

The Effect of Cocoa Beans Heavy and Trace Elements on Safety and Stability of Confectionery Products

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Abstract. The aim of the study was to evaluate cocoa beans quality produced in Cameroon, Ecuador, Nigeria and Ghana from safety position determining heavy and trace metals concentration and evaluating the oxidative stability of confectionery products prototypes (trials) with analysing cocoa beans. For evaluation of oxidative stability of confectionery products, the main ingredients - butter and cocoa beans kernels were tested making trials as milk chocolate prototype.

The composition of confectionery ingredients affects quality of products; therefore it is very important to evaluate quality of raw materials in confectionery industry, as they are purchased practically in all regions of the world. Mercury, arsenic, lead, cadmium concentration was determined in whole cocoa beans as their presence in foods have toxic effect on human beings and their concentration are strictly limited as maximum residue limits for processing. Cocoa shells can be used as additive to confectionery products recipes therefore the object of the study was cocoa beans and cocoa shells.

Analyzing cocoa beans quality indices there was established that lead, cadmium, aluminium and zinc concentrations vary in cocoa beans significantly. Differences in lead concentration in cocoa beans from Ghana, Cameroon and Ecuador were significant ($p < 0.05$) compared with concentration of lead in cocoa beans from Nigeria ($p > 0.05$). Cadmium concentration in cocoa beans from Cameroon was significantly different comparing with cocoa beans from Nigeria, Ecuador and Ghana ($p > 0.05$). Differences in aluminium concentration in cocoa beans kernels were significant ($p < 0.05$) in all analyzed samples. Concentration of zinc was higher in shells of cocoa beans, especially in shells of cocoa beans from Ecuador ($p < 0.05$). The presence of cocoa products in milk chocolate prototypes inhibited the speed of lipid peroxidation. The different trace and heavy metals concentrations in cocoa beans should be taken into account choosing ingredients and components for confectionary products production particularly those with high content of cocoa (chocolates, sweets, cocoa fillings, cocoa creams and others) with the aim to prevent oxidation process during shelf-life of products.

Key words: cocoa beans, heavy, trace metals, peroxides.

Introduction

Cocoa products are widely consumed foods worldwide. Cocoa beans are raw materials for production of chocolate, candies, cocoa powder and beverages. Heavy and trace metals presence in these products is a result of their accumulation in the cocoa beans during vegetation. The concentration of cadmium, lead, copper and arsenic in cocoa beans is of the interest as these metals or trace elements (in high concentrations) are generally considered as toxic to human beings. A lot of researchers have investigated the content of cadmium (Cd), copper (Cu), lead (Pb), and arsenic (As) in cocoa beans from various countries as well as in some chocolate products. Heavy metals such as Pb, Cd, and trace element -Cu are generally regarded as environmental

contaminants and their presence in foods have toxic effect in human.

Due to the importance of heavy metals on human health, the European Commission has set up maximum residue limits for specific heavy metals in cocoa beans in Regulations setting maximum levels for certain contaminants in foodstuffs (Setting maximum levels for certain contaminants in foodstuffs, 2006; Maximum levels of cadmium in foodstuffs, 2014). Therefore, it is very important to evaluate the quality of raw materials in confectionery industry, as they are purchased practically in all regions of the world.

Ingredients that are used in production of confectionery products and desirable constituents which are formed during production processes and shelf-life affect

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nutritional value of products (Fennema, 1985). One of the factors that can reduce the quality of products and can have a negative effect on human health is fat oxidation products in the form of peroxides in food.

Peroxides/hydroxiperoxides and free radicals can be undesirable compounds in food products (Erickson, 2002; Pokorny, 2006). Peroxides are formed from lipids in the presence of oxygen. This process can be promoted by the presence of metal ions as well as heavy and trace elements that contain ingredients in cocoa beans. For prevention of oxidation process antioxidants are added in confectionery products production. Beside food additives, a lot of confectionery ingredients have antioxidant properties due to high concentration of phenolic compounds or fat soluble vitamins.

The aim of the study was to evaluate cocoa beans quality produced in Cameroon, Ecuador, Nigeria and Ghana from safety position determining heavy and trace metals concentration and evaluating the oxidative stability of confectionery products prototypes (trials) with analysing cocoa beans.

Materials and Methods

The object of the study was Forastero type of cocoa beans from different producers. Heavy metals and trace elements concentration was analysed in cocoa beans purchased from Cameroon, Ecuador, Nigeria and Ghana. ISO 2451:2014 standard specifies the requirements for sampling of cocoa beans. Cocoa beans were selected from 10 bags of 60 kg net per bag with a shelf life of around four months. Cocoa beans samples were taken from middle, top and bottom of each bag. It was 10% of the batch. Cocoa beans were mixed and 200 g of cocoa beans were selected and weighted for analyses.

Selenium, zinc and aluminium content was determined in cocoa beans kernels and shells. Analyses of heavy and trace metals were made in Food Safety and Animal Health and Environmental Research Institute "Bior".

Mercury, arsenic, lead and cadmium concentrations were determined according to standard procedures. Mercury was analysed according to ISO 6637-1984 (E) standard procedure, arsenic, lead and cadmium ac-

ording to AOAC 986.15. (1995) method.

Trace elements (selenium, zinc and aluminium) were determined in cocoa beans kernels and shells according to AOAC 986.15. (1995) method.

Forecasting different heavy metals and trace elements concentrations in cocoa beans and their influence on confectionery products quality, oxidative stability of main confectionery ingredients was tested making trials with butter and 36 % of roasted and ground cocoa beans kernels. Cocoa concentration in experimental samples was similar to cocoa concentration in classical milk chocolate. Sweet cream butter (producer – SC Riga dairy) with the fat content of 82.5 % and moisture content of 16 % was used for the experiments. Peroxide value of butter prior investigation was 0.26 mmol kg⁻¹.

Peroxide value was determined according to Wheeler's method (Matisseks, Snepels, & Steiner, 1998). Peroxide value was tested in butter with 36 % roasted and ground cocoa beans kernels after 30 days of incubation at 28±2°C. All samples were prepared in the same conditions and mixed for one minute. Mixed samples were put into Petri plates and kept in an incubator. After that the quantity of peroxides was determined. Chosen parameters correspond to accelerated food shelf-life testing in confectionery industry.

Statistical data analysis was used analyzing differences between cocoa beans and their oxidative stability during accelerated food shelf-life testing. Data were analyzed by one factor dispersion analysis using MS Excel and SPSS program package SPSS 11.0. All tests were regarded as statistically significant when $p < 0.05$.

Results and Discussion

The concentration of heavy metals determined in different origin cocoa beans showed in Table 1.

The results revealed that heavy metal concentration especially lead and cadmium significantly varied in the cocoa beans from different countries. No differences were observed among the countries for mercury and arsenic concentrations in cocoa beans. The highest total concentration of Cd was found in cocoa beans from Ecuador.

Table 1

The concentration of heavy metals in cocoa beans

Indicators	Limit mg kg ⁻¹	Cocoa beans origin			
		Cameroon, mg kg ⁻¹	Ecuador, mg kg ⁻¹	Nigeria, mg kg ⁻¹	Ghana, mg kg ⁻¹
Mercury*	0.1	< 0.01	< 0.01	< 0.01	< 0.01
Arsenic*	1.0	< 0.06	< 0.06	< 0.06	< 0.06
Lead	1.0	0.37 ± 0.05b	0.33 ± 0.04b	0.52 ± 0.07a	0.32 ± 0.04b
Cadmium	0.5	0.05 ± 0.01b	0.20 ± 0.04a	0.020 ± 0.003c	0.017 ± 0.003c

*The method allows determination of value starting from 0.01 mg kg⁻¹

The number of replicates n=3; a,b,c – samples with a similar letter superscripts do not differ significantly ($p > 0.05$)

The highest total concentration of Cd was found in cocoa beans from Ecuador. In the analysed samples cadmium residues range from 0.017 – 0.2 mg kg⁻¹ (Table 1). Data on Cd residues in cocoa beans is scarce probably due to the fact that Cd contamination in agricultural soils is rare. Consequently, the European Union (Maximum levels of cadmium in foodstuffs, 2014) has set a maximal allowable residue limit of 0.5 mg kg⁻¹ for Cd in cocoa powder. However, the level of cadmium in cocoa beans analyzed in this work may not pose any significant health hazard due to relatively low concentration.

Pb residues in cocoa beans obtained from different countries varied from 0.32 to 0.52 mg kg⁻¹. Cocoa beans obtained from Ghana and Ecuador had Pb residues significantly lower than beans obtained from Nigeria. All purchased cocoa beans had Pb residues under maximum permissible levels (1.0 mg kg⁻¹) set by Commission Regulation No 1881/2006. Lead is a toxic chemical and may cause damages to kidneys, cardiovascular, immune, hematopoietic, central nervous and reproductive systems (European Food Safety Authority, 2006). A potentially important source of lead contamination in cocoa beans is tetra-ethyl lead additive in

gasoline, which is still common in many African countries (Rankin *et al.*, 2005). For example, Nigerian gasoline contains 0.4–0.8 g L⁻¹ lead, which is among the highest in the world (Rankin *et al.*, 2005). Overall, it might be difficult to name precisely the source of Pb in cocoa plantations but the fact remains that the level of Pb in cocoa beans is traceable to Pb content in the soil.

According to information mentioned in literature sources Ghana is the second largest cocoa bean producer in the world. Undeniably, cocoa from Ghana is revered to be of the highest quality with high demand in the world market. Due to these quality characteristics of Ghana's cocoa beans, they are mostly used as reference standard for cocoa beans produced from other parts of the world (Fold, 2008). The situation is becoming alarming due to the fact that a lot of cocoa farmers now apply insecticides, herbicides, fungicides and fertilizers on their cocoa farms to control pests and to enhance maximum bean yield. These activities are likely to increase heavy or trace metals like Cd, Fe, Pb, Cu, Mn and Zn into the soil which eventually will end up in the edible parts of the crops through phytoextraction by the crops and translocation throughout the plant system (Thomas, 2015).

Table 2

Selenium, zinc and aluminium concentration in cocoa beans

Place of cocoa beans origin	Kernels			Shells		
	Se* mg kg ⁻¹	Zn mg kg ⁻¹	Al mg kg ⁻¹	Se* mg kg ⁻¹	Zn mg kg ⁻¹	Al mg kg ⁻¹
Cameroon	< 0.1	50 ± 5a	9.2 ± 0.9d	< 0.1	60 ± 6b	4.6 ± 0.5c
Ecuador	< 0.1	58 ± 6a	12 ± 1c	< 0.1	190 ± 20a	9.1 ± 0.9b
Nigeria	< 0.1	49 ± 5a	16 ± 2b	< 0.1	61 ± 6b	9.8 ± 0.9b
Ghana	< 0.1	51 ± 5a	54 ± 5a	< 0.1	68 ± 7b	68 ± 7a

The method allows determination of value starting from 0.1 mg kg⁻¹

The number of replicates n=3; a,b,c - samples with a similar letter superscripts do not differ significantly (p>0.05)

Cocoa bean shells are equivalent to kernels by content of trace elements with some exceptions. Zinc concentration ranged from 49 to 58 mg kg⁻¹ in kernels and from 61 to 190 mg kg⁻¹ in shells. There was no significant difference (p > 0.05) in Zn content among the analyzed kernels samples. Concentration of zinc was higher in shells of cocoa beans, especially in shells of cocoa beans from Ecuador and differences between samples are significant (p < 0.05). The results showed (Table 2) that the content of Zn exceeded recommended dietary allowance per day (average 14 mg for adults and the upper limit is set at 40 mg day⁻¹ for all foods, water and supplements) (Ministry of Health, 2008). The results have revealed that the average concentration of

zinc in cocoa bean shells from Ecuador was the highest comparing with cocoa bean shells data from Nigeria, Ghana, and Cameroon. The most important information reported on zinc toxicity is its interference with copper metabolism. The symptoms that an acute oral Zn dose may provoke are tachycardia, vascular shock, dyspeptic nausea, vomiting, diarrhoea, pancreatitis and damage of hepatic parenchyma (European Food Safety Authority, 2006). Selenium was not detected in any samples of cocoa beans kernels and shells.

Great interest is focused on cocoa and cocoa products for their beneficial health effect because of the high levels of antioxidants they contain. The European Food Safety Authority (EFSA) has approved that fla-

vonoids in cocoa and chocolate products are associated with a lower risk of cardiovascular disease (European Food Safety Authority, 2012).

The antioxidants potential of cocoa beans components was approved through accelerated food shelf-life testing results of experimental samples that are showed in Table 3. Authors decided to measure peroxide value of experimental samples only after 30 days of incubation and obtained results to compare with butter perox-

ide value data. In this case we analysed different oxidation speed of samples with and without cocoa beans additives.

The experiment showed that there were not significant differences between samples with cocoa beans kernels from Ghana and Nigeria during storage time ($p > 0.05$) and their oxidative stability was practically the same.

Table 3

Peroxide value of analysed samples

Samples	Peroxides value, mmol kg ⁻¹ before storage	Peroxides after 30 days of storage, mmol kg ⁻¹
Butter (control sample)	0.26 ± 0.02	0.65 ± 0.01a
Butter with roasted cocoa beans kernels from Cameroon	-	0.35 ± 0.02c
Butter with roasted cocoa beans kernels from Ecuador		0.16 ± 0.01d
Butter with roasted cocoa beans kernels from Ghana		0.49 ± 0.01b
Butter with roasted cocoa beans kernels from Nigeria		0.51 ± 0.02b

The number of replicates n=3; a,b,c,d- samples with a similar letter superscripts do not differ significantly ($p > 0.05$)

It was established that cocoa shells have antioxidants effect (Bruna *et al.*, 2010; Vitola & Strautnieks, 2004; Vitola, Karklina, & Strautnieks, 2005) but in this study we concluded that cocoa bean kernels could have antioxidant potential, too. The research established that the most effective peroxides formation was eliminated in the sample with Ecuador cocoa beans (Table 3). This statement we could explain by analysing zinc results (58 mg kg⁻¹ in kernels and 190 mg kg⁻¹ in shells) because the ability of zinc to retard oxidative processes has been recognized for many years (Powel, 2000). The presence of cocoa products in samples inhibited lipid peroxidation but according to findings of Andujar and co-authors (Andujar *et al.*, 2012) had no effect on the hydroxyl radical, nor did it exhibit ferrous chelating activity. Metal chelating capacity reduces the concentration of the catalyzing transition metal in lipid peroxidation (Schinella *et al.*, 2010) and with this statement we can explain our study results. However, because the polyphenol-rich cocoa extract showed neither ferrous nor copper chelating activity, it most likely acts as a chain-breaking antioxidant (Andujar *et al.*, 2012). Cocoa beans composition was heavy and trace elements could influence lipids stability fastening or delaying peroxides formation in confectionery products.

Conclusions

1. Lead, cadmium, aluminium and zinc concentrations significantly vary in analyzing cocoa beans. No differences were observed among the countries for mercury and arsenic concentrations.
2. The different trace and heavy metal concentrations in cocoa beans should be taken into account by choosing ingredients and components for confectionery products production with the aim to prevent oxidation process during shelf-life of products.
3. The research established that the higher zinc concentration in the sample with Ecuador cocoa beans kernels prevents peroxide formation comparing with Cameroon, Ghana and Nigeria cocoa beans kernels.

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