Uncertainty estimates for evaluating the significance of bias of PXRF measurements using the SdAR-H1, SdAR-M2 and SdAR-L2 reference materials

Annex to Reference Material Data Sheets
SdAR-H1 Metalliferous sediment
SdAR-M2 Metal-rich sediment
SdAR-L2 Blended sediment

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Purpose of this document

When XRF instruments such as hand-held portable XRF (PXRF) are used for analysis, the mass of the test-portion analyzed may be significantly lower than the recommended minimum mass for laboratory analysis (0.2 g) specified on the relevant data sheet. In particulate heterogeneous materials, the occurrence of small-scale heterogeneity of analytes may then lead to increased uncertainties compared with those quoted for the reference values on the data sheet. Indeed, this issue can also affect routine XRF measurements, due to the limited critical penetration depth of fluorescence X-rays from low atomic number elements.

In this document, revised estimates of the uncertainties of SdAR reference values are given for 18 oxides/elements in SdAR-H1 (Appendix 1), 17 oxides/elements in SdAR-M2 (Appendix 2) and 16 oxides/elements in SdAR-L2 (Appendix 3), for use when materials are analysed with a PXRF instrument at two different beam sizes[1]. The revised uncertainty data are provided for nominal primary X-ray beam diameters of 8 mm and 3 mm, based on measurements made with a Niton PXRF model XL3t Ultra on the following presentations of the test material:

a) Compressed powder pellets (here, 13 mm diameter x 7 mm thickness, formed from powder moistened uniformly with a few drops of 2% PVA solution at a pressure of 8 tonnes and dried)

b) Loose powders (here, filling a 25 mm diameter sample cup to a depth of 25 mm)

The increased uncertainty in reference values requires reassessment of experimental bias evaluated using this reference material. Two worked examples of a typical evaluation are given, one where bias is found to be significant at the 95% confidence level, and one where bias is found to be not significant.

Note that other PXRF equipment may use different nominal beam sizes and there may also be differences between geometries of X-ray detection systems.

Assessing the significance of bias measurements – Basic Principles

The uncertainty on the reference value (RV) effectively expresses the limited range of measured values around the reference value that can arise without indicating significant bias in the analytical method. Both the reference value and each measurement have uncertainty and both of these uncertainties should be taken into account when evaluating whether bias is significant.

The estimation of analytical bias is normally undertaken as part of the validation of an analytical method and is usually monitored as part of routine QC. Bias can be estimated from repeated measurements (e.g. on both sides of a single pellet) made on one or more RMs that are approximately matrix matched in terms of analyte mass-fraction, bulk composition and grain size. It is not recommended to use a single measurement on one RM for the estimation of bias, because it is then impossible to provide a reliable estimate of uncertainty on the measurement result (Um).

The principles outlined in **ERM Application Note 1**[2] state that bias is not considered significant if:

$\Delta_m \leq U_\Delta$

where Δ_m is the absolute difference between mean measured value and reference value, and U_Δ is the uncertainty on Δ_m. This is calculated as:

$U_\Delta = \sqrt{(U_m^2 + U_{RV}^2)}$

U_m = uncertainty of the measurement result
U_{RV} = uncertainty of the reference value

U_m (2s) for single measurement values can be estimated using the methods described in the Eurachem/CITAC guide[3], with coverage factor adjusted for the number of replicates measured, if applicable (i.e. less than 8 independent measurements). Alternatively 'n' replicate measurements can be made on the RM over a period, and the standard error of the mean value (calculated as standard deviation(s) divided by $\sqrt{n}$), and doubled to give an estimate of U_m, as uncertainty on the mean value (i.e. $U_m = 2s/\sqrt{n}$).

When the test portion mass is known to be above the minimum of 0.2 g then U_{RV} can be read as the 2 sigma uncertainty from the Appendices provided in the SdAR data sheets. When measurements are made using PXRF it is recommended that appropriate revised values from the Appendices presented in this document are used. These values include a measured component of uncertainty that is caused by small-scale heterogeneity of the analyte, at the specified beam size.

Worked example for deciding whether a value of bias estimated by measurement is statistically significant

Measured values for As are given for the 8 mm beam and the 3 mm beam diameters in **Table 1**. The values are measurements made, for this example, on both sides of 6 pellets made from the SdAR-H1 reference material, using the same PXRF.

Table 1 Twelve measurements of As in SdAR-H1 using 8 mm and 3 mm beam sizes

8 mm beam (mg kg^{-1})	405, 443, 438, 427, 416, 378, 426, 457, 404, 469, 416, 414
3 mm beam (mg kg^{-1})	439, 372, 414, 410, 457, 369, 383, 385, 374, 456, 428, 449

Methods of estimating U_m are described in ERM Application Note 1[2]. At the most basic level, uncertainty can be estimated as 2 x the standard error of a number of successive measurements of the reference material. In this case it is recommended that the reference material sample be moved to different positions between each measurement in order to incorporate heterogeneity effects into the estimate. The measured value would then be the arithmetic mean of these measurements and U_m calculated (from **Table 1**) as

$$U_m = 2 \times \frac{\text{Standard deviation of 12 measurements}}{\sqrt{12}}$$

Summary inputs to the calculation of bias significance are shown in **Table 2**. RV (Reference Value) and $U_{RV\ beam}$ (Uncertainty 8 mm beam, pellet sample) have been taken from **Appendix 1**, and U_m has been calculated as above.

Table 2 Summary of inputs to bias significance calculation (As)

	Measured mg kg^{-1}	U_m mg kg^{-1}	RV mg kg^{-1}	$U_{RV\ beam}$ mg kg^{-1}
8 mm	425	14	396	24
3 mm	411	20	396	60

<u>Bias significance calculations</u>

<u>8 mm beam</u>

$U_\Delta = \sqrt{(U_m^2 + U_{RV}^2)}$ = **28** mg kg^{-1}

Δ_m = | measured value – RV | = **29** mg kg^{-1}

$\Delta_m > U_\Delta$ therefore the bias of **29 mg kg^{-1}** is considered **significant** at 95% confidence.

<u>3 mm beam</u>

$U_\Delta = \sqrt{(U_m^2 + U_{RV}^2)} = \mathbf{63}$ mg kg^{-1}

$\Delta_m = |$ measured value – RV $| = \mathbf{15}$ mg kg^{-1}

$\Delta_m < U_\Delta$ therefore the bias of **15 mg kg^{-1}** is considered **not significant** at 95% confidence.

When multiple CRMs are used for the estimation of analytical bias as a function of mass fraction, then a model of measured versus certified value can be fitted with least-squares regression or FREML[4]. The statistical significance of the bias can be tested by inspecting the confidence limits of the slope and intercept coefficients of the model, to see whether the confidence intervals include unity or zero respectively.

References

1. Rostron P. and Ramsey, M.H. (2017), Quantifying heterogeneity of small test portion masses of geological reference materials by PXRF: implications for uncertainty of reference values. Geostandards and Geoanalytical Research, doi:10.1111/ggr.12162, onlinelibrary.wiley.com/doi/10.1111/ggr.12162/full

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3. Ramsey M.H. and Ellison S.L.R. (eds.) 2007 Eurachem/EUROLAB/CITAC/Nordtest/AMC Guide: Measurement uncertainty arising from sampling: a guide to methods and approaches. Eurachem (2007) Available from the Eurachem secretariat. https://eurachem.org/images/stories/Guides/pdf/UfS_2007.pdf

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This annex to the reference material information sheet is based upon published research[3], and was approved on behalf of the Reference Material and Certification Committee of the International Association of Geoanalysts.

Appendix 1 - SdAR-H1 Metalliferous Sediment

Reference values with revised uncertainty estimates						
			8 mm beam instrument		3 mm beam instrument	
Oxide/ Element	Reference Value g $100g^{-1}$	Bulk uncertainty g $100g^{-1}$	Uncertainty pellet g $100g^{-1}$	Uncertainty powder g $100g^{-1}$	Uncertainty pellet g $100g^{-1}$	Uncertainty powder g $100g^{-1}$
Al_2O_3	11.83	0.07	0.9	1.3	0.7	3
CaO	1.46	0.01	0.2	0.01	0.22	0.07
Fe_2O_3	6.45	0.04	0.05	0.05	0.09	0.15
K_2O	4.17	0.03	0.07	0.07	0.09	0.15
MnO	0.515	0.005	0.012	0.01	0.03	0.021
SiO_2	65.45	0.18	3	1.9	3	7
TiO_2	0.56	0.004	0.02	0.03	0.08	0.06
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
As*	396	24	24	40	60	60
Ba	866	12	12	30	12	50
Cu	1160	20	40	21	50	50
Mo	64	3	3	7	10	24
Nb	21.9	0.9	2.2	1.2	11	4
Pb	3890	80	80	90	130	120
Rb	152	3	3	3	3	6
Sr	182	3	4	4	4	6
V	73.2	1.7	7	1.7	5	5
Zn	3680	60	109	90	170	180
Zr*	258	60	60	70	70	80

*** Given as information values on reference material data sheet.**
Revised uncertainties have been adjusted to the coverage factor for 95% confidence using the Students t-distribution for 11 degrees of freedom in the uncertainty estimates.

Appendix 2 - SdAR-M2 Metal-rich Sediment

Reference values with revised uncertainty estimates						
			8 mm beam instrument		3 mm beam instrument	
Oxide/ Element	Reference Value g 100g^{-1}	Bulk uncertainty g 100g^{-1}	Uncertainty pellet g 100g^{-1}	Uncertainty powder g 100g^{-1}	Uncertainty pellet g 100g^{-1}	Uncertainty powder g 100g^{-1}
Al_2O_3	12.47	0.06	0.7	0.4	1.3	0.7
CaO	0.84	0.01	0.25	0.01	0.3	0.06
Fe_2O_3	2.63	0.02	0.05	0.05	0.14	0.08
K_2O	5	0.03	0.09	0.09	0.11	0.15
MnO	0.134	0.002	0.003	0.008	0.007	0.016
SiO_2	73.45	0.17	1.7	1.9	4	3
TiO_2	0.3	0.003	0.02	0.019	0.05	0.04
	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}	mg kg^{-1}
As*	76	5	10	6	30	12
Ba	990	12	24	40	12	40
Cu	236	4	13	10	19	50
Mo	13.3	0.4	1.5	1.2	0.4	1.7
Nb	26.2	0.7	1.8	1.5	4	3
Pb	808	14	15	21	21	24
Rb	149	2	4	2.5	2	3
Sr	144	3	3	5	3	3
Zn	750	13	24	13	60	60
Zr	259	7	60	25	30	80

*** Given as information values on reference material data sheet.**
Revised uncertainties have been adjusted to the coverage factor for 95% confidence using the Students t-distribution for 11 degrees of freedom in the uncertainty estimates.

Appendix 3 - SdAR-L2 Blended Sediment

Reference values with revised uncertainty estimates						
			8 mm beam instrument		3 mm beam instrument	
Oxide/ Element	**Reference Value g $100g^{-1}$**	**Bulk uncertainty g $100g^{-1}$**	**Uncertainty pellet g $100g^{-1}$**	**Uncertainty powder g $100g^{-1}$**	**Uncertainty pellet g $100g^{-1}$**	**Uncertainty powder g $100g^{-1}$**
Al_2O_3	11.58	0.05	0.6	0.5	1.4	1.4
CaO	1.06	0.01	0.17	0.04	0.19	0.07
Fe_2O_3	3.63	0.02	0.12	0.11	0.15	0.11
K_2O	4.1	0.02	0.05	0.12	0.12	0.15
MnO	0.099	0.001	0.003	0.003	0.005	0.009
SiO_2	74.48	0.11	1.8	2.3	4	4
TiO_2	0.62	0.003	0.03	0.04	0.12	0.07
	mg kg^{-1}	**mg kg^{-1}**	**mg kg^{-1}**	**mg kg^{-1}**	**mg kg^{-1}**	**mg kg^{-1}**
Ba	809	10	30	110	16	70
Cu	50.8	1.1	1.1	7	9	5
Nb	63	1.5	1.7	3	6	4
Pb	183	3	5	9	7	4
Rb	120	1	1.3	1.6	1	1.1
Sr	150	2	2.2	5	3	2.4
V	35	0.8	0.8	0.8	4	1.8
Zn	201	3	3	5	9	14
Zr	618	10	60	50	90	100

Revised uncertainties have been adjusted to the coverage factor for 95% confidence using the Students t-distribution for 11 degrees of freedom in the uncertainty estimates.