Forensic Isotope Ratio Mass Spectrometry (FIRMS) Report

FM299 - (Round 299) 10 May 2021

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Science for a safer world

LGC Proficiency Testing
1 Chamberhall Business Park | Chamberhall Green | Bury | United Kingdom | BL9 0AP
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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 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;

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

X = Assigned value
SDPA = Standard deviation for proficiency assessment
$u(x_{pt})$= Uncertainty of the assigned value

$$Expanded\ SDPA = \sqrt{SDPA^2 + u(x_{pt})^2}$$

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
|z| ≤ 2.00	Satisfactory result	Green
2.00 < |z| and < 3.00	Questionable result	Amber
|z| ≥ 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.

Method distribution charts

Results which have been classified as gross errors or blunders are truncated for display purposes on this chart. The dotted lines on the graph show the minimum or maximum values for results which will be displayed without truncation. Where results are truncated they are displayed with a value of the min/max limit +/- half of the applicable SDPA. If no dotted line is present this indicates that there are no gross errors or blunders to plot.

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.

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Report Authorisation

This report was authorised and electronically signed by: Wayne Gaunt - Technical Manager on Mon May 17 16:33:00 UTC 2021

Sample Details

Samples were despatched: 22 March 2021

Reporting Deadline Date: 10 May 2021

The following samples were distributed in FIRMS Round 299:

1: 1 x 0.5g poly vinyl chloride for the determination of delta 2H and 13C.
2: 1 x 0.5g caffeine for the determination of delta 2H, 13C, 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 (poly vinyl chloride)

Analyte	Within participant SD	Between participant SD
Delta 2H	0.659534	3.916756
Delta 13C	0.14748	-

Sample 2 (caffeine)

Analyte	Within participant SD	Between participant SD
Delta 2H	1.172191	9.077674
Delta 13C	0.055161	0.095433
Delta 18O	0.201602	4.213012
Delta 15N	0.048696	0.293561

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 (poly vinyl chloride)	delta 13C	-26.5946 (0.1728)	Pass
2 (caffeine)	delta 13C	-39.1801 (0.0695)	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) [1]

Lab ID	Method	Result	z score[1]
FM0003	Isotope Ratio Mass Spectrometry	36.40	1.08*
FM0018	Isotope Ratio Mass Spectrometry	32.93	0.06*
FM0026	Isotope Ratio Mass Spectrometry	28.33	-1.29*
FM0038	Isotope Ratio Mass Spectrometry	21.40	-3.33*
FM0048	Isotope Ratio Mass Spectrometry	32.50	-0.06*
FM0054	Isotope Ratio Mass Spectrometry	37.67	1.46*

[1] Due to low numbers of results, performance scores are shown for information purposes only.

*** Please note, participant performance 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.**

Quantitative Statistics

Assessment Statistics	Unit	Assigned Value	Uncertainty of Assigned Value	SDPA	Exp.SDPA	Satisfactory Range	Satisfactory %	Questionable %	Unsatisfactory %
ALL		32.72	3.054	1.5	3.402	25.91 to 39.52	83.3%	0.0%	16.7%

Result Statistics	Unit	Number of Results	Number of Excluded Results	Mean	Median	Standard Deviation	Robust Standard Deviation	Result Range
ALL		6	0	31.54	32.72	5.953	5.984	21.40 to 37.67

Technical comments

Sample: 01 - FIRMS sample 1

Analyte: delta 13C (VPDB)

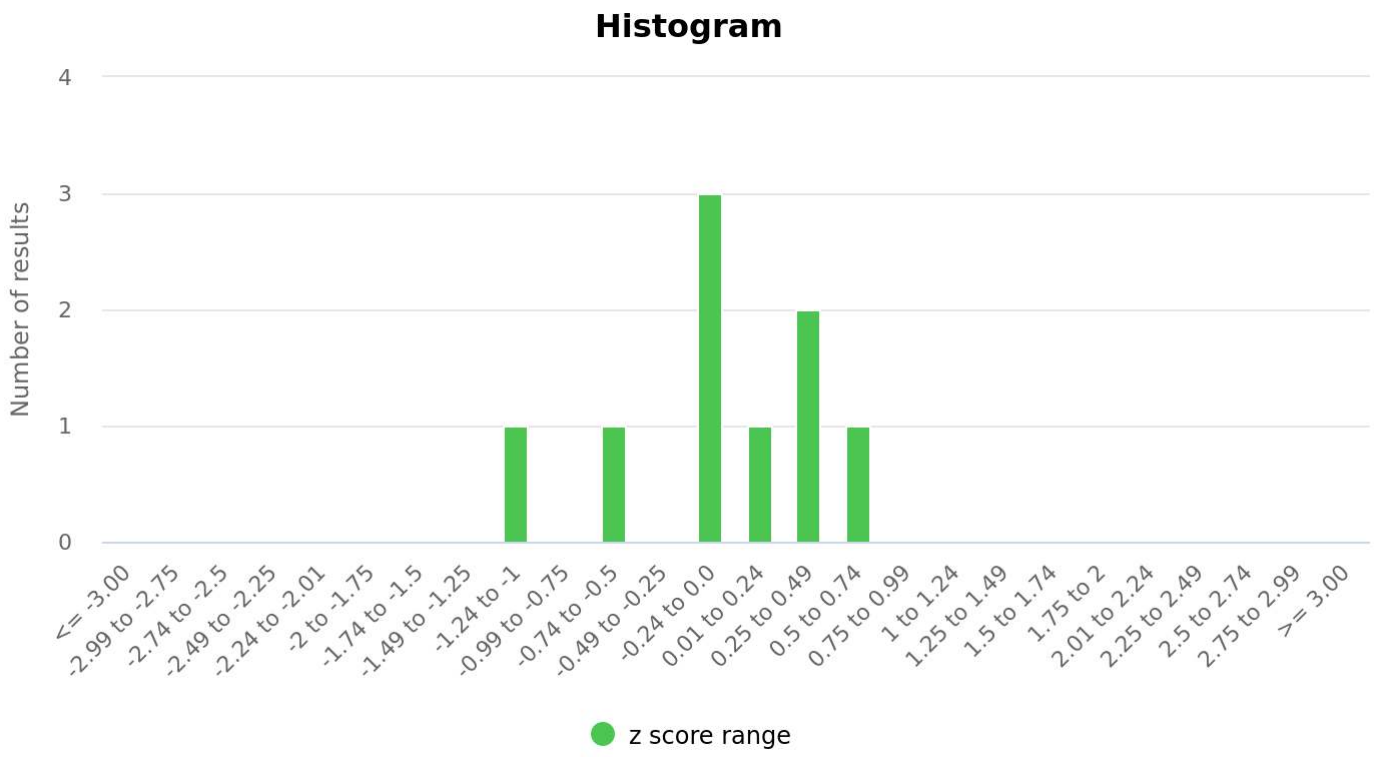
Lab ID	Method	Result	z score
FM0003	Isotope Ratio Mass Spectrometry	-26.39	0.27
FM0014	Isotope Ratio Mass Spectrometry	-26.36	0.47
FM0018	Isotope Ratio Mass Spectrometry	-26.35	0.53
FM0019	Isotope Ratio Mass Spectrometry	-26.43	0.00
FM0026	Isotope Ratio Mass Spectrometry	-26.43	0.00
FM0036	Isotope Ratio Mass Spectrometry	-26.44	-0.07
FM0038	Isotope Ratio Mass Spectrometry	-26.40	0.20
FM0048	Isotope Ratio Mass Spectrometry	-26.52	-0.60
FM0054	Isotope Ratio Mass Spectrometry	-26.59	-1.07

Quantitative Statistics

Assessment Statistics	Unit	Assigned Value	Uncertainty of Assigned Value	SDPA	Exp.SDPA	Satisfactory Range	Satisfactory %	Questionable %	Unsatisfactory %
ALL		-26.43	0.025	0.15	N/A	-26.73 to -26.13	100.0%	0.0%	0.0%

Result Statistics	Unit	Number of Results	Number of Excluded Results	Mean	Median	Standard Deviation	Robust Standard Deviation	Result Range
ALL		9	0	-26.43	-26.43	0.077	0.059	-26.59 to -26.35

Histogram



Sample: 01 - FIRMS sample 1

Analyte: delta 13C (VPDB)

Quantitative Methodology Summary

Method	Results			Unit	Median	Robust SD	Range	Sat %	Unsat %	Questionable %
	Number	Excluded	% of Total							
Isotope Ratio Mass Spectrometry	9	0	100		-26.43	0.06	-26.59 to -26.35	100.0	0.0	0.0

Sample: 02 - FIRMS sample 2

Analyte: delta 2H (VSMOW) [1]

Lab ID	Method	Result	z score[1]
FM0003	Isotope Ratio Mass Spectrometry	-140.30	0.67*
FM0018	Isotope Ratio Mass Spectrometry	-137.72	0.96*
FM0026	Isotope Ratio Mass Spectrometry	-162.38	-1.82*
FM0034	Isotope Ratio Mass Spectrometry	-152.23	-0.67*
FM0038	Isotope Ratio Mass Spectrometry	-165.30	-2.15*
FM0054	Isotope Ratio Mass Spectrometry	-131.72	1.64*

[1] Due to low numbers of results, performance scores are shown for information purposes only.

*** Please note, participant performance 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.**

Quantitative Statistics

Assessment Statistics	Unit	Assigned Value	Uncertainty of Assigned Value	SDPA	Exp.SDPA	Satisfactory Range	Satisfactory %	Questionable %	Unsatisfactory %
ALL		-146.27	8.737	1.5	8.865	-163.99 to -128.54	83.3%	16.7%	0.0%

Result Statistics	Unit	Number of Results	Number of Excluded Results	Mean	Median	Standard Deviation	Robust Standard Deviation	Result Range
ALL		6	0	-148.28	-146.27	13.810	17.121	-165.30 to -131.72

Technical comments

Sample: 02 - FIRMS sample 2

Analyte: delta 13C (VPDB)

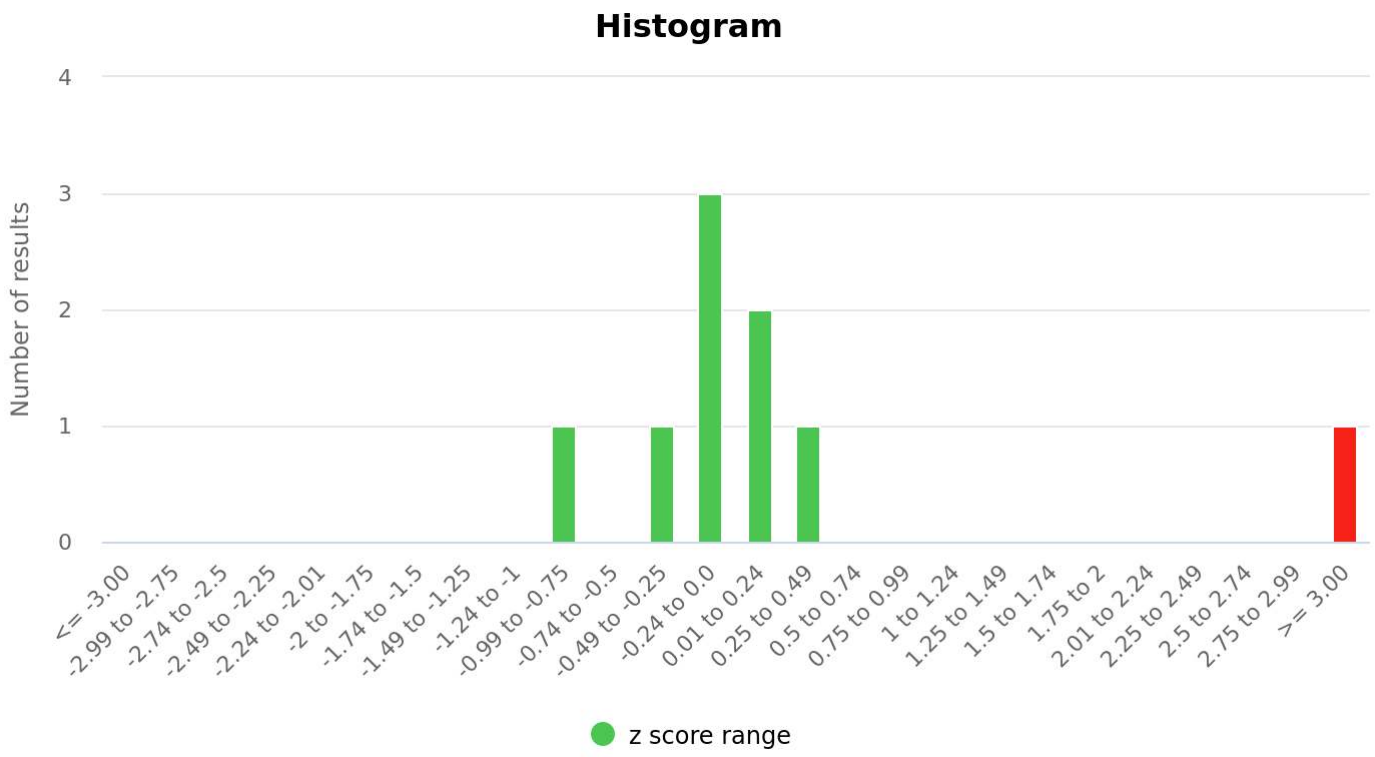
Lab ID	Method	Result	z score
FM0003	Isotope Ratio Mass Spectrometry	-39.30	-0.80
FM0014	Isotope Ratio Mass Spectrometry	-39.12	0.40
FM0018	Isotope Ratio Mass Spectrometry	-39.24	-0.40
FM0019	Isotope Ratio Mass Spectrometry	-39.18	0.00
FM0026	Isotope Ratio Mass Spectrometry	-39.21	-0.20
FM0034	Isotope Ratio Mass Spectrometry	-38.72	3.07
FM0036	Isotope Ratio Mass Spectrometry	-39.15	0.20
FM0038	Isotope Ratio Mass Spectrometry	-39.16	0.13
FM0054	Isotope Ratio Mass Spectrometry	-39.18	0.00

Quantitative Statistics

Assessment Statistics	Unit	Assigned Value	Uncertainty of Assigned Value	SDPA	Exp.SDPA	Satisfactory Range	Satisfactory %	Questionable %	Unsatisfactory %
ALL		-39.18	0.019	0.15	N/A	-39.48 to -38.88	88.9%	0.0%	11.1%

Result Statistics	Unit	Number of Results	Number of Excluded Results	Mean	Median	Standard Deviation	Robust Standard Deviation	Result Range
ALL		9	0	-39.14	-39.18	0.166	0.044	-39.30 to -38.72

Histogram



Sample: 02 - FIRMS sample 2

Analyte: delta 13C (VPDB)

Quantitative Methodology Summary

Method	Results			Unit	Median	Robust SD	Range	Sat %	Unsat %	Questionable %
	Number	Excluded	% of Total							
Isotope Ratio Mass Spectrometry	9	0	100		-39.18	0.04	-39.30 to -38.72	88.9	11.1	0.0

Sample: 02 - FIRMS sample 2

Analyte: delta 18O (VSMOW) [1]

Lab ID	Method	Result	z score[1]
FM0003	Isotope Ratio Mass Spectrometry	19.20	1.00*
FM0018	Isotope Ratio Mass Spectrometry	16.80	-4.34*
FM0026	Isotope Ratio Mass Spectrometry	19.04	0.65*
FM0034	Isotope Ratio Mass Spectrometry	34.06	34.09*
FM0038	Isotope Ratio Mass Spectrometry	17.70	-2.34*
FM0048	Isotope Ratio Mass Spectrometry	18.75	0.00*

[1] Due to low numbers of results, performance scores are shown for information purposes only.

*** Please note, participant performance 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.**

Quantitative Statistics

Assessment Statistics	Unit	Assigned Value	Uncertainty of Assigned Value	SDPA	Exp.SDPA	Satisfactory Range	Satisfactory %	Questionable %	Unsatisfactory %
ALL		18.75	0.373	0.25	0.449	17.85 to 19.65	50.0%	16.7%	33.3%

Result Statistics	Unit	Number of Results	Number of Excluded Results	Mean	Median	Standard Deviation	Robust Standard Deviation	Result Range
ALL		6	1	18.30	18.75	1.021	0.667	16.80 to 19.20

Technical comments

Sample: 02 - FIRMS sample 2

Analyte: delta 15N (AIR)

Lab ID	Method	Result	z score
FM0003	Isotope Ratio Mass Spectrometry	-0.96	0.12*
FM0014	Isotope Ratio Mass Spectrometry	-0.87	0.67*
FM0018	Isotope Ratio Mass Spectrometry	-0.99	-0.06*
FM0019	Isotope Ratio Mass Spectrometry	-0.72	1.58*
FM0026	Isotope Ratio Mass Spectrometry	-0.57	2.49*
FM0034	Isotope Ratio Mass Spectrometry	0.61	9.65*
FM0036	Isotope Ratio Mass Spectrometry	-1.09	-0.67*
FM0038	Isotope Ratio Mass Spectrometry	-1.09	-0.67*
FM0048	Isotope Ratio Mass Spectrometry	-0.98	0.00*
FM0054	Isotope Ratio Mass Spectrometry	-1.24	-1.58*

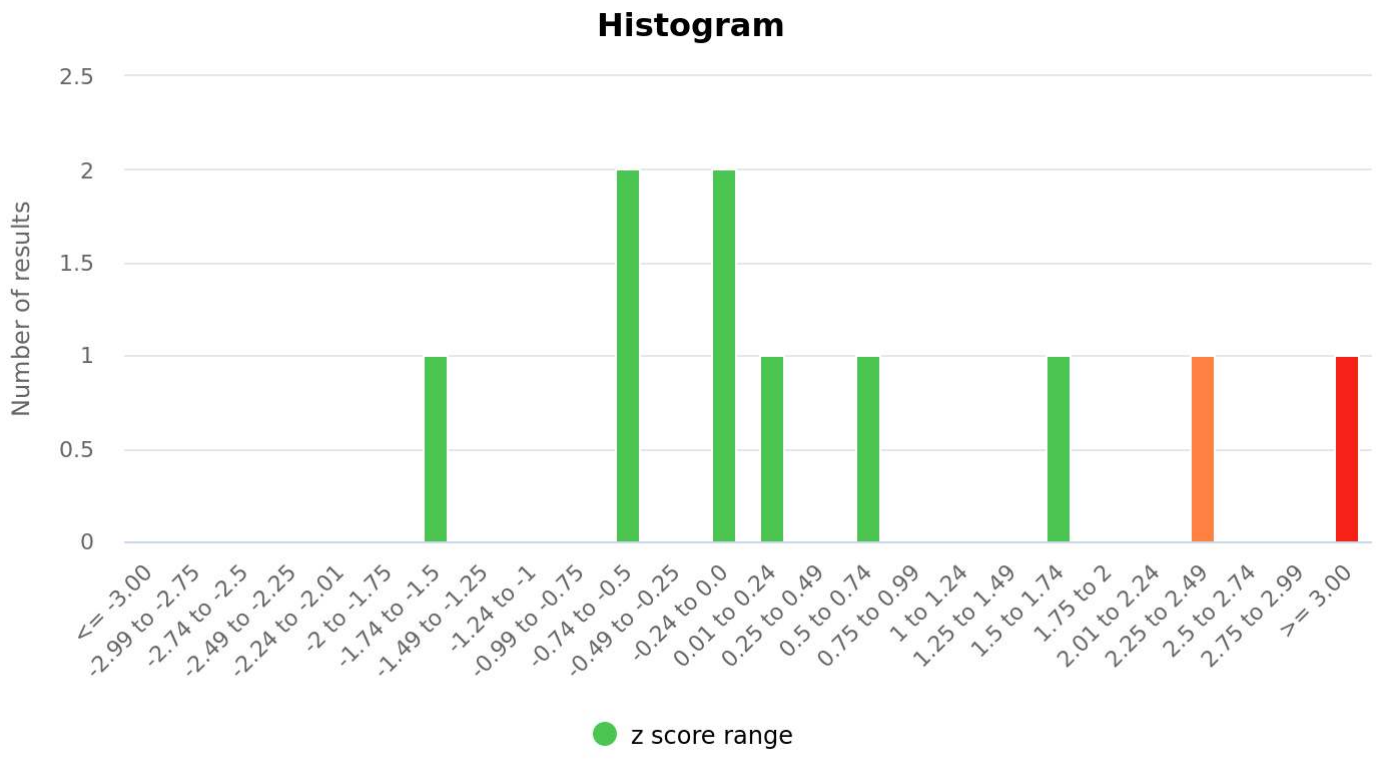
*** Please note, participant performance has been assessed using a z' score, rather than a z score, in order to account for the measurement uncertainty of the assigned value which is not negligible when compared to the SDPA.**

Quantitative Statistics

Assessment Statistics	Unit	Assigned Value	Uncertainty of Assigned Value	SDPA	Exp.SDPA	Satisfactory Range	Satisfactory %	Questionable %	Unsatisfactory %
ALL		-0.98	0.068	0.15	0.165	-1.31 to -0.65	80.0%	10.0%	10.0%

Result Statistics	Unit	Number of Results	Number of Excluded Results	Mean	Median	Standard Deviation	Robust Standard Deviation	Result Range
ALL		10	1	-0.95	-0.98	0.203	0.163	-1.24 to -0.57

Histogram



Sample: 02 - FIRMS sample 2

Analyte: delta 15N (AIR)

Quantitative Methodology Summary

Method	Results			Unit	Median	Robust SD	Range	Sat %	Unsat %	Questionable %
	Number	Excluded	% of Total							
Isotope Ratio Mass Spectrometry	10	1	100		-0.98	0.16	-1.24 to -0.57	80.0	10.0	10.0

Technical comments