FIRMS - Forensic Isotope Ratio Mass Spectrometry PT Scheme

Round: 233

Issue Number 1

Issued 05 November 2015

Scheme Information

Aims of Scheme

The primary aim of the Forensic Isotope Ratio Mass Spectrometry Proficiency Testing Scheme (FIRMS) is to enable laboratories performing isotope ratio analysis of a range of test materials to monitor their performance and compare it with that of their peers. The FIRMS scheme also aims to provide information to participants on technical issues and methodologies relating to isotope ratio analysis.

Further information on the scheme organisation, the test materials, and the statistical analysis of data are available in the FIRMS Scheme Description and the LGC PT General Protocol.

Performance Assessment

Once a PT round has closed, the results will be analysed and the assigned value determined for each analyte, according to the criteria provided in the Scheme Description. Information regarding the traceability of each calculated assigned value is also provided in the Scheme Description.

For quantitative data, the participant's result, x, (or $\log_{10} x$ for microbiological data) is converted into a z score using the following formula;

$$z = \frac{(x - X)}{SDPA}$$

X =   Assigned value
SDPA = Standard deviation for proficiency assessment

For quantitative data, the uncertainty of the assigned value is calculated to ensure that it would have a negligible effect on participants' performance scores. If the uncertainty of the assigned value is greater than 0.3 x SDPA, then this is not considered negligible. In this situation, a z' (z prime) performance score is automatically calculated rather than a z score, in order to take account of the measurement uncertainty of the assigned value. The z' score is calculated using the following formula;

$$z' = \frac{(x - X)}{\sqrt{(SDPA^2 + UxAV^2)}}$$

X =   Assigned value
SDPA = Standard deviation for proficiency assessment
UxAV= Uncertainty of the assigned value

Expanded SDPA = $\sqrt{(SDPA^2 + UxAV^2)}$

Trend graphs will use a mixture of z and z' scores, i.e. the 'performance score' for the round.

For quantitative data, gross errors or blunders are removed from the data by removal of any results that are greater than the assigned value ± 5 x SDPA. These results are not used in the final calculation of the assigned value and other summary statistics and will be included in the number of 'Excluded Results'. All results, including excluded results, will be given a performance score.

For the purposes of performance assessment for a single round, z and z' scores are interpreted as follows:

z/z' score	Interpretation	Colour coding
$\lvert z \rvert \le 2.00$	Satisfactory result	Green
$2.00 < \lvert z \rvert$ and < 3.00	Questionable result	Amber
$\lvert z \rvert \ge 3.00$	Unsatisfactory result	Red
No score given	See below	No colour coding

Performance scores will not be given for the following:

- For qualitative results, where satisfactory performance is based on the participants reporting the same result as the assigned result. e.g. detected, not detected. For these results, colour coding of green (satisfactory) or red (unsatisfactory) will apply.

- For results of zero; such a result is not normally appropriate and should not be reported, the result should be reported as less than the detection limit rather than zero.
  Note: for a very small number of analytes it may be appropriate to report a result of zero, depending on the type of measurement scale being used.

- For quantitative results where the analyte under test is present in the test material but participants report non-numerical results e.g. 0, <1, >300. In these cases, it is not possible to allocate a performance score and participants should assess their performance based on the assigned value and satisfactory range given.

- For quantitative results, for microbiological test materials, where the analyte under test is not present in the test material, the assigned value will be classified as 'Absent'. Results reported as 'less than' at or below the detection level for our method of confirmation will be assessed as satisfactory (green colour code). Results reported at a higher detection level will not be assessed and participants will need to use their own judgement to determine whether their result is fit for its intended use. Results reporting a positive count will be assessed as unsatisfactory (red colour code).

In some cases, performance scores may not be provided or may be provided but with colour coding suspended (indicating that scores need to be interpreted with caution). For example:

- For small data sets where less than 8 results have been submitted and the assigned value is derived using a consensus value from the participants' results. In these circumstances, there may be increased uncertainty of the assigned value, given the low number of participants, and performance scores will be given for information only.

- In cases where the distribution of the results gives cause for concern e.g. bi-modal data sets. These circumstances will be dependent on the statistical design that is in place.

- If the assigned value falls below a concentration threshold (only applies to some schemes).

In these or similar circumstances, further explanation as to the reasons for suspension of performance scoring or colour coding, and on the interpretation of results, will be given in the report.

Note: Data displayed in the report will have been rounded to the required number of decimal places. However statistical calculations will have been performed on unrounded data. For this reason, there may appear to be differences between displayed data and calculated data, but this does not affect results in any way.

Confidentiality
A unique laboratory reference code is used to report results in order to ensure confidentiality.

Contact details
The Technical Scheme Coordinator is Wayne Gaunt

Please contact **ptcustomerservices@lgcgroup.com** if you have any questions or comments regarding the scheme.

Authorisation

This report was authorised by Matthew Whetton, Head of Chemistry on the 05 November 2015

Sample Details

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Quality Control

Samples were despatched on 21 September 2015
The reporting deadline was 30 October 2015.

The following samples were distributed in FIRMS Round 233:

1: 1 x 0.5g Polyethylene for the determination of delta 2H and 13C
2: 1 x 0.5g Carving wax for the determination of delta 2H and 13C

Further information regarding assigned values, performance assessment and technical comments can be found under the individual sample and analyte results.

Calculated within and between participant standard deviations

Sample 1 (Polyethylene)

Analyte	Within participant SD	Between participant SD
Delta 2H	0.8401	0.7655
Delta 13C	0.0780	0.0173

Sample 2 (Carving wax)

| Analyte	Within participant SD	Between participant SD
Delta 2H	1.2180	0.9231
Delta 13C	0.1199	0.0211

Sample: 01 - FIRMS sample 1

Analyte: delta 2H (VSMOW)

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-93.30	0.77
FM0006	Isotope Ratio Mass Spectrometry	-99.27	-1.06
FM0007	Isotope Ratio Mass Spectrometry	-102.35	-2.00
FM0010	Isotope Ratio Mass Spectrometry	-96.45	-0.20
FM0014	Isotope Ratio Mass Spectrometry	-94.48	0.41
FM0018	Isotope Ratio Mass Spectrometry	-95.56	0.08
FM0027	Isotope Ratio Mass Spectrometry	-96.06	-0.08
FM0028	Isotope Ratio Mass Spectrometry	-92.00	1.17
FM0032	Isotope Ratio Mass Spectrometry	-89.68	1.88
FM0035	Isotope Ratio Mass Spectrometry	-97.40	-0.49

Data Statistics

	Value
Number of Results	10
Number of Excluded Results	0
Mean	-95.66
Median	-95.81
Standard Deviation	3.617
Robust Standard Deviation	3.040
Result Range	-102.35 to -89.68

Performance Statistics

	Value
Assigned Value	-95.81
Uncertainty of Assigned Value	1.20
SDPA	3.04
Expanded SDPA	3.268
Satisfactory Range	-102.35 to -89.27
Satisfactory z' scores	100.0%
Questionable z' scores	0.0%
Unsatisfactory z' scores	0.0%
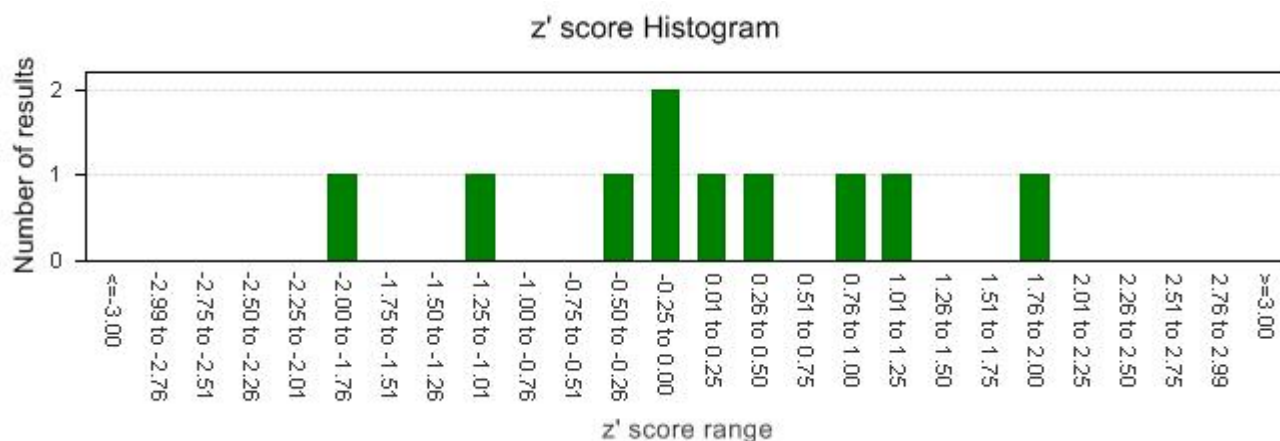
z' score Histogram

Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	10	0	100	-95.81	3.040	-102.35 to -89.68	100.0
All	10	0	100	-95.81	3.040	-102.35 to -89.68	100.0

Comments

The participants in the FIRMS scheme were allowed to report up to 10 results, for the purposes of calculating individual and group summary statistics, plus a mean result, which was used to calculate the summary statistics subsequently applied in the assessment of performance.

In this round most participants obtained satisfactory performance scores for most parameters. Performance scores are currently calculated using the robust standard deviation obtained from the data reported for delta 2H and from a fixed SDPA that has been implemented for delta 13C.

Sample: 01 - FIRMS sample 1

Analyte: delta 2H (VSMOW)

Participant FM0037 has returned results for delta 2H under the 'Other' method category; although no other information was provided.

*Please note, participant performance for this analyte has been assessed using a z' score, rather than a z score, in order to account for the measurement uncertainty of the assigned value which is not negligible when compared to the SDPA.

Sample: 01 - FIRMS sample 1

Analyte: delta 13C (VPDB)

Lab ID	Method	Result	z score
FM0002	Isotope Ratio Mass Spectrometry	-31.54	-0.93
FM0003	Isotope Ratio Mass Spectrometry	-31.33	0.47
FM0006	Isotope Ratio Mass Spectrometry	-31.35	0.33
FM0007	Isotope Ratio Mass Spectrometry	-31.46	-0.40
FM0010	Isotope Ratio Mass Spectrometry	-31.40	0.00
FM0014	Isotope Ratio Mass Spectrometry	-31.40	0.00
FM0018	Isotope Ratio Mass Spectrometry	-31.45	-0.33
FM0027	Isotope Ratio Mass Spectrometry	-31.45	-0.33
FM0028	Isotope Ratio Mass Spectrometry	-31.39	0.07
FM0033	Isotope Ratio Mass Spectrometry	-31.17	1.53
FM0035	Isotope Ratio Mass Spectrometry	-31.46	-0.40
FM0037	Other	-31.19	1.40

Data Statistics

	Value
Number of Results	12
Number of Excluded Results	0
Mean	-31.38
Median	-31.40
Standard Deviation	0.110
Robust Standard Deviation	0.082
Result Range	-31.54 to -31.17

Performance Statistics

	Value
Assigned Value	-31.40
Uncertainty of Assigned Value	0.03
SDPA	0.15
Satisfactory Range	-31.70 to -31.10
Satisfactory z scores	100.0%
Questionable z scores	0.0%
Unsatisfactory z scores	0.0%
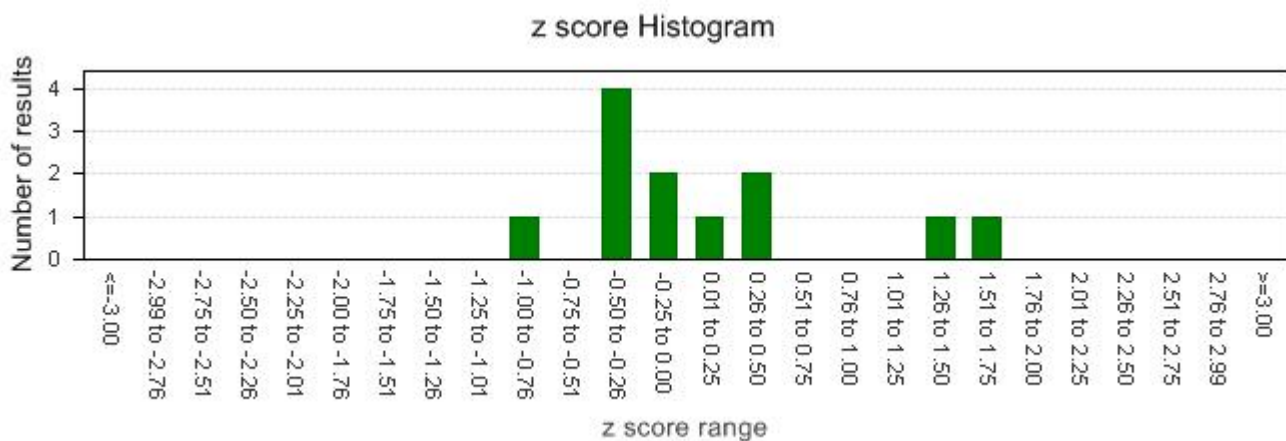
z score Histogram

Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	11	0	91.67	-31.40	0.074	-31.54 to -31.17	100.0
Other	1	0	8.33	-31.19	0.000	-31.19 to -31.19	100.0
All	12	0	100	-31.40	0.082	-31.54 to -31.17	100.0

Comments

Sample: 02 - FIRMS sample 2

Analyte: delta 2H (VSMOW)

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-83.17	0.86
FM0006	Isotope Ratio Mass Spectrometry	-93.81	-2.14
FM0007	Isotope Ratio Mass Spectrometry	-87.72	-0.43
FM0010	Isotope Ratio Mass Spectrometry	-86.17	0.01
FM0014	Isotope Ratio Mass Spectrometry	-81.51	1.33
FM0018	Isotope Ratio Mass Spectrometry	-86.87	-0.19
FM0027	Isotope Ratio Mass Spectrometry	-86.24	-0.01
FM0028	Isotope Ratio Mass Spectrometry	-84.60	0.45
FM0032	Isotope Ratio Mass Spectrometry	-79.62	1.86
FM0035	Isotope Ratio Mass Spectrometry	-89.05	-0.80

Data Statistics

	Value
Number of Results	10
Number of Excluded Results	0
Mean	-85.88
Median	-86.21
Standard Deviation	4.011
Robust Standard Deviation	3.300
Result Range	-93.81 to -79.62

Performance Statistics

	Value
Assigned Value	-86.21
Uncertainty of Assigned Value	1.30
SDPA	3.3
Expanded SDPA	3.547
Satisfactory Range	-93.30 to -79.12
Satisfactory z' scores	90.0%
Questionable z' scores	10.0%
Unsatisfactory z' scores	0.0%
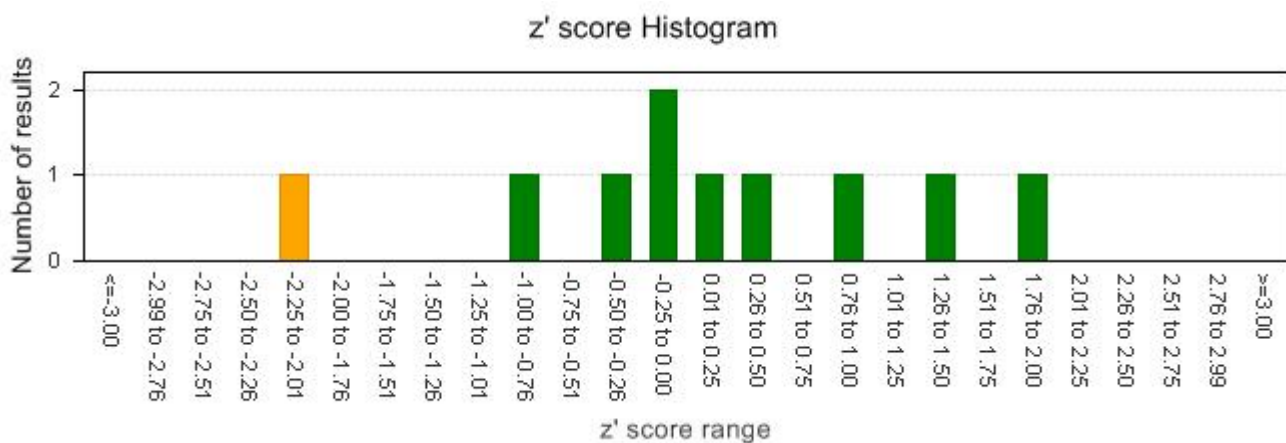
z' score Histogram

Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	10	0	100	-86.21	3.300	-93.81 to -79.62	90.0
All	10	0	100	-86.21	3.300	-93.81 to -79.62	90.0

Comments

*Please note, participant performance for this analyte has been assessed using a z' score, rather than a z score, in order to account for the measurement uncertainty of the assigned value which is not negligible when compared to the SDPA.

**Sample: 02 - FIRMS sample 2**

Analyte: delta 13C (VPDB)

Lab ID	Method	Result	z score
FM0002	Isotope Ratio Mass Spectrometry	-23.19	-0.40
FM0003	Isotope Ratio Mass Spectrometry	-23.06	0.47
FM0006	Isotope Ratio Mass Spectrometry	-23.10	0.20
FM0007	Isotope Ratio Mass Spectrometry	-23.11	0.13
FM0010	Isotope Ratio Mass Spectrometry	-23.12	0.07
FM0014	Isotope Ratio Mass Spectrometry	-23.07	0.40
FM0018	Isotope Ratio Mass Spectrometry	-23.14	-0.07
FM0027	Isotope Ratio Mass Spectrometry	-23.14	-0.07
FM0028	Isotope Ratio Mass Spectrometry	-23.17	-0.27
FM0033	Isotope Ratio Mass Spectrometry	-23.04	0.60
FM0035	Isotope Ratio Mass Spectrometry	-23.26	-0.87
FM0037	Other	-23.16	-0.20

Data Statistics

	Value
Number of Results	12
Number of Excluded Results	0
Mean	-23.13
Median	-23.13
Standard Deviation	0.061
Robust Standard Deviation	0.052
Result Range	-23.26 to -23.04

Performance Statistics

	Value
Assigned Value	-23.13
Uncertainty of Assigned Value	0.02
SDPA	0.15
Satisfactory Range	-23.43 to -22.83
Satisfactory z scores	100.0%
Questionable z scores	0.0%
Unsatisfactory z scores	0.0%
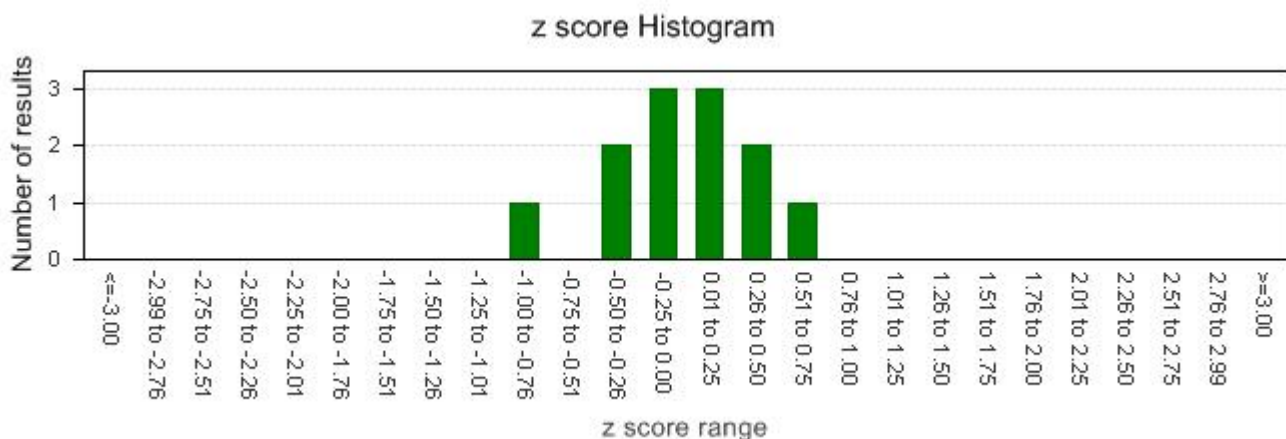
z score Histogram

Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	11	0	91.67	-23.12	0.074	-23.26 to -23.04	100.0
Other	1	0	8.33	-23.16	0.000	-23.16 to -23.16	100.0
All	12	0	100	-23.13	0.052	-23.26 to -23.04	100.0

Comments