

Chocolate and Cocoa Products as A Source of Essential Elements in Nutrition

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Abstract

In order to test current quality and nutritional merits of chocolate, 54 dark, plain and milk chocolate samples as well as cocoa were collected from the Austrian market and analyzed for many nutrient, essential and non essential elements, including the non-metals B, Si, S, and I. The cocoa contents ranged from 20-100%. Among the non-wanted trace elements, nickel was Gaussian distributed with a rather high mean of 4.9 mg/kg. Cd largely ranged below 0.20 mg/kg, but a few were higher, reaching 0.90 mg/kg. Contrary to previous studies, the same sample set was used to determine the contents of several element groups to look for interelement effects. Compared with element levels met in other sweets, element contents in chocolate were significantly higher. Many trace elements, like B-Co-Cr-Cu-Fe-Mn-Zn, ranged at levels met in green plants. Nickel concentrations were surprisingly high and about Gaussian distributed. Silicon was frequently higher than aluminium. Contaminants Pb, As, V, and Tl were very low, Cd was variable. Factor analysis grouped the element concentrations into B-Co-Cu-Mg-Mn-Ni- P-S-Zn, Al-Cr-Fe-Si, and Ca-J-Na, which might represent a component from the cocoa bean, its outer shell, and milk. Contrary to other sweets, consumption of 100 g of chocolate satisfies the recommended daily intake for Cr-Cu-Fe, and 300 g for Mg and Zn, which is particularly important for the adequate trace element supply of children and vegans.

Keywords: Trace elements; Contaminants; Essential elements; Non-metals; Cocoa; Chocolate

Introduction

Within the frame of the Austrian National action plan for nutrition [1], chocolate ranges among the sweets together with bakery products and candies, because it contains significant amounts of sugar. This group of food contributes about 10% to the daily energy intake. Sweets supply about half of total sugar intake for all groups of age, and may reach 90% in the group of too heavy children and teenagers. In spite of a broad offer of food in the industrialized countries, children have a certain risk of malnutrition in trace elements and vitamins, if they keep too much on sweets and chips. Too high sugar consumption can lead to diabetes mellitus and adipositas. A reasonable food mix is therefore recommended to meet all requirements. Element screening of chocolate and cocoa products might show if trace element supply can be improved when chocolate is selected instead of other sweets. In general, the elements Ca-Mg-Cu-Mn-Fe-Zn-Co-Mo-Se-I are regarded as important trace elements, they are frequently added to commercial feedstuffs designed for domestic animals [2]. In particular, the levels of iodine and sulfur in local nutrition are largely unknown. Though not regarded as essential, Sr has got some merits to harden teeth and bones [3]. Lecithin as an emulsifier has got plenty of phosphorus. Another aspect for a broad element screening is to detect the levels of unwanted (toxic) elements like Cd, Pb and maybe others (As, Ba, Be, Bi, Cr, Ni, V, Tl). Apart from complexation capabilities to selected ligands, Al and Si might indicate the contamination from dust during the processing stages. Boron is a strong indicator for green plant origin. During the processing of the cocoa bean, phytate is largely lost, making Fe and other trace elements significantly more available than from common vegetarian food [4]. This is particularly important for vegans and lacto-vegetarians.

ICP-OES multi-element technique allows analyzing many elements simultaneously, which offers the chance to discover new inter element relationships, characteristic element proportions, and unknown ingredients of the food product. Contrary to most previous papers,

main elements, essential elements, so-called “heavy metals”, and non-metals could be done from the same samples.

Some data found in the literature seem to have been done by inadequate methods. Thus, 0.29 mg/kg Cd, 1.36 mg/kg Pb, and 0.90 mg/kg As were found by ICP-AES in milk chocolate from Malaysia, as well as 0.39 mg/kg Cd, 1.82 mg/kg Pb and 1.17 mg/kg As, which seem dangerously high [5]. Similarly, Dahiya et al. [6] obtained a mean value of 1.92 mg/kg for Pb and 0.24 mg/kg for Cd in dark chocolates after open perchloric acid digestion and flame AAS. According to the experience of the author from the analysis of mineral fertilizers, Pb in phosphate matrices, done by flame AAS gets too high near the detection limit, and all three As- emission lines are quite matrix sensitive. However, 8 mg/100g for Zn, 5 mg/100g for Cu and 5 mg/100g for Mn have been confirmed in this work [4] (see below).

It is well known that the fraction available to the organism is less than total and depends on the solubility, the current needs regulated by homeostasis, and the presence of blockers like phytate. For vegetables, sequential leaching methods have been designed imitating the acid conditions in the stomach as well as the slightly alkaline gut [7]. Chocolate, however, contains significant amounts of lipids, which have to be removed prior to simple in vitro leaching; removal of fat by organic solvents or degradation by lipases was too complex to be done within this study.

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From some countries, data about the consumption of chocolate and cocoa products have been available. In Italy, mean chocolate intake has been calculated as 9 g per day [8]. In India, the ingestion rate of chocolate for children has been estimated at 20 g per day [6]. In Turkey, the most preferred chocolate type is milk chocolate (33%), followed by chocolate with pistachio (21%), chocolate with hazelnut (16%), with caramel (15%), and plain (12%) [9]. In Austria, the consumption of chocolate and cocoa products is not outlined per se, however [1]. This paper, however, is about to show that replacement of candies by chocolate and cocoa products is a reasonable strategy to improve the status of some trace elements.

Material and Methods

19 samples of milk chocolate (17 wrapped as Easter Bunnies), 9 dark chocolates (50% cocoa), 15 very dark chocolates (70% cocoa), 3 cocoa samples, 6 chocolates with fillings and 2 cocoa drinks were taken from the Austrian market by the authorities. The data set included the trade marks Bella, Bendsorp, Choceur, Frey, Goutier, Lindt, Manner,

Moser, Rausch, Ritter, Schneekoppe, Spar, Suchard, and Verival. 0.6 grams of finely chopped chocolate sample (remark: for green plants, 1 g sample weight is possible) were weighed into PTFE pressure digestion vessels, 8 ml of potassium chlorate- nitric acid digestion solution was added, the vessel was closed and the samples digested by microwave assisted heating. As microwave digestion unit, a “mls 1200 mega high performance microwave digestion unit” (MLS GmbH, D-88299 Leutkirch) was used, running the subsequent program time/ power program: 3 min 250 W / 2 min 0 / 5 min 250 W / 5 min 400 W / 5 min 500 W. The temperature could not be recorded. After cooling and opening, one further ml of digestion solution was added, and the sample made up to 25 ml in plastic volumetric flasks. Contact with glass has to be avoided because of blanks from boron and silicon [10,11]. ICP-multi-element analysis was done at a Perkin-Elmer Optima 3000 XL horizontal plasma for Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, and Zn versus KClO₃-matrix matched calibrants. Because of K containing reagent solution, K and Rb could not be determined. As most calibrant stock solutions have been kept in glass vessels, and

Element	Median mg/kg	Range mg/kg	corr with % cocoa	Honey. median mg/kg	Recommended daily intake (DACH-values)	Thresholds mg/kg
% Cocoa		20 – 100	X			
P	2200	1546 - 4773	0.5923	42.1	800	
Mg	1205	530 – 2521	0.8559	17.2	300 – 400	
Ca	1058	518 – 2423	0.4535	44.5	800	
S	797	523 – 1618	0.6852	n.d.		
Na	194	14.2 – 1281	0.7272	11.3		
Fe	88.1	20.1 – 167	0.6448	0.60	10 – 15	
Si	45.5	7.0 - 84.8	0.5974	n.d.		
Al	24.8	4.58 - 60.1	0.5998	0.77		
Zn	22.3	10.20 - 52.3	0.8484	0.57	15	
Mn	12.3	2.73 - 26.2	0.8007	0.66	10 – 30	
Cu	9.87	3.47 - 31.6	0.8103	0.14	2	50 [*]
B	5.87	1.63 - 13.04	0.8224	5.07		
Sr	4.53	1.63 - 8.19	0.8188	0.059		
Ba	4.17	0.89 - 9.92	0.8284	0.073		
Ni	2.84	0.611 - 8.97	0.7558	0.030		
Cr	0.82	0.145 - 2.272	0.5020	0.007	0.05 - 0.5	
Co	0.272	0.050 - 0.789	0.7614	0.004		
Mo	0.186	0.091 - 2.126	0.1459	0.003	0.075 - 0.25	
I	0.161	0.013 - 1.112	0.6771	n.d.	0.15	
V	0.091	<0.03 – 0.243	0.4156	0.006		
Cd	0.043	0.010 – 0.626	0.3351	0.001		0.050 ^{**}
Pb	0.034	0.012 – 0.395	0.0956	0.011		2.0 [*] / 0.30 ^{**}
As	< 0.01	< 0.01 – 0.032	X	n.d.		1.0 [*]
Bi	0.006	< 0.001 – 0.091	X	<0.0002		
Be	0.0032	< 0.003 – 0.009	X	<0.0002		
Tl	0.001	< 0.0005 - 0.030	X	0.0004		

n.d. not determined

^{*} limits in Malaysia (citation from 1985) [5].

^{**} limits in Poland (citation from 2006) [20].

Table 1: Concentration ranges found (95% probability), and relation to cocoa contents and nutritional value, compared with honey after [14] (about equal sample numbers of floral and wood honey)

The elements marked by symbols in italics have been taken from ICP-MS, others from ICP-OES, and arsenic from hydride- AAS

The correlation coefficient given in the first column, equals ±1 for perfect correlation, and 0 for ideal independence; it can be calculate e.g. by EXCEL.

may contain sulfate as a counter ion, the non-metals B, Si, P and S were determined within a second run. In this case, the dilutor could not be used because it contains glass parts. Finally, the main elements Ca, Mg, Na, P, as well as Sr for control reasons were determined from 1+19 dilutions versus aqueous calibrants.

For ICP-MS measurements at a Perkin Elmer Sciex ICP mass spectrometer ELAN DRC II, the samples were 1+9 diluted, indium was added as an internal standard, and the elements Bi, Cd, Co, Mo, Ni, Pb, Tl were read. Total iodine was determined in a separate run by standard addition as the iodate, because it is seriously interfered by P-177 in the optical system. Arsenic was determined by hydride AAS in batch mode (Perkin Elmer MHS-20). Occasional foaming during hydride generation limited the applicable sample volume to 2 ml per shot. As quality checks, recoveries from amounts added prior to the digestion, as well as ring tests from the IPE (International Plant Exchange Wageningen NL; code WELE 136) were used. For silicon, no reference value could be found. Each series contained at least 2 blanks. Recovery of 5 µg and 10 µg of B-I-Ge-Si-Sn was > 85 %. For details, see references [11-13].

Results

All results are given with respect to fresh weight, as it is usual in food analysis. Because the water contents are usually not much for these items, differences to dry weight, however, are not large. As, Bi, Be, Ge and Tl were largely below the detection limits of the ICP-MS, and Sn and Sb below the detection limit of the ICP-OES. The concentration ranges met in chocolate and cocoa were similar to the levels encountered in green plants (per dry mass), but not quite equal. Linear correlations with the cocoa contents could be especially established with (in alphabetical order) barium, boron, copper, magnesium, manganese, sulfur, strontium, and zinc (Table 1). As a consequence, many elements also correlate well with each other, e.g. Ni with Cu, B with Cu-Mg-Zn, and even B with Sulfur. As a model substance for sweets, median data for honey are shown for comparison (details and ranges covering both wood and floral honey) [14]. All element levels in honey have been found significantly lower than in chocolate, except for boron.

When the concentration data are grouped according to chocolate types, correlations with cocoa contents can be roughly recognized; samples containing additions other than milk were excluded from Table 2. Details will be discussed for each element separately. The data found in this work were quite different to the data given in a comprehensive book about cocoa products [4].

Statistical evaluation was done by factor analysis, neglecting those element concentrations which were partly below detection limit (As, Be, Bi, Tl, V; Table 2). Component 1 can be interpreted as the contribution from the cocoa beans. Component 2 looks like dirt or soil. Component 3 represents the milk powder in the milk chocolates. Graphic display (Figure 1) reveals that calcium, and at a lesser extent iodine and sodium- concentrations, show a non-linear dependency versus the cocoa content, with a minimum at about 60% cocoa, whereas others (e.g. B, Cu, Mg, and Zn) depend approximately in a linear way. This reflects the input of Ca-I-Na by the milk powder, which is usually more than from the cocoa for these elements. Many multivariate statistical methods require approximately linear relationships among the variables, therefore conditions presented in figure 1 have to be considered before other evaluations.

Rotated Component Matrix			
	Component		
	1	2	3
Al	0.273	0.913	0.259
B	0.803	0.409	0.298
Ba	0.680	0.484	0.406
Ca	0.026	-0.218	-0.934
Co	0.805	0.296	0.401
Cr	0.248	0.870	0.107
Cu	0.880	0.367	0.235
Fe	0.366	0.862	0.234
K	0.243	-0.030	0.037
I	-0.344	-0.197	-0.825
Mg	0.891	0.372	0.232
Mn	0.841	0.441	0.274
Na	-0.270	-0.264	-0.896
Ni	0.825	0.438	0.218
P	0.951	0.225	-0.098
S	0.948	0.216	-0.060
Si	0.234	0.867	0.283
Sr	0.889	0.316	0.266
Zn	0.885	0.316	0.289

Table 2: Rotated component matrix after factor analysis of concentrations found in chocolate. From the original variables, new combination variables can be formed for reasons of simplification, which are weighted by factors given in Table 2, after Varimax rotation (program: SPSS 19). Factor weights > 0,80 have been marked yellow for easier interpretation

Discussion

General

In the EU, general maximum tolerable intake limits have been set for the ingestion of entire food within a week, for cadmium at 7 µg/kg body weight, and for lead at 25 µg/kg body weight [15]. Special threshold concentrations for cocoa and its products have been issued in Malaysia [5] for Cu, Pb and As long ago. In addition to cocoa products (cocoa powder and cocoa butter), the chocolates have a number of ingredients such as white sugar, milk powder, vegetable oils, emulsifiers, dried fruits, nuts etc [9]. For the production of milk chocolate, milk solids are introduced in the form of milk powder or milk crumbs, and dry mixed with chocolate liquor and sugar [16]. With respect to the commonly investigated toxic elements among the ingredients for milk chocolate, cocoa powder contained significantly more As, Hg, Cd, and Pb than milk powder, but all means were below 0.2 mg/kg [9]. Ingredients like milk powder and sugar do not contribute to the metal contents of the finished products [5]. Other additives might be nuts or raisins, which might contribute significantly to trace element loads [9]. To avoid this bias, this work has been restricted to plain and milk chocolate only (Table 3).

Significant differences between candies and chocolate composition have been also found for items sold in Nigeria [17]. Chocolates contained significantly more Ca, Cd, Cu, Pb, Mn, Co, Zn, Mg, whereas the concentration ranges for Ni, Cr, and Fe were overlapping. As

	Milk chocolate (19)		Dark chocolate (9)		very-dark chocolate(15)		Cocoa (3)	
% cocoa	31.8	30.5 - 35.7	51	50 - 55	70	70 - 75	100	100 - 100
Al	15.4	4.58 - 30.9	37.9	22.6 - 40.5	44.8	19.2 - 62.5	39.9	22.9 - 158
As	< 0.01	< 0.01	< 0.01	< 0.01 - 0.018	< 0.01	< 0.01 - 0.016	0.014	< 0.01 - 0.023
B	2.22	1.08 - 3.37	6.62	4.13 - 11.37	9.93	6.29 - 12.6	26.8	22.4 - 27.2
Ba	1.59	0.89 - 2.22	4.29	2.86 - 4.66	5.01	4.25 - 8.99	12.7	10.5 - 12.9
Be	0.003	< 0.003 - 0.008	< 0.003	<0.003-0.006	0.003	<0.003- 0.007	0.012	<0.003-0.015
Bi	0.007	0.003 - 0.027	0.003	<0.001 - 0.007	< 0.001	< 0.001- 0.0914	< 0.001	< 0.001
Ca	1945	1422 - 2447	601	449 - 1421	652	573 - 890	1554	1295 - 1741
Cd	0.017	0.008 - 0.041	0.037	0.025 - 0.246	0.194	0.043 - 0.510	0.122	0.112 - 0.171
Co	0.093	0.050 - 0.268	0.244	0.194 - 0.316	0.422	0.286 - 0.668	0.92	0.79 - 0.97
Cr	0.65	0.15 - 1.05	1.03	0.72 - 2.27	1.36	0.41 - 2.12	1.47	0.92 - 6.26
Cu	4.27	3.09 - 6.10	10.31	8.51 - 15.05	16.9	9.91 - 26.7	55.9	44.7 - 56.2
Fe	48.5	20.1 - 88.1	91.5	86.6 - 150	147	45.7 - 162	167	111 - 450
I	0.740	0.376 - 1.246	0.193	0.134 - 0.342	0.102	< 0.01 - 0.138	0.107	0.045 - 0.152
Mg	651	460 - 693	1263	1104 - 1457	1810	1467 - 2383	5443	4968 - 5467
Mn	4.60	2.73 - 6.02	11.6	10.2 - 15.3	16.6	13.1 - 21.5	49.0	38.8 - 53.4
Mo	0.166	0.112 - 0.49	0.152	0.111 - 0.195	0.201	0.145 - 2.64	0.420	0.270 - 0.452
Na	1135	634 - 1281	54	45 - 435	36	10 - 304	131	115 - 295
Ni	0.98	0.52 - 1.43	3.07	2.64 - 4.89	4.26	2.57 - 7.93	15.33	10.77 - 17.12
P	2053	1670 - 2423	2055	1546 - 2228	2702	1880 - 3392	6632	6125 - 7148
Pb	0.030	0.015 - 0.063	0.039	0.014 - 0.063	0.059	0.019 - 0.114	0.033	0.002 - 0.196
S	773	551 - 882	801	669 - 1098	896	735 - 1443	2500	2433 - 2545
Si	25.6	6.9 - 48	59	30 - 72	65	27 - 100	60	40 - 205
Sr	2.33	1.46 - 2.75	4.65	3.90 - 5.36	6.36	5.74 - 7.81	19.1	16.8 - 20.0
Tl	< 0.002	< 0.002	0.002	< 0.002-0.006	0.003	< 0.002-0.030	0.003	< 0.002 - 0.018
V	0.07	< 0.03 - 0.17	0.10	0.04 - 0.15	0.13	0.02 - 0.28	0.19	0.04 - 0.46
Zn	11.9	9.11 - 17.0	22.6	18.5 - 25.9	34.8	22.4 - 41.5	78.8	75.6 - 82.0

Addendum: results achieved in ring test analysis of plant material after KClO₃ digestion of IPE 2011.3 (issued by Agricultural University Wageningen, NL). K and Rb are not possible.

			result	median	mean	std.dev	participants	
Oak	Al	mg/kg	9.3	11.7	10.35	± 6.49	21	ICP
	Ba	mg/kg	6.13	5.95	5.80	± 0.54	11	ICP
	Be	µg/kg	< 0.5	<			-	ICP
	B	mg/kg	12.8	12.0	11.84	± 1.31	82	ICP
	Ca	g/kg	1.90	2.08	2.056	± 0.197	111	ICP
	Cd	µg/kg	45.1	40.0	39.16	± 7.05	23	ICPMS
	Co	µg/kg	28.2	24.0	23.35	± 3.4	18	ICP-MS
	Cr	µg/kg	39	164	121	± 116	22	ICP
	Cu	mg/kg	7.80	6.85	7.80	± 0.57	102	ICP
	Fe	mg/kg	30.1	27.2	26.8	± 5.23	103	ICP
	Li	µg/kg	89	145			4	ICP
	Mg	g/kg	0.61	0.702	0.701	± 0.046	111	ICP
	Mn	mg/kg	36.4	16.5	39.35	± 2.90	104	ICP
	Mo	µg/kg	504	504	501	± 42	27	ICPMS
	Na	mg/kg	45.8	45.4	43.3	± 11.2	58	ICP
	Ni	µg/kg	1018	881	856	± 125	29	ICP
	Pb	µg/kg	95	143	127	± 54	24	ICPMS
	S	g/kg	0.78	0.95	0.946	± 0.098	62	ICP

	Sr	mg/kg	4.27	4.52	4.47	± 0.29	11	ICP
	V	µg/kg	< 40	27.6	-		4	ICP
	P	g/kg	1.47	1.50	1.503	± 0.082	112	ICP
	Zn	mg/kg	13.2	11.57	11.5	± 1.35	100	ICP
Grass	Al	mg/kg	458	476.6	471.9	± 72.2	25	ICP
	Ba	mg/kg	11.81	9.575	9.40	± 0.79	12	ICP
	Be	µg/kg	14.5	21.1			4	ICP
	B	mg/kg	10.41	9.42	9.4	± 1.20	82	ICP
	Ca	g/kg	5.48	5.53	5.512	± 0.293	113	ICP
	Cd	µg/kg	93.5	80.0	80.17	± 8.08	29	ICPMS
	Co	µg/kg	197	169.3	169.5	± 19.5	25	ICP-MS
	Cr	µg/kg	1496	1760	1742	± 281	27	ICP
	Cu	mg/kg	8.01	7.50	7.54	± 0.50	103	ICP
	Fe	mg/kg	515	502	505	± 49.4	105	ICP
	Li	µg/kg	937	964			4	ICP
	Mg	g/kg	2.11	2.00	1.996	± 0.141	113	ICP
	Mn	µg/kg	87.2	78.9	78.81	± 5.83	105	ICP
	Mo	µg/kg	1788	1687	1697	± 100	29	ICPMS
	Na	mg/kg	3323	3267	3284	± 192	68	ICP
	Ni	µg/kg	1300	1499	1476	± 176	29	ICP
	Pb	µg/kg	1317	1180	1172	± 110	31	ICPMS
	S	g/kg	2.63	3.32	3.35	± 0.306	63	ICP
	Sr	mg/kg	22.2	20.8	21.25	± 1.43	11	ICP
	V	µg/kg	1307	1233	1261	± 143	11	ICP
	P	g/kg	3.60	3.84	3.85	± 0.178	113	ICP
	Zn	mg/kg	29.9	32.7	32.8	± 2.30	102	ICP
Tobacco leaves	Al	mg/kg	222	252	251.9	± 48.7	25	ICP
	Ba	mg/kg	26.4	21.74	22.32	± 2.76	12	ICP
	Be	µg/kg	6.5	10.5			4	ICP
	B	mg/kg	43.4	41.6	41.8	± 4.68	82	ICP
	Ca	g/kg	30.5	30.8	30.83	± 2.03	112	ICP
	Cd	µg/kg	2985	2570	2550	± 288	34	ICPMS
	Co	µg/kg	391	297.5	299.1	± 49.9	24	ICP-MS
	Cr	µg/kg	5960	6274	6309	± 1041	27	ICP
	Cu	mg/kg	12.6	12.4	12.32	± 1.16	102	ICP
	Fe	mg/kg	317	323	325	± 40.6	104	ICP
	Li	µg/kg	6850	7493			4	ICP
	Mg	g/kg	4.90	4.73	4.739	± 0.328	112	ICP
	Mn	mg/kg	309	293.5	295	± 23.8	104	ICP
	Mo	µg/kg	1328	1217	1212	± 160	29	ICPMS
	Na	mg/kg	336	248	248	± 43	65	ICP
	Ni	µg/kg	1146	1151	1080	± 244	29	ICP
	Pb	mg/kg	5626	5549	5688	± 789	36	ICPMS
	S	g/kg	4.45	5.31	5.37	± 0.388	63	ICP
	Sr	mg/kg	82.2	82.2	82.5	± 2.58	11	ICP
	V	µg/kg	546	650	684	± 87	9	ICP

	P	g/kg	4.29	4.61	4.61	± 0.281	112	ICP
	Zn	mg/kg	181	186	186	± 13.8	101	ICP
Wheat grains	Al	mg/kg	110	123.4	123.9	± 26.7	25	ICP
	Ba	mg/kg	2.52	2.02	2.066	± 0.38	11	ICP
	Be	µg/kg	0.5	2.67			2	ICP
	B	mg/kg	0.90	1.445	1.384	± 0.89	68	ICP
	Ca	g/kg	0.725	0.74	0.727	± 0.085	111	ICP
	Cd	µg/kg	17.4	16.8	16.22	± 3.91	21	ICPMS
	Co	µg/kg	43.8	41.6	39.6	± 7.6	19	ICP-MS
	Cr	µg/kg	289	349	338	± 112	24	ICP
	Cu	mg/kg	3.56	4.20	4.20	± 0.44	103	ICP
	Fe	mg/kg	148	164.7	166.2	± 22.4	105	ICP
	Li	µg/kg	154	152			4	ICP
	Mg	g/kg	1.22	1.203	1.202	± 0.075	112	ICP
	Mn	mg/kg	14.2	12.27	12.35	± 1.36	104	ICP
	Mo	µg/kg	825	823	811	± 99	28	ICPMS
	Na	mg/kg	65.2	48.4	46.7	± 15.1	60	ICP
	Ni	µg/kg	172	190	191	± 48	25	ICP
	Pb	µg/kg	192	199	189	± 32	26	ICPMS
	S	g/kg	1.23	1.15	1.154	± 0.106	62	ICP
	Sr	mg/kg	4.71	4.72	4.83	± 0.40	11	ICP
	V	µg/kg	155	234	243	± 51	10	ICP
	P	g/kg	3.26	3.45	3.46	± 0.201	113	ICP
	Zn	mg/kg	25.6	27.35	27.4	± 2.11	102	ICP

Table 3: Median and concentration ranges found (95%) found in different types of chocolates, mg/kg fresh weight (Element symbols in italics mark ICP-MS- data).

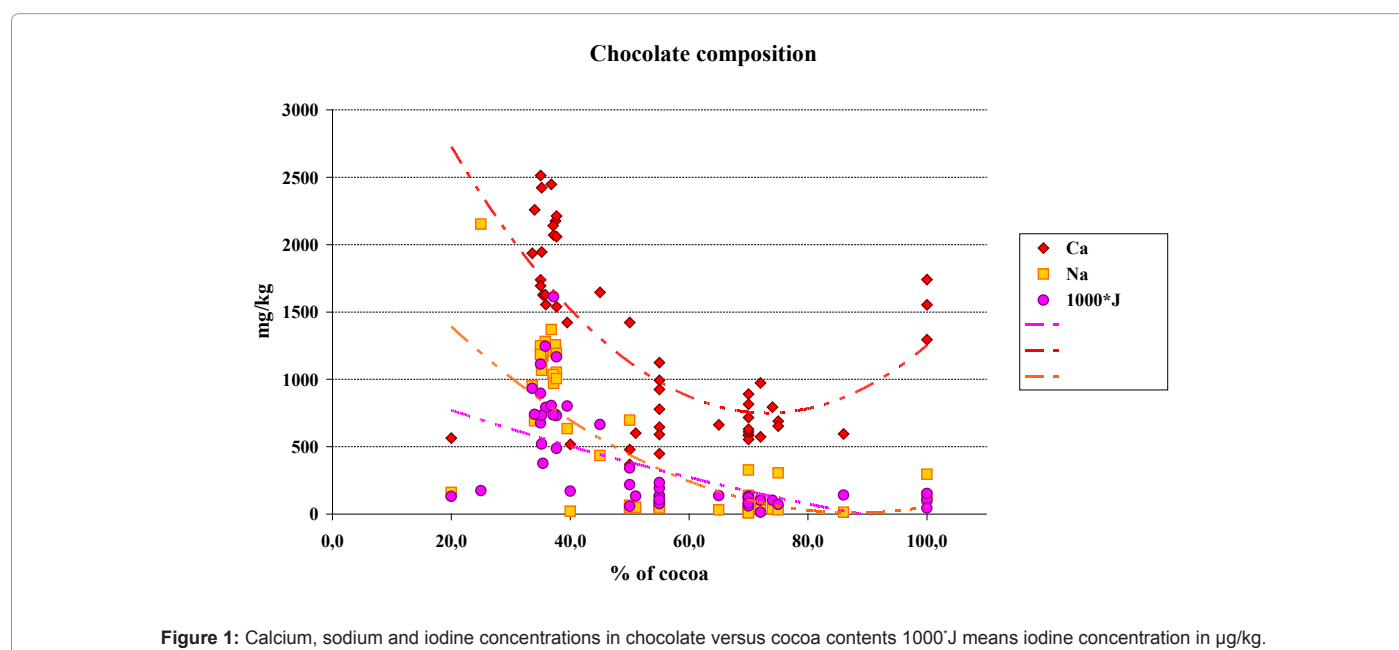


Figure 1: Calcium, sodium and iodine concentrations in chocolate versus cocoa contents 1000*J means iodine concentration in µg/kg.

possible contamination sources, steel containers and catalysts used in the preparation of hydrogenated vegetable oils were identified [17].

Subsequently, current results have been compared with existing data, discussed one by one, to make it easier for the reader to find the element in which he/she is particularly interested. The range of results presented in Table 1 covers the 95 % confidence level, as the 5 highest and the 5 lowest data have been omitted. The term “median” means the most probable value. If within a given dataset, the highest and the lowest are alternatively omitted, the median remains. Use of medians does not necessitate Gaussian data distributions.

Aluminum

In this work, a median concentration of 24.8 mg/kg (range 4.6 – 60.1) was found. This is similar to data found in Germany at 37 mg/kg Al (range 10 – 110) in dry mass, which was higher than for most vegetables and herbs [18]; just some condiments have more. In chocolate sold in Italy, mean Al concentration was found to be 9.2 ± 7.5 mg/kg, the correlation coefficient with cocoa contents was 0.78. Dark chocolates ranged 9.9 – 30.1 mg/kg, and milk chocolates 4.1 – 8.5 mg/kg [8].

Tracing the origin of aluminum, it should be considered than at least in this work, aluminum is part of a component Al-Si-Fe-Cr (see Table 2). Attack of Al wrappings is improbable, as foodstuffs with neutral pH and low salt contents are largely inert because of its natural oxide layer [8].

The acceptable daily intake for aluminum is 1 mg/kg body weight [8], which is reached by consumption of 3 kg chocolate for grown-ups, and about 1 kg for small children (of 20 kg), which is hardly reached in daily life.

Arsenic

In this work, arsenic concentrations were largely at or below detection limit (range < 0.01 – 0.032 mg/kg; hydride method), and within the same range of the data given from Germany [19] 30 years ago (0.022 – 0.066 mg/kg). In Poland, Figurska-Ciura et al. [20] found even less, 0.0029 ± 0.0017 mg/kg in dark chocolates, and 0.0025 ± 0.0021 mg/kg in milk chocolates. From Malaysia, higher values were reported, but might be doubtful because of insufficient background correction in the ICP-OES at those times [5].

Barium

In this work, median concentration of barium was found at 4.17 mg/kg, which resembles the data given by Anke [21] for barium in cocoa (5.4 ± 1.6 mg/kg) and chocolate (4.6 ± 1.6 mg/kg). Barium was found to range at a level like in lentils, and to be higher than in bread and cereals, but lower than in spinach, lettuce and tree barks [21].

Boron

Boron concentrations in cocoa and chocolate (median 5.87; range 1.62 – 13.04 mg/kg) range at about half the levels encountered in green leaves [10]. Due to factor analysis (Table 2), its source is the cocoa bean. No other values about boron in cocoa were found for comparison. In honey, boron gets enriched because buds accumulate it as a natural fungicide [14].

Calcium

In cocoa and chocolates, calcium concentrations are very high and depend parabolically from the cocoa contents (Figure 1). Cocoa

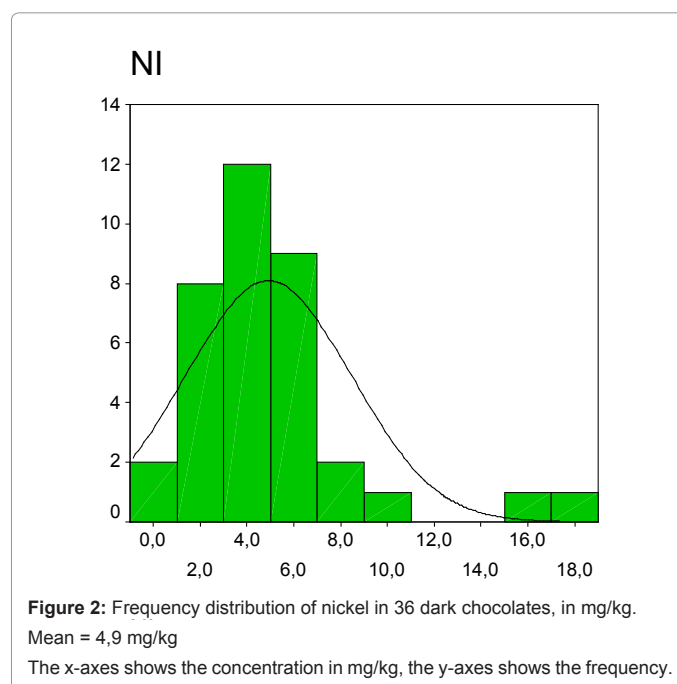
had about 1500 mg/kg, dark chocolate 500 – 1000 mg/kg, and milk chocolate 1500 – 2500 mg/kg. Thus, milk chocolate has double calcium than milk and dairy products, and 5 times more than whole-meal bread [22-24]. 300 g of milk chocolate cover the daily calcium needs.

Cadmium

Most of the cadmium concentrations found in chocolate in this work, have been quite low (median = 0.043 mg/kg), but some higher outliers appeared also (7 values > 0.30 mg/kg), and there was no Gaussian frequency distribution. The 3 highest Cd data came from pralines with fruits inside (Figure 2). The European Commission has set the tolerably weekly intake for Cd at 7 µg/kg body weight [15]. Taking the median value of this study, this means, a child of 20 kg body weight might ingest 3300 g of chocolate per week without any harm from cadmium, but for the worst case, this would be just 220 g. This justifies controlling cadmium concentrations in the respective products. 30 years ago, in Germany, cadmium in chocolates was determined (by graphite furnace AAS) at 0.13 mg/kg for 45% cocoa and 0.35 mg/kg for 60% cocoa contents, but covering a rather broad range. At this time, samples from Malaysia and the Caribbean had higher Cd-levels than products from Africa or the South Pacific region, mainly more than the contemporary recommended value of 0.3 mg/kg [25]. Milk chocolate in Malaysia contained 0.29 mg/kg (range 0.26 – 0.42), and dark chocolate 0.30-0.42 mg/kg [5]. In 2004, mean cadmium in chocolates sold in India was 0.07 mg/kg (range 0.01 – 0.85), which is about the same as in this work [3]. In Poland, the Polish National standard for cadmium in chocolates (0.050 mg/kg) was not reached by any of the samples investigated [6,20], however. Apart from progress in trace element analytical techniques and blanks, concerns about cadmium might have led levels to decrease.

Chromium

Chromium found in this work (median 0.82, range 0.145 – 2.27 mg/kg) is within the range met in green plants, and lower than for chocolates sold in Nigeria (mean 1.9, range 1.1 – 3.0 mg/kg) [17]. Due



to factor analysis, Cr correlates with Al, Fe and Si, thus its source is rather soil than stainless steel, or just the physiology of the cocoa bean.

Cobalt

Cobalt concentrations in this work are much lower than half of the nickel, which is usual in geological samples, and range from 0.050 to 0.789 mg/kg (median 0.272), which is more than in wheat and potatoes [22]. For cocoa, no other data were found.

Copper

Copper concentration in cocoa and its products (median 9.87; range 3.47 – 31.6 mg/kg) ranges among the top values, it is more than in pig liver (per wet weight; pig liver is a top copper carrier) [26], double of whole-meal bread [24], and thrice of eggs. This is not new, however. In the US, chocolate drinks and chocolate cakes were found to range among the 20 top foods for copper. The total dietary copper intake by males and females was positively associated with the consumption of chocolate foods, which is a main source of Cu-intake. Milk chocolate candies contained 4.55 ± 0.64 mg/kg Cu [27]. 100g of chocolate satisfies the recommended daily intake. Among chocolate foods, the dark chocolate made the highest contribution to the mean daily copper intake within a 3-day dietary record study, followed by chocolate pie and chocolate milk [28]. In addition, high proportions of polyunsaturated fatty acids favor copper retention [29].

Similarly, in Malaysia, mean Cu in milk chocolate was 3.59 mg/kg (range 2.92 – 4.62), and in dark chocolate 5.17 mg/kg (range 4.12 – 6.34) [30]. Chocolate brands had significant higher metal levels of Cu than candies [17]. Among nutrients important to feed babies and small children in Poland (milk, cheese, eggs baby food, honey), chocolate contained significantly more Cu (5.2 ± 2.1) mg/kg than milk, honey and eggs [30]. Apart from the physiology of the cocoa bean, a possible source might be its extense use in cacao plantations [9]. Cocoa shells contained more than double of copper concentration, but they are not used for chocolate production [5].

Iodine

Iodine levels have been found rather low, at a median of 0.161 (range 0.013 – 1.11 mg/kg), and 1 kg of chocolate is needed to reach the recommended daily intake of 150 mg. Like for Ca, iodine concentration versus cocoa contents exerts a parabolic function, and more is met in milk chocolate (Figure 1). Because milk is the main source, milk chocolate candies in the US contained even more iodine (0.41 ± 0.01 mg/kg) [27].

Iron

Iron concentrations were determined at 88.1 mg/kg as the median (range 20.1– 167), which is 3 times like whole-meal bread, but less than in pig liver (pig liver is a top Fe-carrier among animal derived foods) [26]. The recommended daily intake is thus easily reached from 200 g chocolate, making it a significant source of Fe, particularly for vegetarians. In the US, milk chocolate candies contained 8 times less Fe than dark chocolate [27]. Iron present in cocoa powder is 93%, and P is 85% bioavailable, because there is almost no phytate present [4].

Among nutrients important to feed babies and small children in Poland, chocolate contained significantly more Fe (25 ± 10) mg/kg than milk, honey and eggs [30].

Magnesium

Cocoa and chocolate are a strong source for Mg (median 1205 mg/

kg, range 530-2521), and range like whole-meal bread and potatoes [22]. Cocoa contains 4-5 times more Mg than peas, white wheat, corn, and rice [24]. The recommended daily intakes of 300-400 mg Mg are covered by about 300 mg chocolate.

Manganese

Manganese levels in cocoa and its products (median 12.3 mg/kg, range 2.73-26.2) are slightly less than in cereals, but more than in potatoes, maize and meat of any kind [22,24,26]. It is not realistic to meet the recommended daily intake of 10-30 mg Mn from chocolates. In Poland, (milk, cheese, eggs baby food, honey), chocolate contained significantly more Mn (8.3 ± 3.8) among nutrients important to feed babies and small children than milk and honey and eggs [30]. In the US, mean Mn concentration met in milk chocolate candies was 3.37 mg/kg [27].

Nickel

With respect to other food items (e.g. vegetables), nickel levels in cocoa and cocoa products were rather high (median 2.84 mg/kg, range 0.61-8.97; for dark chocolates see Figure 3), and followed a Gaussian frequency distribution. Just nuts might contain more, but vegetables and fruits much less [31]. Data of this work resemble those found in India for milk chocolate (median 1.74; range 0.14 -8.29) and dark chocolate (2.76; range 0.05 – 8.29 mg/kg) [6]. Also, in Turkish chocolates, highest nickel concentrations were found in plain chocolate (4.78 mg/kg) [9]. A special survey for nickel in cocoa and its products in the Netherlands resulted in 9-16 mg/kg nickel in cocoa, 3-4 mg/kg in dark chocolate, and 1 mg/kg in milk chocolate. White chocolate contained only cocoa butter, and contained just 0.06 – 0.12 mg/kg Ni [31]. Daily needs for nickel have been estimated as low as 0.05 – 0.075 mg, and are exceeded anyway. Up to 100 mg ingested nickel, no toxic effects have been observed, except in case of nickel allergies [31]. As the pH of the fermented cocoa beans ranges between 5.2 and 5.6, hydrogen addition to unsaturated fats in presence of nickel catalysts, and nickel containing devices might be sources of nickel contaminations [6].

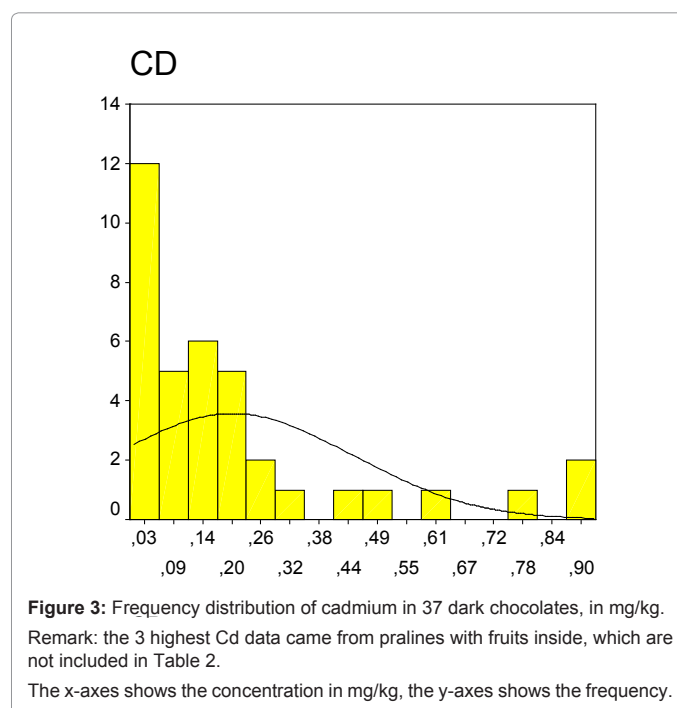


Figure 3: Frequency distribution of cadmium in 37 dark chocolates, in mg/kg. Remark: the 3 highest Cd data came from pralines with fruits inside, which are not included in Table 2. The x-axes shows the concentration in mg/kg, the y-axes shows the frequency.

Lead

In this work, Pb has been found to occur in cocoa and its products at a median concentration of 0.034 mg/kg (range 0.012 – 0.395). This is within the range found in Poland recently (0.044 ± 0.011 for dark chocolates and 0.049 ± 0.026 for milk chocolates) [20], but significantly lower than recent values of samples reported from India (range 0.24 – 8.04 mg/kg for dark chocolate and 0.23- 2.62 mg/kg for milk chocolate) [3] and Nigeria (<0.4 – 2.3 mg/kg) [17]. In Poland, lead concentrations in chocolates ranged at about 15-20% of the national threshold level of 0.30 mg/kg, which was not reached at all [20]. As a main source of Pb-contamination, atmospheric deposition is presumed during roasting the cocoa beans in the open [32]. In the chocolate production process, however, Pb levels get significantly lowered with respect to the levels encountered in cocoa beans [5]. Cocoa beans sampled 1977-79 and analyzed by graphite furnace-AAS, contained 0.05 – 1.4 mg/kg Pb, the highest levels were found in samples from the Caribbean and Sri Lanka. At this time, milk chocolate sold in Germany contained 0.10 mg/kg and dark chocolate 0.28 mg/kg Pb [33]. Since then, Pb-levels have been obviously decreasing in Europe. The European Commission has set the tolerably weekly intake for Pb at 25 µg/kg body weight [15].

Silicon

Silicon levels met in this work (median 45.5; range 7.0 – 84.8 mg/kg) resemble those found in whole meal bread or unpeeled rice. Just a few data are available about the occurrence of silicon in food, highly siliceous plant parts, like reeds or straw, are unsuitable for human nutrition. Silicon is also enriched in brans of cereals [23], but its availability seems to be rather low. High uptake rates are achieved from beer and from soups [34]. The availability of silicon from plant-based food is thought to be at 1-2 %, but as high as 40- 70% from infant formula and milk. Belgian normal diet was calculated to contain 9-43 mg silicon per day. Though silicon is not considered to be an essential element, silicon has an important role in bone mineralization, and prevents from osteoporosis, the ageing of skin, and atherosclerosis. The daily intake was estimated for Belgium at 19 mg, for Britain at 31 mg, and for China at 139 mg Si [35].

Strontium

Within this work, strontium was found at a median of 4.53 mg/kg (range 1.63-8.2), which is about the same like published for German food within a double portion study at 14 locations (range 3.7 - 12 mg/kg; [3]). Strikingly, no strong correlation between calcium and strontium could be established, though green plants usually cannot discriminate between calcium and strontium. A possible explanation of this phenomenon might be the addition of lime or dolomite to neutralize the slightly acid (pH 5.2-5.6) fermented cocoa beans.

Zinc

Median zinc in chocolate and cocoa was 22.3 mg/kg (range 10.2-52.3), which is about the same level than in meat and sausages (based on fresh weight; [26,36]). The recommended daily intake of 15 mg can be hardly reached.

In Poland, Zn in milk chocolate (12 ± 3 mg/kg) was at the same level as Zn in milk, honey and eggs [30].

Conclusions

From elemental composition it can be concluded that it is justified to discriminate cocoa and chocolate from other sweets, like bakery

products, candies and honey within national nutrition plans and diet statistics, because of their significantly different element contents. In particular, essential elements might significantly contribute to healthy nutrition, but also aluminum, cadmium and nickel have to be taken into consideration. As cocoa composition is the main contributor to the composition of plain and milk chocolate, quality control should focus on cadmium and nickel in cocoa. To the knowledge of the author, data on boron, silicon and iodine have been given for chocolate for the first time. Chocolate is sold to consumers usually at 300 g, 100g and also smaller sizes. Referring to median values given in this work, 100g cover the daily needs for copper, 200g for iron, 300 g for magnesium, and 300 g milk chocolate for calcium. It is of particular importance for vegetarians that the availability of iron and other trace elements is quite high, because of low levels of phytic acids therein (93 % iron availability due to [4]). To the contrary, supply with cobalt, zinc, manganese, molybdenum and iodine, is at medium levels. Essential trace element intake is thus much improved, if children get (quality controlled) chocolate or milk chocolate instead of candies or sweet bakery products. In order to find relationships between various elements, simultaneous determination of cations and anions in the food matrix seems to be useful. This shows that the source of chromium is more likely due to an input of a tropical soil than from abrasion of vessels, as it correlates with aluminum, silicon and iron.

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