codex alimentarius commission

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

WORLD HEALTH ORGANIZATION

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Agenda Item 5b) **CX/MAS 05/26/7-Add.1**

JOINT FAO/WHO FOOD STANDARDS PROGRAMME

CODEX COMMITTEE ON METHODS OF ANALYSIS AND SAMPLING
Twenty-sixth Session
Budapest, Hungary, 4 – 8 April 2005

CONVERSION OF THE METHODS FOR TRACE ELEMENTS INTO CRITERIA

(prepared by the Nordic Committee on Food Analysis, NMKL)

INTRODUCTION

At the 25th Session of the Codex Committee on Methods of Analysis and Sampling 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.

According to the Procedural Manual regarding General Criteria for the Selection of Methods of Analysis, it is recommended that preference should be given to methods of analysis whose reliability has 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 should be given preference over methods which apply only to individual commodities.

Based on the Codex documents listed in the list of References (p. 3), the Nordic Committee on Food Analysis, NMKL, with the assistance of ISO, has collected information on method characteristics of the trace element methods recommended by Codex.

THE CRITERIA - METHOD CHARACTERISTICS

Reviews of a number of methods for trace elements referred to in Codex Standards have been carried out. The characteristics are listed in the enclosed table along with the element, method, method type and commodities of interest. The following criteria, method characteristics, have been evaluated:

Applicability: Which matrices the method is applicable to. If very few matrices have been included in the study, these are given in parenthesis in the table.

Validated range: The range of concentrations measured in the collaborative study. The method is usually applicable to a considerably wider concentration range than the validated range.

Detection limit: Defined as $+3\sigma$ of the mean field blank signal where σ is the standard deviation.

Repeatability: Given as the relative standard deviation, RSD_r, describing the variation within laboratories.

Reproducibility: Given as the relative standard deviation, RSD_R, describing the variation within and between laboratories.

HorRat: Dr. W. Horwitz established the Horwitz trumpet and the equation $RSDo_R = 2^{(1-0,5\log C)} = 2C^{-0,1505}$ where C is the concentration ratio (e.g. 5 mg/kg, C = 0.000005= $5 \cdot 10^{-6}$). The Horwitz function is a useful estimate of the expected reproducibility standard deviation at concentration ratio above 10^{-7}. For lower concentration, the $RSDo_R$ = 22%. The HorRat value is RSD_R /$RSDo_R$.

Specificity: The freedom from uncompensated matrix or spectral interference effects. It reflects the ability of the instrumentation to measure only the signal of the determined analyte.

The method characteristics are not established for *Withdrawn* or *Surplus Methods,* which are methods thought not to be in current use for various reasons, such as the purpose for which the method was developed no longer exists, the product for which the method was developed is no longer marketed or the method has been replaced by other methods. The table includes only methods listed in Codex Stan 234-199 and 228-2001, respectively, there are however other suitable official methods and standards for determination of trace elements.

CONCLUSION AND RECOMMENDATIONS

A study of the method characteristics for a number of methods for determination of trace elements shows that the specificity of the methods is excellent (few interferences) and the precisions satisfying for concentration levels about 5 times the detection limits. Generally the methods have acceptable accuracy and are applicable to a wide range of foods. Thus the following criteria could be recommended for a method for determination of trace elements in foodstuffs:

Applicability:	The method should be applicable to a wide range of foodstuffs and hence been studied for more than a few matrices.
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 detection limit.
Detection limit:	No more than 1/5 of specified maximum limits below 0.1 mg/kg, and no more than 1/10 of specified maximum limits above 0.1 mg/kg.
Precision of the method:	HorRat < 2; For levels of ~ 10 mg/kg, $RSD_R \approx 10\%$ For levels of ~ 1 mg/kg, $RSD_R \approx 15\%$ For levels of ~ 0.1 mg/kg, $RSD_R \approx 20\%$ For levels of lower than 0.1 mg/kg, $RSD_R \approx 22\%$ RSR_r should be smaller than RSD_R. The RSD_R and HorRat values should preferably be estimated from results of collaborative studies.
Specificity	No uncompensated matrix or spectral interferences permitted.

REFERENCES

1. Recommended Method of Analysis and Sampling – Codex stan 234-1999.
2. General Codex Methods for Contaminants - Codex stan 228-2001, Rev.1 2004.

3. CX/MAS 98/5 Criteria of Evaluating Acceptable Methods of Analysis for Codex Purposes prepared by the United Kingdom and Canada.
4. Report of the 27th Session of the Codex Committee on Methods of Analysis and Sampling. ALINORM 04/27/23.
5. Codex Alimentarius Commission Procedural Manual, 14th Ed., FAO, ROME, 2004
6. M. Thompson, Analyst, 2000, 125, 385-386

Provision	*Commodity Standards*	*Method*	*Principle*	*Type*	*Method Characteristics*
Arsenic	Cocoa products and chocolate Fruit juices Honey Sugars Vinegar Fats and oils	AOAC 952.13 IUPAC 3.136 (Codex general method)	Colorimetry (diethyldithiocarbamate)	II III	- *the AOAC method surplus in 1993*
Arsenic	Fats and oils Fruit juices	AOAC 942.17 (Codex general method)	Colorimetry (molybden blue)	III	- *the AOAC method surplus in 1993*
Arsenic	Fruit juices Natural mineral waters Fats and oils	AOAC 986.15 (Codex general method)	AAS after generation of metal hydrides	III II	Applicability: foods and feeding stuff (tested on chicken, apple) Validated level: 0.017-1.9 mg/kg Detection level: 0.02 mg/kg RSDr (%): 9-55 RSDR(%): 15-147 (the very high RSDR is for the validated level below the detection level) HorRat: <1.5 (except for the lowest validated level which is below detection level) Specificity: excellent
Arsenic	Food grade salt	ESPA/CN-E/105-1996	Photometry	II	References/method are requested from ESPA
Arsenic	Natural mineral waters	ISO 6595:1982 (confirmed 1995)	Spectrophotometry	IV	- *the ISO method is withdrawn*
Arsenic	Sugars	ICUMSA GS2/3-25 (1994)	Colorimetry (diethyldithiocarbamate)	IV	Not collaboratively validated – data unavailable
Cadmium	All foods except fats and oils	NMKL 139 (1991) AOAC 999.11	AAS after dry ashing	II	Applicability: all foods (incl. fats and oils) Validated level: 0.19-0.53 mg/kg Detection level: 0.003 mg/kg RSDr (%): 14-17 RSDR (%): 18-21 HorRat: < 1.5 Specificity: excellent
Cadmium	All foods except fats and oils	NMKL 161 (1998) AOAC 999.10	AAS after microwave digestion	III	Applicability: all foods except fats, oils and fatty products Validated level: 0.0124 – 0.764 mg/kg

Provision	*Commodity Standards*	*Method*	*Principle*	*Type*	*Method Characteristics*
					Detection level: 0.003 mg/kg RSDr(%): 4.6-15 RSDR(%): 11-20 HorRat: < 1.5 Specificity: excellent
Cadmium	Food grade salt	ESPA/CN-E/107-1997	AAS	III *	References/ method are requested
Cadmium	Natural mineral waters	ISO 8288-1986	AAS	III	Applicability: water Validated level: 4.0–30.2 ug/L (0.004-0.0302 mg/L) Detection level: RSDr(%): 2.3-7.5 RSDR(%): 4.3-10 HorRat: < 1.5 Specificity: excellent
Cadmium	Natural mineral waters	AOAC 974.27	AAS	III	Applicability: water Validated level: 10–100 ug/L (0.010-0.100 mg/L) Detection level: RSDr(%): RSDR(%): 8-61 HorRat: < 2 Specificity: excellent
Cadmium	Natural mineral waters	AOAC 986.15 (Codex general method)	Anodic stripping voltammetry	III	Applicability: all foods and feeding stuff (tested on chicken & apple) Validated level: 0.014 – 1.0 mg/kg Detection level: 0.05 mg/kg RSDr (%): 9-127 (high value at levels lower than DL) RSDR(%): 16- 214 HorRat: < 1.5 (except for the lowest validated level which is below the detection level) Specificity: good
Copper	All foods except fats and oils	NMKL 139 (1991) AOAC 999.11	AAS after dry ashing	II	Applicability: all foods (incl. fats and oils) Validated level: 7.1-45 mg/kg Detection level: 0.1 mg/kg RSDr(%): 3.5 – 20 RSDR(%): 11-22

Provision	*Commodity Standards*	*Method*	*Principle*	*Type*	*Method Characteristics*
					HorRat: < 1.5 Specificity: excellent
Copper	All foods except fats and oils	NMKL 161 (1998) AOAC 999.10	AAS after microwave digestion	III	Applicability: all foods except fats, oils and fatty products Validated level: 0.254-107.5 mg/kg Detection level: 0.09 mg/kg RSDr(%): 1.5-7.2 RSDR(%): 3.0-28 HorRat: < 1.5 Specificity: excellent
Copper	Chocolate Cocoa butter Cocoa powders (cocoa) and dry cocoa sugar mixtures Edible casein products. Whey powders Natural mineral water	AOAC 960.40 (Codex general method) IDF 76A:1980 ISO 5738:1980 (confirmed 1995)	Colorimetry (diethyldithiocarbamate)	II III*	- *the AOAC method surplus in 1993*
Copper	Cocoa (cacao) nib, Cocoa (cacao)mass, Cocoa press cake and cocoa dust (cocoa fines) for use in the manufacturing of cocoa and chocolate products. Cocoa butter confectionery Fruit juices Honey Vinegar	AOAC 971.20 (Codex general method)	AAS	II III*	Applicability: all foods (tested for tea only) Validated level: 5 - 194 mg/L Detection level: 0.5 mg/L RSDr: RSDR (%): 9-18 HorRat < 1.5 Specificity: good
Copper	Cocoa butters Fats and oils	AOAC 990.05 ISO 8294:1994 IUPAC 2.631 AOCS Ca 18b-91(03) (Codex general method)	AAS	II	Applicability: Fats and oils Validated level: 0.03- 0.15 mg/kg Detection level: 0.01 mg/kg RSDr(%): 5.4 – 15 RSDR(%): 15-21 HorRat: < 1.5 Specificity: Excellent

Provision	*Commodity Standards*	*Method*	*Principle*	*Type*	*Method Characteristics*
Copper	Food grade salt	ESPA/CN-E/101-1994	Photometry	III*	References are requested
Copper	Natural mineral waters	ISO 8288:1986 (confirmed 1995)	AAS	III*	Applicability: Water Validated level: 5.7- 41 ug/L (0.0057-0.041 mg/L) Detection level: RSDr (%): 3.5-8.0 RSDR(%): 12-17 HorRat: < 1.5 Specificity: excellent
Copper	Whey powders	AOAC 985.35	AAS	III*	Applicability: all foods and feeding stuffs Validated range: 0.56-4.76 mg/kg Detection limit: 0.05 mg/kg RSDr (%): 4.8-7.0 RSDR(%): 4.8-13 HorRat: < 1.5 Specificity: excellent
Iron	All foods except fats and oils	NMKL 139 (1991) AOAC 999.11	AAS after dry ashing	II	Applicability: all foods (incl. fats and oils) Validated range: 3.8-212 mg/kg Detection limit: 0.08 mg/kg RSDr(%): 8.2-12 RSDR(%): 11-12 HorRat: < 1.5 Specificity: excellent
Iron	All foods except fats and oils	NMKL 161 (1998) AOAC 999.10	AAS after microwave digestion	III	Applicability: foods except fats, oils and fatty products Validated range: 3.3 –484 mg/kg Detection limit: 0.05 mg/kg RSDr(%): 4.2 – 5.6 RSDR(%): 5.7 – 47 HorRat: <1.5 Specificity: excellent
Iron	Cocoa butters Fats and oils	AOAC 990.05 ISO 8294:1994 IUPAC 2.631 AOCS Ca 18b-91(03) (Codex general method)	AAS	II	Applicability: fats and oils Validated range: 0.13-0.96 mg/kg Detection limit: 0.05 mg/kg RSDr(%): 6.2-21 RSDR(%): 19-27

Provision	*Commodity Standards*	*Method*	*Principle*	*Type*	*Method Characteristics*
					HorRat: <1.5 Specificity: excellent
Iron	Cocoa butters	BS 684 Section 2.17: 1976	Colorimetry	III	Not succeded to get the information from BS
Iron	Fruit juices Vinegar	IFJU Method No 15, 1964	Photometry	III*	
Iron	Milk products	IDF 103A:1986 ISO 6732:1985 (confirmed 1995)	Photometry (bathophenanthroline)	IV	Not collaboratively validated – data unavailable
Lead	All foods except fats and oils	NMKL 139 (1991) AOAC 999.11	AAS after dry ashing	II	Applicability: all foods (incl. fats and oils) Validated range: 0.045-0.25 mg/kg Detection limit: 0.006 mg/kg RSDr (%): 26-40 RSDR(%): 26-40 HorRat: <1.6 Specificity: excellent
Lead	All foods except fats and oils	NMKL 161 (1998) AOAC 999.10	AAS after microwave digestion	III	Applicability: foods except fats, oils and fatty products Validated range: 0.005-1.62 mg/kg Detection limit: 0.014-0.055 mg/kg RSDr(%): 16-57 RSDR(%): 16-59 HorRat: < 1.5 Specificity: excellent
Lead	Bouillons and consommés Cocoa butters Cocoa powders (cocoa) and dry cocoa sugar mixtures Processed meat and poultry products and soups and broths	AOAC 934.07	Colorimetry (dithizone)	III*	- *the method surplus in 1993*
Lead	Butter Cocoa (cacao) nib, Cocoa (cacao)mass, Cocoa press cake and cocoa dust (cocoa fines)	AOAC 972.25 (Codex general method)	AAS	II	Applicability: all foods Validated range: 2.2 - 29.0 mg/kg Detection limit: RSDr(%): 4.8–10.5 RSDR(%): 4.9-36

Provision	*Commodity Standards*	*Method*	*Principle*	*Type*	*Method Characteristics*
	for use in the manufacturing of cocoa and chocolate products. Cocoa butter confectionery Canned corn beef Cooked cured chopped meat, ham, pork shoulder Edible casein products Fruit juices Honey Luncheon meat Vinegar Whey powders			III*	HorRat: 0.5-2.5 Specificity: excellent
Lead	Chocolate Cocoa powders (cocoa) and dry cocoa sugar mixtures	AOAC 986.15 (Codex general method)	Anodic stripping voltammetry	II	Applicability: all foods and feeding stuff (tested on chicken and apple) Validated range: 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 validated range close to the detection limit) Specificity: Good
Lead	Cocoa butters	IUPAC Method (Pure and Appl. Chem. 63, 1191-1198)	AAS	III	Applicability: fats and oils Validated range: 0.02-0.09 mg/kg Detection limit: 0.03 mg/kg RSDr(%): 4.5-10 RSDR(%): 10-28 HorRat: <1.5 Specificity: excellent
Lead	Edible casein products	IDF 133A:1992	Spectrophotometry (1,5 diphenylthiocarbazone)	III	To be checked
Lead	Fats and Oils	AOAC 994.02 IUPAC 2.623 ISO 12193:1994 (2004) AOCS Ca 18c-91(03) (Codex general method)	AAS	II	Applicability: edible oils and fats Validated range: 0.018-0.090 mg/kg Detection limit: 0.05 mg/kg RSDr(%): 3.5-11 RSDR(%): 5.9-30

Provision	*Commodity Standards*	*Method*	*Principle*	*Type*	*Method Characteristics*
					HorRat: <1.1 Specificity: excellent
Lead	Food grade salt	ESPA/CN-E/108-1994	AAS	III*	References are requested
Lead	Natural mineral water	ISO 8288:1986 (confirmed 1995)	AAS	III*	Applicability: water Validated range: 0.0197-0.977 mg/L Detection limit: RSDr(%): 1.1-3.8 RSDR(%): 2.8-4.2 (surprisingly good) HorRat: <1.5 Specificity: excellent
Lead	Natural mineral water	AOAC 974.27	AAS	III	Applicability: water Validated range: 0.05-0.20 mg/L RSDr(%): RSDR(%): 30-76 HorRat: 3.0-3.7 Specificity: excellent check the reference again
Lead	Sugars	AOAC 997.15	AAS	III*	Applicability: sugars & syrup (sucrose and fructose) Validated range: 0.100 mg/kg Detection limit: 0.05 mg/kg RSDr(%): 2.7-6.5 RSDR(%): 14-19 HorRat: <1.5 Specificity: excellent
Mercury	Fish and fishery products	AOAC 977.15	AAS	III	Applicability: fish Validated range: 0.275-0.944 mg/kg Detection limit: 0.05 mg/kg RSDr (%): RSDR (%): 4-49 HorRat: 0.24-2.5 Specificity: excellent
Mercury	Food grade salt	ESPA/CN-E/106-1994	AAS (cold vapour)	II	References are requested

Provision	*Commodity Standards*	*Method*	*Principle*	*Type*	*Method Characteristics*
Mercury	Natural mineral waters	ISO 5666-3:1984 (confirmed 1995)	AAS	II	*-this ISO method is withdrawn*
Mercury	Natural mineral waters	AOAC 977.22	AAS	III	Applicability: drinking surface and saline waters Validated range: 0.28-3.7 ug /L Detection limit: 0.2 ug/L RSDr: RSDR(%): 29-79 HorRat: <1.5 Specificity: excellent
Tin	Bouillons and consommés Cooked cured chopped meat, Cooked cured ham Cooked cured pork shoulder Luncheon meat Processed meat and poultry products and soups and broths Canned corned beef	AOAC 985.16 (Codex general method)	AAS	II	Applicability: canned foods Validated range: 50-250 mg/kg Detection limit: 10 mg/kg RSDr(%): 2.2 –12 RSDR(%): 3.3-15 HorRat: < 1.5 Specificity: excellent
Tin	Fruit juices	AOAC 980.19 (Codex general method)	AAS	II	*The method surplus 1986* *Final Action 1996*
Zinc	All foods except fats and oils	NMKL 139 (1991) AOAC 999.11	AAS after dry ashing	II	Applicability: all foods (incl. fats and oils) Validated range: 6.6-37 mg/kg Detection limit: 0.06 mg/kg RSDr(%): 4.3-5.1 RSDR(%): 4.3-5.3 HorRat: < 1.5 Specificity: excellent
Zinc	All foods except fats and oils	NMKL 161 (1998) AOAC 999.10	AAS after microwave digestion	III	Applicability: all foods except fats, oils and very fatty products Validated range: 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

Provision	*Commodity Standards*	*Method*	*Principle*	*Type*	*Method Characteristics*
					Specificity: excellent
Zinc	Fruit juices Vinegar	AOAC 969.32 (Codex general method)	AAS	III*	Applicability: all foods Validated range: 5.0-60 mg/kg (ppm) Detection limit: 0.5 mg/kg RSDr: RSDR(%): 1.6-12 HorRat: <1.5 Specificity: excellent
Zinc	Fruit juices	AOAC 986.15 (Codex general method)	AAS	III	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 As the method is validated for one level only (the detection limit) the study does not fulfil the criteria for a collab study. [For Zinc, AOAC 986.15 should have been type IV.]

***** 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.