This document is a brief description of CBMM's procedures for ferroalloy manual sampling and Nb content analysis. Part I addresses 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 automatic 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.

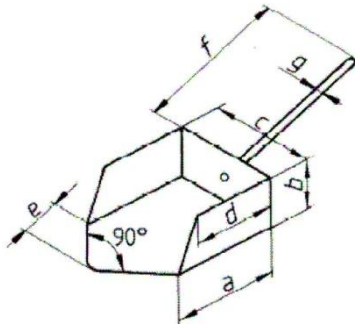

Figure 1: Illustration of a scoop for increment sampling (Source: ISO 3713:1987).

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 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 #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-tonne 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 AUTOMATIC SAMPLING AND ANALYSIS OF Nb CONTENT IN STANDARD FeNb

1. FeNb - Sampling Method in the Crushing Plant

During crushing of the lot, the sample is collected automatically at timed intervals depending on the tonnage of the lot, as described below:

Tonnage	Time intervals between increments
≥ 50	8 min.
30-49.9	6 min.
10-29.9	4 min.
2-9.9	2 min.
≤ 1.9	1 min.

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

2. 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 and the element Nb is analyzed by ICP at the 269.701-nm line with Mo 281.615 nm used as an internal standard.

3. Equipment

ICP Perkin Elmer Optima 4300, ICP Optima 5300 and ICP Optima 7300.

4 Sample Preparation

4.1. Divide the gross sample in 4 equal parts.
4.2. Crush 1 part of the sample to < 10 mm.
4.3. Divide this part until attaining 7 kg using a riffle divider.
4.4. Blend and crush the sample to < 5 mm.
4.5. Divide until reaching a sample of 1.2 kg.
4.6. Grind the 1.2-kg sample to < 100 mesh for instrumental analysis.

5. Sample Digestion

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

6. Calibration

6.1. ICP calibration should be performed using reference material prepared like the sample.
6.2. CBMM uses the following FeNb international standards: EURO CECA 579/01 (62.9% Nb), EURO CECA 579/01 (65.1% Nb) and JSS 755-2 (68.1% Nb).

7. Analysis

7.1. Verify every 4 analyses with an internal reference standard.
7.2. Perform at least 3 replicates for consignments < 80 tonnes.
7.3. Perform at least 6 replicates for consignments > 80 tonnes.

8. Quality Control

8.1. The acceptance criterion for the reference standard result is that the difference between the conventional value and the result must be < 0.2% (absolute).
8.2. The acceptance criterion for the product analyses results is that the difference between the replicate values must be < 0.2% (absolute).

PART III - 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.

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.

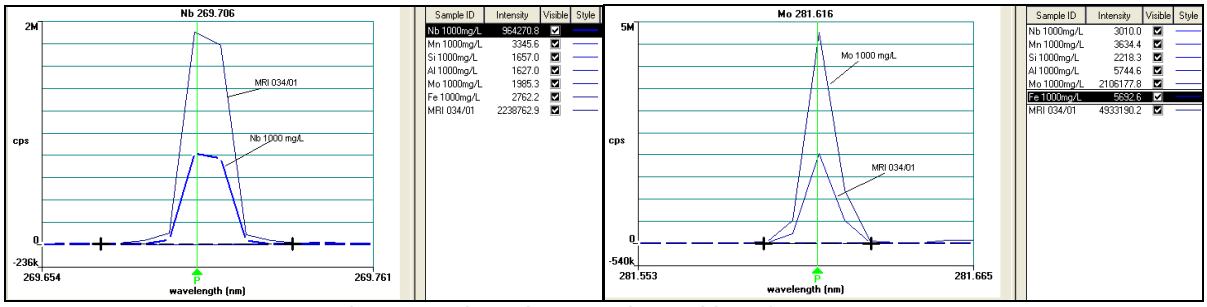

Figure 2: Nb and Mo peaks and interferences.

2. Accuracy

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

2.2 Comparing the measured value (mean value) and the true value (certificate value) in Table 3 illustrates that CBMM's methodology achieves the approval criteria, particularly in the 62.9% to 68.42% range, which corresponds to the Nb content of CBMM's products. Results in this range are near 100%.

Table 3: Accuracy test results of certified materials and an internal control sample (IRM* 034/01. 81/09. 82/09. 83/09)

Accuracy										
	CRM 576-1	NBS	F/20	CRM 579-1	SL 28-06	IRM 034/01	JSS 755-1	IRM 081/09	IRM 082/09	IRM 083/09
Real Value	43.9	57.51	57.28	62.87	65.05	66.8	68.14	65.4	67.6	68.42
ICP 4300	45.67	58.15	58.44	62.84	64.94	66.63	68.08	65.10	68.29	67.39
Accuracy	104.02%	101.12%	102.03%	99.95%	99.83%	99.75%	99.91%	99.54%	101.03%	98.49%
ICP 5300	46.21	58.43	58.67	62.90	64.98	66.68	68.03	65.40	67.74	68.48
Accuracy	105.26%	101.60%	102.43%	100.05%	99.89%	99.82%	99.84%	100.00%	100.21%	100.09%
ICP 7300	46.00	58.32	58.58	62.87	65.01	66.80	68.12	65.19	67.45	68.28
Accuracy	104.78%	101.40%	102.28%	99.99%	99.94%	100.00%	99.97%	99.68%	99.77%	99.80%
Critical Decision (%)	98-102	98-102	98-102	98-102	98-102	98-102	98-102	98-102	98-102	98-102

*Internal reference material.

3. Precision

3.1. Precision evaluates the dispersion of results of repeated independent assays of a single sample, similar samples or standards, under defined conditions. The precision of the internal method was evaluated using internal reference material (IRM).

3.2. 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 4 and 5 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 4: Repeatability (ICP* 4300 and 5300)

Repeatability												
	ICP 4300						ICP 5300					
Sample	IRM 078/09	IRM 079/09	IRM 080/09	IRM 081/09	IRM 082/09	IRM 083/09	IRM 078/09	IRM 079/09	IRM 080/09	IRM 081/09	IRM 082/09	IRM 083/09
Sample 1	65.4	66.2	65.4	65.4	67.5	68.4	65.5	66.3	65.4	65.3	67.4	68.4
Sample 2	65.4	66.3	65.3	65.4	67.6	68.3	65.4	66.1	65.6	65.4	67.5	68.4
Sample 3	65.4	66.3	65.3	65.2	67.6	68.4	65.5	66.1	65.5	65.4	67.4	68.4
Sample 4	65.4	66.2	65.3	65.4	67.6	68.4	65.4	66.1	65.5	65.4	67.6	68.5
Sample 5	65.5	66.2	65.4	65.3	67.5	68.5	65.4	66.1	65.5	65.2	67.5	68.5
Sample 6	65.4	66.2	65.4	65.3	67.5	68.5	65.4	66.1	65.5	65.3	67.6	68.5
Sample 7	65.4	66.2	65.4	65.4	67.4	68.5	65.4	66.2	65.5	65.4	67.6	68.4
Average	**65.4**	**66.2**	**65.4**	**65.3**	**67.5**	**68.4**	**65.4**	**66.2**	**65.5**	**65.3**	**67.5**	**68.4**
STD	**0.029**	**0.040**	**0.045**	**0.052**	**0.064**	**0.081**	**0.058**	**0.063**	**0.053**	**0.069**	**0.059**	**0.067**
RSD	**0.045**	**0.061**	**0.069**	**0.080**	**0.095**	**0.118**	**0.089**	**0.096**	**0.082**	**0.106**	**0.088**	**0.098**
Repeatability Limit	**0.08**	**0.11**	**0.13**	**0.15**	**0.18**	**0.23**	**0.16**	**0.18**	**0.15**	**0.19**	**0.17**	**0.19**
Max	**65.5**	**66.3**	**65.4**	**65.4**	**67.6**	**68.5**	**65.5**	**66.3**	**65.6**	**65.4**	**67.6**	**68.5**
Min	**65.4**	**66.2**	**65.3**	**65.2**	**67.4**	**68.3**	**65.4**	**66.1**	**65.4**	**65.2**	**67.4**	**68.4**
Difference	**0.08**	**0.11**	**0.12**	**0.15**	**0.18**	**0.20**	**0.18**	**0.17**	**0.16**	**0.18**	**0.16**	**0.16**

*Inductively coupled plasma.

Table 5: Repeatability (ICP* 7300)

Repeatability						
	ICP 7300					
Sample	IRM 078/09	IRM 079/09	IRM 080/09	IRM 081/09	IRM 082/09	IRM 083/09
Sample 1	65.6	66.1	65.4	65.3	67.5	68.3
Sample 2	65.5	66.1	65.5	65.2	67.5	68.3
Sample 3	65.5	66.0	65.4	65.3	67.5	68.3
Sample 4	65.4	66.0	65.4	65.3	67.5	68.3
Sample 5	65.6	66.2	65.4	65.3	67.5	68.3
Sample 6	65.5	66.2	65.4	65.3	67.4	68.3
Sample 7	65.5	66.2	65.4	65.2	67.5	68.3
Average	**65.5**	**66.1**	**65.4**	**65.3**	**67.5**	**68.3**
STD	**0.054**	**0.087**	**0.037**	**0.049**	**0.029**	**0.029**
RSD	**0.082**	**0.132**	**0.056**	**0.075**	**0.043**	**0.042**
Repeatability Limit	**0.15**	**0.24**	**0.10**	**0.14**	**0.08**	**0.08**
Max	**65.6**	**66.2**	**65.5**	**65.3**	**67.5**	**68.3**
Min	**65.4**	**66.0**	**65.4**	**65.2**	**67.4**	**68.3**
Difference	**0.15**	**0.21**	**0.10**	**0.10**	**0.10**	**0.07**

*Inductively coupled plasma.

4. Linearity

4.1 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.

4.2 The evaluation made by visual analysis of the graph and the linearity result of 0.998 (shown in Figure 3) confirms that the ICP methodology can be considered linear from 43.9% Nb to 68.1% Nb.

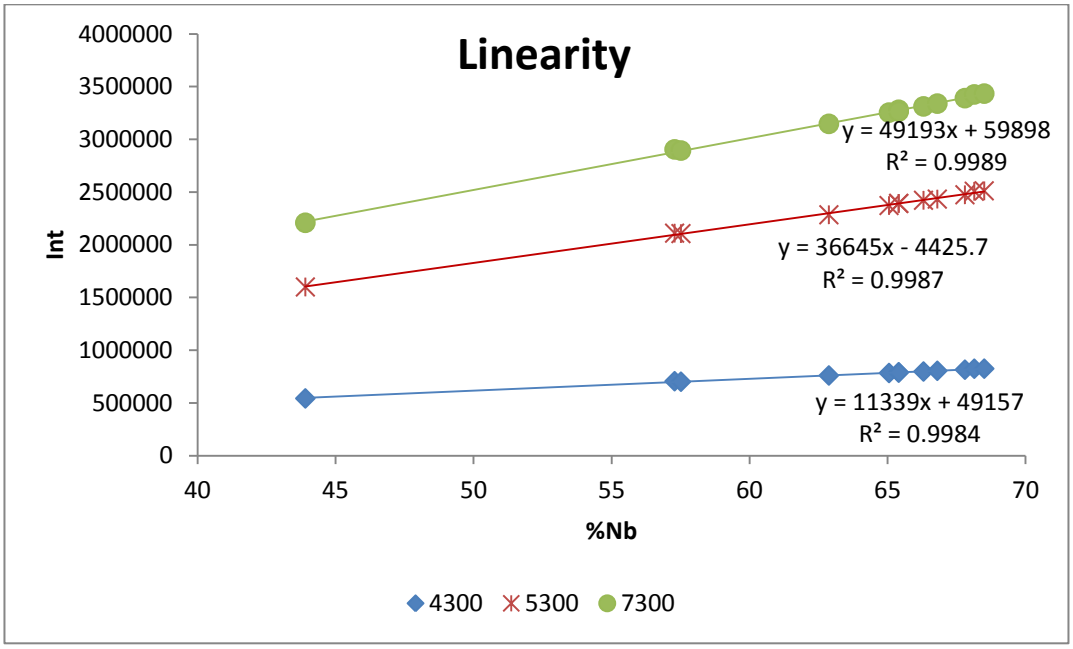

Figure 3: Linearity evaluation of Nb in FeNb using ICP (4300, 5300, 7300).

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

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

5.2 As shown in Table 6, 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 automatic sampling can be used as a reference method.

Table 6: Comparison of manual and automatic sampling methodologies.

Lot	Weight (tonnes)	Size (mm)	Automatic 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**	

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

6.1 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.

6.2 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.

6.3 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.

6.4. CBMM's main uncertainty sources are shown in Figure 4.

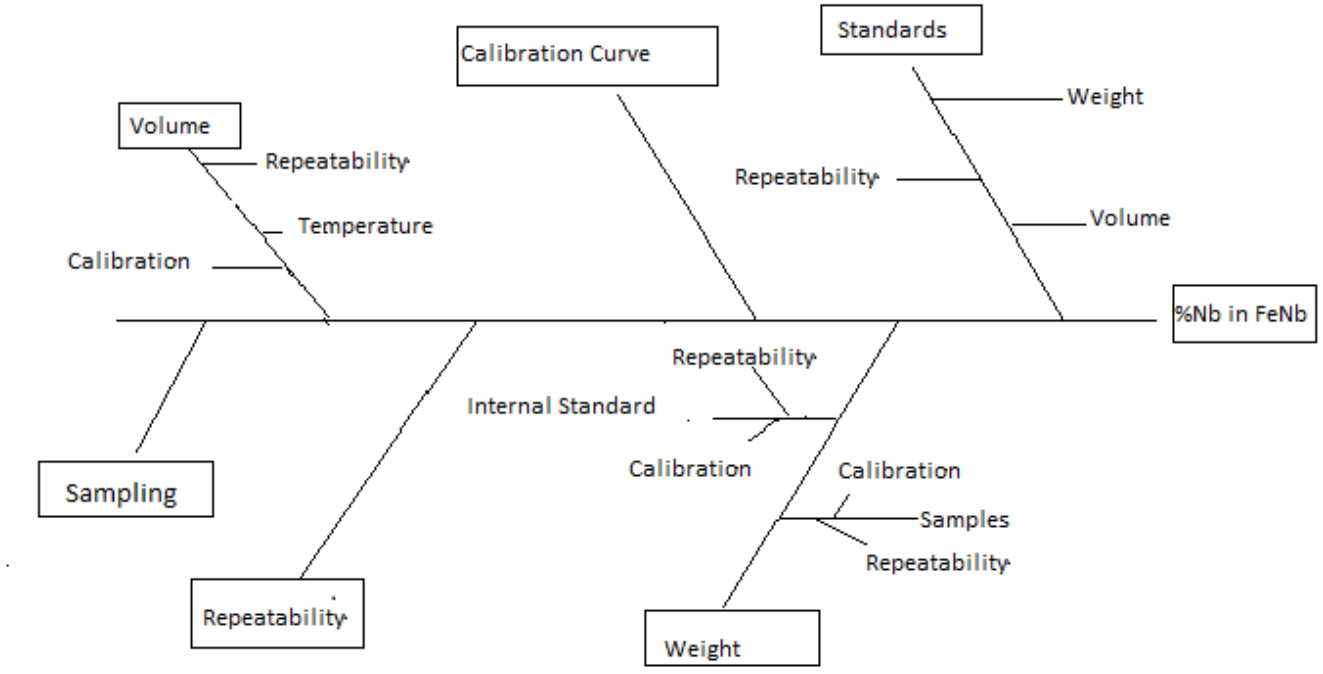

Figure 4: Uncertainty sources.

6.5. The expanded uncertainty is +/- 0.2% for the entire range from 62.9% Nb to 68.1% Nb.

Table 7: Expanded uncertainty for the 62.9% Nb to 68.1% Nb range.

%Nb	62.9	65	65.7	66.4	66.8	67.6	68.1	68.4
Expanded Uncertainty (K = 1.96)	*0.23*	*0.23*	*0.23*	*0.24*	*0.22*	*0.23*	*0.22*	*0.22*

7. Conclusions

7.1 The ICP methodology is not specific for niobium, however it is selective when Nb 269.701 nm and Mo 281.615 nm wavelengths are used.

7.2 CBMM's methodology achieves the approved criteria for accuracy for the entire 62.9% to 68% Nb range. For CBMM's products, the accuracy results are near 100%.

7.3 The repeatability limits for ICP 4300, 5300 and 7300 equipment are below 0.2%, which is in compliance with CBMM internal criteria (the difference between the conventional value and the result is < 0.2% absolute).

7.4 The evaluation made by visual analysis of the graph and linearity (correlation coefficient of 0.998) confirms that the ICP methodology can be considered linear from 43.9% Nb to 68.1% Nb.

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

7.6 The expanded uncertainty is +/- 0.2% for the entire range from 62.9% Nb to 68.1% Nb.