TECHNOLOGICA ACTA

JOURNAL OF SCIENCE PROFESSIONAL FROM CHEMISTRY AND TECHNOLOGY - FACULTY OF TECHNOLOGY TUZLA

ISSN 1840-0426
ISSN 2232-7568

Vol. 6
Number 2
December, 2013. year

UNIVERSITY OF TUZLA
FACULTY OF TECHNOLOGY

TECHNOLOGICA ACTA

Journal of Science-professional from Chemistry and Technology Faculty of Technology Tuzla
Vol. 6 Number 2, page 1-46, Tuzla, december 2013. year

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Publisher / Izdavač
Faculty of Technology University in Tuzla

Printing / Štampa
IN SCAN d.o.o. Tuzla

Journal prints two times of year

Technologica Acta is indexed in the following database: CAB Abstracts, COBISS, Index Copernicus Journal Master List, EBSCO

This number of Technologica acta is supported by the Federal Ministry of Education, Science and Culture of Bosnia and Herzegovina

Edition / Tiraž: 200

Editorial Office / Uredništvo
Secretary / Sekretar: Nermina Jahić
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Tel/fax: +387 35 320 740

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THE EFFECT OF THE DISTILLATION SYSTEMS ON THE QUALITY OF APPLE DISTILLATES

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT

Apple distillates are a common drink in Western European regions and considered as a high quality product. There are many factors that will influence the production and the quality of apple distillates.
The aim of this work was to produce apple distillates by column devices with different rectification index (1, 1.75 and 2.6) and by *alambic* device (classic process and double distillation). Distillates were analyzed to determine chemical composition, aroma profile and sensory properties.
Apple distillates produced by column process had significant higher ethanol content, but lower aldehydes, higher alcohols, esters and monoterpenes. All samples had very low concentration of methanol and furfural. Apple distillates produced by column process had significant higher grades of sensory properties.

Key words: *apple distillate, distillation, quality*

INTRODUCTION

Alcoholic beverages are complex mixtures mainly comprised of ethanol, water and a large number of minor compounds that may be present in the raw materials or formed during the distinct stages of the manufacturing process such as: alcohols, acids, esters, aldehydes, polyphenols, metals, aminoacids, etc. (Rodríguez Madrera & Suárez Vales, 2007).
Production of apple distillates (also called cider brandy or calvados in France or applejack in USA) is mentioned as far back as the 8th century. Cider brandy is a common drink in Western European regions where, because of peculiar climatic characteristics, grape-vine cultivars are not viable. In these countries, cider brandy is considered a high quality product and a factor of important economic repercussion. There are many factors that will influence the production and the quality of apple distillates. These include the type of cultivar, geographical origin, processing of the apples, fermentation, distillation processes and maturation of the distillate in oak barrels to produce the final aged brandy (Mangas et al., 1996). Apple distillate aroma depends more on technological parameters (Askew & Lisle, 1971) in addition to maturation in wood barrels (Onishi et al., 1977; Profumo et al., 1988), than on the raw material, since volatile compounds are formed during fermentation, distillation and aging from their precursors. However, the process of distillation is one of the most important factors to consider (Leaute, 1950). For instance, the extended length of heating in double distillation systems produces cider brandies with higher contents in furfural due to degradation of residual sugars (Rodriguez Madrera et al., 2003), thus imparting a caramel aroma.
Distillation is usually carried out in a traditional alembic pot still or in modern column still (single continuous distillation). The usual arguments for and against the two processes are that the column process gives the fresh and clean apple flavour but with less complexity. On the other hand, a traditional practice in the production process gives the distillate complexity and renders it suitable for longer aging (Guan and Pieper, 1998; Picinelli et al., 2005) as well as increase consumer approval of products.

In this work distillates were produced by distillation of fermented apple pulp in column devices with different rectification index (1, 1.75 and 2.6) and by simple *alambic* device (classic process and double distillation). Produced apple distillates were analyzed to determine chemical composition, aroma profile and sensory properties.

MATERIALS AND METHODS

Preparation of apple distillates

Preparations of apple distillates were carried out in Zvečevo d.d. food industry Požega. Apple pulp (*Golden Delicious* varieties) was prepared and then treated with SO_2 (50 mg/L), as recommended by Nikićević and Tešević (2010). Fermentation was carried out in a fermenter at temperatures between 18-20°C with selected yeast *Feromol-Bouqet 125* (*S. cerevisiae*, LSA Pascal Biotech). The duration of fermentation was 12 days.

After fermentation samples were distilled in industrial copper clip distillation device, according to the distillation protocol:

Apple distillate (AD1): Column process with rectification index 1

Apple distillate (AD2): Column process with rectification index 1.75

Apple distillate (AD3): Column process with rectification index 2.60

Apple distillate (AD4): Classic process of distillation in *Alambic*

Apple distillate (AD5): Double distillation in *Alambic*

Chemical analysis of distillates

Chemical analysis of distillates (ethanol, extract, SO_2, aldehydes, higher alcohols, total acids, esters, methanol and furfural) was conducted according to standard AOAC (1995) procedures.

Analyses of aroma substances

Gas chromatography analyses were performed by gas chromatograph (Hewlett-Packard, type 5890) with a split/splitless injector and an FID detector. For analysis of distillates a Stabilwax (Restec); 30 m; i.d.=0,25 μm capillary column was used. Initial oven temperature was kept at 35°C for 7 min, then raised at 10°C/min to 80°C followed by 25°C/min to 200°C, and kept for 4 min at 200°C. Qualitative analysis was done by comparing the standard retention times (analytical grade from *Merck KGaA Darmstad,* Germany) with the corresponding peaks of samples. The quantification was carried out by comparing the peak areas to those of the Merck standards.

Sensory analyses

A sensory analysis of samples was performed according to the method of positive scoring factor according to the German DLG model (Koch, 1986).

This model was based on 4 sensorial experiences: colour, clearness, odour and taste, which are marked with grades 0 to 5, including 0, while the average grade is multiplied by the significance factor.

Sensory assessment was conducted in two repetition cycles by ten sensory testing experts.

RESULTS AND DISCUSSION

Chemical analyses

Chemical composition of apple distillates (AD) is presented in Table 1 and was in accordance with results reported by Rodriguez Madrera et al. (2006) and Versini et al. (2009).

Distillates had ethanol content ranging from 61.60% to 71.5%, where AD produced by column process had significant higher ethanol content: AD1, 69.91%; AD2, 69.7%; AD3 71.5%; AD4, 63.27% and AD5, 61.6%.

The content of total extract in distillates was in range 14.0-68.0 mg/L where AD4 had the highest value of 68.0 mg/L, followed by AD5 (58.0 mg/L), AD1 (41.0

mg/L), AD2 (34.0 mg/L) and AD3 (14.0 mg/L).

The presence of free SO_2 in distillates ranging from 3.85 to 4.55 mg/L is the result of addition of 50 mg/L SO_2 during production process. SO_2 is important for the protection of pulp from degradation processes and non-controlled fermentation (Nikićević and Tešević, 2010).

Adehydes content were in range from 280.00 to 374.00 mg/L and higher alcohols from 1830.71 to 2845.57 mg/L, where AD produced by *alambic* process had higher level of adehydes and higher alcohols. As regards the higher alcohols quantities, it should be noted that their concentration in AD4 and AD5 is clearly higher than the minimum value accepted by the European Community Council Regulation of 2000 mg/L of a.a. These alcohols, except for 2-butanol, are formed from amino acids during the fermentation of apple pulp therefore their level in the final distillate depend on several factors such as raw material, yeast strains and fermentation conditions (Suarez Valles et al., 2005; Rodriguez Madrera et al., 2006).

The content of total acids and esters shows higher values for the AD produced by *alambic* process compared with the AD produced by column process. As from the literature referred both to distillates (Genovese et al., 2003), and to fermented products like beer (Meilgaard, 1975), these compounds are responsible for a so-called sweet alcoholic-floral-basic aroma on which interact other sensory active substances typical of the beverages.

Methanol is not a yeast fermentation product, but this volatile is cleaved from pectins, and its concentration depends on several factors as apple variety and ripening state (Suarez Valles et al., 2005). In this respect, the results obtained for AD shows values clearly below the maximum content of 12 g/L established by *Regulation,* 2009.

Differences of furfural content are not noted between the AD. Furfural formation in distillation is basically due to the presence of pentose residue in the mash as well as to a possible amadori decomposition product via 1,2-enolisation (Versini et al., 2009). The five AD presented furfural values ranging from 0.001 to 0.003 mg/L.

Table 1 Chemical composition of apple distillates

	AD1	AD2	AD3	AD4	AD5
Ethanol (% vol.)	69.91	69.70	71.50	63.27	61.60
Extract (mg/L)	41.0	34.0	14.0	68.0	51.0
SO_2 (mg/L)	4.54	3.95	3.85	4.55	4.04
Aldehydes (mg/L a.a.)	280.00	305.00	307.00	374.00	370.00
Higher alcohols (mg/L a.a.)	1955.14	1830.71	1880.27	2845.57	2837.39
Total acids (mg/L)	217.60	185.00	184.20	384.20	447.00
Esters (mg/L a.a.)	768.23	828.23	591.00	997.80	933.10
Methanol (g/L a.a.)	0.02	0.02	0.01	0.04	0.04
Furfural (mg/L a.a.)	0.002	0.001	0.001	0.002	0.003

AD1: distillate by column process with rectification index 1; AD2: distillate by column process with rectification index 1.75; AD3: distillate by column process with rectification index 2.60; AD4: distillate by classic process of distillation in *Alambic*; AD5: distillate by double distillation in *Alambic*

Analyses of aroma substances

Table 2 shows the average contents (mg/L) of the volatile components of apple distillates (AD). Among the different substances that determine the specific flavour of distillate spirits, volatile compounds are the most important.

Analysis of these substances allows characterization of the product. Beech and Carr (1977) showed that cider brandies present differences in relation to the levels of low-temperature boiling compounds. On the other hand, typical aromatic compounds (alcohols, esters, allyl derivatives, etc.) have been associated with apple-like odours (Williams et al., 1977; Mangas et al., 1996). Scheirer et al. (1978) investigated the changes in aroma composition during apple-brandy production. Quantitative determinations of 97 aroma components have shown that the aroma of unaged apple brandy is characterised by components produced as a result of the yeast fermentation and technological steps such as mashing and heating rather than by the genuine apple aroma components.

Distillation enhanced the concentration of ethyl esters and many of the higher alcohols (Scheirer et al., 1978). Generally, AD produced by *alembic* process had higher concentration of esters. Ethyl acetate content was in range 44.31-57.49, where AD4 had the highest level of 57.49 mg/L, followed by AD5 57.27 mg/L, AD1 56.57 mg/L, AD2 54.2 mg/L and AD3 44.31 mg/L. Ethyl acetate is the main ester in many fresh distillates, the aroma of which is described as glue/varnish (Rodriguez Madrera et al., 2006). The levels of this compound in distillates are related to the quality of the raw materials used. It may be formed during fermentation or during distillation by esterification of acetic acid with ethanol. Its low boiling point (77°C) and minor solubility in water (10%) make it a typical product of first fractions during distillation (Rodriguez Madrera et al., 2006). Other esters were in lower concentration: isoamyl acetate 24.96-27.35; acetaldehyde 12.22-28.68; ethyl octanoate 12.69-19.18; ethyl decanoate 10.91-11.74; 2-phenylethyl acetate 1.87-2.84; ethyl hexanoate 0-2.84 and ethyl lactate 0-4.10. The ethyl esters of fatty acids from hexanoate to ethyl decanoate related to a ripe fruits aroma (Salo, 1970) were at medium to low level which is in accordance with Versini et al. (2009). Ethyl lactate is present with rather low values in AD, a fact that indicates a reduced presence of lactic or malo-lactic fermentation in the apple pulp (Versini et al., 2009).

2-phenylethanol was of fermentative origin according to Williams (1975) and Schreier et al. (1978). Its presence in spirits, with respect to other alcohols, must be attributed to the fact that this alcohol is predominant in tails, due to its high boiling point, and which furthermore presents low solubility in water, which promotes a low recovery in spirit. This alcohol could contribute to the aroma of AD with floral or rose notes (Salo, 1970; Rodriguez Madrera et al., 2006; Versini et al., 2009). The levels of 2-phenylethanol detected in AD were in range 2.97-4.75.

Monoterpenes level can derive from the free forms often after acid catalysed rearrangements during the distillation, as well as from bound forms present in the mash (Skouroumounis & Sefton, 2000; Versini et al., 2009). Cis and trans furanic linalool oxides dominate (linalool, α-terpineol, 4-terpineol). These compounds contribute to the floral aroma of products (Versini et al., 2009).

Table 2 Average contents (mg/L) of the volatile components of apple distillates

	AD1	AD2	AD3	AD4	AD5
Ethyl acetate	56.57	54.20	44.31	57.49	57.27
Isoamyl acetate	25.60	25.80	24.96	27.32	27.35
Acetaldehyde	12.76	12.96	12.22	28.68	28.51
Ethyl octanoate	15.92	12.69	12.92	19.18	17.18
Ethyl decanoate	11.74	10.91	11.18	11.20	11.19
2-phenylethyl acetate	2.37	1.87	1,97.	2.84	2.76
Ethyl hexanoate	2.47	1.57	n.i.	2.82	2.74
Ethyl lactate	3.07	1.41	n.i.	4.10	3.95
2-phenyl ethanol	2.97	3.52	3.45	4.75	4.73
Linalool	0.63	0.87	1.33	0.11	0.02
α-terpineol	3.1	3.78	3.17	5.23	5.17
4-terpineol	3.01	3.02	3.45	5.40	5.50
Limonene	11.14	12.16	13.27	7.23	16.16

AD1: distillate by column process with rectification index 1; AD2: distillate by column process with rectification index 1.75; AD3: distillate by column process with rectification index 2.60; AD4: distillate by classic process of distillation in *Alambic*; AD5: distillate by double distillation in *Alambic*

Sensory analyses

Sensory analyses of apple distillates (AD) were conducted according to German *DLG* model (Koch, 1986). Total points of sensory analyses of AD ranged from 80.60 to 98.50 (Table 3). Different sensory characteristics of AD can be addressed to distillation protocol, since other factors in the production of distillates were same for all AD. AD produced by column process had significantly higher grades of sensory properties. The best evaluated sample was AD3 (produced by column process with rectification index 2.60) which had 98.5 total points, followed by AD1 (96.5), AD2 (96.3), AD5 (81.0) and AD4 (80.6).

The samples produced in column with different index of rectification had pleasant recognizable apple fruity aroma, without sharp odour tones (caused mainly by malic acid).

Table 3 Results of sensory analyses of apple distillates (*German DLG model*)

Sample	Assessment characteristics				**TOTAL** (max 100 points)
	Colour (max 15 points)	**Clearness** (max 15 points)	**Odour** (max 25 points)	**Taste** (max 45 points)	
AD1	14.80	14.80	24.50	42.40	96.50
AD2	14.80	14.80	23.50	43.20	96.30
AD3	15.00	15.00	24.50	44.00	98.50
AD4	14.70	14.40	15.50	36.00	80.60
AD5	14.70	14.70	15.50	36.00	81.00

AD1: distillate by column process with rectification index 1; AD2: distillate by column process with rectification index 1.75; AD3: distillate by column process with rectification index 2.60; AD4: distillate by classic process of distillation in *Alambic*; AD5: distillate by double distillation in *Alambic*

CONCLUSIONS

Apple distillates produced by column process had significantly higher ethanol content, but lower adehydes and higher alcohols. Distillates produced by *alambic* process had higher alcohols concentration than the minimum value accepted by the EU Regulation of 2000 mg/L of a.a. All samples had very low concentration of methanol and furfural. Distillates produced by *alembic* process had higher concentration of esters and monoterpenes compared to those produced by column process.

Apple distillates produced by column process had significantly higher grades of sensory properties. The best evaluated sample was produced by column process with rectification index 2.60 which had 98.5 total points (max 100).

Increasing the index of rectification could be promising approach in processing of the apples distillates for industrial productions of apple brandy.

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INFLUENCE OF PHYSICAL AND CHEMICAL CONDITIONS OF SOIL ON AVAILABILITY OF COPPER AND CADMIUM

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT

There are many factors which have impact on the intake and bioavailability of heavy metals from soil into plant. Taking into consideration, that heavy metals can be attached to the clay and other soil colloidal particles, such as organic, part, it is very important to know the way of their binding. In this small study, the content of copper and cadmium has been estimated, as well as other factors of soil. Based on the concentration of copper and cadmium in soil, and in soil solutions, using available computer software, such as MINETQ and Medusa, predication of complex forms have been estimated, as well as fractional distribution of those metals in clay, soil solution and in organic matters. Experimental data used in this work, have been obtained using electrochemical method, differential pulse anodic stripping voltammetry.

Results obtained in this work have showed that estimation of mobility and bioavailability are keys of monitoring of intake of heavy metals from soil to plants.

Key words: copper, cadmium, soil, complexes,

INTRODUCTION

Heavy metals can be distributed and bond in soil to different phases, such as clay, organic matter, be dissolved in soil solution and the rest. The distribution of heavy metals in soil depends on many factors, including acidity, the content of organic matter, CEC, ionic strength, etc.

The main factors, which can have impact on realizing and binding of heavy metals in soil are pH and the content of organic matter. In study, performed by Kim, 2010, differences in the soil pH and organic matter contents of the two shooting ranges explained the differences in trace element fractions and chemical species, which in turn influenced the bioavailability and mobility of the trace elements present. Therefore, identification of the risks of contaminated soil to their surrounding environment through continuous monitoring of soil at the shooting ranges is very important[5].

The knowledge of the binding of metals with the different soil phases and components is of major interest to assess the connections with other biotic and a biotic elements of the environment Nevertheless, as Cabral and Lefebvre indicate, the metal speciation is a more complex task that determination of total metal contents[2]. It is widely recognized that to assess the environmental impact of soil pollution, the determination of the metal speciation will give more information about the potential for release of contaminants and further derived processes of migration and toxicity[6,11].

To have the regular monitoring of heavy metals in soil and in its solutions, their mobility is controlled by the chemical forms or complexes in which they occur in the pore water of soils[10].

However, different chemical methods and techniques can be used, such as differential pulse anodic stripping voltammetry (ASV) in order to determine the concentration of ‘‘labile’’ metal such as Pb, Cu and Cd in contaminated soils.

In general, different research show different conclusion on availability of heavy metals in soil. The absence of mobile forms of Pb eliminates the toxic risk both in the tropic chain and its migration downwards the soil profile. The results, obtained in researches also indicate that most of the metals have high abundance in residual fraction indicating lithogenic origin and low bioavailability of the metals in the soil. The average potential mobility for the metals giving the following order: Sn > Cu > Zn > Pb > Cr > As[1].

Metal in soils can be divided into two fractions (Rachou and Sauvé, 2008): (i) inert fraction, assumed as the non-toxic fraction, and (ii) the labile fraction, assumed to be potentially toxic. To assess the availability of heavy metals, only the soil labile fraction is taken into account because this fraction is often called, by extension, the bioavailable fraction[3]. However, the bioavailable fraction can differ from one metal to another and from one receptor to another. The availability of metals for plants and micro-organisms in soil depends on the composition of the different compartments of soil such as carbonates, (oxy) metal hydroxides, organic matter and silica[8].

In research of binding of heavy metals such as Cu and Pb, have showed that they are mostly bound to organic matter and metallic (oxy) hydroxides in the proportions of 54.26% (Cu) and 26.43% (Pb). The study of the potential mobilization showed that metals are retained by co-precipitation or incorporation into crystalline particles. So, aggressive conditions could release them. The soil treatment with hydrochloric acid at pH 0.5 allow the extraction up to 69% of total Cd, eliminating more than 34% of the portion bound to silica, 23.84% (Cu), 65.52% (Zn) and 31.62% (Pb)[9].

MATERIALS AND METHODS

Preparation of samples, including soil and other was performed by conventional methods of digestion; dry burning and wet mineralization.

Copper and cadmium were determined by simultaneous and individual analyses.

Standard solutions for heavy metals determinations used in experiment are suprapure chemicals produced by Merck.

Analyses of copper and cadmium were performed in various supporting electrolytes, including, KNO_3, KCl with the instrumental parameters given in Table 1.

Table 1. Instrumental parameters for determination of copper and cadmium in soil samples

Metal	Initial Potential	Final Potential	Deposition Time	Speed of Scanning	Deaeration Time	Amplitude
Copper	- 0,3 V	0,1 V	300 seconds	2 mV/s	120 seconds	0,05 V
Cadmium	-0,9 V	-0,6 V	300 seconds	2 mV/s	120 seconds	0,05 V

In table no. 1, parameters for determination of concentration of copper and cadmium in soil samples were given, with other necessary parameters for estimating of those metals content which are set by electrochemical method DPASV (Differential Pulse Anodic Scanning Volattmetry) method. The limits of detection for heavy metals, cadmium and copper were given, and based on the current which is obtained by DPASV method, concentration of those metals has been calculated using graphic methods.

The equipment which is used in determination of content of heavy metals in soil, consists of electrochemical cell, type Princeton Applied Research (EG & G) model 303A with Working (HMDE), Referent (Ag/AgCl) and Supporting (Pt-wire) Electrodes, as well as potenciostat/galvanostat, PAR, model 263 A, and software Model 270/250 Research Electrochemistry Software, version 4.3.

RESULTS AND DISCUSSION

In order to use the soil for the laboratory observation of heavy metals intake, some analyses are performed such as organic matter, alumosilica, ox-redox potential, conductivity, capacity of cation exchange, capacity of anion exchange,

Results of mentioned analyses: - Capacity of cation exchange, 25,7 cmol/kg, - Capacity of anion exchange, 1,62 cmol/kg, - Conductivity, 1120 µS/cm, - Soil texture, 50% sand, 27% clay i 23% dust, - Soil pH 7,45

Using above mentioned results of soil and content of copper and cadmium in soil, and soil fractions, the next diagrams are performed in order to obtain the percentage of copper and cadmium in different soil fractions.

The figure no. 1 shows the copper distribution among different soil fractions.

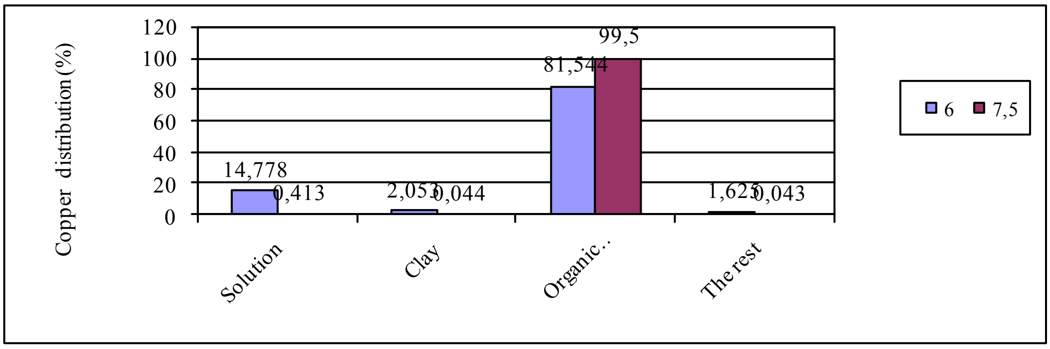


Figure 1. Fractional distribution of copper in soil with its natural content

Speciation of copper in soil has showed that it is the most present in organic part. At pH = 6, the most of copper has been bound to the organic fraction, 81,544 %, and the lowest value in which copper was bound is the rest, 1,624 %, also at pH = 6, e.g. acidic soil conditions, and in soil solution it was present in amount of 14,887%.

In the figure no. 2, the fractional distribution of copper in soil, with its increased concentration, has been presented.

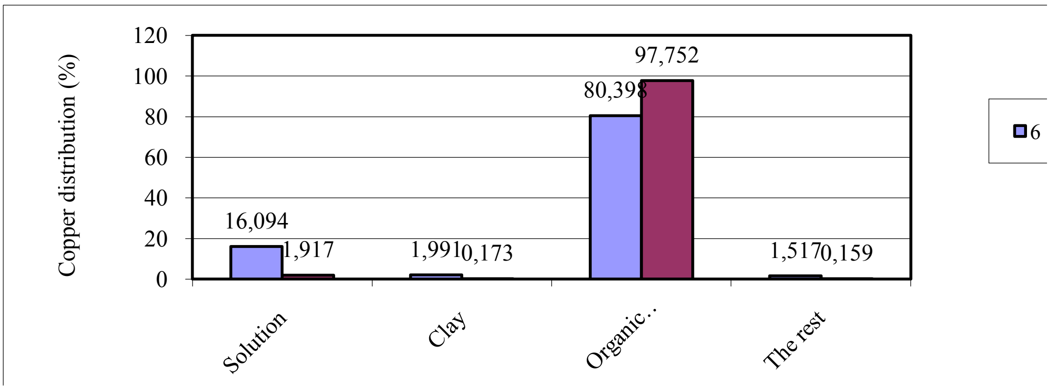


Figure 2. Fractional distribution of copper with is increased content

The figure 2. shows the results of speciation of copper, have showed that all copper in soil solution was bind to the organic fraction, at pH = 7,5, 97,752 %, but very small concentration was present in solution, at pH=7,5, 1,917 %. In the table no. 2, there are possible ionic forms of copper in soil, obtained using available computer software for speciation.

Table 2. Possible copper complexes in soil solution with different pH, with its normal content in soil

pH =6		pH=7,5	
Complex	Concentration (M)	Complex	Concentration (M)
$Cu(CO_3)_2^{-2}$	$8{,}19E \cdot 10^{-12}$	$Cu(CO_2)_2^{-2}$	$4{,}27 \cdot 10^{-10}$
$Cu(OH)_2$	$2{,}18 \cdot 10^{-16}$	$Cu(OH)_2$	$1{,}26 \cdot 10^{-15}$
Cu^{+2}	$9{,}33 \cdot 10^{-11}$	Cu^{+2}	$6{,}90 \cdot 10^{-13}$
$CuCl^{+}$	$1{,}40 \cdot 10^{-13}$	$CuCl^{+}$	$8{,}08 \cdot 10^{-16}$
$CuCO_3$	$7{,}27 \cdot 10^{-10}$	$CuCO_3$	$3{,}54 \cdot 10^{-10}$
$CuHCO_3^{+}$	$7{,}0 \cdot 10^{-8}$	$CuHCO_3^{+}$	$1{,}19 \cdot 10^{-9}$
$CuOH^{+}$	$4{,}70 \cdot 10^{-13}$	$CuOH^{+}$	$9{,}5 \cdot 10^{-14}$
$CuSO_4$	$4{,}72 \cdot 10^{-12}$	$CuSO_4$	$2{,}21 \cdot 10^{-14}$

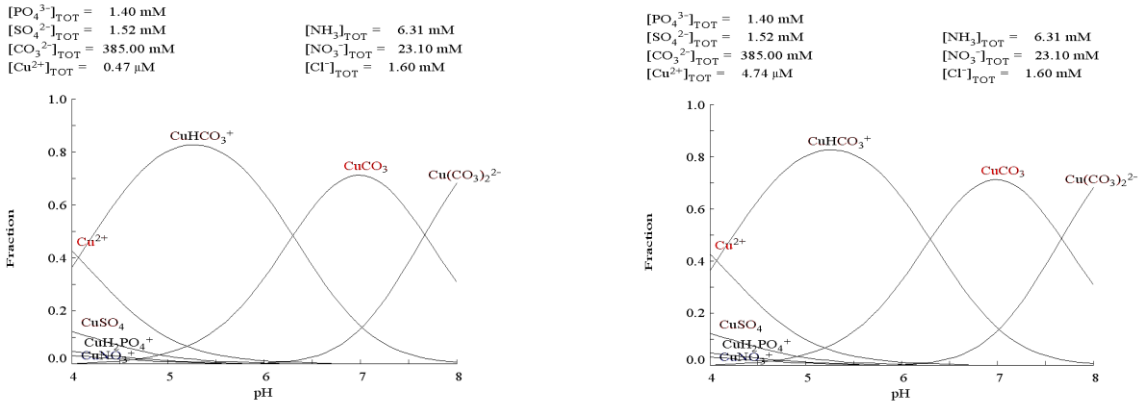
The copper was mostly bound to the hydrogen carbonate, whose concentrations were at natural content $7{,}0 \cdot 10^{-8}$ M, pH=6 i $1{,}19 \cdot 10^{-9}$ M, pH=7,5.

Table 2. Possible copper complexes in soil solution with different pH, with its increased content in soil

pH =6		pH=7,5	
Kompleks	Konc. (M)	Kompleks	Konc. (M)
$Cu(CO_3)_2^{-2}$	$8{,}9 \cdot 10^{-11}$	$Cu(CO_3)_2^{-2}$	$1{,}98 \cdot 10^{-8}$
$Cu(OH)_2$	$2{,}38 \cdot 10^{-15}$	$Cu(OH)_2$	$5{,}87 \cdot 10^{-14}$
Cu^{+2}	$1{,}02 \cdot 10^{-9}$	Cu^{+2}	$3{,}21 \cdot 10^{-11}$
$CuCl^{+}$	$1{,}53 \cdot 10^{-12}$	$CuCl^{+}$	$3{,}76 \cdot 10^{-14}$
$CuCO_3$	$7{,}91 \cdot 10^{-9}$	$CuCO_3$	$1{,}64 \cdot 10^{-8}$
$CuHCO_3^{+}$	$7{,}62 \cdot 10^{-7}$	$CuHCO_3^{+}$	$5{,}52 \cdot 10^{-8}$
$CuOH^{+}$	$5{,}14 \cdot 10^{-12}$	$CuOH^{+}$	$4{,}42 \cdot 10^{-12}$
$CuSO_4$	$5{,}07 \cdot 10^{-11}$	$CuSO_4$	$1{,}02 \cdot 10^{-12}$

The copper in soil, was also mostly bound to the hidrgencarbonate, whose concentrations were with its increased content, $7{,}62 \cdot 10^{-7}$ M, pH=6 and $5{,}52 \cdot 10^{-8}$ M, pH=7,5, respectively. The content of exchangeable forms of copper was very low.

The Figure 3. presents forms of copper to which it was bound in different soil solutions, which are present in this work.



a) Natural content in soil

b) Increased content in soil

Figure 3. Ionic forms of Cu^{2+} and its complexes in pH interval from 5 to 8

The figure no. 3, presents the diagrams of speciation of copper in soil, obtained using commercial software «Meduza», have also showed that it was mostly bound to hidrogencarbonate. It is also important to mention that the content of exchangeable form of copper was reducing with decreasing of pH.

3.1. Complexes of cadmium

The figure no. 4 shows the fraction distribution of cadmium in soil, with different pH of soil, and with its natural content in soil.

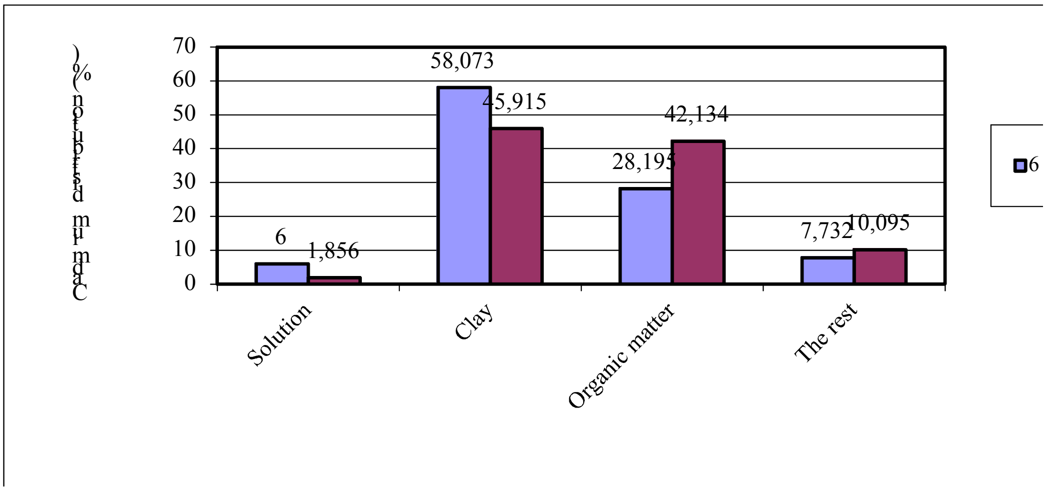


Figure 4. Fractional distribution of cadmium with its natural content in soil

Cadmium with both values of pH and its natural content in soil mostly is bound to the clay fraction, 58,073 %, pH = 6, and 49,915 %, pH = 7,5. The lowest content of cadmium was in soil solution in both cases, with acidic and alkali soil conditions, 6 %, at pH 0 6, and 1,856 % at soil pH = 7,5.

The figure no. 5 shows the fractional distribution of cadmium in soil with its increased content.

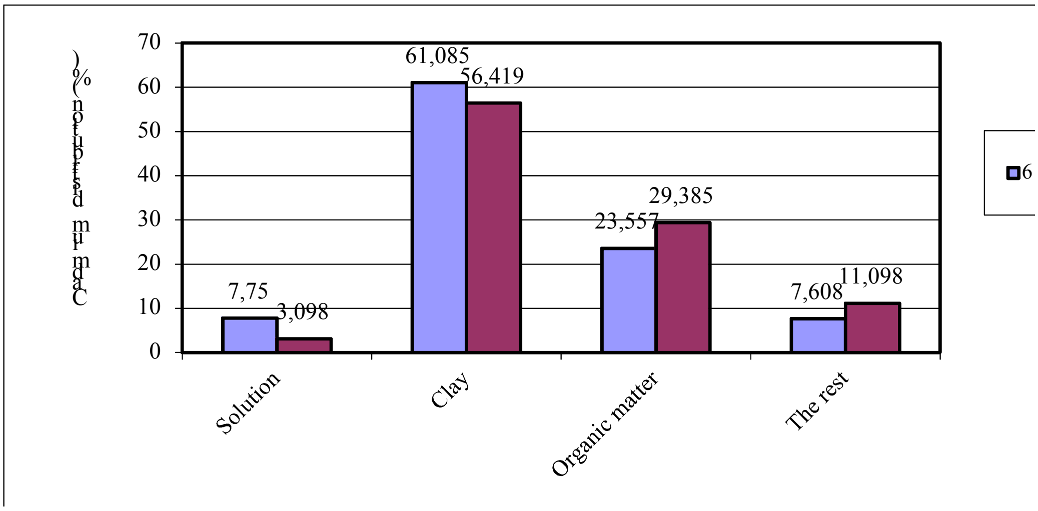


Figure 5. Fractional distribution of cadmium with its increased content in soil

There is similarity with increased cadmium content in soil and in its normal concentration, because it is the most present in clay fraction, 61,085 %, at pH=6 and 56,419 % at pH = 7,5, while also the lowest concentration was in soil solution.

Table 4.-Possible cadmium complexes in soil solution with different pH, with its normal content in soil

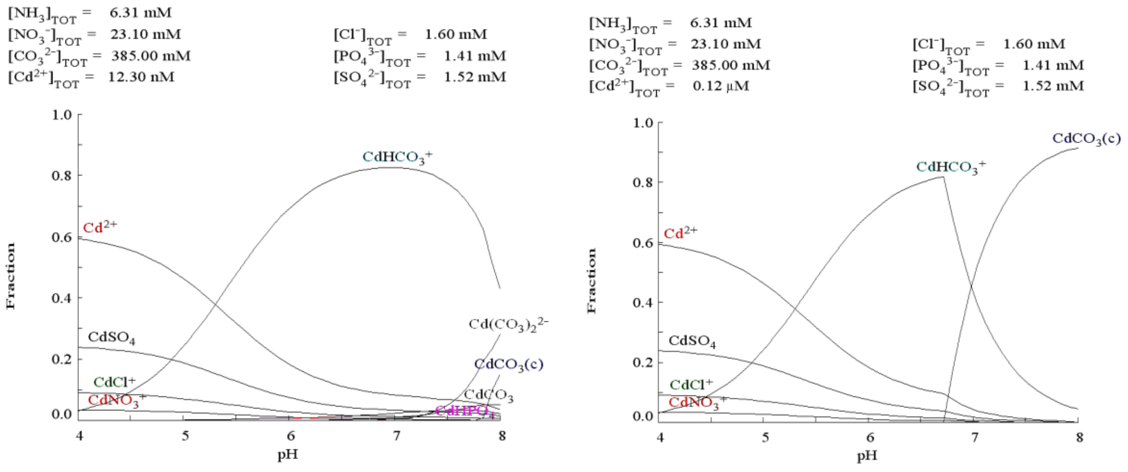
pH =6		pH=7,5	
Complex	Concentration (M)	Complex	Concentration (M)
$Cd(OH)_2$	$1{,}15 \cdot 10^{-19}$	$Cd(OH)_2$	$2{,}88 \cdot 10^{-17}$
Cd^{+2}	$6{,}67 \cdot 10^{-10}$	Cd^{+2}	$2{,}12 \cdot 10^{-10}$
$CdCl^{+}$	$4{,}28 \cdot 10^{-11}$	$CdCl^{+}$	$1{,}06 \cdot 10^{-11}$
$CdCl_2$	$1{,}62 \cdot 10^{-13}$	$CdCl_2$	$3{,}3 \cdot 10^{-14}$
$CdOH^{+}$	$9{,}26 \cdot 10^{-15}$	$CdOH^{+}$	$8{,}05 \cdot 10^{-14}$
$CdSO_4$	$4{,}17 \cdot 10^{-11}$	$CdSO_4$	$8{,}42 \cdot 10^{-12}$

With natural cadmium content in soil, the most presentable its form is ionic, at concentrations ranging from $6{,}67 \cdot 10^{-10}$ M, at pH = 6, to $2{,}12 \cdot 10^{-10}$, at pH = 7,5.
In the table no. 5, possible forms of cadmium complexes are present.

Table 5. Possible cadmium complexes in soil solution with different pH,with its increased content in soil

pH =6		pH=7,5	
Complex	Concentration (M)	Complex	Concentration (M)
$Cd(OH)_2$	$1{,}49 \cdot 10^{-18}$	$Cd(OH)_2$	$4{,}8 \cdot 10^{-16}$
Cd^{+2}	$8{,}62 \cdot 10^{-9}$	Cd^{+2}	$3{,}54 \cdot 10^{-9}$
$CdCl^{+}$	$5{,}51 \cdot 10^{-10}$	$CdCl^{+}$	$1{,}77 \cdot 10^{-10}$
$CdCl_2$	$2{,}08 \cdot 10^{-12}$	$CdCl_2$	$5{,}49 \cdot 10^{-13}$
$CdOH^{+}$	$1{,}19 \cdot 10^{-13}$	$CdOH^{+}$	$1{,}34 \cdot 10^{-12}$
$CdSO_4$	$5{,}29 \cdot 10^{-10}$	$CdSO_4$	$1{,}4 \cdot 10^{-10}$

There is similarity with increased and normal content of cadmium in soil, and concentration is from $8{,}62 \cdot 10^{-9}$ M, at pH = 6 to $3{,}54 \cdot 10^{-9}$ M, at pH = 7,5. The second form in soil solution in which cadmium is present is $CdCl^{+}$, whose concentrations are, at pH = 6, $4{,}28 \cdot 10^{-11}$ M and at pH = 7,5, $1{,}06 \cdot 10^{-11}$ M. With increased cadmium content in soil, there is similar situation, and concentrations ranging from $5{,}51 \cdot 10^{-10}$ M, for slightly acid solution to $1{,}77 \cdot 10^{-10}$, for slightly alkali solution.



a) Natural content of cadmium in soil b) Increased content of cadmium in soil

Figure 6. Ionic form of Cd^{2+} and its complexes in pH interval from 5 to 8

The figure no. 6 presents diagrams of the complexes of cadmium obtained using commercial software.

Both diagrams show the speciation of cadmium in soil solution, with its natural and increased content in soil, in which cadmium is mostly bound, is hidrogencarbonate and carbonate, while other forms are less present in soil solution. As the content of cadmium in soil solution is very small, there is not considerable difference between natural and increased concentration of cadmium in soil.

CONCLUSIONS

Based on above results, the following can be concluded:

- Commercial software and estimated analyses of heavy metals in soil can be used for prediction of bioavailability of heavy metals, as well as their complex forms in soil solutions
- Estimated on the copper and cadmium content, and available software, copper was mainly bound to hidrogencarbonate with slightly acid and slightly alkali soil conditions, and cadmium was in ionic form,
- Comparing results obtained in this work, it is possible to estimate the fractional distribution of heavy metals, such as for copper it was mostly bound to organic form, in part which is available, depending on soil solutions such as content of organic matter and acidity,
- With reducing of acidity, e.g. increasing of pH, free available ionic forms of copper and cadmium, is reducing also.

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POSSIBILITIES OF PRODUCING p.a. NaCl FOR MEDICAL AND PHARMACEUTICAL INDUSTRY BY USING SOMET PROCEDURE

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT

Application of Somet procedure is based on the fact that mixtures of specific organic solutions and water express significant differences during solution of inorganic salts, in type of salt and its comparison to solubility in pure water.

Solubility of chlorides of alkali metals decreases by adding small amounts of alcohol, thus solubility is insignificant in pure alcohol.

In this work we have discussed conditions of p.a. sodium chloride production by desalting it with 96% ethyl alcohol. Special attention was paid to amount of ethyl alcohol for sodium chloride recovery. Results showed that optimal alcohol/water ratio for desalting is 0,4 mol of C_2H_5OH per mol of H_2O.

Key words: sodium chloride p.a., salting , ethyl alcohol, solubility

INTRODUCTION

During last ten years success of chemistry in general is, without doubt, extraordinary. Additionally, success and development of pure bonds is quite significant. New chemistry group named *pure and very pure bonds* was established [1]. Fifty years ago ''better prepared'' bonds consisted of minimal 10^{-2} -10^{-3} % impurities but now in pure substance production impurities are included only in traces (10^{-8} to 10^{-10} %) [2]. Production of such pure products requires specially equipped room with filtered air, total absence of metal objects and exclusive application of Teflon and special plastic materials [3].

Pure class reagents can be used in different conditions in different laboratories, either scientific either manufacturing. Reagents, pure for analytics, as given in name, are intended to be used in analytical examinations requiring high accuracy class. Impurities content is so small that it has no negative effects on analysis accuracy. Those reagents can be used in scientific-research experiments [4].

Materials marked as special pure and intended to be used in special applications, even ones containing less than 10^{-6} are not allowed. Main area of application of such materials is semiconductor, radio electronics and quant electronics industry [5].

EXPERIMENTAL PART

Materials

To produce p.a. NaCl technical sodium chloride, ethyl alcohol (96%) and distilled water have been used. Technical salt used for this type of production should contain small amount of chemical impurities ($CaCl_2$, $MgCl_2$, SO_4^{2-}). Higher content of chemical impurities requires chemical purification of saturated solution while mechanical impurities needs filtration. Purification of saturated chemical solution would significantly increase manufacturing costs thus having negative effect on process profitability which leads us to justifying special attention paid to selection of technical salt for this process.

The characteristics of NaCl, used in experiments, are given in Table 1.

Table 1. Technical salt characteristics used to produce p.a. NaCl

Technical salt component content	%
NaCl	99,61
Insoluble in water	0,126
Sulfates (SO_4^{2-})	< 0,0020
Phosphates (PO_4^{3-})	0,0013
Bromide (Br^-)	< 0,01
Total Nitrogen (N)	< 0,001
Heavy metals (Pb^{2+})	0,0008
Iron (Fe^{3+})	0,00030
Barium (Ba^{2+})	0,001
Calcium (Ca^{2+})	0,008
Magnesium (Mg^{2+})	0,001
Potassium (K^+)	0,01
Arsenic (As^{3+})	-
Reduced matery with MnO_4	-
pH (5% solution at 20^0C)	5,98

Ethyl alcohol used to produce pa NaCl in this experiment by Somet procedure was 96% while demineralised water was taken from columns for cation and anion water softening process. Based on observation of raw base, energy, equipment, operating conditions etc. we came to conclusion that for our process following procedures are applicable [6]:
1. p.a. NaCl production by desalting with 96% ethyl alcohol (Somet Procedure) [7]
2. p.a. NaCl production by saturated solution drying

In this work have discussed desalting by ethyl alcohol – Somet procedure.

Somet procedure – p.a. NaCl production by desalting with ethyl alcohol

Production of p.a. NaCl–by desalting it with 96% ethyl alcohol is based on different solubility of salt in water and ethyl alcohol [8,9]. If we add methanol or ethanol into saturated solution balance solubility diverges and we will have pure salt precipitation.
This procedure is divided in few phases:

1. Preparation of saturated salt solution
2. Saturated solution filtration
3. Desalting
4. Precipitation
5. Centrifuging
6. Drying
7. Distillation

Aforementioned operations and procedures were performed on apparatus given in Figure 1 while results are shown in tables 2 and 3.

Saturated salt solution preparation was performed in enameled reactor 1 (Picture 1). Specific amount of distilled water and technical salt are added until saturated solution was gotten [10]. Amount of added salt is calculated from reactor volume and solubility of salt in water. Prepared solution is then filtrated to remove mechanical impurities. Filtration is done by vacuum 2. Upon removing mechanical impurities solution flows freely into reactor 3 where C_2H_5OH is added providing separation of pure NaCl crystals. Mixture of crystals and alcohol is left to remain still for some time to provide precipitation 4.

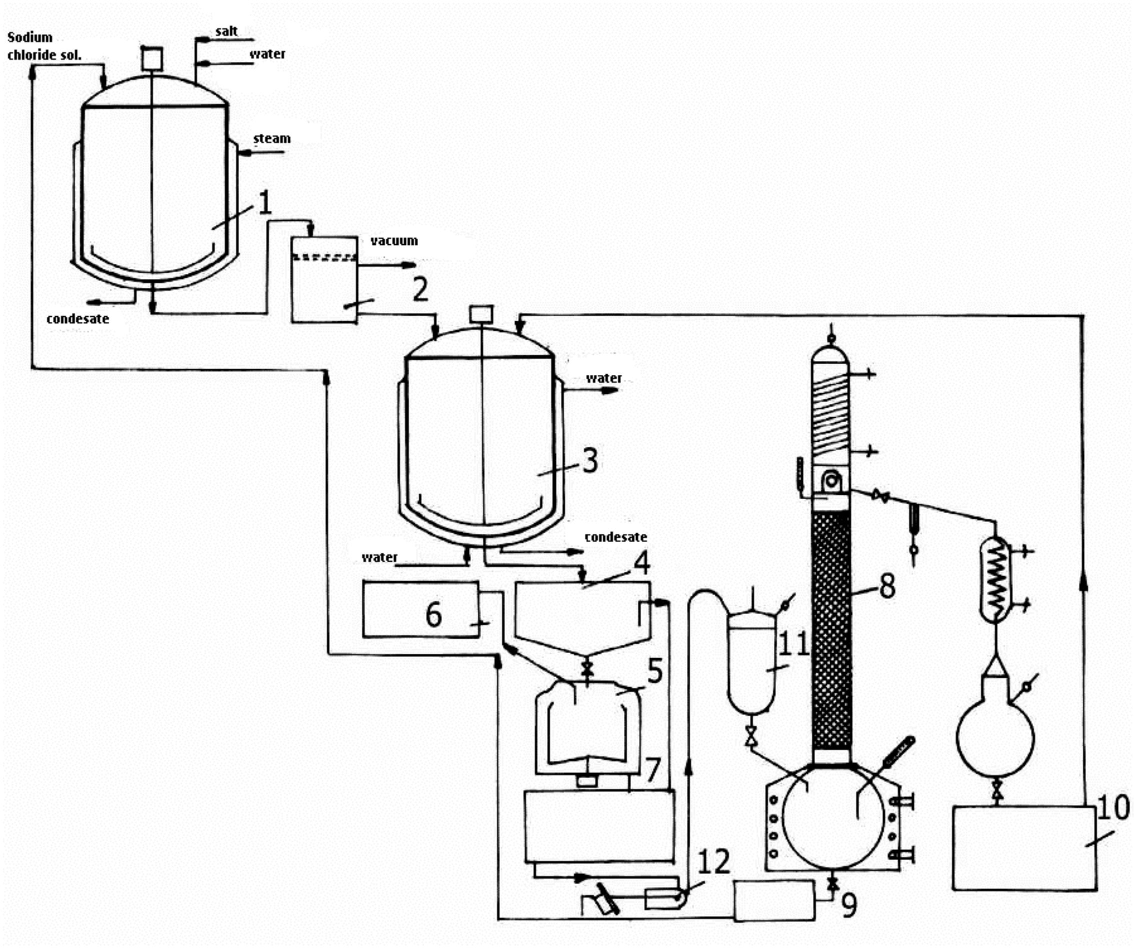

Figure 1. Somet procedure apparatus for p.a. NaCl production

1, 3 - reactors 2 - vacuum filter 4 – precipitator *5 - centrifuge 6 – dryer 7 – tank*
8 – distillation column 9 – alcohol collector 10 – tank 11 - feeder 12 - pump

After precipitation process mixture of salt and alcohol solution above NaCl crystal is separated into collecting tank 7. Crystals with minor content of lye are transferred into centrifuge where crystals are separated from lye and then forwarded to drying 6.

Drying is performed either in vacuum dryer or out in the air. Salt (completely free of surface moist) is collected in plastic bags and then transported in very dry storage rooms (due to high hygroscopes of NaCl).

Salt and alcohol solution mixture is pumped (12) from tank 7 into dosing tank 11. From dosing tank it is sent into distillation column 8. In distillation column alcohol is distilled and collected in tank 10. From this tank alcohol is returned again into desalting process in reactor 3. When alcohol evaporates NaCl solution is sent to collecting tank 9. From this tank NaCl is sent again into production process.

After separating crystal from lye (consisting of salt water and alcohol) crystals are sent to drying and lye is transferred into distillation column. Distillation column is used to regenerate ethyl alcohol from lye so we can use salt water again in production process and recovered ethyl alcohol in further desalting procedures.

Solution heating in distillation balloon can be made by electrical power or steam. In this thesis we based heating energy calculation on steam. Heated mixture of alcohol and slat water is boiling at temperature slightly higher than boiling temperature of alcohol. Boling temperature depends on mol content of alcohol. For various mol content from

$$0{,}7/\ \frac{molC_2H_5OH}{molH_2O}\ \text{to}\ 0{,}1/\ \frac{molC_2H_5OH}{molH_2O}$$

Boiling temperatures vary between 78,4 °C to 80° C. during boiling process temperature in distillation balloon is rising since alcohol evaporates and salt water remains. End of distillation process is characterized by rapid increase in temperature at top of distillation column – indicating boiling temperature of distilled component.

Alcohol steams from distillation balloon go into column filled with glass pipes where it is treated with returning reflux which concentrates easily evaporated components. Alcohol steam goes into cooler where it is concentrated and then sent back as reflux, and bigger part is sent to heat exchanger to cool down to room temperature. Deflagmator contains pipe cooler with water as cooling fluid so alcohol steam condensates on pipe walls of cooling instrument. This kind of distillation gives very good results without having to care about alcohol loss.

RESULTS AND DISCUSSION

Determination of optimal amount of alcohol for desalting

Since different amounts of alcohol separate different amounts of NaCl from saturated salt solution it is important to determine optimal quantity of alcohol that will provide sufficient results. First step is to create diagram (grams of NaCl) as function of mol content (x) of C_2H_5OH in solution. Eight different desalting experiments were made with different amounts of alcohol

(different mol ration of alcohol and water – Table 2):

$$(0{,}l;0{,}2;0{,}3;0{,}4;05;06;07\ /\frac{molC_2H_5OH}{molH_2O}/.$$

Table 2. Optimal amount of alcohol determination

Num Of exp	NaCl techn. (g)	H_2O dist. (ml)	Solution density	V C_2H_5OH ml	C_2H_5OH %	density C_2H_5OH	NaCl (g)	x mol. rate C_2H_5OH
1	100	280	1,199	92	96 %	0,81	16	0,1
2	100	280	1.199	185	96 %	0,81	30	0,2
3	100	280	1,198	250	96 %	0,81	37	0,3
4	100	280	1,200	368	96 %	0,81	43	0,4
5	100	280	1,199	460	96 %	0,81	47,5	0,5
6	100	280	1,200	560	96 %	0,81	51	0,6
7	100	280	1,200	646	96 %	0,81	55	0,7

The diagram presentation of the obtained results can be seen on Figure 2.

- desalting increases significantly up to 01,-04 $/\frac{molsC_2H_5OH}{molsH_2O}/$.
- in range between 04–07 curve downslope is slightly slower, indicated that small difference in NaCl needs large difference in added alcohol (in relation to 0,4).

c

For 0,4 $/\frac{molsC_2H_5OH}{molsH_2O}/$. (368 ml) from

saturated salt water solution of 100 grams – afterd esalting approximately 43,0 grams of NaCl while for 0,7 $/\frac{molsC_2H_5OH}{molsH_2O}/$. (646 ml) we got 55,0 grams of NaCl were gotten.

This fact leads to conclusion that at 0,4 mol ratio with 368 ml of alcohol we extract 43 grams of NaCl while at 0,7 mol ratio with 646 ml of alcohol we extract slightly better 55 grams of NaCl.

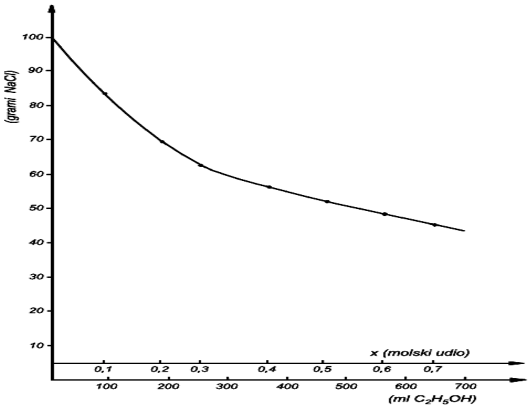

Figure 2. Optimisation of alcohol for NaCl desalting

In respect to alcohol recovery – salt water distillation it is much easier to distill 368 ml and produce 43 grams of NaCl than to distill 646 ml of alcohol and produce 55 grams of NaCl. Difference in produced NaCl is not equivalent to heat energy that must be used to distill two times greater amount of alcohol.

Based on aforementioned results the optimal alcohol-water ratio for NaCl desalting is

$$0,4\ /\frac{molsC_2H_5OH}{molsH_2O}/).$$

Table 3. Laboratory results-saltin

No.	NaCl technical grade	H_2O Dist.	V (ml) C_2H_5OH	% C_2H_5OH	m (g) yield NaCl.p.a.	V ml grove	V sol. NaCl	V (ml) C_2H_5OH	t ^{0}C dist.
1.	200	560	736	96	85,2	1240	510	730	78
2.	200	560	736	96	84,6	1250	520	726	78
3.	200	560	736	96	85,5	1250	504	735	78
4.	200	560	736	96	86,8	1250	527	718	78
5.	200	560	736	96	82,5	1260	540	725	78
6.	200	560	736	96	84,5	1260	570	684	78

In the experiment, salt water that remains after distillation can be later used for dissolution of technical salts and the remaining alcohol, obtained by distillation, can be used in further experiments.

Quality of sodium chloride obtained in this work is given in Table 4.

Table 4. Product quality (NaCl p.a.) manifacture salting of ethyl alchol

Exp no	Insol.in water %	pH (5% sol.) 20^0C	SO_4^{2-} %	PO_4^{3-} %	J^- %	N %	Heavy metals as Pb %	Fe %	Ba %	Ca %	Mg %	K %
1	0,002	5,65	<0,002	<0,0005	<0,01	<0,001	<0,0008	<0,0003	<0,001	<0,004	trace	<0,01
2	0,003	5,65	<0,002	<0,0005	<0,01	<0,001	<0,0008	<0,0003	<0,001	<0,004	trace	<0,01
3	0,001	5,65	<0,002	<0,0005	<0,01	<0,001	<0,0008	trace	<0,001	<0,004	trace	<0,01
4	0,003	5,65	<0,002	<0,0005	<0,01	<0,001	<0,0008	trace	<0,001	<0,004	trace	<0,01
5	0,0025	5,65	<0,002	<0,0005	<0,01	<0,001	<0,0008	trace	<0,001	<0,004	trace	<0,01
6	0,001	5,65	<0,002	<0,0005	<0,01	<0,001	<0,0008	trace	<0,001	<0,004	trace	<0,01

CONCLUSION

Main aim of this work was to define production conditions of p.a. NaCl by desalting it with 96% ethyl alcohol. Based on these results optimum amount of alcohol for desalting process was determined. Alcohol losses during distillation process are insignificant, Table 3. Main loss of alcohol reflects in alcohol that remains in p.a. NaCl crystals. Meanwhile, during drying process losses can be decreased if it is dried with vacuum centrifuge.

Somet procedure ensures NaCl p.a. quality production that can be used in medical and pharmaceutical industry and laboratories as well.

This procedure of p.a. NaCl desalting is surely quite convenient for production both of pure sodium chloride and other salts for analytical chemistry and other applications of less interest for industrial use.

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INFLUENCE OF ADSORPTION PARAMETERS ON REMOVAL OF ORGANIC MATTER FROM NATURAL WATERS

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT

Increased content of organic matter in natural waters intended for drinking and food industry poses a health risk and requires the application of appropriate treatment processes for their removal. In this paper, the influence of basic parameters of adsorption (adsorbent dose, contact time and pH value) on the efficiency of removal of organic matter from surface and groundwater, using three types of commercial activated carbon, was researched. The results showed a non-linear increase in the efficiency of adsorption of organic matter as a function of dosage of activated carbon and increased contact time, and a significant effect of pH on the amount of organic matter removed from the water.

INTRODUCTION

There is a constant increase in water consumption, followed by the increasingly stricter requirements regarding the quality of this valuable resource. The lack of high-quality water resources of such capacity that would satisfy not only the needs of population with drinking water, but also industrial applications, imposes the need for the process treatment of available sources. Natural water normally contain a certain amount of organic matter, and a particular problem which is related to the presence of organic matter in water occurs at the stage of processing water, because the present organic matter can be transformed during chlorine disinfection, in different toxic and potentially carcinogenic organochlorine compounds[1]. Therefore, it is necessary to predict the appropriate technical and technological solutions for the removal of these compounds from water, at the stage of processing[2]. The characteristic of many food processing plants of Tuzla Canton is that they mostly rely on their own sources of water supply. Therefore, it is about the exploitation of water from their own wells which are drilled within the factory. Organic matter that gives water an unpleasant smell and taste, forms toxic by-products during the process of disinfection of water by chlorination and ozone[3], and unwanted substances of these raw waters are commonly present. One of the important sources of surface water of Tuzla Canton, which is used for water supply to the population and industrial sector, is Lake Modrac. However, conducted research works indicate that the water system of lake is characterized, among others, by the presence of organic matter[4,5].

In order to ensure water quality according to the prescribed legal standards for drinking water and the food industry[6], it is necessary to implement appropriate treatment to reduce organic matter within the permitted limits.

Activated carbon is a non-selective adsorbent which removes almost all the natural organic matter present in waters and results in rapid decrease in its capacity to accumulate toxic organics[7,8]. Adsorption on activated carbon is a very efficient technique to reduce organic pollution of water[9], it is very widely used, and most often as a post treatment as its cost would be excessive for concentrated pollution [10,11,12]. In this paper, the influence of basic parameters of adsorption (adsorbent dose, contact time and pH value) on the efficiency of removal of organic matter from surface and groundwater was investigated.

MATERIALS AND METHODS

Two types of natural waters - groundwater of the company "Corn Flips" Srebrenik and surface water of Lake Modrac - were researched. The average physical and chemical properties of the water samples that were used are presented in Table 1.

Table 1. Average physical and chemical properties of groundwater "Corn Flips" and surface water of Lake Modrac

Parameter	**Referent value***	**Corn Flips**	**Modrac**
Turbidity (NTU)	4	0.53 – 0.9	6.5 – 21
Colour (°Co-Pt)	20	29-52	15-40
Ph	6.5 – 9.5	6.65 – 6.8	7.8 – 9.1
Conductivity (μs cm^{-1})	2500	805 – 985	850 – 910
Ammonia (mg/l)	<0.50	0.1	1.98 – 2.8
Nitrates (mg/l)	50	0.18 – 2.5	0.068-0.442
Nitrites (mg/l)	0.5	0.001-0.002	0.004-0.031
COD-Mn (mg O_2/l)	5.0	1.87-5.1	5.35 – 9.4
Total iron (mg/l)	0.2	0.55-0.679	0.017-0.47
Manganese (mg/l)	0.05	0.566-2.436	0.012-0.084
Chlorides (mg/l)	250	26 -30	4 – 8

**Maximum permissible level according to the legislation of Bosnia and Herzegovina*[6]

The examination of the adsorption of organic matter from waters was carried out using three commercial activated carbons:

- Norit Row 0.8 Supra (R),
- Norit Gac 830 Plus (G), and
- Norit PK 1-3 (P).

The specifications of carbons are listed in Table 2.

Table 2. Specifications of active carbons

Activated carbon (symbol)	**Type**	**Particle size (mm)**	**Manufacturer**
NORIT ROW 0.8 SUPRA (**R**)	Extruded activated carbon	0.6-0.8	Norit Nederland BV
NORIT GAC 830 PLUS (**G**)	Granulated activated carbon	0.425 – 2.36	Norit Nederland BV
NORIT PK 1-3 (**P**)	Granulated activated carbon	0.7 – 3.15	Norit Nederland BV

This paper investigates the following factors affecting the process of adsorption of organic matter from waters:

- the amount of dosage of activated carbon,
- contact time, and
- pH.

The experiment was conducted using batch mode. The first set of experiments was carried out with underground water source "Corn Flips", while the next set was done with surface water of Lake Modrac.

The influence of dosage of active carbon on organic matter removal was investigated using the following dosages: 0.05, 0.1, 0.5, 1.0 and 2.0 g/l. The stated amounts were added to glass beakers filled with 500 ml of raw groundwater and water of Lake Modrac, then agitated 200 rpm with a temperature-controlled magnetic agitator at 25 °C for 60 min.

The effect of contact time on the adsorption of natural organic matter was investigated using the activated carbon in a quantity of 0.05 g/l, by adding it into glass beakers filled with 500 ml of water samples and stirring it with a magnetic stirrer 200 rpm, at 25 °C, during the following contact periods: 15, 30, 60, 120 and 360 minutes.

The influence of pH value on the adsorption of organic matter was investigated using the activated carbon in the amount of 0.05 g/l, which was added to glasses with 500 ml of groundwater and surface water samples. All raw water samples were pretreated by adding the appropriate amount of 10% NaOH and 0.1 M HCl to adjust the pH of samples, ranging from 6,5 to 9. Reading the pH of the water was carried out using a pH meter OAKTON pH / CON 510 series. Contact time of adsorption was 60 minutes, with agitation speed of 200 rpm, at 25 °C. Each experiment was repeated twice, the water samples were filtered at the end of the experiment on filter paper for rapid filtration (black belt) and analyzed. The determination of organic matter in the treated samples was performed using a volumetric method, through consumption of $KMnO_4$.

The efficiency of removal of organic matter (Om %) is expressed by the difference between their initial content (Om_i) in a sample of raw water and final content in a treated sample (Om_f), according to the formula:

$$Om\ \% = \frac{Om_i - Om_f}{Om_i}$$

RESULTS AND DISCUSSION

The result of the influence of the amount of activated carbon dosage on the removal of organic matter from the groundwater samples is shown in Fig. 1a), while the effect of the amount of activated carbon on the removal of organic matter from the samples of surface water is shown in Figure 1b).

The results suggest that the efficiency of removal of organic matter increased with the amount of dosage of activated carbon, in both types of treated waters. The linear increase of the dose of activated carbon did not linearly increase the amount of adsorbed organic matter.

Fig. 1a) and 1b) show a significant effect of adsorption of organic substances on activated carbon at the highest dosage of carbon (2 g/l). The greatest amount of organic matter removed from groundwater (71.89%) was achieved when Norit PK 1-3 was used, at a dose of 2 mg/l, while the lowest removal at the same dose was obtained using Norit Row 0.8 Supra, (35.82%).

Using the graphical dependence given in Figures 1a and 1b, the mathematical dependence of the efficiency of removing organic matter from groundwater and surface water Om (%) in function of dosage of activated carbon m (g) is determined.

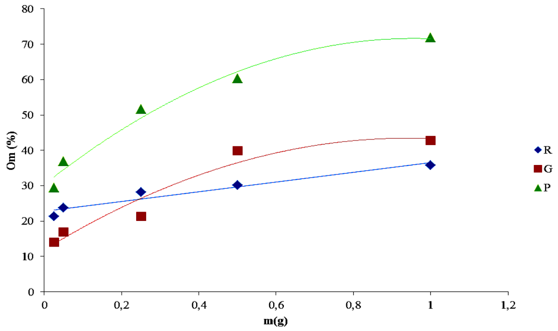

Fig. 1.a) Influence of adsorbent dosage on the efficiency of removal of organic matter from groundwater; m(g) – dosage of activated carbon; Om(%)- efficiency of removal

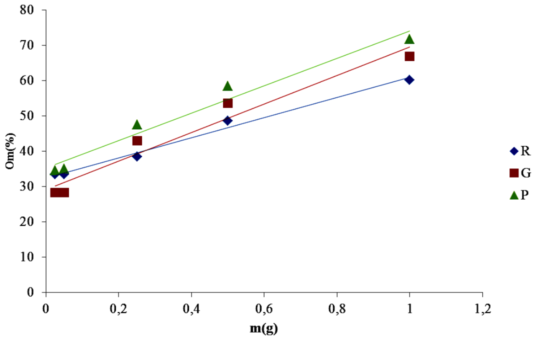

Fig. 1b) Influence of adsorbent dosage on the efficiency of removal of organic matter from surface water;
m(g) – dosage of activated carbon;
Om(%)- efficiency of removal

Table 3. Efficiency of removing organic matter in function of dosage of activated carbon

Activated carbon (symbol)		**Om (%) as mathematical function from m(g)**	**Correlation coefficient, r**
R	Ground water	Om(%) = 13.6·m(g)+22.876	0.971
	Surface water	Om(%) = 28.396·m(g)+32.453	0.995
G	Ground water	Om(%) = -35.547·m^2(g)+66.984·m(g)+11.882	0.972
	Surface water	Om(%) = 40.353·m(g)+29.215	0.977
P	Ground water	Om(%) = -45.127·m^2(g)+86.317·m(g)+30.356	0.989
	Surface water	Om(%) = 38.683·m(g)+35.299	0.983

Based on the value of regression coefficient which ranged from 0.971 to 0.995, it is concluded that the efficiency of removal of organic matter, depending on the amount of added activated carbon may well fit using linear equations and second degree polynomial. The highest degree of regression (0.995) was obtained for surface water during the implementation of activated carbon, type R.

In the case of surface water, the highest efficiency of removal of organic matter (71.65%) was achieved using Norit PK 1-3, at a dose of 2 mg/l, while the lowest removal at the same dosage of active carbon (60.19%) was obtained using Norit Row 0.8 Supra. Fig. 1a) and 1b) also show that the weakest effect of the removal of organic matter in both waters showed Norit Row 0.8 Supra, at all dosage amounts. In the case of groundwater and surface water, a nonlinear relation between increasing dosages of adsorbents and effectiveness of the removal of organic matter by adsorption was obtained. It can be noticed that differences in the efficiency of different activated carbons in removing of organic matter are more marked in the case of groundwater. Figures 2a) and 2b) show the effect of contact time on the efficiency of removal of organic matter from groundwater "Corn Flips" and water of Lake Modrac by using various types of commercial activated carbon.

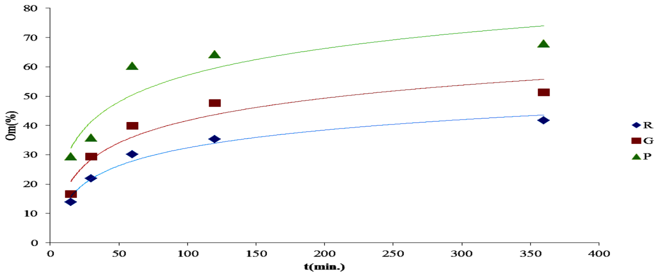

Fig. 2a) The effect of contact time on the efficiency of removal of organic matter from groundwater; t(min) – contact time; Om(%)- efficiency of removal

The results in Fig. 2a) and 2b) show that the percentage of removal of organic matter from water increases with the contact time. Maximum efficiency in removing of organic matter was achieved during the longest contact time (360 min), for both types of water.

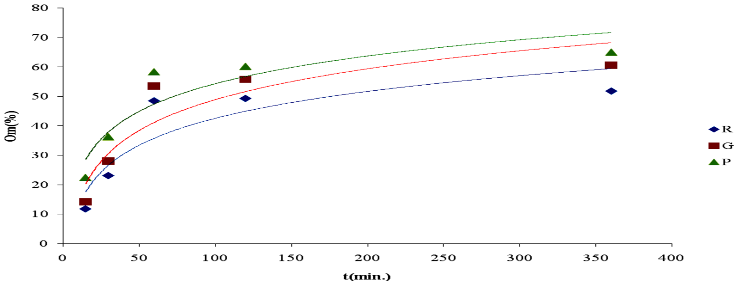

Fig. 2b) The effect of contact time on the efficiency of removal of organic matter from surface water; t(min) – contact time; Om(%)- efficiency of removal

Using the graphical dependence given in Figure 2a, mathematical dependence of the efficiency of removing organic matter from groundwater Om (%) as a function of contact time t (min) is determined.

Table 4. Efficiency of removing organic matter in function of dosage of contact time

Activated carbon (symbol)	Om (%) as mathematical function t(min)	Correlation coefficient, r
R (Ground water)	Om(%) = 8.7685·lnt-8.0203	0.986
G (Ground water)	Om(%) = 10.992·lnt-8.9425	0.956
P (Ground water)	Om(%) =13.147·lnt-3.3913	0.919

Based on the regression coefficient which ranged from 0.919 to 0.986, it was concluded that the efficiency of removal of organic matter, depending on the contact time t may well fit logarithmic equation. The highest degree of regression (0.986) was obtained for the ground water using activated carbon, type R (0.986).

Graph in Figure 2b, can be divided into two parts. In the first 60 minutes we have a linear dependence with a large slope efficiency of removing organic matter in function of contact time, indicating a pronounced effect of contact time. After a contact time of 60 minutes, we had a slight influence of contact time on the efficiency of removal of organic matter.

When samples of groundwater were treated, the highest efficiency of removal of organic matter at contact time of 360 minutes was achieved with the application of Norit PK 1-3 (67.91%) and the lowest efficiency at the same contact time was when Norit Row 0.8 Supra was used (41.71%).

The effect of contact time on the efficiency of removal of organic matter from surface water is shown in Fig. 2b), where it can be seen that the longest contact time had the strongest effect on the removal of organic substances when Norit PK 1-3 was used (65.04%), while the lowest adsorption at time of 360 min, was achieved by using activated carbon Norit Row 0.8 Supra (51.86%).

The results of the influence of pH on the removal of organic matter from the groundwater samples are shown in Fig. 3a), while the effect of pH on their removal from the water samples of Lake Modrac is shown in Fig. 3b).

In both series of experiments, the percentage of removal of organic matter by adsorption decreased with an increase in the pH of the water.

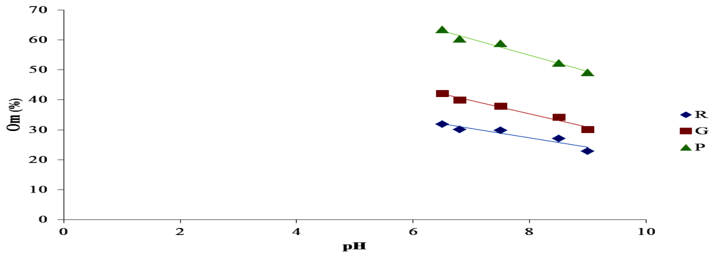

Fig. 3a) The effect of pH on the adsorption of organic compounds from groundwater; Om(%)-efficiency of removal

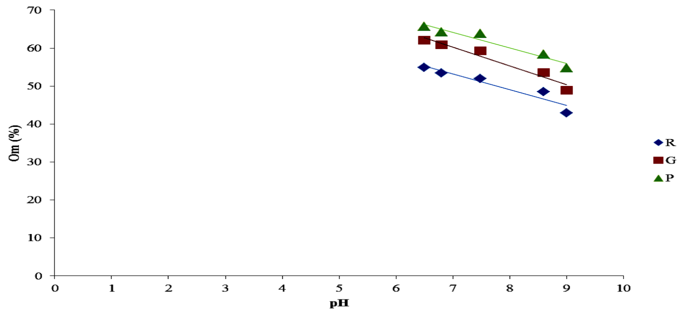

Fig. 3b) The effect of pH on the adsorption of organic compounds from surface water; Om(%)-efficiency of removal

Using the graphical dependence given in Figures 3a and 3b mathematical dependence of the efficiency of removing organic matter from surface and groundwater Om (%) in function of acidity expressed through pH was determined.

Table 5. Efficiency of removal of organic matter in function of pH

Activated carbon (symbol)		**Om (%) as mathematical function from m(g)**	**Correlation coefficient, r**
R	Ground water	Om(%) = -3.1129· pH+52.181	0.945
	Surface water	Om(%) = -4.1528· pH+82.223	0.948
G	Ground water	Om(%) = -4.409· pH+70.571	0.986
	Surface water	Om(%) = -4.9431· pH+94.856	0.975
P	Ground water	Om(%) = -5.4446· pH+98.448	0.989
	Surface water	Om(%) = -4.0851· pH+92.707	0.966

Based on the regression coefficient which ranged from 0.945 to 0.989, it is concluded that the removal efficiency of organic matter, depending on the acidity or pH may well fit using linear equations. The highest degree of regression (0.989) was obtained for the ground water during the application of activated carbon, type P.

In the first series of experiments, with groundwater, the maximum removal of organic matter occurred at pH 6.5 (63.4%), when Norit PK 1-3 was used and the lowest adsorption of organic matter at the same pH value of water occurred by using activated carbon Norit Row 0.8 Supra (31.89%). The greatest amount of organic matter was removed at pH 9 (49.12%), when Norit PK 1-3 was used, while the lowest removal of organic matter (22.8%) was obtained using Norit Row 0.8 Supra. The best results of removal of organic matter from surface water (65.64%) at a pH of 6.5 were obtained when Norit PK 1-3 was used and the lowest adsorption at the same pH was with Norit Row 0.8 Supra (54. 9%). When the pH of surface waters changed to 9, the highest level of removal of organic matter (54.7%) was achieved using Norit PK 1-3, while the lowest level of removal at the same pH was obtained with Norit Row 0.8 Supra (42.87 %).

Similar effects of pH on the adsorption were observed and discussed earlier by many authors[13,14,15] who generally claim that the amount of adsorption of some anionic adsorbates on the adsorbent with a positive surface charge, often shows decreasing trend with the increase of pH, due to less attractive or more repulsive electrostatic interaction at higher pH values.

CONCLUSION

The influence of dosage of activated carbon, contact time and pH value on the removal of organic matter from natural waters (groundwater "Corn Flips" and surface water of Lake Modrac) using commercial activated carbons (Norit Row 0.8 Supra, Norit Gac 830 Plus, Norit PK 1-3) was investigated. The first series of experiments was conducted with groundwater "Corn Flips" while the next series was performed with surface water.

All three applied activated carbons showed the efficiency of removal of organic matter in increasing doses of activated carbon. The highest percentage of removal was achieved with a dose of 2 g/l of activated carbon Norit PK 1-3, which was used in both series of experiments (71.89% for groundwater, 71.65% for surface water). It can also be concluded that the increase of the efficiency of the removal of organic matter was not linear with the increase of dosage amounts of activated carbon.

In the experiment on the effects of contact time on the adsorption of organic matter on the basis of the results it can be concluded that the amount of adsorbed organic matter on activated carbon increased significantly within the first 60 minutes, after which adsorption continuously decreased. In the experiment on the influence of pH in the range from 6.5 to 9 on the removal of organic matter from water all three tested activated carbons showed a drop of adsorption efficiency with the increase of pH.

Comparing the results of the adsorption of organic matter from surface and natural waters using different active carbons, it can be concluded that all activated carbons which are used have similar adsorption characteristics, and the differences between them relate only to the degree of efficiency in the removal of organic matter. The results also suggest that in the case of lower initial concentration of organic matter in raw water, the difference in the efficiency of adsorption using different activated carbons are more pronounced.

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HEAVY METALS IN FRUITS AND VEGETABLES FROM MARKETS IN SARAJEVO, BOSNIA AND HERZEGOVINA

PROFESSIONAL PAPER

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ABSTRACT

In this study, Cu, Pb, Cd, Ni, Cr, Co, Mn, Fe, and Zn metal levels of 24 fruits and 17 vegetables were determined by using atomic absorption spectrometry, flame technique. Presence of heavy metal in randomly collected samples of different types of fruits and vegetables from various markets and shopping centers in Sarajevo city was detected. The levels of metals in almost all samples (washed) were found bellow from the maximum permissible limit recommended by WHO/FAO. All the fruits and vegetables could generally be characterized by low levels of cadmium (0.25-0.66 µg/g), chromium (0.74-1.66 µg/g), nickel (0.33-9.33 µg/g), lead and cobalt (levels were below detection limit), and relatively high levels of zinc (0.62-55.41 µg/g), copper (0.86-68.41 µg/g), iron (5.74-173.22 µg/g) and manganese (0.72-258.78 µg/g).

Key words: Heavy metals, fruits, vegetables, markets, Sarajevo

INTRODUCTION

Large quantities of pollutants have continuously been introduced into ecosystems as a consequence of urbanization and industrial processes. Heavy metals contamination is a major problem of our environment[1, 2]. Prolonged human consumption of unsafe concentrations of heavy metals in foodstuffs may lead to the disruption of numerous biological and biochemical processes in the human body. Heavy metal accumulation gives rise to toxic concentrations in the body, while some elements act as carcinogens and others are associated with developmental abnormalities[3]. Agricultural foodstuffs cultivated on urban sites experience strong man-made impacts[4]. Dietary intake of heavy metals through contaminated fruits and vegetables may lead to various chronic diseases. Biotoxic effects of heavy metals depend upon the concentrations and oxidation states of heavy metals, kind of sources and mode of deposition[1,5]. Contamination of fruits and vegetables with heavy metal may be due to irrigation with contaminated water, the addition of fertilizers and metal-based pesticides, industrial emissions, transportation, the harvesting process, storage and/or at the point of sale[6,7]. Plant analyses are necessary for botanical and environmental purposes. The plants absorb heavy metals from the soil as well as from surface deposits on the parts of plants exposed to polluted air. The content of heavy metals in plants depends on the location of their growth and harvest, as well as on the capacity of the plants to accumulate various substances from soil, water (sewage, fertilizers) and air (dust, particulates, fumes)[8, 9, 10].

The overall objectives of the monitoring of food product contamination are to safeguard consumers' health, to improve the management of food and agricultural resources and to prevent economic losses[11].Vegetables and fruits are rich sources of vitamins, minerals and fibers, and also have beneficial antioxidant effects. Vegetables and fruits are part of daily diets in many households forming an important source of vitamins and minerals required for human health. They are made up of chiefly cellulose, hemi-cellulose and pectin substances that give them their texture and firmness[12]. However, intake of heavy metal-contaminated vegetables and fruits may cause a risk to human health and hence heavy metal contamination of food items is one of the most important aspects of food quality assurance.

A very limited published data are available on the heavy metal contamination in fruits and vegetables on market sites. The main objective of this study was to determine the heavy metal (Cu, Pb, Cd, Ni, Cr, Co, Mn, Fe, and Zn) levels in 24 different fruits and 17 different vegetables using atomic absorption spectrometry, flame technique. Fruits and vegetables were purchased in markets and shopping centers in the area of Sarajevo.

MATERIALS AND METHODS

Chemicals and reagents

All the chemicals and reagents were of analytical grade and were purchased from Merck (Germany). Standard solutions of heavy metals were also provided by Merck. The standards were prepared from the individual 1 g/L standards. Working standards were prepared from the stock solutions. In the digestion and extraction procedures, concentrated nitric acid (65%), hydrochloric acid (37%), and hydrogen peroxide (30%) were used.*Sampling and pre-treatment*

A wide colection of fruits (pineapple, banana, peach, blueberry, cranberry, white and red grapes, red and yellow grapefruit, apple, kiwi, pear, blackberry, lemon, raspberry, tangerine, apricot, orange, nectarine, walnut, fig, plum, sour cherry, cherry) and vegetables (mangold, broccoli, beet-root, kale, fennel, potato, red and yellow cabbage, carrot, red and yellow pepper, tomato, collards, spinach, eggplant, zucchini and lettuce) were collected from different markets and shopping centers of the Sarajevo city from January to June 2012. Samples of each commodity were collected randomly in sufficient quantities (2 kg) to provide a representative samples.

All samples were put in plastic bags to avoid contamination and taken to the laboratory for analyses. The samples were thoroughly washed with running tap water and rinsed with double distilled water to remove any soil particles attached to the plant surfaces. After that, samples were cut to small peaces and air-dried for two weeks. The percentages of moisture lost during the air-drying of fruit and vegetable samples are presented in Table 1.

Table 1. The percentages of moisture lost during the air-drying of fruit and vegetable samples

Fruit samples	Moisture (%)	Vegetable samples	Moisture (%)
Pineapple	60.31	Mangold	80.34
Banana	49.89	Broccoli	70.36
Peach	60.58	Beet-root	67.00
Blueberry	55.61	Kale	61.38
Cranberry	57.49	Fennel	75.84
White grapes	52.33	Potato	50.84
Red grapes	50.61	Red cabbage	72.50
Red grapefruit	65.28	Yellow cabbage	74.44
Yellow grapefruit	63.36	Carrot	62.22
Apple	49.90	Red pepper	82.94
Kiwi	60.11	Yellow pepper	80.36
Pear	51.38	Tomato	82.00
Blackberry	54.73	Collards	79.44
Lemon	61.30	Spinach	80.32
Raspberry	61.32	Eggplant	78.46
Tangerine	58.65	Zucchini	59.99
Apricot	60.72	Lettuce	86.66
Orange	59.87		
Nectarine	60.10		
Walnut	1.44		
Fig	51.60		
Plum	51.78		
Sour cherry	58.30		
Cherry	56.28		

The plant materials was then ground using pestle and motar in order to obtain a homogeneous sample from which representative samples were taken.

Heavy metals in fruit and vegetable samples were extracted following acid digestion procedure as follows: about 2 g portion of the plant sample was placed into a porcelain crucible. The samples were ashed in a muffle furnace at 470 °C for 3 h. The ash was digested by adding 10 mL of mixture of concentrated HNO_3 and concentrated HCl (2:1) and 1 mL of 30 %

H_2O_2. After the evaporation, the residue was passed through a blue band filter paper. The final volume of solution was 50 mL. The sample and blank analyses were performed in triplicate.

Analytical and measuring methods

Concentration of heavy metals in the acidic solution was estimated using atomic absorption spectrometer, flame technique (Spectra AA-10, AA240FS, Varian, Australia) using an air-acetylene flame for the nine heavy metals. The values of the detection limits (LOD) for Cu, Pb, Cd, Ni, Cr, Co, Mn, Fe, and Zn were 0.009, 0.008, 0.02, 0.007, 0.01, 0.05, 0.01, 0.04 and 0.009 µg/mL, respectively.

Daily intake (mg/kg day) is calculated based on the assumptions that:
1) body weight is 60 kg[14], and
2) daily intake of fruits and vegetables is 200 g[13].

Daily intake (mg/kg day) = metal concentrations in fruits and vegetables × 200/1000/60[14].

Agency for Toxic Substances and Disease Registry[15] has defined MRL (minimum risk level) values for individual toxic substances. MRL values are given for Cd, Co, Cu and Zn. For oral intake for the intermediate period of exposure (15 to 364 days) MRL value for Cd is 0.0005, for Cu and Co 0.01, and Zn 0.3 mg/kg day.

Analitycal quality assurance

To ensure the reliability of the results, appropriate quality procedures and precautions were taken. All the reagents were of analytical grade. For washing the vegetables, double distilled water is used. Blank and standards were run after five determinations to calibrate the instrument. Spike sample analysis (or known addition) is used to test the method at varying concentrations of analyte. Known amounts of analyte are added to a sample and the percent recovery is calculated. The acceptable percent recovery of known additions were obtained (96-101%).

RESULTS AND DISCUSSION

Plant species have a variety of capacities in removing and accumulating heavy metals causing a serious health risk to human[16]. Heavy metals enter the environment mainly as a result of industrial and agricultural practices. They are stable unlike some potentially toxic organic compounds[17].

The present study reports heavy metal contents (Cu, Pb, Cd, Ni, Cr, Co, Mn, Fe, and Zn) in some fruits and vegetables collected from different markets of Sarajevo. Observed concentrations of Cu, Cd, Co, Cr, Fe, Ni, Pb and Zn in the fruits and vegetables were compared with recommended limit (FAO/WHO) to assess food contamination.

Table 2. Concentration (mean±standard deviation) of heavy metals in random samples of fruits (µg/g air-dry weight)

Sample	Heavy metals				
	Cu	**Fe**	**Mn**	**Ni**	**Zn**
Pineapple	1.29±0.04	12.16±1.60	33.61±1.86	nd	5.12±0.17
Banana	0.31±0.91	8.24±3.18	9.83±0.13	nd	4.21±0.31
Peach	4.68±0.18	12.49±1.09	4.87±0.15	nd	9.81±0.65
Blueberry	17.28±7.20	28.12±1.2	258.78±1.01	0.75±0.24	7.42±0.51
Cranberry	1.99±0.45	52.02±6.80	174.01±8.87	0.75±0.24	10.41±2.20
Grapes (white)	2.11±0.87	12.50±1.80	1.73±0.23	nd	0.87±0.17
Grapes (red)	3.16±0.35	39.54±4.45	2.53±0.31	nd	0.75±0.01
Grapefruit (red)	nd	13.50±4.20	0.85±0.086	nd	5.20±1.11
Grapefruit (yellow)	0.86±0.14	45.04±4.74	0.79±0.12	nd	1.80±0.98
Apple	1.75±0.86	8.49±2.10	1.61±0,23	nd	5.21±0.70

Kiwi	6.25±0.24	10.22±3.42	4.44±0.42	0.49±0.10	8.32±0.15
Pear	2.11±0.49	40.14±1.89	0.98±0.13	nd	5.91±0.81
Blackberry	2.37±0.09	26.17±2.45	90.63±6.74	nd	7.41±0.99
Lemon	1.46±0.14	8.66±0.28	1.18±0.01	nd	3.62±0.80
Raspberry	3.13±1.88	29.44±1.04	18.92±1.03	nd	14.91±0.36
Tangerine	2.25±0.23	40.24±1.06	2.77±0.19	nd	2.41±0.46
Apricot	nd	27.50±4.54	0.72±0.17	nd	14.52±0.92
Orange	1.61±0.44	61.50±1.40	2.64±0.20	0.37±0.17	2.51±0.77
Nectarine	3.73±0.36	22.91±3.51	4.08±0.012	nd	6.10±0.35
Walnut	2.65±0.31	46.24±12.10	17.46±0.35	0.83±0.14	32.91±5.31
Fig	68.4±0.18	15.91±2.45	1.55±0.19	nd	3.92±1.10
Plum	nd	39.66±8.22	1.37±0.23	nd	16.10±.2.31
Cherry	1.37±0.14	5.74±1.61	4.68±0.25	nd	1.52±0.52
Sour Cherry	nd	6.99±1.15	nd	nd	0.62±0.18
Maximum allowed concentrations (WHO&FAO)	40	425	500	60	60

nd=Not detected - levels were below detection limit

Tables 2 and 3 shows the mean concentrations of heavy metals investigated in fruits and vegetables. The values are given as mean ± SD and the results are means of three replicates. The heavy metal levels determined were based on plants air-dry weight. It is a known fact that fruits and vegetables can be eaten fresh or in dried form.

A number of reports are available on heavy metal concentration in fruits and vegetables sold in the markets of different countries[12, 18, 19, 20] but there are no any published reports available on heavy metal content in the fruits and vegetables sold in Sarajevo markets.

Fruits

The different types of fruits were analysed for the heavy metals. Metal concentrations in fruits vary with plant species.

Fruit samples were also analyzed for the presence of Cr, Co, Cd and Pb, but the values were below the detection limits, except in the following cases:

- cranberry: Cr (1.66±0.37 µg/g);
-blueberry: Cr (0.74±0.35 µg/g), Cd (0.49±0.25 µg/g);
- white grape, red grapefruit, raspberry, plum: Cd (0.25±0.01µg/g);
- walnut: Cd (0.66±0.14 µg/g).

The levels of metals in all fruit samples were bellow the maximum allowed concentration recommended by WHO/FAO (Cd: 0.2; Co: 50; Cr: 2.3 and Pb: 0.3 µg/g) except in the case of copper in fig sample. Since, in this paper, we used air-dried samples the heavy metal content in fresh samples would probably be even lower.

The highest concentrations of **copper** were in fig (68.41 µg/g) and blueberry (17.28 µg/g). In other fruit samples, the copper content was below 7 µg/g, while the lowest content was found in a banana (0.30 µg/g). Daily intake values for copper ranged from 0.001 mg/kg day to 0.228 mg/kg day. In 29.17% of cases the daily intake was higher than the MRL value, 0.01 mg/kg day[15].

The highest **iron** content was found in orange (61.51 µg/g), then in the cranberry, walnut, yellow grapefruit, tangerine, pear, red grape and plum. The lowest iron content was found in cherry. The highest **manganese** content was found in cranberry (174.01 µg/g) and blueberry (258.78 µg/g). The lowest content of manganese was found in apricot (0.72 µg/g), and the yellow and red grapefruit (0.79 µg/g and 0.85 µg/g). **Nickel** content varied from non-detectable amounts to 2.31 µg/g in fig.

The content of **zinc** ranges from 0.62 to 32.77 µg/g which is within the safe limit with respect to FAO/WHO. The highest zinc content was found in the walnut, and the lowest in sour cherry. In all other samples, the zinc content was below 20 µg/g. Daily intake values for zinc ranged from 0.002 to 0.11 mg/kg day. In all cases the daily intake was below the MRL value, 0.3 mg/kg day.

The highest mean concentrations of heavy metals were determined in blueberry, cranberry and walnut. By concentrations, the elements were arranged as the following diminishing series Fe>Mn>Zn>Cu>Cr>Ni>Cd.

Vegetables

Metal concentrations in the analyzed vegetables vary with plant species. Results are presented in Table 3.

Table 3. Concentration (mean±standard deviation) of heavy metals in random samples of vegetables (µg/g air-dry weight)

Sample	Heavy metals				
	Cu	Fe	Mn	Ni	Zn
Mangold	7.57±0.59	57.57±2.67	97.68±4.92	nd	55.41±2.40
Broccoli	5.32±0.57	48.99±2.71	13.71±0.61	0.90±0.25	45.20±1.01
Beet-root	6.79±0.36	113.31±3.71	20.28±1.23	nd	2.40±0.12
Kale	2.50±0.26	29.90±3.40	7.14±0.40	nd	18.20±1.50
Fennel	2.74±0.23	29.59±1.06	5.74±0.18	nd	13.07±0.78
Potato	nd	22.91±1.61	1.94±0.20	0.29±0.10	2.50±1.40
Cabbage (red)	nd	12.92±1.15	5.92±0.22	nd	4.50±0.10
Cabbage (yellow)	nd	28.91±6.82	6.37±0.11	nd	10.60±0.18
Carrot	nd	74.61±2.23	10.66±0.36	nd	8.30±1.20
Pepper (yellow)	5.53±0,14	62.82±6.05	8.23±0.21	9.33±0.14	7.92±0.29
Pepper (red)	1.39±0.11	17.81±3.11	3.64±0.39	2.23±0.65	5.40±0.50
Tomato	3.51±0.93	13.16±0.58	6.30±0.33	nd	7.80±0.87
Eggplant	nd	13.20±0.91	4.59±0.01	nd	5.90±0.29
Collard	2.93±0.03	35.49±8.57	20.83±0.91	0.33±0.14	15.24±1.09
Spinach	8.71±3.68	173.22±6.21	112.81±8.65	0.74±0.39	49.30±0.53
Zucchini	2.21±0.27	28.61±4.21	6.99±0.42	1.70±0.10	26.50±0.53
Lettuce	11.76±0.23	109.10±3.72	97.68±4.92	0.33±0.14	39.81±3.87
Maximum allowed concentrations (WHO&FAO)	40	425	500	60	60

nd=Not detected - levels were below detection limit

Vegetable samples were also analysed for the presence of Cr, Co, Cd and Pb, but the values were below the limit of detections, except in the following cases:

- spinach: Cd (0.66 ± 0.15 µg/g), Cr (1.01 ± 0.10 µg/g)
- potato: Cd (0.25 ± 0.01 µg/g), Cr (0.49 ± 0.25 µg/g)

The levels of metals in all vegetables samples were bellow the maximum allowed limit recommended by WHO/FAO.

The **copper** levels in the samples tested varied between 0.11 – 11.76 µg/g with lettuce and spinach maintaining the lead. In other samples of vegetables, the copper content was below 7 µg/g, while the lowest content was found in red pepper. Daily intake values for copper were lower than 0.039 mg/kg day. In 41.18% of cases the daily intake was higher than the MRL value, 0.01 mg/kg day. The results showed that the levels of **iron** ranged from 12.92 µg/g (red cabbage) to 173.00 µg/g (spinach). Also, high concentrations of iron were found in beet-root and lettuce. Spinach in this work accumulated high concentrations of metals analyzed especially Fe. The highest **manganese** content was found in spinach (112.81 µg/g), lettuce (97.68 µg/g) and mangold (71.62 µg/g). The lowest manganese content was found in potato (1.94 µg/g). The maximum concentration of **nickel** was in yellow pepper (9.33 µg/g) and the minimum in potato (0.29 µg/g). The lowest content of **zinc** was found in beet-root (2.40 µg/g), while the highest content was found in lettuce (39.81 µg/g), broccoli (45.20 µg/g), spinach (49.30 µg/g) and mangold (55.40 µg/g). Daily intake values for zinc ranged from 0.008 to 0.185 mg/ kg day. In all cases the daily intake was below the MRL value, 0.3 mg/kg day.

The highest mean concentrations of heavy metals were determined in spinach, lettuce and mangold. By concentrations, the elements were arranged as the following diminishing series Fe>Mn>Zn>Cu>Ni>Cr>Cd.

Comparing the metal content in the fruit and vegetable samples we can conclude as follows: Content of Cu, Fe, Ni and Zn was generally higher in the vegetable samples. The same applies to manganese except in the cases of blueberries and cranberries where the manganese content was significantly higher compared to all other analyzed samples.

CONCLUSIONS

Heavy metal concentrations varied among the tested vegetable and fruit, which reflect the differences in their uptake capabilities and their further translocation to edible portion of the plants. The metals (Cu, Pb, Cd, Ni, Cr, Co, Mn, Fe, and Zn) investigated in this paper were detected in almost all the vegetable and fruit samples, but their concentrations were below the recommended allowed concentration given by WHO/FAO. All the fruits and vegetables could generally be characterized by low levels of cadmium (0.25-0.66 µg/g), chromium (0.74-1.66 µg/g), nickel (0.33-9.33 µg/g), lead and cobalt (levels were below detection limit), and relatively high levels of zinc (0.62-55.41 µg/g), copper (0.86-68.41 µg/g), iron (5.74-173.22 µg/g) and manganese (0.72-258.78 µg/g).

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INCIDENCE AND POTENTIAL HEALTH RISK OF DEOXYNIVALENOL IN WHEAT SAMPLES HARVESTED IN EASTERN CROATIA

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT

People are exposed to various natural or synthetic chemical compounds that may have a negative effect on their health. One of the most important groups of natural toxins is mycotoxins. Mycotoxins are secondary metabolite products of moulds that occur during the cultivation of plants or during their storage. Due to their toxicity and effects caused in the human body, following mycotoxins are usually monitored: aflatoxin, ochratoxin, patulin, fumonisin (FUM), zearalenone (ZEA) and deoxynivalenol (DON). These mycotoxins often occur in grains, fruits, hazelnuts, almonds, seeds, as well in animal feed and in foodstuffs consisting of or produced from these plants.

The aim of this work was to determine the incidence and potential health risk of deoxynivalenol in wheat samples collected from twenty five storage tanks in the area of eastern Croatia after the harvest 2009. In 4 of 25 wheat grains samples (16%) the deoxynivalenol was found at detectable levels.

Key words: deoxynivalenol, wheat grains, Croatia, potential health risk

INTRODUCTION

Mycotoxins are secondary metabolites of fungi or moulds which can develop in field grains, damaged grains or improperly stored feeds and their occurrence was detected in rice, maize, barley and wheat[1]. It is assumed that there are more than thousand mycotoxins but only 300 of them have been identified[2]. Many epidemiological studies confirmed negative effects of mycotoxins on human health such as neurotoxicity, carcinogenicity, teratogenicity, damages of kidney and liver, gastroenteritis, hemorrhagic diathesis, skin irritation, necrosis and breading problems[3,4]. The presence of mycotoxins usually is unavoidable and therefore testing of raw materials and products is required to keep food and feed safe. So, prevention of mycotoxins appearance is important because once they are developed, they become stable at environment temperature and very resistant to thermal changes[5].

Occurrence and frequency of mycotoxins in wheat grains depend of several factors such as moisture content, temperature, insect damage, mechanical injury, mineral nutrition of the plant, chemical treatment, rapidity of drying, leakage in storage and hot spots[6].

Trichothecenes are the group of numerous structurally related toxic compounds primarily produced in cooler climates by some species of *Fusarium, Myrothecium, Stachybotrys, Trichoderma* and *Cephalosporium.* Trichothecenes are characterized by strong immunosuppressive and cytotoxic effects to many cell types and diagnosis of trichothecene-related toxicosis can be difficult[7,8,9].

Deoxynivalenol (DON) or vomitoxin belongs to the trichothecenes type “B” group – the large group of agriculturally important mycotoxins produces by *Fusarium graminearum* and *Fusarium culmorum* and it appears predominantly in wheat, soybean, corn, barley and other cereals.The occurrence of deoxynivalenol in corps and its intoxication can decrease hematopoiese by damages to the bone marrow and cause damage to the nervous, gastrointestinal and cardiovascular systems and more concerning is the fact that the presence of DON usually indicates the presence of other more toxic mycotoxins from trichothecenes[7,9,10,11].

Croatian legislation and Regulations of maximal permissible contaminants in food (Official Gazette 154/08)[12], that has been in compliance with the regulations existing in the European Union and Commission Regulation No 1881/2006[13], set maximum permissible level (MPL) for deoxynivalenol in cereals and cereal-based products as it follows: unprocessed cereals other than durum wheat, oats and maize (1250 µg/kg), unprocessed durum wheat and oats (1750 µg/kg), unprocessed maize (1750 µg/kg), cereal flour, including maize flour, maize grits and maize meal (750 µg/kg), pasta (dry, 750 µg/kg), bread (including bakery products), pastries, biscuits, cereal snacks and breakfast cereals (500 µg/kg), and processed cereal-based food for infants and young children and baby food (200 µg/kg).

Due to the above mentioned, the Croatian Food Agency conducted this study with the aim to determine the incidence and potential health risk of deoxynivalenol in wheat grain samples collected from twenty five storage tanks in the area of eastern Croatia after the harvest 2009, based on the provisional maximum tolerable daily intakes (PMTDI) for deoxynivalenol.

MATERIALS AND METHODS

Sampling

Samples of wheat grains were collected from twenty five storage tanks after the 2009 harvest during October and November 2009 in the area of eastern Croatia. All samples were stored in a dark and dry place until analysis. Sampling, sampling preparation and sample analysis were completed according to Croatian Regulations (Official Gazette 45/08)[14].

Determination of deoxynivalenol (DON)

Concentrations of deoxynivalenol in the collected samples of wheat grains were determined by immunoassay CD-ELISA Veratox test kits (Neogen Europe Ltd.). For absorbance reading the Stat Fax Microplate Reader (Awarenes Technology, Inc.) was used as instructed by the kit manufacturer. The method used is a direct immunoenzymatic competitive test (CD-ELISA), which allow us to obtain accurate concentrations in parts per billion (ppb or µg/kg). All methods are validated and are officially accredited for DON analyses.

Analysis of potential health risk

The potential health risk of mycotoxin deoxynivalenol in wheat grains for the eastern Croatian population were estimated using Joint FAO/WHO Expert Committee on Food Additives (JECFA)[15] data about total DON intake based on a combination of mean food consumption levels with weighted-mean contamination levels of the five GEMS/Food (Global Environment Monitoring System/Food Contaminants Monitoring and Assessment Programme) regional diets (African, European, Far Eastern, Latin American and Middle Eastern), average adult weight in Croatia, tolerable daily intake (TDI) of 1 µg/kg bw/day that Scientific Committee on Food (SCF) and Joint FAO/WHO Expert Committee on Food Additives (JECFA) estimated considering the year-to-year variability of the contamination of cereals and grains with DON in Europe and Croatian weighted-mean contamination levels of wheat with DON in four counties for 2009 year. Dietary intakes including information on consumption of raw but processed foods were not used to estimate dietary intake.

Comparison of DON incidence and wheat grain quality

It is known that the occurrence and frequency of mycotoxins in wheat grains depend on several factors. Since incidence of *Fusarium* is strongly associated with humid conditions and temperature[6,10,11,16], in this study two climate parameters during the growth of wheat and harvest period were measured (precipitation and air temperature) and following wheat grain quality data were determined: moisture content (ICC 110/1)[17], protein content (ICC ICC 105/2)[18] and starch content (ICC 122/1)[19]. All the measurements were done in triplicate. Obtained measurement results of climate parameters and wheat grain quality were compared with DON incidence to detect the possible connection.

RESULTS AND DISCUSSION

In four out of twenty five wheat grain samples (16%) the deoxynivalenol were found at detectable level, and the results are given in Table 1. As is shown in Table 1, the minimum value of DON registered was 50µg/kg while the maximum DON value was 850µg/kg. Comparing the obtained results with MPL for deoxynivalenol according to Croatian Regulations of maximal permissible contaminants in food (Official Gazette 154/08)[12], it can be seen that the detected values are lower than MPL.

Table 1. DON concentrations detected in wheat grain samples taken from 25 silos in the area of eastern Croatia (after harvest 2009).

NO. SAMPLE	1	2	3	4	5	6	7	8	9	10	11	12	13
DON *(µg/kg)*	BDL	BDL	BDL	BDL	**50**	BDL	BDL	BDL	BDL	**50**	BDL	BDL	BDL
No. sample	14	15	16	17	18	19	20	21	22	23	24	25	*BDL- *Below Detection Limit*
DON *(µg/kg)*	**850**	BDL	BDL	BDL	BDL	BDL	BDL	**90**	BDL	BDL	BDL	BDL	

Potential health risk of the eastern Croatia population exposed to deoxynivalenol via wheat grains was estimated using method previously described in detail. Due to used evaluation method, it was calculated that the average intake of DON for Croatian populations via wheat grain and wheat and grain-based food were 0.67 µg/kg bw/day which is 33% lower than the TDI value proposed by JECFA and 47% lower TDI than Serrano et al.[1] calculated for European region. However, if the TDI was calculated based on the highest detected DON concentration of 850 µg/kg total intake was 2.185µg/kg bw/day which was twice as high as the TDI value proposed by JECFA. It should be noted that potential health risk was expressed for adults and risk for infants or children is higher because total intake and impact on the health is in the relationship with body weight. So it is necessary to control the DON concentration in wheat grains, especially in the silo where the highest DON concentration was detected.

In this study climate data (monthly precipitation and air temperature) during the growth of wheat and harvest period 2009 were collected (Fig. 2) and some grain quality parameters of taken samples (moisture content, protein content, starch content) were analyzed and compared with DON occurrence (Fig. 2).

The shown values of average monthly precipitation and average air temperature in Figure 1 are consistent with the fact that investigated area of eastern Croatia is located in the continental climate belt characterized by a usually warm and humid harvest period.

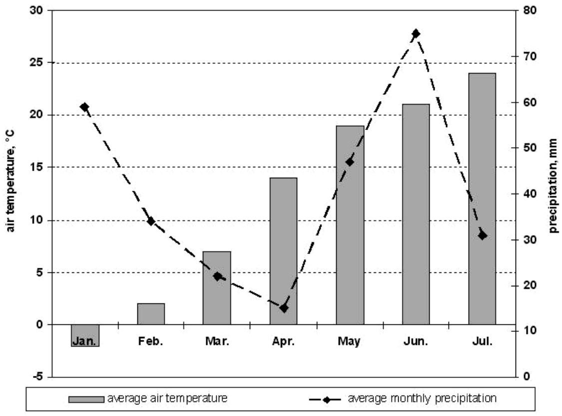

Figure 1. Average monthly precipitation and average air temperature in the area of eastern Croatia during the growth of wheat and harvest period 2009.

Investigating the occurrence of DON in crops of neighbouring Serbia, Jajić et al.[16] emphasized that optimal temperature for *Fusarium graminearum* growth is 25°C at water activity above 0.88 and for *Fusarium culmorum* growth is 21°C at water activity above 0.88. Although from Fig. 1 it can be seen that average air temperatures during June and July (21-24°C) were favourable for *Fusarium* growth, the very low average amount of precipitation during July was not favourable for growth of moulds. The good quality control in grain discharge terminals also contributed to the low incidence of DON in wheat grain samples taken from 25 silos.

Figure 2 shows comparison of three grain quality parameters (moisture content, protein content, starch content) and DON incidence in the taken samples. The moisture content (Fig. 2A) of the analysed wheat grain samples were between 11.1 and 13.1% which were lower than maximum recommended moisture content of 14%[21]. Increased percentage of moisture of wheat grains during the storage period causes and accelerates biochemical processes in grains. All above mentioned also implies that wheat grains were properly stored and contributed to low occurrence of DON.

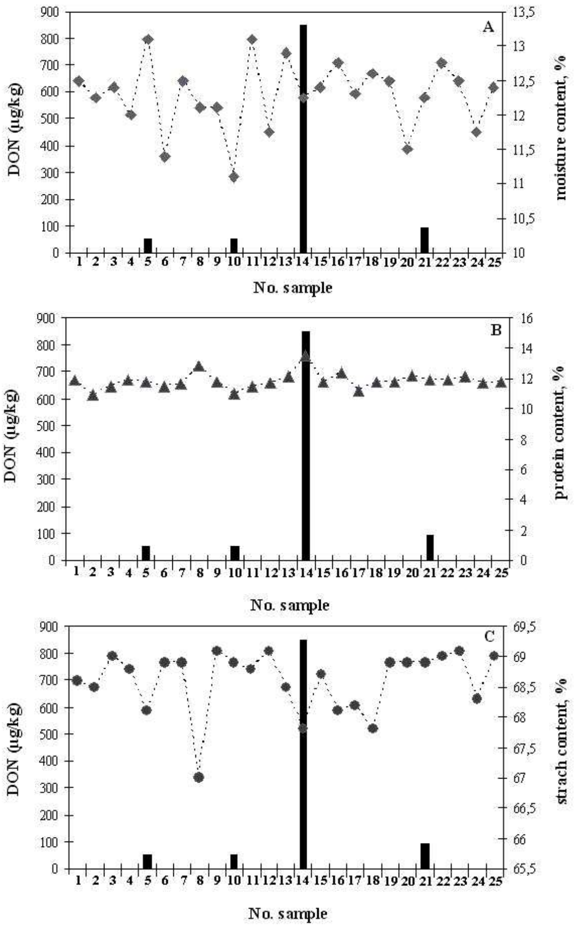

Figure 2. Comparison of deoxynivalenol concentrations (DON) and (A) average moisture content, (B) average protein content and (C) average starch content

Figure 2B shows comparison of wheat grain protein content and incidence of DON. In general, the location, soil type and cultivars have a high influence on wheat grain protein content and wheat protein content is the basis parameter for its classification and determines usage of the grains. The most of the examined samples had grain protein content between 11.5 and 12% of dry matter. It can be seen in Fig. 3B that higher protein content of 13.6% was detected in grain samples with higher DON concentration. However, this incidence was not observed in other grain samples.

Figure 2C shows the occurrence of DON and starch content. Starch is polysaccharide that is mostly placed in wheat endosperm.

The starch content of analyzed wheat grain samples was between 67 and 69.1% of dry matter. According to Fig. 2C DON incidence is not related with starch content.

CONCLUSIONS

This study analysed the incidence and potential health risk of mycotoxin deoxynivalenol in wheat grains sampled after the harvest 2009 at 25 silos in the area of eastern Croatia. In 4 of 25 wheat grains samples (16%) the DON was ranging from 50µg/kg to 850µg/kg.

The potential health risk of mycotoxin deoxynivalenol was estimated using JECFA data about total DON intake, regional diets, average adult weight in Croatia and tolerable daily intake of DON (1 µg/kg bw/day). It was calculated that the average intake of DON for Croatian populations was 0.67 µg/kg bw/day which is 33% lower than the TDI value proposed by JECFA, but twice as high as for the highest detected DON concentration of 850µg/kg (2.185 µg/kg bw/day).

Observing the climate conditions (monthly precipitation and air temperature) it was concluded that the very dry harvest period probably contributed to lower DON incidence. Analyzing and comparing the values of three grain quality parameters (moisture content, protein content, starch content) with DON incidence, no relations were observed.

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SUMMARY OF 3RD INTERNATIONAL SYMPOSIUM “ENVIRONMENTAL RESOURCES, SUSTAINABLE DEVELOPMENT AND FOOD PRODUCTION”

Summary of the two-days of 3rd International Symposium “Environmental resources, sustainable development and food production”, held in the period 14-15 November 2013 in the Congress Hall of Hotel Tuzla, organized by the Faculty of Technology, University of Tuzla

The presentation was organized in three ways:

- Plenary lectures,
- Oral presentations,
- Poster presentations.

The symposium had a rich and quality content with over 50 presentations of recently scientific achievements from Slovenia, Croatian, Serbia, and Macedonia. This was an ideal opportunity to exchange experiences in various scientific fields and the establishment of cooperation between the Faculty of Technology, University of Tuzla and faculties and factories in the region. The program of the Symposium is organized through the following sections:

1. Water-soil (mutual interactions), control, monitoring,
2. Energy efficiency and renewable sources of energy,
3. Environmentally sustainable technologies and food production, the environment and tourism,
4. Control systems in the environment (waste management and recycling)

The 3rd International Symposium contributed to the new findings in the field of environmental protection, chemical and food engineering and applied chemistry through the presented papers and discussions.

All papers will be referred to a review and get a chance to be published in the Journal Tehnologica Acta. This year, like years before, the organization of the Symposium has been financial supported by the companies from the Tuzla Canton and by the other companies from the region.

Thanks givings received after the symposium (impressions of our guests)

Dear Prof. Odobašić,
thank you for your hospitality and pleasant days at your conference.
I was really glad to participate.
Glad to meet you and I hope to have more opportunities for cooperation.
I wish you every success in your future work.
Best regards,
Ljerka Krehula

Dear Prof. Zoran,
I would like to thank you again and congratulations on a really good organized symposium. I hope that we will see again next year. Since that some papers could be very interest for our colleagues (biofuels, nutrition, environment) I am interested if it will be accessible on the website as

a pdf form or I would like to request that you send us a Journal of Tehnologica acta with papers from this conference.

Kind regards from Maribor!

Mitja Kolar

Dear Zoran,
thank you very much for the hospitality that you have given to me last week at a scientific conference in Tuzla. The conference was well organized, both scientifically and socially.
I wish you a lot of success in your future work!
Best regards,
Zoran Mandic

Hello Zoran,
I have heard from Despina only praises for your held symposium. She was very pleased with the organization and kindness of you and interesting lectures that were exposed to the Symposium.
Thank you very much for everything.
Best regards to you, to dean of faculty and to prof. Jasic

Jadranka Blazevska Gilev, DrSc
Associate Professor
University Sts Cyril and Methodius
Faculty of Technology and Metallurgy Rudjer Boskovic 16
Skopje, Republic Macedonia

INSTRUCTIONS FOR AUTHORS OF PAPERS

1. The manuscript which is to be submitted to the Editorial Board should be written in two columns with double spacing on one side of A4 paper, with all margins of 2.54 cm (1 "), font Times New Roman 12 pt. The work will be sent in electronic form, prepared solely using word processing program Microsoft Word, ending with the 2003 versions. The file should be named as follows: TA_last name of first author _first word of title.doc. The extension must match the image format (tif, pcx, jpg, png ....). Images should have a resolution of min. 300 dpi and should be prepared so that they can be printed well in B / W technique. Each individual image should not be greater than one third of A4 format. Image labels should be written below the picture.

2. The size of the article (text, along with summaries, pictures and drawings and with a list of literature references, not counting titles and signatures, as well as information about authors) should be limited to 6 pages (two illustrations correspond to approximately one page). An exception can be negotiated with the editorial board, and to receive a larger volume of work if the content and quality justifies it.

3. For successful inclusion of articles published on BCS languages in international information flows, parts of the manuscript should be written in the language of the article, as well as in English, namely: the text in tables, figures, diagrams and drawings, their titles, and signatures, and a list of abbreviations and marks.

4. Abstracts should be attached to the manuscripts:

- Summary (synopsis) in the language of article of the maximum volume of a one printed site. It must explain the purpose of the paper, and must include the important data and conclusions, as well as keywords. This summary should be entered in the manuscript right after the header of the article.
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5. The paper should contain the full official address, phone and e-mail address of all authors (on a separate sheet). Emphasize the correspondence author, with whom will the editorial board consult.

6. The title of the article should be specific and informative, in order to better determine the content of the paper. It is desirable to be as short as possible. The title should be cited on one of the BCS languages and in English.

7. Text should be clear, concise, and grammatically correct without spelling errors, written in third person (impersonal).

8. Papers should be written with the assumption that readers know the discussed subject. Thus in (a short) introduction should briefly be stated only what is necessary for understanding of the text.

9. Experimental technique and device should be described in detail only if they deviate significantly from the description already published in the literature; for the known techniques and devices only source of necessary information is provided.

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1. J. J. Sangiovanni, A. S. Kesten, Chem. Eng. Sci. 26 (1971) 533.

Example of citing patents:

2. J. Ehrenfreund (Ciba Geigy A. -G.), Eur. Pat. Appl. 22748, 21 Jan 1981; C. A. 95 (1981) 7078b.

Example of book citation:

3. W. Mehl, J. M. Hale, Insulator Reactions, in: P. Delahay and C. W. Tobias (ed.), Advances in Electrochemistry and Electrochemical Engineering. Vol. 6, Interscience Publ., New York, 1967, pp. 399-458.

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