INSTITUTE OF METROLOGY OF BOSNIA AND HERZEGOVINA

LABORATORY FOR PRECIOUS METALS

IMBIH

3RD PROFICIENCY TESTING SCHEME: **IMBIH.LH-PT.15**

FINAL REPORT
TC project.No.1370; 2016-05-25

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- **Introduction**

Proficiency tests are a useful and necessary tool to proof the technical competence of the participating laboratories. The Institute of metrology of Bosnia and Herzegovina, Laboratory for precious metals, has organized the Proficiency Testing Scheme – IMBIH.LH-PT.15 on precious metals alloy in order to provide an objective review of their performance and technical competence to the participating laboratories. The whole process follows the international standard ISO/IEC 17043 – *Conformity assessment – General requirements for proficiency testing*.

The Proficiency Testing Scheme – IMBIH.LH-PT.15 on precious metals alloy is linked to **EURAMET TCMC project No. 1370 and is not meant to support CMC claims.**

- **Organiser**

The 3rd proficiency testing scheme for comparison on precious metals alloy is organized by the Institute of Metrology of Bosnia and Herzegovina – Laboratory for Precious Metals (IMBIH-LH), here in after referred as PT provider.

The comparison measurement was executed as a multilateral comparison measurement.

All information in connection with this comparison will be kept confidential between the participants.

The role of the pilot calibration laboratory was to accompany the process and to evaluate the measurement results. The methodical approach is according ISO/IEC 17043.

- **Participating laboratories**

Fourteen laboratories from eight countries have participated in this PT Scheme. A list of the participating laboratories with contact data and person is enclosed in Annex 1 of this document.

- **Test procedures**

Participating laboratories carried out the test procedures on PT sample according to the instructions provided in Statistical Protocol IMBIH.LH-PT.15 previously delivered by PT Provider.

The test on yellow gold material (750 ‰ approx.) followed the standard method - ISO 11426 – *Determination of gold in gold jewelry alloys – Cupellation method (fire assay)*.

- **Test sample**

The test sample – **MA/Au.03** was prepared in form of wire and it has the following nominal composition:

Au	Cu	Ag	Zn
750 ‰	190 ‰	30 ‰	30 ‰

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- **Homogeneity test**

In the following the executed homogenity test and the related results are described.

Sub-samples were prepared by cutting the wire into equal pieces that were coded prior to carrying out the homogeneity test. Ten pieces of the testing material (sub-samples) were analysed, each in two test portions. Analyses were performed under repeatability conditions within the same laboratory and same analyst using the standard analytical method ISO 11426.

The degree of homogeneity of test material was tested applying the following criterion in accordance with ISO 13528 – *Statistical method for use in proficiency testing by interlaboratory comparisons*. The following criterion must be fulfilled.

$$s_s \leq 0.3 \, \sigma_p$$

where s_s is the between-sample standard deviation and σ_p is the standard deviation for proficiency assessment; $\sigma_p = 0.5 ‰$).

The related calculations are as follows:

Between test-portion mean
$$x_t = \left| \frac{x_1 - x_2}{2} \right| \qquad (1)$$

Between test-portion range
$$w_t = |x_1 - x_2| \qquad (2)$$

Standard deviation of the average
$$s_{\overline{x}} = \sqrt{\frac{\sum(x_t - \overline{x})^2}{g - 1}} \qquad (3)$$

Within sample standard deviation
$$s_w = \sqrt{\frac{\sum s_t^2}{2g}} \qquad (4)$$

Between sample standard deviation
$$s_s = \sqrt{s_{\overline{X}}^2 - \frac{s_w^2}{2}} \qquad (5)$$

Results of the homogeneity test for the sample MA/Au.03 are shown in Table 1; *all data in ‰*

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Sub-samples	x_1	x_2	x_t	w_t	w_t^2
A	734.1	734.2	734.1	0.083	0.007
B	734.6	734.3	734.4	0.277	0.077
C	734.2	734.4	734.3	0.162	0.026
D	734.2	734.4	734.3	0.230	0.053
E	734.1	734.3	734.2	0.238	0.056
F	733.9	734.3	734.1	0.342	0.117
G	734.5	734.4	734.5	0.059	0.003
H	734.2	734.4	734.3	0.138	0.019
I	734.5	734.4	734.5	0.052	0.003
J	734.6	734.6	734.6	0.017	0.000

g	10
$\overline{x}$	734.3
$s_{\overline{x}}$	0.15
s_w	0.13
s_s	0.12
$0.3\sigma_p$	0.15

0.12 < 0.15

Table 1 Results of homogeneity test for MA/Au.03

The obtained results have fulfilled the criterion for homogeneity according to ISO 13528 of bulk test material. The determined homogeneity was considered satisfactory for the purpose of this PT scheme. The equal pieces with an approx. mass of 1 g of bulk test material were distributed to all participants.

Solid precious metals alloys are stable materials; therefore stability is very high, thus a stability check of bulk test material was not performed.

- **Assigned value**

The assigned value for the test material was determined by the PT provider according to IUPAC Technical Report - *The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories* (*3.2.1 – Measurement by a reference laboratory*). The method used for obtaining the assigned value is the standard method ISO 11426. The sample was analysed under within-laboratory reproducibility conditions. For preparing the control sample, as required in the stated method, the certified reference material NIST SRM 685-R (Au 999.99 mg/g) was used providing the appropriate metrological traceability for the assigned value.

The assigned value was determined as the mean value of the test results, after applying outlier tests. Values generated during the homogeneity test were treated as the first series since the same test method was used for both purposes. The second series of values were generated by applying the same test method but with another analyst and shift in analysis time.

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Results used to determine the assigned value for the sample MA/Au.03 is shown in Table 2; *all data in ‰*

	1st series (homogeneity)	2nd series (reproducibility)
	734.1	734.6
	734.4	734.5
	734.3	734.6
	734.3	734.6
	734.2	734.6
	734.1	734.8
	734.5	734.5
	734.3	734.5
	734.5	734.6
	734.6	
	734.1	

n	18
x_a	734.45
$s_{\bar{x}}$	0.19

Table 2 Results of assigning the value for MA/Au.03

The calculated assigned value is 734.45 ‰!

- **Measurement uncertainty of the assigned value**

The expanded measurement uncertainty of the assigned value is determined by the PT Provider according to ISO 21748 – *Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation* and EUROLAB Technical report No.1/2007 – Alternative approaches to uncertainty evaluation. The used approach named "empirical method" is based on the principle that:

Reliability of the results = precision + trueness (bias)

Precision was estimated by incorporating data from intra-laboratory verification procedures under conditions of intra-laboratory reproducibility corresponding to the routine laboratory work. The estimated value of precision is **0.18 ‰**.

Contribution of the bias was evaluated using data from inter-laboratory comparisons that laboratory PT provider participated in. Comparisons was organized by IAAO (International Association of Assay Offices) designed for the field of interest since there are no key or supplementary comparisons in this field organized by EURAMET CIPM MRA. The difference between the laboratory results and the assigned value of the comparison was used to estimate the contribution of the bias within the overall uncertainty. The four different comparisons were used to estimate the value of bias that is **0.15 ‰**.

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The overall measurement uncertainty was expressed using following formula:

$$u_{xa} = \sqrt{u_{prec}^2 + u_{bias}^2} \qquad (6)$$

$$u_{xa} = \sqrt{0.18^2\text{‰} + 0.15^2\text{‰}}$$

$$\boldsymbol{u_{xa} = 0.23}\text{ ‰}$$

The estimated value of the combined measurement uncertainty is 0.23 ‰ (*k*=1)!

- **Performance assessment**

Statistical evaluation of are defined according to these documents:

- ISO 13528 - *Statistical methods for use in proficiency testing by interlaboratory comparisons*
- ISO/IEC 17043 – *Conformity assessment – General requirements for proficiency testing*
- *The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories*

The PT results were processed using *z'*-scores incorporating the measurement uncertainty of the assigned value according to eq. (7):

$$z' = \frac{x - x_a}{\sqrt{u_{xa}^2 + \sigma_p^2}} \qquad (7)$$

where is:

- (x_a) ASSIGNED VALUE,
- (u_{xa}) UNCERTAINTY ON THE ASSIGNED VALUE,
- (σ_p) STANDARD DEVIATION FOR PROFICIENCY TESTING
- (x) INDIVIDUAL LABORATORY MEAN OF THREE REPLICATES
- z'-SCORES

The criteria of acceptability are defined by the values of *z'*-scores in accordance with the following conditions, as defined in ISO 13528:

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If ∣z'∣ ≤2 then the result is considered as "satisfactory";

If 2<∣z'∣ ≤3 then the result is considered as "questionable";

If ∣z'∣ >3 then the result is considered as "unsatisfactory"

- **Results**

The results of the participating laboratories are shown in the Table 3 below as well as the general statistical parameters of this PT.

lab	x_1	x_2	x_3	x	s	z'
DZM	734,3	734,3	734,2	734,27	0,06	-0,33
BoM	734,8	735,0	734,8	734,87	0,12	0,76
KMA	734,0	733,9	733,8	733,90	0,10	-1,00
DMDM	734,5	734,7	734,6	734,60	0,10	0,27
RAO-Warsz.	734,1	734,3	734,5	734,30	0,20	-0,27
RAO-Bialys.	734,7	734,7	734,8	734,73	0,06	0,52
RAO-Gdansk	734,5	734,6	734,5	734,53	0,06	0,15
RAO-Bydgosz.	734,4	734,4	734,4	734,40	0,00	-0,09
RAO-Wroc.	734,6	734,6	734,6	734,60	0,00	0,27
RAO-Krakow	734,6	734,6	734,7	734,63	0,06	0,34
RAO-Lodzi	734,8	734,5	734,4	734,57	0,21	0,21
MSI-RS	733,5	733,5	733,5	733,50	0,00	-1,72
KGC	734,2	734,3	734,6	734,34	0,24	-0,19
SCA	734,6	734,4	734,4	734,47	0,12	0,03

Number of participating laboratories	p	14
Assigned value	x_a	734.45
Measurement uncertainty of the x_a	u_{xa}	0.23
Standard deviation of proficiency assessment	σ_p	0.50

Table 3 Participants' results and Statistical parameters; all data in ‰

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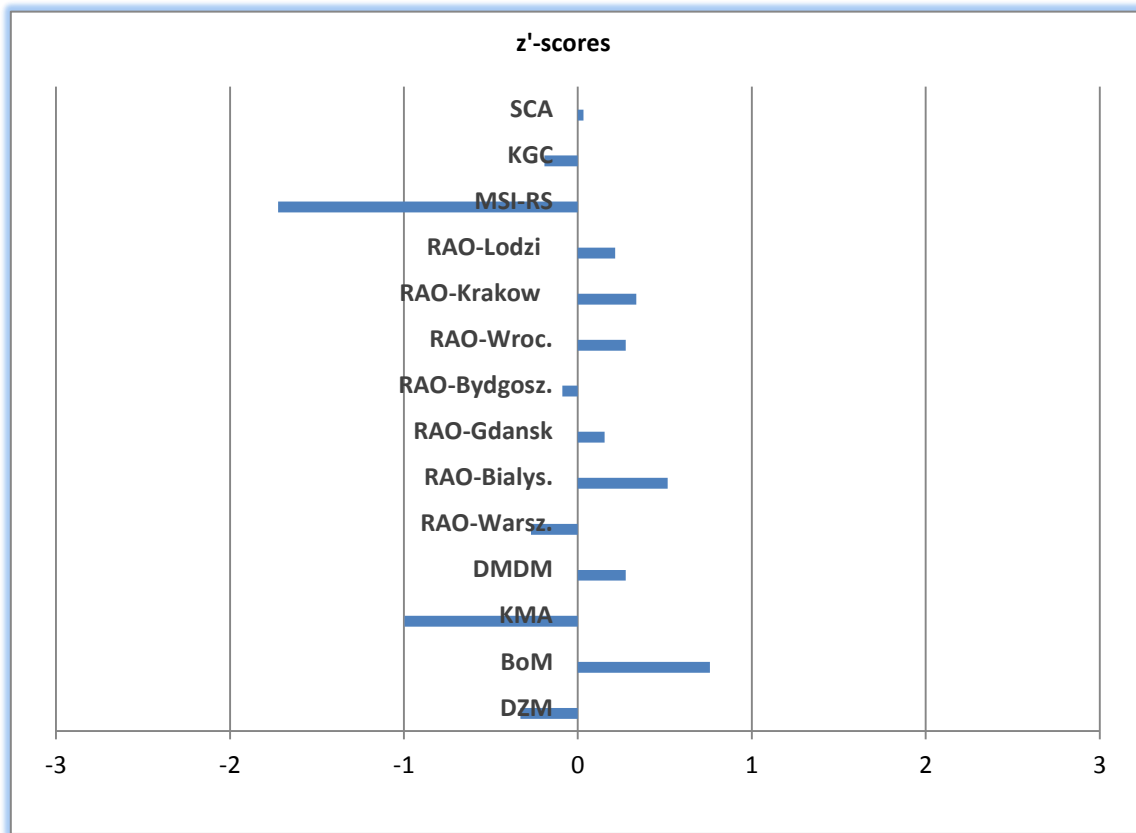The participants' z'-scores are presented on the bar chart shown at the Figure 1.

Figure 1 Participants z' -scores

The results of all participating laboratories were within acceptable satisfactory limits with values |z'| ≤ 2.

The participants' mean values with standard deviations of three replicates as well as assigned value are shown at the Figure 2.
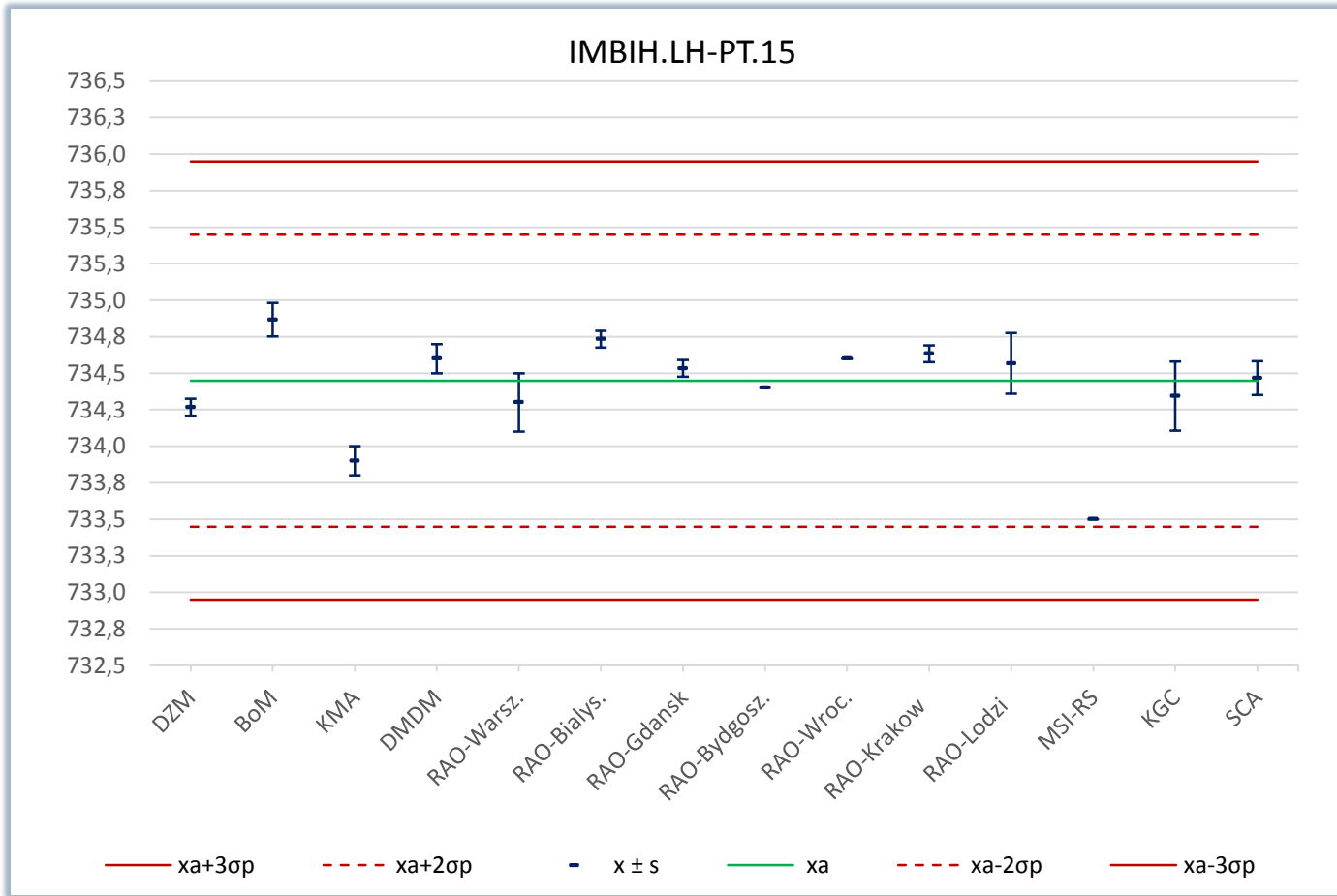

Figure 2 Participants' mean values

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Annex 1: Degrees of equivalence

a) *The degree of equivalence of laboratories for each laboratory* with respect to the assigned value is given by:

$$D_i = x_a - x_i$$

where is:

- (x_a) ASSIGNED VALUE,
- (x_i) INDIVIDUAL LABORATORY MEAN OF THREE REPLICATES

Expanded uncertainty (k=2) is given by:

$$U_{Di} = 2\sqrt{u_{xi}^2 + u_{xa}^2}$$

where is:

- (u_{xa}) UNCERTAINTY ON THE ASSIGNED VALUE (k=1)
- (u_{xi}) INDIVIDUAL LABORATORY MEASUREMENT UNCERTAINTY (k=1)

The values of the degrees of the equivalence of the participating laboratories are shown in the Table 4 below. Unfortunately, only three laboratories provide the measurement uncertainty of results.

lab	x_i	u_{xi}	D_i	U_{Di}
DZM	734,27	n/a	-0.18	n/a
BoM	734,87	n/a	0.42	n/a
KMA	733,90	n/a	-0.55	n/a
DMDM	734,60	**0.25**	**0.15**	**0.68**
RAO-Warsz.	734,30	n/a	0.15	n/a
RAO-Bialys.	734,73	n/a	0.28	n/a
RAO-Gdansk	734,53	n/a	0.08	n/a
RAO-Bydgosz.	734,40	n/a	-0.05	n/a
RAO-Wroc.	734,60	n/a	0.15	n/a
RAO-Krakow	734,63	n/a	0.18	n/a
RAO-Lodzi	734,57	n/a	0.12	n/a
MSI-RS	733,50	**0.13**	**-0.95**	**0.39**
KGC	734,34	n/a	-0.11	n/a
SCA	734,47	**0.10**	**0.02**	**0.41**

Table 4 Participants' results and degrees of equivalence values; all data in ‰

The participants' D_i values as well as their measurement uncertainties are shown at the Table 5 and Figure 3, respectively.

lab	x_i	u_{xi}	D_i	U_{Di}
MSI-RS	733.50	0.13	-0.95	0.52
DMDM	734.60	0.25	0.15	0.68
SCA	734.47	0.10	0.02	0.50
IMBiH	734.45	0.23	0.0	0.65

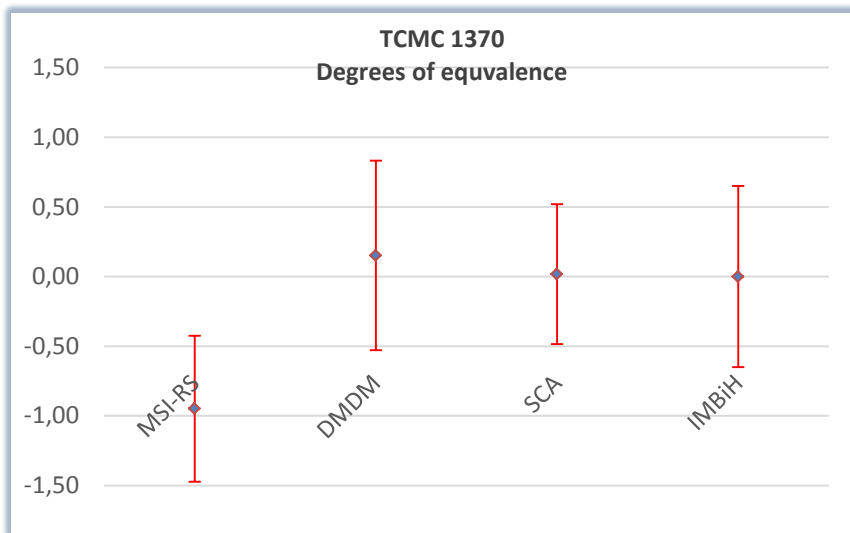*Table 5 Participants' results and degrees of equivalence values; all data in ‰*

Figure 3 Degrees of equivalence and expanded uncertainty (k=2) expressed in ‰.

b) *The degree of equivalence between two laboratories i and j* is given by:

$$D_{ij} = (x_i - x_j)$$

and its expanded uncertainty (k=2):

$$U_{ij} = 2\sqrt{u_{xi}^2 + u_{xj}^2}$$

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The values of the degrees of the equivalence between *i* and *j* laboratories are shown in the Table 6 below.

LAB i ↓			LAB j →								
			MSI-RS		DMDM		SCA		IMBiH		
	D_i	U_i	D_i	U_i	D_i	U_i	D_i	U_i	D_i	U_i	
MSI-RS	-0,95	0,52			-1,10	0,86	0,97	0,32	-0,95	0,52	
DMDM	0,15	0,68	1,10	0,86			0,13	0,72	0,15	0,68	
SCA	0,02	0,5	-0,97	0,32	-0,13	0,72			0,02	0,50	
IMBiH	0	0,65	0,95	0,49	-0,15	0,59	-0,02	0,50			

Table 6 Participants' degrees of equivalence between i and *j values; all data in ‰;*

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Annex 2: List of participating laboratories in Proficiency Testing on Precious Metals Alloys

	COUNTRY:	CONTACT INFO:
MSI-RS	Bosnia and Herzegovina	Republic of Srpska Metrology and Standardization Institute; Laboratory for physical-chemical measurement; Šabačkih đaka bb, 76300 Bijeljina Contact person: Savo Lalović e-mail: savo.lalovic@orao.aero
DZM	Croatia	State Office for Metrology; Service for Precious Metals and Chemical Measurement; Ulica grada Vukovara 284/6 10000, Zagreb Contact person: Josipa Alerić e-mail: josipa.aleric@dzm.hr
KMA	Kosovo	Kosovo Metrology Agency; Laboratory for precious metals; King Pleurat 12, 20000 Prizren Contact person: Esma Shotka e-mail: esma.shotka@rks-gov.net
BoM	Macedonia	Bureau of Metrology; Laboratory for Testing Precious Metals; blvd. Jane Sandanski 109a, 1000 Skopje Contact person: Beti Vukovojac e-mail: beti.vukovojac@bom.gov.mk
RAO-Warsz.	Poland	Regional Assay Office Warszawa; Chemical Laboratory; Elektroralna 2, 00-139, Warszawa Contact person: Katarzyna Nadara e-mail: lab.oup.warszawa@gum.gov.pl
RAO-Bialys.	Poland	Regional Assay Office Warszawa, Branch in Bialystok; Chemical Laboratory; M. Kopernika 89, 15-396, Bialystok Contact person: Adam Wojtulewicz e-mail: a.wojtulewicz.oup@gum.gov.pl
RAO-Gdansk	Poland	Regional Assay Office Warszawa, Branch in Gdansk; Chemical Laboratory; Polanki 124 C 80-308, Gdansk Contact person: Anna Wiezorek e-mail: oup.warszawa.gdansk@gum.gov.pl
RAO-Bydgo.	Poland	Regional Assay Office Warszawa, Branch in Bydgoszcz; Chemical Laboratory; Ul. Zygmunta Augusta 16, 85-082, Bydgoszcz Contact person: Wieslawa Bromka e-mail: oup.warszawa.bydgoszcz@gum.gov.pl
RAO-Wroc.	Poland	Regional Assay Office Krakow, Branch in Wroclaw; Chemical Laboratory; Mlodych Technikow 61/63 53-654, Wroclaw Contact person: Agneieszka Nowak e-mail: oup.krakow.wroclaw@gum.gov.pl
RAO-Krakow	Poland	Regional Assay Office Krakow; Chemical Laboratory Rakowicka 3 31-511, Krakow Contact person: Anna Hindan e-mail: oup.krakow.krakow@gum.gov.pl
RAO-Lodzi	Poland	Regional Assay Offiice Warszawa, Branch in Lodzi, Chemical Laboratory; Narutowicza 75 90-132, Lodz Contact person: Justina Pozycka e-mail: oup.warszawa.lodz@gum.gov.pl

DMDM	Serbia	Directorate for measures and precious metals; Control and supervision sector/Section for control of precious metals articles - Laboratory for precious metals; Mike Alasa 14, 11000 Belgrade Contact person: Danka Pavlović e-mail: danka@dmdm.rsl
SCA	Switzerland	Federal Customs Administration; Central Office for Precious Metals Control; Monbijoustrasse 40, 3003 Bern Contact person: Steeve Humbert e-mail: steeve.humbert@ezv.admin.ch
KGC	Turkey	Koza Gold Company; Ovacik Gold Mine Laboratory Ovacik Koyu pk14-15, Bergana / Izmir Contact person: Mustafa Akbay e-mail: mustafa.akbay@kozagold.com

For further information or questions please contact:

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