



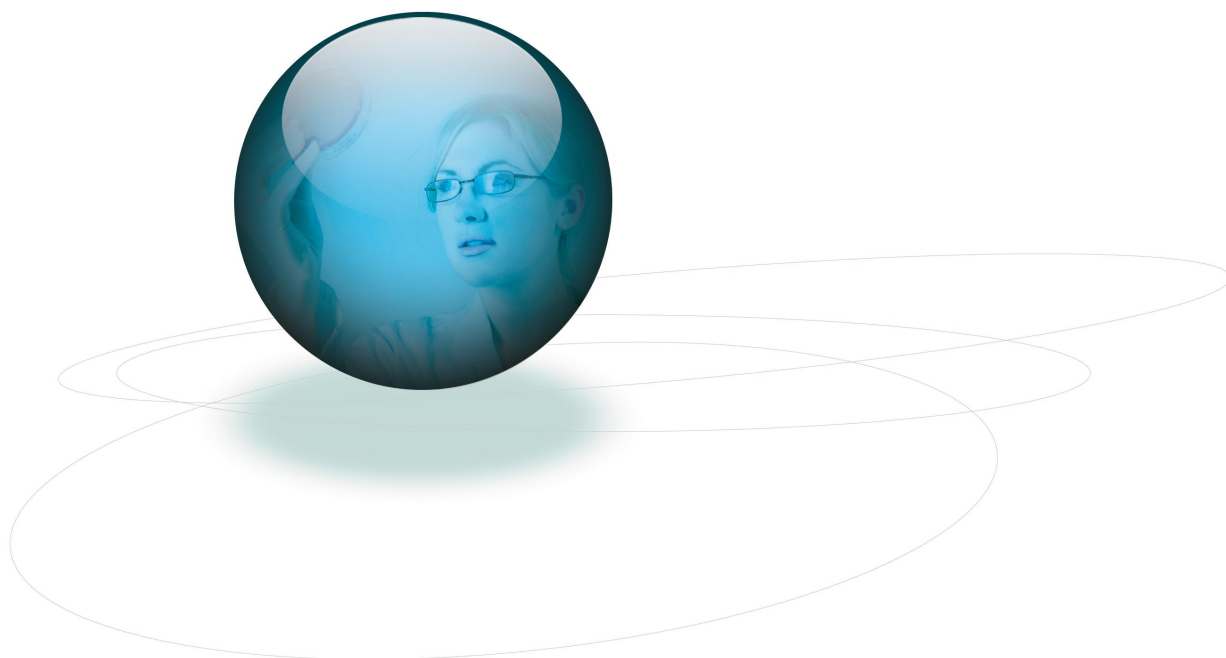
Excellence through measurement

FIRMS - Forensic Isotope Ratio Mass Spectrometry PT Scheme

Round: 209

Issue Number 1

Issued 26 November 2013



LGC Standards Proficiency Testing

1 Chamberhall Business Park, Chamberhall Green, Bury BL9 0AP, UK

Telephone: +44 (0) 161 762 2500 Fax: +44 (0) 161 762 2501

Email: customerservices@lgcpt.com Website: www.lgcpt.com

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;

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

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.

Authorisation

This report was authorised by Matthew Whetton, Head of Chemistry on the 26 November 2013



Sample Details

Samples were despatched on 23 September 2013
The reporting deadline was 01 November 2013

The following samples were distributed in FIRMS Round 209:

- 1: 1 x 0.5g ground hemp sample for the determination of delta 2H, 13C, 15N and 18O
- 2: 1 x 0.5g vegetable oil sample for the determination of delta 2H, 13C, and 18O

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 (Hemp)

delta 2H

Within participant SD = 2.9268

Between participant SD = 4.5257

delta 13C

Within participant SD = 0.1404

Between participant SD = 0.0378

delta 15N

Within participant SD = 0.1309

Between participant SD = 0.0491

delta 18O

Within participant SD = 0.4952

Between participant SD = 0.7186

Sample 2 (Vegetable Oil)

delta 2H

Within participant SD = 10.2109

Between participant SD = 1.0080

delta 13C

Within participant SD = 0.0632

Between participant SD = 0.0274

delta 18O

Within participant SD = 7.3491

Between participant SD = 0.7329

Quality Control

All homogeneity assessments have been conducted in accordance with the principles stipulated in ISO 13528 ^[1] and/or 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 (Hemp)	delta 13C	-28.084 (0.258)*	Pass
2 (Oil)	delta 13C	-28.525 (0.144)*	Pass

*Results were scaled to the NBS19-LSVEC scale.

Analysis carried out for the purposes of homogeneity testing was 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 (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 - hemp**Analyte: delta 2H (VSMOW)**

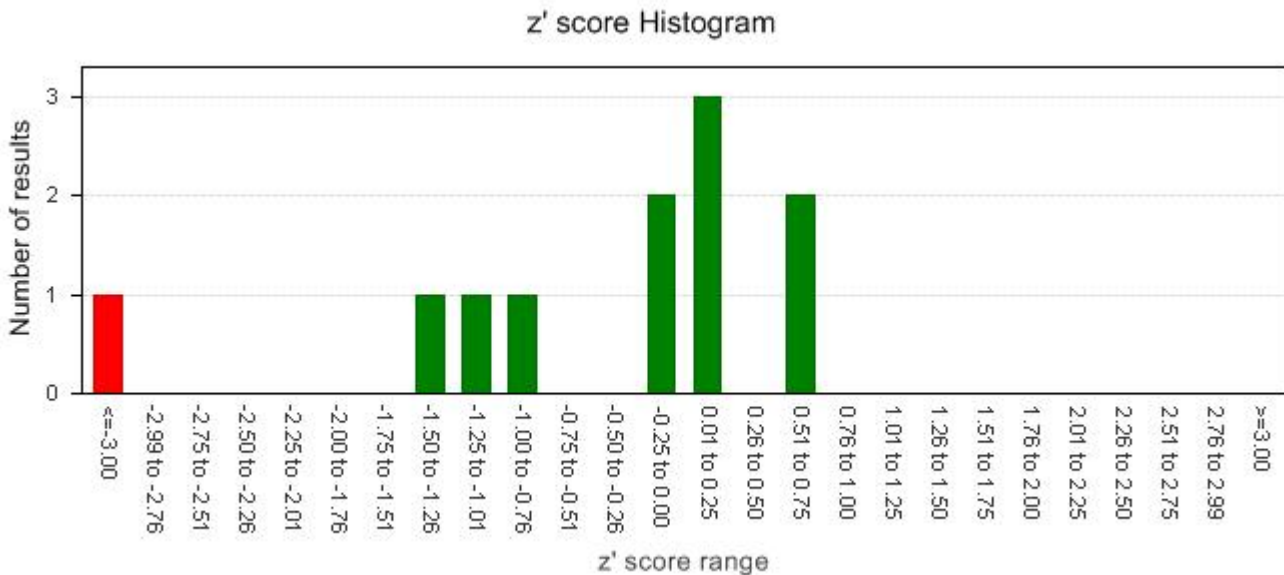
Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-101.91	-1.08
FM0006	Isotope Ratio Mass Spectrometry	-104.57	-1.32
FM0007	Isotope Ratio Mass Spectrometry	-82.31	0.64
FM0009	Isotope Ratio Mass Spectrometry	-123.91	-3.02
FM0010	Isotope Ratio Mass Spectrometry	-89.55	0.00
FM0014	Isotope Ratio Mass Spectrometry	-86.97	0.23
FM0015	Isotope Ratio Mass Spectrometry	-91.97	-0.21
FM0016	Isotope Ratio Mass Spectrometry	-89.22	0.03
FM0018	Isotope Ratio Mass Spectrometry	-87.94	0.14
FM0022	Isotope Ratio Mass Spectrometry	-82.36	0.63
FM0024	Isotope Ratio Mass Spectrometry	-100.67	-0.98

Data Statistics

	Value
Number of Results	11
Number of Excluded Results	0
Mean	-94.67
Median	-89.55
Standard Deviation	12.302
Robust Standard Deviation	10.663
Result Range	-123.91 to -82.31

Performance Statistics

	Value
Assigned Value	-89.55
Uncertainty of Assigned Value	4.02
SDPA	10.663
Satisfactory Range	-112.34 to -66.76
Satisfactory z' scores	90.9%
Questionable z' scores	0.0%
Unsatisfactory z' scores	9.1%

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

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	11	0	100	-89.55	10.663	-123.91 to -82.31	90.9
All	11	0	100	-89.55	10.663	-123.91 to -82.31	90.9

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.

As was seen in the previous round the inclusion of test materials and compounds with exchangeable hydrogen for 2H analysis has many pitfalls unless a strict protocol is provided, to which participants must adhere. In this case participants were allowed to use their routine method of analysis and as a result results which ranged from -82.31 to -123.91 were reported. The spread of data, as defined by the robust standard deviation was also comparatively large 10.663. In comparison the range of results returned for 13C in the hemp sample was -28.00 to -28.56, with a robust standard deviation of just 0.111.

As in round 203, the SDPA used in this round of the FIRMS scheme for the assessment of the participants is the calculated robust standard deviation. In cases where the results returned are varied, the robust standard deviation will also be large and by definition a wide range of results will be assessed as satisfactory. 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.

A fixed SDPA, which can also be a percentage of the assigned value, is being considered by LGC and the FIRMS advisory group.

*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 - hemp**Analyte: delta 13C (VPDB)**

Lab ID	Method	Result	z score
FM0002	Isotope Ratio Mass Spectrometry	-28.34	0.45
FM0003	Isotope Ratio Mass Spectrometry	-28.42	-0.27
FM0006	Isotope Ratio Mass Spectrometry	-28.28	0.99
FM0007	Isotope Ratio Mass Spectrometry	-28.35	0.36
FM0008	Isotope Ratio Mass Spectrometry	-28.50	-0.99
FM0009	Isotope Ratio Mass Spectrometry	-28.34	0.45
FM0010	Isotope Ratio Mass Spectrometry	-28.51	-1.08
FM0014	Isotope Ratio Mass Spectrometry	-28.46	-0.63
FM0015	Isotope Ratio Mass Spectrometry	-28.42	-0.27
FM0016	Isotope Ratio Mass Spectrometry	-28.56	-1.53
FM0017	Isotope Ratio Mass Spectrometry	-28.00	3.51
FM0018	Isotope Ratio Mass Spectrometry	-28.33	0.54
FM0021	Isotope Ratio Mass Spectrometry	-28.42	-0.27
FM0022	Isotope Ratio Mass Spectrometry	-28.31	0.72
FM0023	Isotope Ratio Mass Spectrometry	-28.55	-1.44
FM0024	Isotope Ratio Mass Spectrometry	-28.02	3.33

Data Statistics

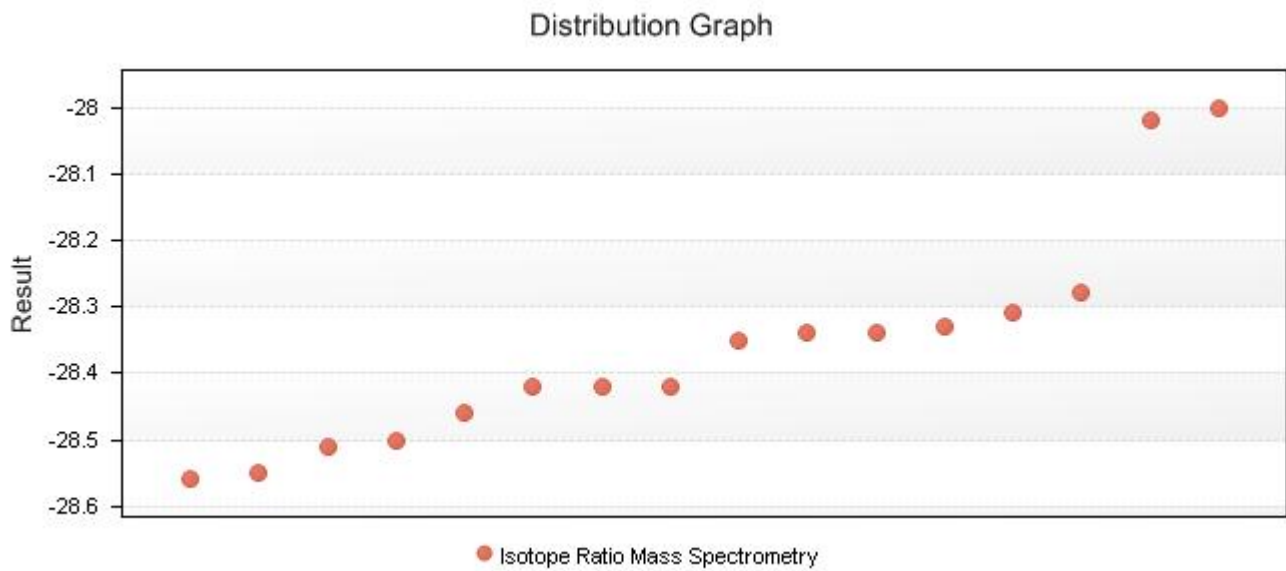
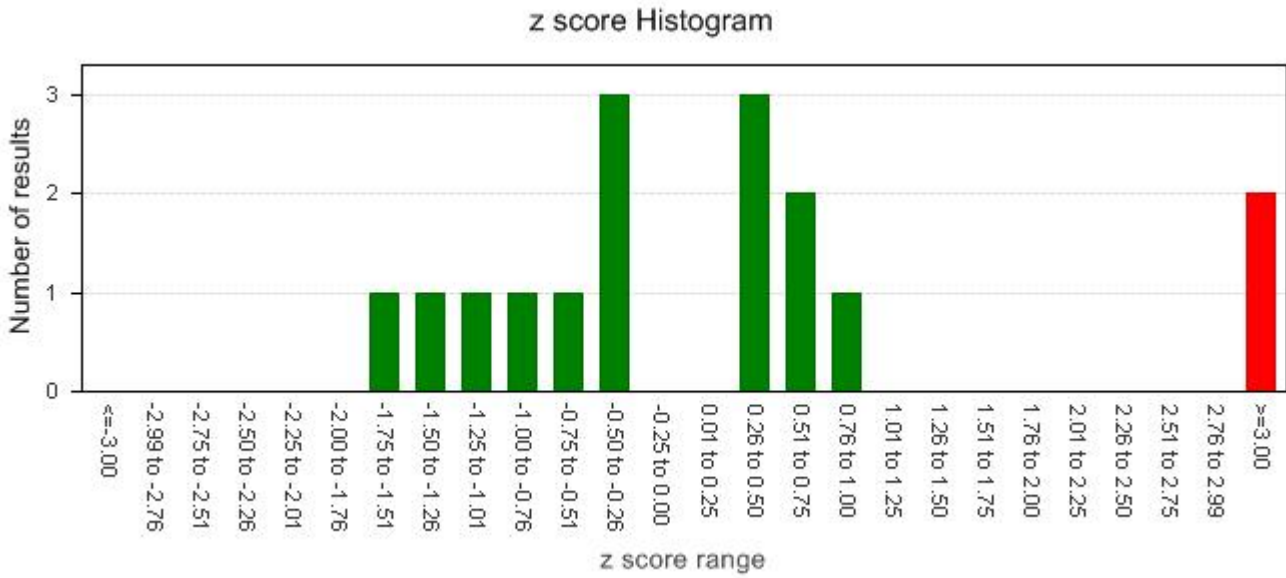
	Value
Number of Results	16
Number of Excluded Results	0
Mean	-28.36
Median	-28.39
Standard Deviation	0.162
Robust Standard Deviation	0.111
Result Range	-28.56 to -28.00

Performance Statistics

	Value
Assigned Value	-28.39
Uncertainty of Assigned Value	0.03
SDPA	0.111
Satisfactory Range	-28.61 to -28.17
Satisfactory z scores	87.5%
Questionable z scores	0.0%
Unsatisfactory z scores	12.5%

Sample: 01 - FIRMS sample 1 - hemp

Analyte: delta 13C (VPDB)



Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	16	0	100	-28.39	0.111	-28.56 to -28.00	87.5
All	16	0	100	-28.39	0.111	-28.56 to -28.00	87.5

Comments

Sample: 01 - FIRMS sample 1 - hemp**Analyte: delta 15N (AIR)**

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	4.67	0.45
FM0003	Isotope Ratio Mass Spectrometry	4.54	-0.53
FM0006	Isotope Ratio Mass Spectrometry	4.52	-0.68
FM0007	Isotope Ratio Mass Spectrometry	4.66	0.38
FM0008	Isotope Ratio Mass Spectrometry	5.00	2.95
FM0009	Isotope Ratio Mass Spectrometry	4.60	-0.08
FM0014	Isotope Ratio Mass Spectrometry	4.94	2.50
FM0015	Isotope Ratio Mass Spectrometry	4.78	1.29
FM0016	Isotope Ratio Mass Spectrometry	4.33	-2.12
FM0017	Isotope Ratio Mass Spectrometry	4.36	-1.89
FM0018	Isotope Ratio Mass Spectrometry	4.53	-0.61
FM0021	Isotope Ratio Mass Spectrometry	4.62	0.08
FM0022	Isotope Ratio Mass Spectrometry	4.39	-1.66
FM0023	Isotope Ratio Mass Spectrometry	4.64	0.23
FM0024	Isotope Ratio Mass Spectrometry	5.39	5.90

Data Statistics

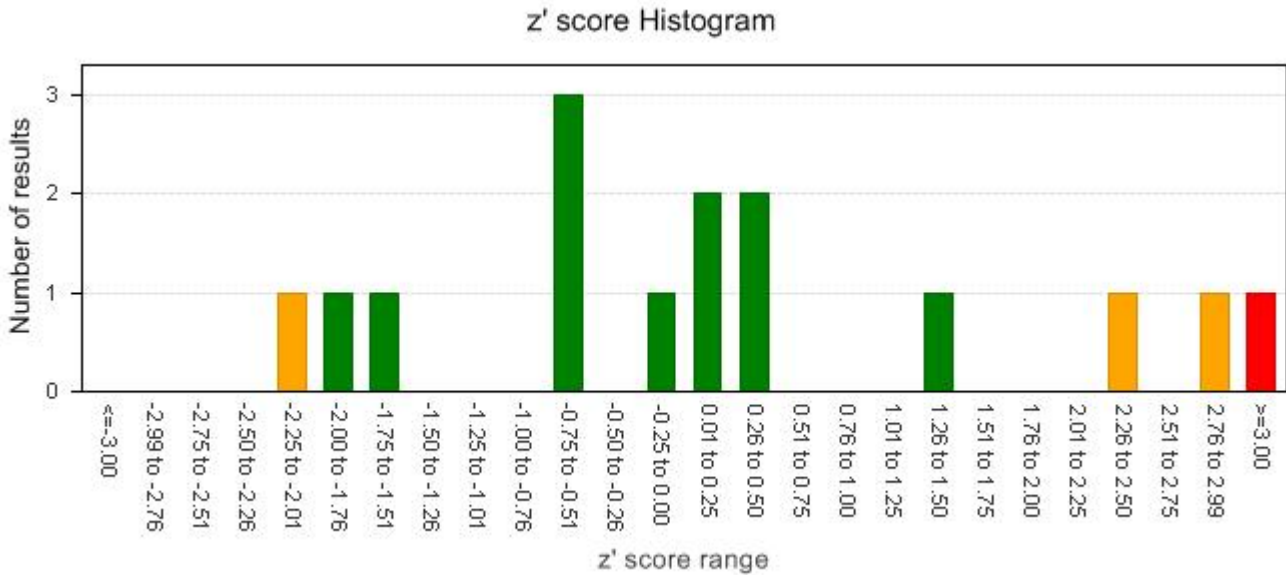
	Value
Number of Results	15
Number of Excluded Results	1
Mean	4.61
Median	4.61
Standard Deviation	0.197
Robust Standard Deviation	0.126
Result Range	4.33 to 5.00

Performance Statistics

	Value
Assigned Value	4.61
Uncertainty of Assigned Value	0.04
SDPA	0.126
Satisfactory Range	4.35 to 4.87
Satisfactory z' scores	73.3%
Questionable z' scores	20.0%
Unsatisfactory z' scores	6.7%

Sample: 01 - FIRMS sample 1 - hemp

Analyte: delta 15N (AIR)



Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	15	1	100	4.61	0.126	4.33 to 5.00	73.3
All	15	1	100	4.61	0.126	4.33 to 5.00	73.3

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 - hemp**Analyte: delta 18O (VSMOW)**

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	22.54	0.62
FM0006	Isotope Ratio Mass Spectrometry	22.36	0.44
FM0007	Isotope Ratio Mass Spectrometry	23.18	1.27
FM0009	Isotope Ratio Mass Spectrometry	21.35	-0.57
FM0015	Isotope Ratio Mass Spectrometry	22.84	0.93
FM0016	Isotope Ratio Mass Spectrometry	21.68	-0.24
FM0018	Isotope Ratio Mass Spectrometry	20.81	-1.12
FM0022	Isotope Ratio Mass Spectrometry	21.92	0.00
FM0024	Isotope Ratio Mass Spectrometry	19.89	-2.04

Data Statistics

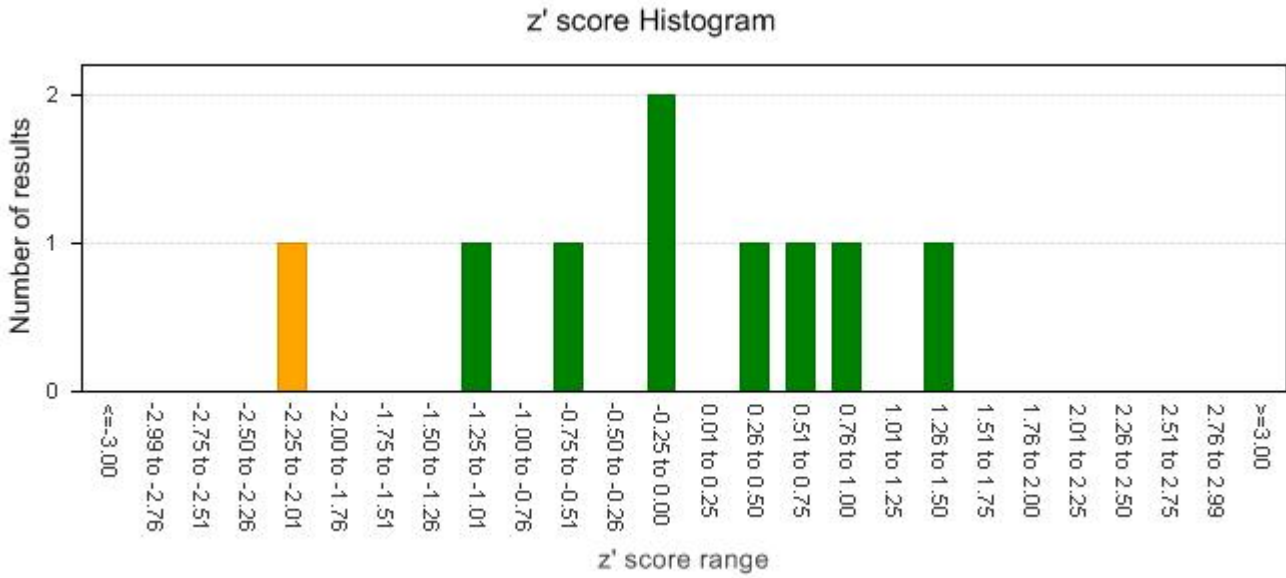
	Value
Number of Results	9
Number of Excluded Results	0
Mean	21.84
Median	21.92
Standard Deviation	1.042
Robust Standard Deviation	0.919
Result Range	19.89 to 23.18

Performance Statistics

	Value
Assigned Value	21.92
Uncertainty of Assigned Value	0.38
SDPA	0.919
Satisfactory Range	19.93 to 23.91
Satisfactory z' scores	88.9%
Questionable z' scores	11.1%
Unsatisfactory z' scores	0.0%

Sample: 01 - FIRMS sample 1 - hemp

Analyte: delta 18O (VSMOW)



Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	9	0	100	21.92	0.919	19.89 to 23.18	88.9
All	9	0	100	21.92	0.919	19.89 to 23.18	88.9

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 - oil**Analyte: delta 2H (VSMOW)**

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-170.84	0.07
FM0006	Isotope Ratio Mass Spectrometry	-163.62	1.79
FM0007	Isotope Ratio Mass Spectrometry	-174.18	-0.72
FM0009	Isotope Ratio Mass Spectrometry	-169.32	0.43
FM0010	Isotope Ratio Mass Spectrometry	-166.75	1.04
FM0014	Isotope Ratio Mass Spectrometry	-173.58	-0.58
FM0015	Isotope Ratio Mass Spectrometry	-171.45	-0.07
FM0016	Isotope Ratio Mass Spectrometry	-173.99	-0.67
FM0018	Isotope Ratio Mass Spectrometry	-172.95	-0.43
FM0022	Isotope Ratio Mass Spectrometry	-165.51	1.34
FM0024	Isotope Ratio Mass Spectrometry	-209.53	-9.11

Data Statistics

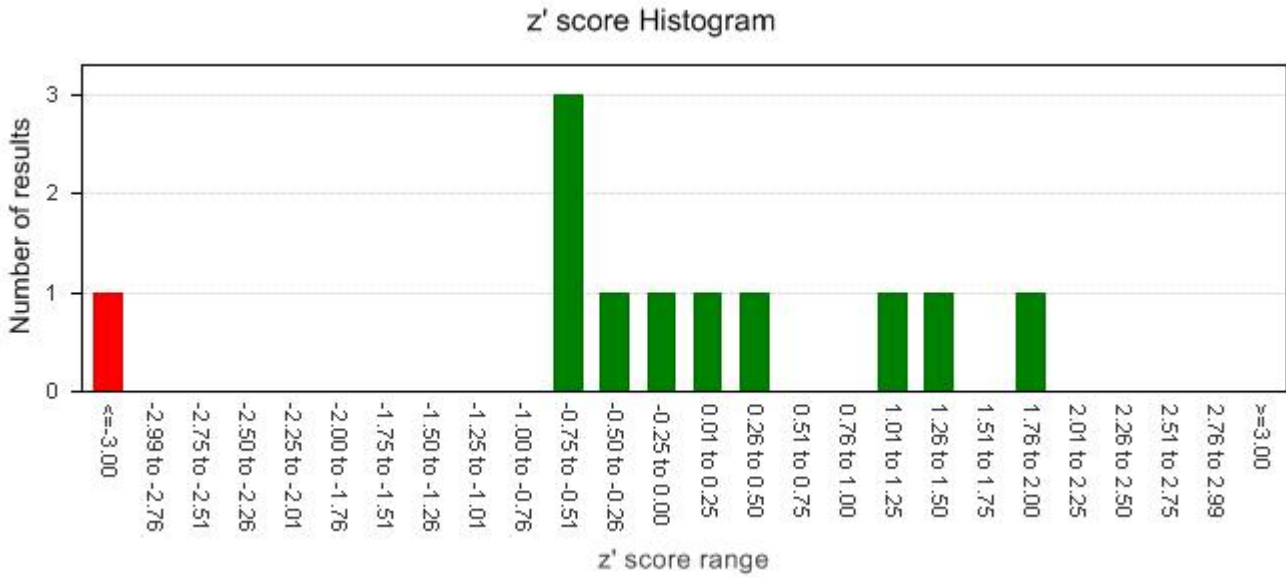
	Value
Number of Results	11
Number of Excluded Results	1
Mean	-170.22
Median	-171.15
Standard Deviation	3.788
Robust Standard Deviation	3.915
Result Range	-174.18 to -163.62

Performance Statistics

	Value
Assigned Value	-171.15
Uncertainty of Assigned Value	1.55
SDPA	3.915
Satisfactory Range	-179.57 to -162.73
Satisfactory z' scores	90.9%
Questionable z' scores	0.0%
Unsatisfactory z' scores	9.1%

Sample: 02 - FIRMS sample 2 - oil

Analyte: delta 2H (VSMOW)



Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	11	1	100	-171.15	3.915	-174.18 to -163.62	90.9
All	11	1	100	-171.15	3.915	-174.18 to -163.62	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 - oil**Analyte: delta 13C (VPDB)**

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	-29.00	-0.21
FM0003	Isotope Ratio Mass Spectrometry	-28.99	-0.11
FM0006	Isotope Ratio Mass Spectrometry	-28.76	2.34
FM0007	Isotope Ratio Mass Spectrometry	-28.90	0.85
FM0008	Isotope Ratio Mass Spectrometry	-29.00	-0.21
FM0009	Isotope Ratio Mass Spectrometry	-28.98	0.00
FM0010	Isotope Ratio Mass Spectrometry	-28.98	0.00
FM0014	Isotope Ratio Mass Spectrometry	-29.04	-0.64
FM0015	Isotope Ratio Mass Spectrometry	-28.87	1.17
FM0016	Isotope Ratio Mass Spectrometry	-29.08	-1.06
FM0017	Isotope Ratio Mass Spectrometry	-28.74	2.56
FM0018	Isotope Ratio Mass Spectrometry	-28.93	0.53
FM0021	Isotope Ratio Mass Spectrometry	-28.92	0.64
FM0022	Isotope Ratio Mass Spectrometry	-28.82	1.70
FM0024	Isotope Ratio Mass Spectrometry	-28.99	-0.11

Data Statistics

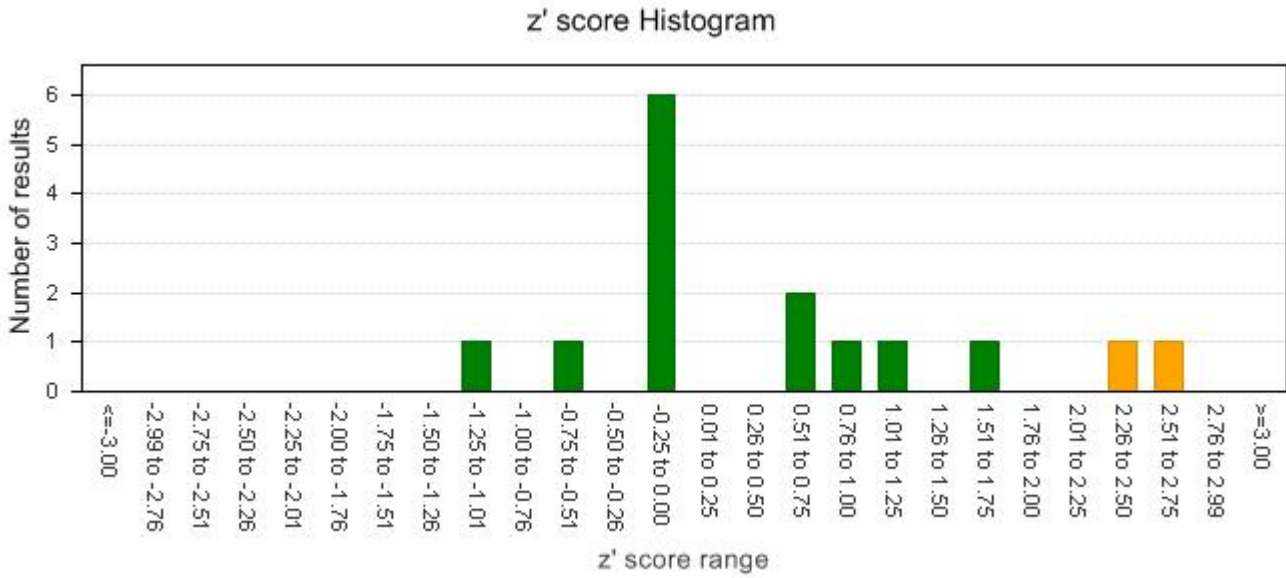
	Value
Number of Results	15
Number of Excluded Results	0
Mean	-28.93
Median	-28.98
Standard Deviation	0.099
Robust Standard Deviation	0.089
Result Range	-29.08 to -28.74

Performance Statistics

	Value
Assigned Value	-28.98
Uncertainty of Assigned Value	0.03
SDPA	0.089
Satisfactory Range	-29.17 to -28.79
Satisfactory z' scores	86.7%
Questionable z' scores	13.3%
Unsatisfactory z' scores	0.0%

Sample: 02 - FIRMS sample 2 - oil

Analyte: delta 13C (VPDB)



Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	15	0	100	-28.98	0.089	-29.08 to -28.74	86.7
All	15	0	100	-28.98	0.089	-29.08 to -28.74	86.7

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 - oil**Analyte: delta 18O (VSMOW)**

Lab ID	Method	Result	z' score*
FM0002	Isotope Ratio Mass Spectrometry	21.56	-0.41
FM0006	Isotope Ratio Mass Spectrometry	22.15	0.05
FM0007	Isotope Ratio Mass Spectrometry	24.67	2.02
FM0009	Isotope Ratio Mass Spectrometry	24.49	1.88
FM0016	Isotope Ratio Mass Spectrometry	22.01	-0.05
FM0018	Isotope Ratio Mass Spectrometry	21.02	-0.83
FM0022	Isotope Ratio Mass Spectrometry	19.19	-2.25
FM0024	Isotope Ratio Mass Spectrometry	22.50	0.33

Data Statistics

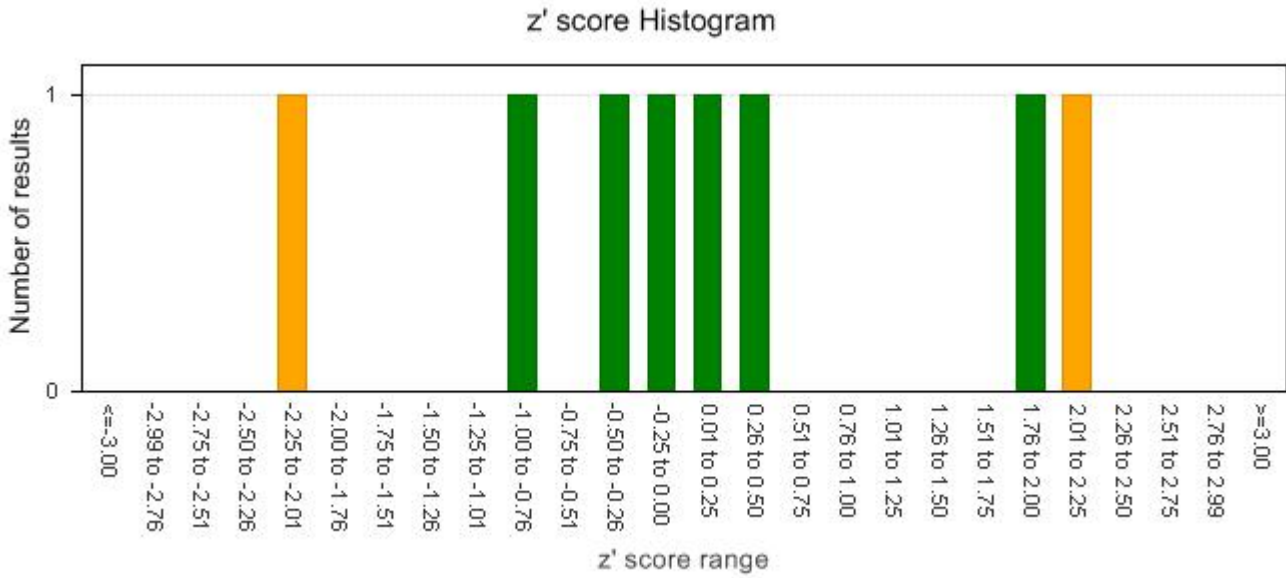
	Value
Number of Results	8
Number of Excluded Results	0
Mean	22.20
Median	22.08
Standard Deviation	1.786
Robust Standard Deviation	1.172
Result Range	19.19 to 24.67

Performance Statistics

	Value
Assigned Value	22.08
Uncertainty of Assigned Value	0.52
SDPA	1.172
Satisfactory Range	19.52 to 24.64
Satisfactory z' scores	75.0%
Questionable z' scores	25.0%
Unsatisfactory z' scores	0.0%

Sample: 02 - FIRMS sample 2 - oil

Analyte: delta 18O (VSMOW)



Methodology Summary

Method	Number of Results	Excluded Results	% of Total	Median	Robust SD	Range	Sat.
							%
Isotope Ratio Mass Spectrometry	8	0	100	22.08	1.172	19.19 to 24.67	75.0
All	8	0	100	22.08	1.172	19.19 to 24.67	75.0

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.