

INCDO-INOE 2000 Research Institute for Analytical Instrumentation

# DETERMINATION OF SOME HEAVY METAL PROFILES IN FOOD OF ANIMAL ORIGIN FROM VARIOUS REGIONS OF ROMANIA



**Institute of Genetics**,

**Physiology and Plant** 

Protection

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## INTRODUCTION

Milk is the fundamental food for baby mammals as it contains essential amino acids, vitamins, antibodies and all essential elements at suitable levels. Also, eggs contain significant levels of vitamins, essential elements, antioxidants and protein. In European Union, milk, cheese and eggs are among the most important consumed food.

Essential elements, beside basic nutrients, have an important role in the function of a human organism and their absence or insufficiency in the human diet may induce metabolic changes or some disease. Some essential elements may become toxic at increased concentrations. Furthermore, the increasing environmental pollution raised concern on the intake of metals in humans. Metals are hazardous as they tend to bioaccumulate in biological organisms. The harmful health effects depend upon the element concentration, human organism resistance and antagonistic effects. Thus the determination of trace element concentrations in raw milk and eggs can be an important direct indicator of quality of milk, as well as an indirect indicator of the pollution degree of milk producing area.

This study aimed to determine the levels of some trace elements (essential and potentially toxic) in raw cow milk and hen eggs from small-scale local producers living in Transylvania, Romania. The obtained results were compared to the levels set by international organizations, for acceptable dietary intakes of nutritional elements and permissible maximum tolerable intakes of potentially toxic trace elements.

# **RESULTS AND DISCUSSIONS**

### Concentrations of metals in food of animal origin

The analytical performance of the analytical method is presented in Table 1. The recovery for the determination of metals in CRMs by GF-AAS and CV-AFS were in the range of 80-120 %.

Table 1. Analysis of reference materials for investigated metals.

	Certified material		Cd	Со	Cr	Cu	Hg	Mn	Pb	Zn
		Certified (µg/g) <sup>a</sup>	0.0005 ± 0.0002	0.0041 <sup>b</sup>	0.0026 ± 0.0007	0.630 ± 0.100	0.0003 ± 0.0002	0.26 ± 0.06	0.019 ± 0.003	46.1 ± 2.2
	NIST 1549 Whole milk powder	Found (µg/g)	0.0004 ± 0.0001	0.0045	0.0023 ± 0.0002	0.680 ± 0.050	< LOQ	0.24 ± 0.04	0.017 ± 0.002	44.3 ± 1.9
	powder	Recovery (%)	80	110	88	98	-	92	90	96
	NIST 8415	Certified (µg/g) <sup>a</sup>	0.005 <sup>b</sup>	0.012 ± 0.005	0.37 ± 0.18	2.70 ± 0.35	0.004 ± 0.003	1.78 ± 0.38	0.061 ± 0.012	67.5 ± 7.60
	Whole egg powder	Found (µg/g)	0.006	0.011 ± 0.004	0.034 ± 0.011	2.79 ± 0.30	< LOQ	1.92 ± 0.41	0.070 ± 0.024	62.7 ± 5.24
		Recovery (%)	120	92.0	92.0	103	-	108	115	93.0

<sup>a</sup>Mean ± U, where U is uncertainty; <sup>b</sup>Information values

# MATERIALS AND METHODS

#### Sampling

The food of animal origin (raw milk and hen eggs) were collected in presumably unpolluted sites (low traffic volume, small-medium villages, no industrial plants, waste incinerators or intensive agricultural activities): 22 small-scale local producers living in rural areas in different parts of Transylvania, Romania (Bistrita, Brasov and Cluj counties) in July-August 2017.

To evaluate seasonal of studied metals, 10 milk and egg samples (of the 22) were also collected during winter (December 2017-January 2018) and analyzed.







Source: www.wikipedia.com

#### Metal analysis

The samples (1 mL milk / 1 g egg) were digested with 8 mL HNO<sub>3</sub> 65% and 3 mL  $H_2O_2$  30% in closed PTFE vessel microwave digestion system (Berghof SpeedWave Xpert, Eningen, Germany) using a three-steps heating program. The digested samples were quantitatively transferred to 20 mL volumetric flasks and diluted to the mark with ultrapure water (Millipore Direct-Q3 UV system, Millipore, Molsheim, France). Three replicate measurements were carried out for each sample.

The concentrations of Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb and Zn in food of animal origin from Transylvania, Romania are given in Table 2.



Table 2. Mean concentrations of metals in food of animal origin.

Metal	Milk (µg/L	ww)	Egg (µg/kg ww)		
Wetai	Summer (n=22)	Winter (n=10)	Summer (n=22)	Winter (n=10)	
Cd	1.01 ± 0.54	1.21 ± 0.42	1.98 ± 0.43	2.04 ± 0.49	
Со	2.24 ± 0.25	4.25 ± 0.84	4.25 ± 1.04	4.43 ± 0.95	
Cr	4.44 ± 1.00	5.25 ± 1.08	76.2 ± 12.3	74.3 ± 10.4	
Cu	52.3 ± 17.6	38.6 ± 10.7	973 ± 146	948 ± 126	
Mn	22.4 ± 7.59	42.4 ± 7.56	961 ± 118	985 ± 103	
Hg	1.01 ± 0.34	$1.48 \pm 0.60$	$1.24 \pm 0.49$	1.38 ± 0.37	
Pb	5.87 ± 0.86	7.23 ± 1.08	1.22 ± 0.15	1.35 ± 0.24	
Ni	24.5 ± 7.69	24.9 ± 5.26	62.1 ± 4.82	66.5 ± 5.02	
Zn	3523 ± 428	2499 ± 364	26125 ± 4128	26356 ± 3258	

According to the European Regulation, EC No. 1881/2006, maximum levels are set only for Pb in raw milk, heat-treated milk and milk for the manufacture of milk-based products, while no maximum levels for the other studied metals are established. The mean concentration of Pb did not exceed the maximum admissible limit of concentrations regulated by legislation.

Regarding the seasonal variations on investigated metals in hen eggs, the obtained mean concentrations of all investigated metals were similar in both seasons. For raw milk, higher concentration of Cu (35%) and Zn (41%) were observed in the summer *i.e.* from cows fed mainly pasture forage, while the content of Mn was approximatively twice in the winter season. The seasonal differences could be associated with the different contents of metals in the feed portion.

The levels of investigated essential elements (Cr, Cu and Zn) in investigated samples were appropriate, their having a positive contribution to daily nutrition of consumers in accordance to Recommended Dietary Allowance (RDA). The potentially toxic element concentrations (Cd, Hg and Pb) were in general low and did not pose any health risk to consumers.

The standard solutions for instruments calibration were prepared from stock standard solution of ultra-pure grade: ICP-MS Multi-Element Standard Solution IV Merck (1000 mg/L) and Mercury ICP Standard Merck (10 mg/L). All reagents used for this research work were of analytical grade and purchase from Merck, Darmstadt, Germany. The certified reference materials, CRMs (NIST SRM-1549 Whole Milk Powder and NIST 8415 Whole Egg Powder) were purchased from LGC Standards GmbH (Wessel, Germany).

The metal concentrations were measured using a PinAAcle 900 T (Perkin Elemr, Waltham, USA) atomic absorbtion spectrometer in furnace mode (GF-AAS) and Cold Vapor Atomic Fluorescence Spectrometer CV-AFS Hydra-AF (Teledyne Instruments, Leeman Labs, USA) - Hg determination.



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