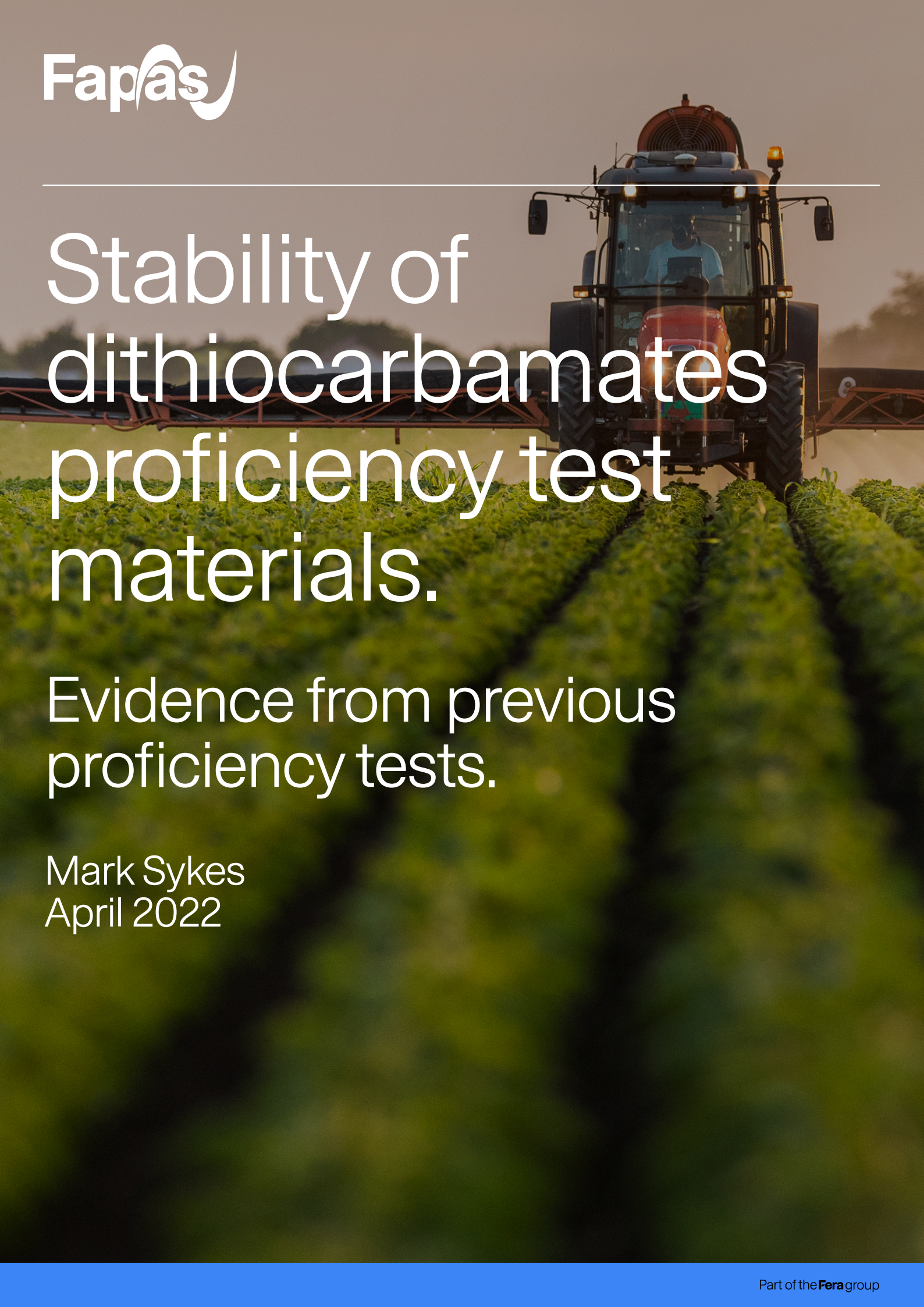


The background of the slide is a photograph of a red tractor with a large sprayer attachment, moving through a vineyard. The tractor is viewed from the front, and the rows of grapevines stretch out on either side, receding into the distance. The lighting suggests it might be early morning or late afternoon, with a soft, warm glow.

Stability of dithiocarbamates proficiency test materials.

Evidence from previous
proficiency tests.

Mark Sykes
April 2022



INTRODUCTION

The analysis of dithiocarbamate pesticide residues most commonly involves the strong acid digestion of the test sample with determination of the carbon disulphide (CS₂) that is released. The analysis is also most commonly undertaken immediately on receipt of test samples at the laboratory, because the pesticides that correspond to the class of dithiocarbamates tend to be unstable and the CS₂ that is released as a result of their breakdown is a gas which is readily lost to the atmosphere.

It is understandable, therefore, that laboratories will be concerned about proficiency test (PT) samples for dithiocarbamates which have been in transit for several days from the PT provider. Some PT samples arrive at the laboratory having completely thawed and having the appearance of a liquid.

Fapas® has been running dithiocarbamate PTs for several years now and the process and stability of the samples is well established. This paper aims to resolve any concerns that laboratories may have on the receipt of their PT samples for this analysis.



SAMPLE PREPARATION

Dithiocarbamate pesticides are typically used on fruit and vegetable produce that naturally have a high water content, such as pears, herbs, salad crops and soft fruit (including grapes).

As with all Fapas® PT materials, the matrix must be uniform in nature, which means that processing the bulk matrix will always result in a quite liquid consistency. After frozen storage, the thawed material will be even more liquid in its consistency.

A dithiocarbamate pesticide is spiked into the material at quite a high concentration before the matrix is further mixed, to ensure homogeneity of the dithiocarbamate residue in the matrix. It is during this part of the preparation that most losses (due to degradation) of the dithiocarbamate occur. It is not unusual to lose 50-75% of the original concentration during this process.

However, experiments undertaken by Fapas® show that the remaining dithiocarbamate will then stabilise to a constant level.

The homogeneity testing that is undertaken at this point will be representative of the stabilised level of the dithiocarbamate, which remains stable during storage and transportation.

SAMPLE DISPATCH

PT samples for dithiocarbamates are stored at Fapas® at -20°C. However, 2-3 days prior to the dispatch date, the samples are frozen at -80°C.

The samples are packed with ice packs in insulated boxes for transportation. This ensures that the samples remain frozen for as long as possible in transit.

EVIDENCE FOR SAMPLE STABILITY IN THE PT DATA

There are three sources of evidence in the PT data that demonstrate stability of the samples:

- **Comparison of the consensus assigned value with the homogeneity mean value**
- **Inspection of the symmetry of the z-score histogram**
- **Comparison of performance by geographic region.**

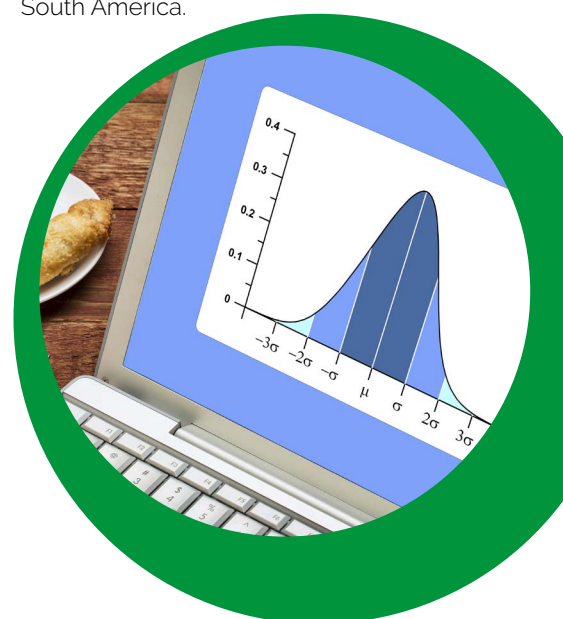
The **homogeneity mean value** is generated from the homogeneity testing carried out on the samples when they are prepared. This is usually a few weeks prior to the PT start date. If there is instability for the test material as a whole, we would expect to see a large negative bias in the assigned value compared to the homogeneity mean value.

The **symmetry of the z-score histogram** is an important indicator of instability due to transportation.

If there was any instability of samples that have spent longer in transit, we would expect to see a large skew (asymmetry) in the z-score histogram, biased towards low concentrations.

All the PT samples are originally shipped from York, UK. **Geographic regions** which are more distant from the UK will have longer transit times. In addition, geographic regions which suffer increased customs inspection or final destinations which transit via one of the EU hubs that operates on behalf of Fapas®, will be expected to have longer transit times.

We look for evidence of instability corresponding to such geographic regions. Geographic regions included in dithiocarbamate PTs are Europe, Middle East, Africa, Asia, Australasia, North America, South America.



NOTE ON OVERALL PERFORMANCE SCORES

The overall performance scores in a PT are provided in the reports – this is the percentage of participants with a z-score $\leq \pm 2$.

This performance statistic mainly provides an indication of the difficulty of the analysis (although method dependency and test material stability can be contributing factors). For the dithiocarbamates PTs in the examples below, the % $|z| \leq 2$ ranges from 64% to 84%. Since the method of analysis is dependent on the digestion of the pesticide

residues to CS₂ gas and headspace determination, we might expect the results to be more variable than for solvent-extracted pesticide residues.

It is not possible to separate the variability of analysis from potential instability only from observation of the overall performance scores.

**For further information,
see the Fapas® Protocol Part 1:
General Principles;**

 [CLICK TO VIEW](#)

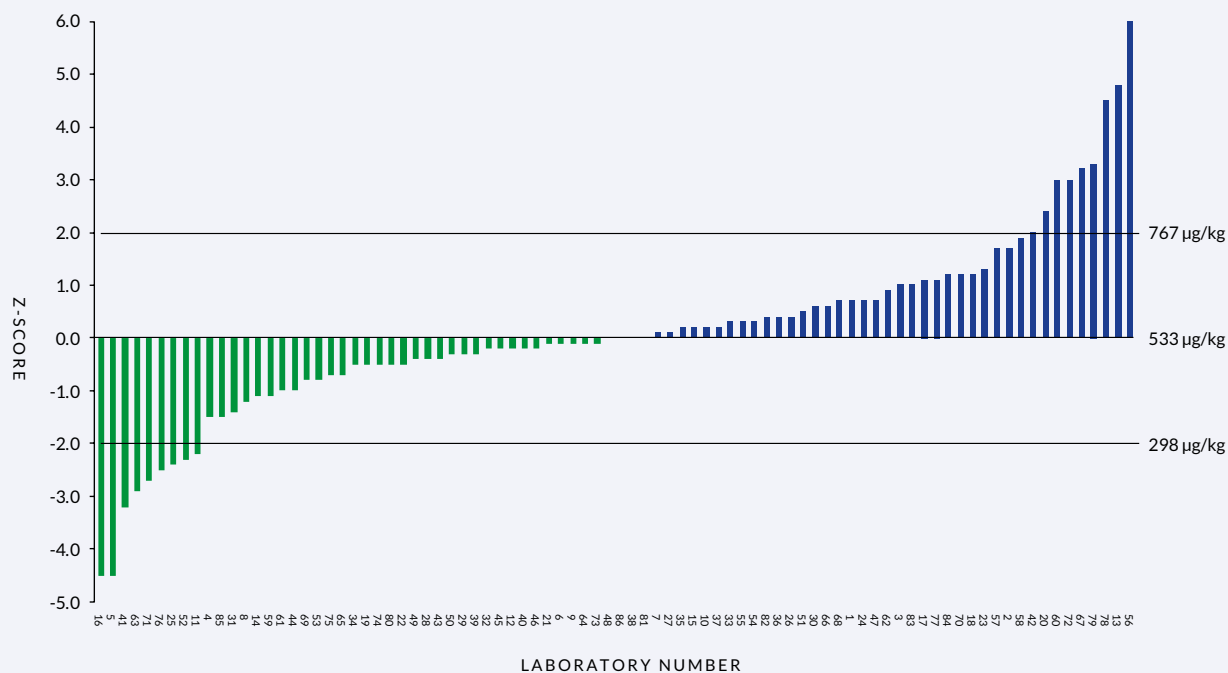
EXAMPLE DATA

The data below are from the most recent Fapas® PTs for dithiocarbamates analysis.

PT	HOMOGENEITY MEAN µg/kg	ASSIGNED VALUE µg/kg	NUMBER OF COUNTRIES	$ Z \leq 2$
19320 Lettuce	497	533	32	80%
19308 Pear	177	107	27	64%
19296 Parsley	980	426	30	74%
19276 Lettuce	487	611	29	76%
19256 Lettuce	612	655	30	84%
19236 Parsley	471	386	27	66%

19320 HISTOGRAM

SYMMETRICAL DISTRIBUTION



19308 HISTOGRAM

ASYMMETRICAL DISTRIBUTION



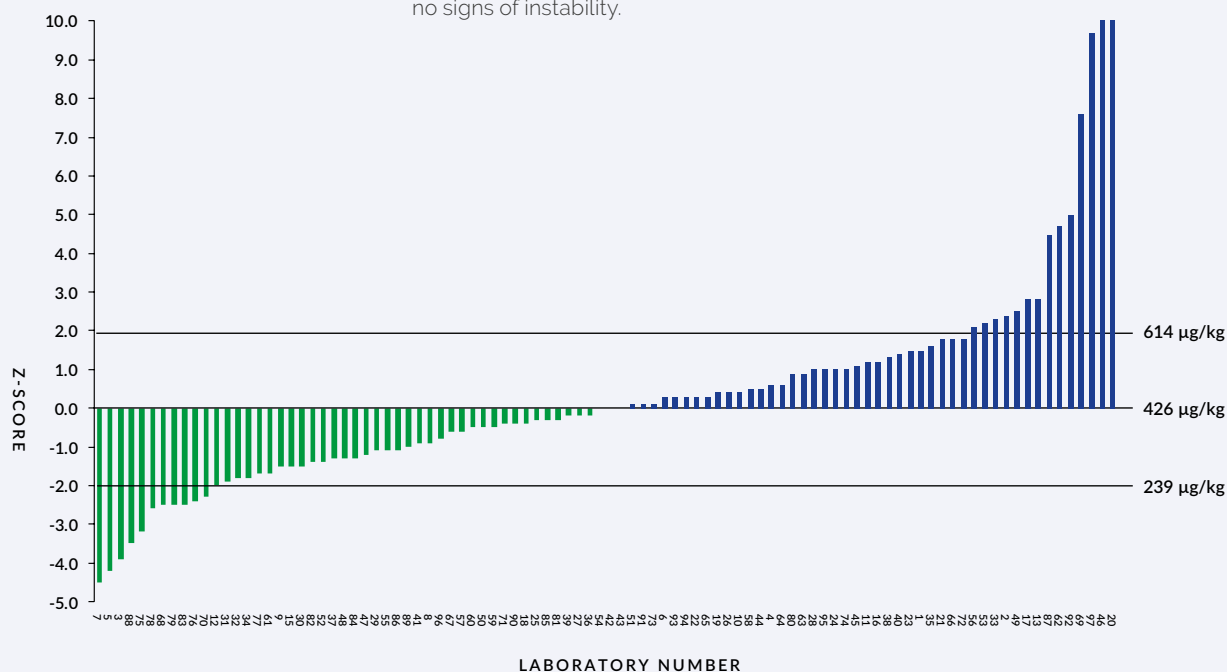
Note that this histogram is asymmetrical but the asymmetry is towards the high concentrations, not the low concentrations. This is the opposite effect of what we would expect if the samples were not stable. This unusual asymmetry also characterises the observed difference between the homogeneity

mean (177 µg/kg) and the assigned value (107 µg/kg). The distribution of z-scores in this PT cannot easily be rationalised but is more likely to be method-related than sample-related.

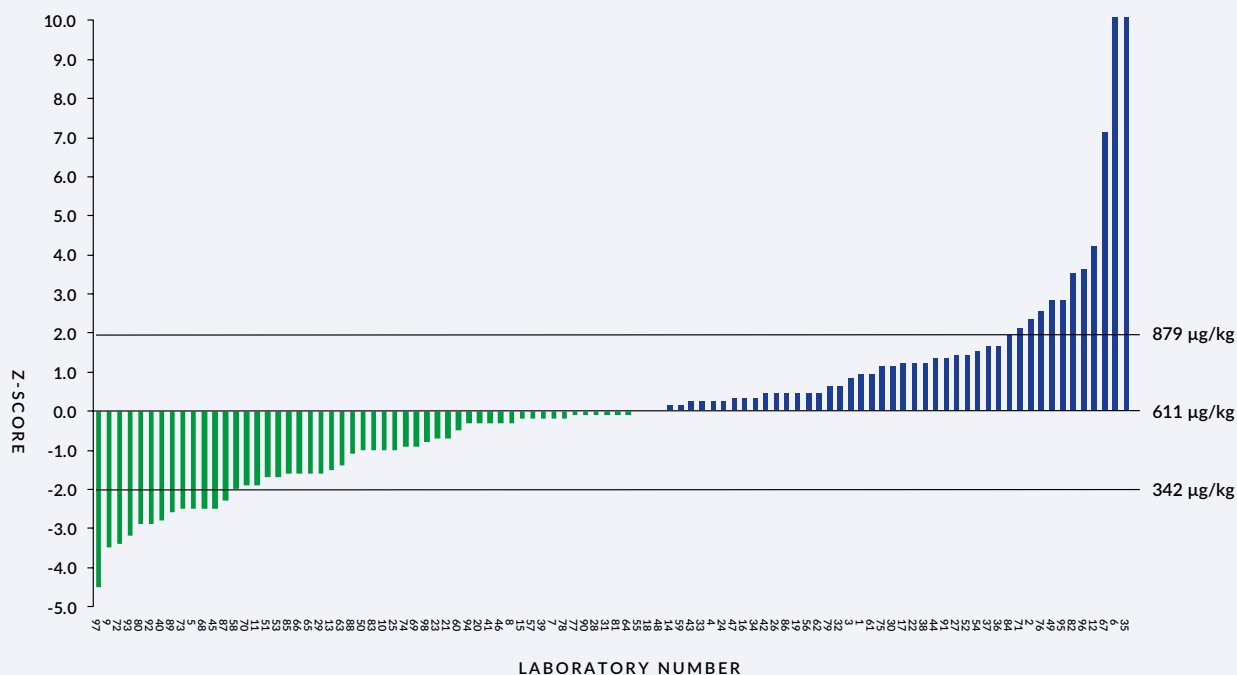
19296 HISTOGRAM SYMMETRICAL DISTRIBUTION

The assigned value (426 µg/kg) in this case is significantly lower than the homogeneity mean value (980 µg/kg). However, the shape of the histogram and the geographic distribution show no signs of instability.

The most likely explanation is the obvious one; the homogeneity testing laboratory used a calibration that was a factor of 2 in error.

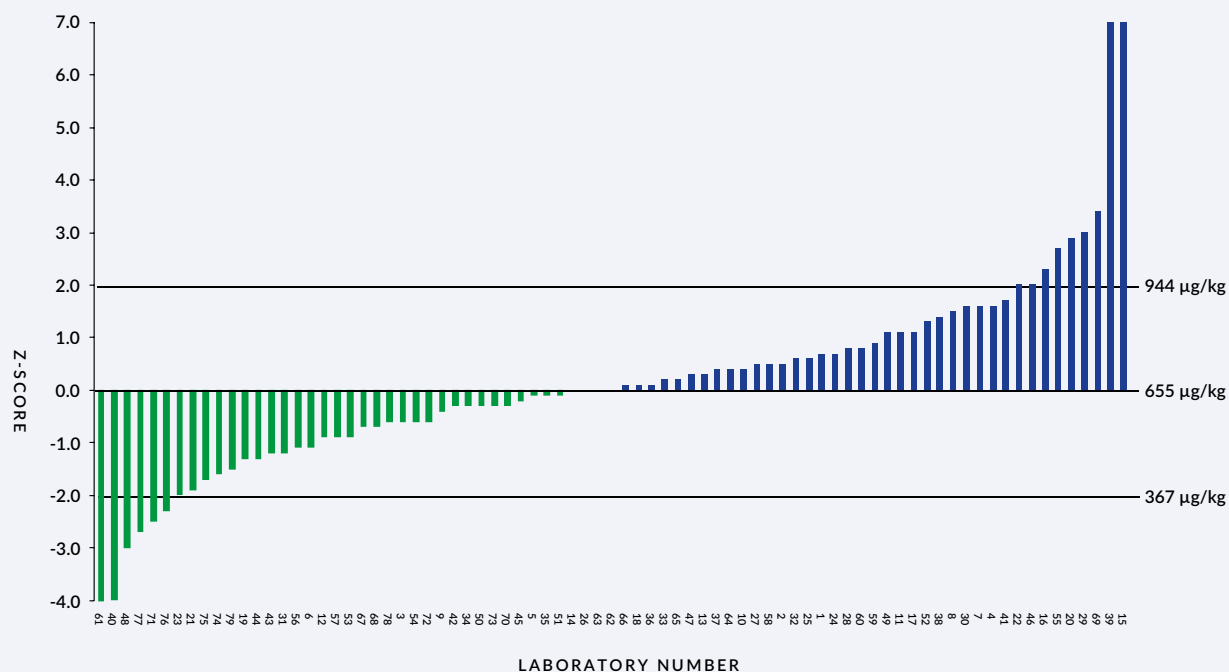


19276 HISTOGRAM SYMMETRICAL DISTRIBUTION



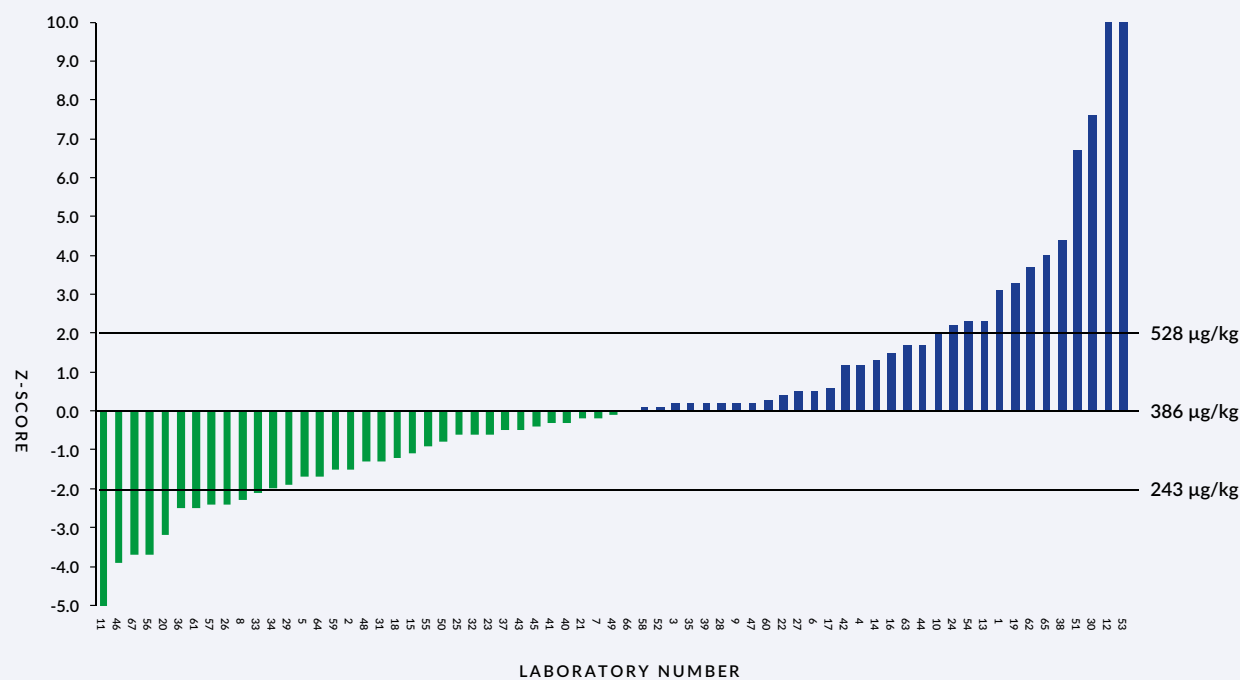
19256 HISTOGRAM

SYMMETRICAL
DISTRIBUTION



19236 HISTOGRAM

SYMMETRICAL
DISTRIBUTION





CONCLUSION

The most recent six Fapas® PTs for dithiocarbamates illustrate that the test materials are fit-for-purpose despite concerns from participants about the stability of the samples that they receive. The PTs continue to attract in excess of 60 participants, so clearly there is trust from participants that the Fapas® PTs provide appropriate performance assessments which support their accredited methods and general quality assurance. There are no indicators of instability in these PTs that adversely affect any individual laboratory's performance.

Fera Science Ltd
York Biotech Campus
Sand Hutton
York
YO41 1LZ

✉ info@fapas.com

☎ +44 (0)1904 462100

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