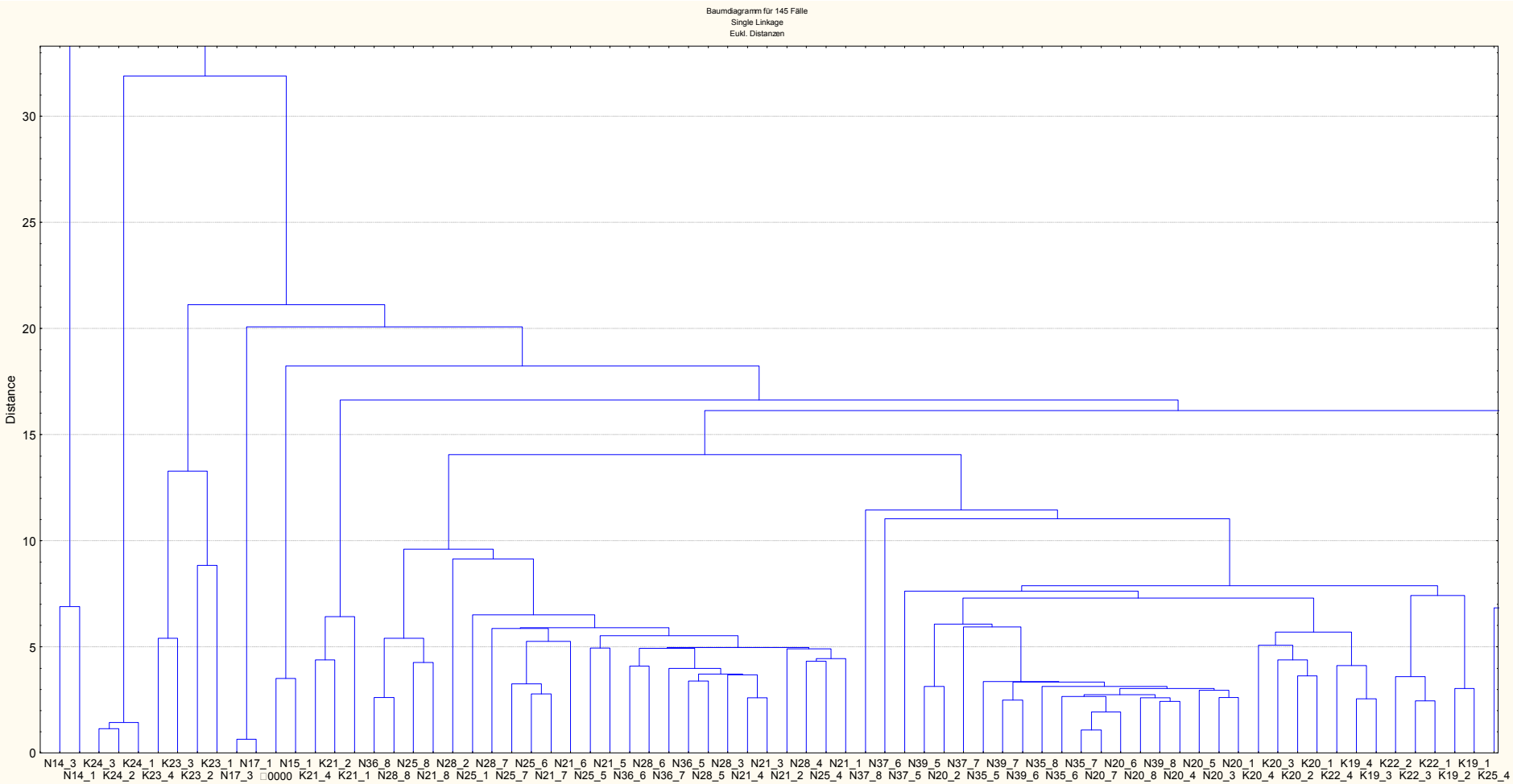
Bundeskriminalamt

Differentiation of NN at risk products

Cluster analysis

K & N series; 27 elements; data not standardised

Magnification, picture 1 of 2



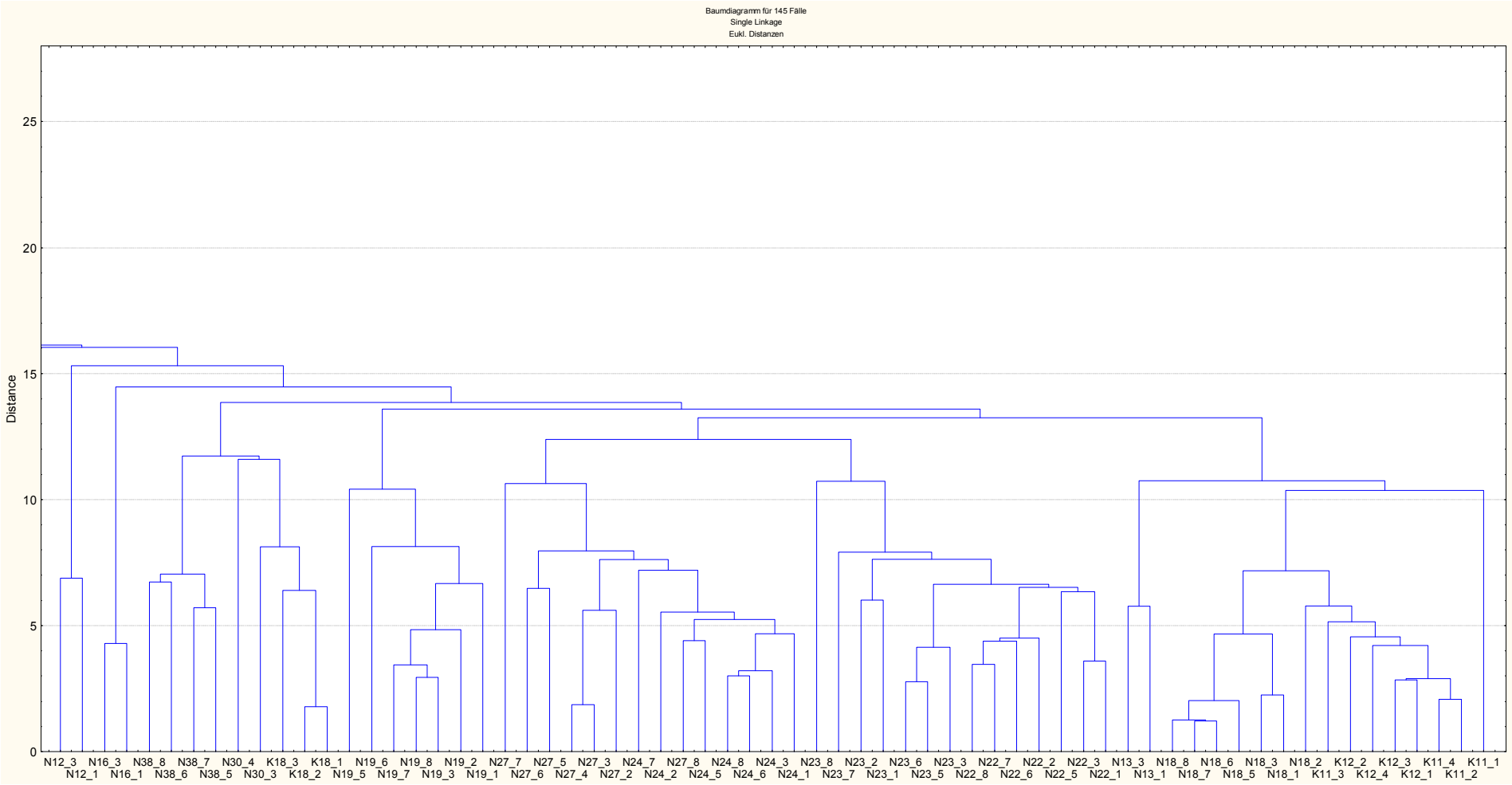
Bundeskriminalamt

Differentiation of NN at risk products

Cluster analysis

K & N series; 27 elements; data not standardised

Magnification, picture 2 of 2

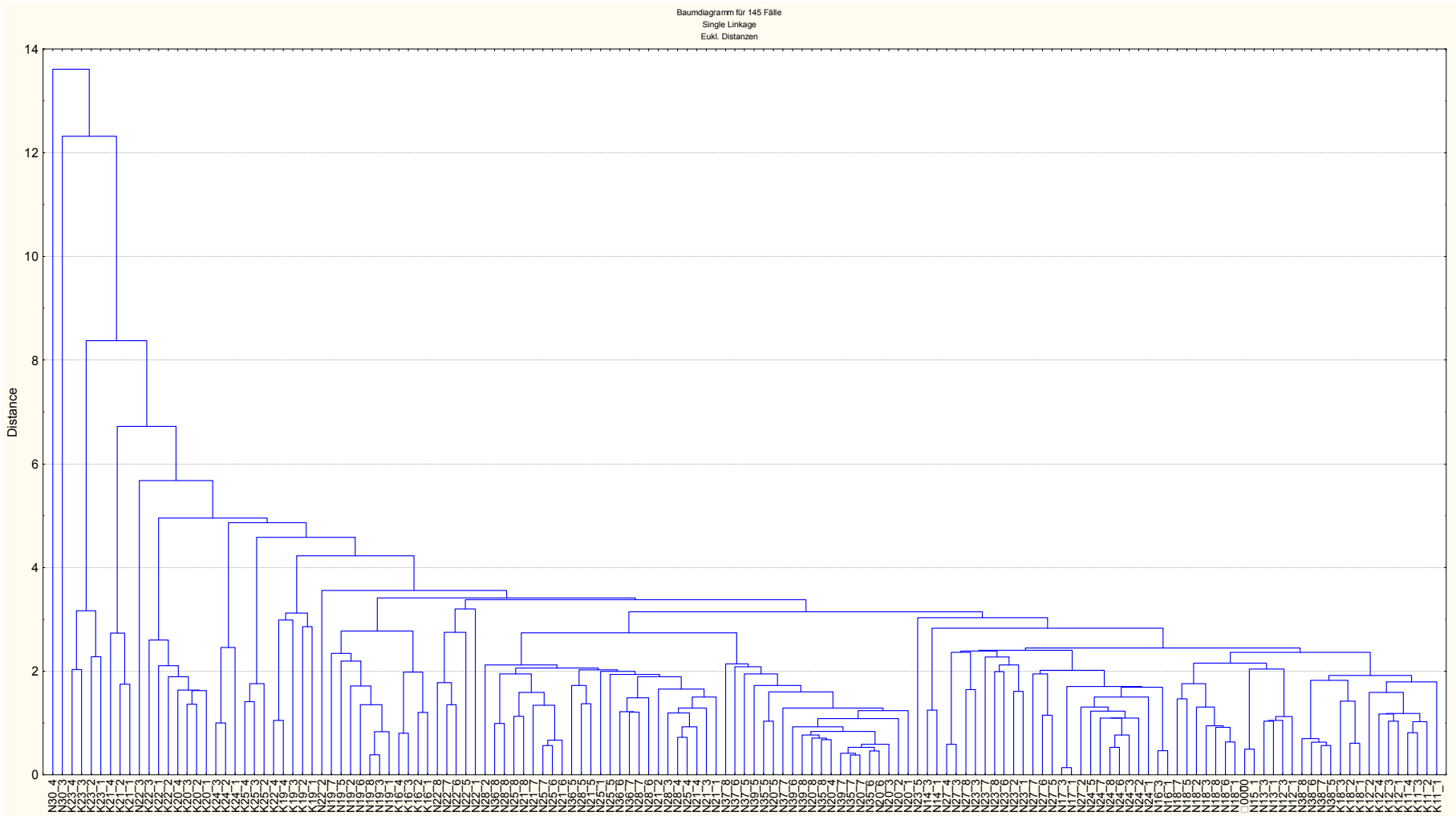


Bundeskriminalamt

Differentiation of NN at risk products

Cluster analysis

K & N series; all elements; data standardised

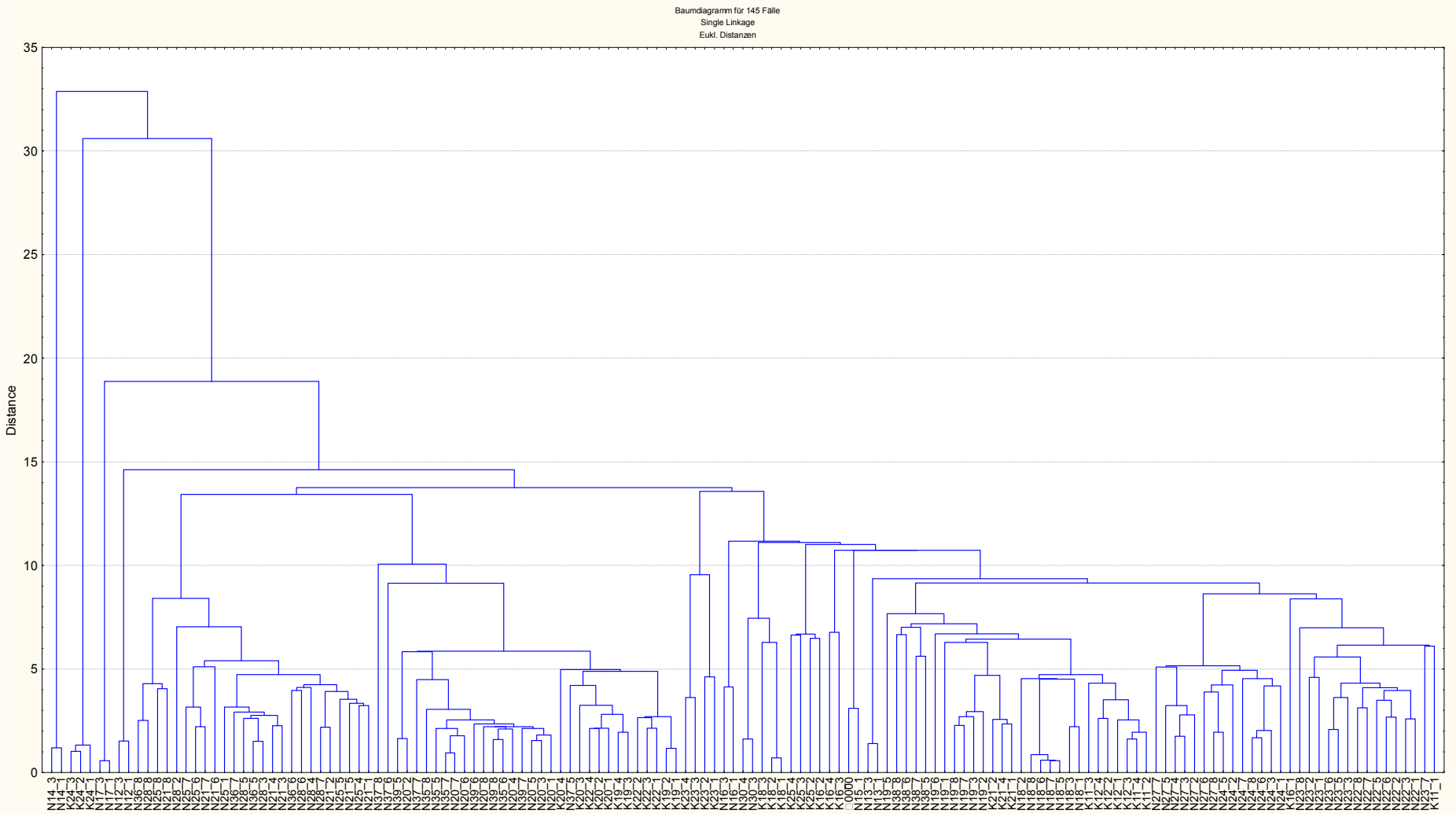


Bundeskriminalamt

Differentiation of NN at risk products

Cluster analysis

K & N series; 9 elements; data not standardised

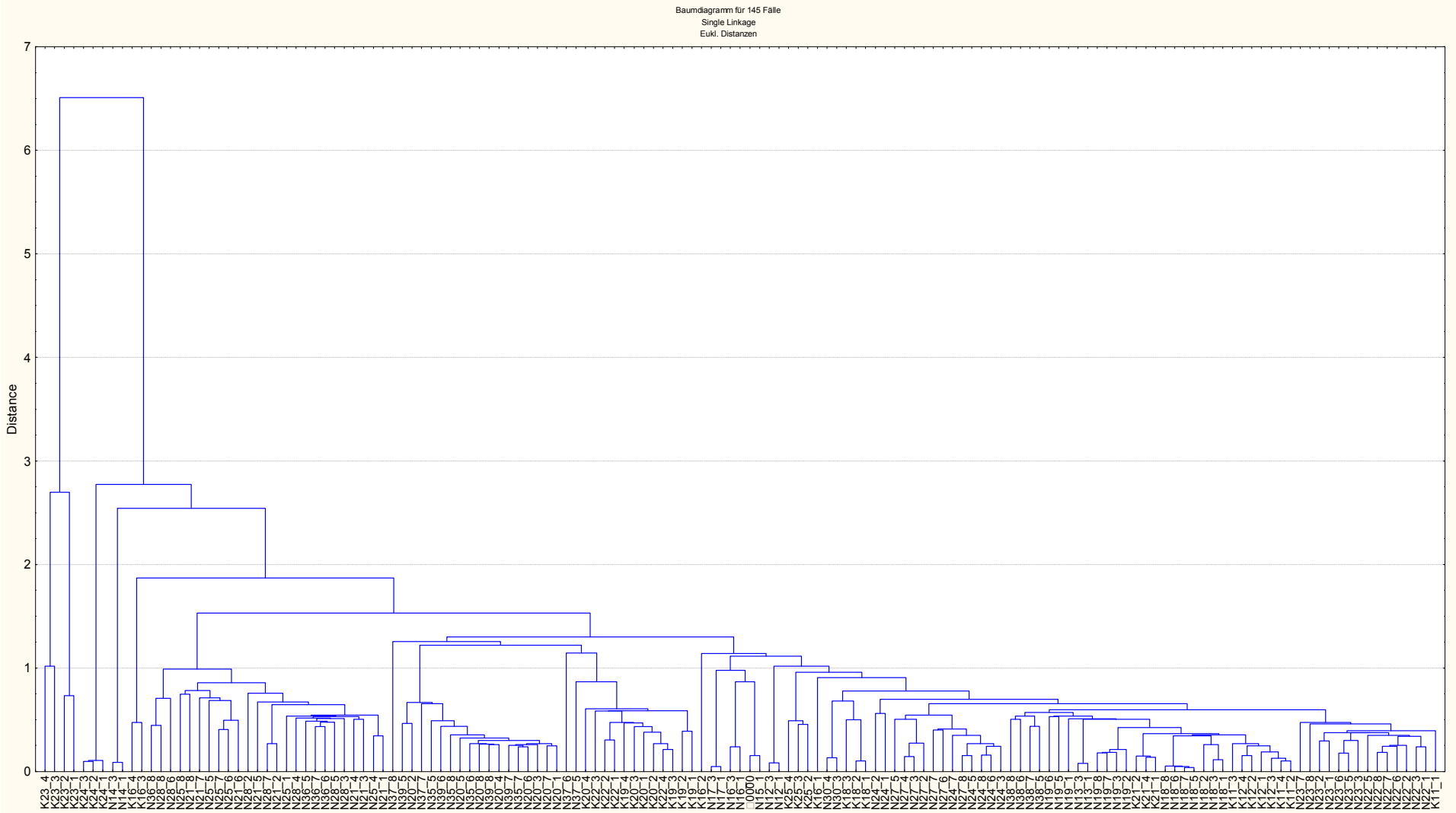


Bundeskriminalamt

Differentiation of NN at risk products

Cluster analysis

K & N series; 9 elements; data standardised



Bundeskriminalamt

Differentiation of NN at risk products

	XRDiffraction Grouping	Descriptive Stat only K-series	Cluster analysis only K-series all elements not standardised	Cluster analysis K & N-series all elements not standardised	Cluster analysis K & N-series all elements standardised	Cluster analysis K & N-series 9 elements not standardised	Cluster analysis K & N-series 9 elements standardised
TSEN–1 nickel sludge	K11	K11	K11	K11	K11	K11	K11
TsEN-2 (ЦЭН–2) Nickel Sludge	K12	K12	K12	K12	K12	K12	K12
Copper Sludge	K16	K21	K21	N18	K16	K16	K16
Sulfating Degree 2 Non-desiliconized Cake	K19	K16	K16	K16	K18	K25	K18
Sulfating Degree 2 Desiliconized Cake	K20	K25	K25	K25	K19	K19	K19
Calcine of synthesis calcinated residues	K21	K19	K19	K19	K20	K20	K20
Platinum-Palladium Concentrate (PPC)	K22	K20	K20	K20	K22	K22	K22
Concentrate of platinum satellite metals - PSMC	K23	K22	K22	K22	K21	K18	K21
Silver-palladium concentrate – SPC	K24	K18	K18	K18	K23	K21	K23
FILTERED COPPER CONCENTRATE URF	N14	K23	K23	K21	K24	K23	K24
FILTERED NICKEL CONCENTRATE URF	N15	K24	K24	K23	K25	K24	K25
Magnetic fraction after matte separation	N16			K24	N12	N12	N12
Nickel Sludge	N18			N12	N13	N30	N14
Copper slime vollständiges data sheet	N19			N13	N14	N14	N15
Nickel Sludge Cinder Cake.	N23			N14	N15	N15	N16
SLAG ANODES	N27			N15	N16	N16	N17
IRIDIUM CONCENTRATE CAKE	N30			N16	N17	N17	N18
OK CONCENTRATE (washed)	N36			N17	N18	N18	N30
Copper sponge (before leaching and washing)	N38			N19	N19	N24	N24
TSEM dried copper sludge	K25			N24	N23	N27	N27
Sulfating Degree 1 Cake	K18			N27	N27	N13	N13
Copper Sludge Cinder Cake	N22			N30	N24	N19	N19
NMZ Copper and Nickel Nis Matte	N12			N38	N30	N38	N38
NZ Copper-Nickel Nis Matte	N13			N22	N22	N22	N22
CRUDE NICKEL ANODES	N17			N23	N38	N23	N23
SECONDARY ANODES.	N24			N21	N21	N21	N21
KP-2 Grade Concentrate (ready, packaged)	N21			N25	N25	N25	N25
LEACHED COPPER SPONGE	N25			N28	N28	N28	N28
CONCENTRATE of OK Grade(final)	N28			N36	N36	N36	N36
KP-1 Grade Concentrate (ready, packaged)	N20			N20	N20	N20	N20
Leached Secondary Sludge	N35			N35	N35	N35	N35
Secondary Sludge Prior to Leaching and Washing	N37			N37	N37	N37	N37
Slime after scrap washing	N39			N39	N39	N39	N39

= no full grouping

Differentiation of NN at risk products

Results

- A full separation of the 33 at risk products based on elemental analysis or X-ray diffractograms is not possible.
- Still a separation into more than twenty sub groups can be achieved.
- Degree of separation / sub grouping based on X-ray diffractograms is similar to the results based on elemental analysis.

Incomplete separation of NN at risk product by using XRD and elemental analysis data ?

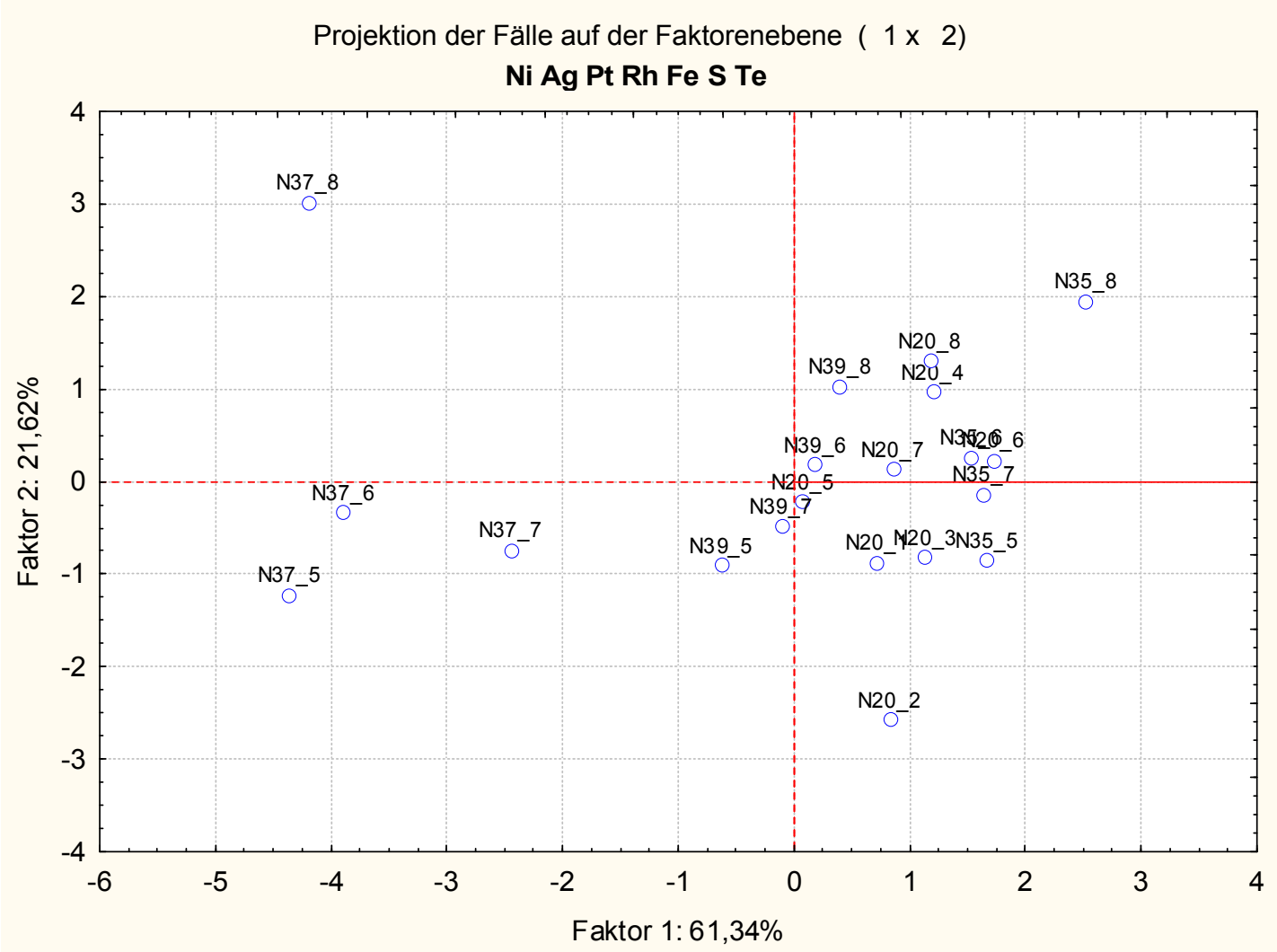
→ Principle component analysis

As an example it was tried to differentiate products N20, N35, N37, N39 and N21, N25, N28, N36 by applying principle component analysis (PCA).

Bundeskriminalamt

Differentiation of NN at risk products

N20, N35, N37, N39



Differentiation of NN at risk products

N20, N35, N37, N39

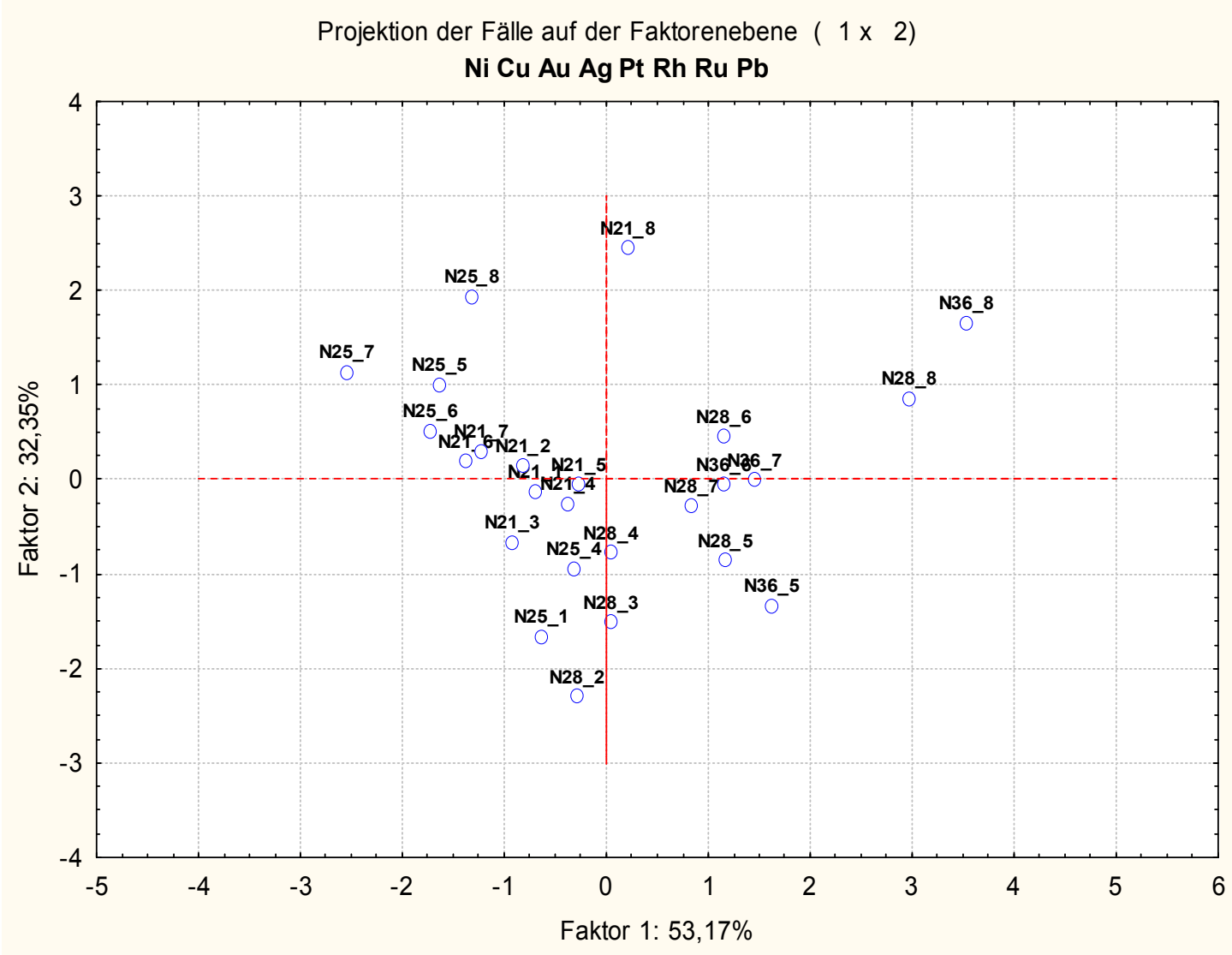
Based on elemental concentrations of Ni, Ag, Pt, Rh, Fe, S, Fe

only a separation of materials from N37 is possible.

Bundeskriminalamt

Differentiation of NN at risk products

N21, N25, N28, N36



Differentiation of NN at risk products

N21, N25, N28, N36

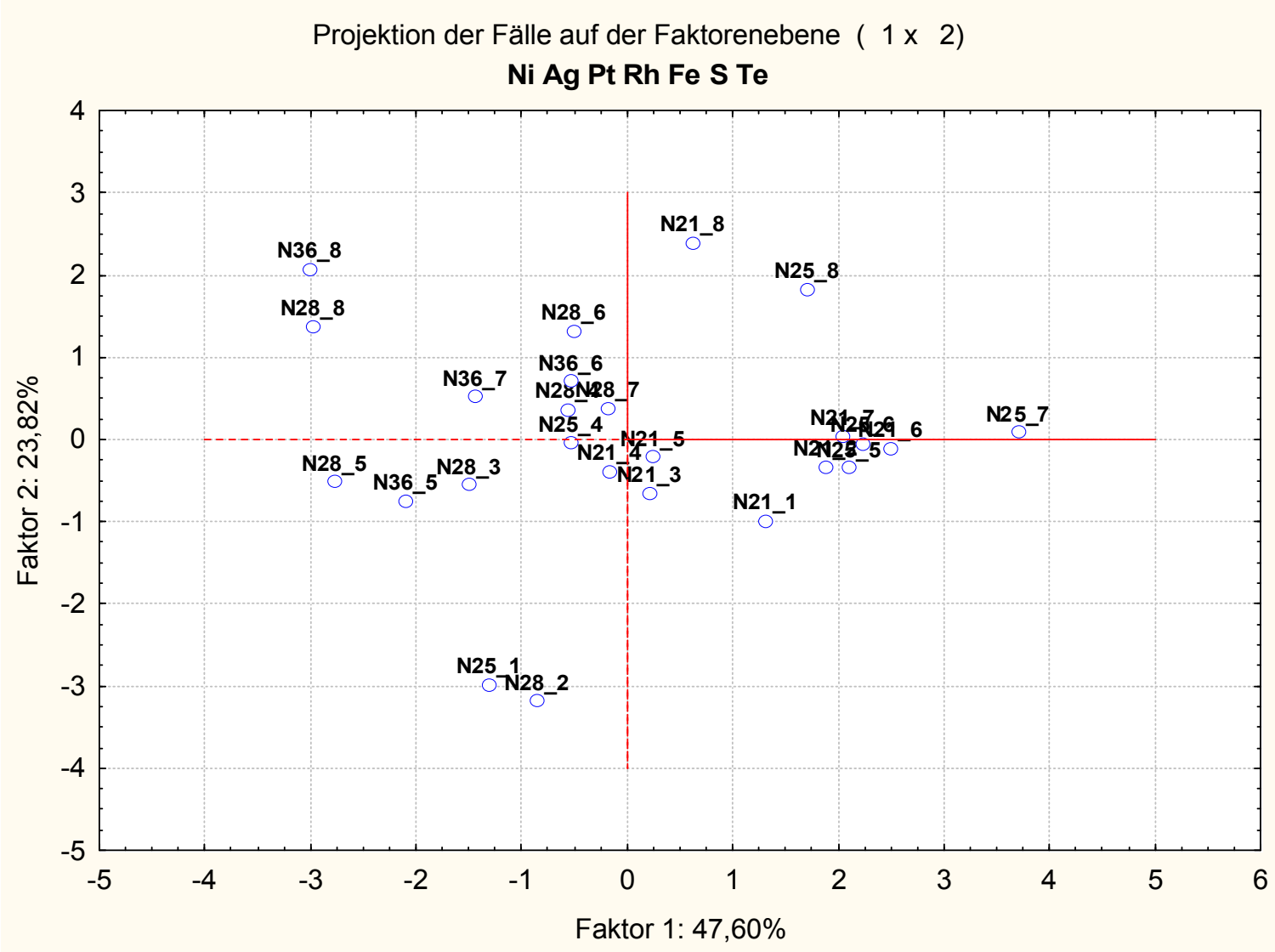
Based on elemental concentrations of Ni, Ag, Pt, Rh, Fe, S, Fe

only no separation is possible.

Bundeskriminalamt

Differentiation of NN at risk products

N21, N25, N28, N36



Differentiation of NN at risk products

Not much further separation was achieved by applying PCA to products N20, N35, N37, N39 and N21, N25, N28, N36.

Differentiation of NN at risk products

Findings consistent with information from material data sheet:

Group consisting of product N20, N35, N37, N39

As stated in material data sheet of N35:

The phase compositions (diffractograms) of leached secondary sludge (N35), secondary sludge prior to leaching and washing (N37), and sludge following scrap washing (N39) are similar….

Differentiation of NN at risk products

Conclusion

No full separation possible based on XRD & elemental analysis data. Separation into more than twenty sub groups is possible.

Differentiation of NN at risk products

Further separation based on SEM type class information as stated in material data sheets of the RDB:

Example for group N20, N35, N37, N39:

Bundeskriminalamt

Differentiation of NN at risk products

		Occurence/ %
Type N20-1	**Pd–Ag–Pt–O–**(As)–Se–(Si)–(Au)–S–(Pb)–Te–(Fe)–(Co)–(Ni)–Cu	70-80
Type N20-2	**Pt**–**Pd**–**Ag**–O–As–Se–(Si)–S–Te–(Fe)–(Ni)–Cu	10
Type N20-3	**Pb**–O–(As)–(Se)–(Pt)–S–Pd–Ag–(Te)–(Cu)	5
Type N20-4	**Pd**–**Ag**–(**Pt**)–(**Sn**)–(**Sb**)–O–S–Pb–(Te)–Cu	5 -15
Type N35–1	**Pd**–**Ag**–**Pt**–(O)–As–Se–(Si)–(Au)–S–(Pb)–(Cl)–Te–(Fe)–(Ni)–Cu	85
Type N35–2	**Pt**–**Pd**–**Ag**–O–As–Se–S–(Pb)–Te–Fe–(Ni)–Cu	1
Type N35–3	**Pb–O–(As)–(Se)–(Pt)–Pd–Ag–(Te)–(Fe)–(Ni)–(Cu)**	5
Type N35–4	**Pd**–**Ag**–**Pt**–**Sn**–(**Sb**)–O–As–Se–(Si)–(Au)–S–Pb–(Te)–Fe–(Ni)–Cu	5
Type N35–5	**Ni**–**O**–(As)–(Se)–(Si)–(Pt)–(S)–(Pb)–(Pd)–(Ag)–(Fe)–(Co)–(Cu)	1
Type N37–1	**Pd–(Ag)–Pt–**O–As–(Se)–(Si)–(Au)–S–(Pb)–(Sn)–(Sb)–Te–Fe–(Co)–Ni–(Cu)	75
Type N37–2	**Pt**–**Pd**–**Ag**–O–As–Se–S–(Ru)–Sn–(Sb)–(Te)–Fe–Ni–(Cu)	10
Type N37–3	**Pb**–O–As–(Se)–(Si)–(Pt)–S–Pd–Ag–Sn–Sb–Te–Fe–(Co)–Ni–(Cu)	10
Type N37–4	**Sn**–**Sb**–**Pd**–**Ag**–(**Pt**)–O–As–(Se)–(Si)–(Au)–S–(Pb)–Te–Fe–Ni–(Cu)	5
Type N39–1	**Pd**–**Ag**–**Pt**–O–As–Se–(Au)–S–(Pb)–(Sn)–(Sb)–Te–(Fe)–(Ni)–(Cu)	75
Type N39–2	**Pt**–**Pd**–**Ag**–O–As–Se–S–(Sn)–(Sb)–Te–Fe–Ni–Cu	10
Type N39–3	**Pb**–O–(As)–(Se)–(Pt)–S–Pd–Ag–(Sn)–(Sb)–(Te)–(Fe)	10
Type N39–4	**Sn**–**Sb**–**Pd**–**Ag**–**Pt**–O–As–(Se)–S–(Pb)–Te–Fe–Ni–(Cu)	5

Special thanks to:

Dr. Sonja Menges - Statistic consultation

Dr. Peter Weis - Elemental analysis

Dr. Erik Krupicka - X-Ray Diffraction

Dr. Gabriele Gorzawski - SEM