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Evaluation of CCME 257-2003 Commissioning Sample Results Employing Kernel Density Analysis (KDA)

Introduction:

The CCME 257-2003 Phase 1 Commissioning Sample Report sent out in November 2002 presents laboratory performance in a tabular format. Kernel Density Analysis (KDA) provides a method for presenting laboratory performance that is particularly suitable for displaying data distributions and laboratory quality control in a visual format. KDA provides direct information with respect to laboratory measurement uncertainty and laboratory bias that can be employed, as a basis for assessing needs for any corrective action or priorities for method improvement.

Background:

The fundamental principles of the KDA analysis are based on procedures published by the Analytical Methods Committee (AMC) of the Royal Society of Chemistry (UK). Examination of a large number of inter-laboratory study (ILS) data sets by the AMC revealed that in the majority of cases the underlying data distributions are multi-modal in nature. Treatment of these distributions employing conventional algorithms in most cases forces the data to a uni-modal fit. In doing so method specific effects are masked, resulting in misleading conclusions concerning laboratory performance.

Recently, the Analytical Methods Committee of the Royal Society of Chemistry (UK) has produced several publications on kernel density calculations as a means of revealing multi-modal structure in the data distributions produced in an ILS. The concept works as follows. From all the results reported for an analyte, a data scale is developed. Then the amount that each data point reported contributes to a given point on the scale is calculated. This contribution is known as a "kernel". All the data "kernels" at a given point are then summed to give the kernel density at that point.



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Kernel Density Charts:

KDA charts are interpreted as follows.

The chart title lists the parameter name.

The laboratory blind alphabetical ID is below and to the right of the chart title.

The blind ID is followed by standard method of test employed by the laboratory.

The **dark blue line** is the data distribution calculated employing kernel density estimates.

The **light blue line** is the cumulative number of labs reporting.

The total number of labs reporting appears in a **blue box** at the right hand side of the graph.

The **reference value and associated confidence limits for the sample under test appear in green** below the x-axis. The reference value and confidence limits have been established through a study or studies entirely independent of the current ILS.

Two dashed vertical green bars appear on the chart.

The green numbers immediately above these two dashed vertical green bars represent the lower and upper limits of the reference value for the sample under test.

The **vertical blue bar** represents the kernel maximum.

This is the scale point with the **highest kernel density**.

The **value of the kernel maximum** appears as a **blue number** in a black box.

The kernel maximum is calculated from the results reported by all ILS laboratories.

The **two solid vertical blue bars and associated values** represent the 95% upper and lower critical benchmark limits of agreement with the “kernel maximum”. These benchmark limits are calculated from the reproducibility standard deviation of the standard method of test according to the principles outlined in ISO 5725 Part 6 as well as confidence limits of the reference sample. In instances where a laboratory reports the use of a method not supported by a method validation study the Horwitz function is employed in conjunction with the reference sample confidence limits to calculate the benchmark limits.



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The laboratory average is plotted as a **black dot** on the kernel distribution curve. For sake of convenience, an **open white circle** representing the laboratory average mirrors this black dot. The **laboratory average highlighted in gray** appears above the open circle.

If the **black dot** falls **within the limits defined by the dashed vertical green bars** then the laboratory has produced an **average result that is unbiased with respect to the reference value**. If the **black dot falls outside of the limits defined by the dashed vertical green bars** but **inside the limits defined by the two solid vertical blue bars** then the laboratory is **capable of producing results within the benchmark limits**. If the **black dot falls outside both of these sets of limits** then the **accuracy of the value reported by the laboratory is suspect**.

In the CCME ILS each laboratory reports 4 mercury values.
The laboratory average is calculated from all four results.
Each laboratory average has horizontal bars representing the range of results reported.

If there are no horizontal bars then the four results reported are identical within rounding error. Taking into account normal sources of random error, this situation is highly unlikely and should be viewed as suspect.

If **the horizontal bars attached to laboratory average are green then laboratory precision is acceptable**. If the **horizontal bars attached to the laboratory average are red then laboratory precision is suspect**. **Suspect precision** indicates a laboratory has not implemented measures to insure the laboratory quality system is sufficiently stable. In the case of **suspect precision laboratory accuracy is also suspect**.

Additional information can be extracted from the precision bars on the graphs.
If both the laboratory average and laboratory precision bars fall within the **limits defined by the dashed vertical green bars then the laboratory quality system has achieved optimum performance for the test sample**.

Examination of the precision bars usually reveals that they are unbalanced or skewed in one direction. This is not unusual when 4 results are involved. However, if the bars are predominantly skewed in one direction this is an indication that one of the 4 results departs significantly from the other three. **This should be investigated, particularly if the precision bars are red**.



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Evaluation of Mercury Analysis by KDA:

Comparison of KDA performance with CCME 257-2003 Phase 1 Commissioning Sample Report.

The KDA graphs of laboratory performance correspond with the summary of laboratory performance presented in Table 2 on page 8 of the CCME 257-2003 Phase 1 Commissioning Sample Report. There are in some instances differences between the numbers on the graphs compared with those in the table. In certain cases the laboratory averages presented on the graphs differ from those in the table. This is because KDA can determine the smallest difference that can be distinguished between any two results. In the case of the commissioning sample this was determined to be 2 ng of mercury. As a result the KDA analysis calculates the laboratory average to the closest even ng of mercury. KDA also calculates slightly wider benchmark limits than appear in the table for the same reason.

KDA of all CCME laboratories

Here is where KDA offers significant advantages over the presentation in the CCME 257-2003 Phase 1 Commissioning Sample Report. Each laboratory graph includes the distribution of results from all laboratories that took part in the commissioning phase as well as the total number of laboratories reporting. Fourteen (14) laboratories took part in commissioning phase. However, three laboratories reported more than 1 set of results accounting for the total of 19 shown in the laboratory graphs.

From the KDA graphs it is evident the kernel maximum corresponds exactly with the reference value determined in the EPRI and ASTM studies for the commissioning sample. This characteristic would not have been revealed by conventional or even robust data analysis.

The KDA distribution clearly reveals three modes of data, 1 centered near 70 ng/g, another near 96 ng/g evident as a low shoulder on the main mode, and the main mode, which has a kernel maximum of 114 ng/g. Comparing the low shoulder on the KDA graph located near 96 ng/g with the table of results attached to this report reveals that almost all of the values associated with this shoulder correspond to laboratories employing EPA 245.5, which has been shown to give low recoveries for coal in past studies. The reasons for the low recovery have been discussed previously in the CCME 257-2003 Phase 1 Commissioning Sample Report. This feature would have been “masked” if normal graphical means of data analysis had been employed.

The mode near 70 ng/g is associated with two laboratories that have significant procedural problems.



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KDA of individual laboratory performance

Here again KDA offers significant advantages over the tabular presentation in the CCME 257-2003 Phase 1 Commissioning Sample Report. It is immediately obvious if laboratory accuracy and precision of is acceptable or suspect. In addition the precision bars reveal to what extent the laboratory results are skewed.

Evaluation of Determination of Ash by KDA:

KDA of all CCME laboratories

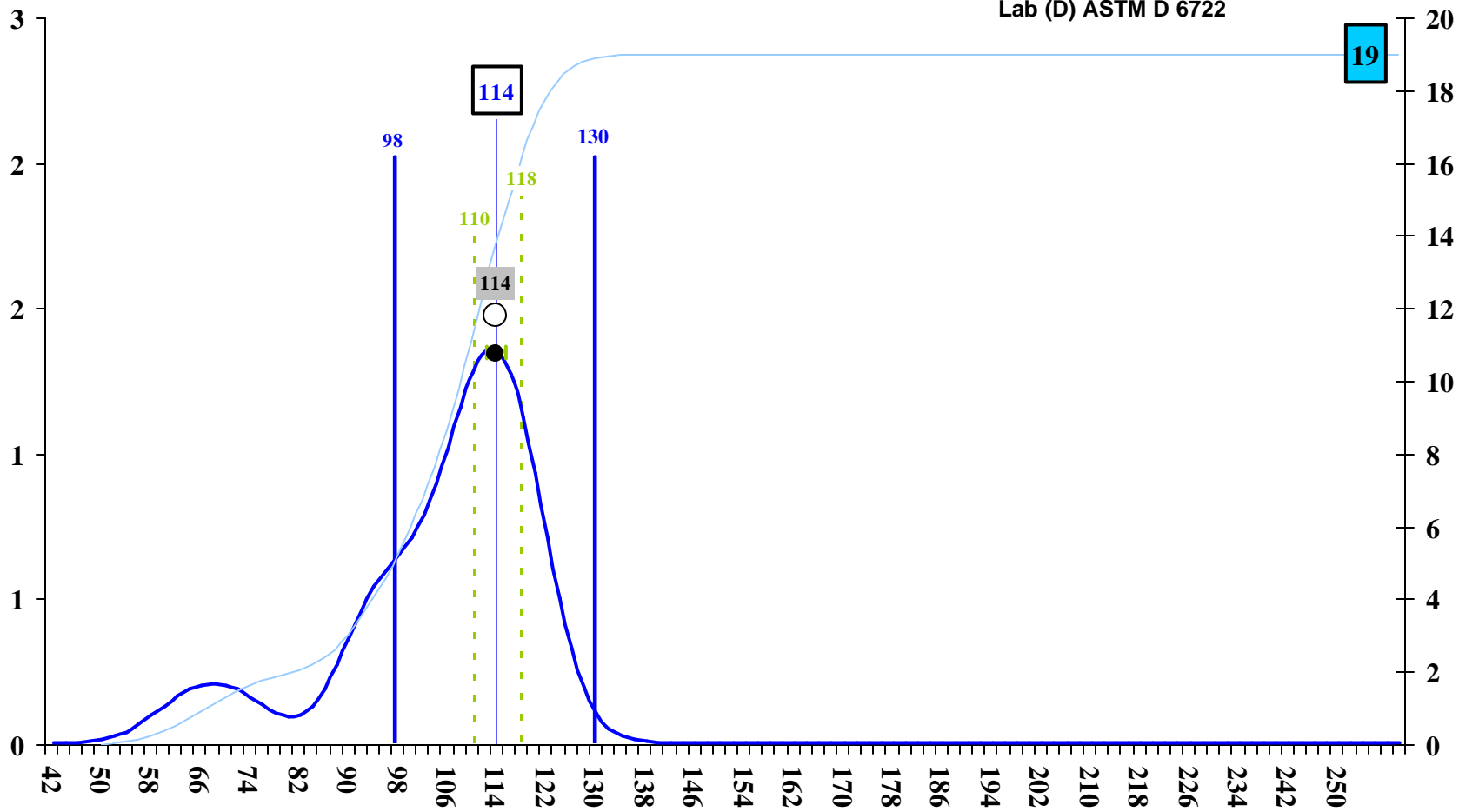
Again KDA offers significant advantages over the presentation in the CCME 257-2003 Phase 1 Commissioning Sample Report. Each laboratory graph includes the distribution of results from all laboratories that took part in the commissioning phase as well as the total number of laboratories reporting. One laboratory did not report any results for the determination of ash. Two laboratories did not treat the commissioning sample under conditions that meet the minimum requirements for complete ignition of the coal sample. One of the two took corrective action to ignite the sample in accordance with minimum specifications. A third laboratory chose to repeat the ash determination after they concluded the calibration of the instrument employed for the determination of ash was biased low. This accounts for the total of 14 laboratories appearing in the KDA graphs.

From the KDA graphs it is evident the kernel maximum is in excellent agreement with the reference value determined in the EPRI and ASTM studies for the commissioning sample.

The KDA distribution reveals three modes of data, one near 7.62 wt %, another near 7.80 wt % evident as a low shoulder on the main mode, and the main mode, which has a kernel maximum of 7.99 wt %. The mode at 7.62 wt % represents the laboratory with the instrument calibration problem. That laboratory reported a corrected value of 8.00 wt %, which is in excellent agreement with the kernel maximum. The distinct mode near 7.80 wt % is sufficiently different from the kernel maximum and the reference value to suggest the laboratories reporting averages near this mode as employing conditions of test such that can result in a lower dry ash content. Identification of these conditions and their impact on the determination of ash content may become more evident upon completion of the CRM and RM component of Phase 1.

CCME-C Mercury ng/g dry basis

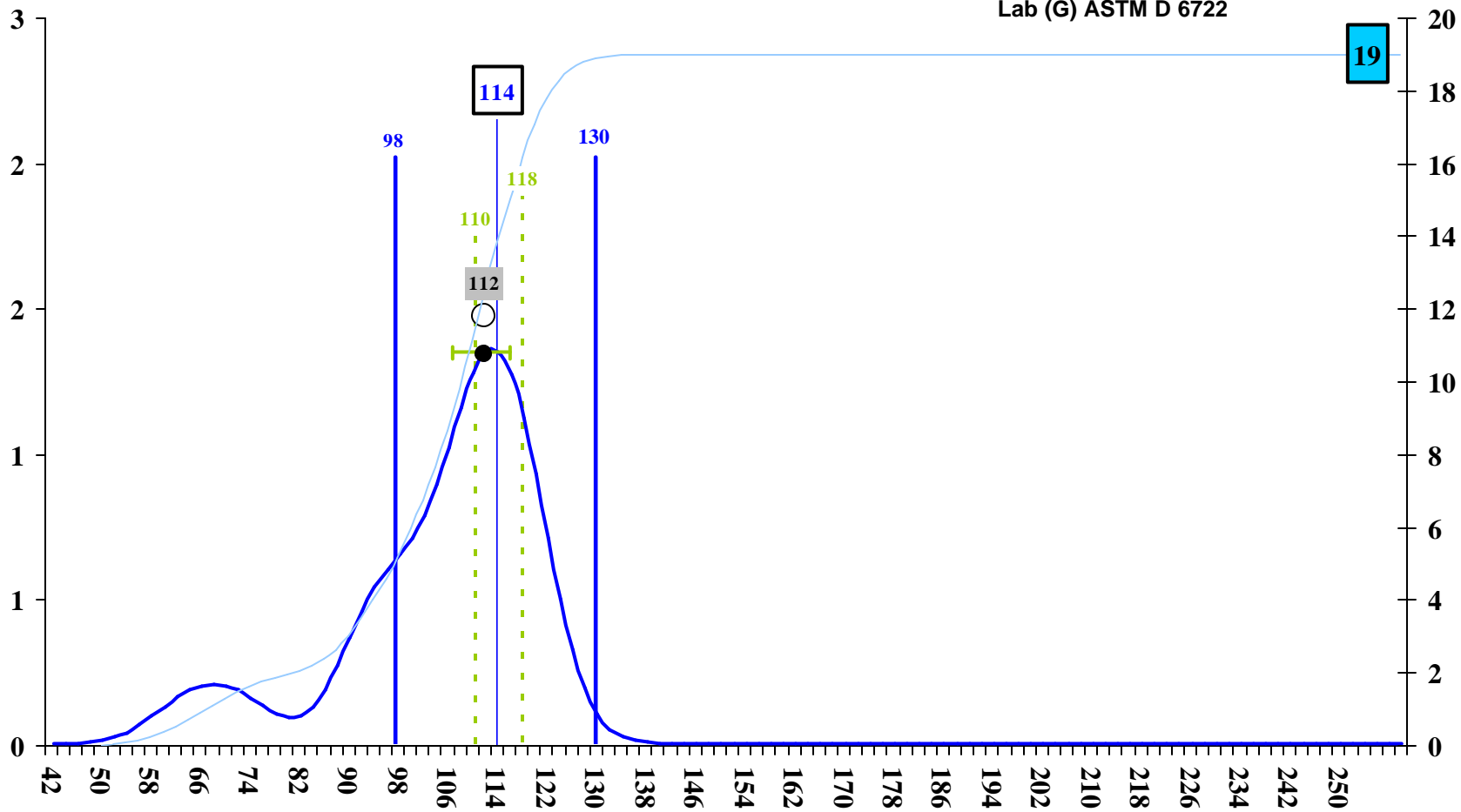
Lab (D) ASTM D 6722



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

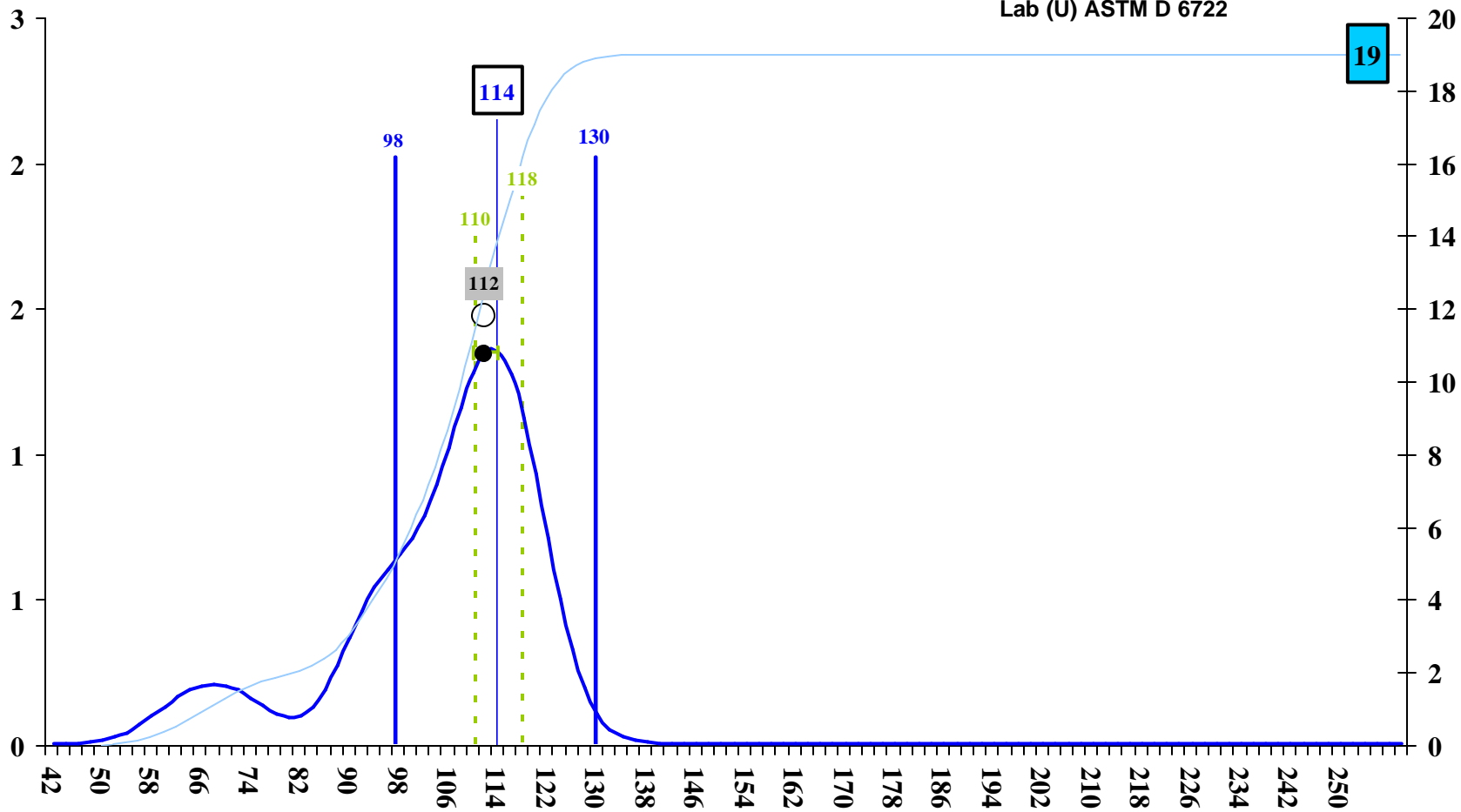
Lab (G) ASTM D 6722



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

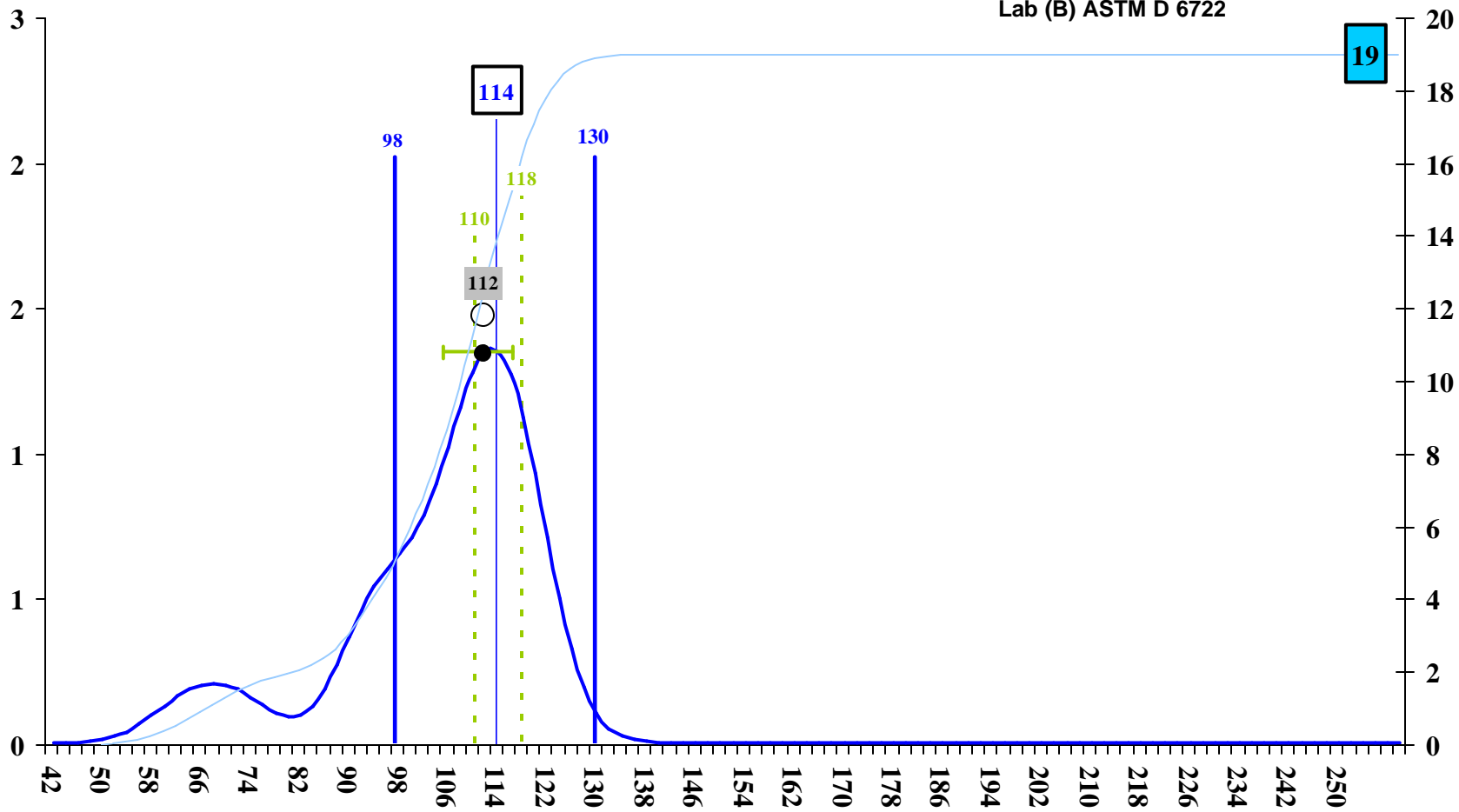
Lab (U) ASTM D 6722



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

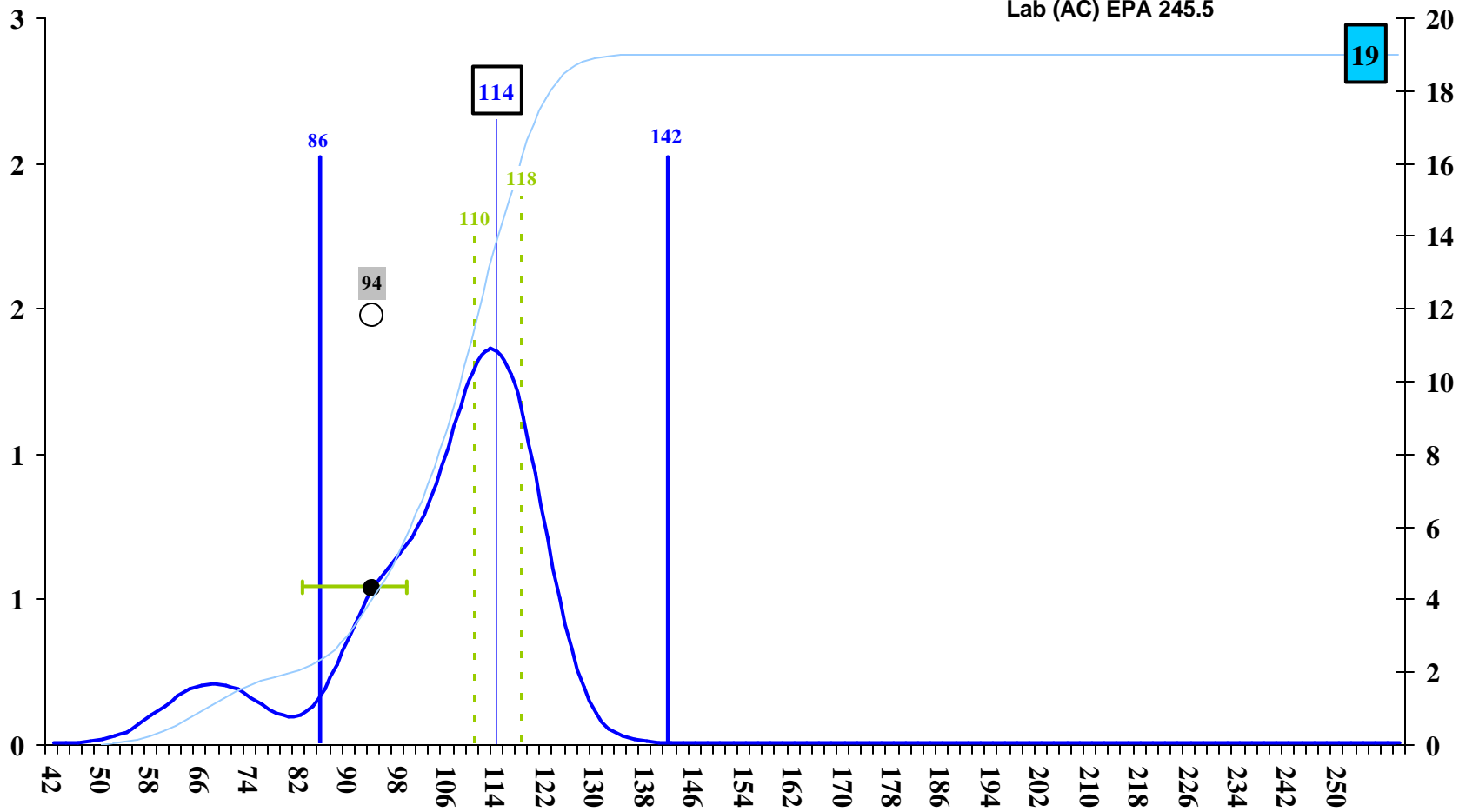
Lab (B) ASTM D 6722



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

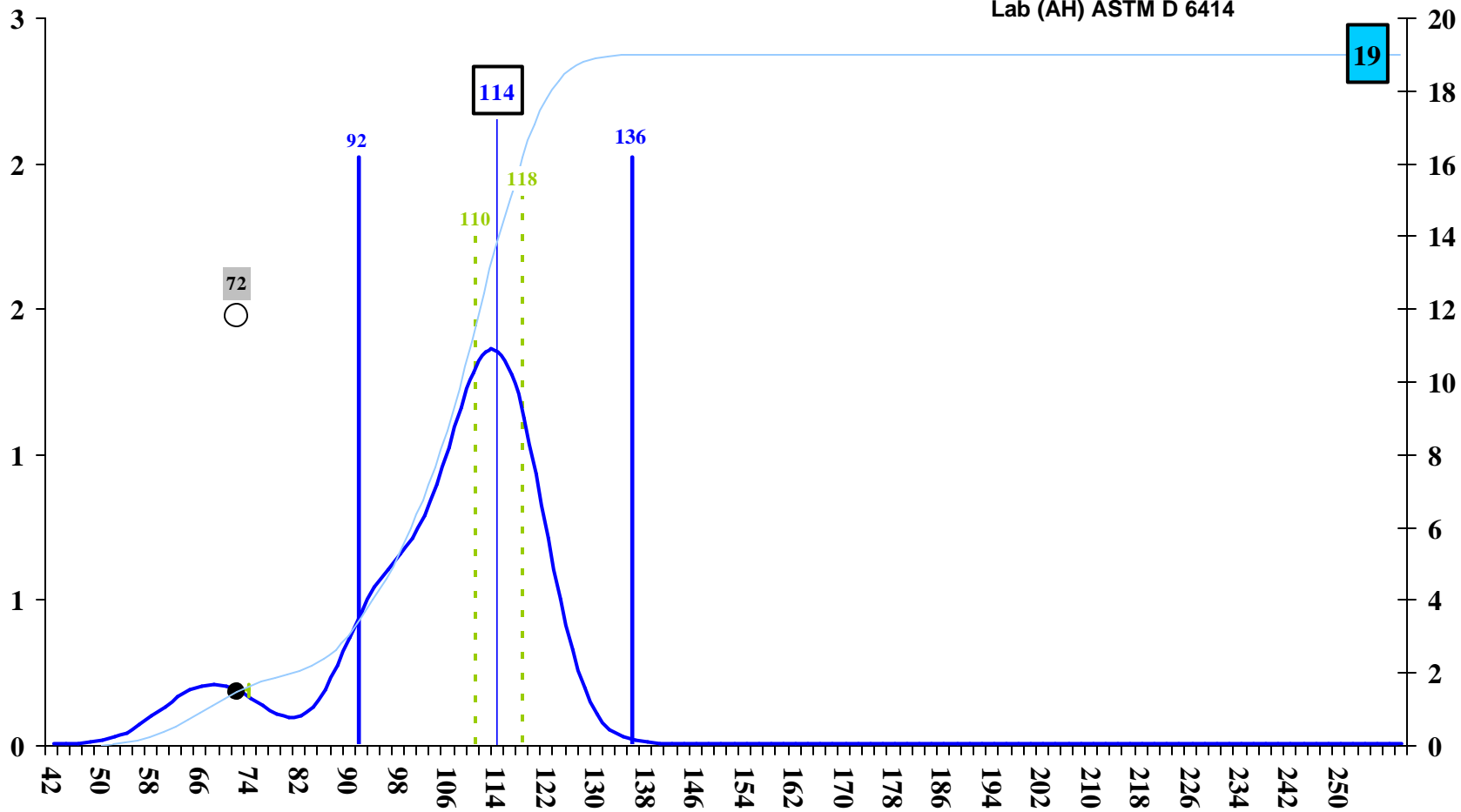
Lab (AC) EPA 245.5



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

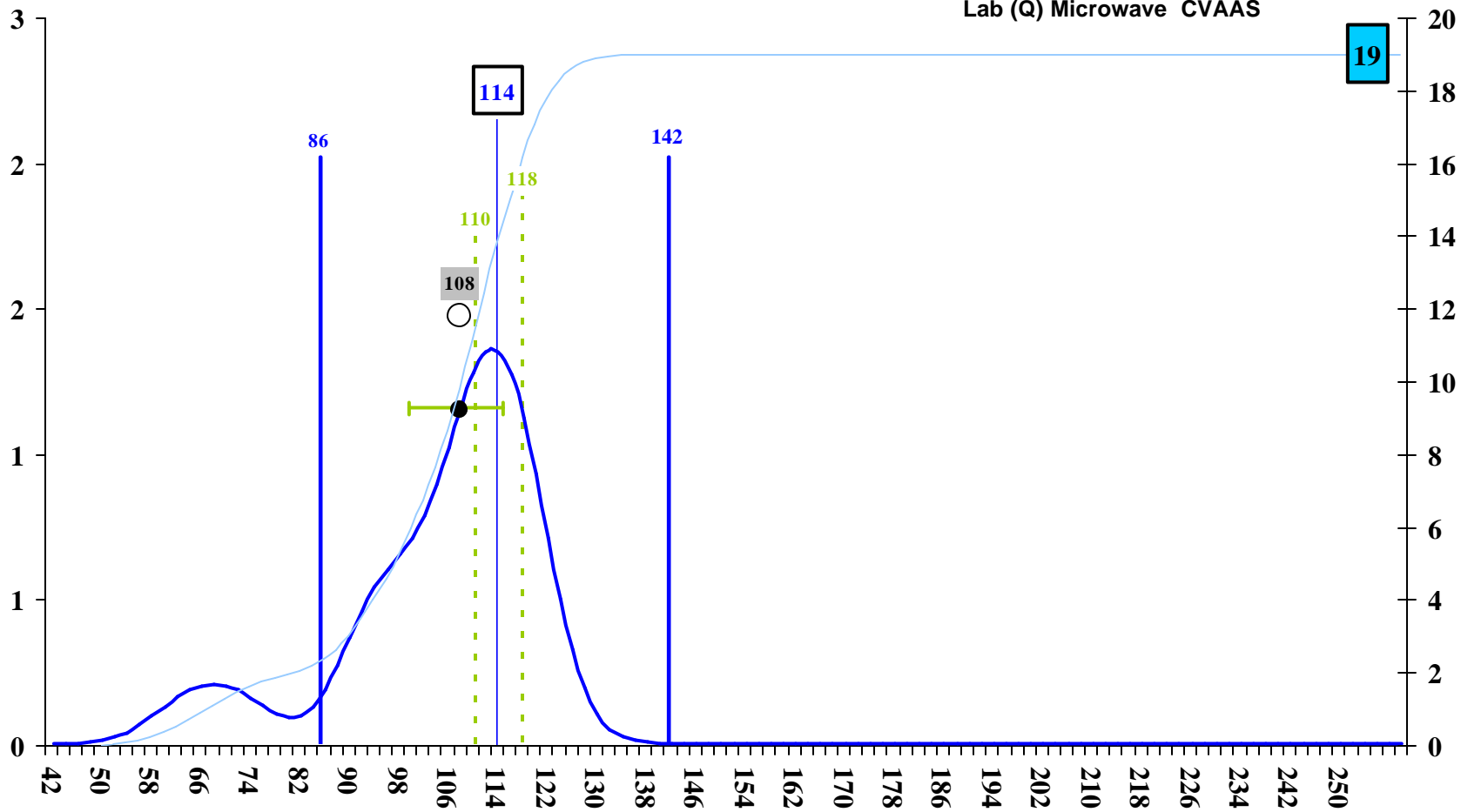
Lab (AH) ASTM D 6414



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

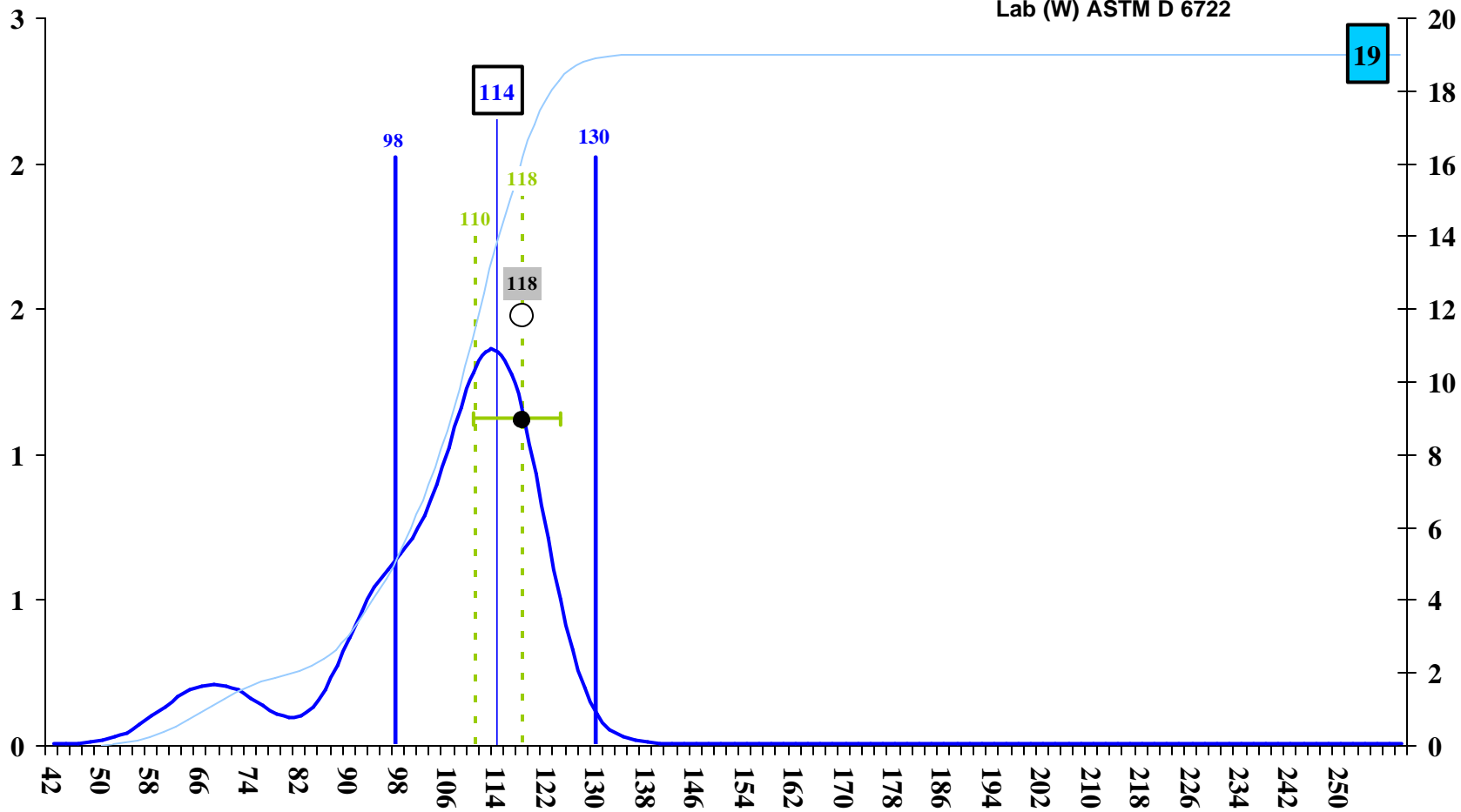
Lab (Q) Microwave CVAAS



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

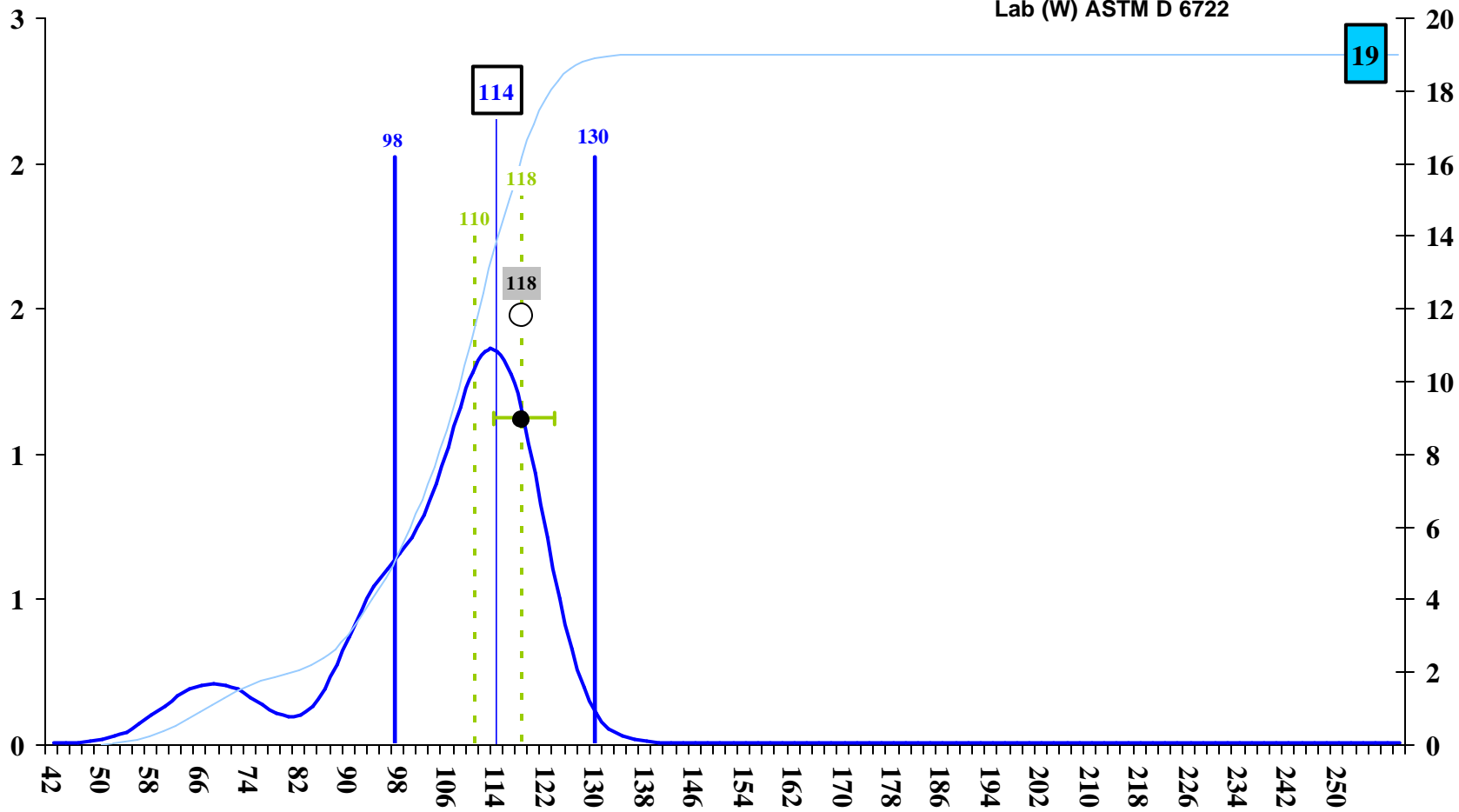
Lab (W) ASTM D 6722



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

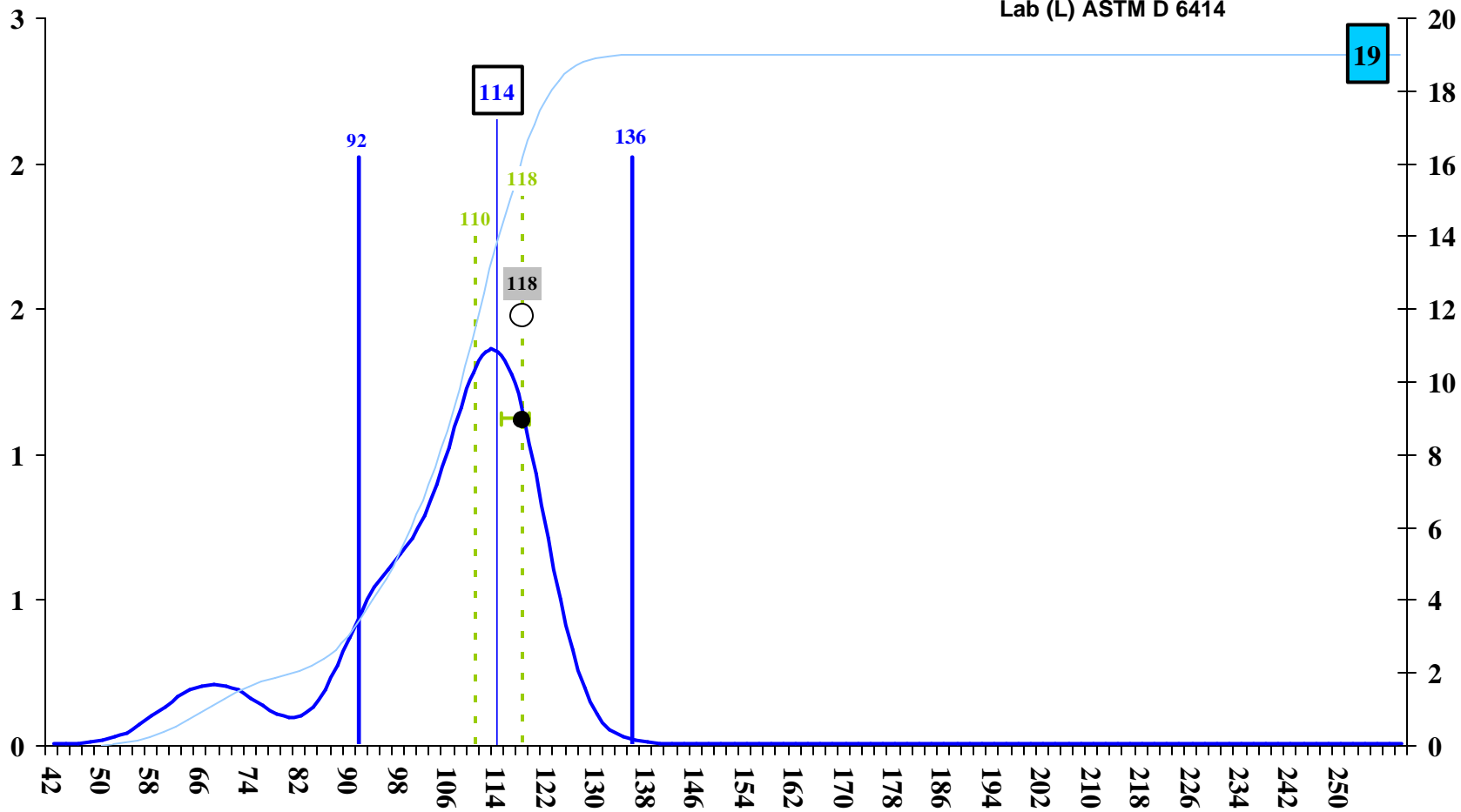
Lab (W) ASTM D 6722



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

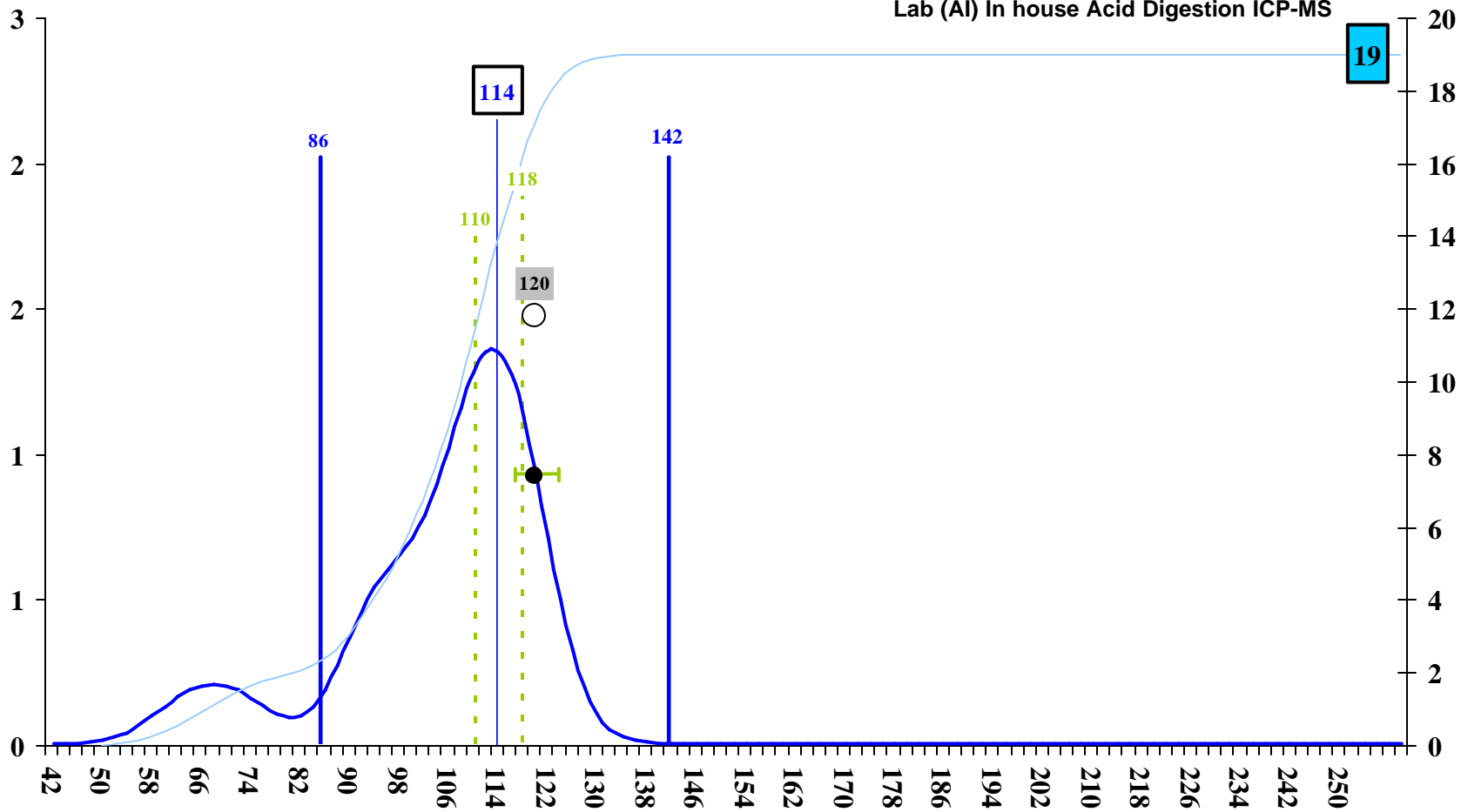
Lab (L) ASTM D 6414



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

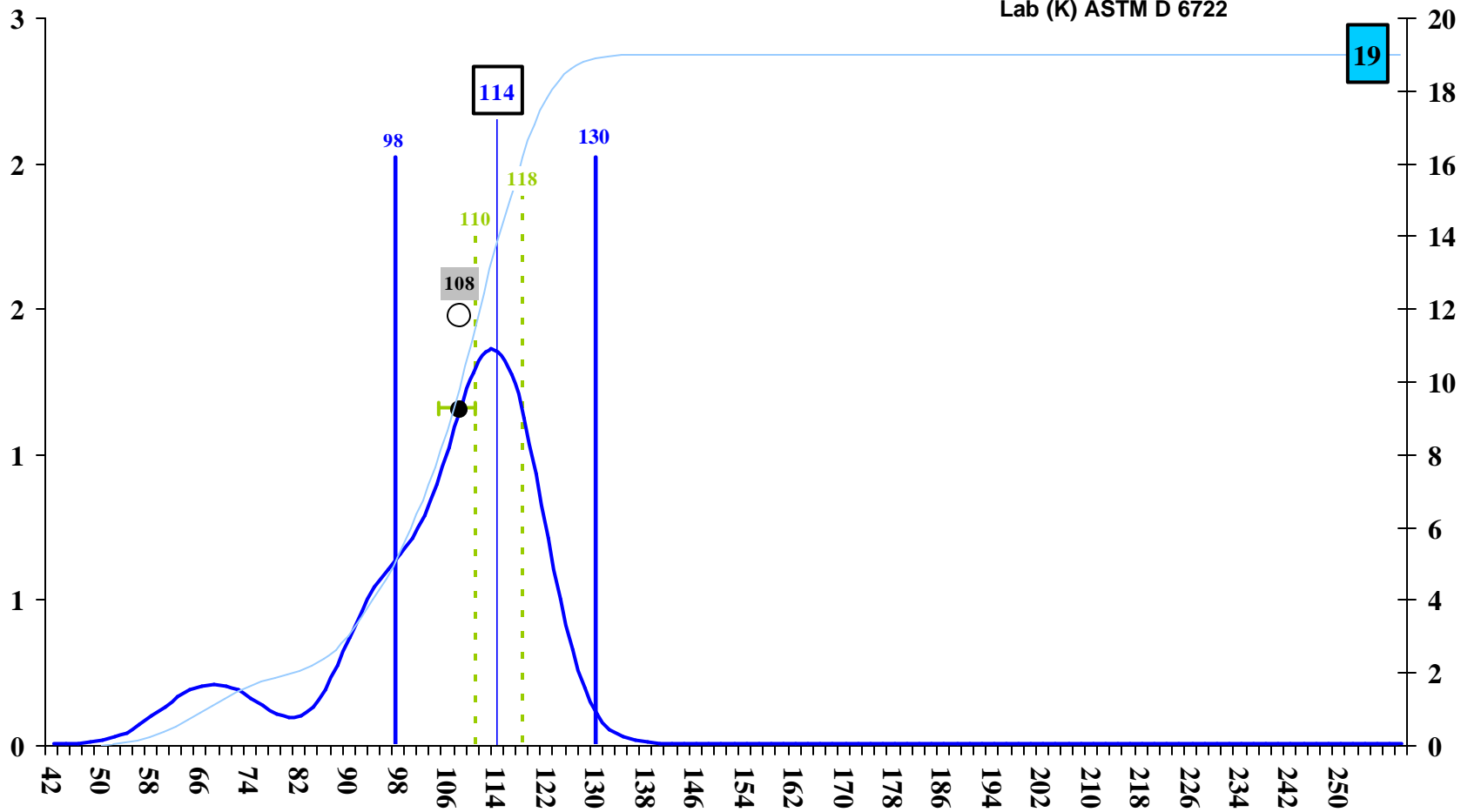
Lab (A1) In house Acid Digestion ICP-MS



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

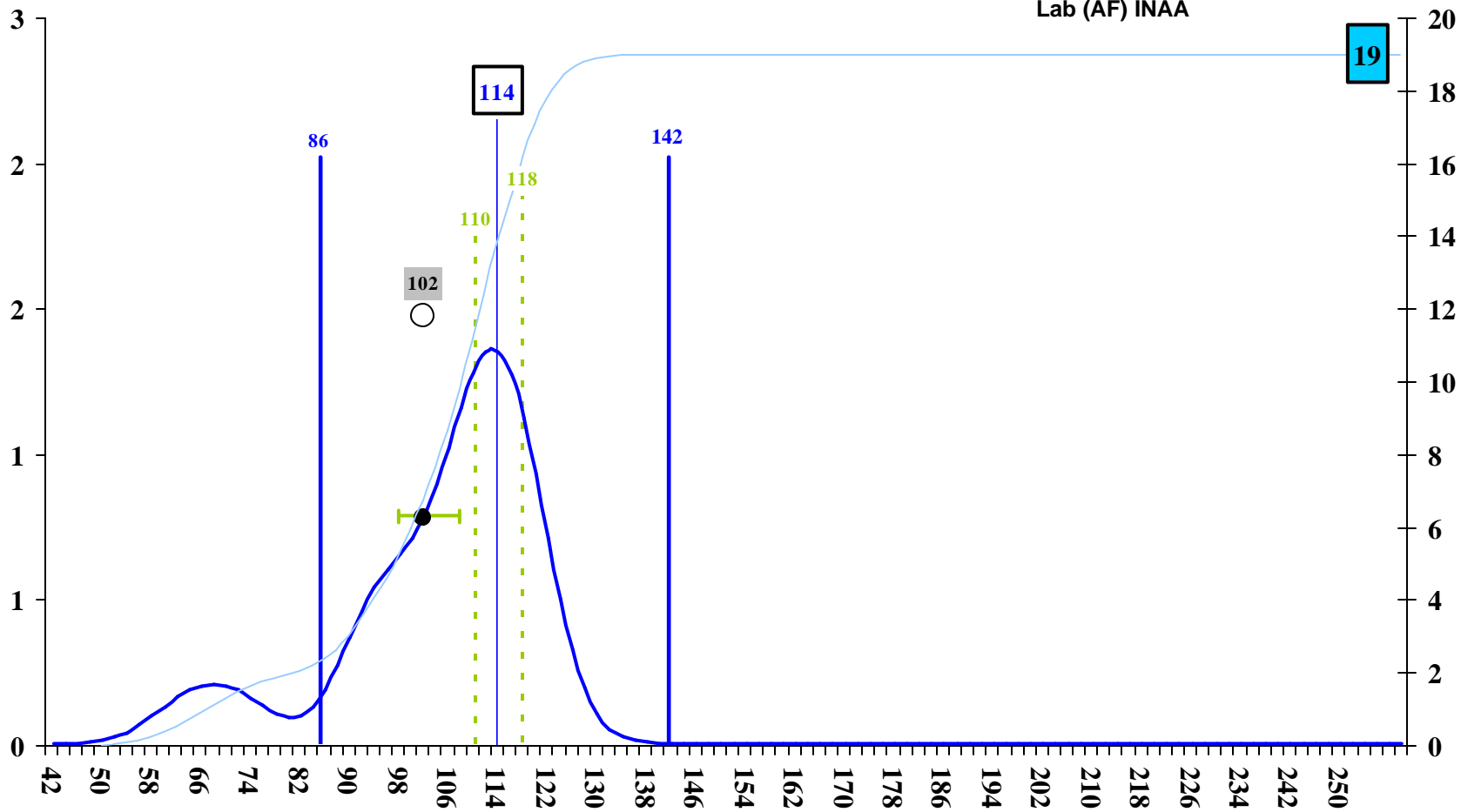
Lab (K) ASTM D 6722



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

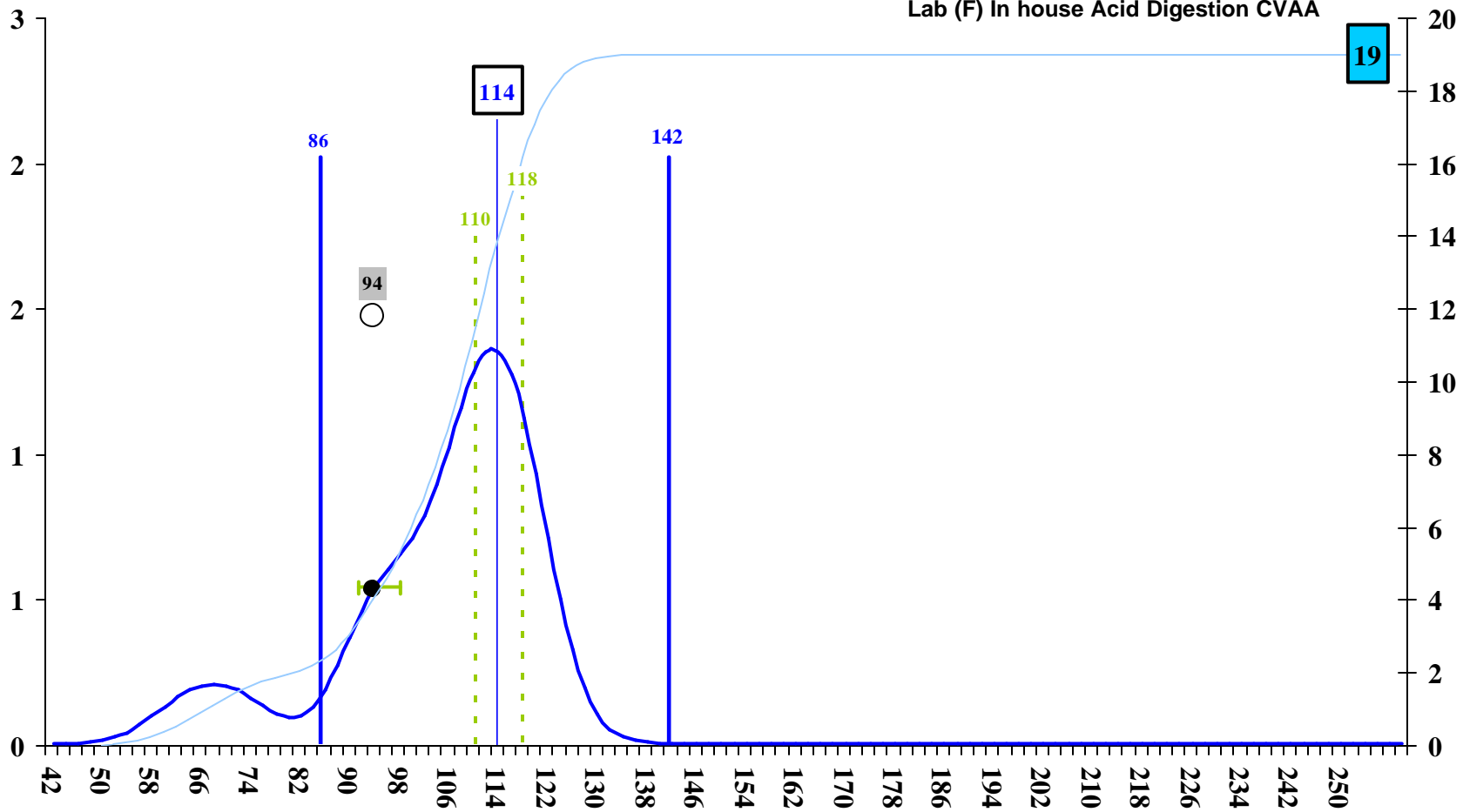
Lab (AF) INAA



Reference Value 114 ± 4

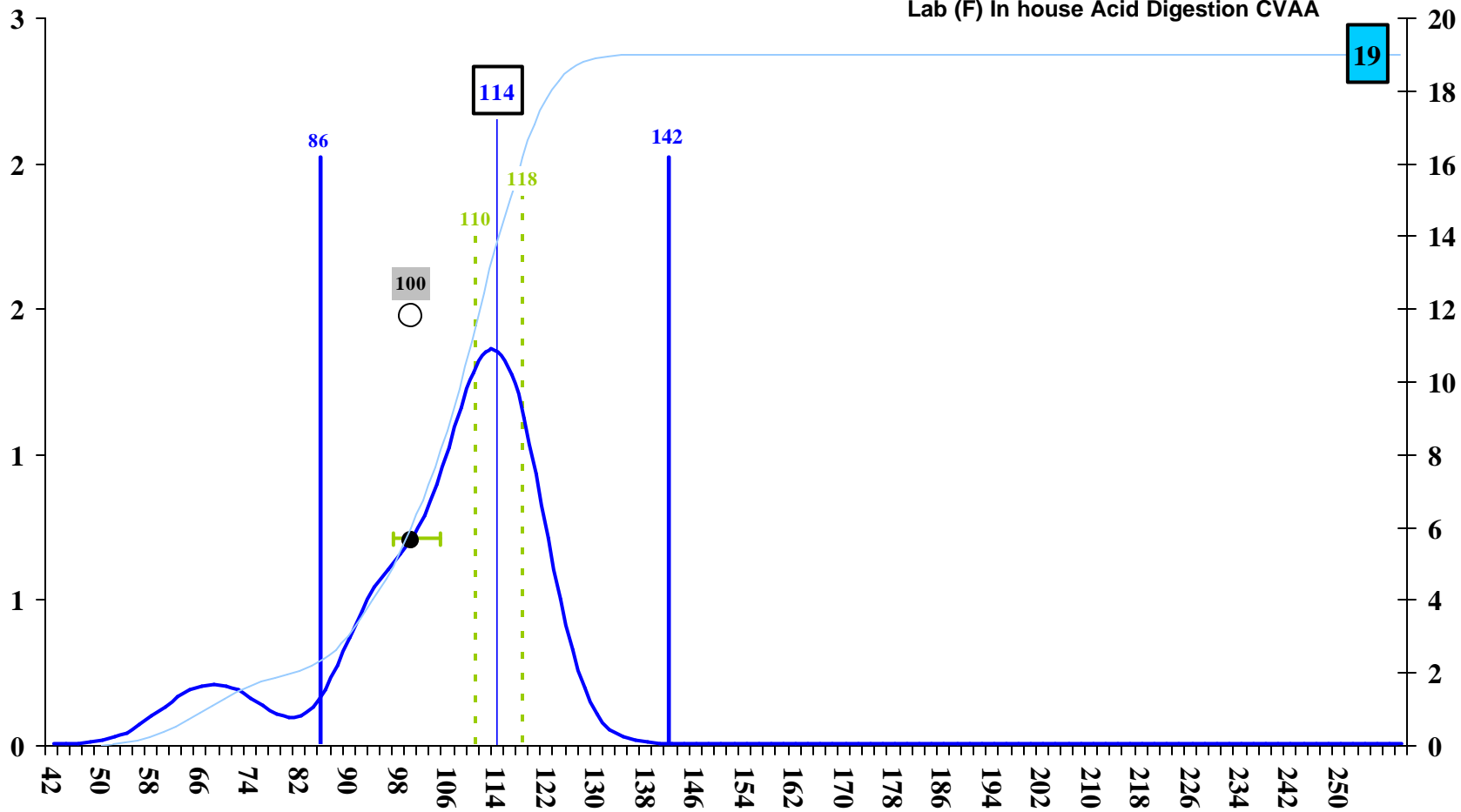
CCME-C Mercury ng/g dry basis

Lab (F) In house Acid Digestion CVAA



CCME-C Mercury ng/g dry basis

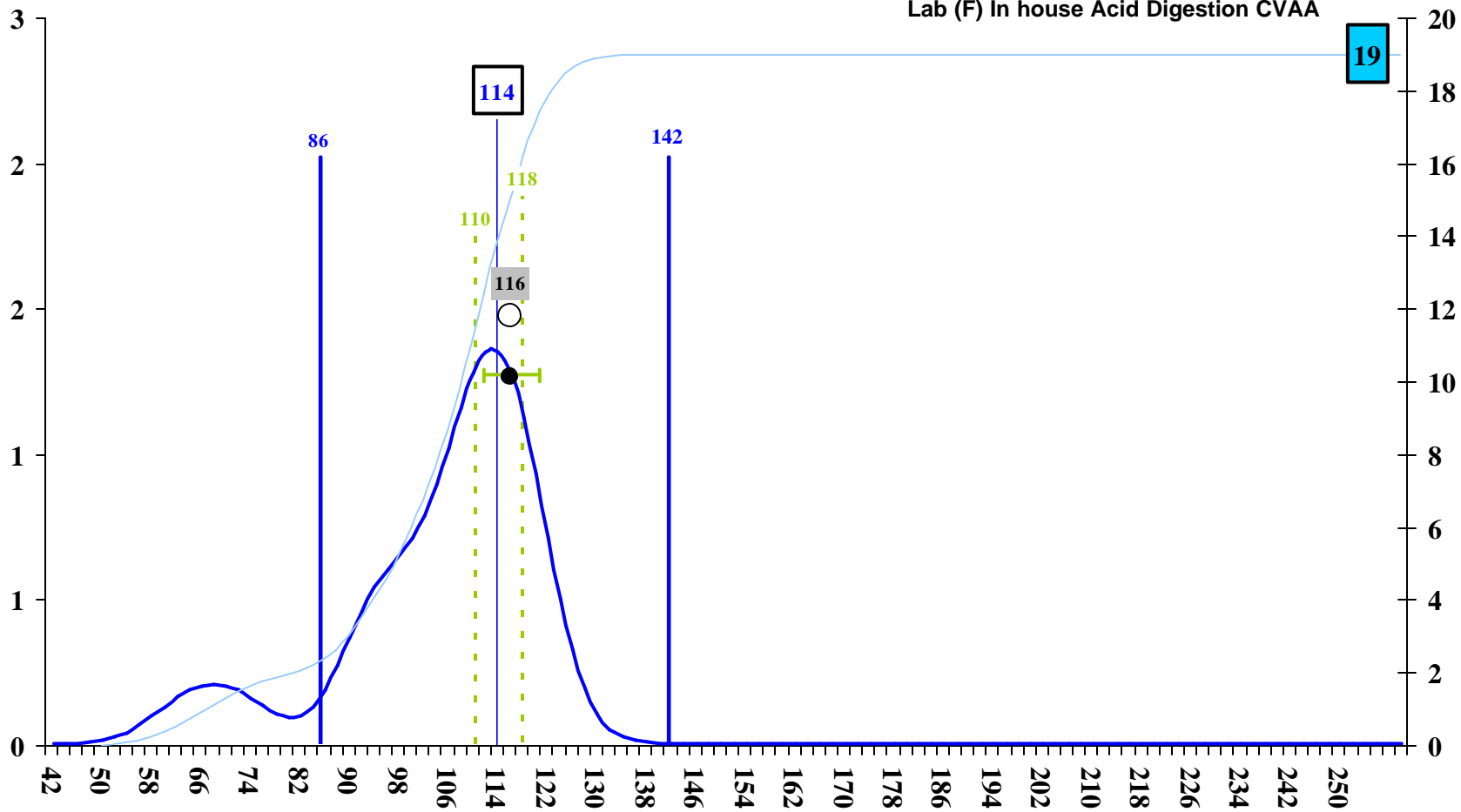
Lab (F) In house Acid Digestion CVAA



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

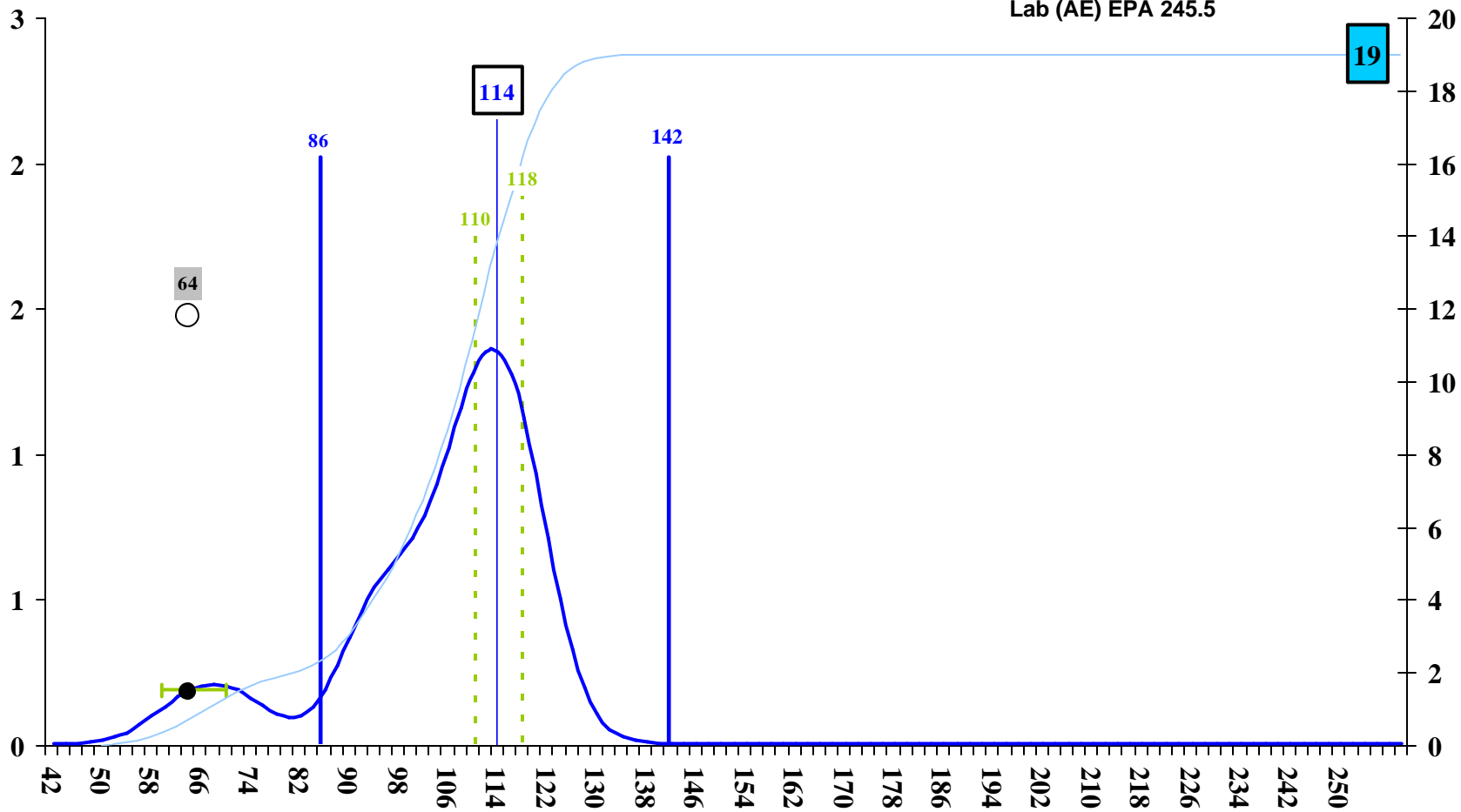
Lab (F) In house Acid Digestion CVAA



Reference Value 114 ± 4

CCME-C Mercury ng/g dry basis

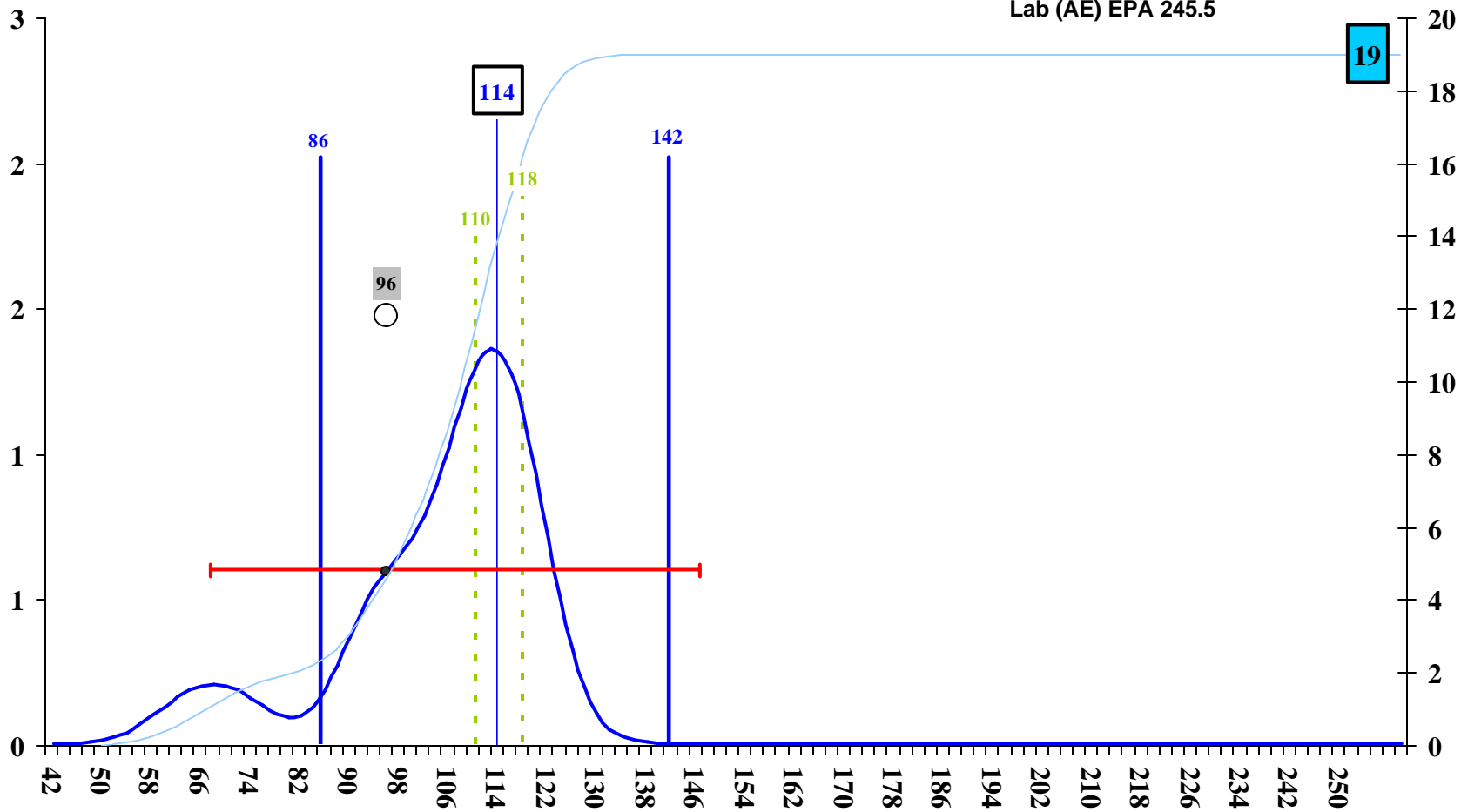
Lab (AE) EPA 245.5



Reference Value 114 ± 4

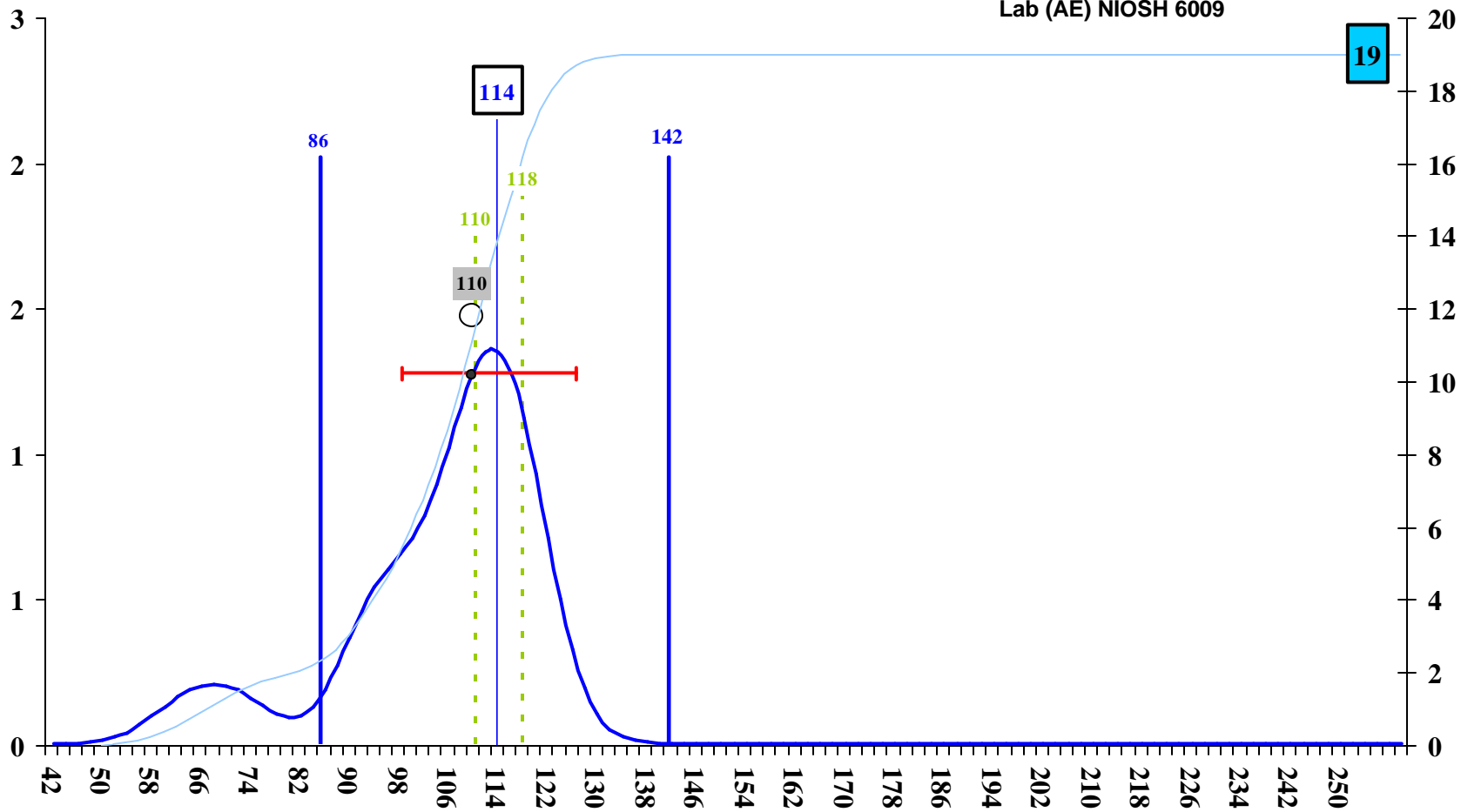
CCME-C Mercury ng/g dry basis

Lab (AE) EPA 245.5



CCME-C Mercury ng/g dry basis

Lab (AE) NIOSH 6009



Reference Value 114 ± 4

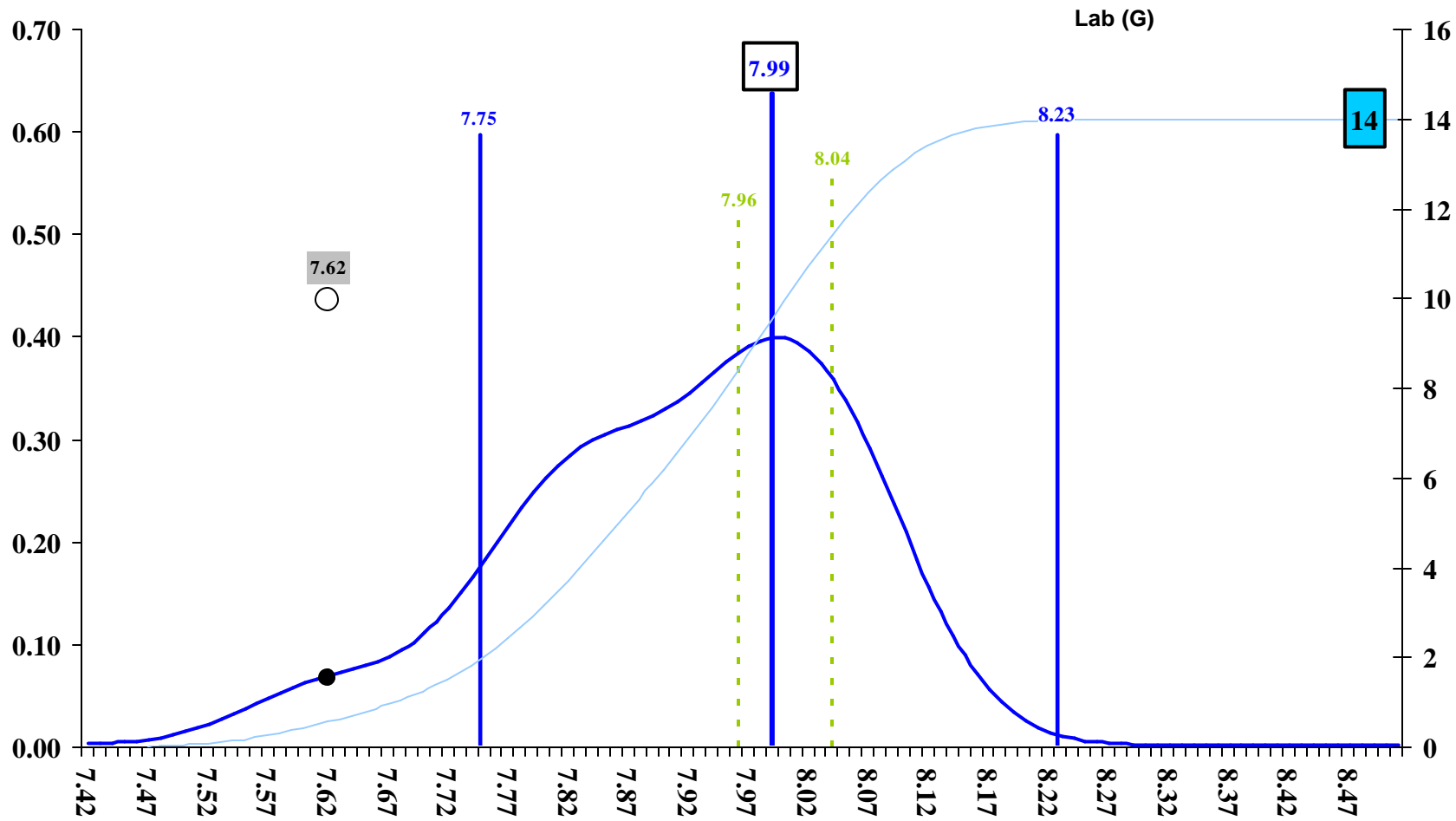
CCME-C

Mercury ng/g dry basis

Number of Laboratories	19
ILS Value	114
ILS Confidence Interval	6

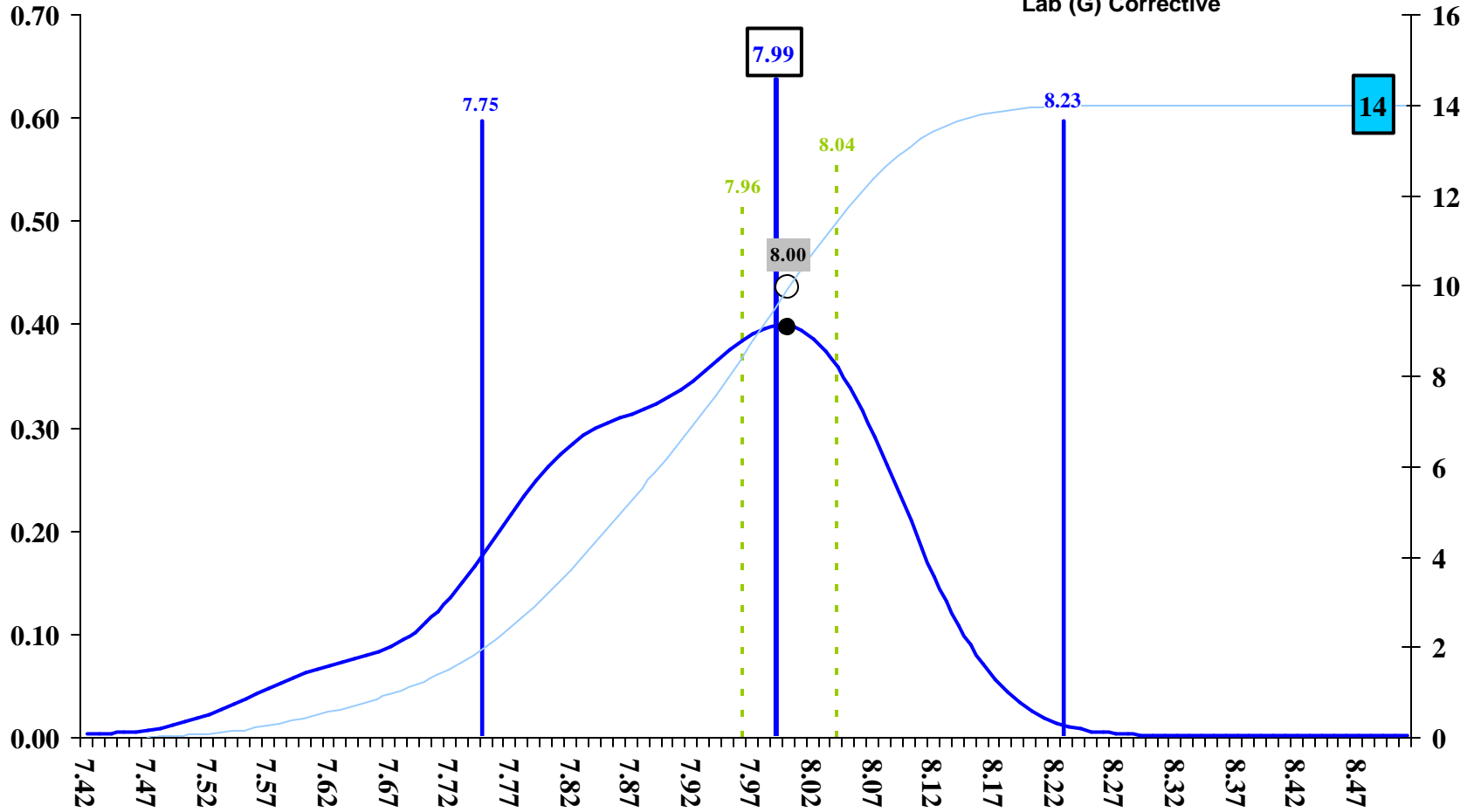
CANSPEX™ CCME-C CODE	Test Result 1	Test Result 2	Test Result 3	Test Result 4	METHOD	COMMENTS
AE	62	63	60	70	EPA 245.5	
AH	71	71	74	73	ASTM D 6414	
F	94	97	90	91	In house Acid Digestion CVAA	
AC	99	97	95	82	EPA 245.5	
AE	95	74	145	66	EPA 245.5	
F	98	100	106	100	In house Acid Digestion CVAA	
AF	104	98	101	108	INAA	
K	110	110	108	104	ASTM D 6722	
Q	110	101	109	116	Microwave CVAAS	
AE	97	104	126	111	NIOSH 6009	
B	105	108	116	116	ASTM D 6722	
G	116	111	115	107	ASTM D 6722	
U	113	115	111	113	ASTM D 6722	
D	114	112	113	115	ASTM D 6722	
F	110	120	114	117	In house Acid Digestion CVAA	
W	117	123	109	120	ASTM D 6722	
L	120	119	115	120	ASTM D 6414	
W	119	124	114	117	ASTM D 6722	
AI	121	116	123	119	In house Acid Digestion ICP-MS	

CCME-C Ash wt % dry basis (ASTM D 5142)



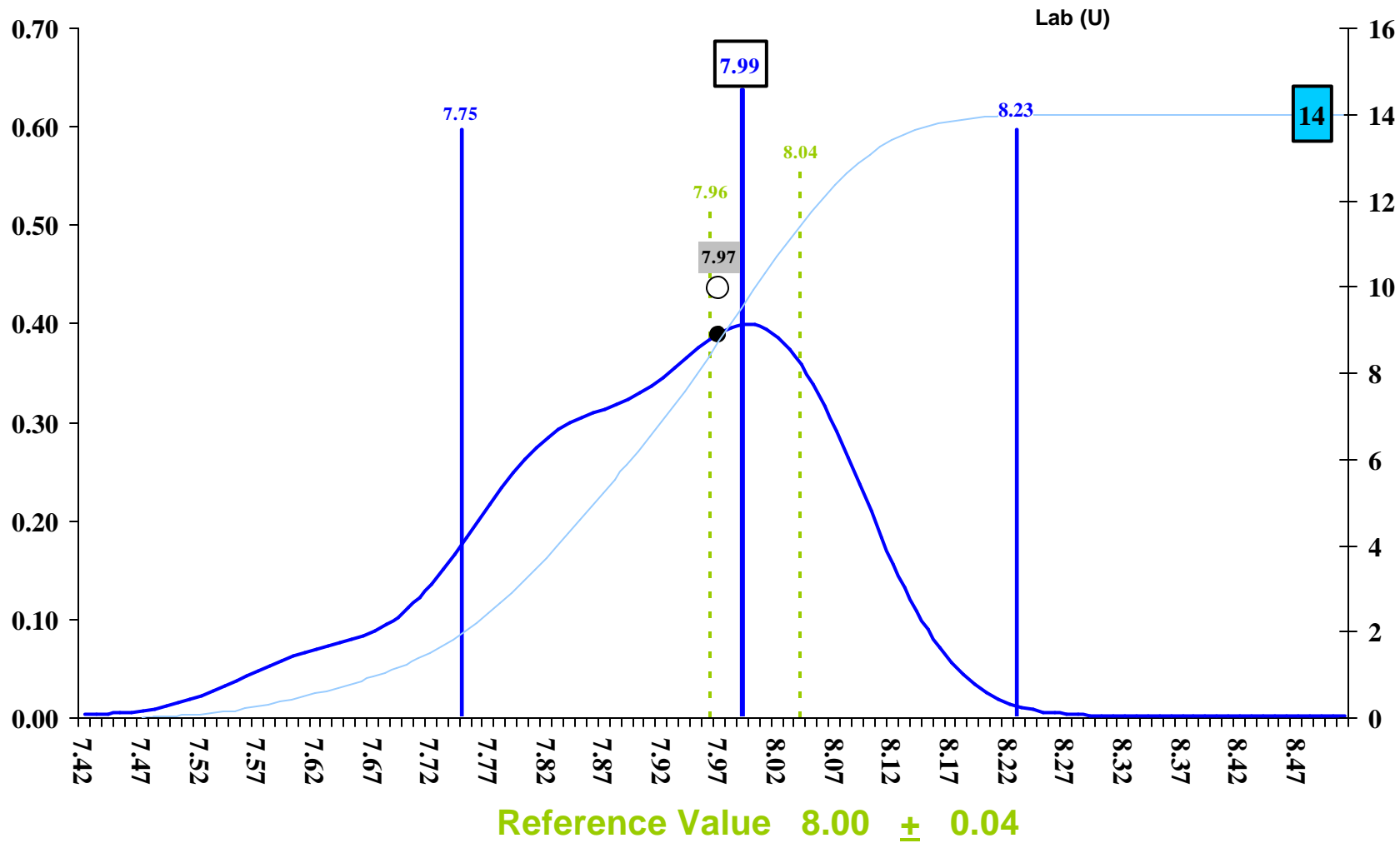
CCME-C Ash wt % dry basis (ASTM D 5142)

Lab (G) Corrective



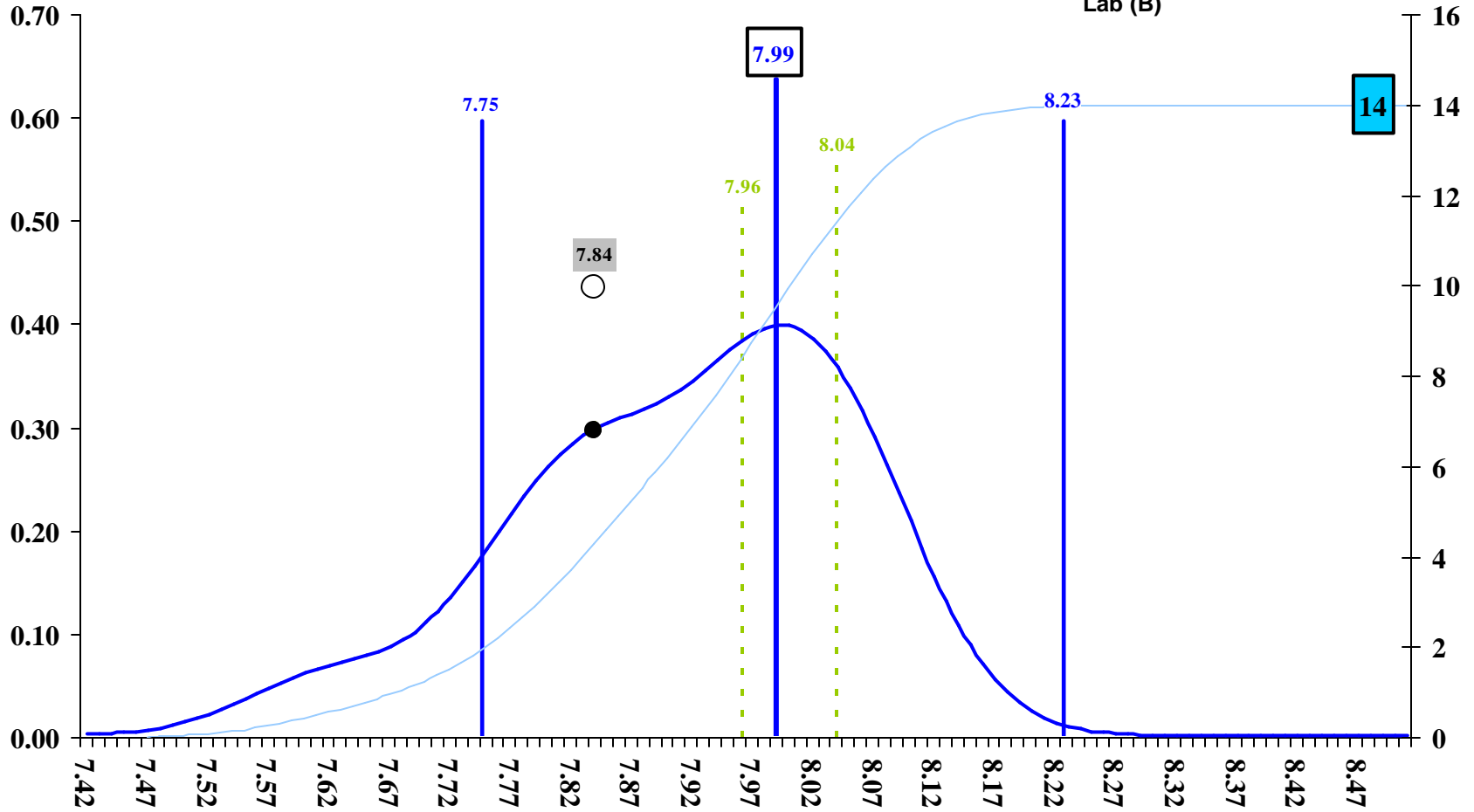
Reference Value 8.00 ± 0.04

CCME-C Ash wt % dry basis (ASTM D 5142)



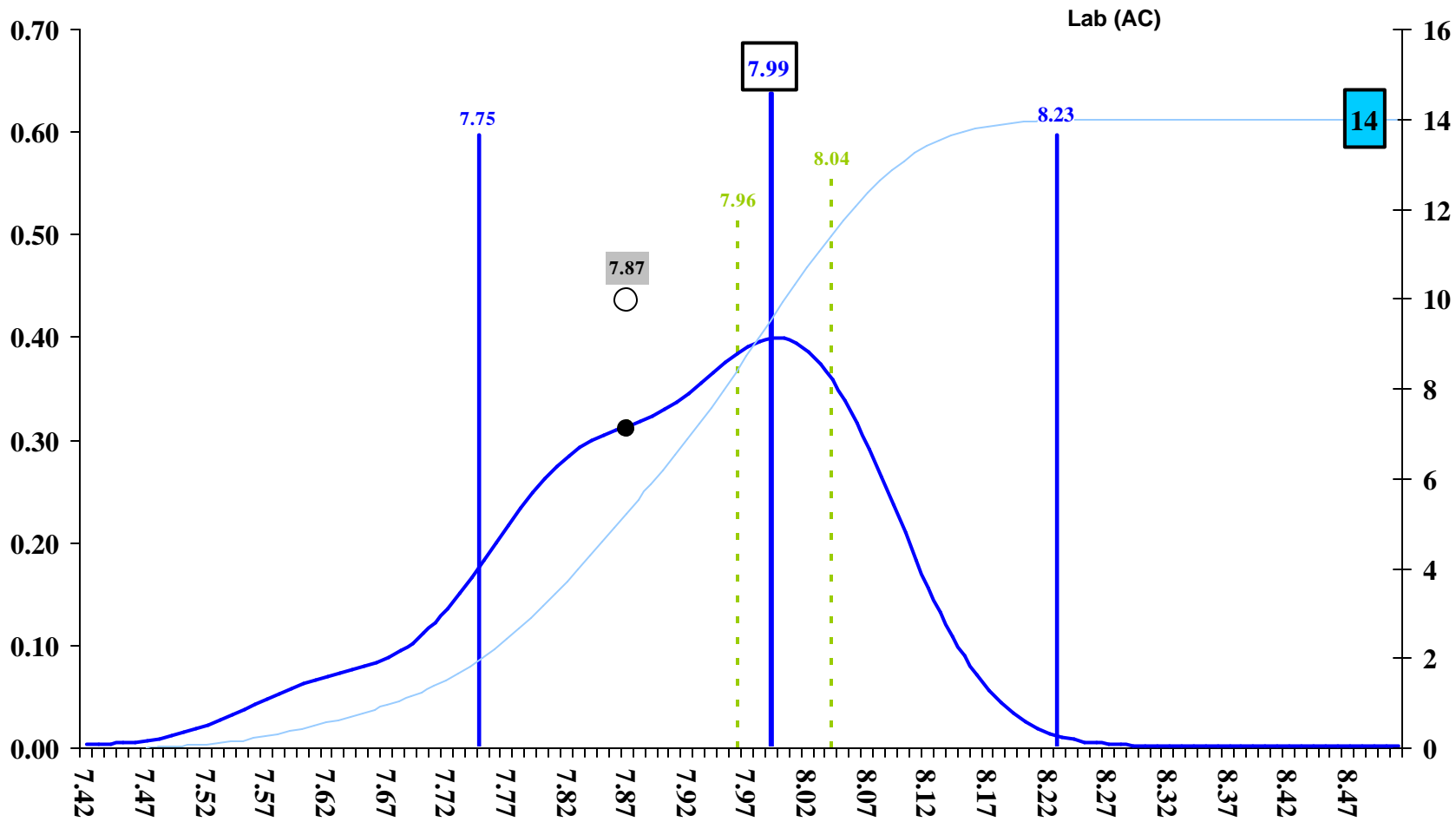
CCME-C Ash wt % dry basis (ASTM D 5142)

Lab (B)



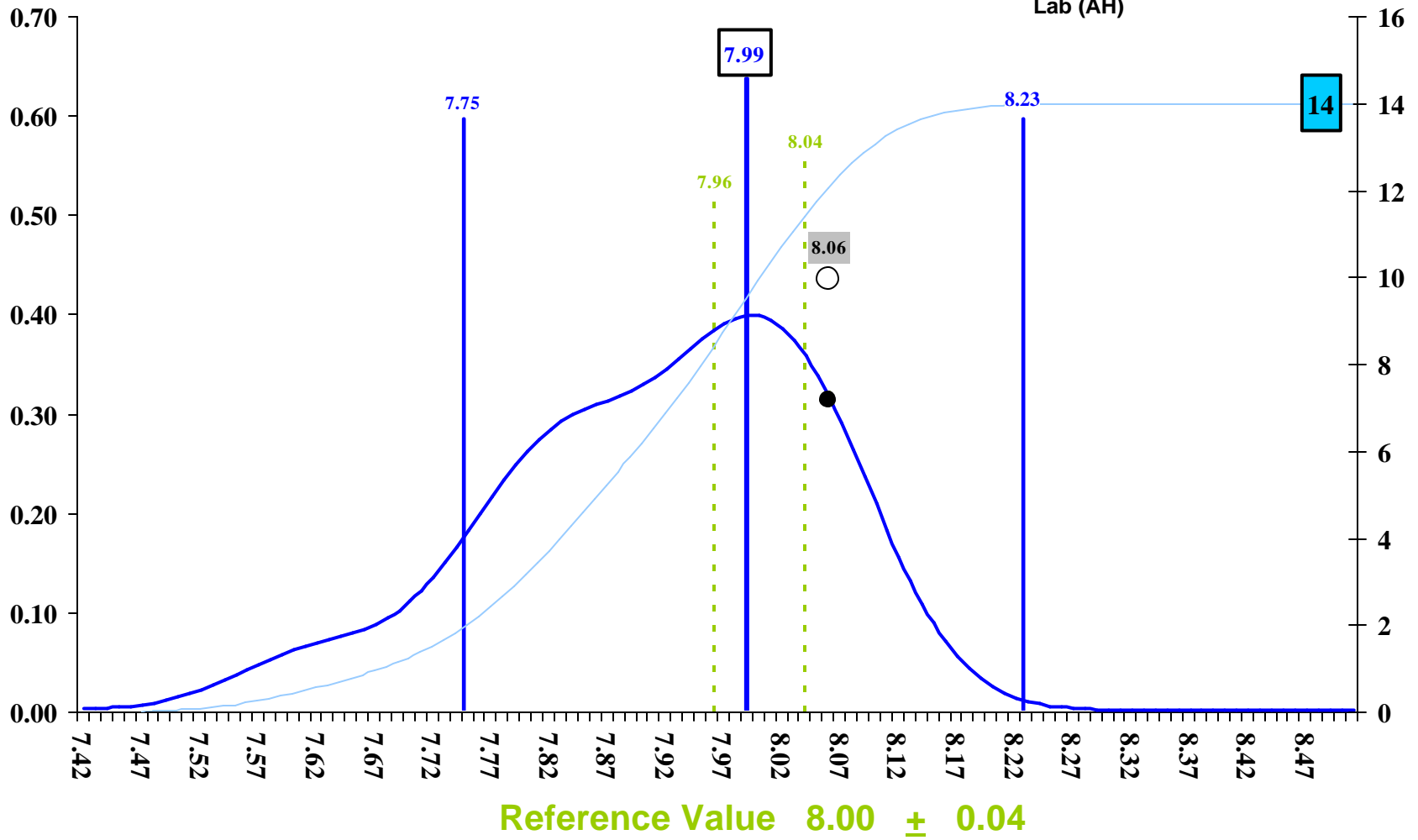
Reference Value 8.00 ± 0.04

CCME-C Ash wt % dry basis (ASTM D 5142)

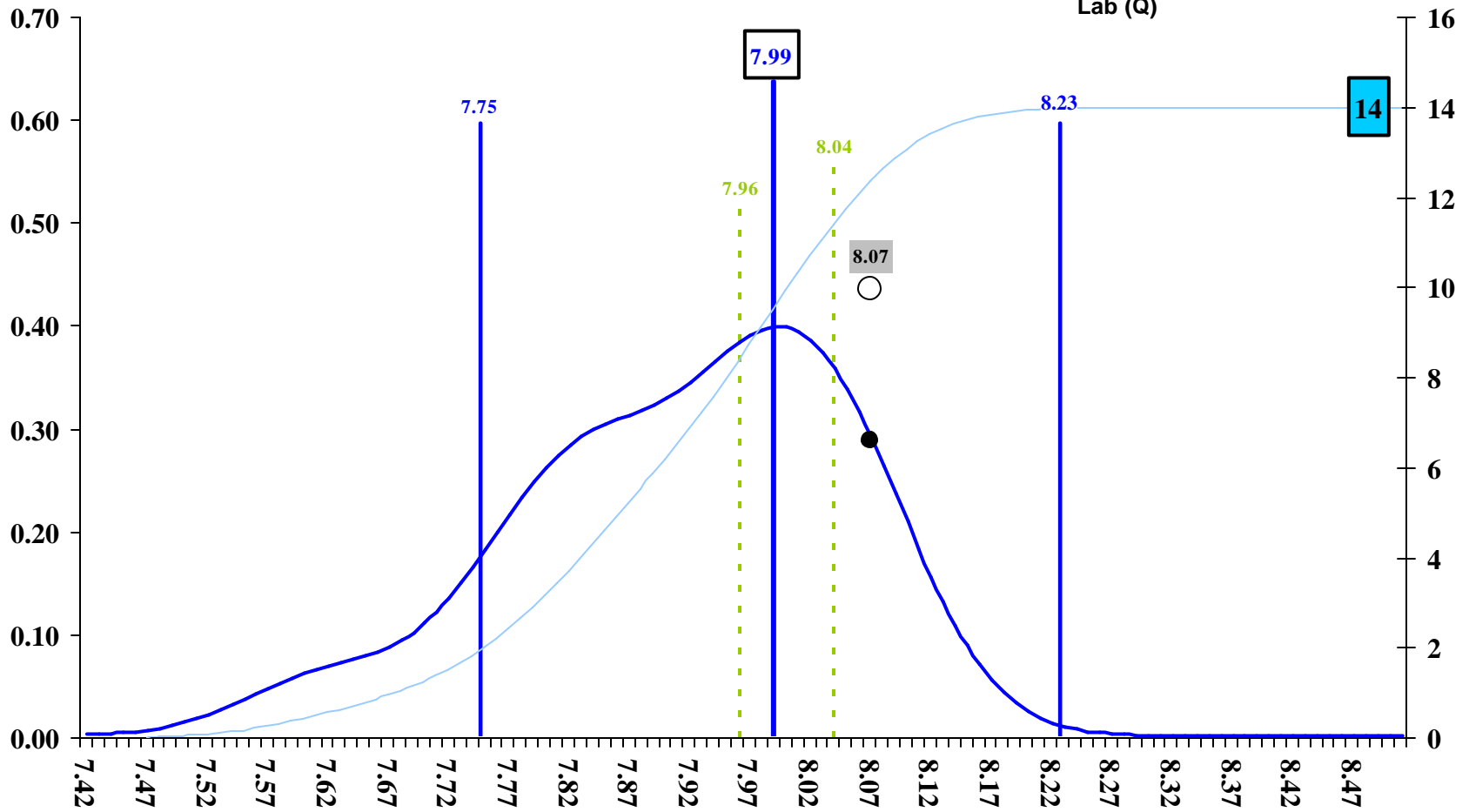


Reference Value 8.00 ± 0.04

CCME-C Ash wt % dry basis (ASTM D 5142)

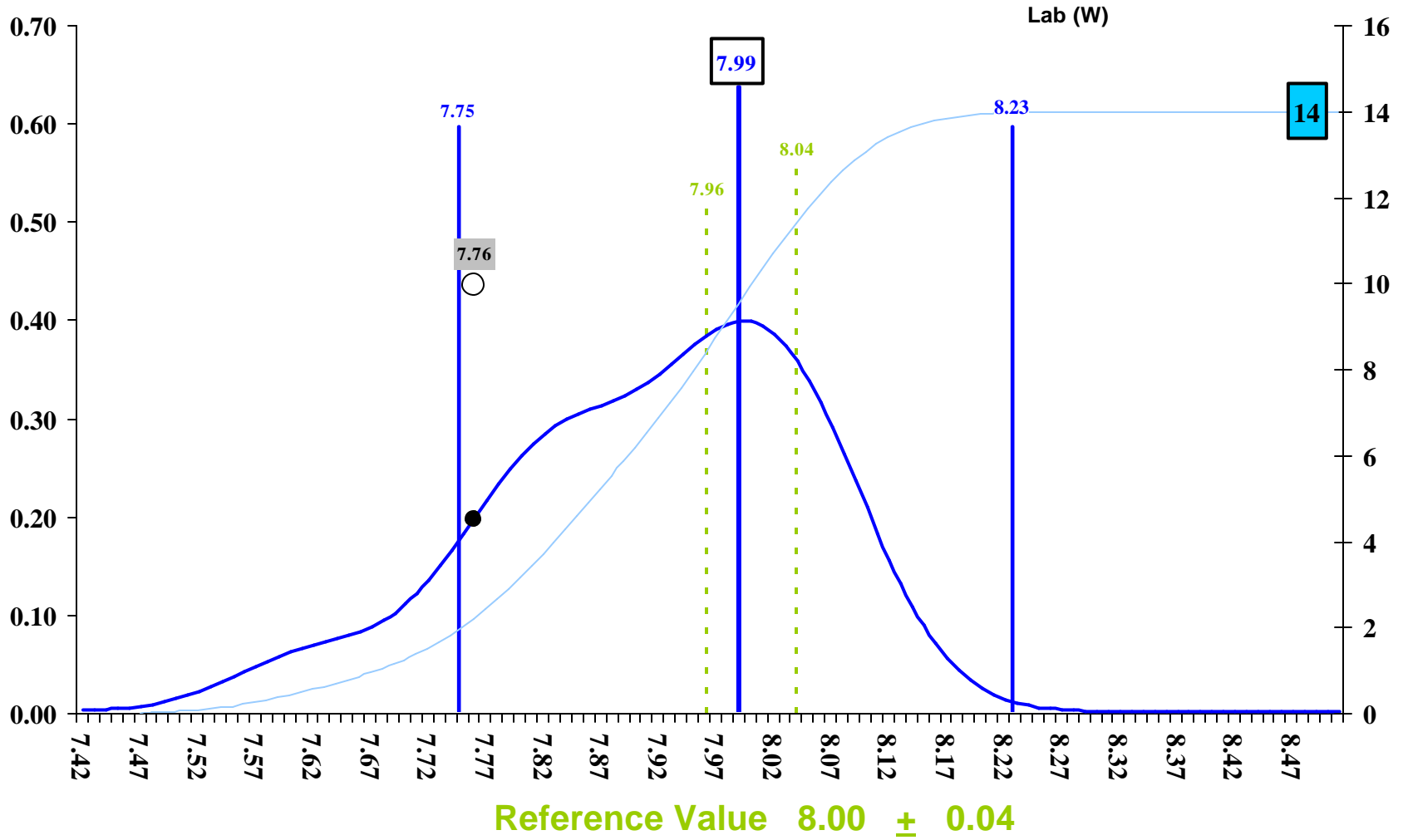


CCME-C Ash wt % dry basis (ASTM D 5142)

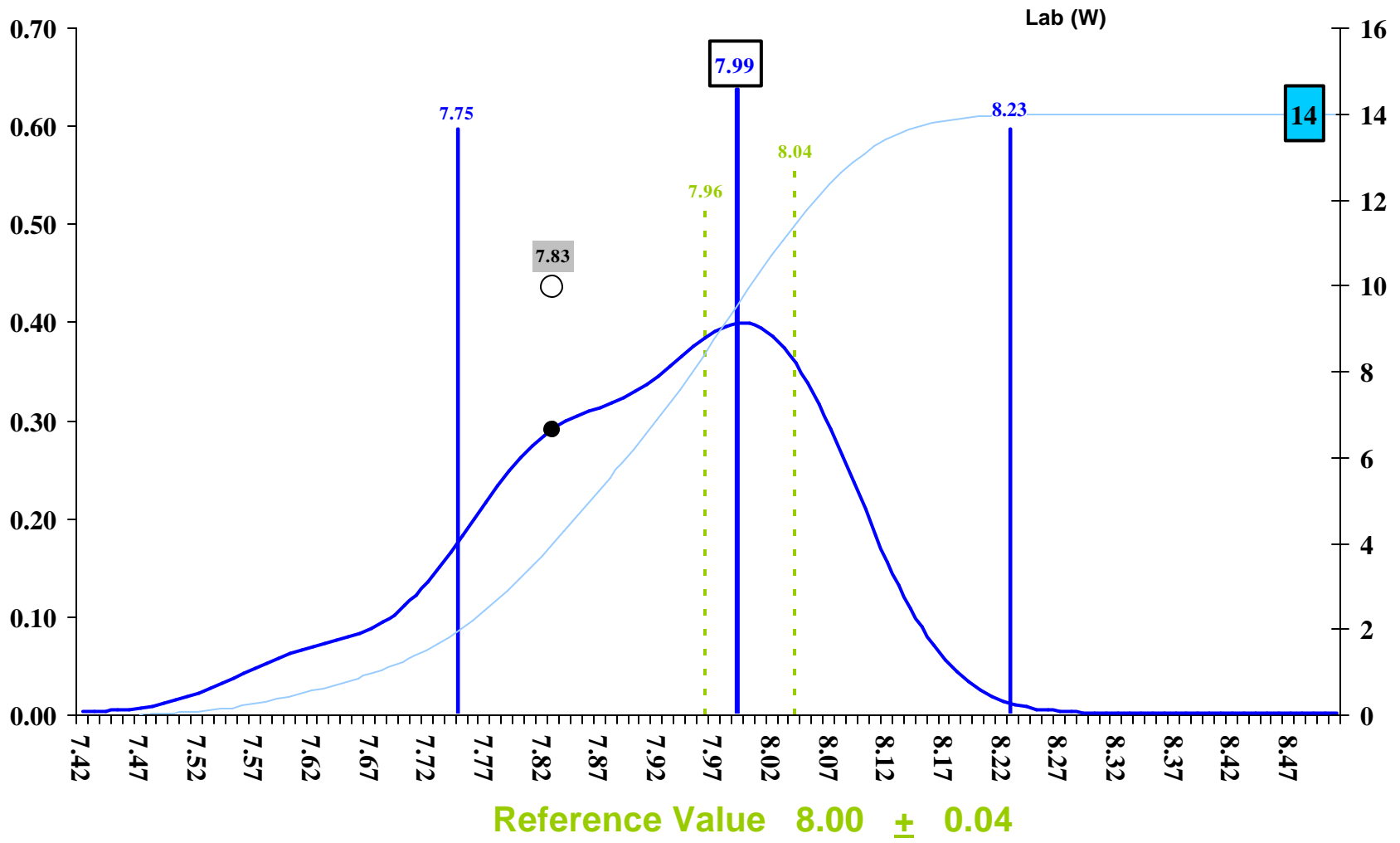


Reference Value 8.00 ± 0.04

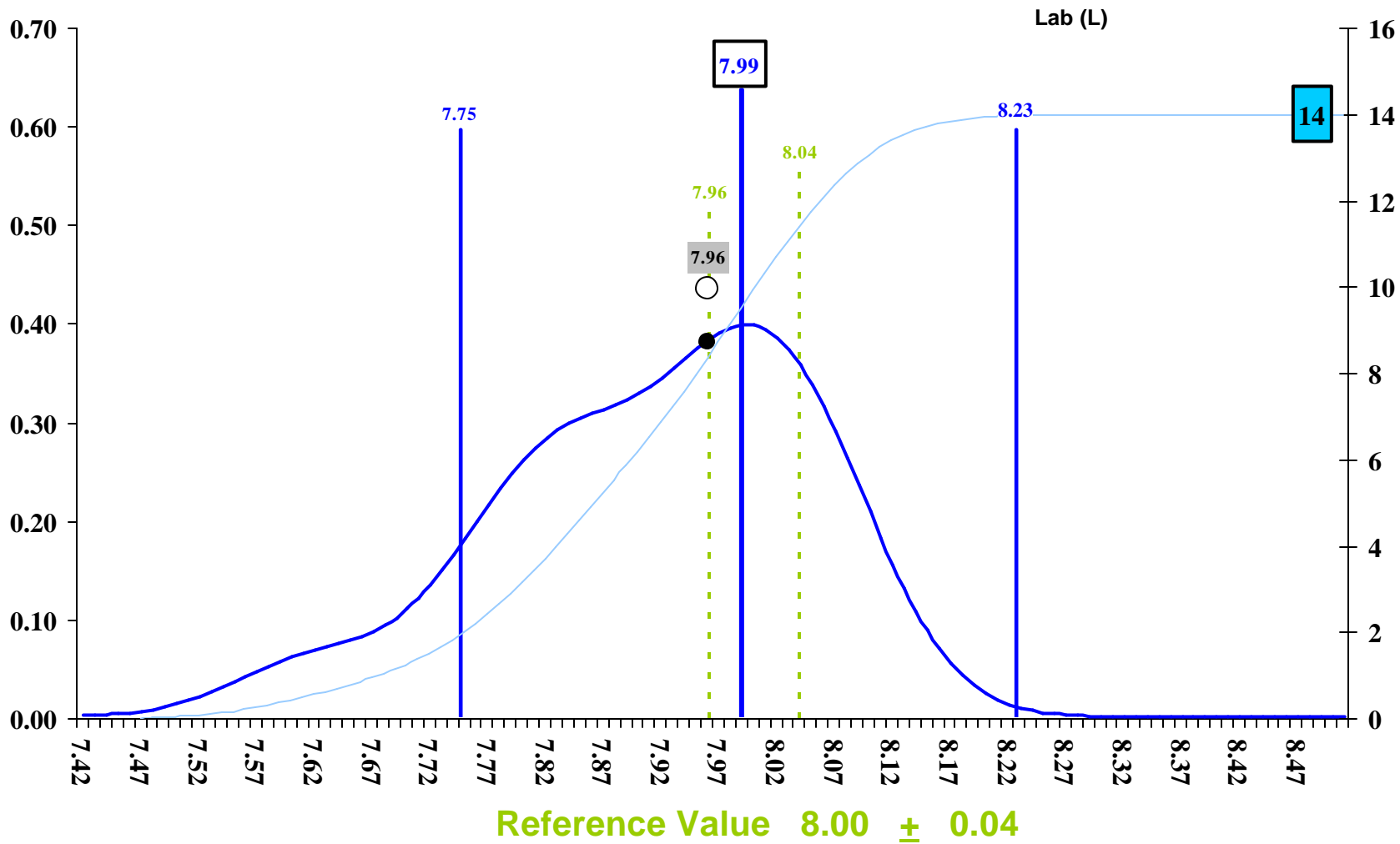
CCME-C Ash wt % dry basis (ASTM D 5142)



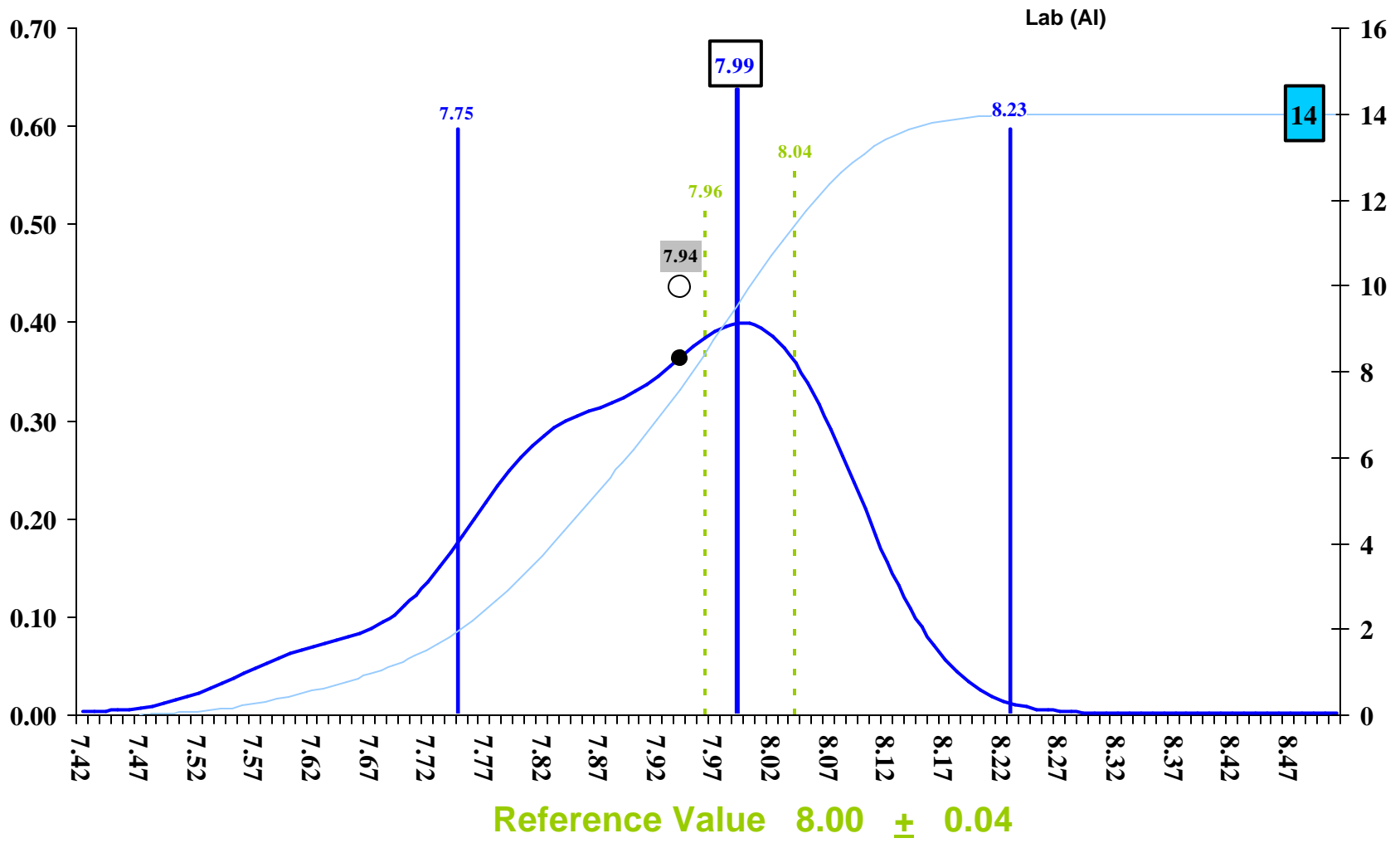
CCME-C Ash wt % dry basis (ASTM D 5142)



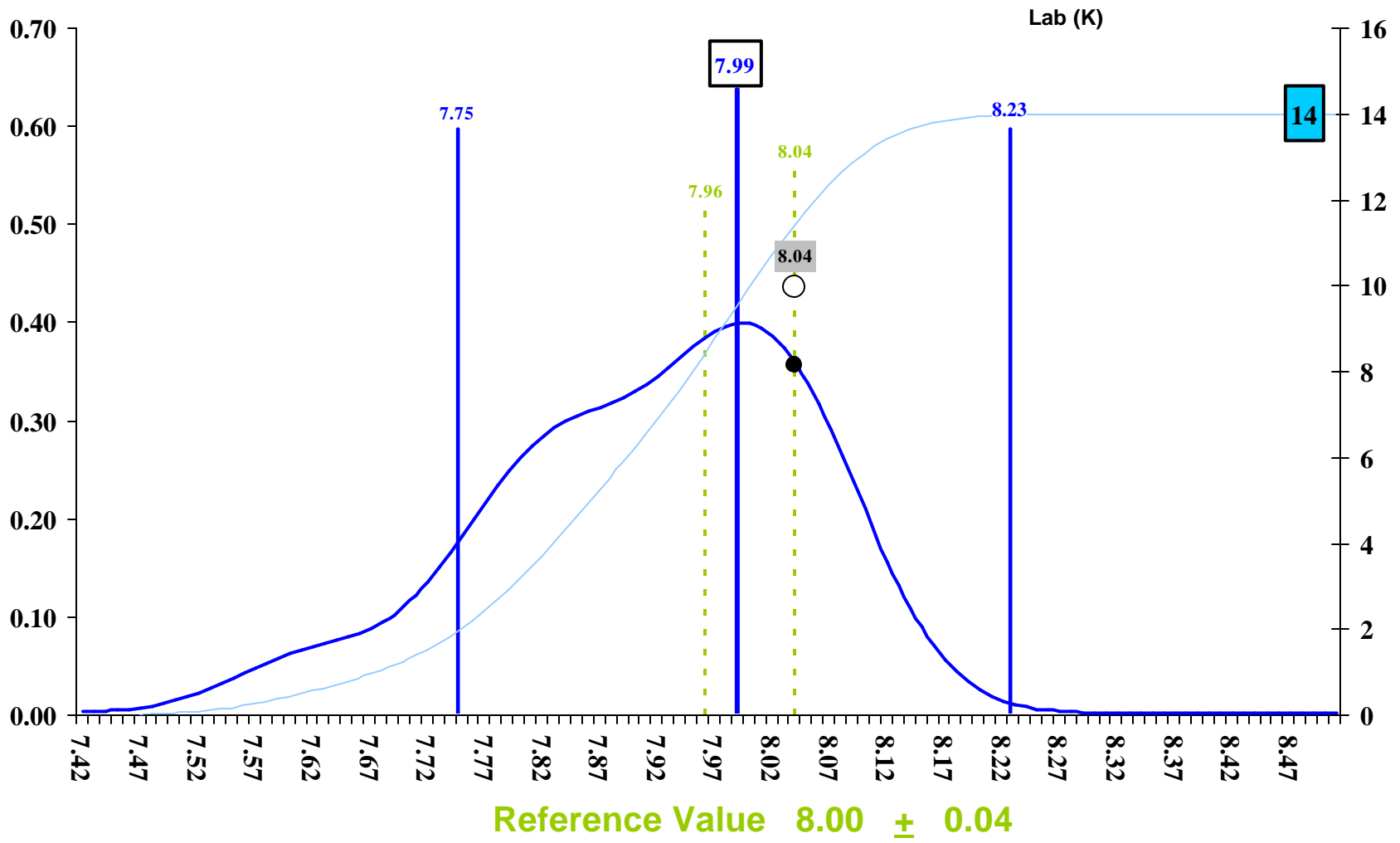
CCME-C Ash wt % dry basis (ASTM D 5142)



CCME-C Ash wt % dry basis (ASTM D 5142)

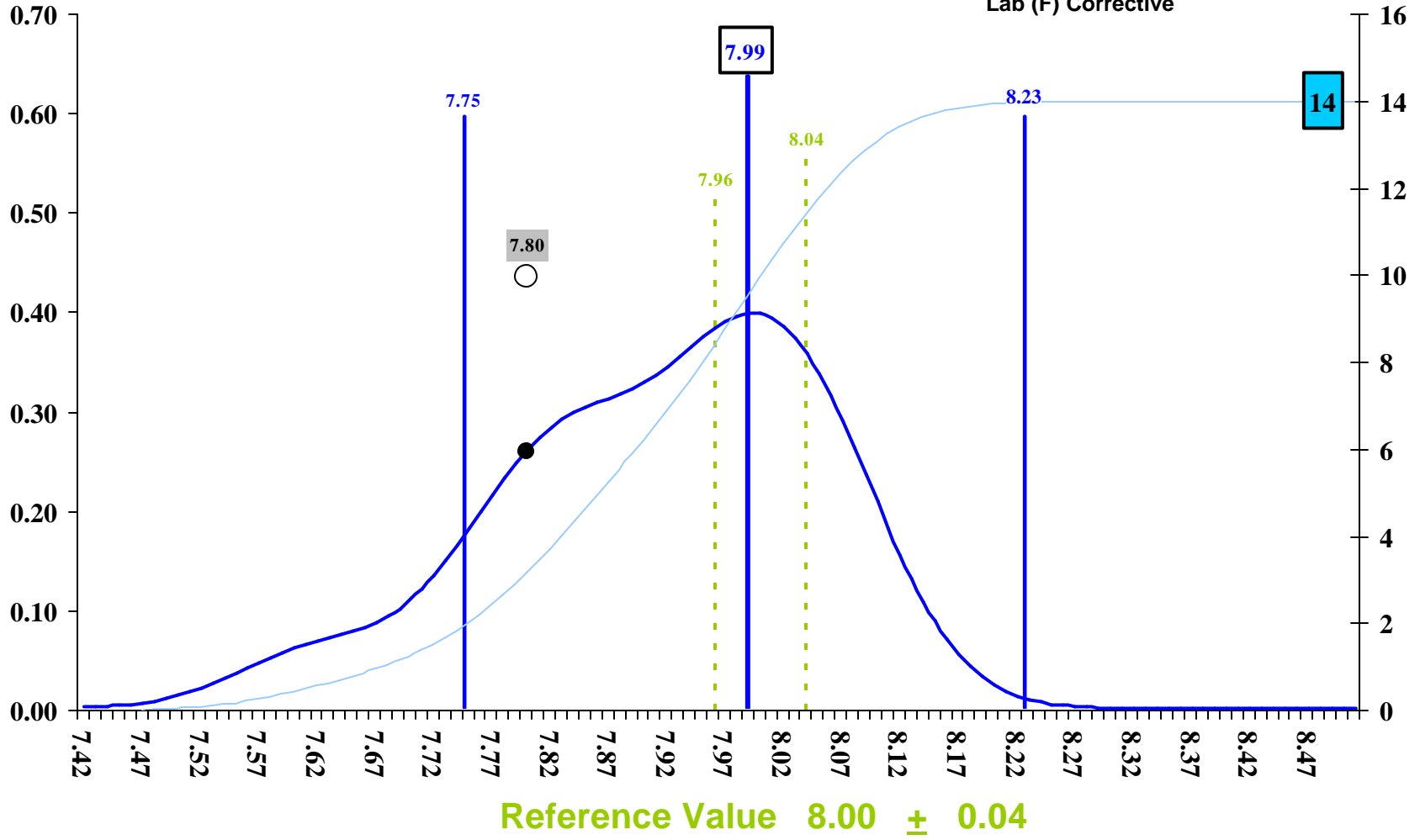


CCME-C Ash wt % dry basis (ASTM D 5142)



CCME-C Ash wt % dry basis (ASTM D 5142)

Lab (F) Corrective



CCME-C

Ash wt % dry basis

Number of Laboratories	14
ILS Value	7.99
ILS Confidence Interval	0.09

CANSPEX™ CCME-C CODE	Test Result 1	METHOD	COMMENTS
G	7.62		
W	7.76		
F	7.80	Corrective	
W	7.83		
B	7.84		
AC	7.87		
AI	7.94		
L	7.96		
U	7.97		
G	8.00	Corrective	
D	8.01		
K	8.04		
AH	8.06		
Q	8.07		
F (C-EXCLUDE)	55.12		(C-EXCLUDE)
F (C-EXCLUDE)	56.45		(C-EXCLUDE)
AE (C-EXCLUDE)	79.82		(C-EXCLUDE)