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Proficiency testing for determination of metals in tomato paste

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Abstract: In this study, the mass fractions of Cd, Cu, Fe, Pb, Sn and Zn in tomato paste were determined by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS). For this purpose, samples were digested with mixture of HNO_3 (65 %, w/w), HCl (30 %, w/w) and H_2O_2 (30 %, w/w). In order to validate a method, some parameters such as limit of detection and quantification, linear range, repeatability, intermediate precision and recovery were investigated. The mass fractions with uncertainties of Cd, Cu, Fe, Pb, Sn, and Zn in the tomato paste with uncertainties were (5.12 ± 0.28) mg/kg, (11.94 ± 0.27) mg/kg, (64.40 ± 3.61) mg/kg, (5.31 ± 0.39) mg/kg, (25.72 ± 0.61) mg/kg, (39.19 ± 1.27) mg/kg, respectively. Homogenized samples were sent to different laboratories for proficiency testing (PT) that was organized in order to evaluate the results and to control the quality of laboratories. As a result of the PT schemes, the participating laboratories can compare their analytical results with those from other laboratories and can improve their method for better measurement accuracy and reliability of their results.

Keywords: Metal; tomato paste; external quality control; proficiency testing; HR-ICP-MS.

1. Introduction

Tomato is a vegetable that is used worldwide in diets because of its natural low calorie content. It contains the carotene lycopene, Vitamin A and C, potassium and folic acid. Lycopene is the pigment that gives the tomato its red colour of tomato and has been linked to the prevention of many types of cancer. Lycopene is also one of the most powerful natural antioxidants which fight free radicals that can interfere with normal cell growth and activity. These free radicals can potentially lead to cancer, heart disease and premature aging. Tomato can be consumed directly or as an ingredient in ketchup, tomato soup, tomato sauce and paste [1].

Trace elements play important roles in our life functioning in wide spectrum. While some of trace elements such as Cd, Pb, Hg and radioactive metals are toxic heavy metals, some of them such as Fe, Cu and Zn have nutritional importance and are essential. Toxic metals usually imitate the action of an essential element in the body, interfering with the metabolic processes to cause illnesses. Thus, the determination of trace elements in various matrices is becoming increasingly important because of

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the heightening interest in monitoring the specific contents of food, biological and environmental samples and nutrients for quality control and public health purposes [2]. Cadmium is a toxic and non-essential element that accumulates mainly in blood, the kidneys and liver tissues. Similarly lead is an abundantly found metal that is highly toxic for health and the environment and serves no essential function in the body. It can damage the kidneys, liver, heart and the vascular, immune and neural systems, especially in young children, and causes a number of hemotological and neurological illness [3,4]. For this reason, the existences of cadmium and lead is unwanted in any sample in any concentration, even at ultra-trace levels. Thus, their determination at the lowest possible concentrations is important and provides a basis for the diagnoses of clinical disorders and intoxication as well as for monitoring environmental pollution. Tin is an essential trace element for animals but some researchers are still unsure of whether tin is essential to human health. Because of its low toxicity, tin-plated metal is used for food packaging, giving the name to tin cans, which are made mostly of steel. Iron is a necessary trace element found in nearly all living organisms and is an essential part of hemoglobin. Copper and zinc are the key components of many enzymes and vital elements for humans, animals, plants and microorganisms. However, as for all essential elements, their excess or deficiency can result in the emergency of chronic or acute disorders. Therefore, the correct and precise determination of maximum level of metals in foods is very important [5-7].

Regulations have been set in many countries in order to restrict the intake of toxic elements and to protect consumers from their harmful effects, as well as to ensure fair practices in food trade. Although the legal limits can vary from one country to another, regulations generally specify an allowed maximum limit for toxic heavy metal content in foods and establish a mechanism to monitor the level of toxic elements in food in order to enforce regulatory standards and assess long-term exposure.

Atomic absorption spectrometry (AAS) [8-10], inductively coupled plasma atomic emission spectrometry (ICP-AES) [8], inductively coupled plasma mass spectrometry (ICP-MS) [11-13], spectrofluorimetry [14], spectrophotometry [15] and electrochemical methods [16] are techniques used for the determination of elements in different food matrices. Recently, ICP-MS has been chosen as a preferred analytical technique, because of its high sensitivity, wide dynamic range, relatively low risk of interferences and rapid multielement capability for each single sampling [17].

Authorised food and feed control laboratories need to be accredited according to the ISO/IEC 17025 standard which obliges laboratories to implement an effective quality control/assurance system into place. Proficiency testing (PT) is an important and essential tool for the determination of laboratory performance. The analysis of an external quality control test material allows individual laboratories to compare their analytical results with those of other laboratories[18-23].

In order to increase awareness of metrological issues in chemical measurements in Turkey generally and to ensure the quality of chemical analyses of metal contents in tomoto paste, TUBITAK UME Chemistry Group Laboratories have been organizing PT schemes in the field of determination of metals in tomato paste since 2005. Laboratories participating in the PT schemes determine Cd, Cu, Fe, Pb, Sn and Zn in a sample of tomato paste provided by TÜBİTAK UME.

In this study, the mass fractions of Cd, Cu, Fe, Pb, Sn and Zn in tomato paste were investigated by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) low, medium and high resolutions. The defined method was validated and the uncertainties of the measurement results were estimated. Subsequently, a PT scheme was organised in which homogenized samples were sent to participating laboratories for analysis so that their results could be evaluated and compared against one another for the purpose of obtaining data on the quality of the measurements performed at each laboratory. As laboratories are informed of the their own results and those of other laboratories, they are able to take steps to improve the methods they utilize for better accuracy and reliability of their measuements.

2. Experimental

2.1. Chemicals and instrumentation

The mass fractions of elements were determined by a Thermo Finnigan Element 2 High Resolution ICP-MS (Bremen, Germany). Instrumental parameters were adjusted according to the manufacturer's recommendations.

The samples were digested and decomposed with CEM MARS5 Microwave digestion system (Matthews, NC, USA). A temperature controlled Teflon PFA vessel (100 mL) was used in the microwave digestion system. The most suitable digestion method for tomato paste was chosen from the microwave digestion manual.

In order to obtain a homogenous mixture, sample was mixed for 4 hours by a Heidolph RZR 2021 mechanical agitator with a Teflon tip (Heidolph, Germany). All reagents used in the analyses were of analytical or higher grade. The stock solutions (1 mg/L and 0.1 mg/L) of the metals were prepared from High Purity Single Element Standard Solutions (1000 mg/L) (High Purity, USA) and further diluted with deionized water (>18.2 MΩ/cm) to prepare reference solutions. Suprapur HNO_3 (65 %, w/w), Suprapur HCl (30 %, w/w) and Suprapur H_2O_2 (30 %, w/w) were purchased from Merck (Germany) and used for the digestion of tomato paste samples. Deionized water obtained from a Millipore MilliQ Academic water purification system with 18.2 MΩ/cm resistivity was used throughout the experiments. Tomato Leaves certified reference material (NIST SRM 1573a) was used for the trueness of method.

2.2. The procedure for the preparation and analysis of the sample procedure

In order to prepare the testing samples which were sent to participant laboratories for analysis, the same manufacturing batch of the tomato paste was used. The mass fractions of analytes in tomato paste for spiking were decided according to EPA/WHO/TSE/EC standards. The sample was spiked with different volumes of analytes (Cd, Cu, Fe, Pb, Sn and Zn) prepared from standard solutions including 1000 mg/L metal, according to the maximum acceptable limits of EPA/WHO/TSE/EC. In order to obtain a homogenous mixture, sample was mixed for 4 hours by mechanical agitator with a Teflon tip. Then the samples of 50 g of the tomato paste were put into glass bottles which were then distributed to the laboratories participating in the PT scheme..

In order to determine the mass fraction of analytes (Cd, Cu, Fe, Pb, Sn and Zn) in tomato paste by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS), the samples were digested with microwave digestion system. For this purpose, the most suitable method for tomato paste was chosen form the microwave digestion manual. The microwave digestion program is given in Table 1.

Table 1. Microwave digestion program

Step	Time (min)	Temperature (º C)	Power (W)
1	5	Ramp to 145	
2	5	Ramp to 180	Up to 1000
3	20	Hold at 180	

Two samples (1.0 g) from each bottle were weighed with 0.1 mg sensitivity in microwave vessels, 7.0 mL of Suprapur HNO_3 (65 %, w/w), 0.5 mL of Suprapur HCl (30 %, w/w) and 0.5 mL of Suprapur H_2O_2 (30 %, w/w) were added, and then the samples were digested according to the chosen method. Then the clear solutions were diluted to 50.0 mL with deionized water. A homogeneous mixture was prepared by taking 10.0 mL from each solution. In order to plot the calibration curve by using the standard addition and internal standard methods simultaneously for analysis of the samples,

different volumes of the standard solutions containing all analytes were added into homogeneous solutions to get “0”, “1”, “3”, “5”, “10”, “30” and “50” µg/L calibration standards.

NIST SRM 1573a Tomato Leaves was used as the certified reference material for the trueness test of the method in this study. 0.5 g of the dried sample was weighed exactly into the microwave vessels with 0.1 mg sensitivity. Then 7.0 mL of Suprapur HNO_3 (65 %, w/w), 0.5 mL of Suprapur HCl (30 %, w/w) and 0.5 mL of Suprapur H_2O_2 (30 %, w/w) were added and the vessels were inserted into the microwave digestion furnace and treated according to the manufacturer’s recommendation in the same process as with the tomato paste samples. Then the digested solutions in the vessels were transferred and diluted to 50 mL with deionized water.

The tomato paste and certified reference material samples were diluted five times by adding the internal standard “Indium” which has a mass concentration of 5 µg/L and deionized water to the samples.

2.3. The proficiency testing scheme procedure

The coordinator, in consultation with technical experts, developed an appropriate protocol and scheme for this analysis. The protocol consisted of the information on sample preparation, sample distribution, sample storage, the programme of the study and the parameters for determination of the analytes. It also included the procedure used to select the participants, the time schedule of the testing scheme and information on methods, reporting of results, evaluation of the results, security and references. The protocol was published on the website of the TÜBİTAK UME. In this PT scheme, the identities of the participating laboratories and their results were kept private through assigning each laboratory a participant number that was used to refer to them and their results in the reporting.

Participants were free to choose the method for the analysis and were advised to use their routine procedure. Participants reported their results using an online interface set up for that purpose.

The homogeneity of PT samples were tested before sending them to the participants. The stability of PT samples were tested through the duration of the PT. The results of the homogeneity and stability tests were evaluated according to ISO 13528 [19]. The results of participants were evaluated statistically and z-scores were calculated for each laboratory according to ISO 17043 [20]. The report was prepared and published on TÜBİTAK UME’s web site. Attendance Certificates were sent to the participants.

3. Results and discussion

3.1. Analysis of samples, validation of the method and calculations of measurement

The use of the validated method is very important for the quality of the results. In this study, the method was validated, the measurement results for each analyte were evaluated statistically and the measurement uncertainties were estimated. In order to validate the method, some parameters such as linearity, limit of detection and quantification, recovery, repeatability and intermediate precision parameters were investigated [24-28].

3.1.1 Linearity

Linearity is the ability of the method to elicit test results that are directly proportional to the analyte concentration within a given range. Linearity is generally reported as a correlation coefficient and the variance of the slope of the regression. A range is defined as the interval between the upper and the lower levels of the analytes within the calibration curve. In order to prepare calibration solutions and to plot a calibration curve by using the standard addition and internal standard methods

simultaneously for analysis of the samples, a homogeneous mixture was prepared by taking 10.0 mL from each digested and diluted sample. The linearity of the method was determined via repeated measurements of calibration solutions. The relationship between the mass concentration of the analyte and the corresponding detector response was calculated using the linear regression method. Calibration curves and residual plots are shown in Supporting Information, Evaluation of Calibration Curves Tomato Paste file.

The acceptance performance criteria of the obtained curves were determined as follows:

- correlation coefficient of the calibration lines for all the isotopes of all analytes monitored higher than 0.989 or better
- equal distribution of points

3.1.2 Limit of detection and quantification

The limit of detection (LOD) is defined as the lowest concentration of an analyte in a sample that can be detected with statistical confidence. The limit of quantification (LOQ) is defined as the lowest concentration of an analyte in a sample that can be determined with acceptable precision and trueness under stated operational conditions of the method [24, 27]. While LOD was estimated as the concentration corresponding to three times the standard deviation (3σ) of the independent blank corrected results obtained from a set of reagent blanks (n = 20), LOQ was estimated as the concentration corresponding to ten times the standard deviation (10σ) of independent blank corrected results obtained from a set of reagent blanks (n = 20). LOD and LOQ that have been determined for the analytes are shown in Table 2.

Table 2. LOD and LOQ for the analytes

	Cd	Cu	Fe	Pb	Sn	Zn
LOD (mg/kg)	0.02	0.03	0.04	0.01	0.04	0.63
LOQ (mg/kg)	0.05	0.26	0.12	0.03	0.14	2.69

3.1.3 Recovery/Trueness

Trueness is determined by using certified reference materials or comparing the new method with a reference method or performing a spike-and-recovery experiment. In this study, in order to confirm the trueness of the complete method including digestion and the measurement, certified reference material (NIST SRM 1573a) was used for Cd, Cu, Fe, Zn and a spike-and-recovery experiment was used for all elements. Tomato Leaves (NIST SRM 1573a) a certified reference material was used and analyzed together with the samples, applying the same digestion and measurement procedure. Results and recovery values for the elements whose values were certified in the CRM are given in Table 3. Recoveries were calculated by using Equation (1) below:

$$\text{Recovery}\,(\%) = \frac{C_{\text{Observed value}}}{C_{\text{Certified value}}} \times 100 \qquad (1)$$

where:

$C_{Observed\ value}$: mass fraction of analyte found, mg/kg

$C_{Certified\ value}$: certified value of analyte in the certificate, mg/kg

Table 3. The analytical results and recoveries for the analytes found in Tomato Leaves (NIST SRM 1573a)

Analytes	Found average mass fraction (mg/kg)	Certified value (mg/kg)	Recovery (%)
Cd	1.53 (1.49, 1.54, 1.55)	1.52±0.04	100.4
Cu	4.82 (4.73, 4.83, 4.89)	4.70±0.14	102.5
Fe	338 (336,338,340)	368±7	91.8
Zn	30.8 (30.3, 30.7, 31.4)	30.9±0.7	99.7

Trueness of all elements was also determined through a spike-and-recovery experiment in which a known amount of analyte is added to the sample matrix, and the two sets of mass fractions are compared with unspiked sample concentrations. Analytes at two different mass fractions (5 and 10 mg/kg) were to be added to the samples. The same procedure was applied to the spiked samples and the unspiked samples. Recoveries were calculated by using Equation 2. There was no discrepancy observed between the results.

Results and recovery values for the elements are given in Table 4 and Table 5. Recoveries were calculated by using Equation (2) below:

$$\text{Recovery}\,(\%) = \left(\frac{C_2 - C_1}{C_o} \right) * 100 \qquad (2)$$

where:

C_2 = Spiked sample mass fraction, mg/kg

C_1 = Unspiked sample mass fraction, mg/kg

C_o = Spiked value, mg/kg

Table 4. Recoveries of analytes for 5 mg/kg spiked samples

Analytes	Recovery (%)	SD	RSD (%)
Cd	98	0.1	0.5
Cu	93	0.3	1.1
Fe	98	1.2	1.2
Pb	97	0.1	0.4
Sn	98	0.1	0.3
Zn	99	2.3	3.5

Table 5. Recoveries of analytes for 10 mg/kg spiked samples

Analytes	Recovery (%)	SD	RSD (%)
Cd	95	0.3	1.3
Cu	95	0.5	1.6
Fe	96	0.4	0.4
Pb	95	0.4	1.5
Sn	96	0.1	0.2
Zn	99	2.4	3.4

3.1.4 Repeatability and intermediate precision

Repeatability is a crucial parameter for method validation. In this study, ten bottles were randomly selected from among the samples prepared for the PT. Two representative samples taken from each of the ten bottles were digested. Twenty independent test results were obtained with the same method on identical test items using the same equipment within one day and the results were evaluated by using Single Factor Analysis of Variance (Single Factor ANOVA) and shown in Table 6 [28]. $F_{experimental}$ obtained were F_{critic}, there is no significant difference between the results.

The intermediate precision expresses the precision where at least one of the conditions for repeatability is not met and reveals. It is the within-laboratory variation due to e.g. different days, different analysts, different equipment, etc. In order to evaluate the intermediate precision of the method, three bottles were randomly selected from among the samples prepared for the PT [28]. Three independent samples were prepared from the selected samples and were analyzed. The same procedure was applied on three different days by the same operator using the same methodology. The obtained results were evaluated by applying one-way ANOVA and shown in Table 6. $F_{experimental}$ were lower than F_{critic}, there was no significant difference between the results. The relative standard deviations for repeatability and intermediate precision were lower than 5 %.

Table 6. Evaluation of the results of the repeatability and intermediate precision testing of the sample by one-way ANOVA

		Cd	Cu	Fe	Pb	Sn	Zn
Repetability	RSD_{rep} (%)	0.5	1.1	1.6	1.5	0.8	0.5
	$F_{experimental}$	2.543	1.406	0.514	1.031	1.974	0.526
	F_{critic}			3.020			
Intermediate precision	RSD_{ip} (%)	1.0	1.1	2.6	1.9	0.9	1.5
	$F_{experimental}$	0.328	3.882	0.502	0.299	0.173	0.328
	F_{critic}			5.143			

3.1.5 Estimation of measurement uncertainties

The mass fractions of analytes in the tomato paste samples were calculated by using Equation (3) below:

$$\text{Mass fraction}\,(mg/\text{kg}) = \frac{(C_{sample} - C_{blank}) \times V_{final}}{m_{Sample}} \times d \qquad (3)$$

where:

$C_{sample:}$: mass fractions of analytes in the sample obtained from the calibration curve, µg/L

C_{blank}: mass fractions of analytes in the reagent blank obtained from the calibration curve, µg/L

V_{final}: final diluted volume after digestion, 0.05 L

d: dilution factor, 5

m_{sample}: amount of sample, g

Measurement uncertainty quantifies the doubt one reasonably has concerning a accuracy of an analytical result. It gives a range in which the "true value" is expected to lie with a certain probability. In principle, there are two different ways to quantify measurement uncertainty. The "top-down" approach starts from the "normal" performance of a method, assumes that the method performed equally well for a particular measurement and estimates the measurement uncertainty based on this previous knowledge of method performance. The "top down" estimation is based on method performance and on the fact that the combined influence of many effects is quantified simultaneously by estimating repeatability, intermediate precision and trueness. The other, called the "bottom-up" approach, it starts at the individual measurement and tries to identify and quantify all potential influence factors and then estimates the measurement uncertainty based on these components. It should be borne in mind that both methods of quantification are equivalent and only differ in terms of the "resolution" of individual uncertainty components [18, 25, 26]. In this study, the bottom-up approach was used for the evaluation of uncertainty.

The following parameters were used for the calculations of uncertainties:

1. Calibration curves, stock solutions of standards and internal standard (C),
2. Samples weight (m_{sample})
3. Final volume of the digested sample (V_{final})
4. Repeatability (rep)
5. Dilution factor (d)

Standard combined uncertainty is a combination of the uncertainties of each parameter which was calculated by using the Equation (4) below:

$$u(C) = \sqrt{u^2(C) + u^2(m_{sample}) + u^2(V_{final}) + u^2(rep) + u^2(d)} \quad (4)$$

The standard combined uncertainties were multiplied by two for the calculation of the expanded uncertainties. Measurement results and their uncertainties are shown in Table 7.

Table 7. Measurement results and their uncertainties for all analytes

	Cd (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Sn (mg/kg)	Zn (mg/kg)
Measurement result ± uncertainty*	5.12±0.28	11.94±0.27	64.40±3.61	5.31±0.39	25.72±0.61	39.19±1.27

*k= 2; 95 % confidence level

3.2. Homogeneity and stability of PT samples

The homogeneity and stability tests of the PT samples were performed according to the ISO 13528 standard [18]. The homogeneity of the samples was tested before they were distributed to the PT participants. In this study, ten bottles were randomly selected from among the samples prepared for PT. Two representative samples taken from each ten bottles were digested. Analysis results obtained from the samples were used for the evaluation of homogeneity of the PT sample. The between-samples standard deviation (s_s) was compared with the standard deviation for proficiency assessment (σ). As the value of s_s was lower than or equal to 0.3σ, so the samples were determined to be adequately homogeneous for use in the PT scheme.

The results for homogeneity were calculated according to the Equations 5-11 below and are shown in Table 8.

$x_{t,k}$

where

t represents the samples (t= 1, 2,….,g)

k represents the test portion (k = 1, 2)

$$x_{t,.} = (x_{t,1} + x_{t,2})/2 \quad (5)$$

$x_{t,.}$: the sample average, mg/kg

$x_{t,1}$ and $x_{t,2}$: concentration of analytes in the test portion for replicate 1 and 2, mg/kg

$$w_t = \left| x_{t,1} - x_{t,2} \right| \quad (6)$$

w_t : between test-portion ranges, mg/kg

$$\bar{x}_{.v} = \sum \bar{x}_{t_v} / g \quad (7)$$

$\bar{x}_{.v}$: general average, mg/kg

$\bar{x}_{t_v}$: test portion average, mg/kg

g: number of samples

$$s_x = \sqrt{\sum (x_{t_v} - \bar{x}_{.v})^2 / (g-1)} \quad (8)$$

s_x : standard deviation of sample averages, µg kg^{-1}

$$s_w = \sqrt{\sum w_t^{\,2} / (2g)} \quad (9)$$

s_w : within-samples standard deviation, µg kg^{-1}

$$s_s = \sqrt{s_x^2 - (s_w^2 / 2)} \quad (10)$$

s_s : between-samples standard deviation, µg kg^{-1}

If,

$$s_s \le 0.3\sigma \quad (11)$$

samples are homogeneous.

σ : standard deviation for proficiency assessment

In order to test the stability of the PT samples, three bottles were selected randomly from among homogeneity samples stored at 4 ^{o}C. Selected samples were analyzed triplicate during the PT duration. The general average of the measurements obtained in the homogeneity test ($\bar{x}_{.v}$) was compared with general average of the measurements obtained in the stability test ($\bar{y}_{.v}$) by using Equation (12).

$$\left| \bar{x}_{.v} - \bar{y}_{.v} \right| \le 0.3\sigma \quad (12)$$

$\bar{x}_{.v}$ general average of the measurements obtained in the homogeneity test, mg/kg

$\bar{y}_{.v}$ general average of the measurements obtained in the stability test, mg/kg

The difference between the general average of the measurements obtained in the homogeneity test and in the stability test was lower than 0.3 σ, consequently the samples were deemed adequately stable for use in the PT scheme during the PT period. The results obtained are shown in Table 8.

Table 8. Measurement results and their uncertainties

	Cd (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Sn (mg/kg)	Zn (mg/kg)
s_s	0.033	0.060	1.603	0.014	0.126	0.542
$\left\|\bar{x}_{.v} - \bar{y}_{.v}\right\|$	0.023	0.165	1.001	0.017	0.498	0.658
0.3σ	0.192	0.396	1.653	0.198	0.756	1.083

3.3. Evaluations of the results of participant laboratories

There is no rule for the determination of assigned values of analytes in PT. Generally, in these studies, the preparation of the samples and the calculation of assigned value and standard deviation for PT assessment is done by the TÜBİTAK UME Inorganic Chemistry Laboratory. However, other methods may used for the determination of the assigned values of analytes. If the results submitted by the participants are significantly lower or higher than TÜBİTAK UME results, the median or mean are used as the assigned values of analytes. In this study, the assigned values were determined from the results of the homogeneity and stability studies conducted by TÜBİTAK UME. The Horwitz Equation was used to determine the standard deviation of the proficiency assessment. A z-score for each laboratory was calculated to evaluate the results using the assigned values and standard deviation for the proficiency assessment. Consequently, it can be used to compare the results of analyses obtained by different methods. It is easy to understand and to interpret the z-score. The z-score is calculated by using Equation (13) below [18, 19]:

$$z = \frac{x - X}{\hat{\sigma}} \tag{13}$$

where:

x : participant's result, mg/kg

X : assigned value, mg/kg

$\hat{\sigma}$: standard deviation for proficiency assessment, mg/kg

A common classification based on z-score can be made as following:

$z \leq 2.0$ Satisfactory

$2.0 < z < 3.0$ Questionable

$z \geq 3.0$ Unsatisfactory

The distribution of all results from the participant laboratories are shown in Table 9. The distribution of the participants' results of Cd, Cu, Fe, Pb, Sn and Zn in the PT are given in Figures 1-6. In the figures, green lines are drawn where z-scores equal to 2 and -2 and red lines are drawn where z-scores to 3 and -3.

Table 9. Distribution of all results

	Cd	Cu	Fe	Pb	Sn	Zn
Participant number (n)	6	6	5	6	6	6
Assigned value (mg/kg)	5.12	11.94	64.40	5.31	25.72	39.19
Standard deviation for PT assessment (mg/kg)	0.64	1.32	5.51	0.66	2.52	3.61
Maximum value (mg/kg)	6	11.9	73.7	5.6	77.5	40
Minimum value (mg/kg)	4.36	8.73	51.05	4.01	15.2	23.2
Spike value (mg/kg)	5	9	40	4	25	30

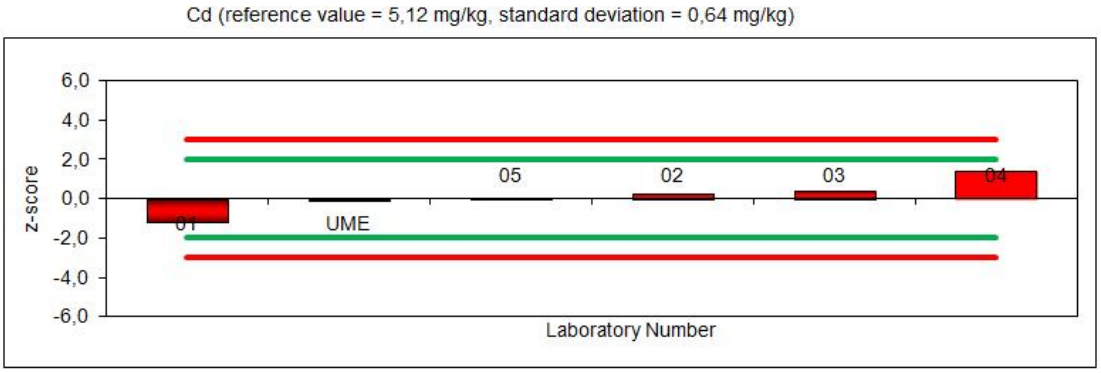

Figure 1. Distribution of Cd results in tomato paste PT scheme

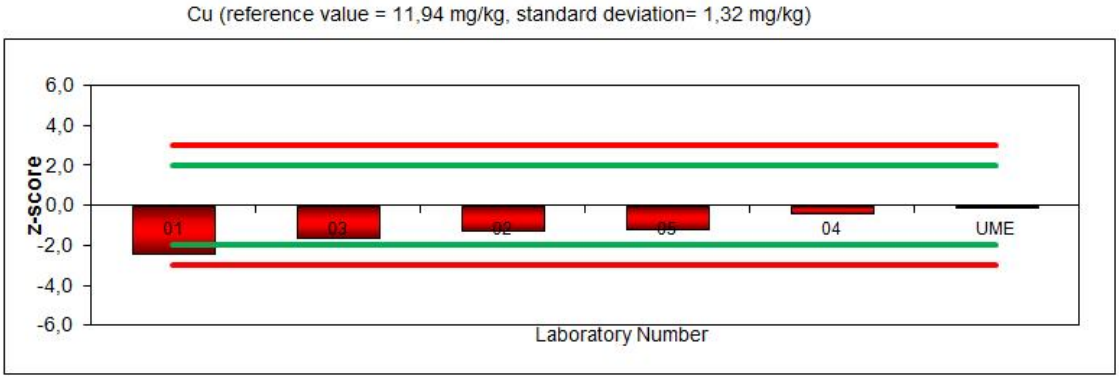

Figure 2. Distribution of Cu results in tomato paste PT scheme

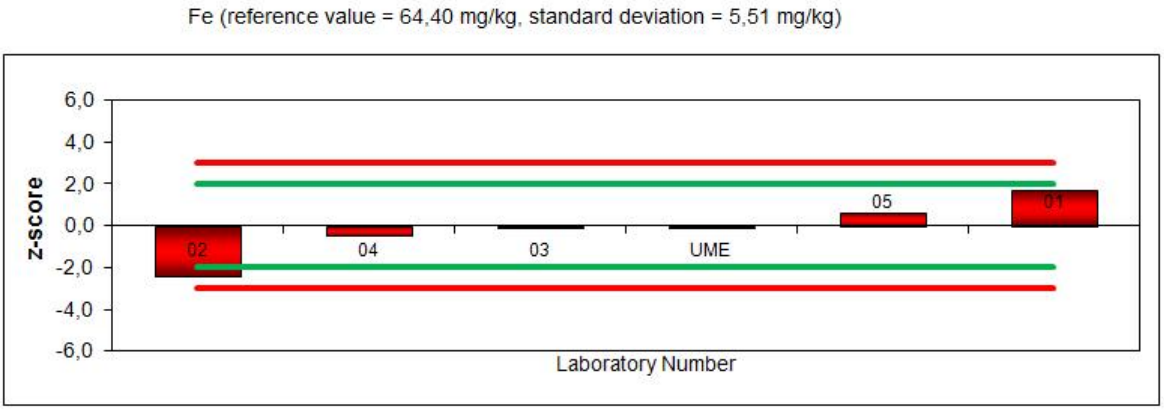

Figure 3. Distribution of Fe results in tomato paste PT scheme

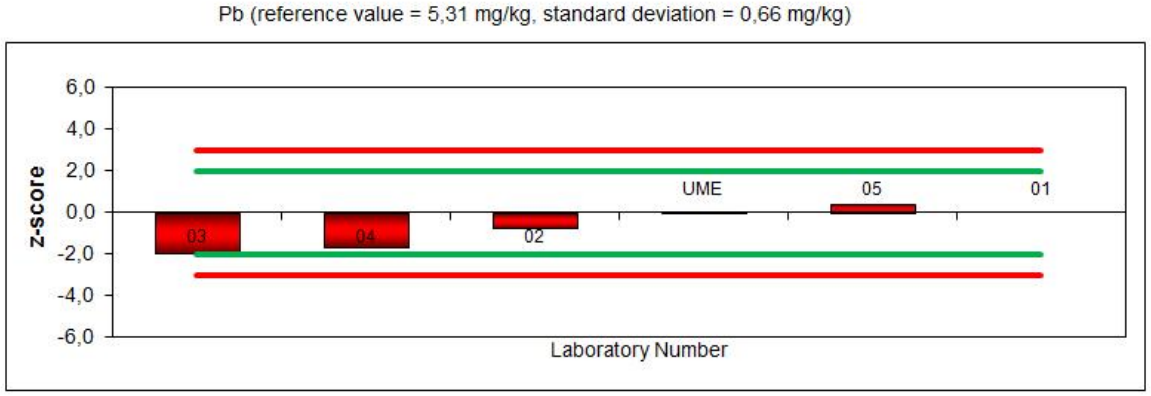

Figure 4. Distribution of Pb results in tomato paste PT scheme

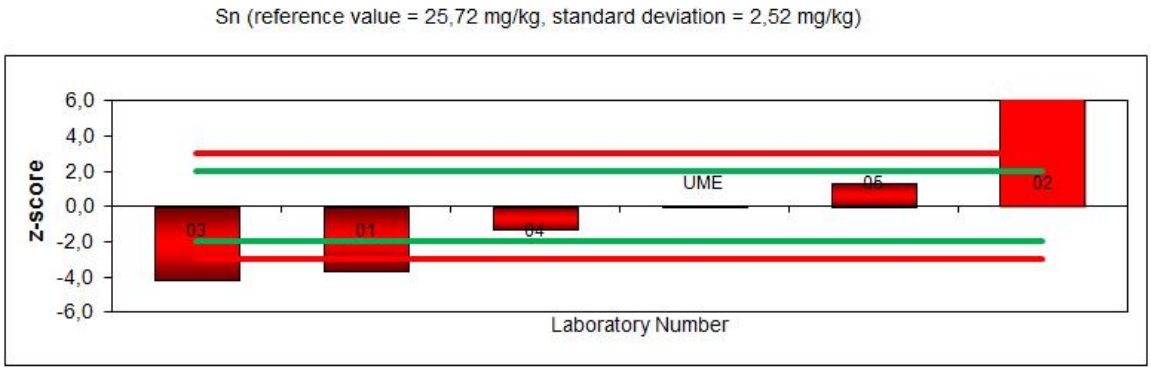

Figure 5. Distribution of Sn results in tomato paste PT scheme

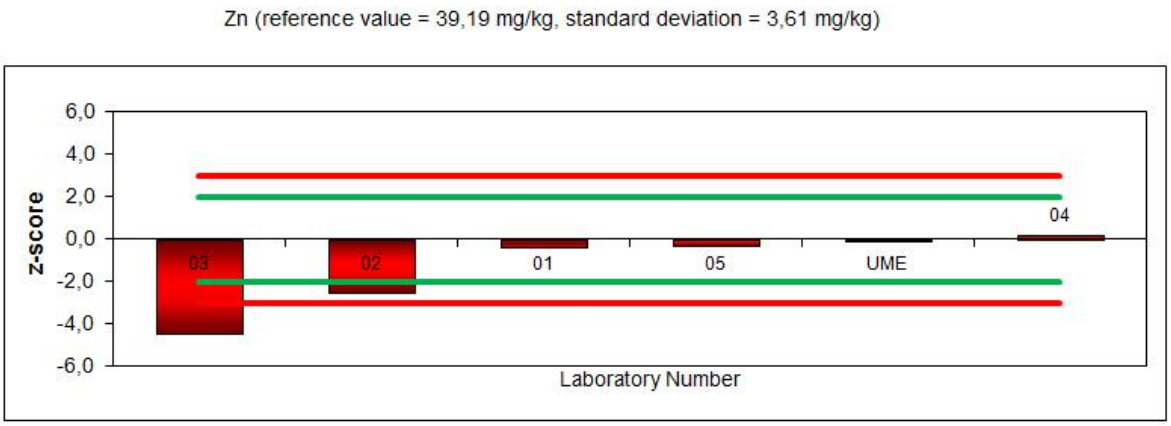

Figure 6. Distribution of Zn results in tomato paste PT scheme

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