

Intercomparison Exercise for the Analysis of Components in Indoor Air

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Approved on behalf of NPLML by Michael Adeogun, Division Head, Analytical
Science.

Intercomparison Exercise for the Analysis of Components in Indoor Air

EXECUTIVE SUMMARY

This report presents the results of an Intercomparison Exercise in which ten components commonly found in indoor air or constructed building atmospheres were analysed by twenty-four participating institutions and the results of these were compared. The ten indoor air components were either gas or liquid loaded onto Tenax® sorbent tubes at NPL. Sets of these tubes were sent for analysis to each of the participants who reported the results that they observed. The results were displayed in terms of the relative difference compared to the assigned reference value. Z-scores were also calculated in order to indicate the performance of participants for each component.

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EXECUTIVE SUMMARY

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1 INTRODUCTION

It has been well documented that atmospheric air quality influences human health, while poor air quality has been linked to higher mortality rates, and other adverse health effects, such as bronchitis and cardiovascular problems. There is significant work being carried out globally to ensure that air quality is being monitored and regulated to minimise negative externalities impacting on public health.

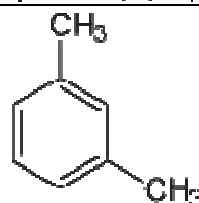
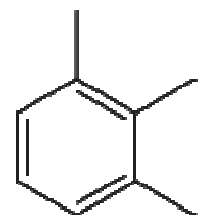
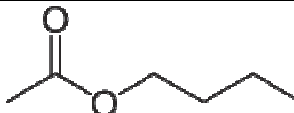
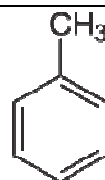
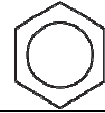
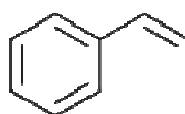
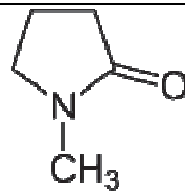
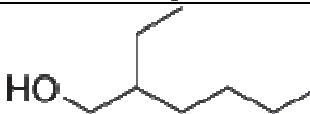
While there has been extensive research on the impact of outdoor air components, it is also crucial that indoor air monitoring is developed to protect public health. According to the US Environmental Protection Agency, indoor air can be two to five times more polluted than outdoor air. As the public spends more time indoors it is necessary that careful monitoring is implemented and for this the development of a traceable measurement infrastructure is required. This is seen as increasingly important within the construction of new buildings and there are European Union construction Products Directives associated with these and other air pollutants. Likewise it is essential that laboratories carrying out analysis of volatile organic compounds (VOCs) found in indoor air ensure that results are comparable and traceable – something that is often assessed via Intercomparison Exercises. The results of the Intercomparison Exercise reported here will add to the understanding of measurement performance in this area and will assist the UK and Europe to fulfil commitments to indoor air and workplace air legislation.

2 INTERCOMPARISON EXERCISE

The Intercomparison Exercise reported here was aimed at laboratories (some of which are ISO 17025 accredited) undertaking the analysis of VOCs from air samples collected on sorbent tubes and analysed using thermal desorption techniques as detailed in ISO 16017-1 [1] and 16017-2 [2]. This Intercomparison Exercise provides an independent means of assessing the analytical system employed including the calibration and the performance of the thermal desorption method.

Participant laboratories were supplied with Silco-treated Tenax® tubes: one blank and three loaded with ten VOC components as listed in table 1. These represent a range of hydrocarbons, terpenes and oxygenated VOCs that have a significant impact on human health due to their presence in indoor air. For continuity, four of these components selected (benzene, toluene, butyl acetate and 2-ethyl-1-hexanol) featured in the previous Intercomparison Exercise organised by NPL [3]. Six additional components were added to represent the range of substances present from building material emissions. Some of these present a greater analytical challenge than those in the previous Intercomparison Exercise.

Table 1 List of components chosen for Intercomparison Exercise

Component	Formula	Structure	CAS number
α -pinene [(+)- α -pinene and (-)- α -pinene]	$C_{10}H_{16}$	 (+)- α -pinene (-)- α -pinene	7785-70-8 (+) 7785-26-4 (-)
<i>m</i> -xylene	C_8H_{10}		108-38-3
1,2,3-trimethylbenzene (1,2,3-TMB)	C_9H_{12}		526-73-8
butyl acetate	$C_6H_{12}O_2$		123-86-4
hexanal	$C_6H_{12}O$		66-25-1
toluene	C_7H_8		108-88-3
benzene	C_6H_6		71-43-2
styrene	C_8H_8		100-42-5
1-methyl-2-pyrrolidone (NMP)	C_5H_9NO		872-50-4
2-ethyl-1-hexanol	$C_8H_{18}O$		104-76-7

3 SAMPLE PREPARATION AND VALIDATION

2-Ethyl-1-hexanol and 1-methyl-2-pyrrolidone were loaded onto ninety-two sorbent tubes from a liquid reference standard. A nominal 5 μL aliquot of a stock solution containing approximately 42,000 ng g^{-1} of 2-ethyl-1-hexanol and 1-methyl-2-pyrrolidone in methanol was injected from a 10 μL syringe through a modified injection port onto each sorbent tube (figure 1). After each injection, zero air was passed over the sorbent tube for a minute at a rate of 150 mL min^{-1} . The dispensing syringe was weighed before and after injection and the loaded mass transferred onto the sorbent tube was determined. The 10 μL syringe was calibrated using gravimetry. The volume of the syringe is set by a Chaney adaptor. The true volume dispensed is determined from the mean and density of methanol at a recorded temperature. This is achieved by carrying out repeated transfer of aliquots of methanol into a sealed 2 mL septum vial by the syringe requiring calibration. The vial is reweighed after each transfer and by subtraction the weight of the methanol dispensed is calculated. An overall mean, standard deviation and co-efficient of variation is determined for the data set.

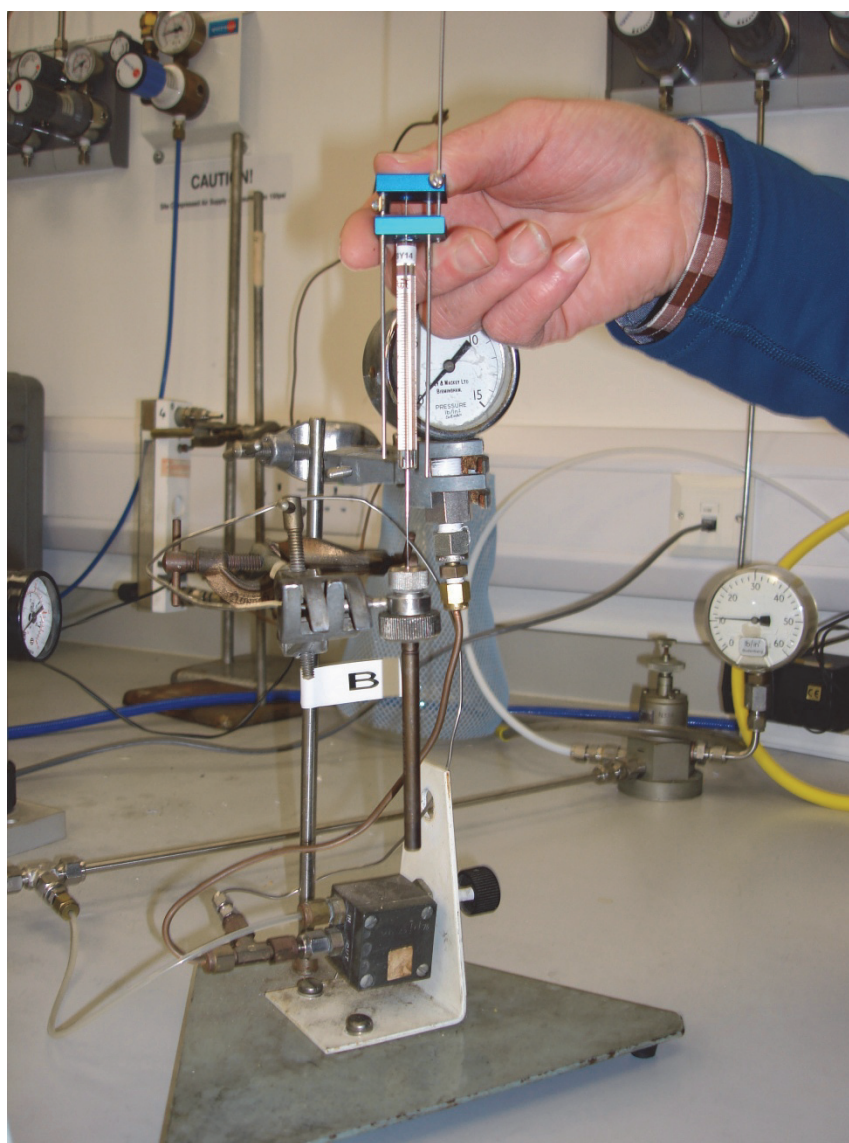


Figure 1 Photograph of rig – using a syringe with a Chaney adaptor an aliquot is injected onto the sorbent tube through the modified port before zero air is passed over for one minute.

The remaining eight components were loaded by flowing a primary reference gas mixture (where the mixture was prepared gravimetrically at the National Physical Laboratory, and validated using independent methods) across the sorbent tube at a controlled rate of approximately 10 mL min^{-1} for 15 minutes (figure 2). The other end of the sorbent tube was connected to a flow meter (BIOS), which was used to record the flow during each tube loading. An average flow rate was determined so that the mass loading of all of the eight components could be determined using the following equation:

$$m = \frac{ftxM}{V}$$

where m is the mass of the analyte loaded in g, f is the volume flow rate in L min^{-1} , t is the time in minutes, V is the molar volume at 293.15 K in L mol^{-1} , x is the amount fraction in mol mol^{-1} and M is the molecular weight of the component in g mol^{-1} .

A minimised dead volume (MDV) connector and a low volume restriction device (used to control sample flow) were employed. The system was purged for 120 minutes before tube loading commenced. The first and last samples loaded were discarded due to the higher possible variance in flow.

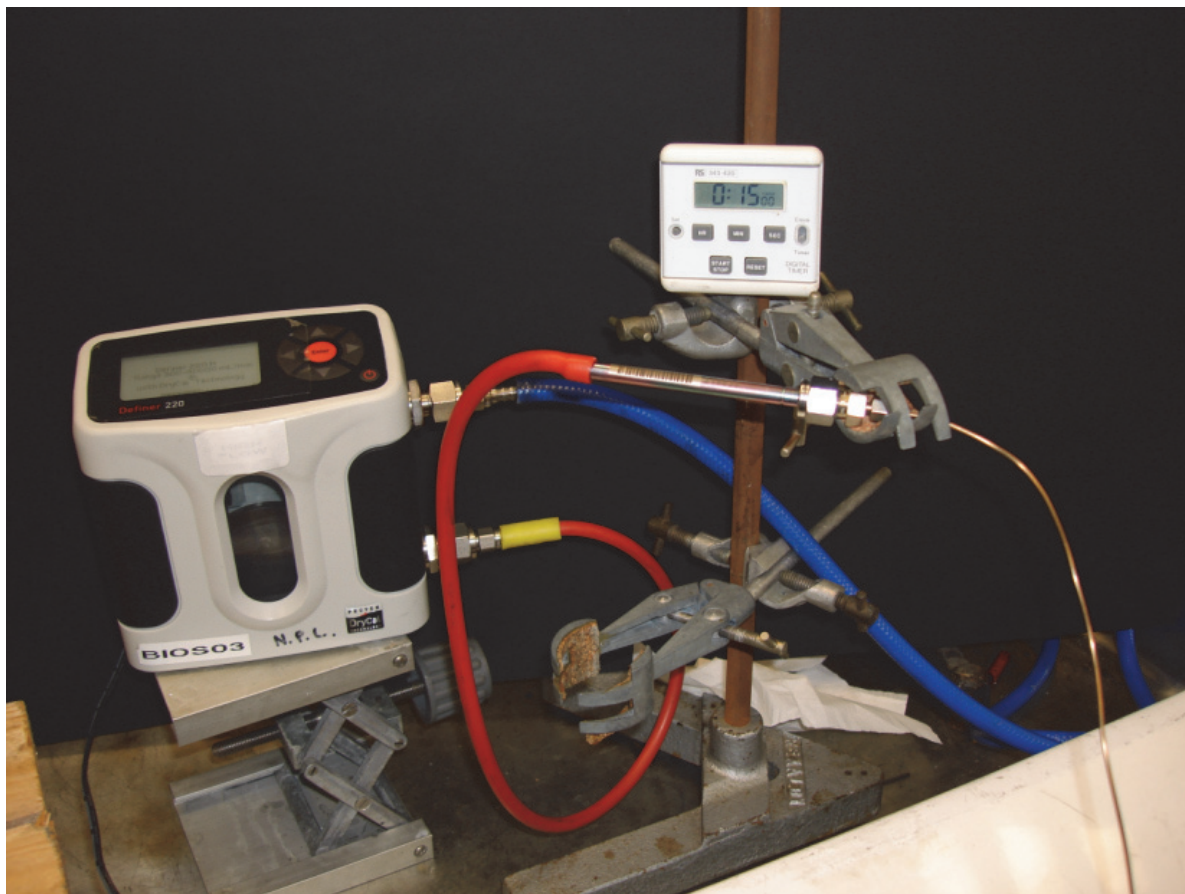


Figure 2 A close up of the tube loading rig. The cylinder is opened and the flow is adjusted using a restriction device (not pictured) before a tube is introduced. The treated tubing shown disappearing (bottom right of the photograph) is connected to the cylinder – this line was purged prior to loading the sorbent tube. The red tubing connects the sorbent tube to the flow meter (BIOS) and the blue tubing goes to the vent.

The primary reference standard used for loading was gravimetrically prepared with all components nominally around 250 nmol/mol (table 2). The primary reference standard was validated against in house standards.

Prior to gas and liquid loading, each sorbent tube used in this exercise was run on a Thermal Desorption Gas Chromatograph Mass Spectrometer (TD-GC-MS) to confirm that no more than 3 ng of each component was observed. Any tubes that did not meet the criteria were rejected.

Table 2 Molecular weight (M) and amount fractions (x) of components in the primary reference gas mixture

Component	M / (g/mol)	x / (nmol/mol)
benzene	78.1	248.6
toluene	92.1	262.8
Butyl acetate	116.2	253.3
hexanal	100.2	242.6
m-xylene	106.2	250.2
α -pinene	136.2	246.3
styrene	104.2	254.5
1,2,3-trimethylbenzene	120.2	237.7

4 SAMPLE HOMOGENEITY AND STABILITY

A sample of eleven tubes was analysed using TD-GC FID and MS as outlined in 16017-2 to interrogate the homogeneity of the batch. The gravimetric loadings of each component were in close agreement with the certified values obtained from the liquid reference standards, and from the gas loading, and the tubes within the set of samples analysed demonstrated good homogeneity. To confirm the stability of the samples, NPL analysed a further set of three sample tubes when the submission date for the participants' results had passed. The results of this analysis compared well with the results for the eleven tubes analysed before the despatch of the sample tubes to participants. Results from this set of three tubes were used as NPL's submission for the Intercomparison Exercise.

5 INTERCOMPARISON EXERCISE Z-SCORE CALCULATIONS

A z-score was assigned to each reported result to give an indication of performance. The z-score assignment was based upon the following equation:

$$z = \frac{x_{lab} - \bar{x}_{res}}{\sigma_{PA}}$$

where z is the z-score, x_{lab} is the reported analytical result from the participating laboratory and $\bar{x}_{res}$ is the assigned value for the performance assessment and σ_{PA} is the standard deviation for performance assessment.

The loadings vary up to 7 % across the suite of tubes because of small changes in flow rate. To account for this, each participant's results were normalised against the gravimetric loading, prior to the calculation of z-scores. For the majority of the components, the median of the gravimetric

loadings of all ninety-two tubes (where data was available) was used as the reference value. A bias was observed between the gravimetric loadings and the NPL validation measurements carried out using an independent set of calibration standards for butyl acetate, hexanal and 1,2,3-trimethylbenzene. The sign of the bias was indicative of some of these components being retained on the sorbent material. Hence for these components, the median of the analytical results from the eleven tubes used in the homogeneity study was taken as the reference value. The standard deviation for performance assessment (σ_{PA}) was set as 12.5 % for butyl acetate, hexanal and 1,2,3-trimethylbenzene. For all other components the σ_{PA} was set as 7.5 %. The σ_{PA} values are set in accordance to BS EN 482 [4].

6 INTERCOMPARISON EXERCISE RESULT SUMMARY

Twenty-four participants took part in the Intercomparison Exercise. Each participant was given one blank and three loaded tubes. Participants were informed of the ten components that had been loaded and that all components were present at masses between 50 ng and 300 ng. Not all participants reported results for all of the sorbent tubes received or for all of the components that were loaded.

Table 3 Each institution was sent a set of tubes for analysis. The institution number corresponds to the value on the x-axis

Set	Tube 1	Tube 2	Tube 3	Blank	Institution
A	218882	218848	218880	Mi117790	1
B	218802	218829	218881	Mi117794	2
C	218806	218851	218867	Mi117786	3
D	218844	218872	218893	Mi117745	4
E	218855	218886	218827	Mi117714	5
F	218813	218850	218859	Mi117774	6
G	218858	218815	218875	Mi117784	7
H	218814	218885	218811	Mi117758	8
I	218857	218891	218869	Mi117757	9
J	218812	218864	218849	Mi117785	10
K	218853	218862	218876	Mi117717	11
L	218803	218896	218899	Mi117716	12
M	218852	218871	218870	Mi117749	13
N	218842	218874	218894	Mi116295	14
O	218900	218884	218836	Mi117738	15
P	218887	218898	218854	Mi116297	16
Q	218865	218828	218808	Mi117755	17
R	218801	218819	218839	Mi117793	18
S	218847	218816	218892	Mi116296	19
T	218843	218807	218868	Mi116291	20
U	218820	218825	218846	Mi117773	21
V	218804	218826	218834	Mi117739	22
W	218873	218824	218833	Mi117721	23
X	218888	218821	218831	218866	24

The plots and tables in the Appendix show the relative difference from the median for each sorbent tube. Numbers one to twenty-four on the x-axis correspond to the participants, as detailed in table 3. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value. The tables below show the results reported for each tube analysis and the corresponding z-score that was assigned.

For Intercomparison Exercises involving BTEX, z-scores of within ± 2 are deemed acceptable, while a z-score between ± 2 and ± 3 is considered to be a questionable result, at a warning level, with $> \pm 3$ an unsatisfactory result. Given the more challenging nature of some of the components in this study, larger z-scores are expected.

7 CONCLUSIONS

Using the results of the twenty-four participants and tabulating the results by their z-score assignment (table 4) it can be observed that for toluene and 1,2,3-trimethylbenzene (which was assigned a greater σ_{PA}) over 75 % of reported results had a z-score within ± 2 of the gravimetric median. Other hydrocarbons components such as benzene, *m*-xylene and styrene also showed higher numbers of participants achieving z-scores within ± 2 of the gravimetric median. Fewer participants achieved z-scores within ± 2 of the gravimetric median for α -pinene with many participants achieving a z-score between ± 2 and ± 3 .

For components containing one or more heteroatoms such as 1-methyl-2-pyrrolidone, 2-ethyl-1-hexanol and hexanal, fewer participants achieve z-scores within ± 2 of the gravimetric median. However, fewer results have been reported for these components. This may be a result of poor chromatography and broader peaks that tend to be observed for oxygenated components such as hexanal. The choice of reference material for more unusual components such as 1-methyl-2-pyrrolidone and 2-ethyl-1-hexanol may also be a contributing factor. However, while z-scores for butyl acetate are similar to benzene it should be remembered that the assigned σ_{PA} was 12.5 % for butyl acetate whereas for benzene it was 7.5 %.

Table 4 Z-score groupings by frequency

Component	z-score				Total
	$-2 < z < +2$	$2 < z < 3$	$3 < z < 5$	$ z > 5$	
benzene	45	5	5	13	68
toluene	54	4	3	9	70
butyl acetate	46	7	9	4	66
hexanal	27	10	17	10	64
<i>m</i> -xylene	44	9	7	10	70
α -pinene	35	15	4	4	58
styrene	43	4	4	13	64
1,2,3-trimethylbenzene	52	1	7	4	64
2-ethyl-1-hexanol	32	8	2	17	59
1-methyl-2-pyrrolidone	30	6	2	18	56

REFERENCES AND USEFUL DOCUMENTATION

- [1] International Organisation for Standardisation, ISO 16027-1:2000. *Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography – Part 1: Pumped sampling.*
- [2] International Organisation for Standardisation, ISO 16027-2:2003. *Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography – Part 2: Diffusive sampling.*
- [3] Woods, P T. *Proficiency Testing for the Analysis of Hydrocarbons using Passive Adsorption Tubes - in support of the EU Construction Products Directive & Related UK Regulations: In Support of the EU Construction Products Directive & UK Regulations* - Presentation to the Meeting on “New Construction Products Regulations” - British Measurement and Testing Association held at Building Research Establishment, 17 November 2010.
- [4] British Standard, BS EN 482:2012. *Workplace exposure - General requirements for the performance of procedures for the measurement of chemical agents*

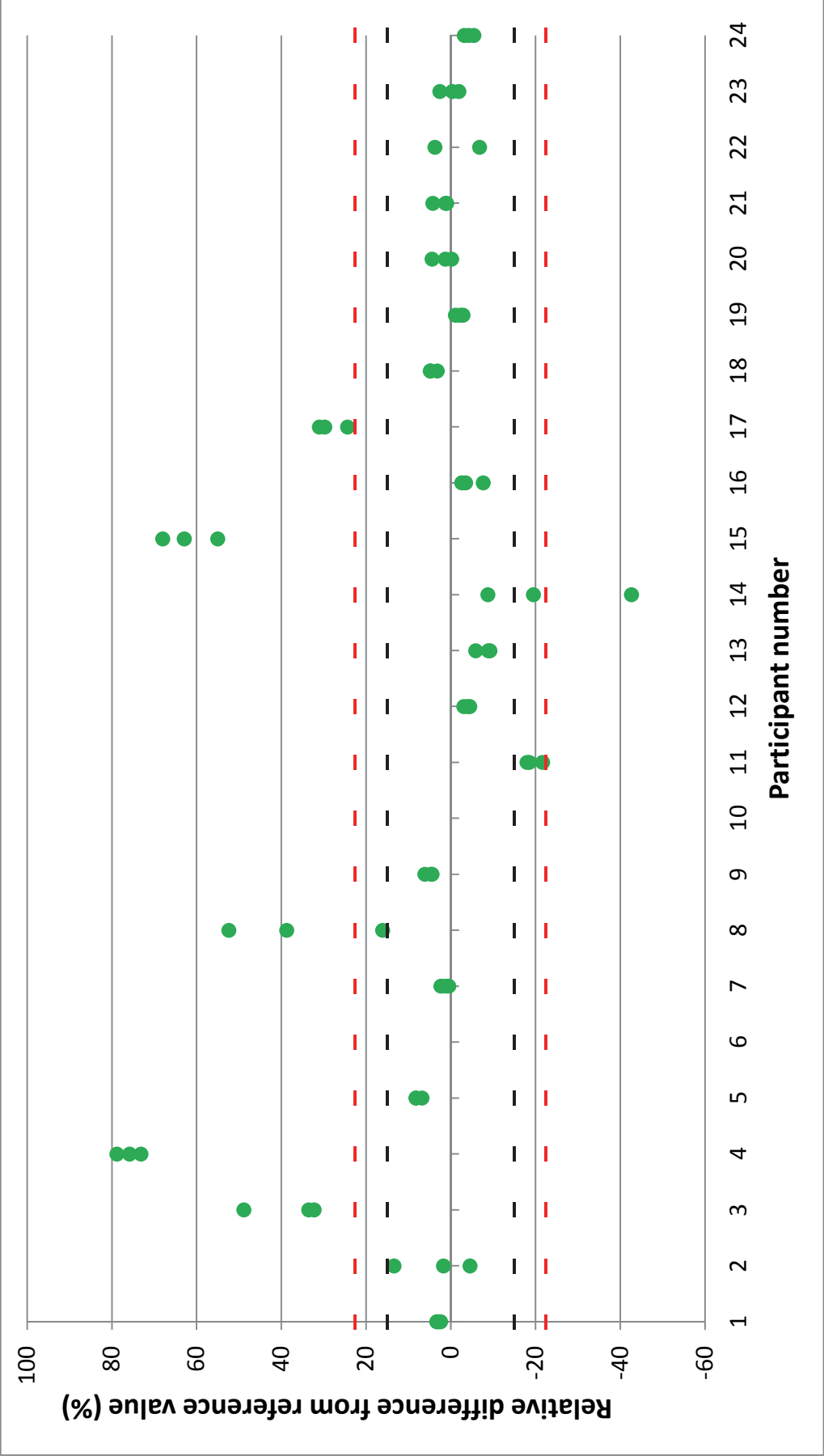


Figure 3a The relative difference of reported results from the reference value for benzene. For institution 6 the points are not depicted in the above figure as the relative differences correspond to values greater than 100 %. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

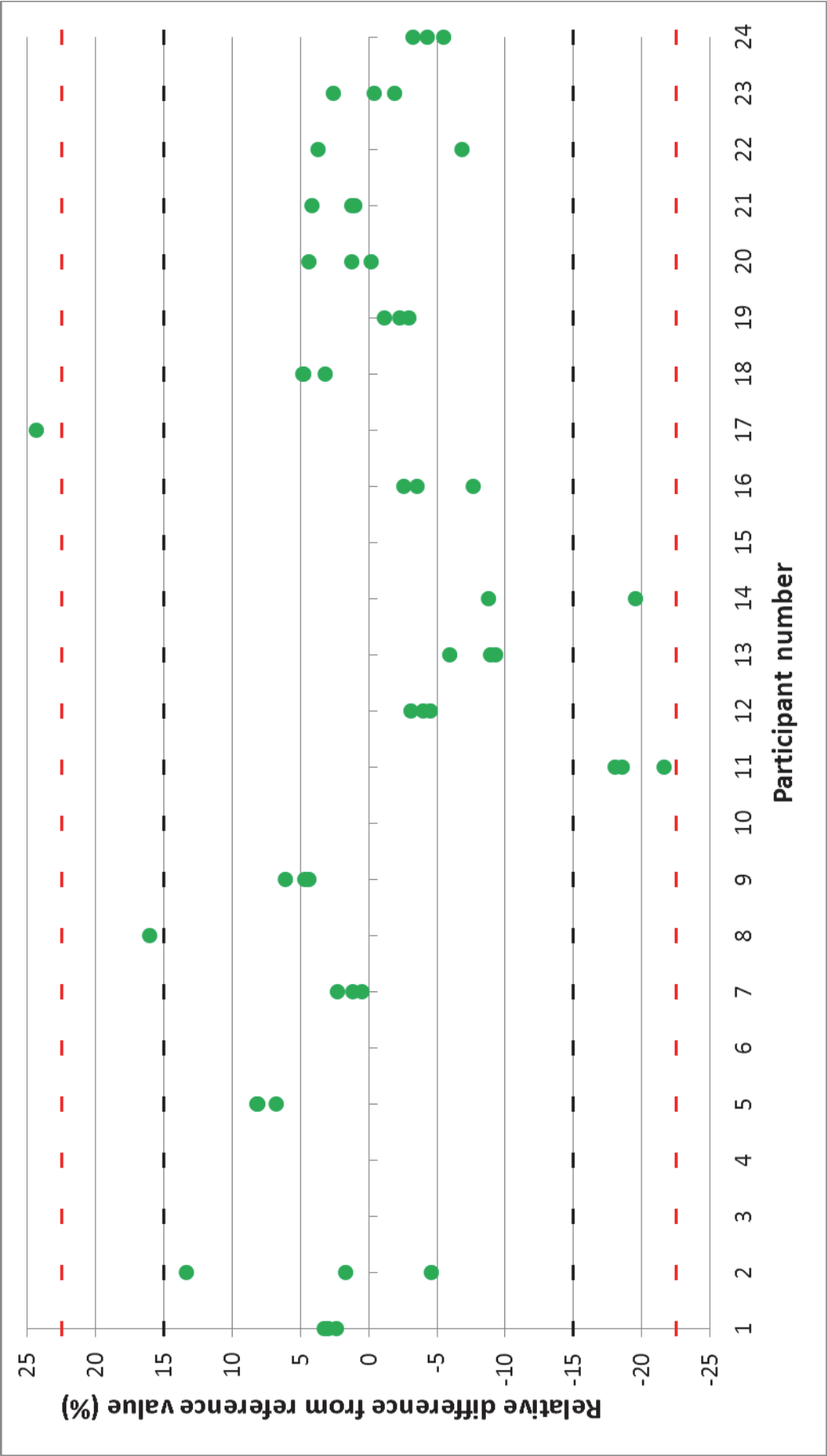


Figure 3b The relative difference of reported results from the reference value for benzene (less than $\pm 25\%$). The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

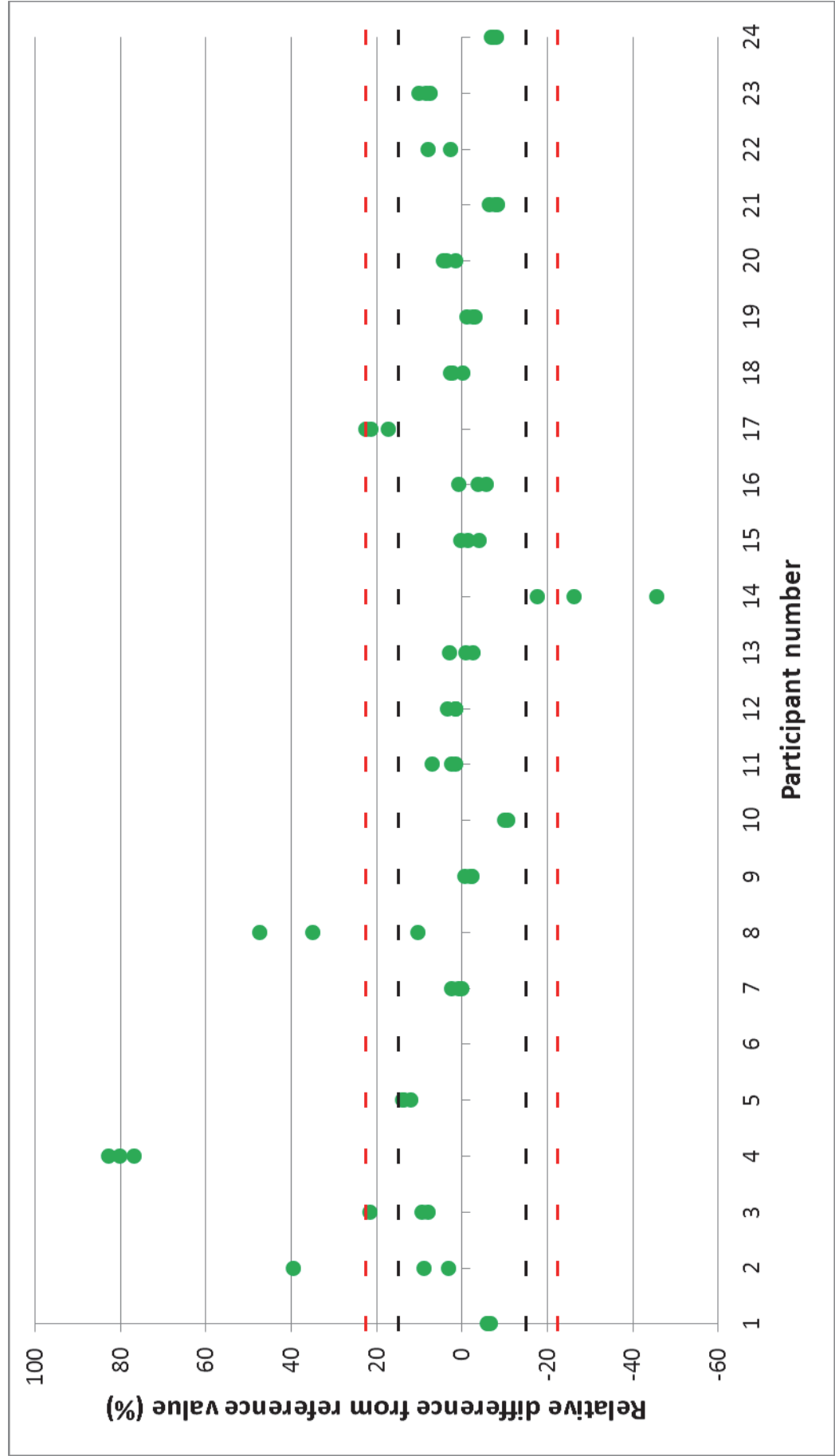


Figure 4a The relative difference of reported results from the reference value for toluene. For institution 6 the points are not depicted in the above figure as the relative differences correspond to values greater than 100 %. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

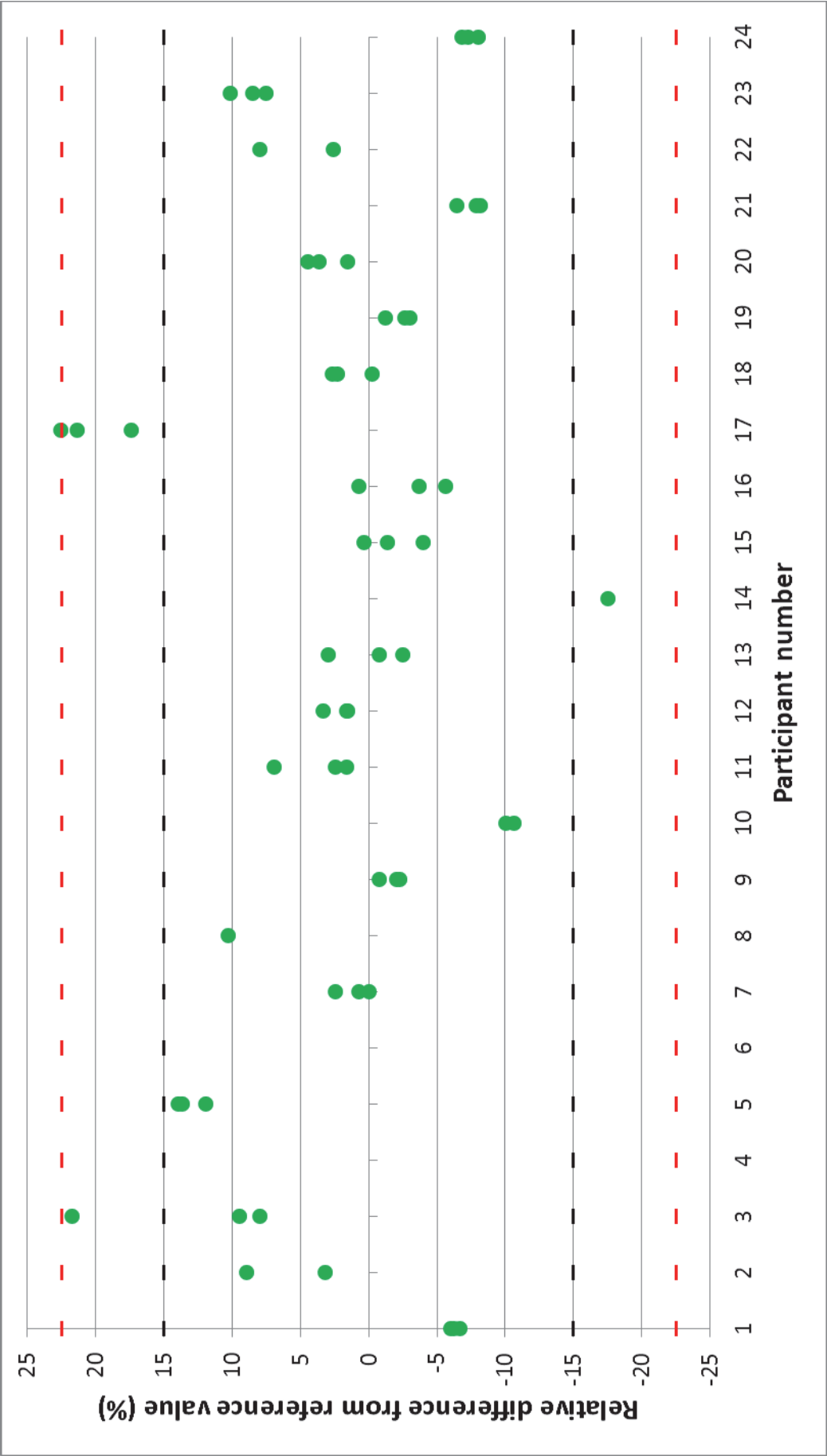


Figure 4b The relative difference of reported results from the reference value for toluene (less than $\pm 25\%$). The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

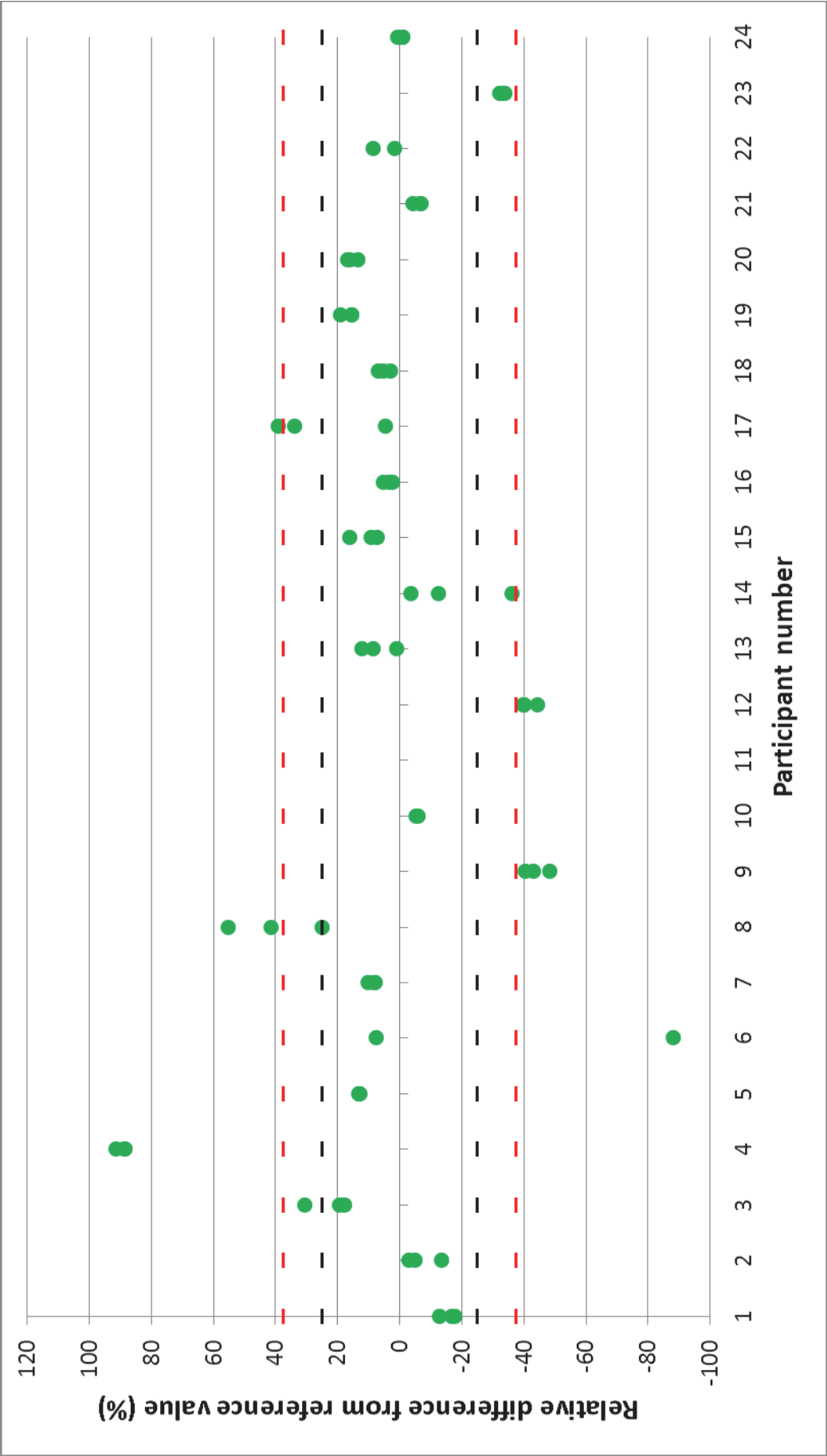


Figure 5a The relative difference of reported results from the reference value for butyl acetate. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

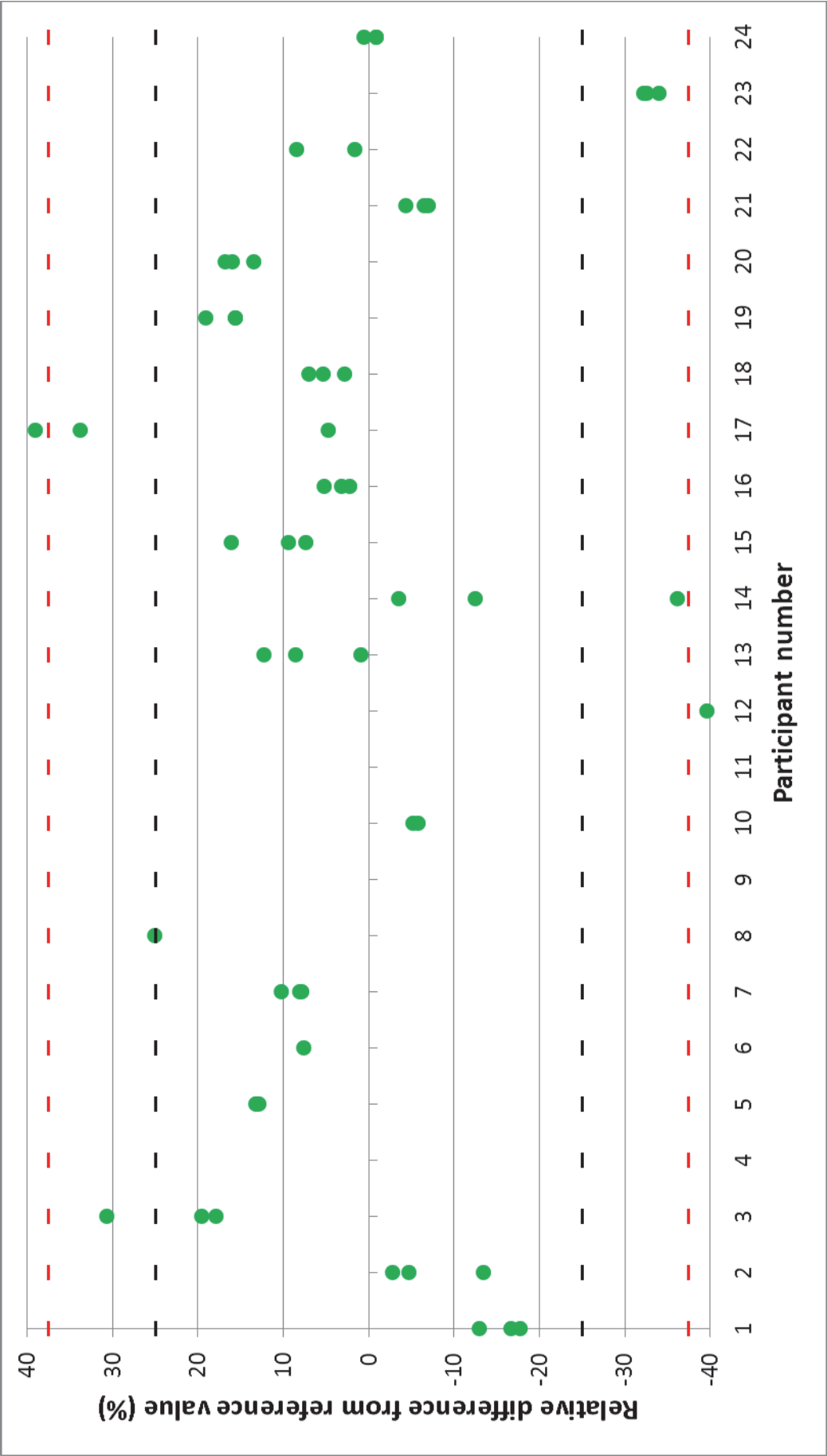


Figure 5b The relative difference of reported results from the reference value for butyl acetate (less than $\pm 40\%$). The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

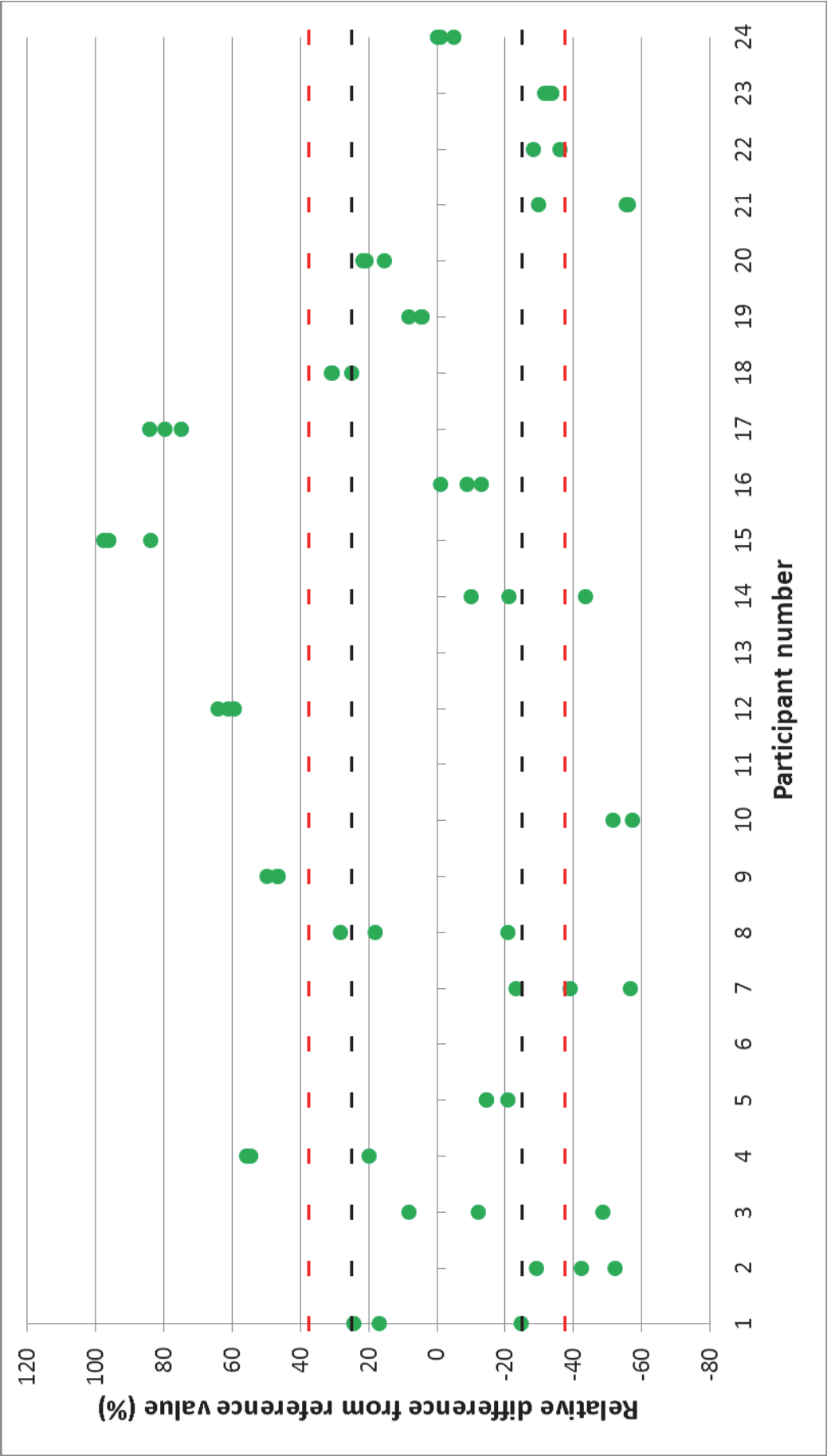


Figure 6a The relative difference of reported results from the reference value for hexanal. For institution 6 the points are not depicted in the above figure as the relative differences correspond to values greater than 100 %. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

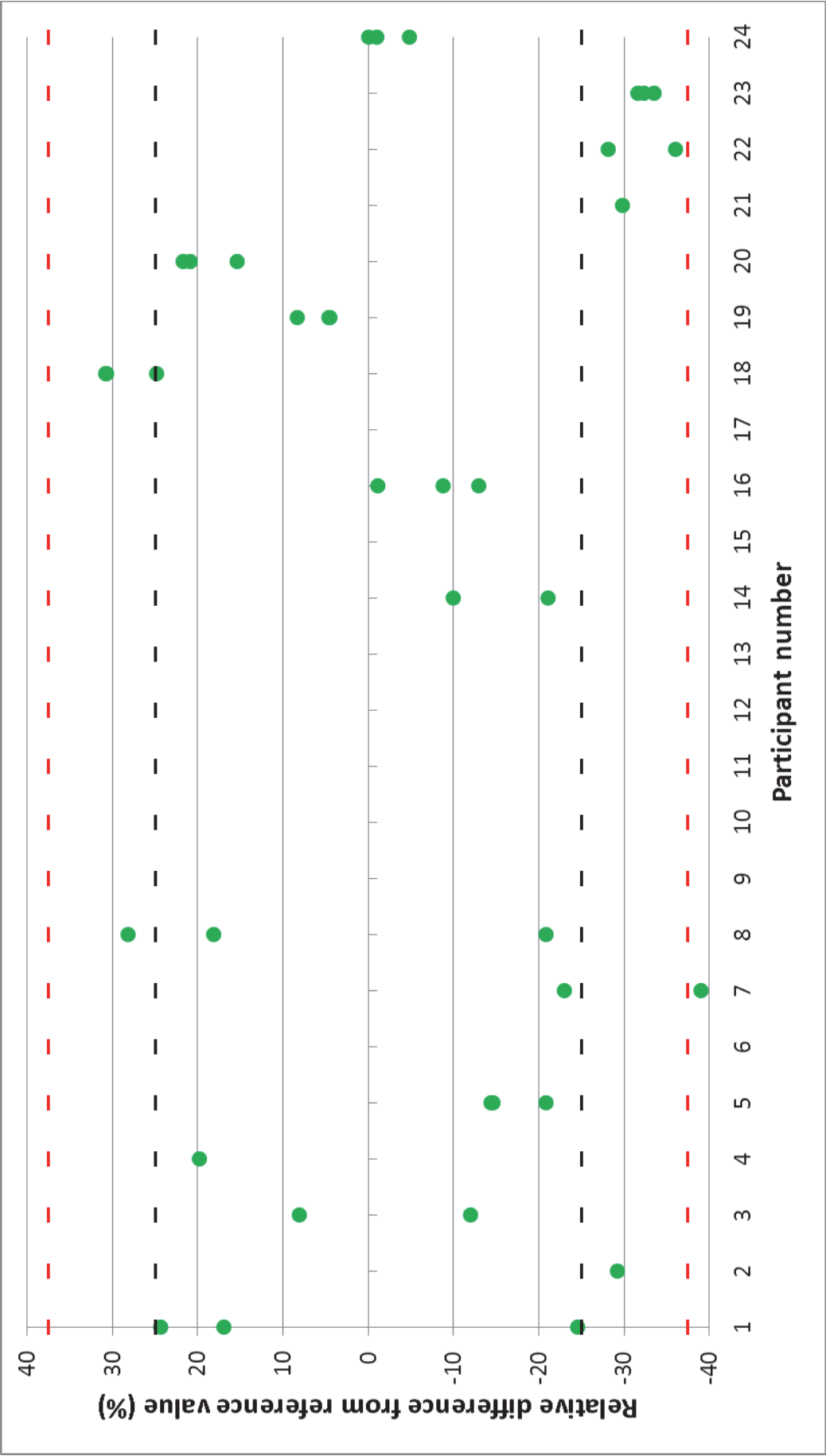


Figure 6b The relative difference of reported results from the reference value for hexanal (less than $\pm 40\%$). The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

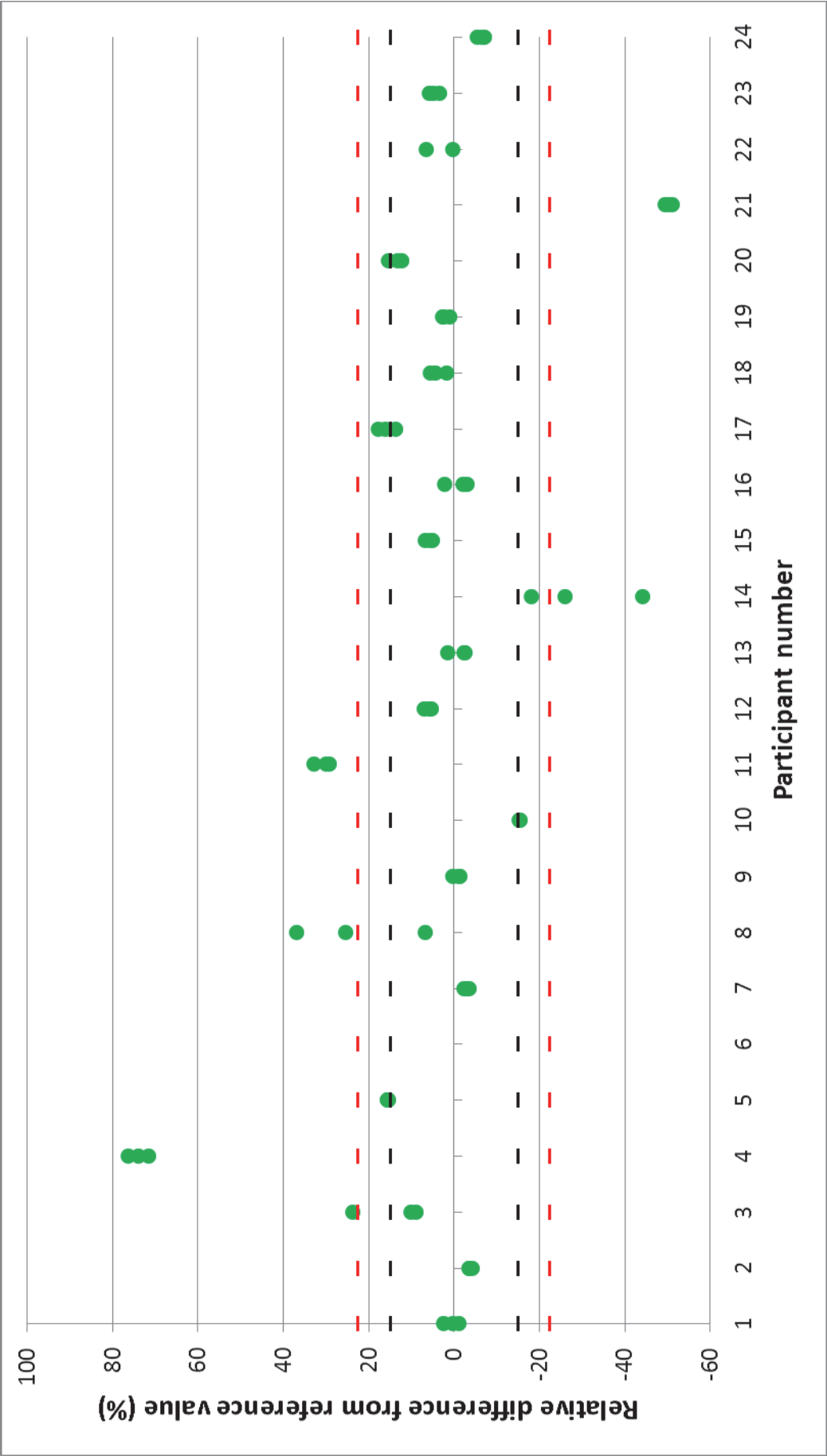


Figure 7a The relative difference of reported results from the reference value for *m*-xylene. For institution 6 the points are not depicted in the above figure as the relative differences correspond to values greater than 100 %. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

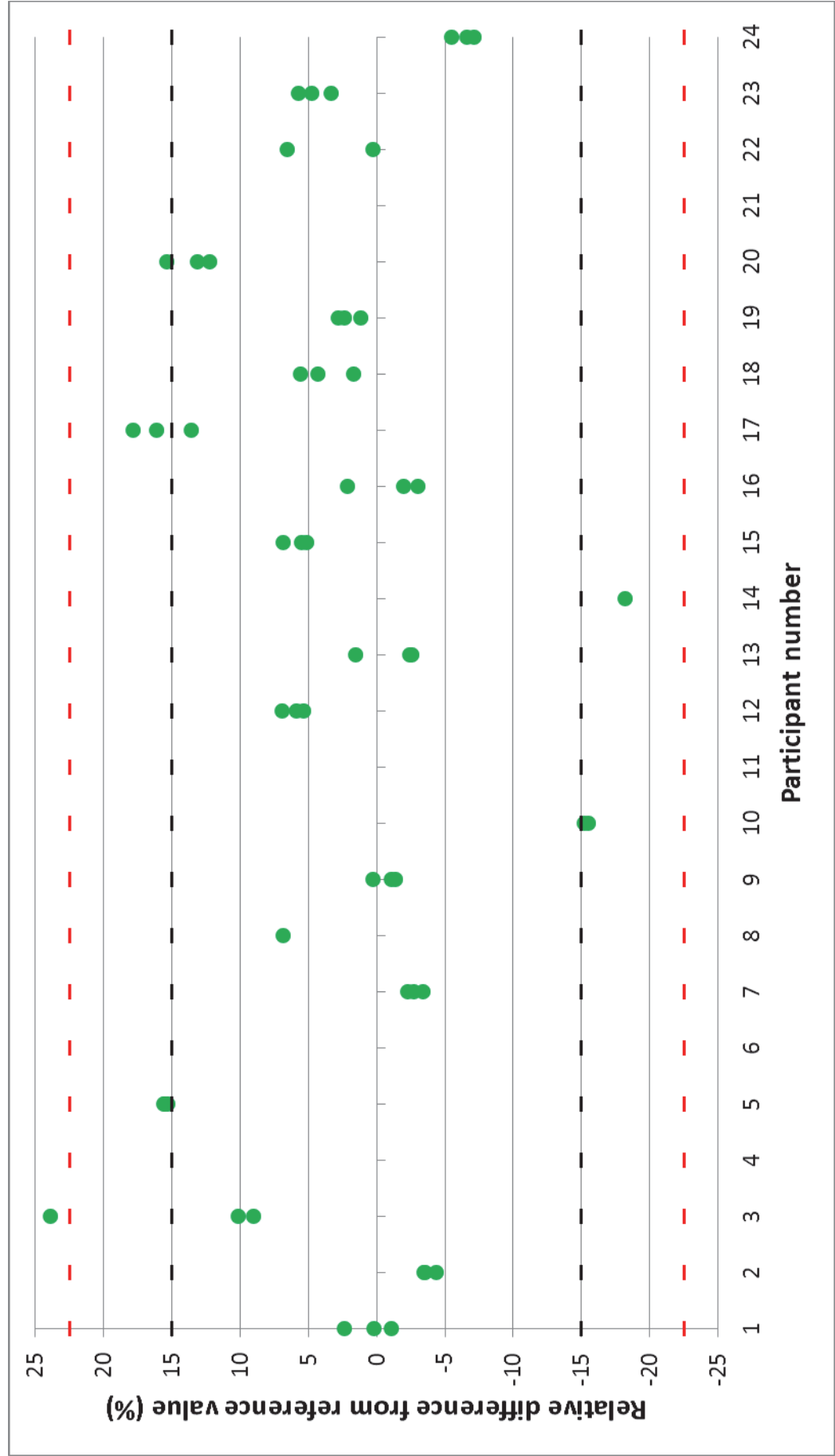


Figure 7b The relative difference of reported results from the reference value for *m*-xylene (less than $\pm 25\%$). The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

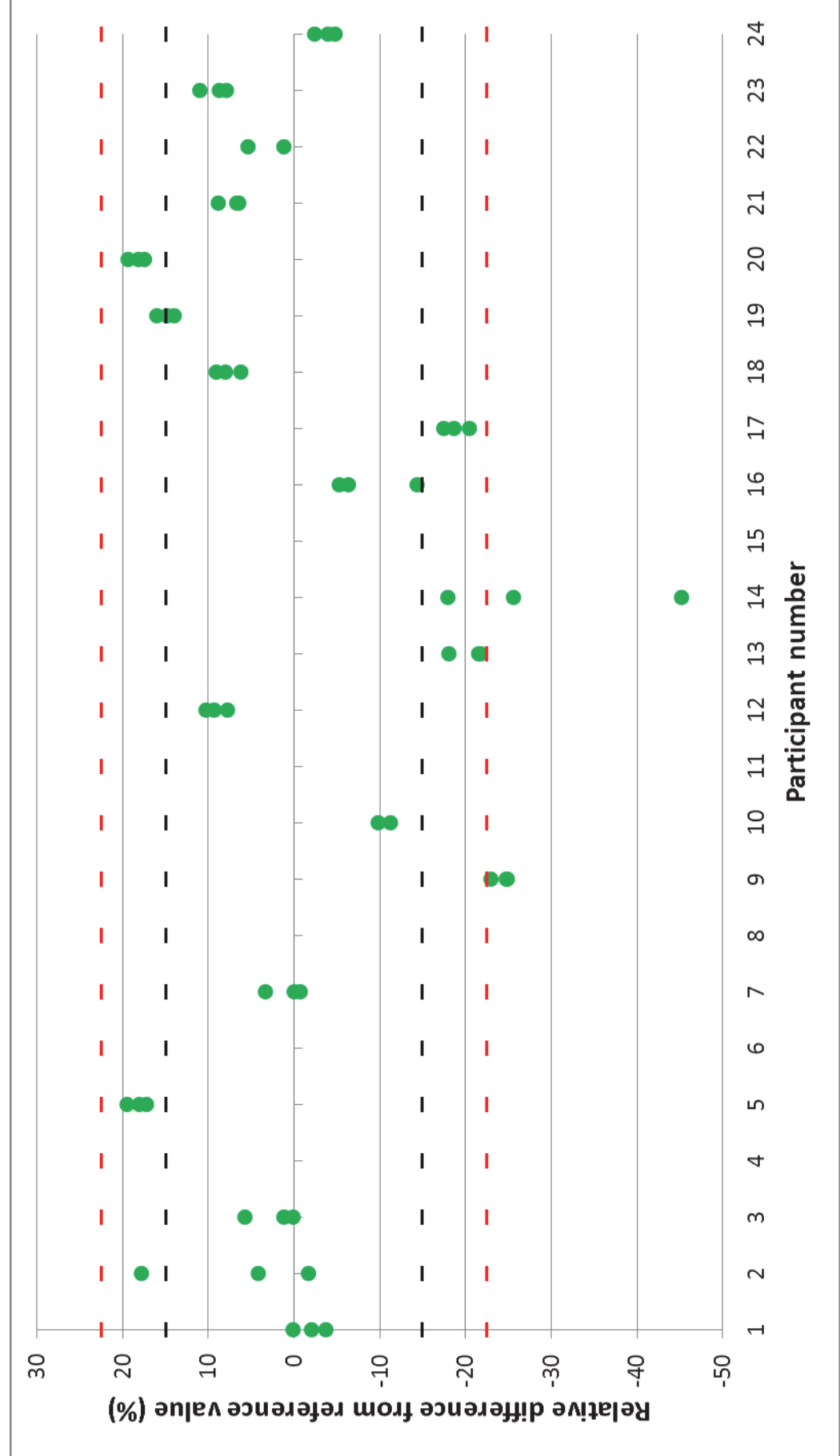


Figure 8a The relative difference of reported results from the reference value for α -pinene. For institution 6 the points are not depicted in the above figure as the relative differences correspond to values greater than 100 %. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

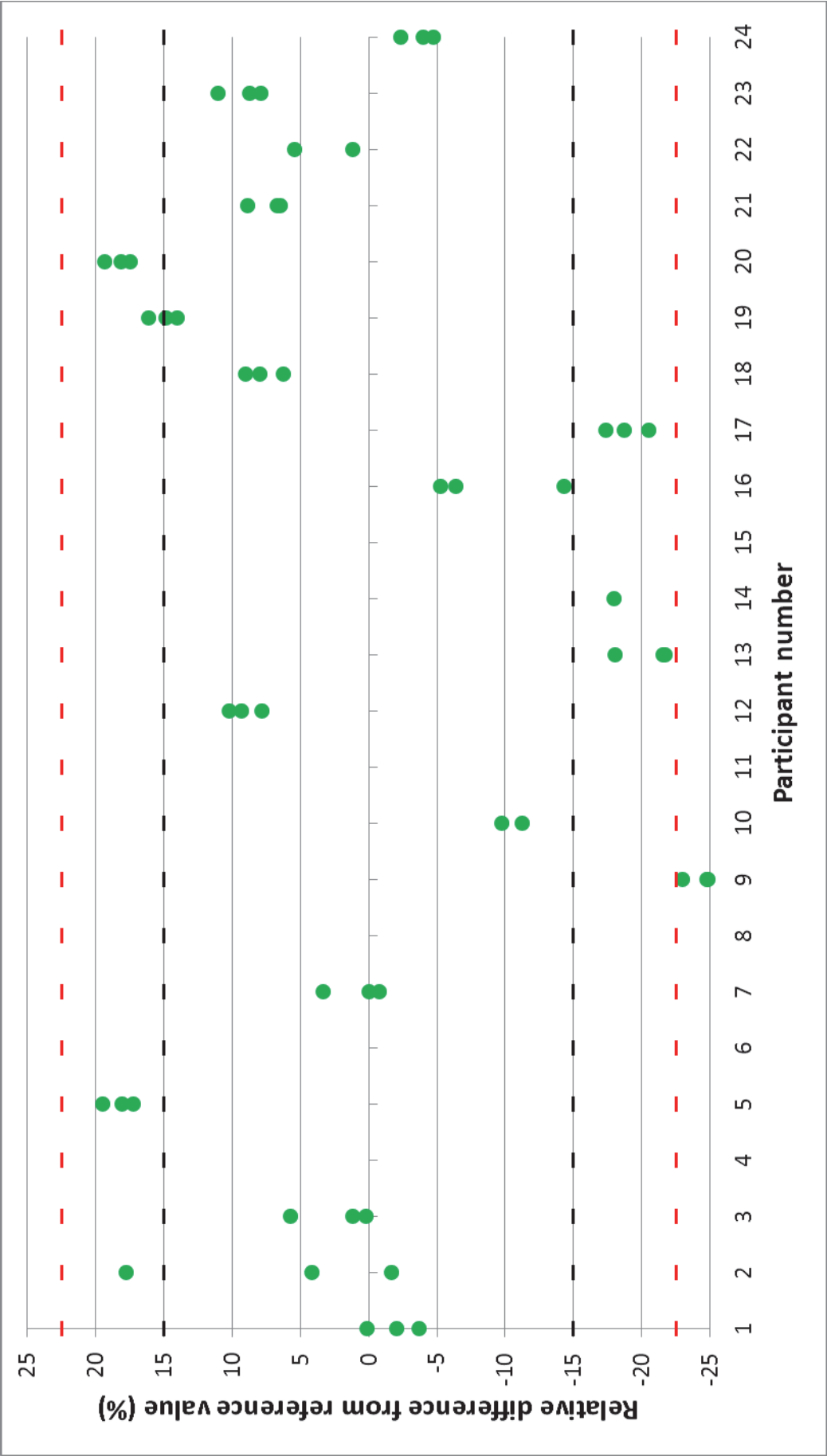


Figure 8b The relative difference of reported results from the reference value for α -pinene (less than $\pm 25\%$). The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

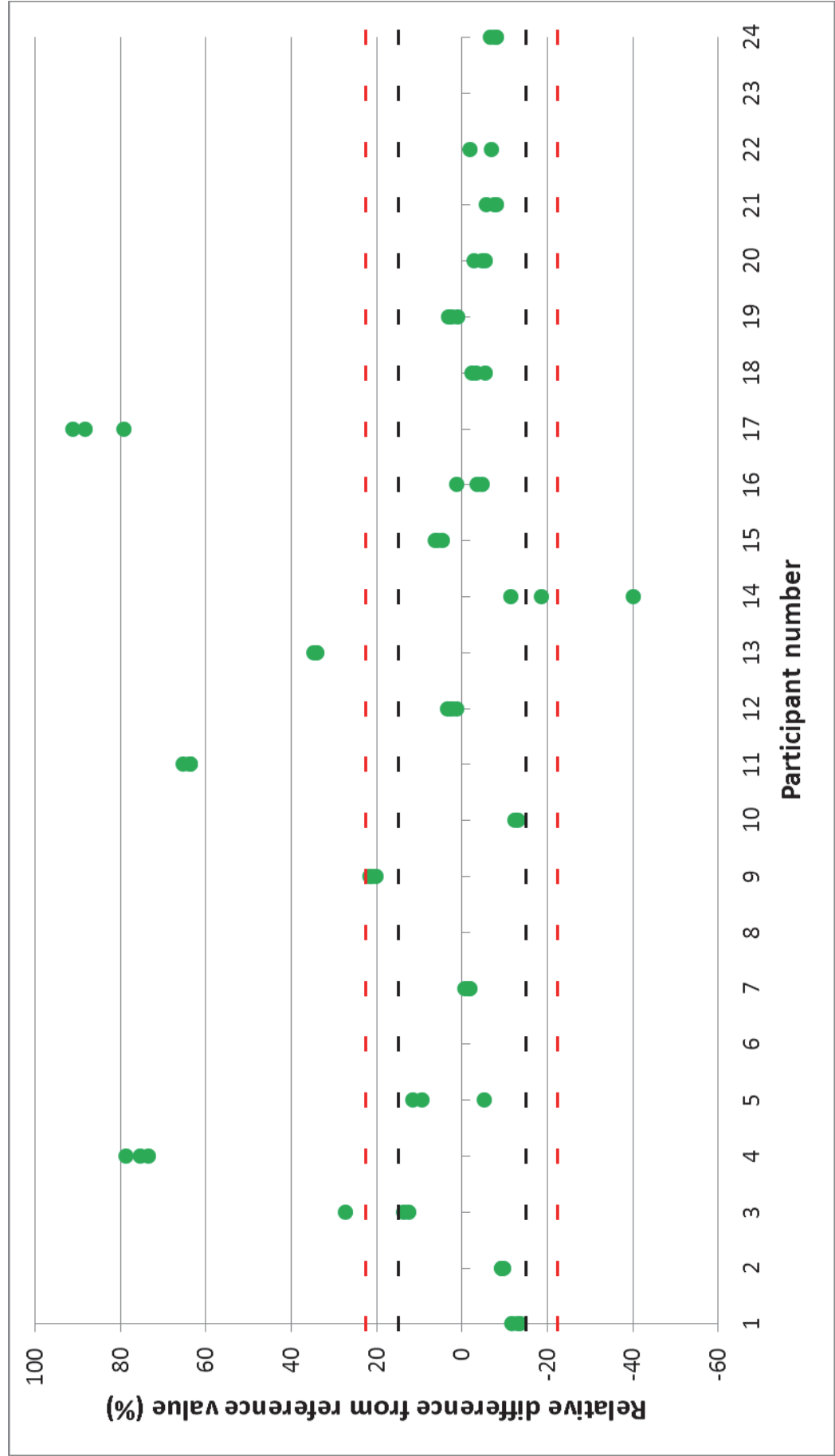


Figure 9a The relative difference of reported results from the reference value for styrene. For institution 6 the points are not depicted in the above figure as the relative differences correspond to values greater than 100 %. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

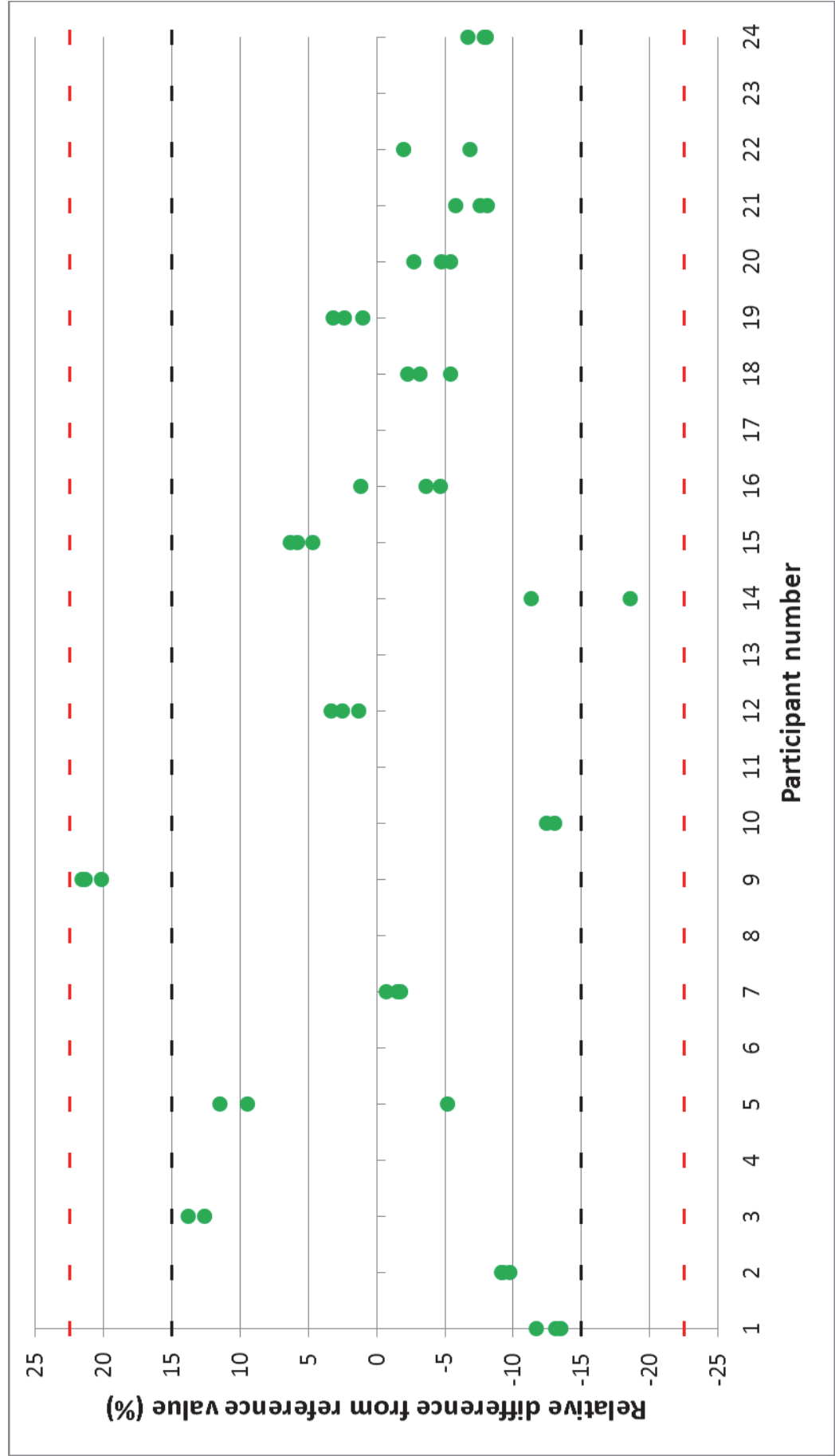


Figure 9b The relative difference of reported results from the reference value for styrene (less than $\pm 25\%$). The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

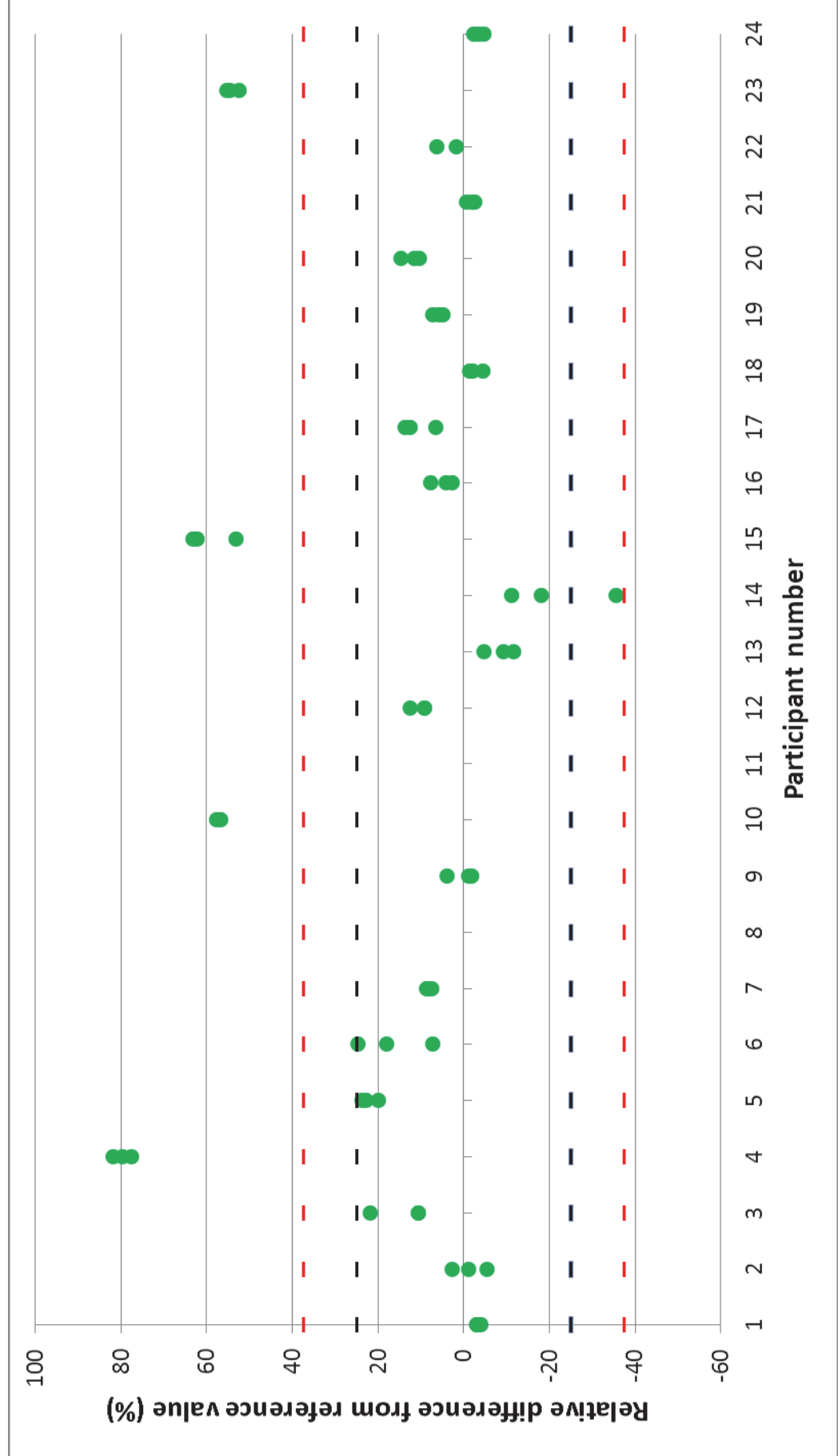


Figure 10a The relative difference of reported results from the reference value for 1,2,3-trimethylbenzene. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

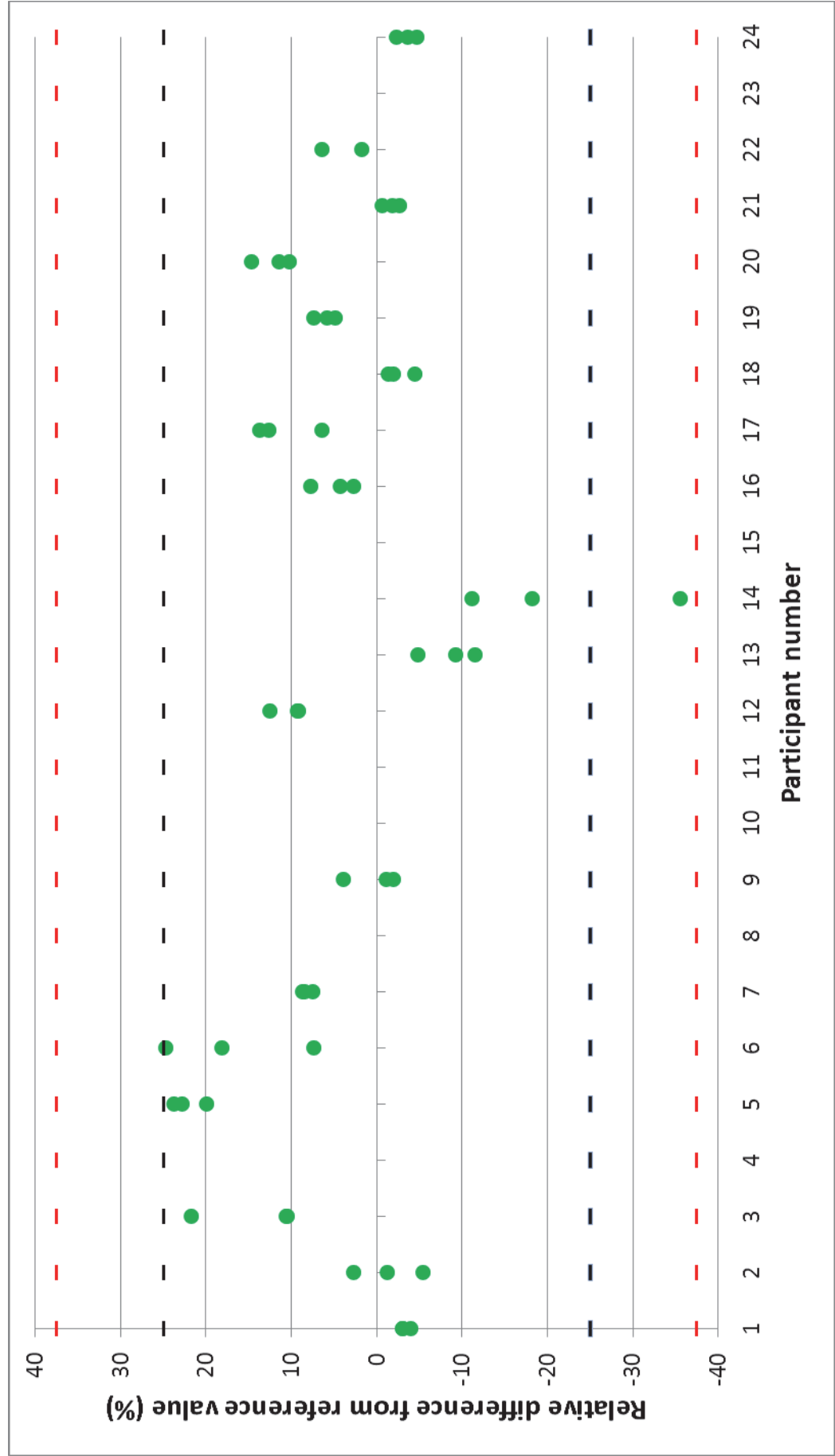


Figure 10b The relative difference of reported results from the reference value for 1,2,3-trimethylbenzene (less than $\pm 40\%$). The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

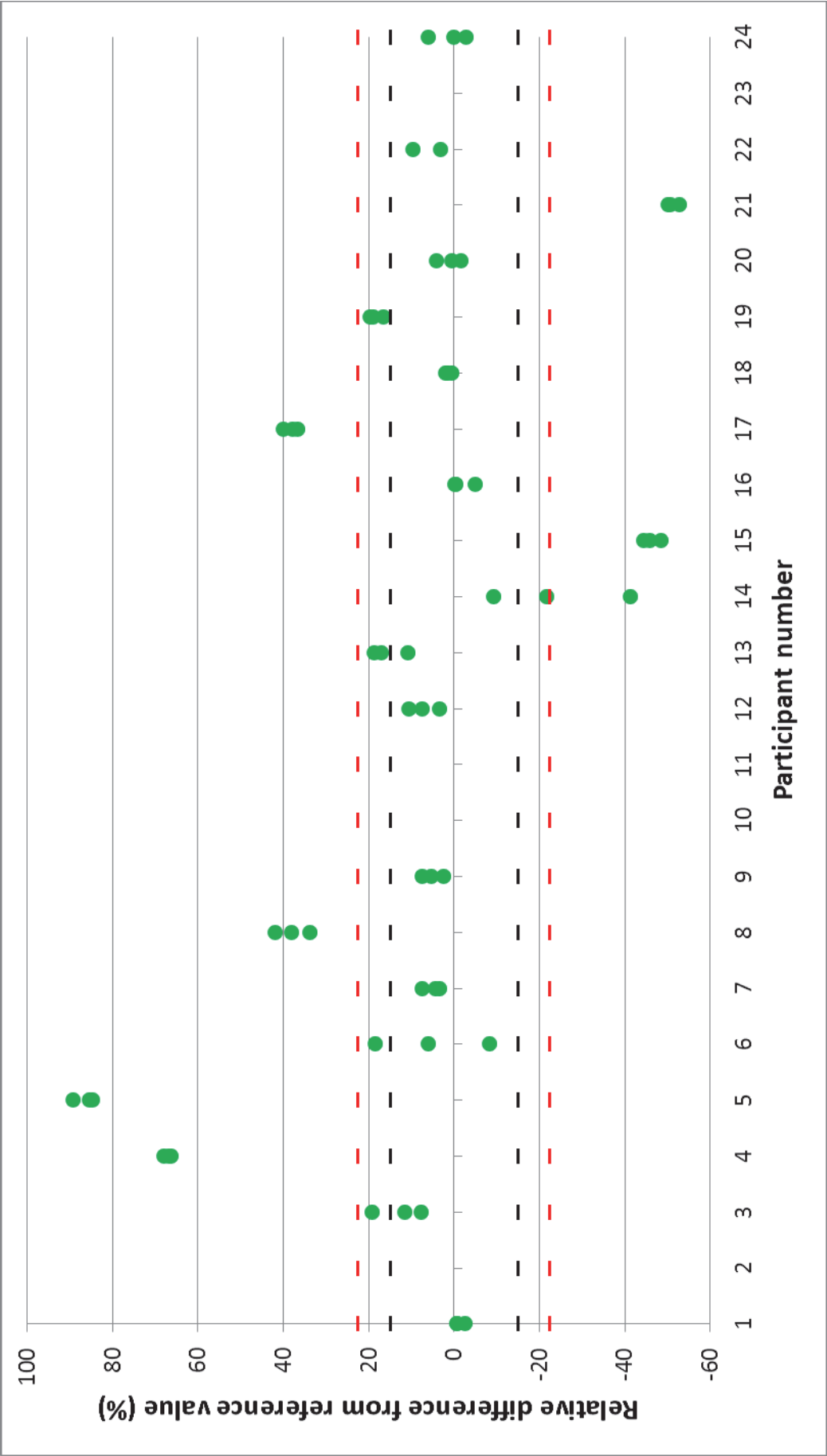


Figure 11a The relative difference of reported results from the reference value for 2-ethyl-1-hexanol. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

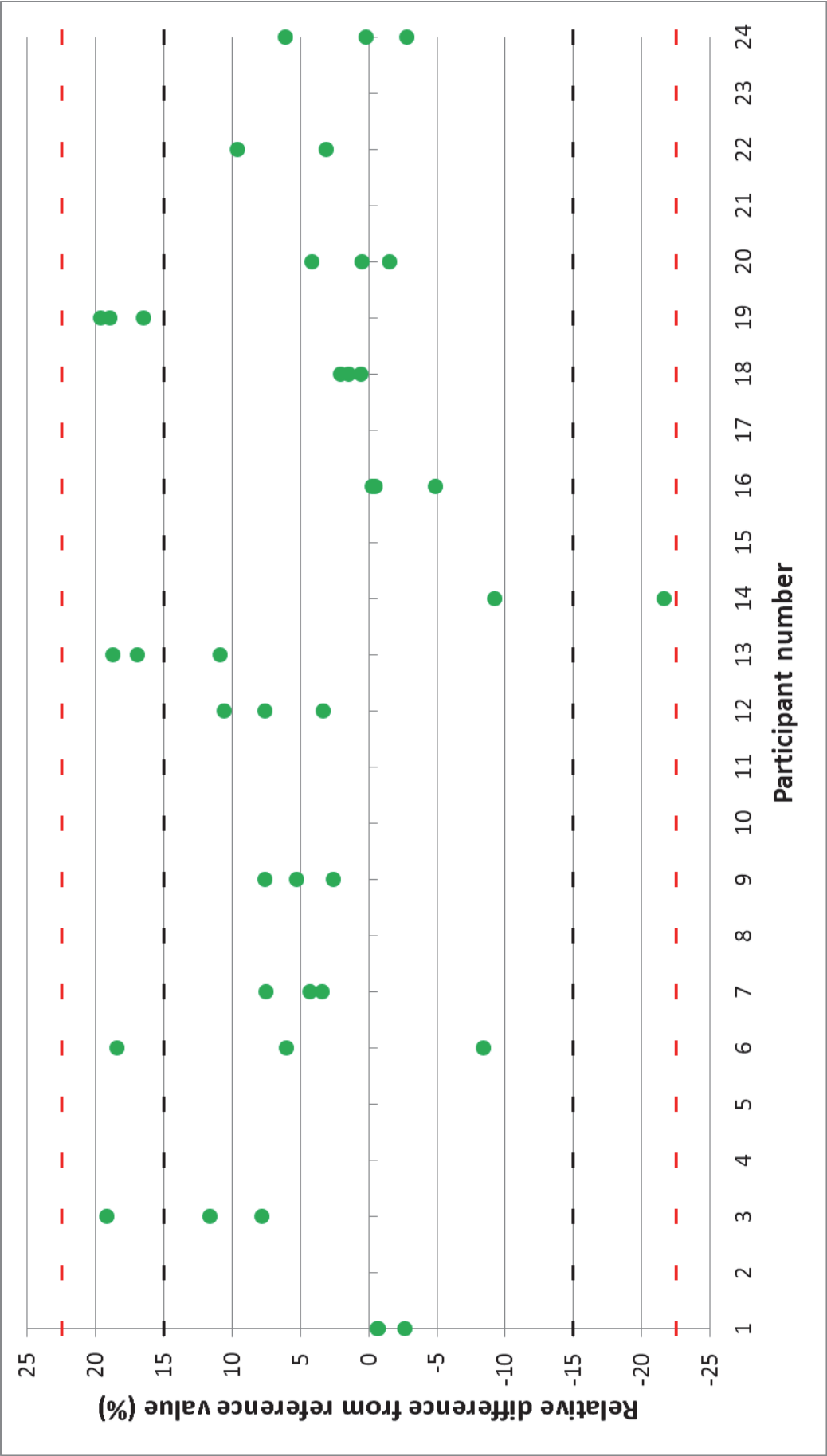


Figure 11b The relative difference of reported results from the reference value for 2-ethyl-1-hexanol (less than $\pm 25\%$). The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

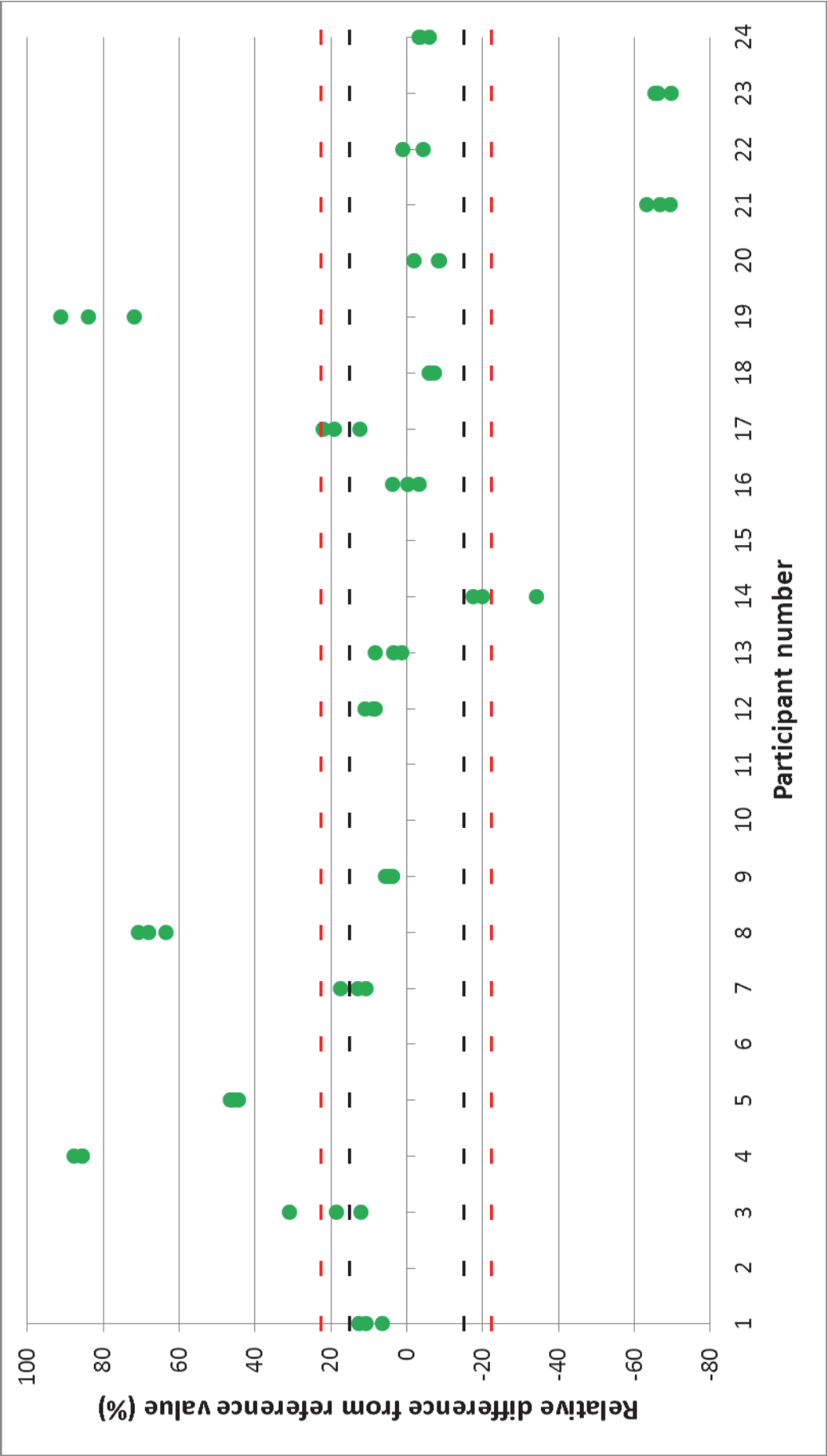


Figure 12a The relative difference of reported results from the reference value for 1-methyl-2-pyrrolidone. The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

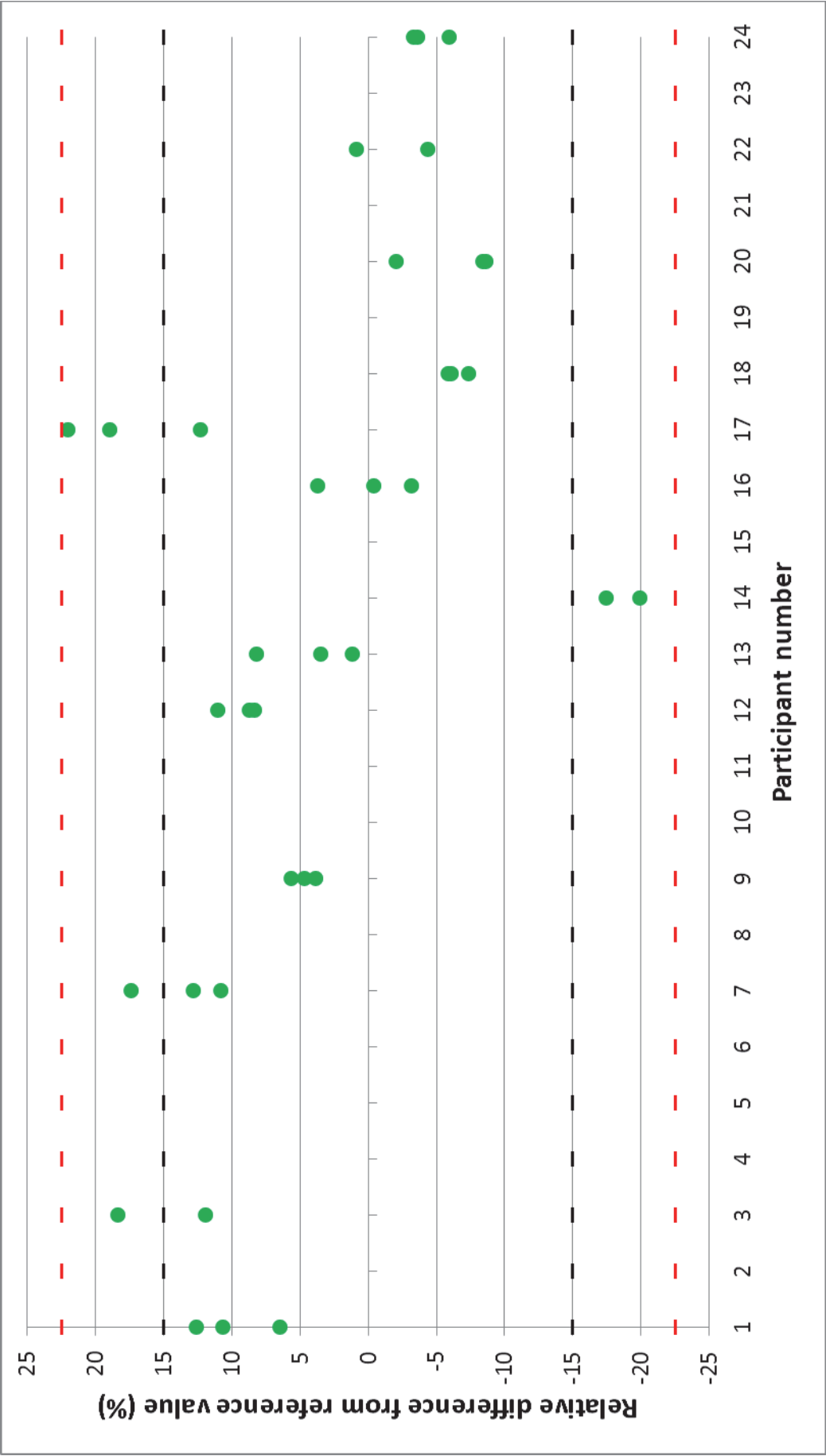


Figure 12b The relative difference of reported results from the reference value for 1-methyl-2-pyrrolidone (less than $\pm 25\%$). The black dotted lines represent a z-score of ± 2 and the red dotted lines represent a z-score of ± 3 either side of the assigned reference value.

APPENDIX

Tables 5-14 Z-score tabulations for the ten indoor air components

Benzene			
Reference value			120.20 ng
σ_{PA}			7.5 %
Set	z-score		
A	0.44	0.40	0.32
B	0.22	1.78	-0.61
C	4.47	6.51	4.30
D	9.74	10.11	10.50
E	0.90	1.09	1.09
F	17.85	20.26	16.13
G	0.31	0.06	0.16
H	2.14	6.98	5.16
I	0.81	0.62	0.59
J			
K	-2.89	-2.47	-2.40
L	-0.41	-0.60	-0.53
M	-0.79	-1.24	-1.19
N	-5.69	-2.60	-1.17
O	7.33	9.06	8.38
P	-1.02	-0.34	-0.47
Q	3.24	4.13	3.96
R	0.63	0.64	0.42
S	-0.39	-0.30	-0.15
T	0.17	-0.03	0.58
U	0.13	0.16	0.56
V		0.50	-0.91
W	0.34	-0.05	-0.25
X	-0.73	-0.43	-0.57

Toluene			
Reference value			149.88 ng
σ_{PA}			7.5 %
Set	z-score		
A	-0.80	-0.83	-0.89
B	1.19	5.26	0.43
C	1.26	2.89	1.06
D	10.26	10.70	11.03
E	1.86	1.59	1.82
F	27.92	31.07	79.02
G	0.32	0.00	0.10
H	1.38	6.32	4.66
I	-0.10	-0.30	-0.27
J	-1.33		-1.42
K	0.22	0.33	0.93
L	0.20	0.22	0.44
M	-0.33	-0.11	0.39
N	-6.09	-3.49	-2.34
O	-0.53	0.05	-0.18
P	-0.75	-0.49	0.10
Q	2.32	3.01	2.85
R	0.35	0.30	-0.03
S	-0.16	-0.35	-0.40
T	0.49	0.21	0.60
U	-0.86	-1.05	-1.09
V		1.07	0.35
W	1.13	1.35	1.00
X	-1.07	-0.91	-0.97

Butyl acetate			
Reference value			165.24 ng
σ_{PA}			12.5 %
Set	z-score		
A	-1.03	-1.34	-1.42
B	-0.38	-0.22	-1.07
C	1.43	2.46	1.56
D	7.09	7.08	7.31
E	1.05	1.03	1.06
F		-7.05	0.61
G	0.82	0.63	0.65
H	2.01	4.43	3.32
I	-3.88	-3.45	-3.22
J	-0.47		-0.42
K			
L	-3.21	-3.17	-3.55
M	0.07	0.68	0.99
N	-2.90	-1.00	-0.28
O	0.59	0.75	1.28
P	0.18	0.26	0.42
Q	0.38	2.70	3.13
R	0.57	0.43	0.23
S	1.53	1.25	1.25
T	1.34	1.08	1.28
U	-0.35	-0.52	-0.56
V		0.13	0.68
W	-2.58	-2.60	-2.72
X	-0.07	0.04	-0.07

Hexanal			
Reference value			116.25 ng
σ_{PA}			12.5 %
Set	z-score		
A	-1.96	1.95	1.36
B	-4.17	-2.34	-3.39
C	-3.89	0.65	-0.96
D	1.58	4.37	4.47
E	-1.67	-1.17	-1.16
F	12.55	23.18	22.42
G	-4.54	-1.84	-3.12
H	-1.67	1.45	2.25
I	3.98	3.74	3.71
J	-4.59		-4.13
K			
L	4.76	4.89	5.13
M			
N	-3.48	-1.69	-0.80
O	6.72	7.70	7.81
P	-1.04	-0.71	-0.09
Q	6.00	6.72	6.38
R	1.99	2.47	2.45
S	0.67	0.36	0.37
T	1.74	1.23	1.67
U	-2.38	-4.49	-4.45
V		-2.88	-2.25
W	-2.68	-2.53	-2.59
X	-0.08	0.00	-0.39

<i>m</i>-xylene			
Reference value			164.41 ng
σ_{PA}			7.5 %
Set	z-score		
A	-0.15	0.32	0.03
B	-0.58	-0.46	-0.47
C	1.20	3.18	1.36
D	9.53	9.85	10.18
E	2.07	2.04	2.08
F	53.46	52.32	64.97
G	-0.36	-0.45	-0.30
H	0.92	4.91	3.39
I	0.04	-0.18	-0.14
J	-2.06		-2.03
K	3.99	3.90	4.38
L	0.79	0.71	0.92
M	-0.35	-0.32	0.20
N	-5.89	-3.47	-2.42
O	0.73	0.91	0.68
P	-0.27	-0.40	0.29
Q	1.81	2.38	2.15
R	0.75	0.57	0.22
S	0.37	0.15	0.32
T	1.75	1.63	2.05
U	-6.60	-6.81	-6.72
V		0.04	0.87
W	0.63	0.76	0.44
X	-0.95	-0.73	-0.88

α-pinene			
Reference value			207.71 ng
σ_{PA}			7.5 %
Set	z-score		
A	-0.49	0.01	-0.27
B	0.56	2.37	-0.22
C	0.02	0.76	0.16
D			
E	2.30	2.40	2.60
F	35.18	40.27	34.99
G	-0.10	0.44	0.00
H			
I	-3.06	-3.31	-3.30
J	-1.50		-1.30
K			
L	1.24	1.04	1.37
M	-2.90	-2.87	-2.41
N	-6.03	-3.41	-2.39
O			
P	-0.85	-0.70	-1.91
Q	-2.73	-2.32	-2.49
R	1.21	1.07	0.83
S	1.87	2.14	1.98
T	2.42	2.33	2.58
U	1.18	0.89	0.87
V		0.16	0.72
W	1.16	1.47	1.06
X	-0.53	-0.31	-0.63

styrene			
Reference value			164.07 ng
σ_{PA}			7.5 %
Set	z-score		
A	-1.56	-1.75	-1.80
B	-1.23	-1.30	-1.22
C	1.68	3.63	1.84
D	9.81	10.05	10.49
E	1.53	1.27	-0.69
F	73.46	77.93	70.36
G	-0.23	-0.20	-0.09
H			
I	2.87	2.85	2.68
J	-1.73		-1.66
K	8.70	8.49	8.48
L	0.34	0.18	0.44
M	4.62	4.53	4.56
N	-5.36	-2.47	-1.51
O	0.84	0.78	0.63
P	-0.48	-0.62	0.15
Q	10.55	12.17	11.77
R	-0.30	-0.43	-0.72
S	0.13	0.31	0.42
T	-0.63	-0.72	-0.36
U	-0.77	-1.08	-1.01
V		-0.91	-0.26
W			
X	-1.07	-0.89	-1.05

1,2,3-trimethylbenzene			
Reference value			182.86 ng
σ_{PA}			12.5 %
Set	z-score		
A	-0.24	-0.25	-0.31
B	-0.10	-0.43	0.21
C	0.84	1.74	0.85
D	6.20	6.39	6.54
E	1.90	1.60	1.82
F	1.45	1.98	0.59
G	0.68	0.69	0.60
H			
I	0.31	-0.09	-0.15
J	4.54		4.61
K			
L	0.73	0.74	1.00
M	-0.92	-0.74	-0.38
N	-2.84	-1.46	-0.89
O	4.24	4.98	5.07
P	0.34	0.21	0.62
Q	0.52	1.10	1.01
R	-0.11	-0.16	-0.35
S	0.39	0.46	0.59
T	0.92	0.82	1.18
U	-0.05	-0.21	-0.15
V		0.14	0.51
W	4.37	4.42	4.19
X	-0.37	-0.18	-0.29

2-ethyl-1-hexanol			
Reference value			164.18 ng
σ_{PA}			7.5 %
Set	z-score		
A	-0.08	-0.10	-0.35
B			
C	1.04	2.56	1.55
D	9.07	8.90	8.85
E	11.29	11.41	11.91
F	-1.12	0.80	2.46
G	0.46	1.00	0.57
H	4.50	5.60	5.08
I	0.34	0.70	1.01
J			
K			
L	1.41	0.45	1.01
M	1.45	2.26	2.50
N	-5.52	-2.88	-1.23
O	-6.12	-5.92	-6.45
P	-0.06	-0.65	-0.04
Q	4.88	5.33	5.05
R	0.28	0.20	0.08
S	2.52	2.61	2.20
T	0.07	-0.21	0.55
U	-6.68	-7.05	-6.76
V		0.42	1.28
W			
X	-0.37	0.82	0.02

1-methyl-2-pyrrolidone			
Reference value			164.36 ng
σ_{PA}			7.5 %
Set	z-score		
A	1.68	0.86	1.43
B			
C	1.59	4.12	2.45
D	11.40	11.39	11.69
E	6.09	5.91	6.19
F			
G	1.44	2.32	1.71
H	8.48	9.42	9.07
I	0.51	0.63	0.75
J			
K			
L	1.12	1.16	1.47
M	0.16	0.46	1.09
N	-4.55	-2.33	-2.65
O			
P	0.49	-0.42	-0.05
Q	1.64	2.93	2.53
R	-0.81	-0.78	-0.98
S	11.20	12.14	9.56
T	-1.15	-1.12	-0.27
U	-8.91	-9.24	-8.45
V		-0.58	0.12
W	-9.30	-8.74	-8.82
X	-0.79	-0.48	-0.44