This document is a brief description of CBMM's procedures for ferroalloy manual sampling and niobium (Nb) content analysis. Part I addresses ferroniobium (FeNb) manual sampling that is based on ISO 4552-2:1987 (Ferroalloys: Sampling and Sample Preparation for Chemical Analysis) and ISO 3713:1987 (Ferroalloys: Sampling and Preparation of Samples – General Rules). Specific details about the procedures can be found in the respective ISO standards. Part II provides a brief description of automated sampling and the Nb analysis procedure established by CBMM. Part III contains the validation data of CBMM's procedures.

PART I - FeNb MANUAL SAMPLING

1. Manual Method of Increment Sampling

1.1. In manual sampling an increment is taken in a single motion at one time with a special scoop suitable for sampling constant masses.

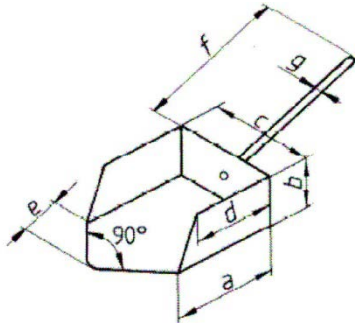

Figure 1: Illustration of a scoop for increment sampling (Source: ISO 3713:1987).

1.2 When sampling to determine the chemical composition of a consignment consisting of particles of different sizes, the size distribution of an increment corresponds to that of the consignment, which is known from the results of the sieve analysis.

1.3 In manual sampling of a ferroalloy in a stationary state, the sampling points are arrayed in a defined order on the surface. A crater is made at each sampling point and an increment is taken using a scoop along the walls of the crater in a straight-line, upward motion. The sampled ferroalloy may not over-fill the scoop. When using this method it is necessary to ensure that bias is not introduced.

2 Sampling a Consignment in Packaged Form

2.1. Sampling a packaged consignment is carried out in two stages. The first stage involves selecting the planned number of packaged units. The planned number of increments is taken from each packaged unit during the second stage.

2.2. Packaged units are selected by systematic sampling or by random sampling using tables of random numbers if the packaged units are numbered.

Table 1: Minimum number of increments and sampling precision*.

Mass of consignment, t		Mininum number of increments	Precision of sampling ± βs %(m/m)			
			FeTi	FeMo	FeW	FeNb
Over	Up to and including		Ti	Mo	W	Nb
40	64	28	0.23	-	-	-
25	40	24	0.25	-	-	-
16	25	20	0.27	0.29	0.29	0.25
10	16	17	0.29	0.32	0.32	0.27
5	10	14	0.32	0.35	0.35	0.29
3	5	11	0.36	0.39	0.39	0.33
1	3	9	0.40	0.43	0.43	0.37
0.5	1	7	0.45	0.49	0.49	0.42
	0.5	5	0.54	0.58	0.58	0.49

Table 2: Mass of increment*.

Nominal top size mm	Minimum mass of increment Kg				
	FeTi	FeMo	FeW	FeNb	FeV
>50	5.0	5.0	5.0	3.5	1.0
50	3.5	3.5	3.5	2.5	0.5
25	1.5	1.5	1.5	1.0	0.2
<10	0.5	0.5	0.5	0.2	0.2

*Source: ISO 4552-2:1987

2.3. Methods of sampling increments from packaged units comply with the steps described in item 1. above. Prior to increment sampling, it is recommended that the contents of the packaged unit be deposited onto a clean surface.

2.4. Increments taken from one consignment are combined into one gross sample.

2.5. If the number of increments is larger than the number of packages, it is necessary to take more than one increment in the same unit. To prevent biased results, sampling large numbers from the same bag is avoided.

Example: For a 5-tonnene lot with a top size of 50 mm, packaged in 20 drums of 250 kg, it is necessary to take 11 increments (11 drums sampled) with each increment containing at least 2.5 kg. The previously described sampling steps are then followed.

PART II – CBMM AUTOMATED SAMPLING

1. FeNb Sampling Method in the Crushing Plant

During crushing of the lot, the sample is collected automatically by following the weight parameters for lots larger than 5 tonnes and time for lots smaller than 5 tonnes, as described in Table 3.

Table 3: Acceptable minimum mass for the sample and respective cut numbers.

Tonnage	Lot top size	Minimum sample weight	Minimum number of increments
≥ 25.1 tonnes	≥ 50.0 mm	140 kg	28
	25.1 – 49.9 mm	100 kg	
	10.1 – 25.0 mm	70 kg	
	≤ 10.0 mm	40 kg	
5.0 to 25.0 tonnes	≥ 50.0 mm	100 kg	20
	25.1 – 49.9 mm	70 kg	
	10.1 – 25.0 mm	50 kg	
	≤ 10.0 mm	30 kg	
≤ 5.0 tonnes	≥ 50.0 mm	70 kg	11
	25.1 – 49.9 mm	50 kg	
	10.1 – 25.0 mm	40 kg	
	≤ 10.0 mm	20 kg	

Each sample increment weighs approximately 3.5 kg. The samples are collected from the conveyor belt after the classification process, intercepting the flow for a few seconds.

2. Comparison of CBMM's Automated Sampling and ISO 4552-2:1987 Manual Sampling

2.1 An analysis of 21 lots with different weights and sizes was used to compare manual and automated sampling. The Student's T-test was applied to verify the test hypothesis.

2.2. As shown in Table 4, the difference between the two different sampling methodologies was lower than the Student's T-test value, which means that the difference was not statistically significant and that automated sampling can be used as a reference method.

Table 4: Comparison of manual and automated sampling methodologies.

Lot	Weight (tonnes)	Size (mm)	Automated sampling (% Nb)	Manual sampling (% Nb)	di= xai-xbi	di^2
1	17.222	1-12.5	65.7	65.5	0.20	0.04
2	33.24	1-12.5	65.5	65.7	-0.20	0.04
3	53.29	1-12.5	64.6	65.0	-0.40	0.16
4	35	1-12.5	65.0	64.7	0.30	0.09
5	40	3-15	65.9	65.9	0.00	0.00
6	10	3-15	66.0	66.3	-0.30	0.09
7	24	5-30	66.1	66.3	-0.20	0.04
8	0.25	5-30	66.0	65.8	0.20	0.04
9	60	5-30	65.6	65.9	-0.30	0.09
10	4	5-30	64.8	64.6	0.20	0.04
11	6	5-30	65.4	65.4	0.00	0.00
12	6	5-30	65.3	64.7	0.60	0.36
13	5	5-30	65.5	65.6	-0.10	0.01
14	24	5-30	65.6	65.4	0.20	0.04
15	30	5-30	66.2	66.3	-0.10	0.01
16	24	5-50	65.7	66.0	-0.30	0.09
17	24	5-50	66.1	66.4	-0.30	0.09
18	24	5-50	65.5	65.4	0.10	0.01
19	24	5-50	65.6	65.4	0.20	0.04
20	40	3-15	64.9	64.8	0.10	0.01
21	30	5-30	66.2	66.3	-0.10	0.01
Total					**0.20**	**1.30**
K					**21**	
d					**0.00952381**	
vd					**0.06490476**	
to					**0.171**	
t tab (20; 0.025)					**2.086**	

PART II – ANALYSIS OF Nb CONTENT AND Fe CONTENT IN STANDARD FeNb

1. Analytical Methodology

CBMM analyzes Nb content in FeNb alloy by the inductively coupled plasma (ICP) method. The sample (< 100 mesh) is digested using acid mixture. Table 5 presents the analysis method for determining the specification of Fe and Nb in the FeNb alloys.

Table 5: Method specification.

Element	Nb	Fe	Mo (Internal Standard)
Wave Length (nm)	269.706	259.940	281.616
Plasma View	Radial		
Calibration Equation	Linear Bracketing		

2. Equipment

ICP Perkin Elmer Optima 7300 (equipment ANA-000101 and ANA-000117)

3. Sample Preparation

3.1. Divide the gross sample in 4 equal parts.
3.2. Crush 1 part of the sample to < 10 mm.
3.3. Divide this part until attaining 7 kg using a riffle divider.
3.4. Blend and crush the sample to < 5 mm.
3.5. Divide until reaching a sample of 1.2 kg.
3.6. Grind the 1.2-kg sample to < 100 mesh for instrumental analysis.

4. Sample Digestion

4.1. Weigh 0.400 g of the sample and 0.400 g MoO_3.
4.2. Dissolve the sample and MoO_3 in 20 mL acid mixture (350 mL HCl + 300 mL ultra pure water + 350 mL HF) and then add 3 mL HNO_3.
4.3. Heat the mixture on a hot plate at ~430° C for 10 min.
4.4. Cool at room temperature.
4.5. Transfer the solution quantitatively to a volumetric flask (100 mL) and complete the volume by adding purified water.

5. Calibration

5.1. ICP calibration should be performed using reference material prepared like the sample.
5.2. CBMM uses the EURO CECA 579/01 and ICRM F20/3 FeNb international standards. The standards are prepared from different weights, as described in Table 6.

Table 6: Calibration curve standards.

Standard Solution	Standard	Nb		Fe		Mo	Final Volume (mL)
		Concentration (% w/w)	Weight (g)	Concentration (% w/w)	Weight (g)	Weight (g)	
CECA 579/1 - 1	CECA 579/1	50.30	0.3200	-	-	0.4000	100
CECA 579/1 – 2	CECA 579/1	62.87	0.4000	-	-	0.4000	100
CECA 579/1 – 3	CECA 579/1	65.05	0.4139	-	-	0.4000	100
CECA 579/1 – 4	CECA 579/1	68.20	0.4339	-	-	0.4000	100
ICRM F20/3 - 1	ICRM F20/3	-	-	26.56	0.3190	0.4000	100
ICRM F20/3 – 2	ICRM F20/3	-	-	29.22	0.3510	0.4000	100
ICRM F20/3 - 3	ICRM F20/3	-	-	33.30	0.4000	0.4000	100
Verification Standard - Fe	SL 28/07	-	-	31.93	0.4000	0.4000	100
Verification Standard - Nb	NCS HC 18606	66.24	0.4000	-	-	0.400	100

6. Analysis

6.1. The calibration curve is performed for a maximum batch of seven samples and verified using the verification standards.
6.2. Three replicates are performed for samples.

7. Quality Control

7.1. The acceptable correlation coefficient for the calibration curve is at least 0.999.
7.2. The acceptance criterion for the reference standard result is that the difference between the conventional value and the result must be < 0.15% (absolute).
7.3. The recovery of the internal standard (Mo) should be 90% to 110%.
7.4. The acceptance criterion for the product analyses results is that the difference between the replicate values must be < 0.2% (absolute).

PART IV - VALIDATION OF Nb ANALYSIS IN STANDARD FeNb (DOQ-CGRE-008 – INMETRO)

1. Selectivity and Specificity

1.1. Specificity refers to a method that produces a response for only a single analyte, while the term selectivity refers to a method that provides responses for a number of chemical entities that may or may not be distinguished from each other.

1.2. Figure 2 shows that the Nb 269.701 nm and Mo 281.615 nm lines have no interferences for the main impurities of standard FeNb. This indicates that the ICP methodology is not specific for Nb, however it is selective when Nb 269.701 nm and Mo 281.615 nm wavelengths are used.

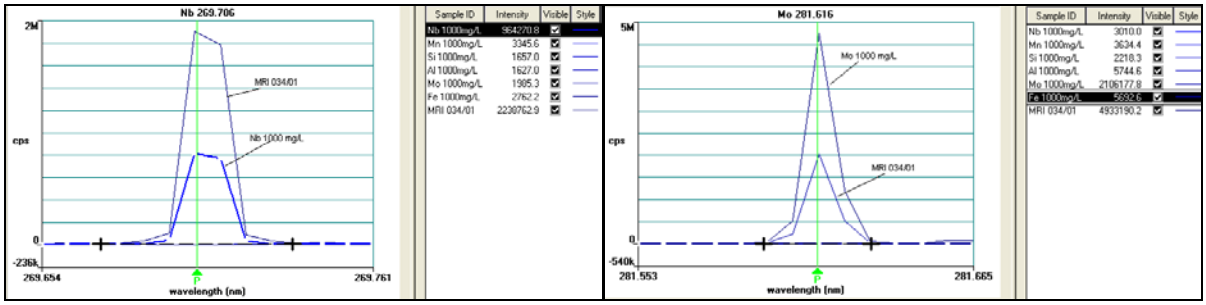

Figure 2: Nb and Mo peaks and interferences.

1.3. Figure 3 shows that the Fe 259.940 nm line has no interferences for the main impurities of standard FeNb. This indicates that the ICP methodology is selective when the Fe 259.940 nm wavelength is used.

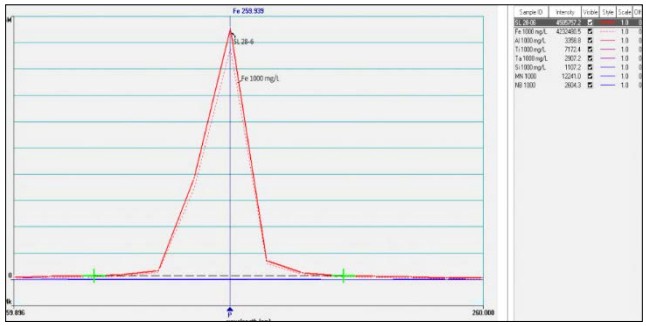

Figure 3: Fe peak and interferences.

1.4. For the selectivity test, two sample groups were prepared, a group with the sample matrix and another without the matrix. Both groups had identical concentrations of analytes of each concentration level of interest.

1.5. A Snedecor F-test and Student T-test were performed based on the results for comparison, adopting a 95% confidence level. The criteria used for the F-test ($F_{cal} < F_{tab}$) indicate that the variances are statistically equal. For the criteria adopted for the T-test ($T_{cal} < T_{tab}$), averages are statistically equal, the matrix did not have a significant effect on the result.

1.6 The results obtained in the selectivity test are shown in Table 7.

Table 7: Results obtained with the F-Snedecor test and Student t-test.

Analyte	Snedecor F-Test			Student T-Test		
	Fcal ANA-000101	Fcal ANA-000117	Ftab	Tcal ANA-000101	Tcal ANA-000117	ttab
Nb	1.03	1.02	4.28	0.594	0.895	1.782
Fe	1.01	1.25		**0.973**	**1.610**	

2. Linearity

2.1. The linearity of an analytical method is its ability to have a proportional result of analyte concentrations in samples within a given range or to be proportional by means of well-defined mathematical transformations. The linear correlation coefficient (R) is often used to indicate how much the line can be considered appropriate as a mathematical model.

2.2. The obtained linear correlation coefficient was greater than 0.995, indicating that the method is linear to Nb (43.9% to 68.45%) and Fe (26.0% to 37.15%).

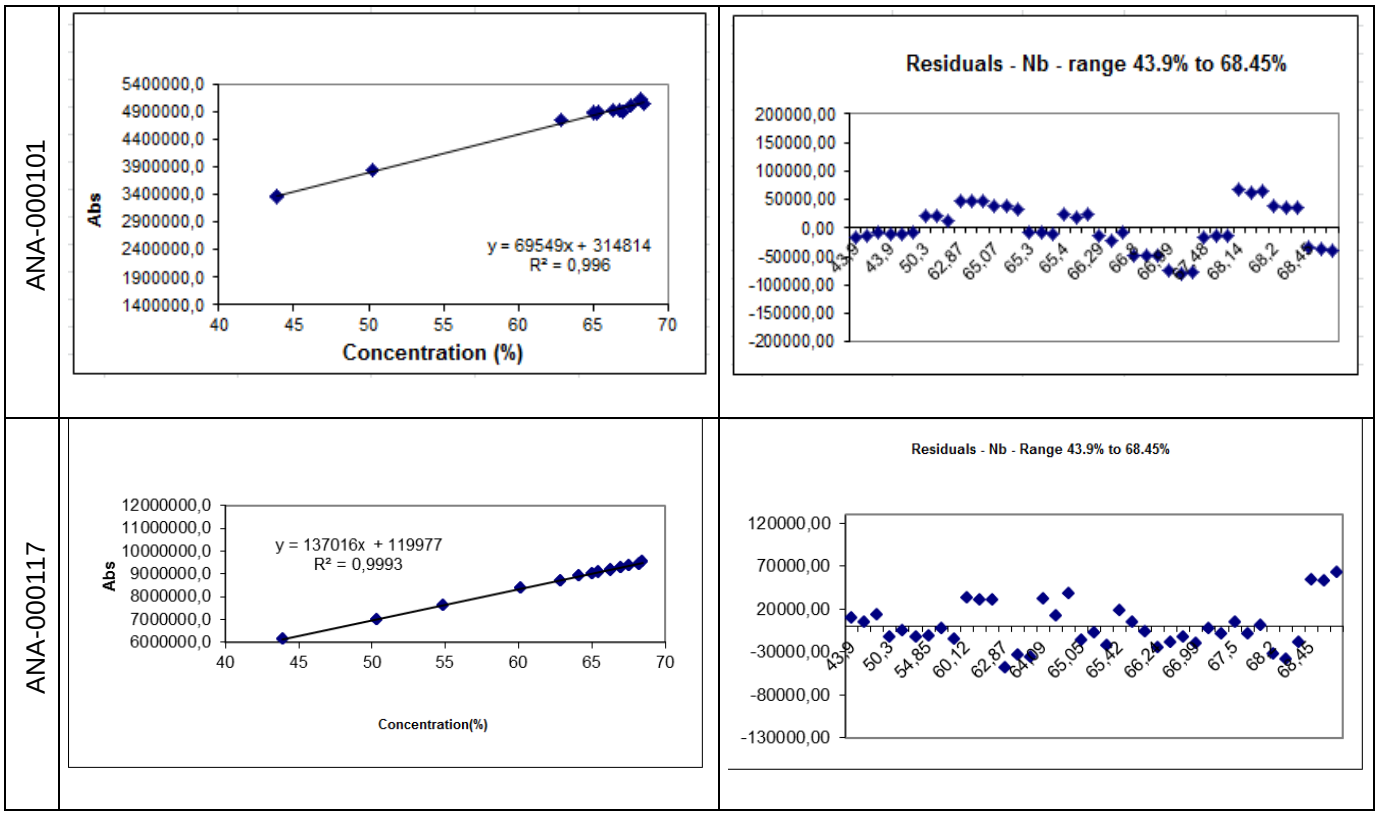

Figure 4: Linearity evaluation of Nb in FeNb.

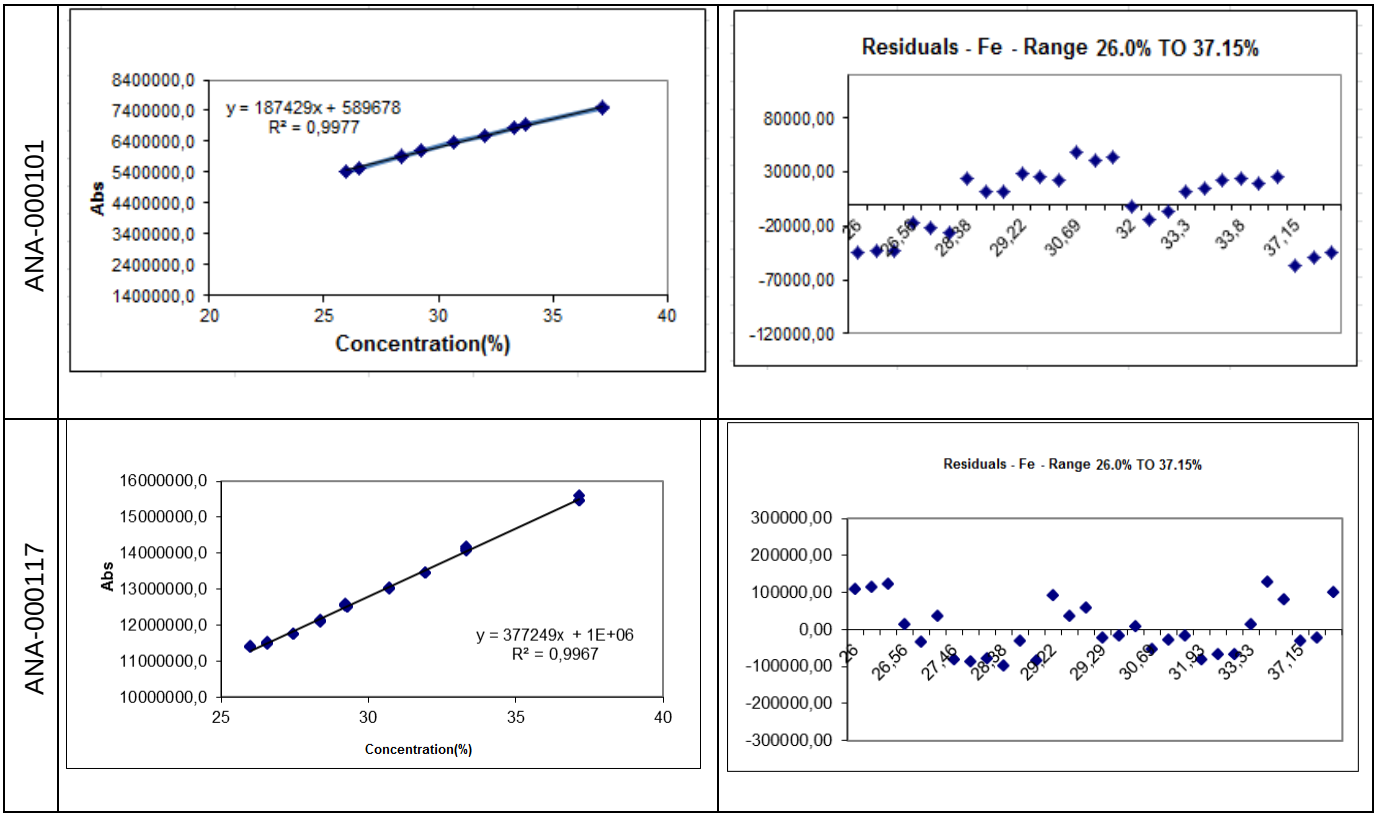

Figure 5: Linearity evaluation of Fe in FeNb.

3. Accuracy

3.1. The accuracy of a measurement system is the degree of measurement concordance of a quantity to that quantity's actual (true) value.

3.2. Comparing the measured value (mean value) and the true value (certificate value) in Table 7 illustrates that CBMM's methodology achieves the approval criteria, particularly in the 43.9% to 68.42% range for Nb and 26% to 37.15% for Fe. Some reference materials were prepared from different weights to obtain concentrations that apply to the entire range studied, as shown in Tables 8 and 9.

3.3. The acceptance criteria considered for the accuracy of Fe and Nb is 98% to 102%.

Table 8: Accuracy test results of certified materials and internal reference material for Nb.

Accuracy - Equipment ANA - 000101														
CRM or IRM	CECA 576-1	CECA 579-1	CECA 579-1	CECA 579-1	CECA 579-1	IRM 081/09	IRM 078/09	IRM 079/09	IRM 034/01	SL 28/03	IRM 082/09	JSS 755-2	CECA 579-1	IRM 083/09
Weight (g)	0.4000	0.2793	0.3200	0.4000	0.4140	0.4000	0.4000	0.4000	0.4000	0.4000	0.4000	0.4000	0.4339	0.4000
Real Value	43.9	43.9	50.3	62.87	65.07	65.3	65.4	66.29	66.8	66.99	67.48	68.14	68.2	68.45
Mens Value (average)	43.8	43.9	50.3	63.0	65.0	65.5	65.6	66.5	66.9	66.8	67.7	68.7	68.1	68.7
Accuracy	99.68%	99.97%	100.09%	100.15%	99.90%	100,31%	100.35%	100.35%	100.20%	99.66%	100.38%	100.84%	99.87%	100.32%

Accuracy - Equipment ANA - 000117															
CRM or IRM	CECA 576-1	CECA 579-1	CECA 579-1	SL 28/09	CECA 579-1	SL 28/07	SL 28/06	CECA 579-1	IRM 078/09	NCS 186069	IRM 068/07	SL 28/03	SL 28/11	CECA 579-1	IRM 083/09
Weight (g)	0.4000	0.3200	0.3490	0.4000	0.4000	0.4000	0.4000	0.4139	0.4000	0.4000	0.4000	0.4000	0.4000	0.4339	0.4000
Real Value	43.9	50.3	54,85	60.12	62.87	64.09	65.05	65.05	65.42	66.24	66.75	66.99	67.5	68.2	68.45
Mens Value (average)	43.68	50.06	54.73	60.39	62.71	64.23%	65.04	64.93	65.50	66.02	66.77	66.64	67.39	67.73	68.51
Accuracy	99.51%	99.53%	99.79%	100.45%	99.75%	100.21%	99.98%	99.81%	100.12%	99.67%	100.02%	99.48%	99.83%	99.31%	100.09%

***IRM: Internal reference material.**

Table 9: Accuracy test results of certified materials and internal reference material for Fe.

Accuracy - Equipment ANA - 000101													
CRM or IRM	SL 28/03	ICRM F20/3	SL 28/03	IRM 082/09	F 20/3	IRM 078/09	IRM 079/09	IRM 034/01	SL 28/06	SL 28/03	ICRM F20/3	SL 28/06	ICRM F20/1
Weight (g)	0.3660	0.3190	0.4000	0.4000	0.3510	0.4000	0.4000	0.4000	0.4000	0.4510	0.4000	0.4405	0.4000
Real Value	26.0	26.56	28.38	28.98	29.22	29.31	29.717	30.3	30.69	32.0	33.3	33.8	37.15
Mens Value (average)	25.9	26.5	28.4	29.2	29.2	29.7	29.9	30.7	30.8	31.8	33.3	33.8	36.8
Accuracy	99.71%	99.72%	100.21%	100.78%	100.03%	101.18%	100.64%	101.24%	100.31%	99.46%	99.94%	100.07%	99.18%

Accuracy - Equipment ANA - 000117										
CRM or IRM	SL 28/09	ICRM F20/3	SL 28/09	SL 28/03	ICRM F20/3	SL 28/11	SL 28/06	SL 28/07	ICRM F20/3	ICRM F20/1
Weight (g)	0.3787	0.3190	0.4000	0.4000	0.3510	0.4000	0.4000	0.4000	0.4000	0.4000
Real Value	26.0	26.56	27.46	28.38	29.22	29.29	30.69	31.93	33.3	37.15
Mens Value (average)	25.89	26.45	27.42	28.11	29.16	29.23%	30.72	31.92	33.30	36.68
Accuracy	99.57%	99.59%	99.87%	99.06%	99.81%	99.80%	100.09%	99.96%	99.99%	98.73%

***IRM: Internal reference material.**

4. Recovery

4.1. The recovery study was made using a FeNb sample with known additions in three concentration levels for Nb

and Fe.

4.2. The sample used in the recovery study for Nb was the FeNb sample 437189 and for Fe it was the FeNb sample 436941.

4.3. The equation used for the recovery calculation was:

$$Recovery\ (\%) = \left(\frac{C_1 - C_2}{C_3}\right) \times 100$$

Where:
C1 – measured concentration in the added sample
C2 – measured concentration in the sample without addition
C3 – added concentration

4.4. Table 10 and 11 show the obtained results. The acceptance criteria for the recovery study was 90%-110%.

Table 10: Obtained Nb recovery in FeNb sample 437189.

Nb Recovery							
Equipment	**Value without addition (% Nb)**	**Addition 1.57% Nb**		**Addition 4.02% Nb**		**Addition 5.28% Nb**	
		Meas.Value (% Nb)	**Recovery (%)**	**Meas.Value (% Nb)**	**Recovery (%)**	**Meas.Value (% Nb)**	**Recovery (%)**
ANA – 0000101	61.91	63.46	98.5	65.72	94.8	66.82	93.0
ANA – 0000117	61.88	63.48	101.9	65.65	93.8	66.87	94.1

Table 11: Obtained Fe recovery in FeNb sample 436941.

Fe Recovery							
Equipment	**Value without addition (% Fe)**	**Addition 0.87% Fe**		**Addition 1.75% Fe**		**Addition 3.53% Fe**	
		Meas.Value (%Fe)	**Recovery (%)**	**Meas.Value (%Fe)**	**Recovery (%)**	**Meas.Value (%Fe)**	**Recovery (%)**
ANA – 0000101	28.89	30.81	105.2	31.63	99.5	33.28	96.0
ANA – 0000117	29.71	30.63	105.8	31.45	99.4	33.21	99.2

5. Precision

5.1. Precision evaluates the dispersion of results of repeated independent assays of a single sample, similar samples or standards, under defined conditions.

5.2. Repeatability is obtained when the analysis is carried out in a laboratory by an operator using equipment in a short period of time. The repeatability limit enables the analyst to determine if the difference between sample analyses is significant using repeatability conditions. Tables 12 and 13 indicate that the repeatability limits for both pieces of equipment are ≤ 0.2%, which complies with CBMM internal criteria (difference between conventional value and the result is < 0.2% absolute).

Table 12: Repeatability for Nb on ICP-OES ANA-0000101 and ANA-0000117 equipment.

Repeatability - Equipment ANA - 000101														
CRM or IRM	CECA 576-1	CECA 579-1	CECA 579-1	CECA 579-1	CECA 579-1	IRM 081/09	IRM 078/09	IRM 079/09	IRM 034/01	SL 28/03	IRM 082/09	JSS 755-2	CECA 579-1	IRM 083/09
Weight (g)	0.4000	0.2793	0.3200	0.4000	0.4140	0.4000	0.4000	0.4000	0.4000	0.4000	0.4000	0.4000	0.4339	0.4000
Real Value	43.9	43.9	50.3	62.87	65.07	65.3	65.4	66.29	66.8	66.99	67.48	68.14	68.2	68.45
Sample 1	43.7	43.95	50.33	62.94	65.08	65.55	65.68	66.53	66.97	66.83	67.76	68.71	68.2	68.64
Sample 2	43.75	43.95	50.33	62.92	65.08	65.55	65.65	66.43	66.98	66.74	67.78	68.64	68.14	68.66
Sample 3	43.81	43.97	50.29	62.95	65.03	65.54	65.65	66.6	66.97	66.79	67.72	68.67	68.15	68.66
Sample 4	43.8	43.87	50.39	63.02	64.93	65.47	65.67	66.56	66.89	66.79	67.69	68.73	68.09	68.69
Sample 5	43.79	43.84	50.39	63.01	64.92	65.55	65.59	66.47	66.94	66.73	67.76	68.76	68.05	68.66
Sample 6	43.75	43.82	50.3	62.97	64.87	65.47	65.57	66.52	66.9	66.75	67.69	68.76	68.03	68.67
Sample 7	43.73	43.81	50.37	62.92	65.11	65.4	65.58	66.54	66.9	66.72	67.75	68.7	68.1	68.68
Average	43.76	43.89	50.34	62.96	65.00	65.50	65.63	66.52	66.94	66.76	67.74	68.71	68.11	68.67
Standard Deviation	0.040	0.068	0.041	0.041	0.095	0.059	0.046	0.056	0.039	0.040	0.036	0.045	0.059	0.016
RSD (%)	0.09%	0.15%	0.08%	0.06%	0.15%	0.09%	0.07%	0.08%	0.06%	0.06%	0.05%	0.07%	0.09%	0.02%
Repeatability Limit	0.11	0.19	0.12	0.11	0.27	0.16	0.13	0.16	0.11	0.11	0.10	0.13	0.17	0.05
Min Value	43.7	43.81	50.29	62.92	64.87	65.4	65.57	66.43	66.89	66.72	67.69	68.64	68.03	68.64
Max Value	43.81	43.97	50.39	63.02	65.11	65.55	65.68	66.6	66.98	66.83	67.78	68.76	68.2	68.69
Difference	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.2	0.0

Repeatability - Equipment ANA - 000117															
CRM or IRM	CECA 576-1	CECA 579-1	CECA 579-1	SL 28/09	CECA 579-1	SL 28/07	SL 28/06	CECA 579-1	IRM 078/09	NCS 186069	IRM 068/07	SL 28/03	SL 28/11	CECA 579-1	IRM 083/09
Weight (g)	0.4000	0.3200	0.3490	0.4000	0.4000	0.4000	0.4000	0.4139	0.4000	0.4000	0.4000	0.4000	0.4000	0.4339	0.4000
Real Value	43.9	50.3	54,85	60.12	62.87	64.09	65.05	65.05	65.42	66.24	66.75	66.99	67.5	68.2	68.45
Sample 1	43.77	50.12	54.86	60.4	62.74	64.29	65.16	64.91	65.56	66.03	66.8	66.75	67.52	67.82	68.59
Sample 2	43.69	50.07	54.79	60.45	62.7	64.25	65.05	64.92	65.52	66.06	66.76	66.64	67.44	67.78	68.49
Sample 3	43.67	50.05	54.71	60.36	62.73	64.24	65.03	64.98	65.51	66.04	66.74	66.65	67.41	67.73	68.48
Sample 4	43.66	50.04	54.75	60.38	62.75	64.2	64.99	64.95	65.47	66.08	66.81	66.6	67.36	67.71	68.43
Sample 5	43.68	50.06	54.67	60.37	62.74	64.22	65.07	64.96	65.51	66.01	66.73	66.65	67.36	67.69	68.55
Sample 6	43.67	50.04	54.66	60.39	62.67	64.18	64.99	64.91	65.44	65.96	66.73	66.6	67.3	67.7	68.51
Sample 7	43.65	50.06	54.69	60.38	62.67	64.2	64.99	64.87	65.46	65.97	66.79	66.58	67.31	67.69	68.51
Average	43.68	50.06	54.73	60.39	62.71	64.23	65.04	64.93	65.50	66.02	66.77	66.64	67.39	67.73	68.51
Standard Deviation	0.040	0.028	0.072	0.029	0.034	0.037	0.062	0.037	0.041	0.045	0.034	0.056	0.077	0.050	0.051
RSD (%)	0.09%	0.05%	0.13%	0.05%	0.05%	0.06%	0.10%	0.06%	0.06%	0.07%	0.05%	0.08%	0.11%	0.07%	0.07%
Repeatability Limit	0.11	0.08	0.20	0.08	0.10	0.10	0.17	0.10	0.12	0.12	0.10	0.16	0.22	0.14	0.14
Min Value	43.65	50.04	54.66	60.36	62.67	64.18	64.99	64.87	65.44	65.96	66.73	66.58	67.3	67.69	68.43
Max Value	43.77	50.12	54.86	60.45	62.75	64.29	65.16	64.98	65.56	66.08	66.81	66.75	67.52	67.82	68.59
Difference	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.2	0.2	0.1	0.2

Table 13: Repeatability for Fe on ICP-OES ANA-0000101 and ANA-0000117 equipment.

Repeatability - Equipment ANA - 000101													
CRM or IRM	SL 28/03	ICRM F20/3	SL 28/03	IRM 082/09	ICRM F20/3	IRM 078/09	IRM 079/09	IRM 034/01	SL 28/06	SL 28/03	ICRM F20/3	SL 28/06	ICRM F20/1
Weight (g)	0.3660	0.3190	0.4000	0.4000	0.3510	0.4000	0.4000	0.4000	0.4000	0.4510	0.4000	0.4405	0.4000
Real Value	26.0	26.56	28.38	28.98	29.22	29.31	29.717	30.3	30.69	32.0	33.3	33.8	37.15
Sample 1	25,92	26,52	28,32	29,22	29,24	29,67	29,94	30,69	30,84	31,85	33,26	33,86	36,81
Sample 2	25,93	26,5	28,26	29,23	29,23	29,66	29,94	30,69	30,77	31,79	33,27	33,83	36,85
Sample 3	25,93	26,48	28,26	29,18	29,22	29,66	29,92	30,68	30,79	31,83	33,31	33,86	36,87
Sample 4	25,9	26,44	28,32	29,17	29,21	29,65	29,93	30,68	30,82	31,79	33,29	33,81	36,87
Sample 5	25,96	26,47	28,3	29,2	29,23	29,67	29,94	30,66	30,79	31,81	33,27	33,78	36,83
Sample 6	25,92	26,49	28,49	29,21	29,26	29,66	29,84	30,69	30,78	31,85	33,29	33,82	36,85
Sample 7	25,92	26,5	28,75	29,23	29,22	29,63	29,84	30,64	30,71	31,86	33,28	33,8	36,85
Average	25.93	26.49	28.39	29.21	29.23	29.66	29.91	30.68	30.79	31.83	33.28	33.82	36.85
Standard Deviation	0,018	0.026	0.0178	0.024	0.016	0.014	0.046	0.019	0.041	0.029	0.017	0.030	0.021
RSD (%)	0.07%	0.10%	0.63%	0.08%	0.06%	0.05%	0.16%	0.06%	0.13%	0.09%	0.05%	0.09%	0.06%
Repeatability Limit	0.05	0.07	0.50	0.07	0.05	0.04	0.13	0.05	0.12	0.08	0.05	0.08	0.06
Min Value	25.9	26.44	28.26	29.17	29.21	29.63	29.84	30.64	30.71	31.79	33.26	33.78	36.81
Max Value	25.96	26.52	28.75	29.23	29.26	29.67	29.94	30.69	30.84	31.86	33.31	33.86	36.87
Difference	0.06	0.08	0.49	0.06	0.05	0.04	0.1	0.05	0.13	0.07	0.05	0.08	0.06

Repeatability - Equipment ANA - 000117										
CRM or IRM	SL 28/09	ICRM F20/3	SL 28/09	SL 28/03	ICRM F20/3	SL 28/11	SL 28/06	SL 28/07	ICRM F20/3	ICRM F20/1
Weight (g)	0.3787	0.3190	0.4000	0.4000	0.3510	0.4000	0.4000	0.4000	0.4000	0.4000
Real Value	26.0	2.56	27.46	28.38	29.22	29.29	30.69	31.93	33.3	37.15
Sample 1	25.9	26.49	27.43	28.12	29.16	29.25	30.7	31.95	33.31	36.73
Sample 2	25.9	26.44	27.45	28.11	29.16	29.27	30.74	31.91	33.3	36.68
Sample 3	25.88	26.45	27.41	28.12	29.17	29.26	30.73	31.92	33.29	36.69
Sample 4	25.9	26.46	27.41	28.11	29.18	29.23	30.7	31.92	33.31	36.68
Sample 5	25.88	26.44	27.41	28.13	29.19	29.22	30.76	31.92	33.28	36.65
Sample 6	25.86	26.43	27.42	28.11	29.13	29.19	30.7	31.88	33.27	36.64
Sample 7	25.89	26.45	27.44	28.1	29.16	29.21	30.7	31.92	33.32	36.68
Average	25.89	26.45	27.42	28.11	29.16	29.23	30.72	31.92	33.30	36.68
Standard Deviation	0.015	0.020	0.016	0.010	0.019	0.029	0.025	0.021	0.018	0.029
RSD (%)	0.06%	0.07%	0.06%	0.03%	0.07%	0.10%	0.08%	0.06%	0.05%	0.08%
Repeatability Limit	0.04	0.05	0.05	0.03	0.05	0.08	0.07	0.06	0.05	0.08
Min Value	25.86	26.43	27.41	28.1	29.13	29.19	30.7	31.88	33.27	36.64
Max Value	25.9	26.49	27.45	28.13	29.19	29.27	30.76	31.95	33.32	36.73
Difference	0.04	0.06	0.04	0.03	0.06	0.08	0.06	0.07	0.05	0.09

6. Intermediate Precision

6.1. Intermediate precision is related to the variation in results observed when one or more factors, such as time, equipment and operator are evaluated in the laboratory.

6.2. Table 14 shows intermediate precision results for Nb and Table 15 shows intermediate precision for Fe, considering factors such as time and analyst.

6.3. The acceptance criteria for the accuracy of Nb and Fe is 98% to 102%.

Table 14: Intermediate precision for Nb on ICP-OES ANA-0000101 equipment.

Analyst	Standard	SL28-03 (0.3759 g)	SL28-06 (0.4000g)	IRM 079/09 (0.4000g)	SL28-03 (0.4000g)	IRM 082/09 (0.4000g)	IRM 083/09 (0.4000g)
	Reference Value	**62.95**	**65.05**	**66.3**	**66.99**	**67.5**	**68.5**
Analyst 1	Sample 1	62.88	64.96	66.15	66.59	67.68	68.63
	Sample 2	62.89	64.95	66.12	66.63	67.64	68.62
	Sample 3	62.87	64.91	66.12	66.61	67.65	68.59
	Sample 4	62.86	64.92	66.13	66.62	67.63	68.59
	Sample 5	62.87	64.9	66.09	66.61	67.62	68.59
	Sample 6	62.86	64.92	66.1	66.61	67.56	68.59
	Sample 7	62.89	64.92	66.25	66.55	67.59	68.57
Analyst 2	Sample 1	62.8	64.76	66.23	66.88	67.39	68.72
	Sample 2	62.83	64.82	66.2	66.9	67.39	68.7
	Sample 3	62.83	64.84	66.21	66.88	67.33	68.66
	Sample 4	62.86	65.1	66.24	66.88	67.42	68.39
	Sample 5	62.86	64.9	66.23	66.87	67.42	68.62
	Sample 6	62.83	64.86	66.21	66.89	67.37	68.63
	Sample 7	62.84	65.09	66.24	66.86	67.43	68.62
Analyst 3	Sample 1	62.94	65.09	66.17	66.64	67.64	68.67
	Sample 2	62.94	65.04	66.11	66.59	67.54	68.61
	Sample 3	62.63	65.02	66.06	66.62	67.56	68.63
	Sample 4	62.89	65.04	66.01	66.65	67.54	68.59
	Sample 5	62.9	65.04	65.99	66.62	67.57	68.58
	Sample 6	62.91	65.03	65.94	66.66	67.55	68.55
	Sample 7	62.89	65.03	65.93	66.64	67.57	68.6
Analyst 4	Sample 1	62.87	65.11	66.16	66.68	67.79	68.62
	Sample 2	62.85	65.07	66.13	66.65	67.79	68.65
	Sample 3	62.85	65.13	66.11	66.69	67.8	68.64
	Sample 4	62.85	65.13	66.13	66.65	67.78	68.68
	Sample 5	62.83	65.11	66.24	66.67	67.82	68.69
	Sample 6	62.8	65.08	66.21	66.65	67.8	68.68
	Sample 7	62.89	65.06	66.16	66.66	67.82	68.66
Average		**62.86**	**64.99**	**66.14**	**66.69**	**67.60**	**68.62**
Standard Deviation		**0.057**	**0.104**	**0.089**	**0.113**	**0.151**	**0.062**
RSD (%)		**0.09%**	**0.16%**	**0.13%**	**0.17%**	**0.22%**	**0.09%**
Reproducibility limit		**0.16**	**0.29**	**0.25**	**0.32**	**0.42**	**0.17**
Accuracy (%)		**99.95%**	**100.11%**	**99.83%**	**100.22%**	**100.01%**	**100.07%**

Table 15: Intermediate precision for Fe on ICP-OES ANA-0000101 equipment.

Analyst	Standard	SL28-03 (0.3759g)	SL28-03 (0.4000g)	SL28-06 (0.4000g)	SL28-03 (0.4510g)
	Reference Value	**26.60**	**28.38**	**30.69**	**32.00**
Analyst 1	Sample 1	26.59	28.3	30.66	31.83
	Sample 2	26.59	28.28	30.67	31.84
	Sample 3	26.57	28.28	30.67	31.84
	Sample 4	26.55	28.27	30.69	31.85
	Sample 5	26.55	28.25	30.69	31.83
	Sample 6	26.55	28.24	30.67	31.79
	Sample 7	26.56	28.24	30.65	31.76
Analyst 2	Sample 1	26.55	28.3	30.62	31.79
	Sample 2	26.57	28.3	30.67	31.85
	Sample 3	26.57	28.29	30.69	31.82
	Sample 4	26.58	28.3	30.77	31.82
	Sample 5	26.58	28.28	30.73	31.79
	Sample 6	26.58	28.3	30.7	31.81
	Sample 7	26.57	28.28	30.76	31.79
Analyst 3	Sample 1	26.58	28.21	30.78	31.82
	Sample 2	26.56	28.19	30.77	31.81
	Sample 3	26.46	28.22	30.78	31.78
	Sample 4	26.55	28.24	30.79	31.78
	Sample 5	26.55	28.24	30.78	31.8
	Sample 6	26.56	28.23	30.78	31.81
	Sample 7	26.54	28.28	30.79	31.82
Average		**26.56**	**28.26**	**30.72**	**31.81**
Standard Deviation		**0.027**	**0.033**	**0.056**	**0.025**
RSD (%)		**0.10%**	**0.12%**	**0.18%**	**0.08%**
Reproducibility limit		**0.08**	**0.09**	**0.16**	**0.07**
Accuracy (%)		**99.85%**	**99.59%**	**100.10%**	**99.41%**

7. Robustness

7.1. The robustness of a method measures its sensitivity to small changes. A method is robust when it is not sensitive to small variations that may occur during testing.

7.2. Table 16 lists the factors for determining the robustness of Nb and Fe determination in FeNb using the ICP method and the variations performed.

Table 16: Variation factors used to study robustness.

Factor		Nominal	Variation
A	Radio frequency (lowest)	1350	1300
B	Delay time (lowest)	30s	15s
C	Flush time (lowest)	25s	15s
D	Integration time (manual)	Automated (1/10)	0.005/1
E	Plasma (lowest)	20	15
F	Background (closed)	-	-
G	Nebulization (lowest)	0.8	0.6

7.3. As shown in Tables 17 and 18, there was no variation, indicating that the developed method is robust.

Table 17: Robustness for Nb.

Element	Niobium							
Result	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
	65.22	65.29	65.2	65.23	65.22	65.2	65.26	65.18
Combination	Average Nominal Factor		Average Variation Factor		Difference		Average	
A or a	65.24		65.22		0.02			
B or b	65.22		65.22		0.0		65.22	
C or c	65.23		65.22		0.015		Standard Deviation	
D or d	65.22		65.24		-0.020		0.035	
E or e	65.2		65.25		-0.05			
F or f	65.21		65.24		-0.025			
G or g	65.23		65.22		0.005			

Table 18: Robustness for Fe.

Element	Iron							
Result	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
	30.75	30.78	30.83	30.79	30.76	30.81	30.88	30.8
Combination	Average Nominal Factor		Average Variation Factor		Difference		Average	
A or a	30.79		30.81		-0.025			
B or b	30.80		30.80		0.010		30.80	
C or c	30.78		30.82		-0.05		Standard Deviation	
D or d	30.81		30.79		0,020		0.041	
E or e	30.80		30.80		-0.005			
F or f	30.78		30.82		-0.05			
G or g	30.81		30.79		0,015			

8. Participation in Proficiency Testing

8.1. Proficiency Test 0912 – FeNb STD

8.1.1. Proficiency test 0912 was organized by the Institute Fur Eignungsprufung GmbH (IfEP). Ten laboratories from six different countries participated in the testing, Table 19. Four of the participants were accredited on the ISO/IEC 17025 and one participant remained anonymous.

Table 19: Proficiency test 0912 participating laboratories – FeNb STD (IfeP).

Laboratory	Country
Alfred H. Knight Internaticional	England
Alternative Testing Laboratories, Inc.	USA
OCAS	Belgium
PLANSEE SE	Austria
Salzgitter Flachstahl GmbH	Germany
ThyssenKrupp Steel AG	Germany
Villares Metals S.A	Brazil
Volkswagen AG Nutzfahrzeuge	Germany
Companhia Brasileira de Metalurgia e Mineração	Brazil
Anonymous	Unknown

8.1.2. CBMM's identification number on this proficiency test was 646 and the result was satisfactory, as shown in Figure 6.

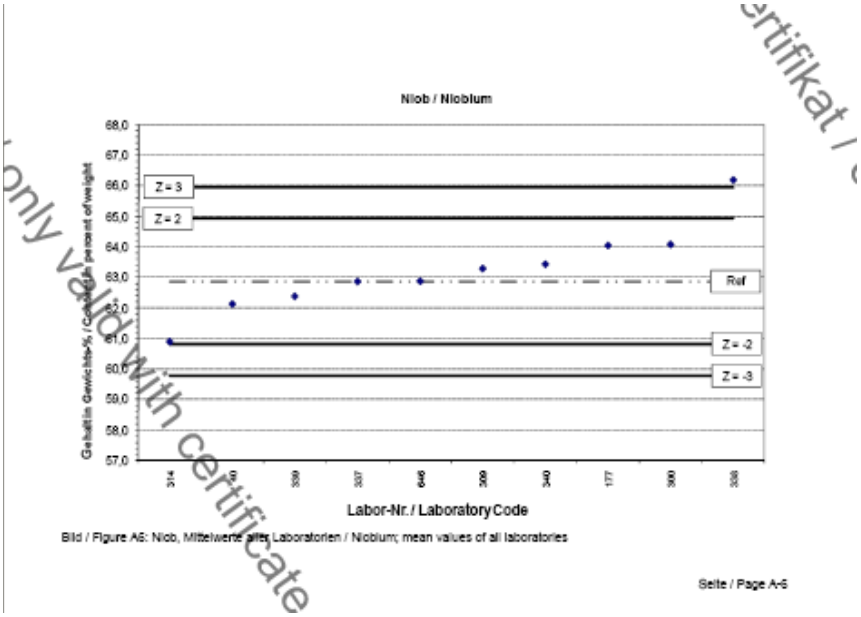

Figure 6: Laboratory results on proficiency test 0912 – FeNb STD – Nb.

8.2. **Proficiency Test 1115 – FeNb STD**

8.2.1. Proficiency test 1115 was organized by the IfEP in 2011/2012. Six laboratories from four different countries participated in the testing, Table 20. Four participants were accredited on ISO/IEC 17025.

Table 20: Laboratory participants of Proficiency Test 1115 – FeNb STD (IfeP) for location

Number of Participating Laboratories	Country
1	USA
1	Belgium
3	Austria
1	Brazil

8.2.2. CBMM's identification number on this proficiency test was 271. Two samples were sent for Nb and Fe analyses. As shown in Figures 7 and 8, the results were satisfactory for Nb and questionable for Fe. Actions were taken to improve the Fe analysis and the problem was solved.

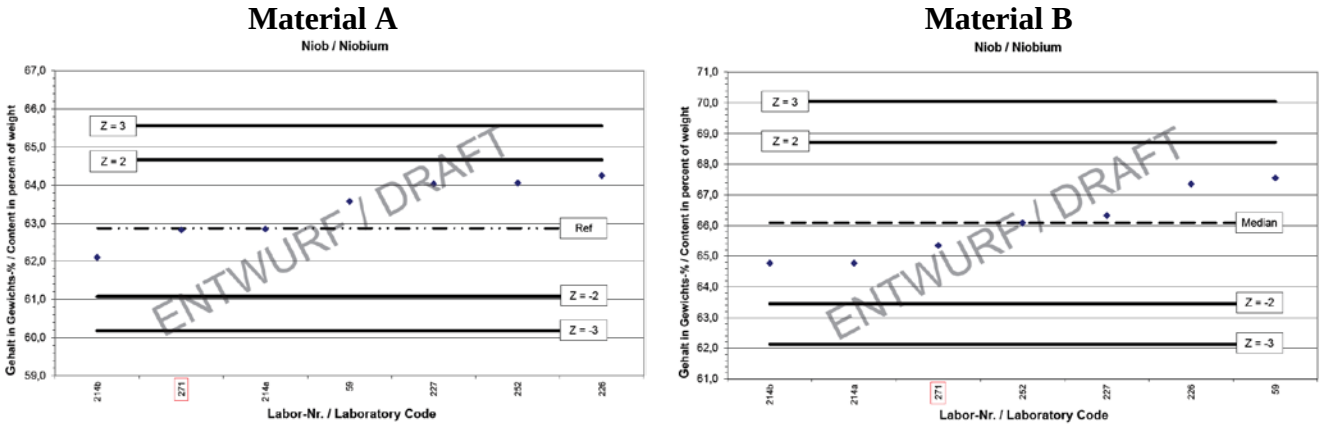

Figure 7: Laboratory results on proficiency test 1115 – FeNb STD – Nb.

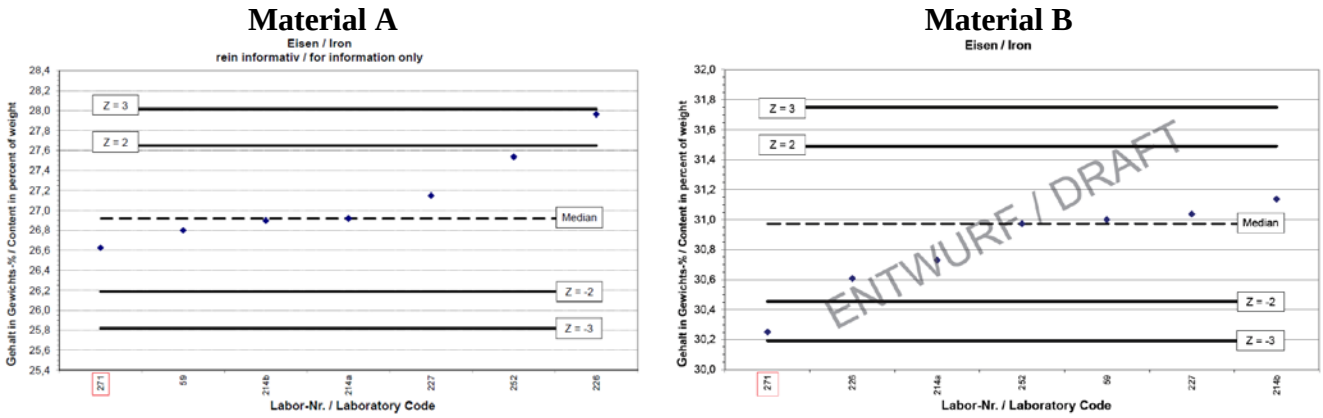

Figure 8: Laboratory results on proficiency test 1115 – FeNb STD – Fe.

9. Uncertainty According to EURACHEM/CITAC Guide CG 4 – Quantifying Uncertainty in Analytical Measurement

9.1. In order to decide whether a result indicates compliance or non-compliance with a specification, it is necessary to take into account the measurement uncertainty associated with the result.

9.2. Definition: A parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

9.3. To estimate the overall uncertainty, it may be necessary to report each source of uncertainty and treat it separately to obtain the contribution from that source.

9.4. CBMM's main uncertainty sources are shown in Figure 9.

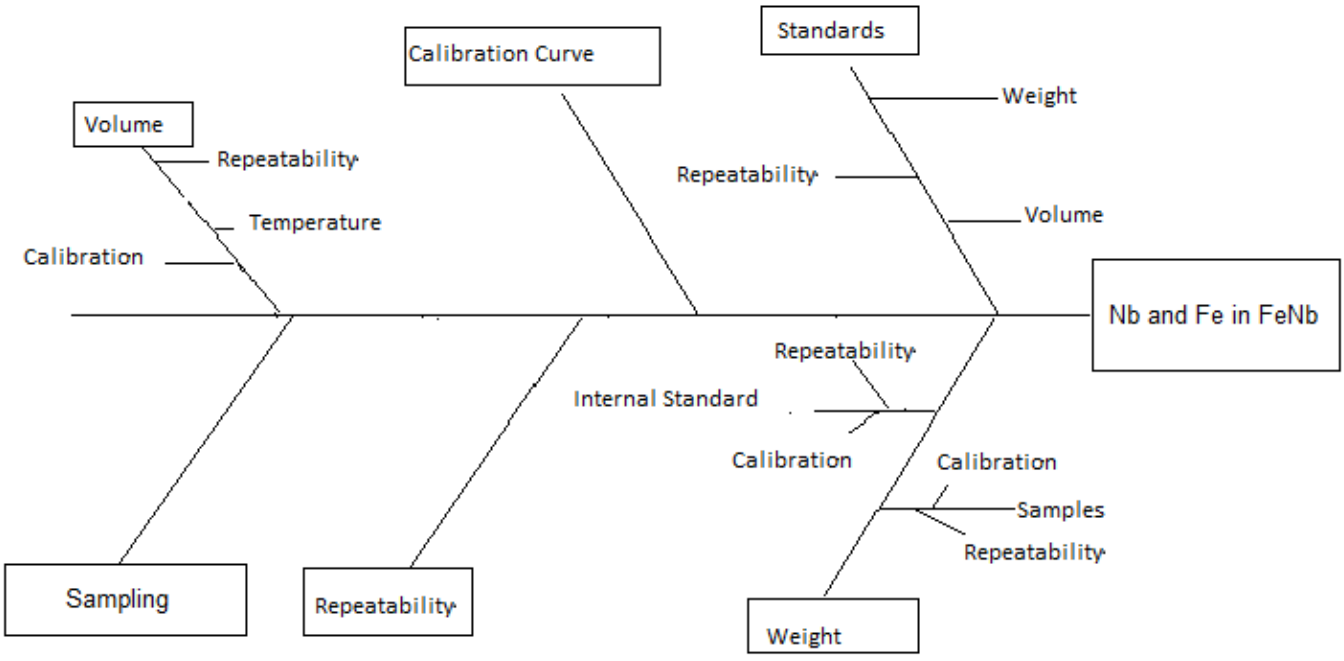

Figure 9: Uncertainty sources.

9.5. The expanded uncertainty is +/- 0.2% for the entire range from 62.9% Nb to 68.1% Nb and 26.0% Fe to 33.3% Fe, as shown in Tables 21 and 22.

Table 21: Expanded uncertainty for the 62.9% Nb to 68.1% Nb range.

Nb Content (%)	Expanded Uncertainty (%)	Coverage Factor (k)
62.9	0.2	1.96
65.1	0.2	1.96
65.4	0.2	1.96
66.3	0.2	1.96
66.8	0.2	1.96
67.0	0.2	1.96
68.2	0.2	1.96
68.4	0.2	1.96

Table 22: Expanded uncertainty for the 26.0% Fe to 33.3% Fe range.

Nb Content (%)	Expanded Uncertainty (%)	Coverage Factor (k)
26.0	0.2	1.96
26.6	0.2	1.96
28.4	0.2	1.96
29.0	0.2	1.96
29.2	0.2	1.96
30.3	0.2	1.96
33.3	0.2	1.96

10. Conclusions

10.1. The inductively coupled plasma (ICP) methodology is not specific for Nb and Fe. However, it is selective when Nb 269.701 nm, Mo 281.615 nm and Fe 259.940 nm wavelengths are used.

10.2. The selectivity tests indicate that the matrix does not influence Fe and Nb results. But, the option was made to use certified reference material (CRM) in the FeNb matrix for the preparation of the calibration curve

10.3. CBMM's methodology achieves the approved criteria for accuracy for the entire 43.9% to 68.4% Nb range and the 26.0% to 37.2% Fe range. For CBMM's products, the accuracy results are near 100%.

10.4. The addition tests show satisfactory recovery of Nb and Fe, with limits between 90% to 110%.

10.5. The repeatability limits for ANA-000101 and ANA-000117 equipment for Nb and Fe are below 0.2%, which is in compliance with internal CBMM criteria (the difference between the conventional value and the result is < 0.2% absolute).

10.6. The intermediate precision studies obtained for Nb and Fe indicate accuracy close to 100% in accordance with internal CBMM criteria (accuracy 98% to 102%).

10.7. The evaluation made by visual analysis of the residual graph and linearity (correlation coefficient of 0.995) confirms that the ICP methodology can be considered linear from 43.9% Nb to 68.4% Nb and from 26.0% to 37.2% Fe.

10.8. CBMM's Laboratory achieved a satisfactory index for all parameters analyzed on interlaboratory 0912 – FeNb STD conducted by IfEP.

10.9. CBMM's Laboratory obtained a questionable finding for the Fe result in the B material on interlaboratory 1115 – FeNb STD conducted by IfEP. Actions were taken to improve the Fe analysis and the problem was solved. The results were satisfactory for all other parameters.

10.10. The difference between the two sampling methodologies (manual following ISO 4552-2:1987 and CBMM's automated sampling) was lower than the Student's T-test value, indicating that the difference is not statistically significant and that CBMM's automated sampling can be used as a reference method.

10.11. The expanded uncertainty is +/- 0.2% for the entire range from 43.9% Nb to 68.2% Nb.

10.12. The expanded uncertainty is +/- 0.2% for the entire range from 26.0% Fe to 37.2% Fe.