ورشة عمل بعنوان تأسيس و بناء نظام الجودة في مختبرات التحاليل النووية والإشعاعية طبقاً لمتطلبات الايزو 17025:2017

عمان-المملكة الأردنية الهاشمية

7-11/05/2023

"Method Validation for "Analyzing Solid Samples Using Wavelength Dispersive X-ray Fluorescence Spectrometer (WDXRF)"

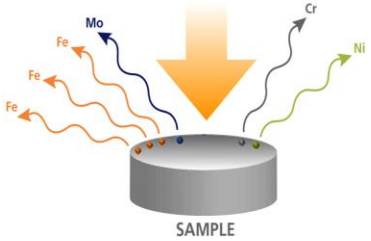
"طريقة التحقق من صحة تحليل العينات الصلبة باستخدام مطيافية الاستشعاع السيني الموجي"

What is XRF ?

- It is an analytical method used for determining the chemical composition of all kinds of materials. The material can be solid, liquid, powder, filters or of other forms.
- The XRF gives quantitative and qualitative values of both major and trace elements of atomic numbers ranging from Sodium (Na) to Uranium (U), in homogeneous samples. The detected concentrations range between ppm level to 100%.

Basics of XRF

- In XRF, X-rays produced by a source irradiate the sample. In most cases, the source is an X-ray tube but alternatively it could be a synchrotron or a radioactive material.
- The elements present in the sample will emit fluorescent X-ray radiation with discrete energies (equivalent to colors in optical light) that are characteristic for these elements. A different energy is equivalent to a different color.



Sample Preparation

- The sample is mixed with a powder binding material with a known ratio, a pressure of (20 tons) are employed using the Hydraulic Press to get a pressed pellet sample .

Press Pellet Preparation

Sample Preparation

- Dissolution of the material at high-temperatures in the presence of a fluxing compound (LithiumTetra borate and Lithium Meataborate) . In the case of XRF analysis, the high-temperature melt is most often cast into a fused bead which is then placed in the instrument for analysis.

Fused Beads Preparation

Sample Analysis

- The first step in the analysis is to determine the top positions and the height of the line profiles.
- The positions of the tops represent the presence of elements and the height of the peak represents the intensities of the elements.
- In quantitative analysis, the net intensities are converted into concentrations.

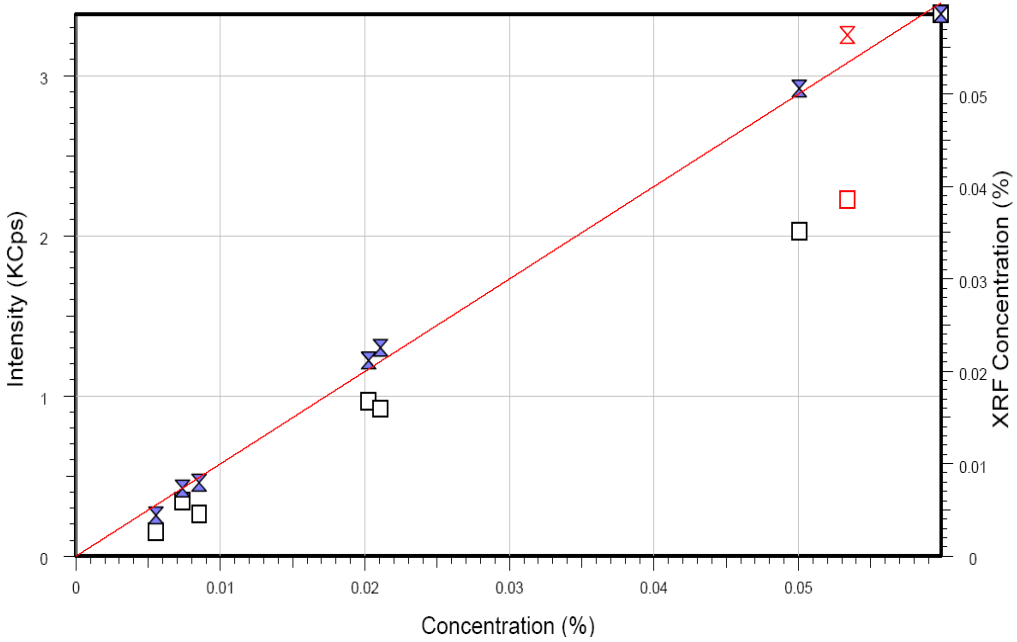
Sample Analysis

- The usual procedure is to calibrate the spectrometer by measuring one or more reference materials. The calibration determines the relationship between the concentrations of elements and the intensity of the fluorescent lines of those elements
- Unknown concentrations can be determined once the relationship is known.

Calibration Curve

The intensities of the elements with unknown concentration are measured, with the corresponding concentration being determined from the calibration.

Uranium calibration curve



What should be included in the method validation report?

- Introduction.
- Performance Characteristics.
- Uncertainty Calculations.
- Limit of Detection or Quantification.
- Calibration and Corrections.

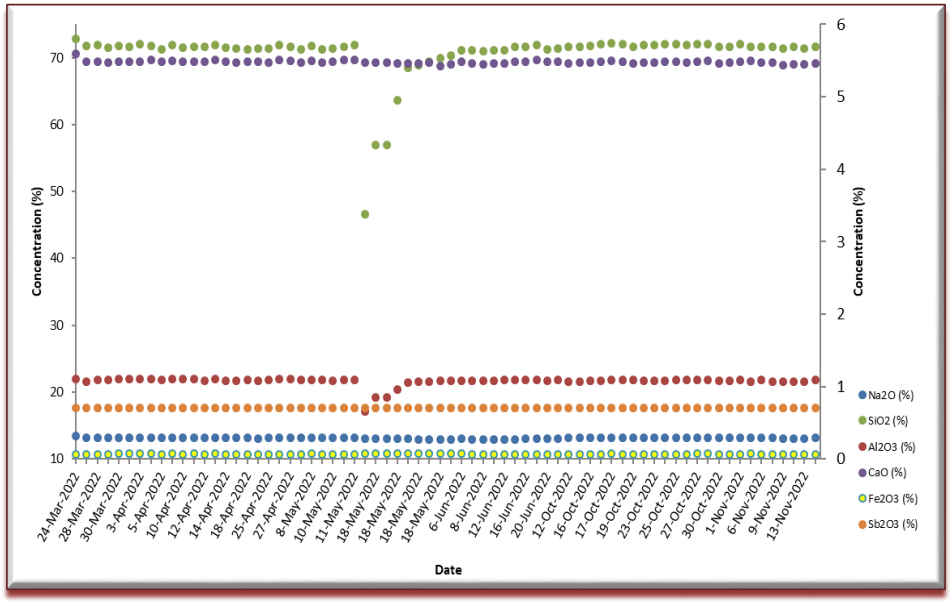
Introduction

Scope	•Analysis of rare earth elements for fused beads samples based on calibration curve method " covering the following analytes (Al_2O_3, CaO, CeO_2 Fe_2O_3, K_2O, La2O3, LOI, MgO, Nb_2O_5, Nd_2O_3, P_2O_5, Pr_6O_{11}, SiO_2, Sm_2O_3, TiO_2 ThO_2, V_2O_5, Y_2O_3 and ZrO_2).
Reference Standards	•Characterization of waste and soil —Determination of elemental composition by X-ray fluorescence. "BS EN 15309:2007"
Relative SOPs	•Analyzing Solid Samples Using Wavelength Dispersive X-ray Fluorescence Spectrometer (WDXRF). "CPAL-SOP-006" •X-Ray Fluorescence Spectroscopy Sample Preparation. "CPAL-SOP-007"
Description of method	•WDXRF is an analytical technique uses a X-Rays that strikes and interacts with constituent elements of the target specimen to produce characteristic X-rays of those elements. The characteristic X-Rays are then detected with a wavelength spectrometer to quantify the collected intensity then turn it into concentration in part per million (ppm) or percentage (%).

Performance Characteristics

- Stability.
- Precision (Repeatability & Reproducibility)
- Turness.
- Linearity.
- Working Range.
- Accuracy.

Stability



Stability tests ensure the reliability and robustness of the analyzing techniques which assesses the stability of the technique's results over time. A high degree of consistency indicates good test-retest reliability.

Linearity

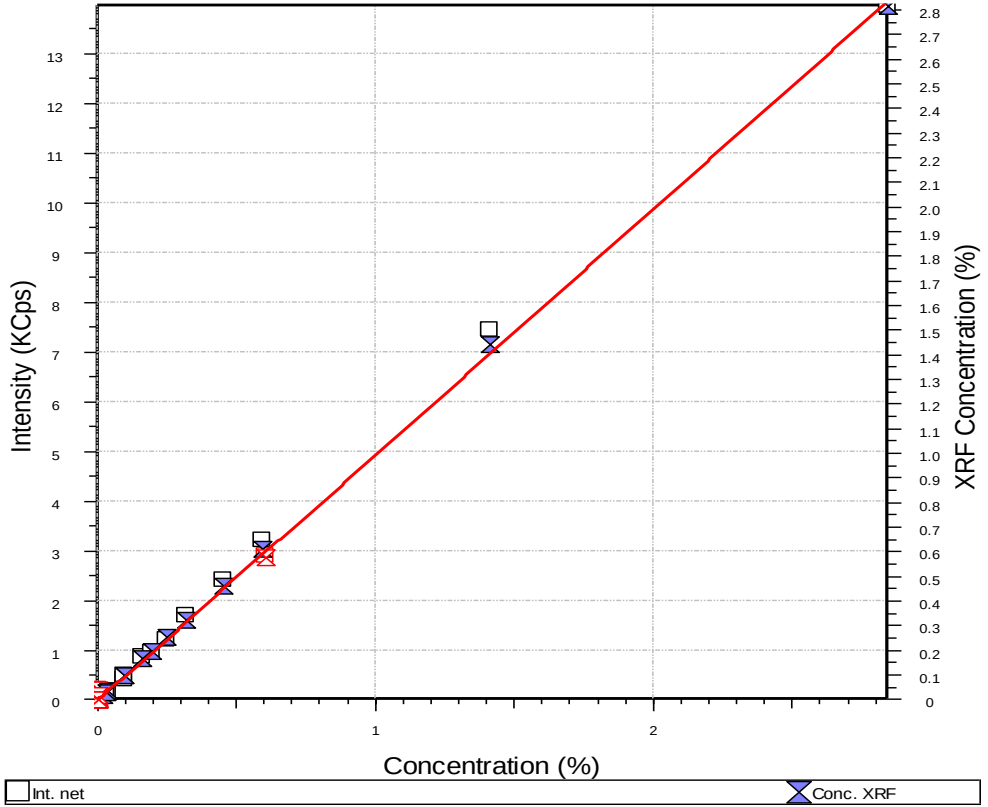
- For an analytical method for which a measurement model defines a relation between the instrumental response and the concentration, the range of applicability of this model must be established.
- For many analytical methods, the instrumental response as a function of concentration is linear within a stated range. This is normally demonstrated by graphical methods.

Working Range

- The ‘working range’ is the interval over which the method provides results with an acceptable uncertainty. The lower end of the working range is bounded by the limit of quantification LOQ. The upper end of the working range is defined by concentrations at which significant anomalies in the analytical sensitivity are observed.

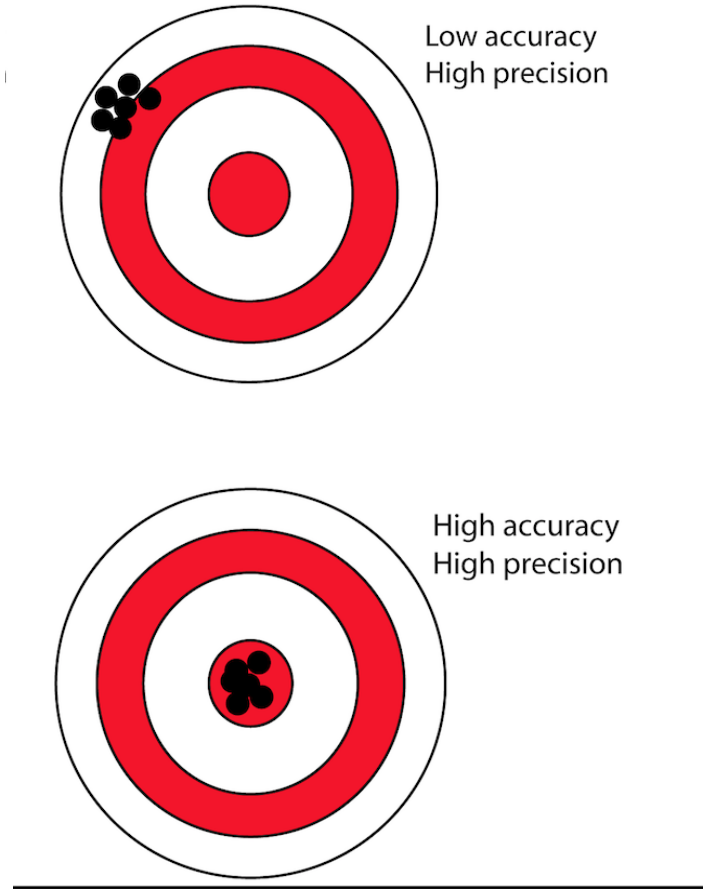
The performance characteristics ‘working range’, ‘linear range’, were identified

- Abridged calibration data for line La LA1-HS-Min.
- 24 standards from 0.00 % to 2.75 % were used.
- Standard deviation: 0.0144 %
- Squared correlation coefficient: 0.999747



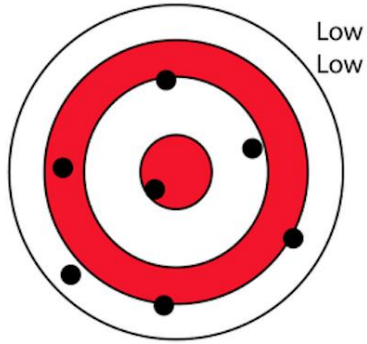
Accuracy

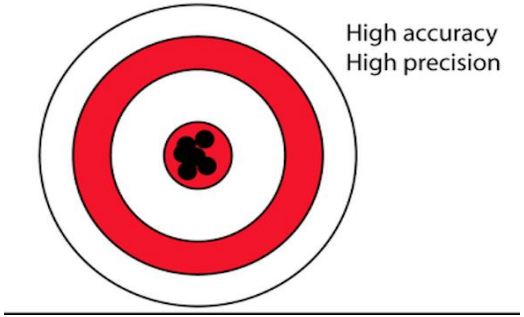
Accuracy is a measure of the quality of a result. Accuracy is, therefore, normally studied as two components: 'trueness' and 'precision'.



Precision

- The precision of a method is a measure of the closeness expected between independent replicate test results conducted under specified conditions.
- Precision is usually stated in terms of the standard deviation (s), or relative standard deviation (RSD) of replicate results. Two measures of precision, termed repeatability and reproducibility are commonly used.





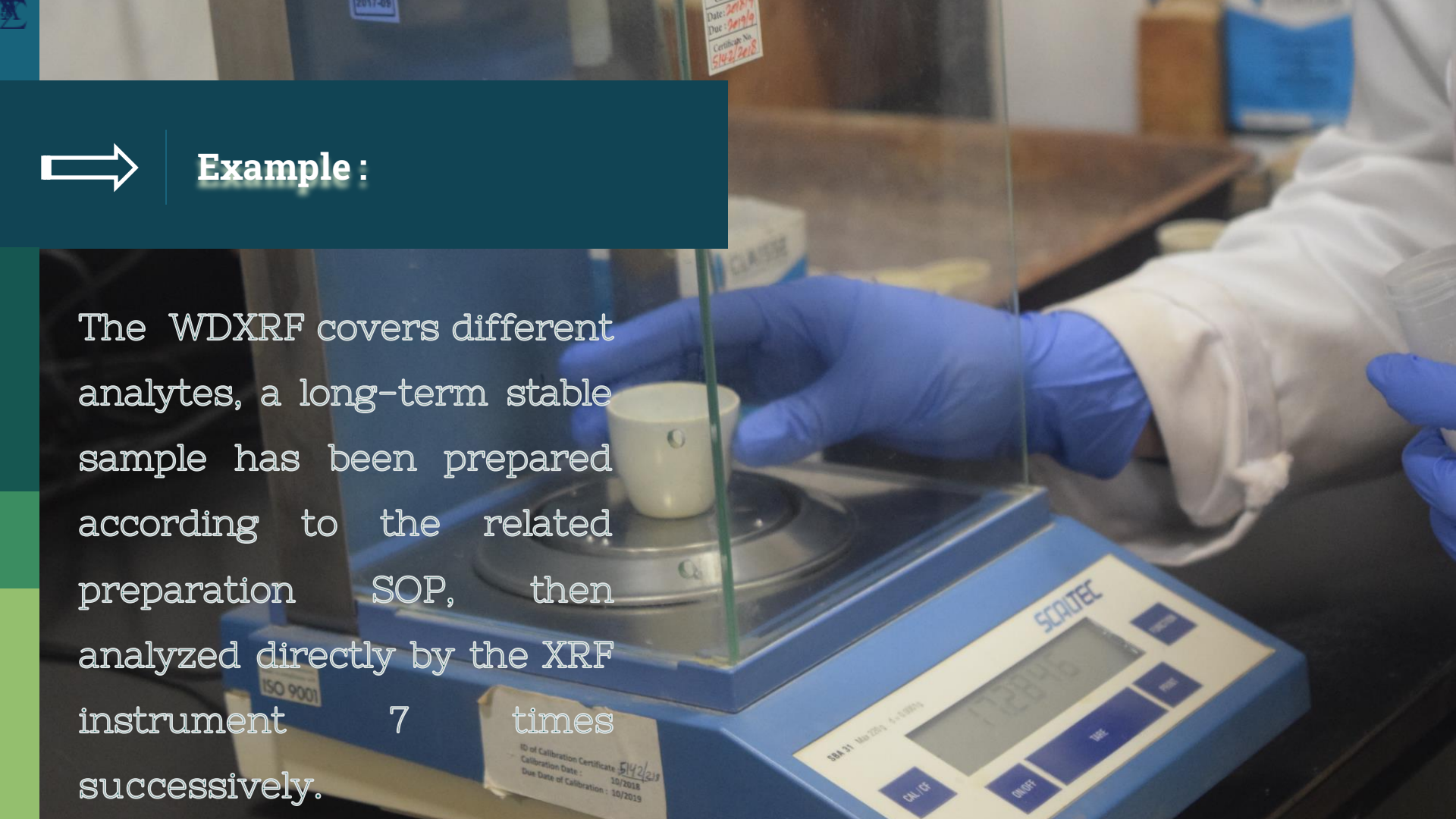
Repeatability

The standards deviation of an element concentration that is determined with the same test method on an identical sample in the same laboratory by the same user with the same XRF instrument within a short amount of time.

To Perform the repeatability test for each analytes; at least 7 replicates must be analyzed successively.

$$s = \sqrt{\frac{\sum(X - \bar{x})^2}{n - 1}}$$

s = Analyte standard deviation
X = concentration value
$\bar{x}$ = mean of concentrations
n = number of replicates



Example :

The WDXRF covers different analytes, a long-term stable sample has been prepared according to the related preparation SOP, then analyzed directly by the XRF instrument 7 times successively.

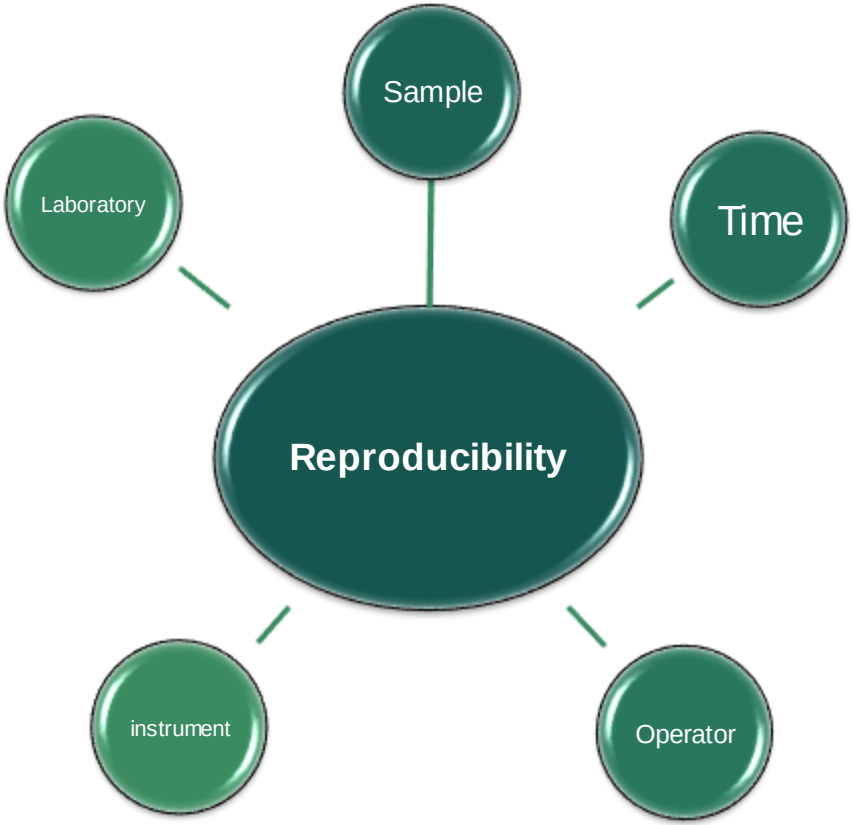
Repatability reults for 7 times analyzed sample

	Repl.1	Repl.2	Repl.3	Repl.4	Repl.5	Repl.6	Repl.7	Avg.	STD.	RSD.
Al_2O_3 (%)	11.09	11.04	11.09	11.14	11.11	11.13	11.1	**11.1**	**0.033**	**0.29**
CaO (%)	1.43	1.42	1.42	1.42	1.42	1.42	1.43	**1.42**	**0.005**	**0.34**
CeO_2 (PPM)	49258	49156	48934	49010	49258	49141	49092	**49121**	**120.62**	**0.25**
Fe2O3 (%)	47.6	47.97	48.86	47.71	47.7	47.93	47.94	**47.96**	**0.42**	**0.88**
K_2O (%)	0.06	0.07	0.06	0.06	0.06	0.06	0.07	**0.06**	**0.005**	**8.13**
La_2O_3 (PPM)	28683	28667	28527	28624	28650	28569	28578	**28614**	**57.53**	**0.20**
MgO (%)	0.79	0.8	0.8	0.8	0.8	0.77	0.79	**0.79**	**0.01**	**1.41**
Nb2O5 (PPM)	6585	6604	6641	6581	6580	6614	6624	**6604**	**23.58**	**0.36**
Nd_2O_3 (PPM)	12986	12783	12909	12850	12822	12911	12908	**12881**	**67.68**	**0.53**
P_2O_5 (%)	8.15	8.14	8.14	8.16	8.16	8.15	8.19	**8.15**	**0.02**	**0.21**
Pr_6O_{11} (PPM)	4506	4545	4496	4467	4415	4507	4557	**4499**	**47.75**	**1.06**
SiO_2 (%)	3.71	3.74	3.75	3.74	3.71	3.72	3.78	**3.74**	**0.03**	**0.67**
Sm_2O_3 (PPM)	2459	2462	2459	2482	2468	2455	2485	**2467**	**11.88**	**0.48**
ThO_2 (PPM)	916	918	912	912	914	913	913	**914**	**2.24**	**0.24**
TiO_2 (%)	10.52	10.48	10.51	10.51	10.52	10.51	10.52	**10.51**	**0.01**	**0.13**
V_2O_5 (PPM)	1095	1093	1088	1088	1091	1091	1095	**1092**	**2.94**	**0.27**
Y_2O_3 (PPM)	612	617	614	607	609	609	612	**611**	**3.41**	**0.56**
ZrO_2 (PPM)	2840	2834	2839	2817	2830	2839	2836	**2834**	**8.10**	**0.29**

On examining the results shown in the table, it is obvious that the standard deviation for all elements is very low. This indicates good precision for all the analyzed elements. All %RSD values are below 2%, indicates that the method can give repeatable results, therefore good precision.

Reproducibility

Reproducibility is the standard deviation for an element concentration that is determined with the same analytical principle but under modified conditions.



Example :

In case of no option to participate in intra-laboratory reproducibility ; an 'intermediate precision' can be performed which indicates the precision relating to reproducibility conditions restricted to a single laboratory.

For single-laboratory validation, the best measure of precision is obtained by replicate analyses of independently prepared test portions of a laboratory sample.

Repreducability reults for 9 replicate sample

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	AVG.	STD.	RSD.
Al2O3 (%)	10.52	10.56	10.61	9.75	10	10.23	10.94	10.99	11	10.5	0.44	4.23
CaO (%)	1.72	1.72	1.71	1.78	1.73	1.79	1.74	1.75	1.75	1.75	0.03	1.49
CeO2 (PPM)	8103	8116	8054	8122	8216	8167	8134	8218	8209	8160	57	0.7
Fe2O3 (%)	48.952	48.802	49.146	48.476	48.373	48.66	49.89	49.21	49.55	49.04	0.5	1.02
La2O3 (PPM)	5942	6010	5928	5931	5925	5912	5938	6018	6018	5953	44	0.74
MgO (%)	1.736	1.73	1.724	1.648	1.632	1.69	1.7	1.69	1.68	1.68	0.04	2.13
Nb2O5 (PPM)	2181	2199	2193	2214	2179	2179	2186	2151	2134	2177	24	1.11
Nd2O3 (PPM)	4135	4147	4162	4225	4308	4211	4261	4322	4291	4254	71	1.67
P2O5 (%)	1.385	1.371	1.365	1.327	1.336	1.35	1.47	1.47	1.44	1.39	0.06	3.99
Pr6O11 (PPM)	1195	1145	1232	1209	1219	1362	1256	1235	1304	1260	63	5
SiO2 (%)	27.01	26.84	26.92	26.02	25.97	26.27	26.72	26.53	26.68	26.44	0.38	1.45
Sm2O3	640	620	656	660	646	654	651	628	637	647	13	2.08
ThO2 (PPM)	346	331	330	325	328	330	354	333	344	335	10	2.94
TiO2 (%)	3.273	3.216	3.22	3.198	3.203	3.208	3.308	3.246	3.245	3.23	0.04	1.13
V2O5 (PPM)	454	450	449	450	449	452	464	462	461	455	6	1.34
Y2O3 (PPM)	226	230	227	228	224	226	228	237	220	227	5	2.03
ZrO2 (PPM)	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	<MQL	/	/	/

On examining the results shown in the table, it is obvious that the standard deviation for all elements is very low. This indicates good precision for all the analyzed elements. All %RSD values are below 2%, indicates that the method can give repeatable results, therefore good precision.

Trueness

It is the comparing the concentration determined by the test method with the certified values of a certified reference material. The difference is referred to “bias”.

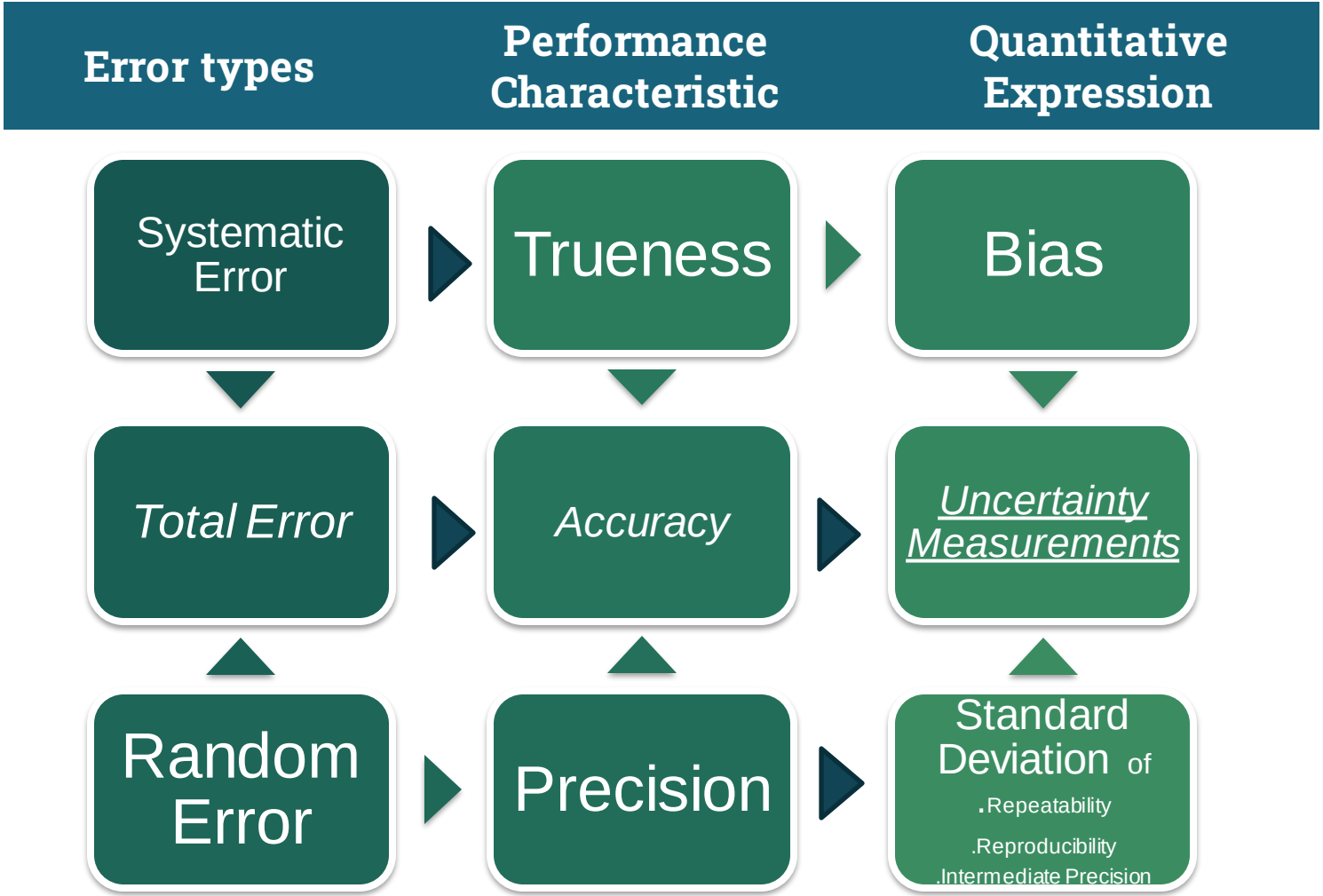
A reference material, containing the analytes of known concentration were used to estimate the bias of a test result. The average bias is best achieved by comparing test results, obtained in different runs over several days, with the known value. The used reference materials should match the matrices and analytes of the samples to be tested by the method.

Analyzing 7 replicate of 6 CRMs which having a matrix and concentration matched with samples.

	Certified Value (%)	1SD	Average of Reading (%)	SD of average	Recovery (%)	Bias (%)
OREAS 460	26.81	0.38	27.04	0.52	**100.8**	**0.23**
OREAS 461	46.09	0.77	45.77	0.56	**99.3**	**0.32**
OREAS 462	48.69	0.75	48.54	0.47	**99.7**	**0.15**
OREAS 463	49.48	1.11	48.99	0.86	**99.0**	**0.49**
OREAS 464	54.38	1.03	53.14	0.93	**97.7**	**1.24**
OREAS 465	49.96	1.31	47.74	0.73	**95.6**	**2.22**

Bias = $Average\ of\ reading - Certified\ value$

Recovery= $\frac{Average\ of\ reading}{Certified\ value} \times 100\%$


Error types
Performance Characteristic
Quantitative Expression
Systematic Error
Trueness
Bias
Total Error
Accuracy
Uncertainty Measurements
Random Error
Precision
Standard Deviation of
.Repeatability
.Reproducibility
.Intermediate Precision

Measurement of Uncertainty

In quantitative XRF analysis, the global (or overall) uncertainty of an analytical result depends on the combination of errors introduced mainly by sample preparation, the measurement of both peak and background intensities, the slope "m" of the calibration line and the corrections for matrix effects. All these errors can be grouped in two main categories: random errors (precision) and systematic errors (accuracy). Reference materials were used to calculate the uncertainty; they were prepared according to the regular chemical sample preparation procedure as described in “CPAL-SOP 007”.

Intermediate Precision Uncertainty

Estimating the uncertainty of the replicate samples to develop a better model for the sample distribution of the mean, the Pooled Standard Deviation (S_{pooled}) is employed. When determining the value of S_{pooled}, individual standard deviations are averaged with more "weight" given to the larger values.

Thus, the pooled variance is defined by:

$$s_{\text{pooled}} = \sqrt{\frac{(n_1-1)s_1^{\,2} + (n_2-1)s_2^{\,2} + \ldots + (n_k-1)s_k^{\,2}}{n_1 + n_2 + \ldots + n_k - k}}$$

Where:

k, number of CRMs

n1, n2, . . ., nk are the number of replicates.

s1, s2, . . ., sk are the relative standard deviation of measured concentrations.

So, the total uncertainty of the pooled standard deviation "U_s" is estimated as:

$$U_s = \frac{S_{pooled}}{\sqrt{\sum n_k}}$$

For "Fe_2O_3" ⟶

$$S_{Pooled} = \sqrt{\frac{(7-1)\times\left(\frac{0.52}{27.04}\times100\right)^2+(7-1)\times\left(\frac{0.56}{45.77}\times100\right)^2+(7-1)\times\left(\frac{.86}{48.99}\times100\right)^2+(7-1)\times\left(\frac{0.93}{53.14}\times100\right)^2+(7-1)\times\left(\frac{0.73}{47.74}\times100\right)^2+(7-1)\times\left(\frac{0.47}{148.54}\times100\right)^2}{(7*6-6)}} = 8.6$$

$$U_s = \frac{8.6}{\sqrt{7*6}} = 1.33$$

The uncertainty of the reference materials "U_{RM}"

Constituent	Certified Value	1SD
Borate Fusion XRF		
CeO_2, Cerium(IV) oxide (ppm)	2213	87.6
Fe_2O_3, Iron(III) oxide (wt.%)	26.81	0.383

Divided the SD from the certificate by the certified value and multiplied by 100 to calculate the RSD.

Carrey out the previous step for all RMs, then the RSD of each RM is squared, and their sum is calculated.

Divided the sum by the total number of RMs; the square root of the resulting number is the value of the total "U_{RM}".

$$RSD = \frac{0.383}{26.81} \times 100\% = 1.43\%$$

The mean U_{RM} = 22.8 %

$$U_{RM} = \sqrt{\frac{22.8}{6}} = 1.95\%$$

Total Uncertinity

Finally, the combined uncertainty will be:

$$U_{Comb.} = \sqrt{(U_{CRM})^2+(U_S)^2}$$

Note that the combined uncertainty must be multiplied by 1.96.

So, the final uncertainty (Expanded uncertainty) is:

$$U_{Exp.} = 1.96^* \; U_{Comb.}$$

For "Fe2O3" ⟶

$$U_{Exp.} = 1.96 \times \sqrt{(1.95)^2 + (1.33)^2} = \underline{4.6\%}$$

Minimum Detection Limit

- The Minimum Detection Limit (MDL) is the lowest concentration of the analyte that can be detected by the method at a specified level of confidence; 95% in this case.

- The lowest level at which the performance is acceptable for a typical application is usually referred to as the Minimum Quantification Limit (MQL).

The LLD was estimated from the slope of the calibration curve

$$LLD = 3.3 \times \frac{S_y}{a}$$

Where:

S_y: is the standard deviation of intercept.

a : is the slope of the calibration curve.

To calculate the value of MQL; the estimated LLD is multiplied by the 'k' factor.

For "Fe2O3":

a= 1.51

$S_{y=}$ 0.04 → $LLD = 3.3 \times \frac{0.04}{1.51} = 0.09$ → LQM= 3× 0.09= 0.26 %

Thank You