Forensic Isotope Ratio Mass Spectrometry (FIRMS)

Round: 275

Issue Number 1

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Science for a safer world

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LGC is the accredited provider of the PT scheme.

UKAS PROFICIENCY TESTING 0001

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

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
$\lvert z\rvert \leq 2.00$	Satisfactory result	Green
$2.00 < \lvert z\rvert$ and < 3.00	Questionable result	Amber
$\lvert z\rvert \geq 3.00$	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 zero results or greater than results. 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 where the analyte under test is present in the test material but participants report a 'less than' value. In these cases, it is not possible to allocate a numeric performance score, however, where the 'less than' value reported is < (AV-3*SDPA) the 'less than' value will be assessed as unsatisfactory (red colour coding), where the less than value reported is between < (AV-3*SDPA) and < (AV-2*SDPA), or > (AV+2*SDPA) the assessment will be questionable (orange colour coding) and it is recommend that you assess whether the method used is fit for purpose, and where the less than value reported is between (AV-2*SDPA and AV+2*SDPA) a satisfactory assessment (green colour coding) will be given as such results are deemed to be consistent with the assigned value.
- 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).
- For quantitative results, for chemistry or clinical test materials, where the analyte under test has not been spiked into the test material, the assigned value will be classified as 'Zero Spike'. A 'less than' value reported at or below the detection level, set as the assigned

value, will be assessed as satisfactory (green colour code). A 'less than' value reported above the 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. Positive, numeric, results which are below the detection level, set as the assigned value, will not be assessed, whilst those that are greater than the assigned value 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 02 May 2019

Sample Details

Samples were despatched on 18 March 2019
The reporting deadline was 26 April 2019

The following samples were distributed in FIRMS Round 275:

1: 1 x 0.5g shark collagen for the determination of delta 2H, 13C, 18O and 15N
2: 1 x 0.5g sodium nitrate for the determination of delta 18O and 15N

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 (shark collagen)

Analyte	Within participant SD	Between participant SD
Delta 2H	2.393655	11.75197
Delta 13C	0.185364	0.183415
Delta 18O	1.054065	0.94112
Delta 15N	0.126948	0.100717

Sample 2 (sodium nitrate)

Analyte	Within participant SD	Between participant SD
Delta 18O	0.412245	1.149486
Delta 15N	0.066404	0.221456

Quality Control

All homogeneity assessments have been conducted in accordance with the principles stipulated in ISO 13528 [1]. Further details regarding the assessment of homogeneity can be found in the LGC Standards Proficiency Testing General Protocol.

Sample	Analyte/Test	Result (SD)	Assessment
1 (shark collagen)	delta 13C	-13.3620 (0.0948)	Pass
2 (sodium nitrate)	delta 15N	9.2370 (0.0876)	Pass

*Results were scaled to the NBS19-LSVEC scale.

Analysis carried out for the purposes of homogeneity and stability testing were sub-contracted by LGC to an external laboratory.

For quantitative testing in this round, a comparison of the standard deviation of the homogeneity results returned and the SDPA expected for the participant assessment was carried out. The samples were considered to be sufficiently homogeneous for use in the PT scheme, based on the values returned.

For qualitative testing, the target analyte must be detected in 100% of test materials analysed.

For any analyte which has not been proven to be sufficiently homogeneous, and any closely related analytes, the value set for the SDPA may be suspended in order to take account of any potential inhomogeneity. The actual value used for the standard deviation for proficiency assessment is shown at the foot of the results and z-score tables in this report.

Often a particular test material does not require homogeneity assessment prior to distribution. Such sample types include standard solutions and aqueous solutions.

[1] ISO 13528 (2015), ‘Statistical methods for use in proficiency testing by inter-laboratory comparison’.

Sample: 01 - FIRMS sample 1

Analyte: delta 2H (VSMOW)

Lab ID	Method	Result	z score
FM0002	Isotope Ratio Mass Spectrometry	2.91	
FM0014	Isotope Ratio Mass Spectrometry	10.17	
FM0018	Isotope Ratio Mass Spectrometry	9.71	
FM0026	Isotope Ratio Mass Spectrometry	13.83	
FM0027	Isotope Ratio Mass Spectrometry	30.41	
FM0048	Isotope Ratio Mass Spectrometry	30.50	

Data Statistics

	Value
Number of Results	6
Number of Excluded Results	0
Mean	N/A
Median	N/A
Standard Deviation	N/A
Robust Standard Deviation	N/A
Result Range	2.91 to 30.50

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.

A wide range of results were reported for delta 2H with values ranging from 2.91 to 30.50. Due to the variation observed it was not possible for a consensus to be determined and so performance scores have not been provided for this analyte.

Sample: 01 - FIRMS sample 1

Analyte: delta 13C (VPDB)

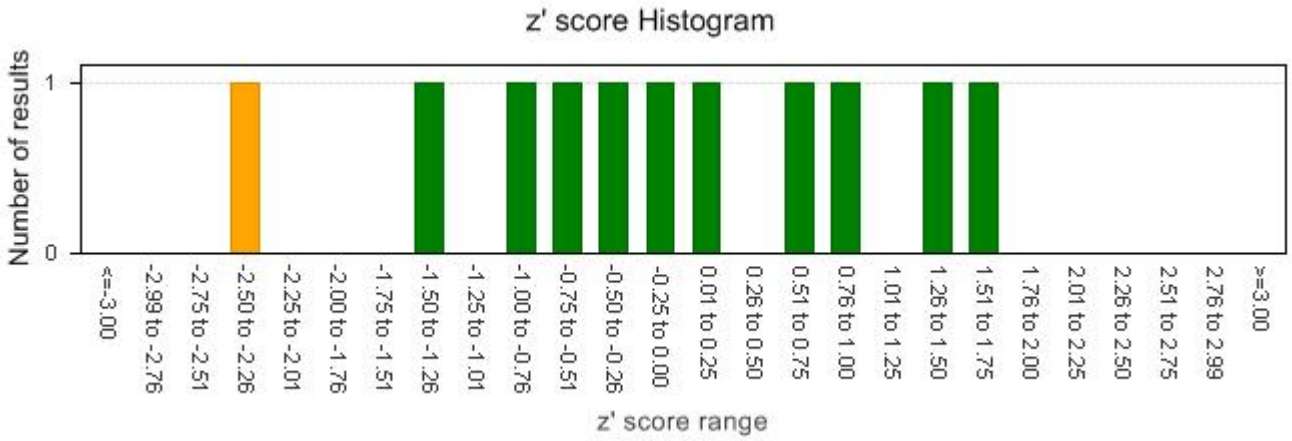
Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-12.99	1.33
FM0003	Isotope Ratio Mass Spectrometry	-12.93	1.69
FM0014	Isotope Ratio Mass Spectrometry	-13.45	-1.45
FM0018	Isotope Ratio Mass Spectrometry	-13.62	-2.48
FM0019	Isotope Ratio Mass Spectrometry	-13.34	-0.79
FM0026	Isotope Ratio Mass Spectrometry	-13.19	0.12
FM0027	Isotope Ratio Mass Spectrometry	-13.30	-0.54
FM0034	Isotope Ratio Mass Spectrometry	-13.05	0.97
FM0036	Isotope Ratio Mass Spectrometry	-13.21	0.00
FM0046	Isotope Ratio Mass Spectrometry	-13.12	0.54
FM0048	Isotope Ratio Mass Spectrometry	-13.28	-0.42

Data Statistics

	Value
Number of Results	11
Number of Excluded Results	0
Mean	-13.23
Median	-13.21
Standard Deviation	0.203
Robust Standard Deviation	0.193
Result Range	-13.62 to -12.93

Performance Statistics

	Value
Assigned Value	-13.21
Uncertainty of Assigned Value	0.07
SDPA	0.15
Expanded SDPA	0.166
Satisfactory Range	-13.54 to -12.88
Satisfactory z' scores	90.9%
Questionable z' scores	9.1%
Unsatisfactory z' scores	0.0%



Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	11	0	100	-13.21	0.193	-13.62 to -12.93	90.9
All	11	0	100	-13.21	0.193	-13.62 to -12.93	90.9

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: 01 - FIRMS sample 1

Analyte: delta 18O (VSMOW)

Lab ID	Method	Result	z' score*
FM0003	Isotope Ratio Mass Spectrometry	18.73	2.47
FM0018	Isotope Ratio Mass Spectrometry	18.00	0.49
FM0026	Isotope Ratio Mass Spectrometry	17.64	-0.49
FM0027	Isotope Ratio Mass Spectrometry	17.41	-1.11
FM0046	Isotope Ratio Mass Spectrometry	15.48	-6.36
FM0048	Isotope Ratio Mass Spectrometry	14.05	-10.25

Due to the low number of results returned, performance scores are shown for information purposes only

Data Statistics

	Value
Number of Results	6
Number of Excluded Results	2
Mean	17.95
Median	17.82
Standard Deviation	0.577
Robust Standard Deviation	0.437
Result Range	17.41 to 18.73

Performance Statistics

	Value
Assigned Value	17.82
Uncertainty of Assigned Value	0.27
SDPA	0.25
Expanded SDPA	0.368
Satisfactory Range	17.08 to 18.56
Satisfactory z' scores	50.0%
Questionable z' scores	16.7%
Unsatisfactory z' scores	33.3%

Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	6	2	100	17.82	0.437	17.41 to 18.73	50.0
All	6	2	100	17.82	0.437	17.41 to 18.73	50.0

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: 01 - FIRMS sample 1

Analyte: delta 15N (AIR)

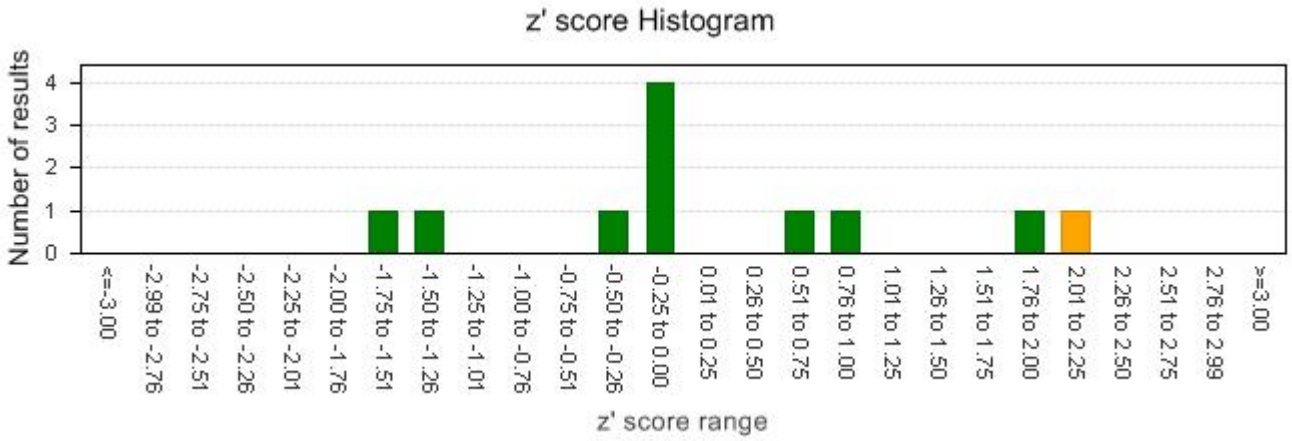
Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	12.33	-0.43
FM0003	Isotope Ratio Mass Spectrometry	12.12	-1.73
FM0014	Isotope Ratio Mass Spectrometry	12.39	-0.06
FM0018	Isotope Ratio Mass Spectrometry	12.19	-1.30
FM0019	Isotope Ratio Mass Spectrometry	12.50	0.62
FM0026	Isotope Ratio Mass Spectrometry	12.54	0.87
FM0027	Isotope Ratio Mass Spectrometry	12.40	0.00
FM0034	Isotope Ratio Mass Spectrometry	12.76	2.23
FM0036	Isotope Ratio Mass Spectrometry	12.38	-0.12
FM0046	Isotope Ratio Mass Spectrometry	12.70	1.86
FM0048	Isotope Ratio Mass Spectrometry	12.40	0.00

Data Statistics

	Value
Number of Results	11
Number of Excluded Results	0
Mean	12.43
Median	12.40
Standard Deviation	0.192
Robust Standard Deviation	0.148
Result Range	12.12 to 12.76

Performance Statistics

	Value
Assigned Value	12.40
Uncertainty of Assigned Value	0.06
SDPA	0.15
Expanded SDPA	0.162
Satisfactory Range	12.08 to 12.72
Satisfactory z' scores	90.9%
Questionable z' scores	9.1%
Unsatisfactory z' scores	0.0%



Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	11	0	100	12.40	0.148	12.12 to 12.76	90.9
All	11	0	100	12.40	0.148	12.12 to 12.76	90.9

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 18O (VSMOW)

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	26.17	-2.56
FM0003	Isotope Ratio Mass Spectrometry	27.29	0.31
FM0018	Isotope Ratio Mass Spectrometry	26.81	-0.92
FM0019	Isotope Ratio Mass Spectrometry	31.30	10.58
FM0026	Isotope Ratio Mass Spectrometry	27.55	0.97
FM0027	Isotope Ratio Mass Spectrometry	27.17	0.00
FM0034	Isotope Ratio Mass Spectrometry	30.00	7.25
FM0046	Isotope Ratio Mass Spectrometry	25.52	-4.23
FM0048	Isotope Ratio Mass Spectrometry	23.86	-8.48

Due to the low number of results returned, performance scores are shown for information purposes only

Data Statistics

	Value
Number of Results	9
Number of Excluded Results	4
Mean	27.00
Median	27.17
Standard Deviation	0.534
Robust Standard Deviation	0.534
Result Range	26.17 to 27.55

Performance Statistics

	Value
Assigned Value	27.17
Uncertainty of Assigned Value	0.30
SDPA	0.25
Expanded SDPA	0.391
Satisfactory Range	26.39 to 27.95
Satisfactory z' scores	44.4%
Questionable z' scores	11.1%
Unsatisfactory z' scores	44.4%

Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	9	4	100	27.17	0.534	26.17 to 27.55	44.4
All	9	4	100	27.17	0.534	26.17 to 27.55	44.4

Comments

The SDPA used in the determination of performance scores is fixed at 0.25 and the satisfactory range has been set as 26.39 to 27.95.

As the results reported for delta 18O ranged from 23.86 to 31.30 just 44% of participants have achieved a satisfactory performance assessment for this analyte.

*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 15N (AIR)

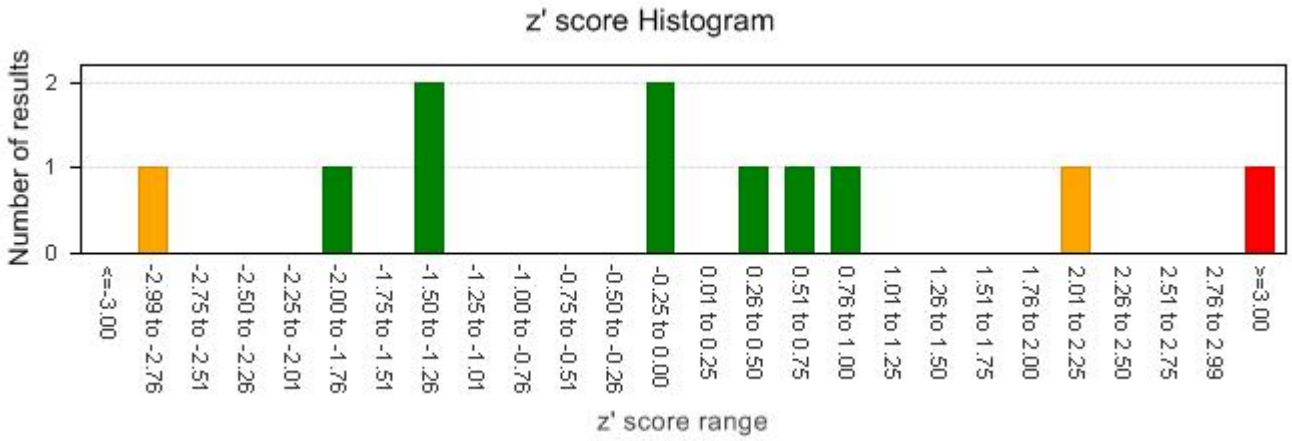
Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	9.00	-1.46
FM0003	Isotope Ratio Mass Spectrometry	9.47	0.91
FM0014	Isotope Ratio Mass Spectrometry	9.29	0.00
FM0018	Isotope Ratio Mass Spectrometry	9.29	0.00
FM0019	Isotope Ratio Mass Spectrometry	9.70	2.07
FM0026	Isotope Ratio Mass Spectrometry	8.74	-2.77
FM0027	Isotope Ratio Mass Spectrometry	9.41	0.60
FM0034	Isotope Ratio Mass Spectrometry	8.94	-1.76
FM0036	Isotope Ratio Mass Spectrometry	9.38	0.45
FM0046	Isotope Ratio Mass Spectrometry	14.05	23.98
FM0048	Isotope Ratio Mass Spectrometry	9.02	-1.36

Data Statistics

	Value
Number of Results	11
Number of Excluded Results	1
Mean	9.22
Median	9.29
Standard Deviation	0.291
Robust Standard Deviation	0.334
Result Range	8.74 to 9.70

Performance Statistics

	Value
Assigned Value	9.29
Uncertainty of Assigned Value	0.13
SDPA	0.15
Expanded SDPA	0.198
Satisfactory Range	8.89 to 9.69
Satisfactory z' scores	72.7%
Questionable z' scores	18.2%
Unsatisfactory z' scores	9.1%



Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat. %
Isotope Ratio Mass Spectrometry	11	1	100	9.29	0.334	8.74 to 9.70	72.7
All	11	1	100	9.29	0.334	8.74 to 9.70	72.7

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.