FINAL REPORT
Supplementary Comparison

DETERMINATION OF VOLUME OF STAINLESS STEEL WEIGHTS

2 kg, 1 kg, 200 g and 1 g
SIM.M.D-S5
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1. Introduction

This report describes the results of a supplementary comparison between SIM NMIs, which is being carried out in order to compare the degree of equivalence in volume measurements of stainless steel mass standards.

In March 2012, a meeting between the participant laboratories was carried out in La Paz – Bolivia as an activity within the framework of the cooperation project PTB–CAN. In that meeting the laboratories discussed critical topics they faced during calibration of weights at a high altitude above sea level; the conclusions were: first, is necessary to measure the density/volume of weights, as well as the determination of mass and with these values calculate the conventional mass; and second, the laboratories have to estimate the air density using the CIPM-2007 formula, both in order to guarantee the traceability for E_1 and E_2 standard weights. Because of that, the laboratories decide to organize a comparison including the calculation of mass and conventional mass, density and volume for E_2 standard weights.

This supplementary comparison was piloted by the Instituto Ecuatoriano de Normalización (INEN, Ecuador) and the Centro Nacional de Metrología (CENAM, Mexico) accepted to be the support laboratory; after the second semester of 2013 the Instituto Nacional de Metrología (INM, Colombia) continued with the activities of the pilot laboratory instead of INEN due to internal situations. Six NMIs took part of this comparison.

For this comparison was selected a set of weights, with the following nominal values: 2 kg, 1 kg, 200 g and 1 g. These values are linked to the values used in the key comparison SIM.M.D-K3.

The travelling standards, accuracy class OIML E_2, are property of the project "***FOMENTO COORDINADO DE LA INFRAESTRUCTURA DE LA CALIDAD EN LA REGIÓN ANDINA, PTB-CAN***".

The goal of this comparison was to compare the measurement results of participant NMIs in volume at 20 °C as reference temperature.

The weights were circulated among the NMIs from April 2012 to January 2013.

2. Participant NMIs

All the participant laboratories are NMIs belonging to SIM and all are signatures of the CIPM MRA. The participant laboratories and their respective technical contacts are listed below:

- *Centro Nacional de Metrología (CENAM) / México.*
    - Luis Omar Becerra
    - Luis Manuel Peña
- *Instituto Nacional de Calidad (INACAL) / Perú.*
    - Aldo Martín Quiroga Rojas
    - Luz Cori Almonte
- *Instituto Nacional Metrología (INM) / Colombia.*
    - Jhon J. Escobar Soto
    - Jorge Daniel García Benavides
    - Álvaro Bermúdez Coronel
- *Instituto Ecuatoriano de Normalización (INEN) / Ecuador.*
    - René Chanchay[7]
    - Wilson Naula
- *Instituto Nacional de Tecnología y Normalización (INTN) / Paraguay.*
    - Arnaldo Florencio
    - María Lourdes Valenzuela
- *Laboratorio Costarricense de Metrología (LACOMET) / Costa Rica.*
    - Francisco Sequeira
    - Sandra Rodríguez

[7] René Chachay left INEN-Ecuador in June 2015.

3. Traveling standards

The traveling standards used for this comparison are class OIML E_2, see figure 1.

Figure 1. Traveling standards.

Nominal values	Identification	Accuracy class	Material	Construction	Shape
2 kg, 1 kg, 200 g, 1 g	141717	E_2	Stainless steel	One single piece, no closed cavities	OIML

Table 1. Characteristics of the travelling standards

4. Circulation Schedule

The set of traveling standards was circulated and measured among participants according to the schedule shown in table 2.

No.	National Metrology Institute	Measurements date
1	CENAM-Mexico	April, 2012
2	INEN-Ecuador	June, 2012
3	INACAL-Peru	July, 2012
4	INTN-Paraguay	August, 2012
5	LACOMET-Costa Rica	October, 2012
6	INM-Colombia	November, 2012
8	INEN-Ecuador	January 2013,

Table 2. Schedule of circulation during the comparison

The traveling standards were examined by each NMI at the reception and departure of the weights in order to register all marks and damages during circulation.

As was agreed in the protocol, before to the pilot laboratory received results from all participants, CENAM and INEN checked consistency among their measurement results, see chapter 7.1.

Measurement results from all participants were received by pilot laboratory after a month of finishing their measurements.

5. Instruments used by participant laboratories

The participant laboratories measured the volume at 20 °C applying their own technical procedures.

For the buoyancy correction, the air density was calculated using the CIPM-2007 equation [1].

For those laboratories that used water density as reference, they calculated the water density using the Tanaka's formula [2].

The resolutions of the weighing instruments used for weighing in air by the participant laboratories are shown in Table 3.

	CENAM	INEN	INACAL	INTN	LACOMET	INM
2 kg	0,1	1	0,2	1	1	5
1 kg	0,1	1	0,1	0,01	0,1	0,001
200 g	0,01	1	0,1	0,01	0,01	0,001
1 g	0,01	0,01	0,1	0,0001	0,001	0,01

Table 3. Resolution of the weighing instruments for weighing in air by laboratory, in milligrams

The resolutions of the weighing instruments used for weighing in liquid by the participant laboratories are shown in in Table 4.

	CENAM	INEN	INACAL	INTN	LACOMET	INM
2 kg	0,1	1	0,2	1	10	5
1 kg	0,1	1	0,1	1	1	1
200 g	0,01	1	0,1	1	0,1	1
1 g	0,01	0,1	0,1	1	0,1	0,01

Table 4. Resolution of the weighing instruments for weighing in liquid by laboratory, in milligrams

For the measurements of the liquid temperature and environmental conditions during the measurements, the resolutions of the instruments used by the participant laboratories are shown in Table 5.

	CENAM	INEN	INACAL	INTN	LACOMET	INM
Temperature (for air density calculation) *t* / °C	0,01	0,1	0,1	0,1	0,1	0,001
Temperature (transfer liquid) *t* / °C	0,001	0,01	0,05	0,001	0,001	0,001
Relative Humidity *hr* / %	0,01	1	0,5	0,1	0,1	0,01
Barometric Pressure *p* / Pa	1	1	10	10	1	0,1

Table 5. Resolution of the environmental conditions equipment by laboratory

Table 6 shows the liquid of reference used by the participant laboratories.

	CENAM	INEN	INACAL	INTN	LACOMET	INM
Liquid of reference / Traceability	Pentadecane / CENAM[8]	Distilled water / Tanaka's equation	Distilled water / Tanaka's equation	Distilled water / Tanaka's equation	Bi-distilled water / Tanaka's equation	Bi-distilled water / Tanaka's equation

Table 6. Liquid of reference and traceability by laboratory

6. Measurement results

The participant laboratories normally used one of the methods described in [3] to measure the volume of weights.

The measurement method used by CENAM, INTN and LACOMET was A1 for all the travelling standards; INACAL used the method A1 for 2 kg, 1 kg and 200 g weights and the method B1 for 1 g weight; INEN used the method C for all weights; and INM used the method D for 2 kg weight, method A2 ii) for 1 kg and 200 g weights, and the method C for 1 g weight [3].

Table 7 shows the volume measurement results as reported by participant laboratories.

Nominal value	2 kg		1 kg		200 g		1 g	
	Volume at 20 °C cm^3	*u* (k = 1) cm^3	Volume at 20 °C cm^3	*u* (k = 1) cm^3	Volume at 20 °C cm^3	*u* (k = 1) cm^3	Volume at 20 °C cm^3	*u* (k = 1) cm^3
CENAM	249,630	0,006	124,903 5	0,003 6	24,973 1	0,002 4	0,124 6	0,000 5
INEN1	249,623 2	0,008 7	124,901 0	0,008 0	24,964 5	0,003 1	0,123 90	0,000 37
INACAL	249,693	0,013	124,912	0,005	24,971	0,005	0,124 9	0,000 4
INTN	249,628	0,025	124,908	0,020	24,973	0,004	0,124 7	0,001 0
LACOMET	249,61	0,39	124,909	0,011	24,974 7	0,002 5	0,128 9	0,002 8
INM	250,10	0,10	124,885 6	0,011 96	24,972 6	0,011 54	0,124 7	0,000 10
INEN2	249,623 2	0,008 8	124,903 0	0,008 7	24,969 6	0,002 5	0,123 66	0,000 42

Table 7. Volume value and standard uncertainty reported by the participant laboratories

[8] The density of the pentadecane was measured at CENAM with a hydrostatic weighing system using as a density standard a zerodur sphere with traceability to PTB - Germany.

The results reported by all the participant laboratories, as well as the uncertainty analysis, were done according to "*Guide to the expression of Uncertainty in Measurements*" GUM [4].

7. Results Analysis

7.1 Consistency between CENAM and INEN

The consistency between CENAM and INEN were checked using the normalized error criterion [5] according to the equation (1)

$$E_n = \frac{\Delta x_{INEN_1} - \Delta x_{CENAM}}{\sqrt{U^2(INEN_1) + U^2(CENAM)}} \quad (1)$$

where

Δx_{INEN_1}: first volume value measured by INEN

Δx_{CENAM}: volume value measured by CENAM

$U^2(INEN_1)$: expanded uncertainty associated to the volume calculated by INEN at the beginning of measurements

$U^2(CENAM)$: expanded uncertainty associated to the volume calculated by CENAM

Table 8 shows the values of normalized error calculated for volume values reported by CENAM and INEN.

Nominal value	**2 kg**	**1 kg**	**200 g**	**1 g**
Normalized error for volume values	-0,19	-0,08	-0,63	-0,39

Table 8. Normalized error between CENAM and the first measurement of INEN

7.2 References values for the comparison

The reference value for volume measurements is calculated using the results reported by each participant laboratory according to the mathematical model of weighted mean [6].

A chi-squared test is used for analyzing the consistency of the estimated value in volume.

The criterion used for the consistency of the estimated value is given for a confidence level of 95 % with a probability p calculated using the inequality

$$p = P\{\chi^2(\nu) > \chi^2_{obs}\}$$

with a number of degrees of freedom $\upsilon = 5$. According to the above criterion, if the probability is more than 0,05, the estimated value is consistent [7]. Table 9 includes the value of volume calculated by each participant laboratory, the estimated reference value of volume $\widehat{V}$ and its uncertainty associated $u(\widehat{V})$.

The chi-squared test is used for analyzing the consistency of the estimated value, taking into account that the critical value for consistency is

$$x^2(\upsilon = 5) = 11{,}070$$

Participant laboratory	Nominal value	V (cm³)	$u(V)$ (cm³)	$\widehat{V}$ (cm³)	$u(\widehat{V})$ (cm³)	χ^2_{obs}
CENAM	2 kg	249,630	0,006	249,640	0,005	41,738 The chi-squared test failed. The reference can't be calculated as weighted mean.
INEN		249,623	0,018			
INACAL		249,693	0,013			
INTN		249,628	0,025			
LACOMET		249,61	0,39			
INM		250,10	0,10			
CENAM	1 kg	124,903 5	0,003 6	124,905 4	0,002 7	4,961
INEN		124,901	0,016			
INACAL		124,912	0,005			
INTN		124,908	0,0220			
LACOMET		124,909	0,011			
INM		124,885 6	0,011 96			
CENAM	200 g	24,973 1	0,002 4	24,973 0	0,001 5	2,403
INEN		24,965	0,006			
INACAL		24,971	0,005			
INTN		24,973	0,004			
LACOMET		24,974 7	0,002 5			
INM		24,972 6	0,011 54			
CENAM	1 g	0,124 6	0,000 5	0,124 7	0,000 1	3,678
INEN		0,123 9	0,000 8			
INACAL		0,124 9	0,000 4			
INTN		0,124 7	0,001 0			
LACOMET		0,128 9	0,002 8			
INM		0,124 7	0,000 10			

Table 9. Estimated reference values for volume of travelling standards, their uncertainties and results for chi-squared consistency tests.

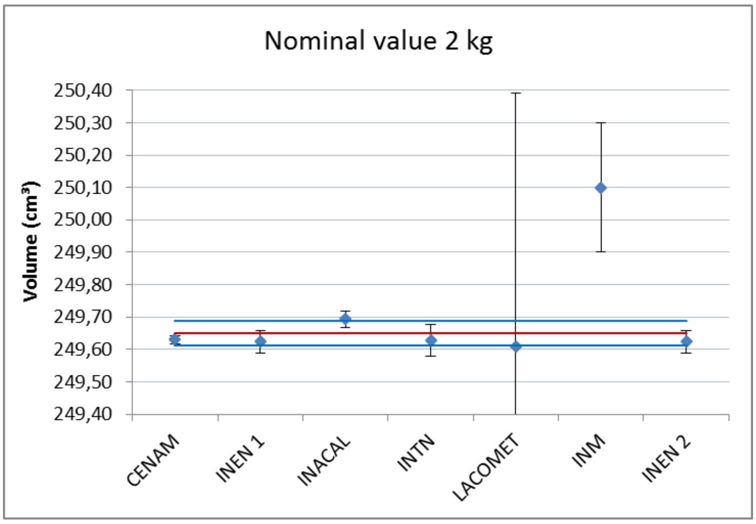
As the chi-squared test failed for the volume of the 2 kg weight, the reference value for this nominal value was calculated by numerical simulation method as the median (procedure B [8]) by the use of the commercial software @Risk for Microsoft Excel 5.5 with 1×10^5 trials, see Annex A.

The reference value calculated for the volume of 2 kg weight is the following:

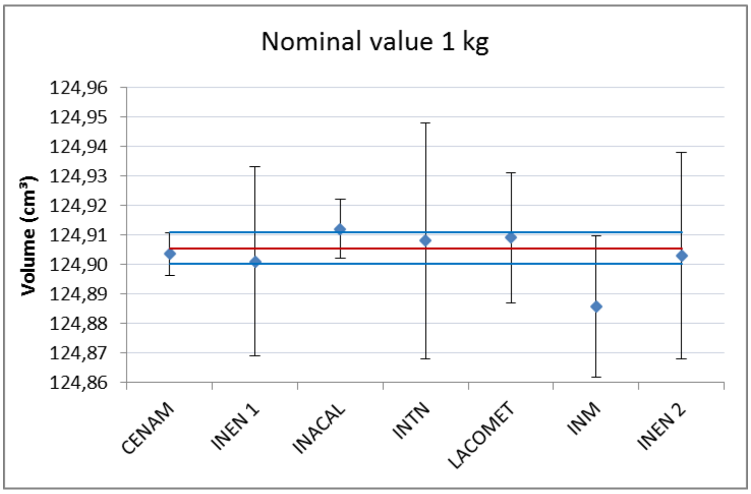
$$V_{ref(2\,kg)} = 249.649\,5 \text{ cm}^3 \pm 0.0188 \text{ cm}^3 \; (k = 1)$$

Result of reference value is shown with more than two digits in order to avoid loss of information.

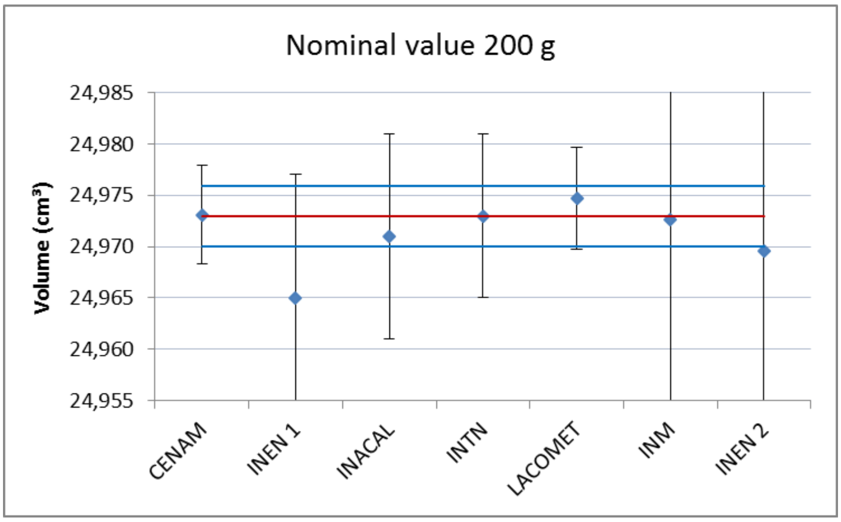
Figures 1 to 4 show the values and the uncertainties reported by each participant laboratory and the reference value and its uncertainty values which are expressed with a coverage factor *k = 2*.



Graphic 1. Reported values of volume for 2 kg weight for each laboratory and the reference value calculated. The reference value is represented by the red line and its uncertainty by the blue lines.



Graphic 2. Reported values of volume for 1 kg weight for each laboratory and the reference value calculated. The reference value is represented by the red line and its uncertainty by the blue lines.



Graphic 3. Reported values of volume for 200 g weight for each laboratory and the reference value calculated. The reference value is represented by the red line and its uncertainty by the blue lines.

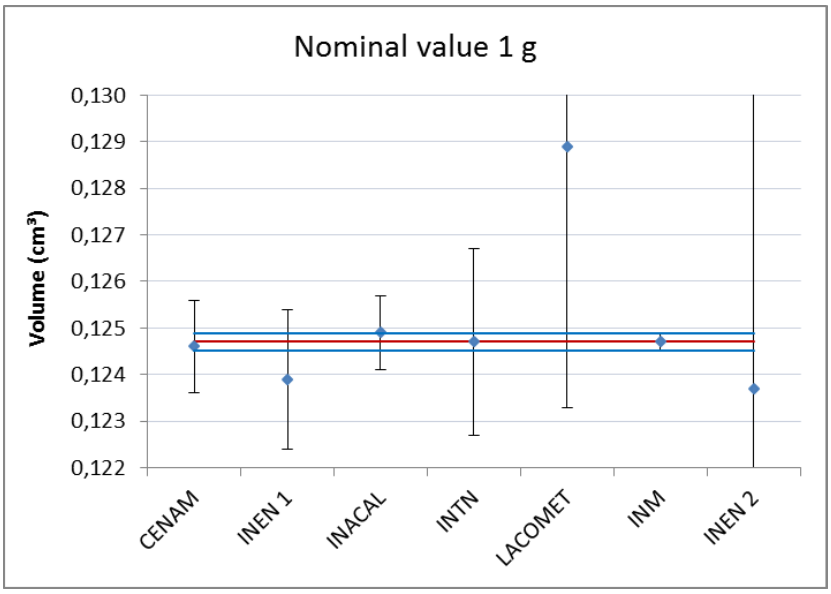


Figure 4. Reported values of volume for 1 g weight for each laboratory and the reference value calculated. The reference value is represented by the red line and its uncertainty by the blue lines.

8. Conclusions

According to the results of this supplementary comparison, it is possible to conclude:

- There is a general consistency of the measurements in volume of weights with nominal values 1 kg, 200 g and 1 g, which is possible to see in the calculated normalized error for each participant laboratory.

- It is possible to see a concordance between different methods of calculation of volume of weights with nominal values 1 kg and 200 g (the laboratories used the methods A1, A2 and C of OIML R 111), and 1 g (the laboratories used the methods A1, B1 and C of OIML R 111). This result assures the correspondence of the calculated values of volume of standard weights independently of the chosen method.

- For 2 kg weight, the chi-squared value calculated during the calculation of the reference value of volume measurements is larger than expectation, as a conclusion the references value calculated for volume are not statistically consistent. All the participant laboratories used the method A1 of OIML R 111 for determining the density of this weight with exception of one laboratory which used the method C and other laboratory which used the method D; the last laboratory mentioned reported the value of density and volume with the strongest deviation comparing against the results reported by other laboratories.

9. References

[1] Davis, R.S., "*Equation for the determination of the density of moist air*" (1981/91). Metrología 29,67 (1992). Giacomo P., "*Equation for the determination of the density of moist air*" (1981), Metrología 18, 33 (1982).

[2] Tanaka, M., Girard, G., Davis, R., Peuto, A., Bignell, N., [NMIJ, BIPM, IMGC, NML], *"Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports"*. Metrología, 2001, 38, n°4 ,pp. 301-309.

[3] OIML R 111-1 Edition 2004 (E). Weights of classes E_1, E_2, F_1, F_2, M_1, M_{1-2}, M_2, M_{2-3} and M_3 Part 1: Metrological and technical requirements. Organisation Internationale de Métrologie Légale.

[4] JCGM 100:2008 Evaluation of measurement data – Guide to the expression of uncertainty in measurements
http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf

[5] Wöger, W., "*Remarks on the E_n – Criterion used in Measurement comparisons*". Internationale Zusammenarbeit PTB – Mitteilungen 109 1/99

[6] Euromet.M.D.K1 (European Project N°339) *Intercomparison of volume standards by hydrostatic weighing.* Final report, August 2000.

[7] Cox, M.G., *“The evaluation of key comparison data: determining the largest consistent subset”*. National Physical Laboratory (NPL), BIPM-NMIJ Satellite Workshop on Key Comparison Data Evaluation, 16 May 2005.

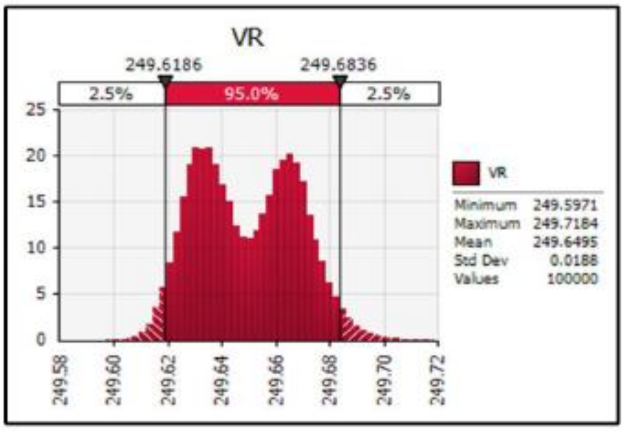
[8] Cox, M.G., “The evaluation of key comparison data”, Metrologia, 2002, 39, 589-595 589

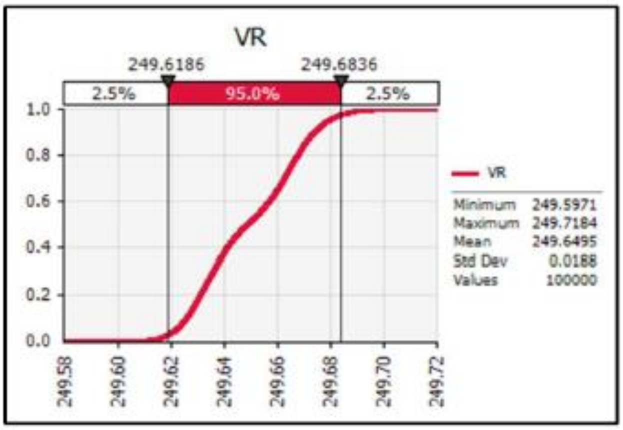
[9] Tovar et al. – Automatización del Sistema de pesada hidrostática para la medición de densidad de líquidos – Proceedings of Symposium of Metrology, October 2010 Querétaro Mexico.
https://www.cenam.mx/sm2010/info/pmiercoles/sm2010-mp07a.pdf

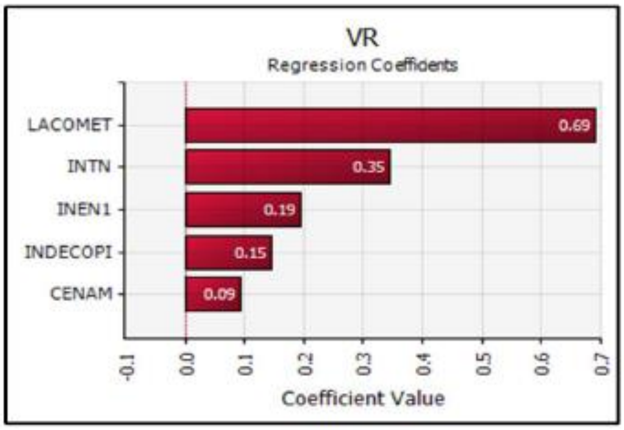
ANNEX A

Calculation of the reference value for 2 kg weight using numerical simulation by Monte Carlo method

For the numerical simulation by Monte Carlo method was used the mathematical model of median as is described in [6]







Simulation Summary Information	
Workbook Name	2 kg Volumen.xlsx
Number of Simulations	1
Number of Iterations	100000
Number of Inputs	6
Number of Outputs	22
Sampling Type	Latin Hypercube
Simulation Start Time	5/14/15 12:35:28
Simulation Duration	00:00:23
Random # Generator	Mersenne Twister
Random Seed	909945326

Summary Statistics for VR			
Statistics		Percentile	
Minimum	249.59713	5%	249.62179
Maximum	249.71844	10%	249.62572
Mean	249.64949	15%	249.62858
Std Dev	0.01877	20%	249.63099
Variance	0.000352278	25%	249.63340
Skewness	0.126992666	30%	249.63575
Kurtosis	2.041928685	35%	249.63830
Median	249.64869	40%	249.64113
Mode	249.63028	45%	249.64446
Left X	249.61858	50%	249.64869
Left P	2.5%	55%	249.65321
Right X	249.68363	60%	249.65694
Right P	97.5%	65%	249.65996
Diff X	0.06505	70%	249.66257
Diff P	95%	75%	249.66509
#Errors	0	80%	249.66759
Filter Min	Off	85%	249.67037
Filter Max	Off	90%	249.67380
#Filtered	0	95%	249.67901

Regression and Rank Information for VR			
Rank	Name	Regr	Corr
1	LACOMET	0.691	0.747
2	INTN	0.345	0.336
3	INEN1	0.195	0.193
4	INDECOPI	0.146	0.139
5	CENAM	0.095	0.095
6	INM	0.000	0.004494475