codex alimentarius commission

Agenda Item 5b) CX/MAS 06/27/6-Add.1

JOINT FAO/WHO FOOD STANDARDS PROGRAMME

CODEX COMMITTEE ON METHODS OF ANALYSIS AND SAMPLING
Twenty-seventh Session
Budapest, Hungary, 15-19 May 2006

CONVERSION OF THE METHODS FOR TRACE ELEMENTS INTO CRITERIA
(Prepared by Sweden)

BACKGROUND

At the 25th Session of CCMAS it was agreed to initiate the conversion of the methods for trace elements into criteria for consideration in the framework of the Agenda Item on Endorsement.

The 26th Session of CCMAS discussed a document prepared by the NMKL. Several delegations supported this work as it could provide clear guidance that would allow a consistent interpretation of the criteria approach across Codex and assist in selecting appropriately validated analytical methods for monitoring compliance with Codex Standards related to trace elements in foodstuffs, so that Commodity Committees would be aware about the quality of methods.

Some delegations drew the attention of the Committee to the need to clarify the validated range of characteristics and precision of the method, definitions and terminology. It was proposed to clarify under which circumstances the lowest validated level should be no more than 3 times the detection limit. It was also noted that recovery might not be appropriate in trace elements analysis, and therefore this should be reflected in the text.

The Delegation of the United Kingdom indicated that in further revision of the document it was necessary to prepare it in a more descriptive way to provide working instructions for the implementation of the criteria approach and conversion of specific methods of analysis to criteria, as described in the Procedural Manual. The Delegation drew the attention of the Committee to the fact that some already adopted Codex methods would not comply with the criteria proposed for trace elements and that this should be stated in the paper.

The 26th Session of CCMAS agreed that the Working Group chaired by Sweden[1], with NMKL as Rapporteur, working electronically would prepare a revised more descriptive version of the document for consideration by the next Session of the Committee, including the status of the document.

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[1] Argentina, Brazil, European Community, Finland, France, Japan, Netherlands, United Kingdom, United States, IDF, ISO and NMKL.

INTRODUCTION

According to the Procedural Manual (15th ed.) regarding General Criteria for the Selection of Methods of Analysis, it is notified that preference should be given to methods of analysis the reliability of which have been established in respect of the following criteria, selected as appropriate:

    i) Specificity
    ii) Accuracy
    iii) Precision; repeatability, intra-laboratory (within laboratory), reproducibility inter-laboratory (within laboratory and between laboratories)
    iv) Limit of detection
    v) Sensitivity
    vi) Practicability and applicability under normal laboratory conditions
    vii) Other criteria which may be selected as required

Further, methods of analysis which are applicable uniformly to various groups of commodities (horizontal methods) should be given preference over methods which apply only to individual commodities.

The Procedural Manual (15th ed.) states regarding the Conversion of Specific Methods of Analysis to Methods Criteria that: When a Codex Commodity Committee submits a Type II or Type III method to CCMAS for endorsement, it should also submit information on the criteria listed below to enable the CCMAS to convert it into suitable generalized analytical characteristics:

- *accuracy*
- *applicability (matrix, concentration range and preference given to 'general' methods)*
- *detection limit*
- *determination limit*
- *precision; repeatability intra-laboratory (within laboratory), reproducibility inter-laboratory (within laboratory and between laboratories), but generated from collaborative trial data rather than measurement uncertainty considerations*
- *recovery*
- *selectivity*
- *sensitivity*
- *linearity*

The CCMAS will assess the actual analytical performance of the method which has been determined in its validation. **This will take account of the appropriate precision characteristics obtained in collaborative trials which may have been carried out on the method** together with results from other development work carried out during the course of the method development. The set of criteria that

are developed will form part of the report of the CCMAS and will be inserted in the appropriate Codex Commodity Standard. **Analytical methods that has undergone collaborative trials will, however, not automatically be accepted**.

In addition, the CCMAS will identify numeric values for the criteria for which it would wish such methods to comply.

A review of the metal methods referred to in Codex Standards have been carried out. The methods' characteristics, for the selected criteria according to this paper, are listed in table 1 along with the element, method index, method type and commodity of interest. Recommended method criteria for commodities and elements along with the methods already referred to in the Codex system are given in table 2. This includes the methods that comply with the criteria as well as the non-complying methods.

METHODS CRITERIA

The criteria described in this document refer to methods for the determination of the total amount of metal present in the sample.

The sample destruction/digestion removes most, or all, of the organic matrix, leaving only the inorganic residue behind. Certain procedures result in concentrated sample solutions (e.g. ashing, due to the large sample weight), whereas others (e.g. microwave digestion, with small sample weights) in rather dilute sample solutions. This factor has an effect on the detection limit.

Accuracy: (*The closeness of agreement between a test result and the accepted reference value*). Based on results from proficiency tests (PT) and/or repeated use of certified reference materials (CRMs). For PT-results a z-score[1] $\leq \pm 2$ is satisfactory. Z-scores between ± 2 and 3 are questionable. For CRM-results, when

used in a collaborative test of the method, a z-score $\leq \pm 2$ is normally satisfactory. Higher z-scores can be accepted, provided that the relative difference between the mean content of the certified material and the experimentally determined mean are within ±10%.

Trueness: (*The closeness of agreement between the average value obtained from a series of test results and an accepted reference value*). Applicable when more than one result is available from e.g. PT-tests.

Applicability: All foods[2].

Selectivity (specificity): Matrix, spectral, isobaric and/or polyatomic interferences are fully compensated for.

Detection limit[3] (LOD)-1 General: The mean plus three times the standard deviation (σ), for the field blank or a standard solution with a concentration near the LOD. Based on ≥ 20 blanks (EN 13804)

Detection limit (LOD)-2 When maximum limits (ML) are defined: No more than 1/5 of specified ML below 0.1 mg/kg, and no more than 1/10 of specified ML above 0.1 mg/kg.

Recovery: 100 %, allowing for measurement uncertainty (MU). Recoveries[4] (based on spiked sample solutions) that are systematically lower or higher than 100% ± MU (usually ±10%) indicate analytical problems with the method. Such problems must be rectified before further use of the method, or another method selected.

The validated range of the method: The validated range should be relevant for the purpose of the analysis and as wide as possible. The lowest validated level should preferably be no more than 3 times the LOD, which approximates the Determination Limit as described in the procedural manual.

Precision of the method: Relative reproducibility standard deviation (RSD_R):

The RSD_{OR} which is calculated from the Horwitz equation ($2C^{-0.1505}$) for a given concentration provides a basis with which the found RSD_R can be compared, e.g.:

For levels of 10^{-5} (10 mg/kg), $RSD_R = 11\%$
For levels of 10^{-6} (1 mg/kg), $RSD_R = 16\%$
For levels of 10^{-7} (0.1 mg/kg), $RSD_R = 23\%$
or levels $< 10^{-7}$ (<0.1 mg/kg), RSD_R = As low as possible

The Horwitz ratio, "HorRat" (RSD_R/ RSD_{OR}) should be ≤ 2

Relative repeatability standard deviation (RSD_r):

RSD_r should be smaller than RSD_R. The usual approximation is that RSD_r is 67% of the RSD_R.

The RSD_R and HorRat values should preferably be estimated from results of collaborative studies.

SELECTION OF METHOD CRITERIA

Method criteria should be based on the need, i.e. fitness for purpose. Setting very strict criteria may have the result that all available methods are unacceptable. In the analysis of trace elements the major problems are usually encountered at very low concentrations, due to contamination and analytical interferences, whereas at very high concentrations the sample solutions are simply diluted, which, in addition, reduces interferences. In other types of analysis the situation can be very different. The method criteria regarding precision should be assigned based on the need and the purpose of the analysis.

In analytical techniques where one or several extraction steps are included the recovery is an important criterion. Methods for the determination of the total amount of elements usually do not include extraction steps, therefore the recovery is not a relevant criterion.

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[1] Z-score is calculated as $z == \dfrac{(\overline{X}_{found} - \overline{X}_{certified})}{\sqrt{\dfrac{SD^2_{found}}{n_{found}} + \dfrac{SD^2_{certified}}{n_{certified}}}}$ as described in NMKL Procedure no. 9, 2002

[2] Foods with a fat content >30%, or pure fats and oils, may require specific methods.
[3] Determination limit: As for detection limit except that 6 or 10 is required rather than 3.
[4] It is recommended that recovery is used with caution in methods such as the determination of the total amount of a metal and where no extraction step is employed. A recovery may seemingly be acceptable, but on false grounds. Likewise, a recovery that is found to be too low, may also be established but on erroneous grounds.

Table 1 serves as an example to illustrate the process of selecting/finding a method that concur with a set of fitness for purpose criteria.

Table 1.

Commodity: Milk Purpose of the investigation, Determination of lead at levels below 0.05 mg/kg	
Requested methods criteria	*Method to which criteria are applicable*
	Method: AOAC 999.10 Determination of Cd, Pb, Cu, Fe and Zn in foods by AAS after microwave digestion (except fats and oils). **Samples in the collaborative test:** Bovine muscle (NIST CRM), Liver, Fish Wheat bran, Mushroom (NFA CRM) Diets E & F (NFA CRMs)
Selectivity: Matrix effects compensated for	Background correction applied
Detection limit (3 x σ): <0.01 mg/kg	0.003 mg/kg
Validated range, measuring range, 0.02 –0.1 mg/kg	$\geq$0.01 mg/kg (0.0124 – 0.768 mg/kg)
Precision RSD_r: <20%	15 – 4.6%
Precision RSD_R: < 30%	28 – 11%
Accuracy (agreement single-certified values)	-
Trueness (agreement mean-certified values based on z-scores using CRMs); z-score <2	Mean 1.3 (-0.1 1.5 1.7 2.2)
Recovery	Not relevant
HorRat: <2	0.6 - 1.0

In cases where a food commodity has been assigned a very low maximum permitted level (ML) it may be very important to set the criterion for the limit of detection accordingly. In the EU the ML for lead in milk is 0.020 mg/kg. According to methods criteria, this would require a method with a limit of detection of 0.004 mg/kg, which many laboratories would have difficulties to match. Edible offal and crustaceans have a ML of 0.5 mg/kg, at which level the analysis is much less demanding.

The HorRat value is a well known tool for evaluating the obtained RSD_R. Generally a HorRat value below 2, or even 1.5, is achievable by most methods for determination of metals in food. However, the estimation of the HorRat value is based on a generalisation and therefore not absolutely true. In trace element analysis there may be differences due to type of instrumentation. The determination of e.g. lead by AAS usually results in a higher uncertainty than the determination of cadmium. At levels below 0.12 mg/kg, *the applicability of the Horwitz Ratio may depend on analyte. For, e.g., lead it is probably not fully applicable, whereas for, e.g., mycotoxins it is applicable. Applying the Thompson equation which states that for concentrations <0,12 mg/kg the RSD is 22% would probably reduce the number of acceptable methods to a minimum.* These factors must be taken into consideration when the HorRat criterion is discussed.

Table 2

Commodity: Fish muscle Purpose of the investigation: Determination of lead at a level 0.4 mg/kg	
Requested methods criteria	*Method to which criteria are applicable*
	AOAC 986.15 (Codex general method). Determination of Cd, Pb, Cu, Fe and Zn in foods by AAS after microwave digestion (except fats and oils). **Samples used in the collaborative test:** Chicken, Apple
Selectivity: Matrix effects compensated for	Specificity good (ASV-method)
Detection limit (3 x σ): ≤0.04 mg/kg	0.03 mg/kg
Validated range, measuring range, 0.1 –1 mg/kg	0.03 – 2.8 mg/kg
Precision RSD_r: ≤15%	98 - 10%
Precision RSD_R: ≤ 20%	106 - 17%
Accuracy (agreement single-certified values)	-
Recovery	>90%
HorRat: <2	-

Accuracy (trueness) is a crucial criterion, as it is the only factor that gives an objective view of the method bias. This can be established in the collaborative study of a method using CRMs with the concentration of the analyte unknown to the analyst at the time of the analysis. The accuracy can also be estimated from results obtained in PT-schemes, using z-scores. A method for the calculation of the bias, based on the z-score is described in NMKL Procedure No. 9, 2002.

It is possible that other analytical techniques may require additional, or other, criteria to those listed in this paper.

In Table 3 the Codex methods for trace elements and heavy metals are arranged into groups according to the selected methods criteria. The methods have also been divided into Complying or Non-complying with basic validation requirements, depending on their methods characteristics.

REFERENCES

Recommended Method of Analysis and Sampling – Codex stan 234-1999.

General Codex Methods for Contaminants -Codex standard 228-2001, Rev.1 2004.

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Codex Alimentarius Commission Procedural Manual, 14th Ed., FAO, ROME, 2004

NMKL Procedure No. 9 (2002). Evaluation of Results Derived from the Analysis of Certified Reference Materials. The Nordic Committee on Food Analysis.

NMKL Procedure No. 4 (2005). Validation of Chemical Analytical Methods. The Nordic Committee on Food Analysis.

EN 13804. 2002. Foodstuffs – Determination of trace elements. Performance criteria, general considerations and sample preparation. European Committee for Standardisation. B-1050 Brussels

Table 31. Methods criteria and methods of analysis for metals, in the Codex system

Element	Applica-bility	Method Criteria	Complying Codex methods and characteristics	Type	Non-complying codex methods and characteristics	Type
Arsenic	All foods	Selectivity: All known interferences compensated for. Measuring range: 0,02 – 2 mg/kg (RSD: 30% – 15%.) HorRat: ≤1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0.02 mg/kg (Recovery: not relevant) Accuracy (bias):			AOAC 986.15 (Codex general method) Food and feed (tested on chicken, apple) Assessed level: 0.017-1.9 mg/kg Detection limit: 0.02 mg/kg RSDr (%): 9-55 RSDR(%): 15-147 HorRat: <1.5 (except for the lowest assessed level which is below detection limit) (Recovery: >90%) Specificity: excellent (*insufficient number of test materials*) ICUMSA GS2/3-25 (1994) (*Not collaboratively validated*)	III II IV
Arsenic	Salt	Selectivity: All known interferences compensated for. Measuring range: 0,005 – 0.5 mg/kg (RSD: 30% – 10%.) HorRat: ≤1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: (Recovery: not relevant) Accuracy (bias):			ESPA/CN-E/105-1996 rock salt, vacuum salt, sea salt) (greater than 0.1 mg/kg) Assessed level: 0.005-0.024 mg /kg Detection limit: RSDr (%): 87,5-430 RSDR(%): 210-680 HorRat: not applicable for so low concentrations. Specificity: 1996 Vertical method (*Assessed level lower than the level of applicability, large RSD*)	II
Cadmium	All foods	Selectivity: All known interferences	NMKL 139 (1991) AOAC 999.11 Applicability: foods (excl. fats and	II		

Element	Applica-bility	Method Criteria	Complying Codex methods and characteristics	Type	Non-complying codex methods and characteristics	Type
		compensated for. Measuring range: 0,01 – 1 mg/kg (RSD: 30% – 10%.) HorRat: <1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0.05 mg/kg (Recovery: not relevant) Accuracy (bias):	oils) Assessed level: 0.19-0.53 mg/kg Detection limit: 0.003 mg/kg RSDr (%): 14-17 RSDR (%): 18-21 HorRat: < 1.5 (Recovery: > 90%) Specificity: excellent NMKL 161 (1998) AOAC 999.10 Applicability: foods (excl. fats and oils) Assessed level: 0.012 – 0.76 mg/kg Detection limit: 0.003 mg/kg RSDr(%): 4.6-15 RSDR(%): 11-20 HorRat: < 1.5 (Recovery: > 90%) Specificity: excellent	III		
Cadmium	Salt	Selectivity: All known interferences compensated for. Measuring range: 0,01 – 1 mg/kg (RSD: 30% – 10%.) HorRat: <1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0.05 mg/kg (Recovery: not relevant) Accuracy (bias):			ESPA/CN-E/107-1997 Applicability: equal to or greater than 0.05 mg Cd per kilogram of salt Assessed level: 0.001-0.011 mg/kg Detection limit: RSDr(%): 20-540 RSDR(%): 93-1040 HorRat: not applicable for so low concentrations Specificity: Vertical method (assessed level lower than the level of applicability), Large RSD	III
Cadmiu	Water	Selectivity: All	ISO 8288-1986	III	AOAC 986.15	III

Element	Applica-bility	Method Criteria	Complying Codex methods and characteristics	Type	Non-complying codex methods and characteristics	Type
m		known interferences compensated for. Measuring range:0,004 – 0,1 mg/kg RSD: 50% - 5%. HorRat: ≤1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0.001 mg/kg (Recovery: not relevant) Accuracy (bias):	Applicability: water 0.004-0.0302 mg/L Detection limit: RSDr(%): 2.3-7.5 RSDR(%): 4.3-10 HorRat: < 1.5 Specificity: excellent AOAC 974.27 Applicability: water 0.010-0.100 mg/L Detection limit: RSDr(%): RSDR(%): 8-61 HorRat: < 2 Recovery: 72-103,4% Specificity: excellent	III	*(insufficient study material)*	
Copper	All foods	Selectivity: All known interferences compensated for. Measuring range: 0,1 – 100 mg/kg (RSD: 20% – 1.5%.) HorRat: ≤1.5 LOD: 0.1 mg/kg (Recovery: not relevant) Accuracy (bias):	NMKL 139 (1991) AOAC 999.11 Applicability: foods (excl. fats and oils) Assessed level: 7.1-45 mg/kg Detection limit: 0.1 mg/kg RSDr(%): 3.5 – 20 RSDR(%): 11-22 HorRat: < 1.5 (Recovery: > 90%) Specificity: excellent NMKL 161 (1998) AOAC 999.10 Applicability: foods (excl. fats and oils) Assessed level: 0.254-107 mg/kg Detection limit: 0.09 mg/kg RSDr(%): 1.5-7.2	II III	AOAC 971.20(Codex general method) Applicability: all foods (*tested for tea only*) Assessed level: 5 - 194 mg/L Detection limit: 0.5 mg/L RSDr: RSDR (%): 9-18 HorRat > 1.5 (Recovery: > 90%) Specificity: good (*insufficient number of test materials*)	II III*

Element	Applica-bility	Method Criteria	Complying Codex methods and characteristics	Type	Non-complying codex methods and characteristics	Type
		Selectivity: All known interferences compensated for. Measuring range: 1 – 10 mg/kg (RSD: 15% –5%.) HorRat: ≤1.5 LOD: 0.05 mg/kg (Recovery: not relevant) Accuracy (bias):	RSDR(%): 3.0-28 HorRat: < 1.5 (Recovery: > 90%) Specificity: excellent AOAC 985.35 Applicability: *all foods and feed* Assessed level: 0.56-4.76 mg/kg Detection limit: 0.05 mg/kg RSDr (%): 4.8-7.0 RSDR(%): 4.8-13 HorRat: < 1.5 (Recovery: > 90%) Specificity: excellent	III*		
Copper	Fats and oils	Selectivity: All known interferences compensated for. Measuring range: 0,03 – 0,15 mg/kg (RSD: 15% – 5%.) HorRat: ≤1.5 LOD: 0.01 mg/kg (Recovery: not relevant) Accuracy (bias):	AOAC 990.05 ISO 8294:1994 IUPAC 2.631 AOCS Ca 18b-91(03) (Codex general method) Applicability: Fats and oils Assessed level: 0.03- 0.15 mg/kg Detection limit: 0.01 mg/kg RSDr(%): 5.4 – 15 RSDR(%): 15-21 HorRat: < 1.5 (Recovery: > 90%) Specificity: Excellent	II	AOAC 971.20(Codex general method) Applicability: all foods (*tested for tea only*) Assessed level: 5 - 194 mg/L Detection limit: 0.5 mg/L RSDr: RSDR (%): 9-18 HorRat > 1.5 (Recovery: > 90%) Specificity: good (*insufficient number of test materials*)	II III*
Copper	Water	Selectivity: All known interferences compensated for. Measuring range:0,005 – 0,1	ISO 8288:1986 (confirmed 1995) Applicability: Water 0.0057-0.041 mg/L Detection limit: RSDr (%): 3.5-8.0	III*		

Element	Applica-bility	Method Criteria	Complying Codex methods and characteristics	Type	Non-complying codex methods and characteristics	Type
		mg/kg RSD: 10% - 2%. HorRat: ≤1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0,002 mg/kg (Recovery: not relevant) Accuracy (bias):	RSDR(%): 12-17 HorRat: < 1.5 (Recovery: > 90%) Specificity: excellent			
Iron	All foods	Selectivity: All known interferences compensated for. Measuring range: 1 – 500 mg/kg (RSD: 50% – 5%.) HorRat: ≤1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0,05 mg/kg (Recovery: not relevant) Accuracy (bias):	NMKL 139 (1991) AOAC 999.11 Applicability: foods (excl. fats and oils) Assessed level: 3.8-212 mg/kg Detection limit: 0.8 mg/kg RSDr(%): 8.2-12 RSDR(%): 11-12 HorRat: < 1.5 (Recovery: > 90%) Specificity: excellent NMKL 161 (1998) AOAC 999.10 Applicability: foods (excl. fats and oils) Assessed level: 3.3 –484 mg/kg Detection limit: 0.05 mg/kg RSDr(%): 4.2 – 5.6 RSDR(%): 5.7 – 47 HorRat: <1.5 (Recovery: >90%) Specificity: excellent	II III	IFJU Method No 15, 1964 (*No da*ta) IDF 103A: 1986 (*No validation data*) ISO 6732: 1985 (*No validation data*)	III*
Iron	Fats and	Selectivity: All known interferences	AOAC 990.05 ISO 8294:1994 IUPAC 2.631 AOCS Ca 18b-91(03)	II	BS 684 Section 2.17: 1976 *(No data)*	*III*

Element	Applica-bility	Method Criteria	Complying Codex methods and characteristics	Type	Non-complying codex methods and characteristics	Type
	oils	compensated for. Measuring range: 0,1 – 1 mg/kg (RSD: 30% – 10%.) HorRat: ≤1.5 LOD: 0.05 mg/kg (Recovery: not relevant) Accuracy (bias):	(Codex general method) Applicability: fats and oils Assessed level: 0.13-0.96 mg/kg Detection limit: 0.05 mg/kg RSDr(%): 6.2-21 RSDR(%): 19-27 HorRat: <1.5 (Recovery: > 90%) Specificity: excellent			
Lead	All foods	Selectivity: All known interferences compensated for. Measuring range: 0,005 – 2 mg/kg (RSD: 50% – 15%.) HorRat: ≤2.0 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0.005 mg/kg (Recovery: not relevant) Accuracy (bias): Trueness: Z-score ≤2	NMKL 139 (1991) AOAC 999.11 Applicability: foods (excl. fats and oils) Assessed level: 0.045-0.25 mg/kg Detection limit: 0.006 mg/kg RSDr (%): 26-40 RSDR(%): 26-40 HorRat: <1.6 (Recovery: > 80%) Specificity: excellent	II	IDF 133A:1992 To be checked	III
			NMKL 161 (1998) AOAC 999.10 Applicability: foods (excl. fats and oils) Assessed level: 0.005-1.62 mg/kg Detection limit: 0.014-0.055 mg/kg RSDr(%): 16-57 RSDR(%): 16-59 HorRat: < 1.5 Recovery: > 90% Specificity: excellent Trueness: Z-scores -0.1 – +2.2	III		
		Selectivity: All			AOAC 986.15 Applicability: all foods and feed (*tested on chicken and apple*)	II

Element	Applica-bility	Method Criteria	Complying Codex methods and characteristics	Type	Non-complying codex methods and characteristics	Type
		known interferences compensated for. Measuring range: 0,03 – 3 mg/kg (RSD: 30% – 20%.) HorRat: ≤1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0.03 mg/kg (Recovery: not relevant) Accuracy (bias):			Assessed level: 0.03-2.8 mg/kg Detection limit: 0.03 mg/kg RSDr(%): 10-98 RSDR(%): 17 –106 HorRat: 1.2-3.9 (HorRat value above 1.5 for assessed level close to the detection limit) (Recovery: > 90%) Specificity: Good (*insufficient study material*) AOAC 972.25 (Codex general method) Applicability: all foods Assessed level: 2.2 – 29 mg/kg Detection limit: RSDr(%): ~ 9 RSDR(%):~ 5 - 35 HorRat: < 2 for most materials Recovery: > 97% Specificity: excellent (*Assessed levels higher than the measuring range*)	II III*
Lead	Fats and oils	Selectivity: All known interferences compensated for. Measuring range: 0,01 – 0.1 mg/kg (RSD: 50% – 15%.) HorRat: ≤2.0 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0.03 mg/kg	IUPAC Method (Pure and Appl. Chem. 63, 1191-1198) Applicability: fats and oils Assessed level: 0.02-0.09 mg/kg Detection limit: 0.03 mg/kg RSDr(%): 4.5-10 RSDR(%): 10-28 HorRat: <1.5 (Recovery: > 95%) Specificity: excellent	III		

Element	Applica-bility	Method Criteria	Complying Codex methods and characteristics	Type	Non-complying codex methods and characteristics	Type
		(Recovery: not relevant) Accuracy (bias):	AOAC 994.02 IUPAC 2.623 ISO 12193:1994 (2004) AOCS Ca 18c-91(03) (Codex general method Applicability: edible oils and fats Assessed level: 0.018-0.090 mg/kg Detection limit: 0.05 mg/kg RSDr(%): 3.5-11 RSDR(%): 5.9-30 HorRat: <1.1 (Recovery: > 95%) Specificity: excellent	II		
Lead	Salt	Selectivity: All known interferences compensated for. Measuring range: 0,025 – 0.808 mg/kg (RSD: 100% – 15%.) HorRat: $\leq$2.0 (This may not be valid for concentrations below 0.1 mg/kg) LOD: (Recovery: not relevant) Accuracy (bias):			ESPA/CN-E/108-1994 Applicability: equal to or greater than 0.5 mg Pb per kilogram of salt Assessed level: 0.025-0.808 mg/kg Detection limit: RSDr(%): 19-193 RSDR(%): 51-626 HorRat = 35 (calculated for the highest validated level (0.808 mg/kg) Specificity: (**Large RSDs Horrat >>2**)	III
Lead	Water	Selectivity: All known interferences compensated for. Measuring range:0,01 – 1 mg/kg RSD: 30% - 5%.	ISO 8288:1986 (confirmed 1995) Applicability: water Assessed level: 0.0197-0.977 mg/L Detection limit: RSDr(%): 1.1-3.8 RSDR(%): 2.8-4.2 (surprisingly	III*		

		HorRat: ≤1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0.005 mg/kg (Recovery: not relevant) Accuracy (bias):	good) HorRat: <1.5 (Recovery: > 95%) Specificity: excellent AOAC 974.27 Applicability: water Assessed level: 0.05-0.20 mg/L RSDr(%): RSDR(%): 30-76 HorRat: 3.0-3.7 (Recovery: > 84%) Specificity: excellent (check the reference again)	III		
Lead	Sugar, syrup	Selectivity: All known interferences compensated for. Measuring range:0,01-0,5 mg/kg RSD: >20% - 15%. HorRat: ≤1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0.05 mg/kg (Recovery: not relevant) Accuracy (bias):			AOAC 997.15 Applicability: sugars & syrup (sucrose and fructose) Assessed level: 0.100 mg/kg Detection limit: 0.05 mg/kg RSDr(%): 2.7-6.5 RSDR(%): 14-19 HorRat: <1.5 Recovery: Specificity: excellent (*Assessed level too limited. Method vertical*)	III*
Mercury	Fish	Selectivity: All known interferences compensated for. Measuring range:0,2 – 1 mg/kg RSD: 50% - 5%. HorRat: ≤1.5 LOD: 0.05 mg/kg (Recovery: not	AOAC 977.15 Applicability: fish Assessed level: 0.275-0.944 mg/kg Detection limit: 0.05 mg/kg RSDr (%): RSDR (%): 4-49 HorRat: 0.24-2.5 Recovery: >90% Specificity: excellent	III		

		relevant) Accuracy (bias):				
Mercury	Salt	Selectivity: All known interferences compensated for. Measuring range: 0.003-0.0,1 mg/kg (RSD: 100% – 50%.) HorRat: (This may not be valid for concentrations below 0.1 mg/kg) LOD: (Recovery: not relevant) Accuracy (bias):			ESPA/CN-E/106-1994 Applicability: salt with Hg content equal to or greater than 0,020 mg/ kg Assessed level: 0.0033-0.0,0060 mg/kg Detection limit: RSDr(%): 64-84 RSDR(%): 346-389 HorRat = not applicable for so low concentrations. Specificity: (Assessed level lower than the level of applicability, large RSD)	II
Mercury	Water	Selectivity: All known interferences compensated for. Measuring range:0,3 – 3 mg/kg RSD: 80% - 30%. HorRat: ≤1.5 LOD: 0.2 mg/kg (Recovery: not relevant) Accuracy (bias):	AOAC 977.22 Applicability: drinking surface and saline waters Assessed level: 0.28-3.7 ug /L Detection limit: 0.2 ug/L RSDr: RSDR(%): 29-79 HorRat: <1.5 (Recovery: > 85%) Specificity: excellent	III		
Tin	Canned food	Selectivity: All known interferences compensated for. Measuring range:50-250 mg/kg RSD: 20% - 5%. HorRat: ≤1.5 LOD: 10 mg/kg	AOAC 985.16 (Codex general method) Applicability: canned foods Assessed level: 50-250 mg/kg Detection limit: 10 mg/kg RSDr(%): 2.2 –12 RSDR(%): 3.3-15 HorRat: < 1.5	II		

		(Recovery: not relevant) Accuracy (bias):	(Recovery: > 95%) Specificity: excellent				
Zinc	All foods	Selectivity: All known interferences compensated for. Measuring range: 5-200 mg/kg (RSD10% – 2%.) HorRat: ≤1.5 (This may not be valid for concentrations below 0.1 mg/kg) LOD: 0.1 mg/kg (Recovery: not relevant) Accuracy (bias):	NMKL 139 (1991) AOAC 999.11 Applicability: all foods (excl. fats and oils) Assessed level: 6.6-37 mg/kg Detection limit: 0.06 mg/kg RSDr(%): 4.3-5.1 RSDR(%): 4.3-5.3 HorRat: < 1.5 (Recovery: > 80%) Specificity: excellent	II	AOAC 986.15 (Codex general method) Applicability: all food and feeding stuff (tested on chicken and apple) Validated range: 0.06 mg/kg (one level only) Detection limit: 0.06 mg/kg (*Insufficient study material , validated for one level only (the detection limit)*)	III
			NMKL 161 (1998) foods (excl. fats and oils) Assessed level: 4.45-181.9 mg/kg Detection limit: 0.002 mg/kg RSDr (%): 1.6-4.0 RSDR(%): 1.7-9.7 HorRat: <1.5 (Recovery: >90%) Specificity: excellent	III		
			AOAC 969.32 (Codex general method) Applicability: all foods Assessed level: 5.0-60 mg/kg Detection limit: 0.5 mg/kg RSDr: RSDR(%): 1.6-12 HorRat: <1.5 (Recovery: > 90%) Specificity: excellent	III *		

- In CODEX STAN 234-1999, these methods are type II methods, however, according to Codex stan 228-2001, Rev.1 2004, these methods becomes type III.