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HEALTH & SAFETY LABORATORY

Certification Report

Reference Material

HSL MSWF-1

Elements in Mild Steel Welding Fume

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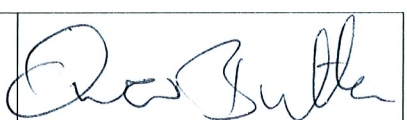
AS/2012/11
Health and Safety Laboratory

Report prepared by	Mr Owen Butler	Principal Scientist Analytical Sciences Unit HSL	
Report approved by	Dr Duncan Rimmer	Unit Head Analytical Sciences Unit HSL	
Report released by	Mr Peter Davies	Director Corporate Information and Services HSL	

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1 INTRODUCTION

Welders can be exposed to fume containing toxic metals and metalloids and occupational hygienists need to assess and ultimately minimise such exposure risks. The monitoring of the concentration of fume in workplace air is one assessment approach whereby fume, from representative welding activities, is sampled onto a filter and returned to a laboratory for analysis. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS) are employed as instrumental techniques of choice for the analysis of such filter samples. Methods have been codified at national level such as US NIOSH Method 7300 [1] and OSHA ID-125G [2] and more recently as international standards such as ISO 15202 (analysis involving ICP-AES) [3,4] and ISO 30011 (analysis involving ICP-MS) [5].

An inherent difficulty with ICP based techniques is that they typically require sample to be presented for analysis in the form of a solution thus, in this case, requiring the dissolution of the filter sample in typically strong mineral acids. Despite promulgated methods, this dissolution step can rely heavily upon the experience of the analyst. A reported study [6] has shown that analytical bias can occur primarily due to errors in performing this dissolution step.

A useful tool in assessing the efficacy of this dissolution step would be the analysis of welding fume reference materials with stated elemental concentrations and whose matrices match as closely as possible the matrix compositions of test welding fume samples. To date, as far is known, only one such welding fume material has been produced [7] certified only for its chromium content (both hexavalent and total content).

This report thus describes the certification of a new bulk welding fume reference material HSL MSWF-1, derived from welding of zinc coated mild steel substrates. This material compliments a second companion material, HSL

SSWF-1, prepared in parallel and derived from the welding of stainless steel substrates [8]. In summary, these two reference materials have been produced to assist analysts in assessing the performance of the digestion procedures they employ in their laboratories when undertaking welding fume analysis.

These materials have been certified for analytical use at a nominal sample aliquot size of 10 mg. This is a compromise value balancing the requirements in weighing out accurately small quantities of finely divided powder with the quantities typically collected on workplace air filters (typically < 1 mg).

Recommended digestion procedures for use with this welding matrix type are tabulated in Section 9.

HSL would like to acknowledge the following who have contributed to the development of this reference material:

- Dr Martin Grosser (Müller-BBM) for procuring the candidate material
- Mr Peter Stacey (HSL) for XRD analysis and
- Participating certification laboratories (summary details provided in Table 13, Annex II).

2 CANDIDATE MATERIAL

The starting material for preparing HSL MSWF-1 was obtained from ventilation ducts above robotic welding stations at an automobile assembly plant. Approximately 1.2 kg of material was recovered and transported to HSL for processing.

Initially the material was dispersed on plastic trays and air dried at a nominal 95 °C before being sieved through a coarse 2-mm sieve to remove debris. This sieved fraction was then passed through a finer 200-μm sieve to remove debris such as (condensed) metal splash beads. Approximately 0.8 kg of material was recovered at this stage.

Welding fume upon generation consists of nm sized particles which quickly condense to form μm sized agglomerates. By nature it is therefore a finely divided particulate powder which is homogenous in nature provided that metal splash particles or other particles from related welding activities such as grinding are absent or removed.

To ensure the best possible homogenisation of this candidate material however, sample mixing was undertaken using both tubular and roller bottle mixers in 2010. The material was initially stored as one lot at a nominal 20 °C. It was then, following remixing, decanted into sample bottles, capped and again stored at a nominal 20 °C. A total of 800 bottles (units), each containing a nominal 1 g of fume, were produced in March 2012.

3 HOMOGENEITY STUDY

3.1 Analytical procedure

Ten bottles were chosen randomly following the sequence of bottling. A quantity of fume was removed from each bottle following shaking, air dried and 10 (± 0.1) mg sample aliquots taken for analysis. Each bottle was sampled in triplicate resulting in 30 test samples. These samples were digested using a hot block digestion procedure involving the use of a nitric / hydrochloric acid mixture at 95°C following a procedure described in ISO 15202-2 Annex H [3].

Solutions thus obtained were analysed by ICP-AES following procedures set out in ISO 15202-3 [4]. These measurements were performed under repeatability conditions after sample randomisation in one instrumental run sequence and employing a single calibration prepared using certified multi-elemental solutions traceable to national standards.

Measurement results obtained in this homogeneity study are presented in Annex I in both tabular (Tables 10-12) and in graphical formats (Figures 2-4). The error bars in the graphical presentations indicate the standard deviation of the mean of triplicate measurements undertaken per bottle unit.

3.2 Data analysis

Estimates of elemental specific inhomogeneity contributions u_{bb} to be included in the total uncertainty budget were calculated according to procedures described in ISO Guide 35 [9] using equations 1 and 2:

$$s_{bb} = \sqrt{\frac{MSamong - MSwithin}{n}} \qquad (1)$$

$$u_{bb}* = \sqrt{\frac{MSwithin}{n}} \sqrt[4]{\frac{2}{N(N-1)}} \qquad (2)$$

where

MS_{among}	is the mean of squared deviations between bottles
MS_{within}	is the mean of squared deviations within bottles
n	is the number of replicates per bottle analyzed
N	is the number of bottles selected for homogeneity study

s_{bb} equates to the between-bottle standard deviation, whereas u_{bb}^* denotes the maximum heterogeneity that can potentially be hidden by insufficient repeatability in the measurement method used. In summary, the larger of these two values has been used as u_{bb}. Equation one has not been applied if $MS_{within} > MS_{among}$.

The calculated relative values of s_{bb}, u_{bb}^* and u_{bb} for the different elements to be certified are reproduced in Table 1.

Table 1 Results of the homogeneity study conducted on HSL MSWF-1

Analyte	**s_{bb} (relative) %**	**u_{bb}^* (relative) %**	**u_{bb} (relative) %**
Iron	$MS_{among} < MS_{within}$	0.37	0.37
Manganese	$MS_{among} < MS_{within}$	0.55	0.55
Zinc	0.25	0.38	0.38

4 STABILITY STUDY

Based upon many years of experience in the repeat analysis of in-house welding fume quality control materials [10], HSL considers this welding fume material to remain stable if stored sealed at ambient temperatures.

HSL however is conducting an ongoing long term stability check study involving the reanalysis, in triplicate every six months, of material from units used in the homogeneity study.

In summary an expiry date of three years, since bottling, has initially been chosen, set at 31st March 2015.

Customers will be informed in the event of any changes/updates to the material certification data.

5 CERTIFICATION STUDY

5.1 Certification laboratories

Thirteen invited laboratories participated in this certification exercise. Summary laboratory details are tabulated in Annex 2 (Table 13). Laboratories were invited to participate based upon the following selection criteria:

- Expertise in the analysis of welding fume samples using recommended national and international standard methods or validated in-house methods
- Expertise in wider trace element analysis of metallurgical based materials

5.2 Certification protocol

Each laboratory received two randomly chosen bottles of candidate fume material. Before analysis, the material had to be dried at a nominal 95 °C overnight. Participants were requested to analyse five subsamples (nominal 10 (± 1.0 mg aliquots) from each of the bottles.

Participants were free to choose a digestion method in use in their facility that they deemed appropriate for the sample matrix. For information, a list of digestion methods deemed appropriate, was supplied by HSL alongside the test samples together with instructions for analysis and data reporting.

All laboratories bar one used ICP-AES as the instrumental technique. One laboratory employed sector field ICP-MS. Calibrations were performed used either liquid standard solutions prepared from pure metals or stoichiometric compounds or from commercial stock calibration solutions traceable to national standards.

Performance check samples were also supplied by HSL to be analysed alongside the candidate material. These consisted of 25-mm diameter mixed cellulose ester (MCE) filters spiked with elements, which upon dissolution, provided test solutions at elemental concentrations similar to that expected in digested fume samples. Blank MCE filters were also supplied so that process blanks could be evaluated.

5.3 Evaluation of returned results

The results returned by the participants and used in this certification are compiled and presented in both tabular and graphical formats on an element by element basis, in Tables 14-16 and Figures 5-7 found in Annex II. The error bars in the graphical presentations indicate the standard deviations of the mean of means from each of the individual laboratories (five replicate aliquots tested from each of two bottles). The error bars associated with the plotted certified values represent the corresponding expanded uncertainties arising from the certification exercise.

Prior to statistical examination of the data, returned participants' results were technically evaluated on the basis of:

- whether the required nominal 10 mg test aliquot was tested?
- data checks for possible transcription errors?
- whether recoveries from spiked MCE filter performance test samples were acceptable? (where the minimum performance requirement was within ± 10 % of spiked values determined at HSL)
- whether the digestion parameters used were suitable for the fume matrix in question? (in particular factors such as digestion temperature, suitability and compatibility of acid mixture to dissolve matrix and to subsequently stabilise elements in solution were considered)

Data sets which passed this evaluation step were then processed statistically using protocols set out in ISO Guide 35 [9] using the software package SoftCRM v1.2.2 [11].
The following statistical tests were carried out and results tabulated in Table 2.

Scheffé multiple t-test:	All data sets compatible two-by-two?
Cochran test:	Outlying variances?
Grubbs, Dixon and Nalimov tests:	Outlying means?
Bartlett test:	Variances homogenous?
Scedecor F-test:	Differences between data sets statistically significant?
Kolmogorov-Smirnov-Lilliefors test:	Normality of the distribution of the means?

As no technical reasons could be identified for two data sets (Iron: Laboratory 0) and (Zinc: Laboratory 2) and that the means were not flagged as a statistical outlier at a confidence level of 99 %, these two data sets were retained for further data processing.

Table 2 Statistical tests carried out on accepted participants' data

Analyte	Number of data sets accepted	Statistical tests								Comment
		Scheffé	Cochran	Grubbs	Dixon	Nalimov	Bartlett	Snedecor	Kolmogorov Smirnov Lilliefors	
		(p = (0.01/0.05)								
Iron	6	No	(-/-)	(-/-)	(-/-)	(-/L0)	yes/yes	yes/yes	yes/yes	Pooling of data not allowed
Manganese	10	No	(-/-)	(-/-)	(-/-)	(-/-)	yes/yes	yes/yes	yes/yes	Pooling of data not allowed
Zinc	9	No	(-/-)	(-/-)	(-/-)	(-/L2)	yes/yes	yes/yes	yes/yes	Pooling of data not allowed

6 CERTIFIED VALUES AND UNCERTAINITIES

The unweighted means of accepted data sets from certification laboratories (Tables 14-16, Annex 2) were taken as the best estimate w_{char} for the elemental mass fractions to be certified. The standard deviation of the mean of the accepted data sets means was taken to derive the uncertainty contributions u_{char} arising from this certification exercise:

$$u_{char} = \frac{SD_M}{\sqrt{N}} \qquad (3)$$

where

SD_M = standard deviation of the mean of means of data sets

N = number of individual data sets

The combined uncertainties $u_{combined}$ were calculated from the spread resulting from this certification exercise and the uncertainty contribution from possible inhomogeneity of the material:

$$u_{combined} = \sqrt{u^2_{char} + u^2_{bb}} \qquad (4)$$

The calculated mass fractions w_{char} and absolute values of the various uncertainty components are reproduced in Table 3.

Table 3 Mass fractions and uncertainty components for analytes in HSL MSWF-1

Analyte	w_{char}	u_{char}	u_{bb}	$u_{combined}$
	% (m/m)			
Iron	42.83	0.22	0.16	0.27
Manganese	1.476	0.010	0.008	0.013
Zinc	21.69	0.34	0.08	0.35

The expanded uncertainties U were obtained by multiplying the combined uncertainties $u_{combined}$ by a coverage factor k:

$$U = k\, u_{combined} \qquad (5)$$

The value of the coverage factor k was chosen to give a level of confidence of approximately 95 % for coverage of the interval ± U around the certified values. An appropriate k value was determined by calculating the effective degrees of freedom ν_{eff} of the linear combinations of u_{char} and u_{bb} using the Welch-Satterthwaite formula [12]. The calculated values for ν_{eff} and the corresponding $t_{95}(\nu_{eff})$ obtained from the Student's t-distribution, giving a level of confidence of 95 %, are provided in Table 4.

Table 4 Effective degrees of freedom of $u_{combined}$ and corresponding $t_{95}(\nu_{eff})$

Analyte	ν_{eff}	$t_{95}(\nu_{eff})$
Iron	10.6	2.23
Manganese	17.1	2.11
Zinc	9.8	2.26

A factor of k = 2.5 was therefore chosen for all analytes to give a level of confidence of approximately 95 %.

The certified mass fractions and their corresponding expanded uncertainties, rounded to an appropriate value, are shown in Table 5.

Table 5 Certified mass fractions and expanded uncertainties of analytes in HSL MSWF-1

Analyte	Number of data sets accepted	Mass fraction	Uncertainty
	n	*% (m/m)*	
Iron	*6*	42.8	± 0.7
Manganese	*10*	1.48	± 0.03
Zinc	*9*	21.7	± 0.9

7 TRACEABILITY

Certified values obtained by analysis of test solutions, prepared via the dissolution of the recommended 10 mg sample amount, are traceable to the SI (Systéme International d'Unites) via calibration using substances with certified purity.

During this certification exercise the following checks were used in the control of the sample dissolution step.

Weighing step

Sample aliquots (10 mg) were weighed out in participating laboratories using calibrated microbalances.

Dissolution step

Published digestion procedures (Table 13, Annex 2), have been used by some participants whose data has been accepted for certification. Such procedures have been produced via an expert peer review process either at a national or international level. Supporting method validation studies have been reported [13] as have independent reviews of the suitability of such methods for determining hazardous substances in workplaces [14].

The in-house digestion procedures used by some other participants (Table 13), upon review by HSL experts, have been deemed suitable given that they are essentially variants of the published procedures.

In summary, when appropriately used, these digestion procedures are deemed effective to ensure the quantitative dissolution of welding fume matrices of this type.

Analysis step

All analyses were carried out with matrix-matched (acid-matched) calibration solutions prepared either from pure metals or stoichiometric compounds or from commercial stock calibration solutions traceable to national standards. Dilution of stock standards or test samples was undertaken using calibrated volumetric vessels and pipettes.

Method performance check

Performance check samples, consisting of 25-mm diameter mixed cellulose ester (MCE) filters spiked with elements, which upon dissolution, provided test solutions at elemental concentrations similar to that expected in digested fume samples, were used to assess the performance of the certification laboratories.

Spiked MCE filters were prepared at HSL specifically for this certification exercise. Nominal elemental spike values were determined by assaying 10 % of this lot by ICP-AES [4] following leaching of filters in dilute nitric acid based upon a procedure described in ISO 15202-2 Annex B [3] .

The minimum performance requirement was that participating laboratories obtain results within ± 10 % of spiked values determined at HSL. Typically the spike filter recovery for participants whose data was accepted was within ± 5 % of spiked values determined at HSL.

8 ADDITIONAL SAMPLE INFORMATION

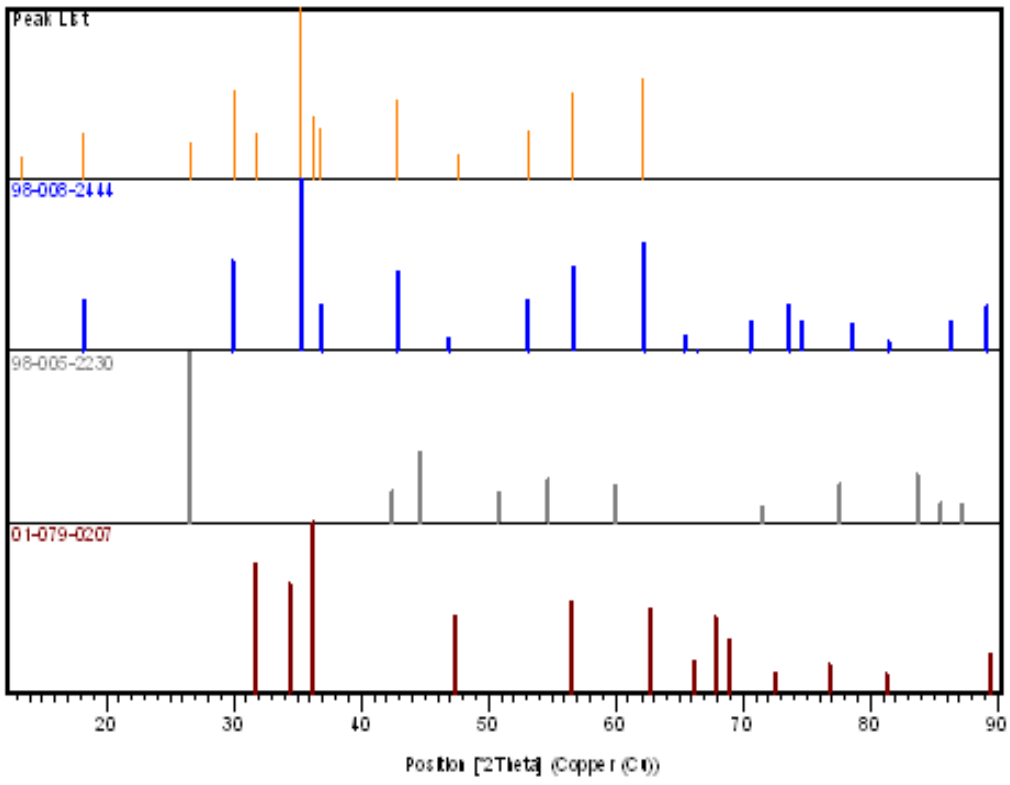
8.1 X-ray diffraction (XRD) scan of a sample of HSL MSWF-1

A qualitative XRD scan (6-65 θ) showed the presence of the following major crystalline phases best described as:

- Fe_3O_4 (ICDD pattern 98-008-2444)
- ZnO (ICDD pattern 01-079-0207)
- Graphitic carbon (ICDD pattern 98-005-2230)

The XRD pattern for the minor MnO phase is masked by the Fe and Zn phases.

Figure 1 XRD scan of a sample of HSL MSWF-1



8.2 Additional analytical data

Additional analytical results obtained in the course of this certification exercise are tabulated in Tables 6 and 7 for information.

Table 6 Indicative analyte mass fractions in HSL MSWF-1

Analyte	**Indicative mass fraction average (range)** ***% (m/m)***	**Data from certification laboratories**
Aluminium	0.42	Results from 1 laboratory
Calcium	0.85	Results from 1 laboratory
Chromium	(0.03 – 0.04)	Results from 3 laboratories
Copper	(0.25 – 0.29)	Results from 11 laboratories
Lead	0.005	Results from 1 laboratory
Nickel	0.01	Results from 2 laboratories
Magnesium	0.08	Results from 1 laboratory

Additional elemental data provided by HSL, derived from analysis (3 x 10 mg aliquots) from a randomly selected bottle (Unit 005) is tabulated below

Table 7 Indicative analyte mass fractions in HSL MSWF-1

Analyte	**Indicative mass fraction** ***% (m/m)***	**Analytical method**
Water soluble Zinc	0.06	ISO 15202-2 Annex A [3]

In July 2010, the candidate material was used as a blind test sample in the course of a round of the HSL WASP proficiency testing scheme. Participants were asked to analyse 10 (± 1.0) mg nominal sample aliquots using dissolution procedures and analytical techniques of their choosing. The PT results returned were evaluated using a robust method of data analysis and are summarised below.

Table 8 Analyte mass fractions measured during a round of the HSL WASP PT scheme

Analyte	**PT mean** *% (m/m)*	**S_R** *% (m/m)*	***n***	**% Recovery against certified value**
Iron	39.9	5.3	*13*	93
Manganese	1.43	0.05	*13*	97
Zinc	22.0	2.3	*13*	101

9 INFORMATION ON THE USE OF HSL MSWF-1

9.1 Transportation

Transportation of this reference material does not require special precautions above protecting against breakages of the glass bottle.

9.2 Storage

On receipt this reference material should be shored, capped at ambient temperature (*ca.* 20°C) in a dry and clean atmosphere.

9.3 Safety instructions

No hazardous effect is to be expected when this material is handled and used in a laboratory setting by trained analytical chemists using appropriate controls. It is recommended however that this material should be handled and disposed of in accordance with guidelines for handling laboratory reagents in force at the site of end use or disposal.

For further product information please refer to the accompanying Material Safety Data Sheet.

9.4 Instructions for use

The material should be used as supplied. The recommended amount of sample to be used is 10 (± 1.0) mg. However before taking a sample, a re-homogenisation by manual shaking of the closed bottle is recommended.

Analytical results have to be corrected to the dry mass content of the material by drying overnight at a nominal 95 °C using a separate sub-sample. Typical values recorded at HSL were *ca*. 0.4 % moisture content.

Recommended digestion procedures for dissolution of welding fume of this matrix type (mild steel fume) include the standard methods shown in Table 9.

Table 9 Recommended digestion procedures for dissolution of HSL MSWF-1 and similar welding fume matrices

Recommended workplace air standard methods	**Comment**
ISO 15202-2:2012 [3]	Recommended International Standard digestion procedures described in Annexes C-H. Procedures described in Annex C and G used by participants in the certification exercise
NIOSH 7300 [1]	Procedure used by a participant in the certification exercise
NIOSH 7301 [15]	-
NIOSH 7303 [16]	Procedure used by a participant in the certification exercise
OSHA ID-125G [2]	Procedure used by a participant in the certification exercise
ASTM D7439-08 [17]	-
ASTM D7035-10 [18]	-
Environmental standard methods that are deemed suitable	
US EPA SW 846 Method 3052 [19]	Procedure used by a participant in the certification exercise
EN 13656 [20]	Procedure used by a participant in the parallel certification exercise for HSL SSWF-1 [8]

9.5 Legal notice

The certified values in this report are HSL's best estimate of the true values within the stated uncertainties and based upon the measurement techniques described within this report. This reference material has been produced in accordance with international guidelines for the preparation and certification of reference materials [9].

In no event shall HSL be liable for any damages (including, without limitation, lost profits, business interruption, or lost information) arising out of the use of or inability to use HSL welding fume reference materials, even if HSL has been advised of the possibility of such damages. HSL will inform purchasers of any updated information regarding the material or its certification values and will refund the purchase price of the material in such circumstances where proven defects in this material have been brought to its attention.

10 REFERENCES

[1] NIOSH Manual of Analytical Methods 4th Edition, Method 7300*: Elements by ICP*, Issue 3 March 2003.

[2] OSHA ID-125G: *Metal and Metalloid particulates in workplace atmospheres (ICP analysis)* September 2002.

[3] ISO 15202-2:2012 *Workplace air -- Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry -- Part 2: Sample preparation*.

[4] ISO 15202-3:2004 *Workplace air -- Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry -- Part 3: Analysis*.

[5] ISO 30011:2010 *Workplace air -- Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma mass spectrometry.*

[6] Butler O. and Stacey P., *Performance of laboratories analysing welding fume on filter samples: Results from the WASP proficiency testing scheme*, Annals of Occupational Hygiene, 2008, 52, 4 287-295.

[7] Certified reference material BCR 545 *Welding dust loaded on a filter* available from the EC JRC Institute for Reference Materials and Measurements, Geel, Belgium.

[8] HSL Certification Report: *Reference Material HSL SSWF-1 Elements in stainless steel welding fume*, AS/2012/12, December 2012, available from the Health and Safety Laboratory, Buxton, United Kingdom.

[9] ISO Guide 35:1996 *Reference materials – General and statistical principles for certification.*

[10] HSL Report: *Investigation into the accuracy and completeness of Material Safety Data Sheet information on the chemical composition of welding fume* IEAS/99/05, February 2000, available from the Health and Safety Laboratory, Buxton, United Kingdom.

[11] SoftCRM *v1.2.2* (downloadable at www.eie.gr/iopc/softcrm/index.html). Information regarding this software can be found in the following published paper "*SoftCRM: a new software for the development of Certified Reference Materials (CRMs)"* Bonas G., Zerou M., Papaeoannou T and Lees M., *Accred. Qual. Assur.* 2003 **8** 101-107.

[12] [NIST Engineering Statistical Handbook http://www.itl.nist.gov/div898/handbook/prc/section3/prc31.htm accessed November 2012.

[13] Butler Owen T. and Howe Alan M., *Development of an international standard for the determination of metals and metalloids in workplace air using ICP-AES: evaluation of sample dissolution procedures through an interlaboratory trial,* Journal of Environmental Monitoring, 1999, 1, 23-32 (and references 2-4 therein).

[14] GESTIS database of analytical methods http://www.dguv.de/ifa/en/gestis/analytical_methods/index.jsp accessed November 2012

[15] NIOSH Manual of Analytical Methods 4th Edition, Method 7301*: Elements by ICP (Aqua Regia Ashing)*, Issue 1 March 2003.

[16] NIOSH Manual of Analytical Methods 4th Edition, Method 7303*: Elements by ICP (Hotblock HCl/HNO_3 Digestion),* Issue 1 March 2003.

[17] ASTM D7439-08 Standard Test Method for *Determination of Elements in Airborne Particulate Matter by Inductively Coupled Plasma-Mass Spectrometry*, Version of August 3, 2007.

[18] ASTM D7035-10 Standard Test Method for *Determination of Elements in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)*, Version of April 1, 2010.

[19] *EPA Method 3052 Microwave assisted digestion of siliceous and organically based matrices December 1996* in US EPA SW 846 (Test Methods for evaluating solid waste: Physical/Chemical Methods, 3rd Edition, Update III, 1997).

[20] EN 13656:2002 *Characterization of waste. Microwave assisted digestion with Hydrofluoric (HF), Nitric (HNO_3) and Hydrochloric (HCl) acid mixture for subsequent determination of elements in waste.*

ANNEX I HOMOGENEITY STUDY RESULTS

Table 10 Iron homogeneity results

Sample ID	Replicate 1	Replicate 2	Replicate 3	MEAN	SD
Random bottle (Unit number)	*% (m/m)*				
1 (005)	42.3	41.7	42.8	42.3	0.6
2 (181)	42.0	43.1	42.4	42.5	0.6
3 (232)	41.9	42.7	42.7	42.5	0.5
4 (271)	42.6	42.5	42.4	42.5	0.1
5 (334)	41.6	43.3	42.8	42.6	0.9
6 (397)	42.3	42.3	43.5	42.7	0.7
7 (453)	42.2	43.2	43.0	42.8	0.5
8 (550)	42.8	42.9	42.8	42.8	0.1
9 (615)	41.9	42.1	42.6	42.2	0.4
10 (755)	43.0	41.6	41.2	41.9	0.9

Figure 2 Iron homogeneity results

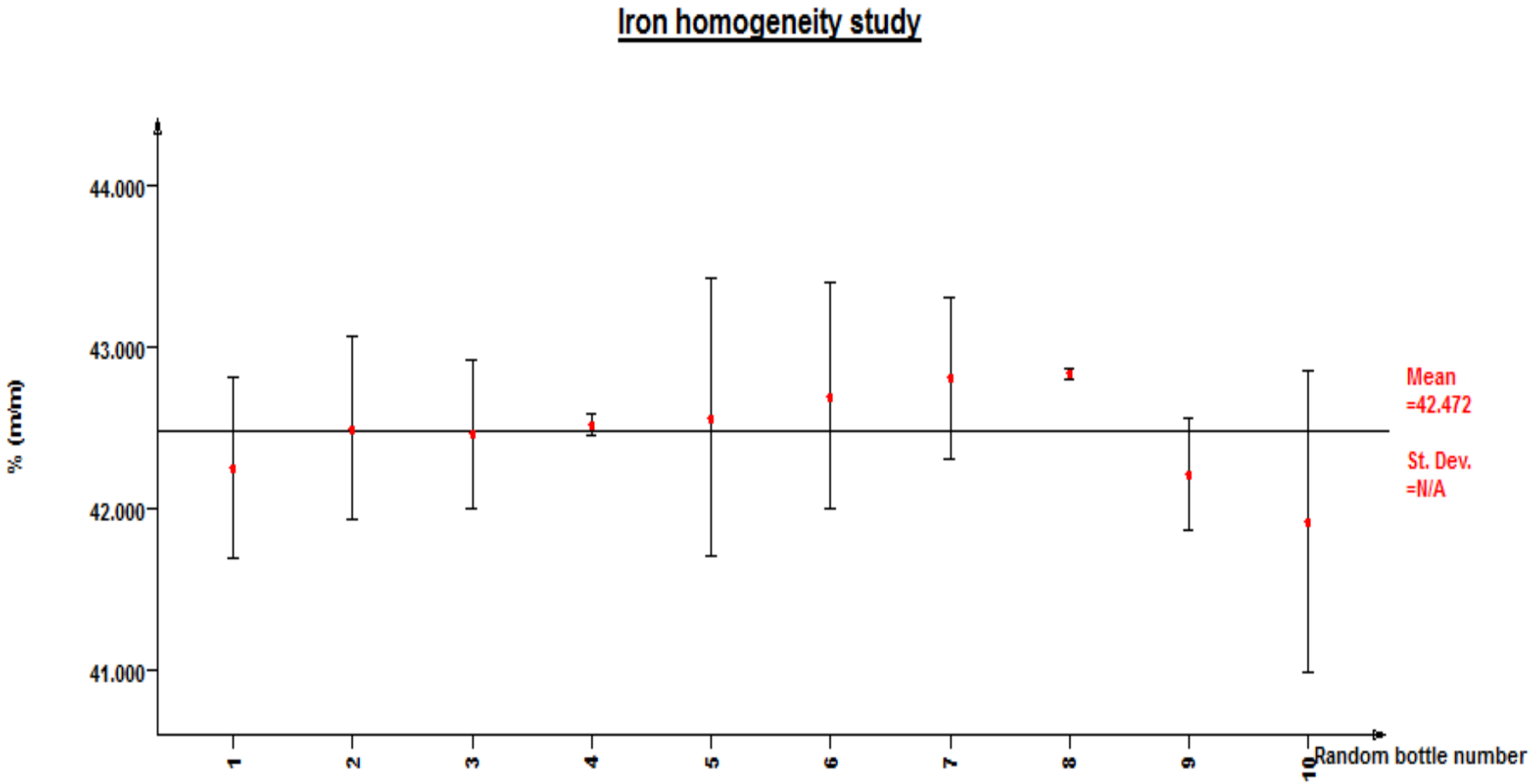


Table 11 Manganese homogeneity results

Sample ID	Replicate 1	Replicate 2	Replicate 3	MEAN	SD
Random bottle (Unit number)	*% (m/m)*				
1 (005)	1.58	1.53	1.60	1.57	0.04
2 (181)	1.55	1.59	1.56	1.57	0.02
3 (232)	1.52	1.56	1.55	1.54	0.02
4 (271)	1.58	1.53	1.56	1.56	0.02
5 (334)	1.52	1.60	1.56	1.56	0.04
6 (397)	1.55	1.56	1.61	1.57	0.03
7 (453)	1.58	1.55	1.56	1.56	0.01
8 (550)	1.56	1.57	1.55	1.56	0.01
9 (615)	1.53	1.54	1.54	1.54	0.01
10 (755)	1.57	1.53	1.53	1.54	0.02

Figure 3 Manganese homogeneity results

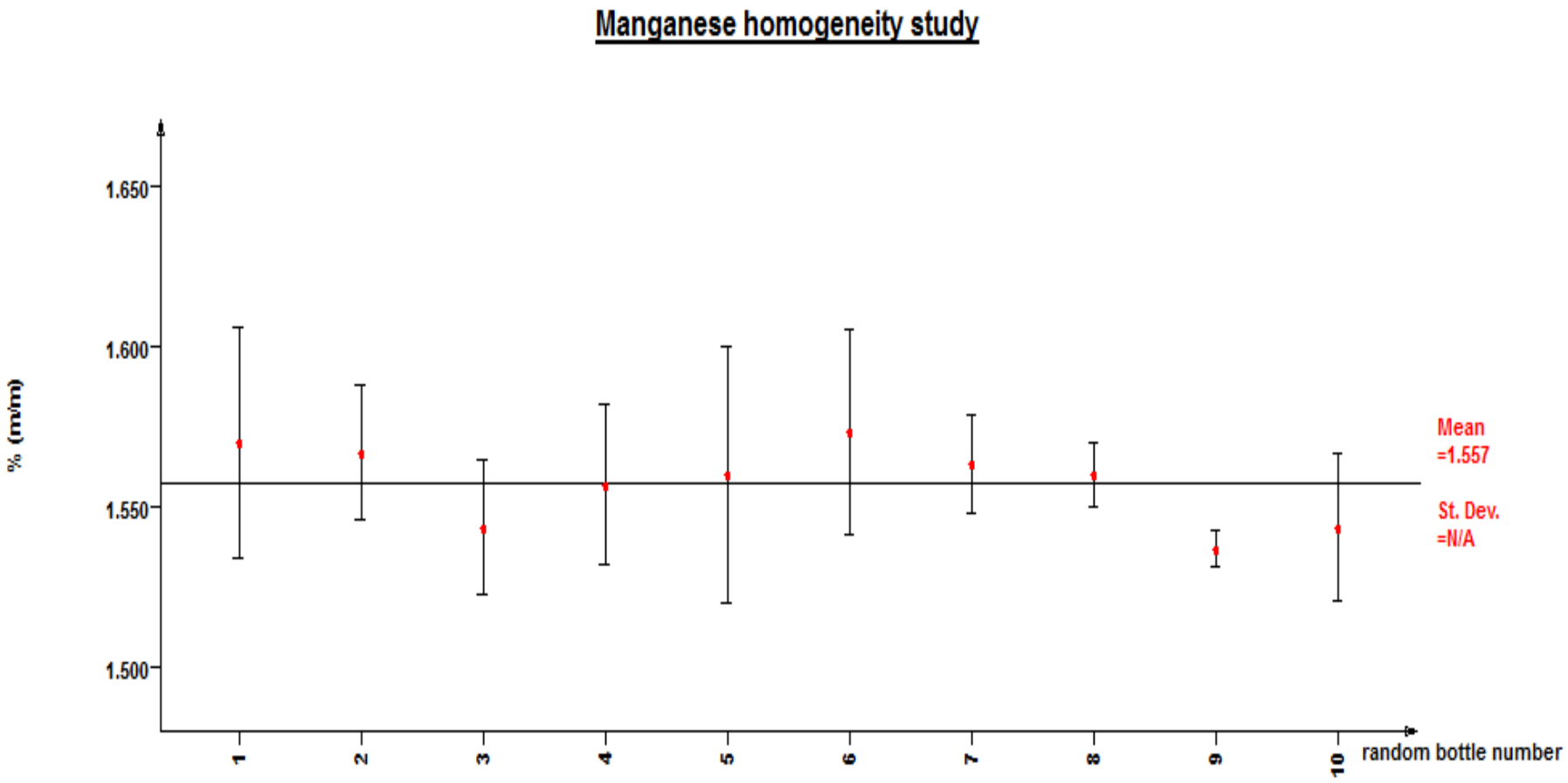
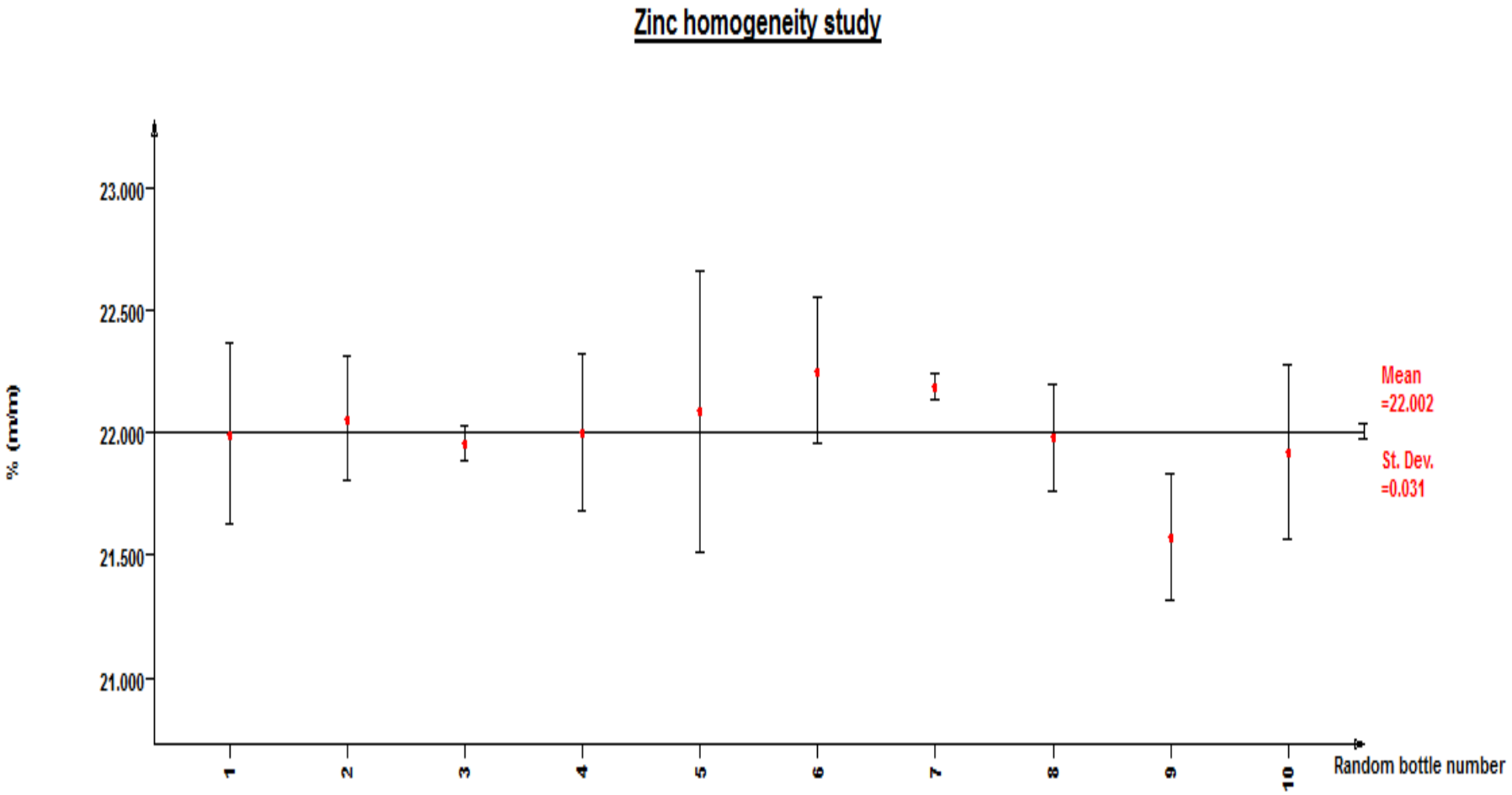


Table 12 Zinc homogeneity results

Sample ID	Replicate 1	Replicate 2	Replicate 3	MEAN	SD
Random bottle (Unit number)	*% (m/m)*				
1 (005)	22.4	21.7	22.0	22.0	0.4
2 (181)	21.8	22.3	22.2	22.1	0.3
3 (232)	21.9	22.0	22.0	22.0	0.1
4 (271)	22.0	21.7	22.3	22.0	0.3
5 (334)	21.5	22.7	22.1	22.1	0.6
6 (397)	22.0	22.2	22.6	22.3	0.3
7 (453)	22.2	22.2	22.1	22.2	0.1
8 (550)	21.9	22.2	21.9	22.0	0.2
9 (615)	21.4	21.9	21.5	21.6	0.3
10 (755)	22.3	21.9	21.6	21.9	0.4

Figure 4 Zinc homogeneity results



ANNEX II CERTIFICATION STUDY RESULTS

Table 13 Participants and their methodologies employed in the certification exercise

Laboratory	Country	Digestion Method	Acid mixture (temperature)	Analytical Technique
ALS Scandinavia	Sweden	US EPA SW846 Method 3052 - closed vessel microwave assisted digestion [19]	HNO_3/HCl/HF (180° C)	ICP- SFMS
Federal Public Service for Employment, Labour and Social Dialogue (FOD WASO/FPS ELSD)	Belgium	ISO 15202-2 Annex C – hotplate digestion [3]	HNO_3/HCl (95° C)	ICP-AES
Flemish Institute for Technological Research (VITO)	Belgium	NIOSH 7303 – hotblock digestion [16]	HNO_3/HCl (95° C)	ICP-AES
Health and Safety Laboratory (HSL)	UK	ISO 15202-2 Annex G - closed vessel microwave assisted digestion [3]	HNO_3/HCl/HF (180° C)	ICP-AES
Instituto Nacional de Seguridad e Higiene en el Trabajo (INSHT)	Spain	ISO 15202-2 Annex G - closed vessel microwave assisted digestion [3]	HNO_3/HCl (180° C)	ICP-AES

Laboratory	Country	Digestion Method	Acid mixture (temperature)	Analytical Technique
Kinectrics Inc	Canada	In-house closed vessel microwave assisted digestion	HNO_3/HCl/HF (?)	ICP-AES
Leibniz-Institut für Kristallzüchtung (IKZ)	Germany	In-house closed vessel microwave assisted digestion	HNO_3 (250° C)	ICP-AES
National Institute of Occupational Health (NIOH)	Hungary	In-house closed vessel microwave assisted digestion	HNO_3/H_2O_2 (200° C)	ICP-AES
National Institute of Occupational Health (STAMI)	Norway	In-house closed vessel microwave assisted digestion	HNO_3/HCl/HF (?)	ICP-AES
National Institute of Occupational Safety and Health (NIOSH)	USA	NIOSH 7300 – hotplate digestion [1]	$HNO_3/HClO_4$ (150 ° C)	ICP-AES
Occupational Safety and Health Administration (OSHA)	USA	OSHA 125g – hotplate digestion [2]	$HNO_3/H_2O_2/H_2SO_4$ (fuming SO_3)	ICP-AES
Ridsdale & Co. Ltd	UK	In-house hotplate digestion	$HNO_3/HClO_4/H_3PO_4$ (fuming)	ICP-AES

Table 14 Accepted Iron results from certification laboratories

Iron	***% m/m***											
Laboratory	**L0**		**L2**		**L3**		**L6**		**L7**		**L8**	
Replicate (Unit)	Bottle 1 (092)	Bottle 2 (692)	Bottle 1 (669)	Bottle 2 (736)	Bottle 1 (061)	Bottle 2 (508)	Bottle 1 (391)	Bottle 2 (632)	Bottle 1 (022)	Bottle 2 (465)	Bottle 1 (300)	Bottle 2 (547)
1	41.9	41.3	41.4	45.3	41.6	43.3	43.2	42.6	43.2	43.3	43.1	44.3
2	42.1	41.3	42.7	44.3	42.5	42.4	43.2	42.3	43.3	42.7	43.7	42.6
3	42.4	42.1	40.6	42.6	45.0	44.0	43.8	42.6	42.8	42.4	42.3	43.2
4	42.3	42.1	43.9	43.5	42.1	43.1	43.0	42.3	42.9	42.3	44.7	44.2
5	41.7	42.1	42.1	43.5	42.7	40.8	42.9	42.4	43	43.2	43.6	44.2
Mean	42.1	41.8	42.1	43.8	42.8	42.7	43.2	42.4	43.0	42.8	43.5	43.7
sd	0.3	0.4	1.3	1.0	1.3	1.2	0.4	0.2	0.2	0.5	0.9	0.8
Mean of mean	41.9		43.0		42.8		42.8		42.9		43.6	
sd	0.2		1.2		0.0		0.6		0.2		0.2	

Figure 5 Accepted Iron results from certification laboratories

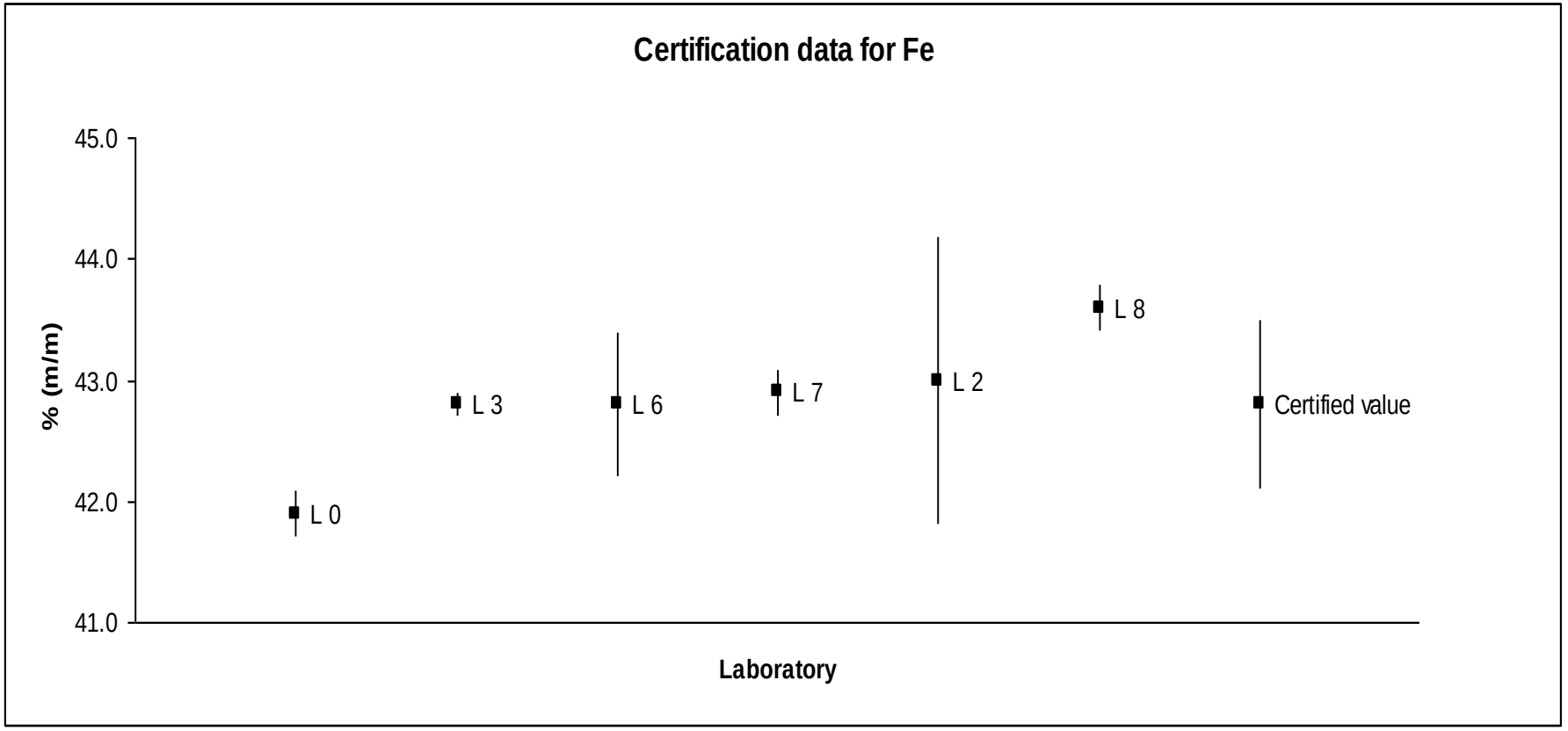


Table 15 Accepted Manganese results from certification laboratories

Manganese	***% m/m***											
Laboratory	**L0**		**L2**		**L3**		**L4**		**L5**		**L6**	
Replicate (Unit)	Bottle 1 (092)	Bottle 2 (692)	Bottle 1 (669)	Bottle 2 (708)	Bottle 1 (061)	Bottle 2 (508)	Bottle 1 (162)	Bottle 2 (526)	Bottle 1 (222)	Bottle 2 (147)	Bottle 1 (391)	Bottle 2 (632)
1	1.49	1.51	1.42	1.57	1.46	1.45	1.45	1.44	1.43	1.51	1.45	1.43
2	1.49	1.52	1.45	1.55	1.48	1.43	1.50	1.46	1.42	1.40	1.46	1.41
3	1.52	1.54	1.45	1.47	1.51	1.44	1.51	1.45	1.41	1.57	1.48	1.44
4	1.52	1.54	1.48	1.49	1.48	1.43	1.52	1.51	1.44	1.45	1.46	1.42
5	1.50	1.53	1.43	1.5	1.46	1.42	1.47	1.62	1.44	1.46	1.45	1.42
Mean	1.50	1.53	1.45	1.52	1.48	1.43	1.49	1.50	1.43	1.48	1.46	1.42
sd	0.02	0.01	0.02	0.04	0.02	0.01	0.03	0.07	0.01	0.07	0.01	0.01
Mean of mean	1.52		1.48		1.46		1.49		1.45		1.44	
sd	0.02		0.05		0.03		0.01		0.04		0.03	

Manganese	***% m/m***							
Laboratory	**L7**		**L8**		**L9**		**L12**	
Replicate (Unit)	Bottle 1 (022)	Bottle 2 (465)	Bottle 1 (300)	Bottle 2 (547)	Bottle 1 (047)	Bottle 2 (799)	Bottle 1 (727)	Bottle 2 (475)
1	1.50	1.5	1.52	1.55	1.43	1.45	1.46	1.47
2	1.51	1.47	1.54	1.51	1.45	1.47	1.44	1.41
3	1.49	1.46	1.49	1.53	1.47	1.52	1.46	1.38
4	1.46	1.48	1.56	1.54	1.47	1.49	1.49	1.40
5	1.51	1.46	1.54	1.55	1.48	1.49	1.44	1.37
Mean	1.49	1.47	1.53	1.54	1.46	1.48	1.46	1.41
sd	0.02	0.02	0.03	0.02	0.02	0.03	0.02	0.04
Mean of mean	1.48		1.53		1.47		1.43	
sd	0.01		0.01		0.02		0.04	

Figure 6 Accepted Manganese results from certification laboratories

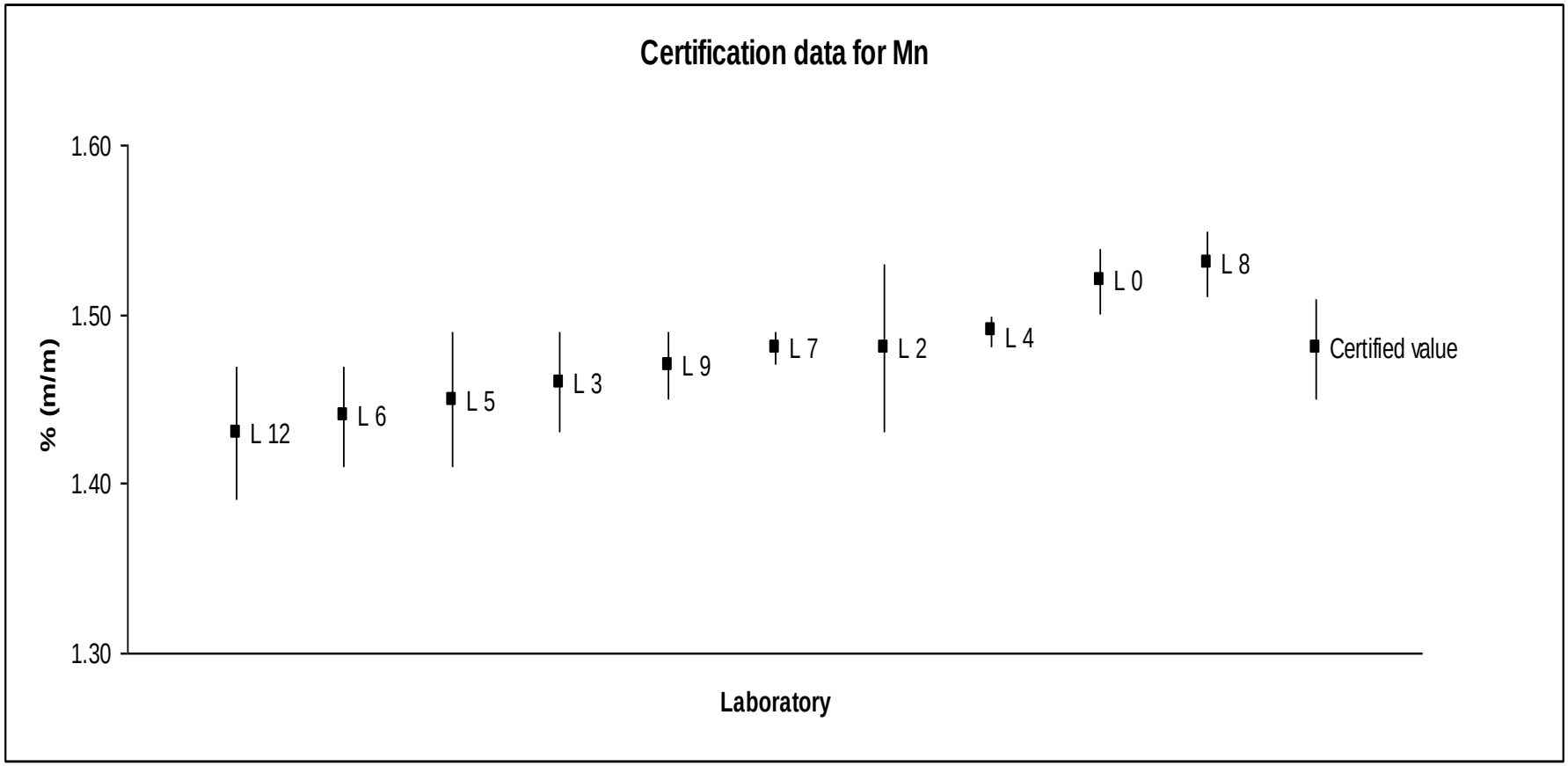


Table 16 Accepted Zinc results from certification laboratories

Zinc	***% m/m***											
Laboratory	**L0**		**L2**		**L3**		**L5**		**L6**		**L7**	
Replicate (Unit)	Bottle 1 (092)	Bottle 2 (692)	Bottle 1 (669)	Bottle 2 (736)	Bottle 1 (061)	Bottle 2 (508)	Bottle 1 (222)	Bottle 2 (147)	Bottle 1 (391)	Bottle 2 (632)	Bottle 1 (022)	Bottle 2 (465)
1	22.0	21.9	22.3	24.9	21.1	21.7	20.1	21.0	21.4	21.2	23.1	23.2
2	21.8	21.9	23.1	24.6	21.5	21.2	19.9	19.6	21.7	21.3	22.7	22.6
3	22.1	22.3	23.3	23.4	23.0	22.1	19.7	22.0	21.9	21.4	22.8	22.0
4	22.1	22.3	23.8	23.8	21.2	21.6	20.3	20.2	21.9	21.1	22.3	22.1
5	21.8	22.1	23.6	23.9	21.7	20.5	20.2	20.2	21.6	21.1	22.6	22.8
Mean	22.0	22.1	23.2	24.1	21.7	21.4	20.0	20.3	21.7	21.2	22.7	22.5
sd	0.2	0.2	0.6	0.6	0.8	0.6	0.2	0.9	0.2	0.1	0.3	0.5
Mean of mean	22.0		23.7		21.6		20.3		21.5		22.6	
sd	0.1		0.6		0.2		0.4		0.3		0.1	

Zinc	***% m/m***					
Laboratory	**L8**		**L10**		**L12**	
Replicate (Unit)	Bottle 1 (300)	Bottle 2 (547)	Bottle 1 (422)	Bottle 2 (111)	Bottle 1 (727)	Bottle 2 (475)
1	20.7	20.8	21.0	21.1	22.2	22.1
2	21.2	20.4	20.7	21.1	21.7	22.2
3	20.3	20.6	21.0	20.9	22.2	21.0
4	21.6	20.6	21.0	20.7	22.7	21.1
5	20.5	21.1	20.8	21.2	22.1	20.7
Mean	20.9	20.7	20.9	21.0	22.2	21.4
sd	0.5	0.3	0.1	0.2	0.4	0.7
Mean of mean	20.8		21.0		21.8	
sd	0.1		0.1		0.5	

Figure 7 Accepted Zinc results from certification laboratories