



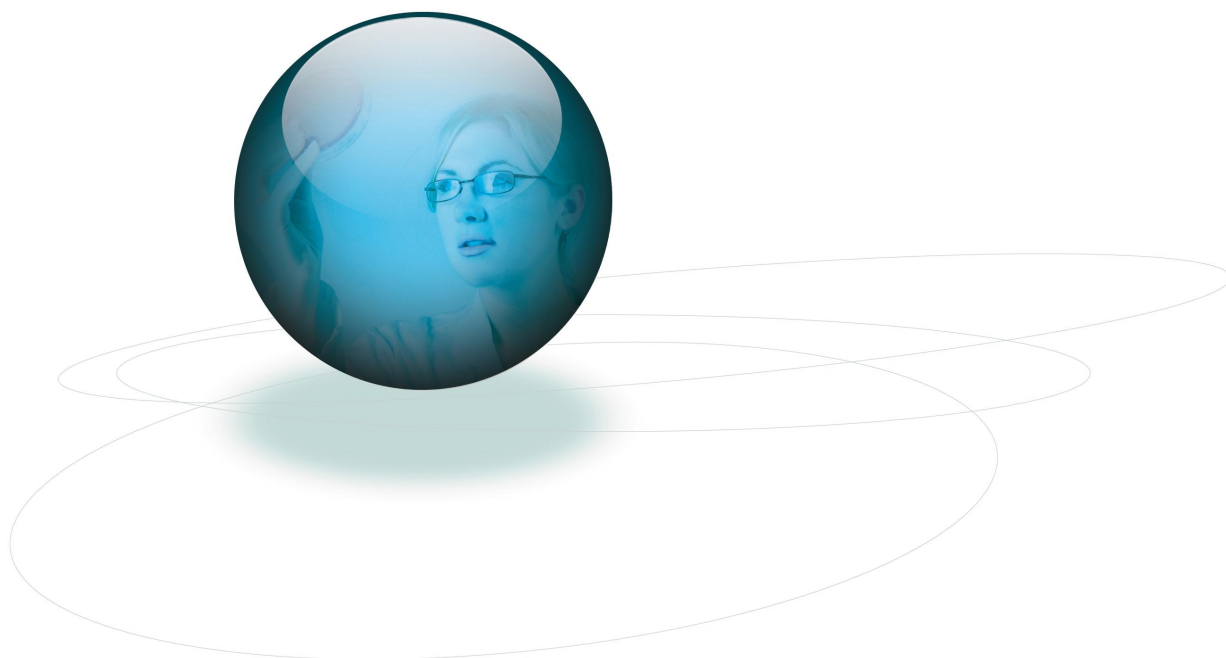
Excellence through measurement

FIRMS - Forensic Isotope Ratio Mass Spectrometry

Round: 203

Issue Number 2

Issued 31 July 2013



LGC Standards Proficiency Testing

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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, according to the criteria given 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;

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

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 $0.3 \times \text{SDPA}$, 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;

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

X = Assigned value

SDPA = Standard deviation for proficiency assessment

Ux = Uncertainty of the assigned value

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 $\pm 5 \times \text{SDPA}$. 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
$ z \leq 2.00$	Satisfactory result	Green
$2.00 < z $ and < 3.00	Questionable result	Amber
$ z \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 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 Matthew Whetton

Please contact customerservice@lqcpt.com if you have any questions or comments regarding the scheme.

Issue Information

This report has been reissued due to the transposition of the QC data in the issue 1. The results for the chitim sample had been mistakenly attributed to the oil sample and vice versa. No participant results or performance assessments have changed as a result of this re-issue.

Authorisation

This report was authorised by Matthew Whetton, Head of Chemistry on the 31 July 2013

A handwritten signature in black ink, appearing to be 'M. H.', located in the upper left quadrant of the page.

Sample Details

Samples were despatched on 29 April 2013
The reporting deadline was 07 June 2013*

The following samples were distributed in FIRMS Round 203:

- 1: 1 x 0.5g Oil sample for the determination of delta 2H, 13C, 15N and 18O
2: 1 x 0.5g Chitin sample for the determination of delta 2H, 13C, 15N and 18O

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

*Deadline was extended to allow reporting of replicate results.

Calculated within and between participant standard deviations

Sample 1

10 x delta 2H

Within participant SD = 0.985223

Between participant SD = 30.88684

10 x delta 13C

Within participant SD = 0.090986

Between participant SD = 7.082325

Sample 2

10 x delta 2H

Within participant SD = 1.347819

Between participant SD = 5.484558

10 x delta 13C

Within participant SD = 0.093806

Between participant SD = 5.742599

10 x delta 15N

Within participant SD = 0.109131

Between participant SD = 1.022194

10 x delta 18O

Within participant SD = 0.351623

Between participant SD = 0.497071

Quality Control

All homogeneity assessments have been conducted in accordance with the principles stipulated in ISO 13528 ^[1] and the IUPAC ^[2] Harmonized PT Protocol. 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 (Oil)	delta 13C	-27.19 (0.050)*	Pass
2 (Chitin)	delta 13C	-21.83 (0.042)*	Pass

*Results were scaled to the NBS19-LSVEC scale.

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 (2005), 'Statistical methods for use in proficiency testing by inter-laboratory comparisons'.

[2] M Thompson, S L R Ellison, R Wood, 'International Harmonised Protocol for the Proficiency Testing of Analytical Chemistry Laboratories', *Pure Appl. Chem.*, 2006, 78, 145-196.

Sample: 01 - FIRMS sample 1**Analyte: 10 x delta 2H (VSMOW)**

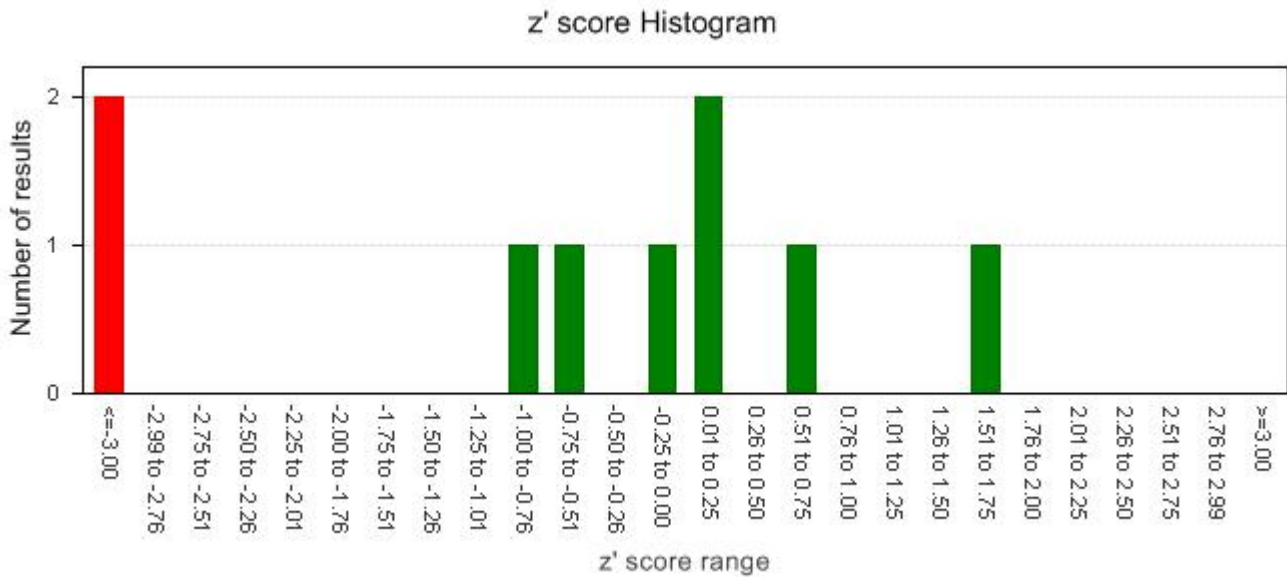
Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-100.50	0.53
FM0009	Isotope Ratio Mass Spectrometry	-105.71	-0.76
FM0010	Isotope Ratio Mass Spectrometry	-983.50	-218.21
FM0012	Isotope Ratio Mass Spectrometry	-102.72	-0.02
FM0014	Isotope Ratio Mass Spectrometry	-95.77	1.70
FM0015	Isotope Ratio Mass Spectrometry	-117.08	-3.57
FM0016	Isotope Ratio Mass Spectrometry	-101.92	0.18
FM0018	Isotope Ratio Mass Spectrometry	-105.48	-0.70
FM0022	Isotope Ratio Mass Spectrometry	-102.57	0.02

Data Statistics

	Value
Number of Results	9
Number of Excluded Results	1
Mean	-103.97
Median	-102.65
Standard Deviation	6.143
Robust Standard Deviation	3.693
Result Range	-117.08 to -95.77

Performance Statistics

	Value
Assigned Value	-102.65
Uncertainty of Assigned Value	1.63
SDPA	3.693
Satisfactory Range	-110.04 to -95.26
Satisfactory z' scores	77.8%
Questionable z' scores	0.0%
Unsatisfactory z' scores	22.2%

Sample: 01 - FIRMS sample 1**Analyte: 10 x delta 2H (VSMOW)****Methodology Summary**

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	9	1	100	-102.65	3.693	-117.08 to -95.77	77.8
All	9	1	100	-102.65	3.693	-117.08 to -95.77	77.8

Comments

The participants in the FIRMS scheme were allowed to report up to 10 results plus a mean result, in order to calculate the summary statistics for the participant group.

It was brought to our attention during the reporting process that participants were requested to report delta values as 10 x delta, whereas 1000 x delta would have been more familiar to participants.

One participant has reported results which are different to the assigned values by a factor of 10 and as a result has obtained large negative z scores.

In this round the SDPA used for the assessment of the participants is the calculated robust standard deviation. Participants are advised to consider the magnitude of this statistic and the absolute difference for their result from the median value (bias), when interpreting the assessment of their performance.

*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: 10 x delta 13C (VPDB)**

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-27.40	0.00
FM0003	Isotope Ratio Mass Spectrometry	-27.06	4.26
FM0009	Isotope Ratio Mass Spectrometry	-27.38	0.25
FM0010	Isotope Ratio Mass Spectrometry	-273.80	-3085.79
FM0012	Isotope Ratio Mass Spectrometry	-27.61	-2.63
FM0014	Isotope Ratio Mass Spectrometry	-27.44	-0.50
FM0015	Isotope Ratio Mass Spectrometry	-27.47	-0.88
FM0016	Isotope Ratio Mass Spectrometry	-27.20	2.50
FM0017	Isotope Ratio Mass Spectrometry	-27.35	0.63
FM0018	Isotope Ratio Mass Spectrometry	-27.45	-0.63
FM0019	Isotope Ratio Mass Spectrometry	-27.40	0.00
FM0021	Isotope Ratio Mass Spectrometry	-27.39	0.13
FM0022	Isotope Ratio Mass Spectrometry	-27.33	0.88

Data Statistics

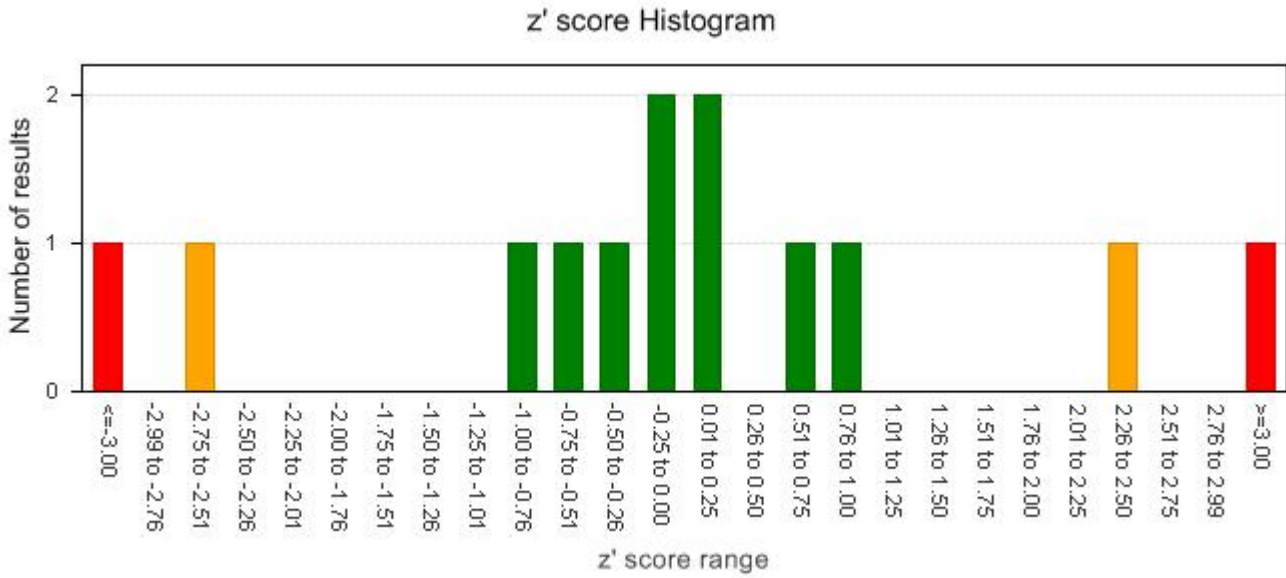
	Value
Number of Results	13
Number of Excluded Results	1
Mean	-27.37
Median	-27.40
Standard Deviation	0.138
Robust Standard Deviation	0.074
Result Range	-27.61 to -27.06

Performance Statistics

	Value
Assigned Value	-27.40
Uncertainty of Assigned Value	0.03
SDPA	0.074
Satisfactory Range	-27.55 to -27.25
Satisfactory z' scores	69.2%
Questionable z' scores	15.4%
Unsatisfactory z' scores	15.4%

Sample: 01 - FIRMS sample 1

Analyte: 10 x delta 13C (VPDB)



Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	13	1	100	-27.40	0.074	-27.61 to -27.06	69.2
All	13	1	100	-27.40	0.074	-27.61 to -27.06	69.2

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: 10 x delta 2H (VSMOW)**

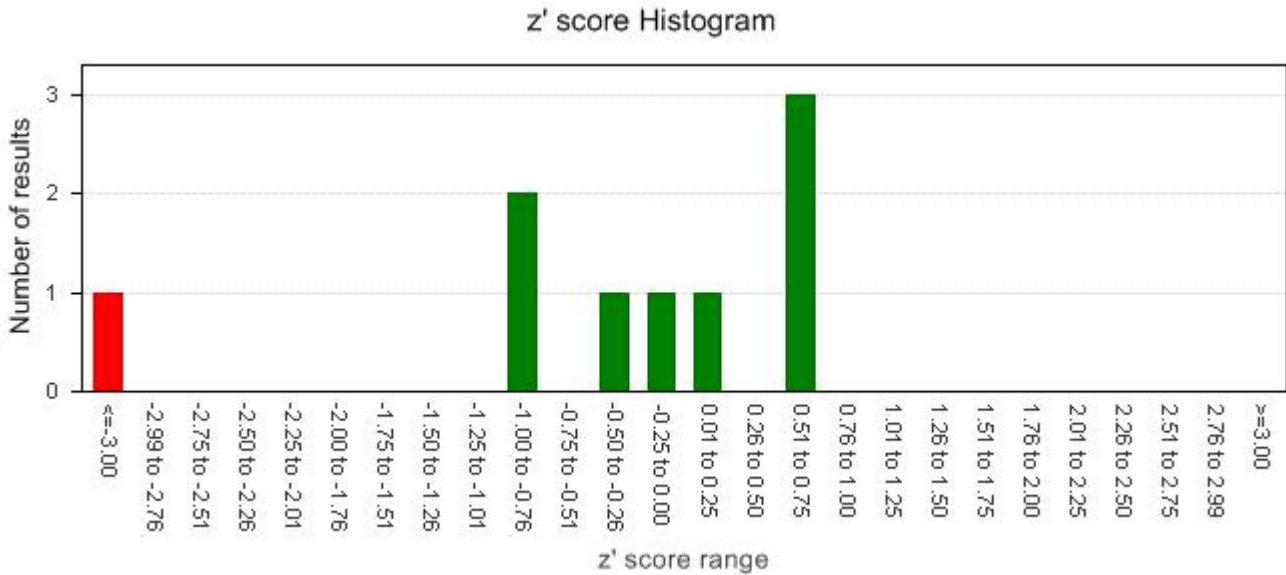
Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-31.30	-0.19
FM0009	Isotope Ratio Mass Spectrometry	-39.10	-0.92
FM0010	Isotope Ratio Mass Spectrometry	-169.40	-12.96
FM0012	Isotope Ratio Mass Spectrometry	-38.85	-0.89
FM0014	Isotope Ratio Mass Spectrometry	-21.59	0.70
FM0015	Isotope Ratio Mass Spectrometry	-22.02	0.66
FM0016	Isotope Ratio Mass Spectrometry	-23.04	0.57
FM0018	Isotope Ratio Mass Spectrometry	-27.10	0.19
FM0022	Isotope Ratio Mass Spectrometry	-32.09	-0.27

Data Statistics

	Value
Number of Results	9
Number of Excluded Results	1
Mean	-29.39
Median	-29.20
Standard Deviation	7.126
Robust Standard Deviation	9.892
Result Range	-39.10 to -21.59

Performance Statistics

	Value
Assigned Value	-29.20
Uncertainty of Assigned Value	4.37
SDPA	9.892
Satisfactory Range	-48.98 to -9.42
Satisfactory z' scores	88.9%
Questionable z' scores	0.0%
Unsatisfactory z' scores	11.1%

Sample: 02 - FIRMS sample 2**Analyte: 10 x delta 2H (VSMOW)****Methodology Summary**

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	9	1	100	-29.20	9.892	-39.10 to -21.59	88.9
All	9	1	100	-29.20	9.892	-39.10 to -21.59	88.9

Comments

In comparison to the data returned for the other measurands, the results for delta 2H in the Chitin sample are varied. A result of this variability in the participant data is a large SDPA, which then defines the satisfactory range for the participant results.

The SDPA for this measurand is greater than 30% of the calculated assigned value (median), which results in a satisfactory range of $\pm 60\%$. The SDPAs calculated for the other measurands in this round are between 0.3 and 6% of the calculated assigned values.

Participants are advised to consider the magnitude of the SDPA used in the calculation of z scores, when interpreting the assessment of their performance.

*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: 10 x delta 13C (VPDB)**

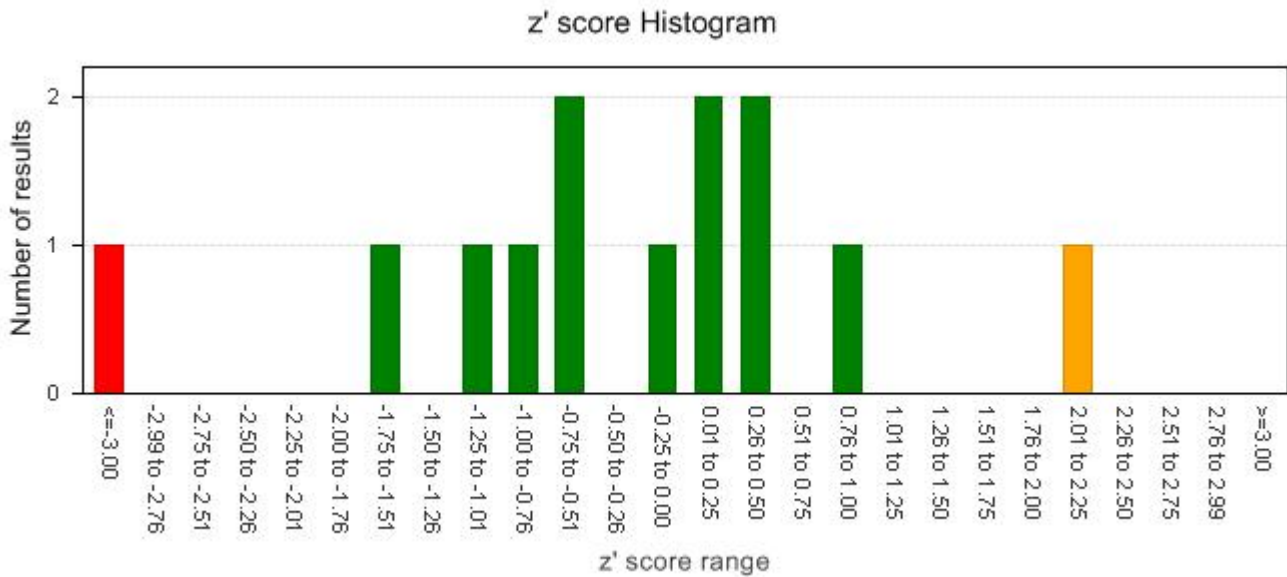
Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-22.06	0.13
FM0003	Isotope Ratio Mass Spectrometry	-22.32	-1.60
FM0009	Isotope Ratio Mass Spectrometry	-22.03	0.33
FM0010	Isotope Ratio Mass Spectrometry	-222.10	-1337.01
FM0012	Isotope Ratio Mass Spectrometry	-21.78	2.01
FM0014	Isotope Ratio Mass Spectrometry	-22.17	-0.60
FM0015	Isotope Ratio Mass Spectrometry	-22.25	-1.14
FM0016	Isotope Ratio Mass Spectrometry	-22.04	0.27
FM0017	Isotope Ratio Mass Spectrometry	-21.96	0.80
FM0018	Isotope Ratio Mass Spectrometry	-22.06	0.13
FM0019	Isotope Ratio Mass Spectrometry	-22.17	-0.60
FM0021	Isotope Ratio Mass Spectrometry	-22.09	-0.07
FM0022	Isotope Ratio Mass Spectrometry	-22.20	-0.80

Data Statistics

	Value
Number of Results	13
Number of Excluded Results	1
Mean	-22.09
Median	-22.08
Standard Deviation	0.143
Robust Standard Deviation	0.141
Result Range	-22.32 to -21.78

Performance Statistics

	Value
Assigned Value	-22.08
Uncertainty of Assigned Value	0.05
SDPA	0.141
Satisfactory Range	-22.36 to -21.80
Satisfactory z' scores	84.6%
Questionable z' scores	7.7%
Unsatisfactory z' scores	7.7%

Sample: 02 - FIRMS sample 2**Analyte: 10 x delta 13C (VPDB)****Methodology Summary**

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	13	1	100	-22.08	0.141	-22.32 to -21.78	84.6
All	13	1	100	-22.08	0.141	-22.32 to -21.78	84.6

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: 10 x delta 15N (AIR)**

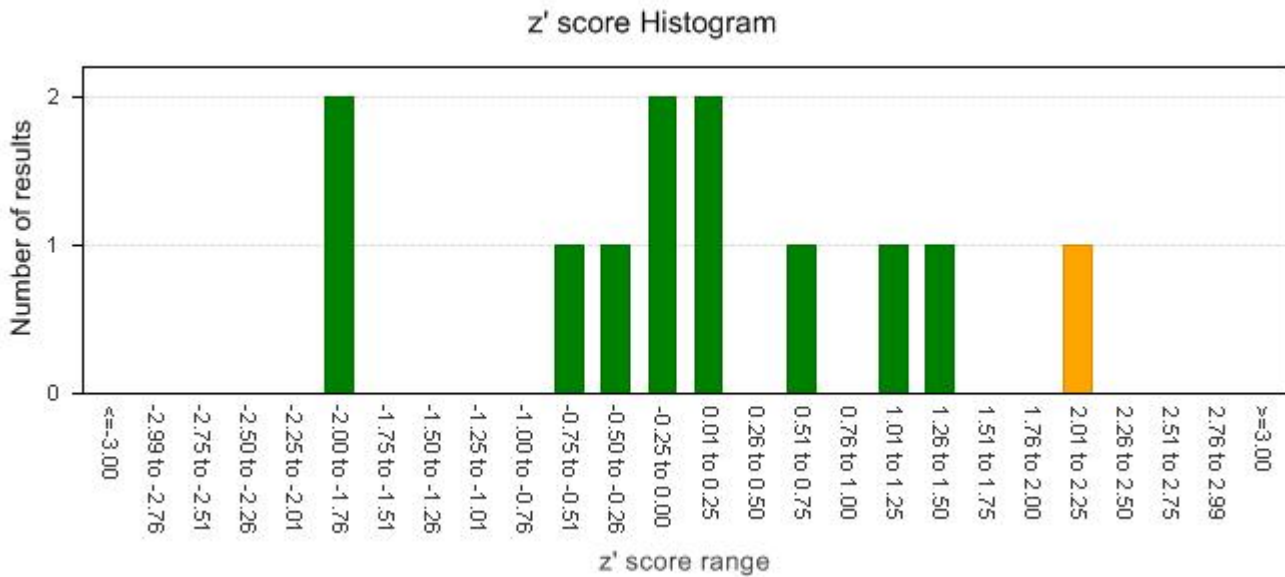
Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-4.71	0.53
FM0003	Isotope Ratio Mass Spectrometry	-4.59	1.17
FM0009	Isotope Ratio Mass Spectrometry	-4.90	-0.48
FM0012	Isotope Ratio Mass Spectrometry	-5.15	-1.81
FM0014	Isotope Ratio Mass Spectrometry	-4.57	1.28
FM0015	Isotope Ratio Mass Spectrometry	-5.14	-1.76
FM0016	Isotope Ratio Mass Spectrometry	-4.78	0.16
FM0017	Isotope Ratio Mass Spectrometry	-4.83	-0.11
FM0018	Isotope Ratio Mass Spectrometry	-4.95	-0.75
FM0019	Isotope Ratio Mass Spectrometry	-4.85	-0.21
FM0021	Isotope Ratio Mass Spectrometry	-4.42	2.08
FM0022	Isotope Ratio Mass Spectrometry	-4.77	0.21

Data Statistics

	Value
Number of Results	12
Number of Excluded Results	0
Mean	-4.81
Median	-4.81
Standard Deviation	0.218
Robust Standard Deviation	0.178
Result Range	-5.15 to -4.42

Performance Statistics

	Value
Assigned Value	-4.81
Uncertainty of Assigned Value	0.06
SDPA	0.178
Satisfactory Range	-5.17 to -4.45
Satisfactory z' scores	91.7%
Questionable z' scores	8.3%
Unsatisfactory z' scores	0.0%

Sample: 02 - FIRMS sample 2**Analyte: 10 x delta 15N (AIR)****Methodology Summary**

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	12	0	100	-4.81	0.178	-5.15 to -4.42	91.7
All	12	0	100	-4.81	0.178	-5.15 to -4.42	91.7

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.

Sample: 02 - FIRMS sample 2**Analyte: 10 x delta 18O (VSMOW)**

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	31.80	0.36
FM0009	Isotope Ratio Mass Spectrometry	29.09	-1.00
FM0012	Isotope Ratio Mass Spectrometry	31.09	0.00
FM0015	Isotope Ratio Mass Spectrometry	31.32	0.12
FM0016	Isotope Ratio Mass Spectrometry	29.75	-0.67
FM0018	Isotope Ratio Mass Spectrometry	32.31	0.61
FM0022	Isotope Ratio Mass Spectrometry	28.80	-1.15

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

Data Statistics

	Value
Number of Results	7
Number of Excluded Results	0
Mean	30.59
Median	31.09
Standard Deviation	1.376
Robust Standard Deviation	1.809
Result Range	28.80 to 32.31

Performance Statistics

	Value
Assigned Value	31.09
Uncertainty of Assigned Value	0.85
SDPA	1.809
Satisfactory Range	27.47 to 34.71
Satisfactory z' scores	100.0%
Questionable z' scores	0.0%
Unsatisfactory z' scores	0.0%

Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	7	0	100	31.09	1.809	28.80 to 32.31	100.0
All	7	0	100	31.09	1.809	28.80 to 32.31	100.0

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.