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Arsenic in Bosnia and Herzegovina market seafood: Effects of matrix modifiers on measured concentration

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Abstract: Arsenic concentration in seafood could potentially reach very high levels and represent a significant health risk for humans. In this study, the concentration of arsenic in various seafood: crabs (shrimp, prawns), molluscs (mussels) and cephalopods (squid) available both fresh on the market and frozen in supermarkets in Sarajevo, Bosnia and Herzegovina, were determined by the electrothermal atomic absorption spectrometry (ETAAS). The results obtained using different matrix modifiers: $\text{Mg}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Pd}(\text{NO}_3)_2$, and mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ were compared. The best recovery rate of 98.4 % arsenic for the reference material ERM-CE278k, was achieved after the addition of the mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$. The mean arsenic concentrations were 1.551 ± 0.836 , 1.298 ± 0.410 and $2.794 \pm 0.958 \text{ mg kg}^{-1}$ for crustaceans, molluscs and cephalopods, respectively, using $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ as the matrix modifier. The arsenic concentrations in the same sample measured using different matrix modifiers varied widely, even above 70 %. With the current consumption rate of seafood products, both cancerogenic and non-cancerogenic risks associated with exposure to arsenic through seafood are very low for the residents of Bosnia and Herzegovina.

Keywords: ETAAS; matrix modifier; target hazard quotient; cancer risk.

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INTRODUCTION

Seafood is a well-known source of numerous nutrients. Many countries have issued national guidelines that support the regular intake of seafood. According to the U.S. Department of Agriculture and U.S. Department of Health and Human Services recommendations, an optimal seafood intake should be an app. 225 g per week.¹ The main reasons that support these claims are based on the content of high-quality proteins found in the seafood. Those proteins are easily digestible because the levels of connective tissue in seafood are significantly lower compared to red meat or chicken. In addition, seafood contains a particular type of polyunsaturated fatty acids (PUFAs) including omega-3 fatty acids that positively impact human health.² Consumption of seafood 1–2 times a week is desirable for adults, while consumption of 3–4 times a week during pregnancy is associated with better functional outcomes of neurodevelopment in children.³ Seafood may or may not be contaminated with toxic elements. The accumulation of this elements in human body from marine organisms, including seafood, depends primarily on their habitat and species and internal factors such as size, weight, age, sex, sexual maturity and stress.⁴

The lethal doses of arsenic for adults are between 100 and 300 mg.⁵ Numerous epidemiological studies have reported a strong association between exposure to arsenic and systemic health effects.⁶ Long-term exposure to arsenic can lead to neurological and cognitive dysfunction in children and adults.⁷ Knowing that most of As ingested with food are very fast excreted from the body,⁸ adverse effects for human health can arise only after excessive exposure.⁹ The International Agency for Research on Cancer (IARC) classifies inorganic arsenic compounds as cancerogenic for humans. On the other hand, organic arsenic compounds are only potentially cancerogenic.¹⁰ However, the cancer risk in humans due to exposure to As through seafood consumption is considered to be low.¹¹

Arsenic toxicity in humans is mainly related to exposure to inorganic arsenic, which through binding to thiol or sulfhydryl groups on proteins can inactivate over 200 enzymes.¹² Most likely, this is the mechanism of action underlying the effects of arsenic on various organic systems. At the same time, inorganic arsenic has been shown to inhibit mitochondrial respiration, which may cause DNA mutation and the development of cancer.¹³ The percent of inorganic arsenic in seafood is, according to different literature sources, less than 2–3 %^{14–18} up to 10–13 %.^{16,19,20} It is generally accepted that inorganic arsenic is critical for human health risk assessment.²¹ However, some findings indicate that organic arsenic compounds undergo biotransformation, leading to trivalent toxic arsenic intermediates or some end products that are more toxic than the parent arsenic.¹³

The use of precise and reliable analytical techniques to determine arsenic at 0.01 mg kg⁻¹ levels has become a standard requirement. Inductively coupled plasma mass spectrometry (ICP-MS) and electrothermal atomic absorption spec-

trometry (ETAAS) are detection techniques that meet this requirement.²² Better control of chemical processes and reduction of interference of the present components of the matrix are the most important goals for analysts who deal with these techniques. They can be achieved by adding certain chemical compounds, known as matrix modifiers that reduce interference by separating the test compound from the matrix.²³

The matrix modifiers achieve their effect by binding to the analyte element, thus preventing its loss at high pyrolysis temperatures, which are sufficient to remove most of the matrix. In general, this can be achieved by two main mechanisms: decreasing the analyte's volatility or increasing the matrix's volatility. Arsenic compounds are highly volatile; therefore, samples can lose arsenic during the preparation phase.²⁴ Test method for ETAAS issued by U.S. EPA²⁴ recommend adding nickel nitrate or palladium nitrate prior to analysis to minimize volatilization losses of arsenic during drying and ashing. Adding nickel enables char temperatures up to 1500 °C can be achieved without an arsenic loss.²⁵ Achieving the highest pyrolysis temperature is not the only prerequisite for the optimal effect of the matrix modifier.²⁶ Therefore, some authors prefer palladium which allows pyrolysis temperatures up to 1300 °C with high sensitivity.²⁷ Palladium nitrate belongs to the platinum group matrix modifiers that catalyse analyte reduction under high pyrolysis temperatures. It forms low volatility intermetallic compounds with the analyte.²⁶ Palladium nitrate is often used to determine arsenic in seafood.²⁸ Given that the classes above of matrix modifiers have different modes of action, an attempt was made to combine the modifiers from both groups. For this purpose, the mixture of palladium nitrate and magnesium nitrate is most often used, which is also considered a universal matrix modifier.²⁷ Although some research has been conducted to examine exposure to heavy metals through fish and seafood in the adult population of Bosnia and Herzegovina,²⁹ there is still insufficient information on the arsenic concentrations in seafood and related health risks.

This study aimed to determine the concentration of arsenic in various seafood: crabs (shrimp, prawns), molluscs (mussels) and cephalopods (squid) available both fresh on the market and frozen in supermarkets in Sarajevo, Bosnia and Herzegovina. In addition, the effect of the use of different matrix modifiers on As concentration was investigated. Finally, the risk to human health from arsenic intake through seafood was assessed.

EXPERIMENTAL

Chemicals

Standard arsenic solution (1 g L⁻¹) in HNO₃ (0.5 mol L⁻¹), CertiPUR®, was obtained from Merck. Matrix modifiers stock solution: magnesium nitrate (10 g L⁻¹), palladium nitrate (2 g L⁻¹) and nickel nitrate (10 g L⁻¹), trace element analyses purity, were obtained from Carlo Erba Reagents, Italy. Nitric acid, HNO₃ (65 %), Suprapur™, was purchased from Thermo

Fisher Scientific. Ultrapure water was obtained from Mili-Q-Direct 8, Millipore, USA. Certified reference material ERM-CE278k (mussel tissue) was purchased from Sigma–Aldrich.

Instruments

Microwave digestion system producer Berghof MWS-3+, Germany; Electrothermal atomic absorption spectrometer – ETAAS – PinAAcle 900T AAS THGA, producer Perkin Elmer, supported by the software WinLab 32.

Samples

Analysis has been performed on a total of 61 samples of three different types of seafood: *crustaceans* ($n = 29$), the molluscs ($n = 17$) and the cephalopods ($n = 15$). More than half of the samples (59 %) were procured fresh on the fish market and stored in the fridge at 4 °C. The other samples (41 %) were acquired frozen from the supermarket and kept in the freezer. All samples were collected between June and the end of September 2019. This study did not take into account seasonal variations and different suppliers in the market. Before the analysis, all the samples were removed from the fridge and freezer to reach room temperature, after which they were prepared by separating the edible portion from the inedible (guts, scales, heads and bones). The animal's commonly edible part (tissue) was selected for analysis and were homogenised by grinding in stainless steel chopper. Arsenic concentration was determined in each sample using all investigated matrix modifiers.

Sample preparation

All samples were treated following the applicable standard methods EN 13804:2015 and EN 13805:2015. The frozen samples were thawed at room temperature. About 0.5 g of comminuted and homogenized sample was taken for microwave digestion in PTFE vessels. After that, 5 ml HNO₃ were added, and the samples were placed on microwave digestion. The digested samples were transferred into polypropylene volumetric flasks, diluted to 25 ml with ultrapure water and used for total As determination.

Electrothermal atomic absorption spectrometry

The determination of arsenic was performed by ETAAS, supported by the software WinLab 32 and following the standard EN 14332:2004. The operating parameters of the ETAAS used during the analysis are shown in Table I. program given by producer of ETAAS for determination arsenic. The injection temperature was 20 °C, and the samples were analysed in duplicate. The injected volume of the sample was 20 µl, while the injected volume of matrix modifiers was 5 µl. The concentrations of all matrix modifiers were 1 µg µL⁻¹.

TABLE I. ETAAS operating parameters

Step		Temperature °C	Ramp time min	Hold time min	Flow of argon mL/min
1a.	Drying	110	1	30	250
1b.		130	15	30	250
2.	Pyrolysis	1200	10	20	250
3.	Atomization	2000	0	3	0
4.	Cleaning	2450	1	3	250

Calibration

Standard arsenic solution (1 g L⁻¹), was diluted to get a calibration curve. The calibration was done with 5 different concentrations (0, 1, 5, 10, 15 and 20 µg L⁻¹) and blank, it was lin-

ear, with correlation coefficients above 0.991. The real samples were analysed without and with adding matrix modifiers. Stock solution matrix modifiers were diluted and used in amount of: 5 µg Mg(NO₃)₂, 5 µg Pd(NO₃)₂, 8 µg mix of 5µg Pd(NO₃)₂ + 3µg Mg(NO₃)₂ and 5µg Ni(NO₃)₂.

Quality control

The certified reference material ERM-CE278k was analysed in each sample series, to perform quality control. Certified As value for ERM-CE278k, given by producer is 6.7±0.4 mg kg⁻¹. Also, solvents and blank were included in each series of digestion and analysis. *LOQ* value of methods is 0,01 mg kg⁻¹. The certified and analysed As values and trueness (recoveries) with different matrix modifiers were presented in Table II. The recoveries were calculated as:

$$\text{Trueness (Recovery), \%} = 100(\text{Analysed As value/Certified As value}) \quad (1)$$

TABLE II. Analysed As values and trueness (recoveries) ERM-CE278k obtained without and with different matrix modifiers;

Matrix modifier (MM)	Analyzed value ^a , mg/kg	Recovery, %
Without MM	2.29±0.1	34.2
Mg(NO ₃) ₂	1.28±0.1	19.1
Pd(NO ₃) ₂	7.09±0.2	105.8
Ni(NO ₃) ₂	3.32±0.2	49.5
Pd(NO ₃) ₂ + Mg(NO ₃) ₂	6.50±0.1	98.4

^aThe data are presented as means ± standard deviation

Risk assessment

Target hazard quotient (*THQ*) and cancer risk (*CR*) have been determined for assessing non-carcinogenic and carcinogenic risk. *THQ* and *CR* were calculated as:³⁰

$$THQ = 10^{-3} E_{fr} \times ED \times FIR \times C / R_{fd} \times BW \times TA \quad (2)$$

$$CR = 10^{-3} E_{fr} \times ED \times FIR \times C \times CSF / BW \times TA \quad (3)$$

In formulas (2) and (3), *E_{fr}* refers to exposure frequency (365 days/year), and *ED* is exposure duration (years), where the average human lifetime of 70 years was used. *FIR* stands for fish (food) ingestion rate (g per day). Since there is no available official data regarding seafood consumption in Bosnia and Herzegovina, *FIR* was estimated by using FAOSTAT food supply quality data for 2018, the latest year with available records. According to this source, 0.04, 0.05, and 0.2 kg per capita per year was the consumption for crabs, molluscs and cephalopods, respectively.³¹ The *C* is the element concentration in the sample (mg kg⁻¹). The concentration of inorganic arsenic, which represents the most toxic arsenic form, was calculated as 3 % of the mean for total arsenic concentration, in line with the approach from other authors from Bosnia and Herzegovina.¹⁷ *BW* stands for average body weight (kg), where an average adult weight of 70 kg was used and *TA* refers to exposure time for non-carcinogens (365 days per year×*ED*). *R_{fd}* refers to oral reference dose mg kg⁻¹ per day), and *CSF* is a carcinogenic slope factor. According to United States Environmental Protection Agency the *R_{fd}* and *CSF* for arsenic are 0.0003 and 1.5 mg kg⁻¹ per day respectively.³²

This research gives a snapshot of the current arsenic levels in seafood available to the citizens of Bosnia and Herzegovina. The performed risk assessment based on the collected

data provides an initial understanding of the situation. To accurately assess the population's exposure to arsenic through this diet, several years of monitoring are needed.

RESULTS AND DISCUSSION

The results of quality control (Table II) showed that recoveries were between 19.1 % (the lowest) with $\text{Mg}(\text{NO}_3)_2$ and 105.8 % (the highest) with $\text{Pd}(\text{NO}_3)_2$ as the matrix modifier (Table II). The recovery obtained with a mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ as matrix modifier was 98.4 %, and this result was considered representative since arsenic concentration was closest to the certified value. Seafood samples were analysed first without matrix modifiers and then with various matrix modifiers as a CRM material. The results are presented in Table III. The arsenic concentrations are shown as mean values with standard deviation, and range for crustaceans ($n = 29$), molluscs ($n = 17$) and cephalopods ($n = 15$). Based on the results obtained by measuring recovery of the reference material, which we consider representative, the As results obtained with the mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ were compared with the results obtained by measuring with the other matrix modifiers. None of the samples, regardless of the matrix modifier used during the analysis, showed an arsenic concentration higher than 15 mg kg^{-1} , defined as the upper limit by state regulation on maximum levels of specific contaminants in food.³³

TABLE III. Total arsenic concentration (mg/kg) in seafood measured with different matrix modifiers and risk assessment results; *THQ* – target hazard quotient; *CR* – cancer risk; * – comparison with mixture $\text{Pd}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$

Sample	Parameter	No matrix modifier	$\text{Mg}(\text{NO}_3)_2$	$\text{Pd}(\text{NO}_3)_2$	$\text{Ni}(\text{NO}_3)_2$	$\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$
Crustaceans $n = 29$	Mean $\pm$ SD	1.281 $\pm$ 0.908	0.773 $\pm$ 0.458	1.601 $\pm$ 0.908	0.795 $\pm$ 0.340	1.551 $\pm$ 0.836
	Range	0.010–3.570	0.020–1.976	0.225–4.144	0.086–1.740	0.252–3.741
	<i>p</i> value*	1.000	< 0.003	0.173	< 0.001	N/A
	<i>THQ</i> /10 ⁻⁴	2.0	1.2	2.5	1.2	2.4
	<i>CR</i> /10 ⁻⁷	0.9	0.5	1.1	0.6	1.1
Cephalopods $n = 15$	Mean $\pm$ SD	1.225 $\pm$ 1.023	0.902 $\pm$ 0.311	1.346 $\pm$ 0.453	0.582 $\pm$ 0.242	1.298 $\pm$ 0.410
	Range	0.020–2.752	0.325–1.487	0.490–1.818	0.135–0.852	0.405–1.706
	<i>p</i> value*	0.108	< 0.001	0.663	< 0.001	N/A
	<i>THQ</i> /10 ⁻⁴	9.6	7.1	10.5	4.6	10.2
	<i>CR</i> /10 ⁻⁷	4.3	3.2	4.7	2.1	4.6
Molluscs $n = 17$	Mean $\pm$ SD	1.367 $\pm$ 0.740	0.774 $\pm$ 0.316	2.537 $\pm$ 0.793	1.042 $\pm$ 0.219	2.794 $\pm$ 0.958
	Range	0.218–2.710	0.163–1.288	1.070–3.851	0.686–1.363	1.106–4.301
	<i>p</i> value*	< 0.001	< 0.001	0.061	< 0.001	N/A
	<i>THQ</i> /10 ⁻⁴	2.7	1.5	5.0	2.0	5.5
	<i>CR</i> /10 ⁻⁷	1.2	0.7	2.2	0.9	2.5

A risk assessment analysis has been performed based on the gained arsenic concentrations to estimate the probability of adverse health effects potentially caused by exposure to arsenic-containing seafood. *THQ* and *CR* were calculated

using the methodology initially developed to determine concentrations of toxic substances ingested through the consumption of edible fish.³⁰ However, this methodology has been used by many authors for assessing the risk from the consumption of seafood as well.^{15,34,35} For the *THQ* values < 1 , adverse health effects are not expected. If the *THQ* value is > 1 , non-carcinogenic adverse health effects could be experienced. On the other hand, according to U.S. EPA,³⁶ carcinogenesis is a phenomenon for which risk evaluation based on the presumption of a threshold is inappropriate. Therefore, *CR* results are evaluated upon acceptable lifetime risk level (*ARL*) equal to 1×10^{-5} as defined by U.S. EPA,³⁷ representing a risk for developing cancer over a human lifetime of 1 in 100,000.

Crustaceans

It is not surprising that a high concentration of this heavy metal can be found in seafood shrimps.¹⁵ However, that was not the case in this research, where the gained arsenic concentration for crustaceans was in the range 0.010–4.144 mg kg⁻¹ (wet weight) with a mean concentration of 1.551 ± 0.836 mg kg⁻¹ observed for the samples analysed with the mixture Pd(NO₃)₂ + Mg(NO₃)₂ as a matrix modifier. The highest observed mean arsenic concentration was 1.601 ± 0.908 mg kg⁻¹ with Pd(NO₃)₂. In contrast, the lowest one was 0.773 ± 0.458 mg kg⁻¹ determined with the Mg(NO₃)₂. It can be noticed that the mean As concentrations obtained with Pd(NO₃)₂ and with a mixture Pd(NO₃)₂ + Mg(NO₃)₂ are very similar (1.601 ± 0.908 and 1.551 ± 0.836 mg kg⁻¹, respectively). This finding indicates that the effect of Pd(NO₃)₂ on reducing the interference of the present matrix components is crucial. Similar mean As values were also obtained with Mg(NO₃)₂ and Ni(NO₃)₂ (0.773 ± 0.458 and 0.795 ± 0.340 mg kg⁻¹, respectively), indicating that these two modifiers work similarly. The mean As concentration obtained without matrix modifier was 1.281 ± 0.908 mg kg⁻¹ and was between the values obtained with Pd (NO₃)₂/(Pd(NO₃)₂ + Mg(NO₃)₂) and Mg(NO₃)₂/Ni(NO₃)₂. Based on these findings, it can be concluded that Mg(NO₃)₂ and Ni(NO₃)₂ interfere with the determination of arsenic and should not be used alone for these purposes.

The most extensive range of concentrations was found for the samples analysed without matrix modifiers, while the smallest was in the group with Ni(NO₃)₂ (Fig. 1). For the individual samples, the highest arsenic concentration of 4.144 mg kg⁻¹ was recorded using Pd(NO₃)₂. The lowest concentration was 0.010 mg kg⁻¹ in the sample without a matrix modifier. Several literature sources reported the mean arsenic values for shrimp in a similar range of 0.27–2.18 mg kg⁻¹.^{38,39} In Olmedo *et al.* work,³⁸ fresh samples had the higher mean As concentrations of 0.739 mg kg⁻¹ than 0.509 mg kg⁻¹ recorded in frozen samples. Other studies have reported much higher arsenic values for shrimp in the range of 19.13–51.18 mg kg⁻¹.¹⁵

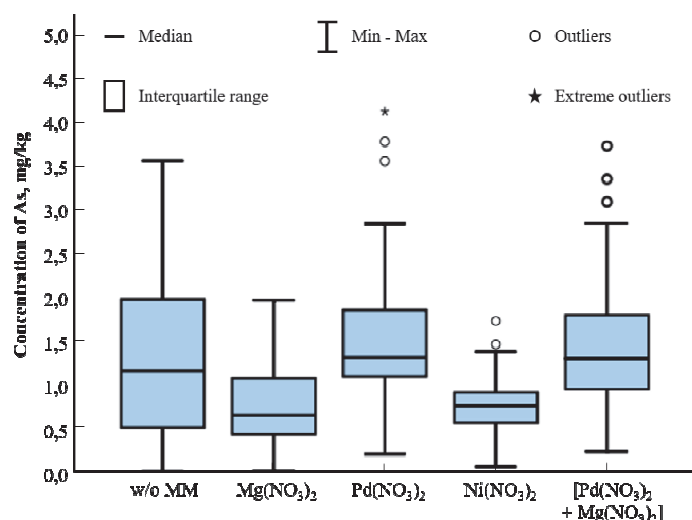


Fig. 1. Arsenic concentration (mg kg^{-1} , wet weight) for crustaceans, measured with different matrix modifiers.

In comparison with the mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$, the results with $\text{Pd}(\text{NO}_3)_2$ and without matrix modifier did not show a significant difference ($p = 0.173$ and $p = 1.000$, respectively). The mean arsenic concentrations were 3.22 % higher and 17.41 % lower, respectively, compared with the values obtained with the mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$. In contrast, the differences between As the concentrations obtained with the mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ and the concentrations obtained with $\text{Mg}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ modifiers have shown statistical significance ($p < 0.05$). The mean arsenic concentration measured with the mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ was 50.17 % higher than the concentration observed with $\text{Mg}(\text{NO}_3)_2$ and 48.74 % higher than the value noticed with $\text{Ni}(\text{NO}_3)_2$.

Estimates for *THQ* and *CR* have shown that consumption of crustaceans does not pose significant non-carcinogenic or carcinogenic health risks. The calculated *THQ* results are far below the limit of 1 regardless of the matrix modifier used and the range between 1.2×10^{-4} and 2.5×10^{-4} . These values are significantly lower than those observed by the Bonsignore *et al.* study, ranging from 0.200 to 0.140.¹⁵ In addition to the lower levels of arsenic reported in this study, a significantly lower ingestion rate strongly contributed to the observed difference. These two factors notably influenced *CR*, calculated as 0.5×10^{-7} – 41.1×10^{-7} . Once again, these levels are much lower than those reported by Bonsignore *et al.*¹⁵

Cephalopods

Results of arsenic concentration in cephalopods are shown in Fig. 2. The mean arsenic concentration was $1.298 \pm 0.410 \text{ mg kg}^{-1}$ for the samples treated

with the mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$, which was the lowest value compared to crustaceans and molluscs (Table III). The observed mean As concentrations ranged from $0.582 \pm 0.242 \text{ mg kg}^{-1}$ for $\text{Ni}(\text{NO}_3)_2$ to $1.346 \pm 0.453 \text{ mg kg}^{-1}$ for $\text{Pd}(\text{NO}_3)_2$ modifier. In contrast, the lowest and the highest single sample arsenic concentrations were 0.020 and 2.752 mg kg^{-1} , respectively, observed in the samples not treated with matrix modifiers (Fig. 3). Pronounced diversity can also be found in the values of As concentration published in the literature. Some authors have reported relatively low arsenic levels below 5 mg kg^{-1} ,¹⁶ while the others have reported a high concentration of 36.63 mg kg^{-1} .⁴⁰ Several authors have reported arsenic levels in broad ranges, including the low and high boundaries mentioned above.^{14,18}

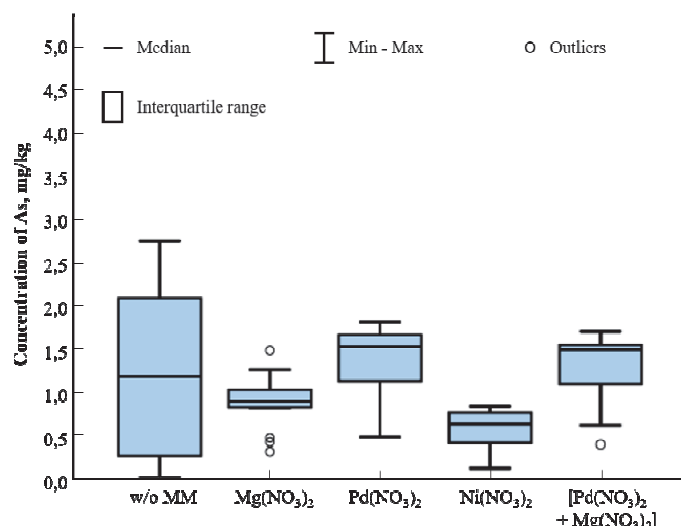


Fig. 2. Arsenic concentration (mg kg^{-1} , wet weight) for cephalopods, measured with different matrix modifiers.

In the same way as for crustaceans, a significant difference ($p < 0.05$) between the mean arsenic concentration measured with the mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ and both $\text{Mg}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ modifiers was observed. The mean As value obtained with the mixture $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ was higher for 30.51 and 44.84 % compared with those measured separately with $\text{Mg}(\text{NO}_3)_2$ and $\text{Ni}(\text{NO}_3)_2$ modifiers. As expected, no significant difference has been determined when the mean As concentration obtained with $\text{Pd}(\text{NO}_3)_2$ was compared to the concentration obtained with $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ mixture ($p = 0.663$). The mean As value with $\text{Pd}(\text{NO}_3)_2$ was just 3.70 % higher than the value with the modifiers mixture. Similarly, the result without the matrix modifier does not show statistical significance ($p = 0.108$). Still, the mean As concentration

obtained with the modifiers mixture was higher by 5.62 % compared with concentration without matrix modifier.

Although the values of arsenic were the lowest in *cephalopods*, both carcinogenic and non-carcinogenic risks are higher comparing to crustaceans and molluscs due to the highest consumption. *THQ* scores were ranged from 1.5×10^{-4} to 5.5×10^{-4} , which is still well below the cut-off value of 1. The results are much lower than those reported by Bonsignore *et al.*, which have ranged from 0.15 to 2.00.¹⁵ A considerable difference was also observed in the results of *CR* scores. Calculated values for inorganic arsenic in this research were in the range 2.1×10^{-7} – 4.7×10^{-7} , whereas the *CR* score for cephalopods reported in the literature was considerably higher, amounted 2.6×10^{-4} – 8.1×10^{-4} .¹⁵

Molluscs

The results of arsenic concentration in molluscs are shown in Fig. 3. The obtained concentration ranged 0.163–4.301 mg kg⁻¹. The highest mean concentration of 2.794 ± 0.958 mg kg⁻¹ was observed in the group of results obtained with the mixture Pd(NO₃)₂ + Mg(NO₃)₂ as a matrix modifier. The lowest one of 0.774 ± 0.316 mg kg⁻¹ was obtained in the case of Mg(NO₃)₂ as a matrix modifier. The single sample's highest and lowest arsenic concentrations were also found in those two groups (4.301 and 0.163 mg kg⁻¹, respectively).

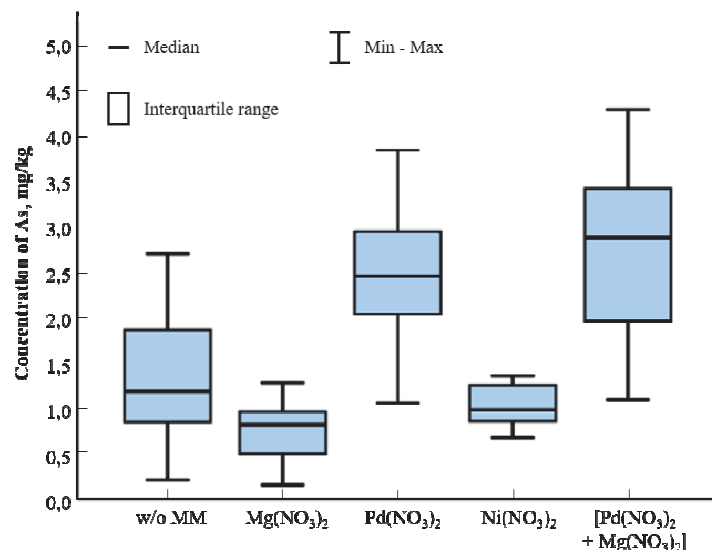


Fig. 3. Arsenic concentration (mg kg⁻¹, wet weight) for molluscs, measured with different matrix modifiers.

Similar to the results for crustaceans, it was again observed that the mean concentrations of As obtained with Pd(NO₃)₂ and a mixture of Pd(NO₃)₂ +

Mg(NO₃)₂, were quite close (2.537±0.793 and 2.794±0.958 mg kg⁻¹, respectively). Relatively close mean concentrations of As were also obtained when Mg(NO₃)₂ and Ni(NO₃)₂ were used (0.774±0.316 and 1.042±0.219 mg kg⁻¹, respectively). This finding again indicates that the mechanism of action of these modifiers, Mg(NO₃)₂ and Ni(NO₃)₂, which primarily eliminate interference from inorganic chlorides, in our research was not helpful. Indeed, according to Welz *et al.* sodium chloride caused very few problems in determining arsenic.²⁷

Most available literature sources have reported arsenic concentrations in molluscs with a similar range as found in our research. Several locations of the Adriatic Sea are the main source of fresh seafood products available at markets in Bosnia and Herzegovina. Mussels collected along the Croatian coast contained total arsenic in 2.33–2.56 mg kg⁻¹,^{28,40} while mussels at the coast of Montenegro contained 1.73–2.41 mg kg⁻¹.⁴² Recent research has shown that the main arsenic concentration in fresh and frozen mussels marketed in Serbia was 3.97 and 1.56 mg kg⁻¹, respectively.⁴³ The differences in arsenic concentration between fresh and frozen products are also described by Olmedo *et al.*, reporting lower As levels in both publications.³⁸

No statistically significant difference was observed between the results with the mixture Pd(NO₃)₂ + Mg(NO₃)₂ in comparison to the results with Pd(NO₃)₂ modifier ($p = 0.061$). The mean As concentration obtained with Pd(NO₃)₂ + Mg(NO₃)₂ mixture was slightly higher (9.20 %). Compared to other results, the mean concentration of As obtained with the mixture (Pd(NO₃)₂ + Mg(NO₃)₂) was significantly higher: 51.07 % than the mean concentration without matrix modifier, 72.30 % than with Mg(NO₃)₂ and 62.71 % than with Ni(NO₃)₂ modifier. All differences were statistically significant ($p < 0.05$). The low range with low mean values observed for the results with Mg(NO₃)₂ and Ni(NO₃)₂ clearly shows that these modifiers are not suitable for determining As.

Compared to crustaceans and cephalopods, molluscs had the highest observed As concentrations (Table III). Nevertheless, those concentrations are still well below the upper limit of 15 mg kg⁻¹ defined by the local Bosnia and Herzegovina regulation.³³ A low consumption rate of only 0.05 kg per capita per year³¹ resulted in very low *THQ* and *CR* scores. Ferrante *et al.* have determined a strong impact of the level of exposure to As through molluscs consumption on both non-carcinogenic and carcinogenic risks.³⁴ Calculated *THQ* scores from this work were in the range of 1.5×10^{-4} – 5.5×10^{-4} , which was much lower than 0.331–2.320 reported by Ferrante *et al.*³⁴ and also than 0.209–0.262 reported by Conte *et al.*¹⁹ Similarly, *THQ* scores calculated *CR* results in the range of 0.7×10^{-7} – 2.5×10^{-7} are still much lower than 1.49×10^{-4} , which was found to be the lowest level of exposure in Conte *et al.*¹⁹

CONCLUSIONS

This research has provided arsenic concentration in seafood available on markets in Sarajevo, the capital of Bosnia and Herzegovina. The obtained results have shown low levels of arsenic, toxic element associated accordingly with low health risks arising from seafood consumption. Since the portion of inorganic arsenic, which has a critical role in the impairment of human health, is minor in seafood, only the excessive exposure could increase health risks. With the current very low consumption rate of seafood products, both cancerogenic and non-cancerogenic risks associated with exposure to arsenic through seafood are very low for the residents of Bosnia and Herzegovina. Under the described conditions, different matrix modifiers did not show a considerably significant impact on the health risk assessment. However, it is essential to emphasize that some differences in As concentrations of the same samples measured using different matrix modifiers were more than 70 %. Additional research is needed to determine why some modifiers had better efficacy than others and to explain the intensive, beneficial response of seafood samples on $\text{Pd}(\text{NO}_3)_2$ matrix addition.

ИЗВОД

АРСЕН НА ТРЖИШТУ МОРСКИХ ПЛОВОДА У БОСНИ И ХЕРЦЕГОВИНИ: ЕФЕКТИ МОДИФИКАТОРА МАТРИЦЕ НА ИЗМЕРЕНУ КОНЦЕНТРАЦИЈУ

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Концентрација арсена у морским плодовима може потенцијално достићи веома високе вредности и представљати значајан здравствени ризик за људе. У овој студији, концентрација арсена у разним морским плодовима, као што су: ракови (шампи, козице), мекушци (дагње) и главоношци (лигње), доступним у свежем и смрзнутом стању на тржишту у Сарајеву, Босна и Херцеговина, одређена је електротермалном атомском апсорпционом спектрометријом (ETAAS). Упоредени су резултати добијени коришћењем различитих модификатора матрице: $\text{Mg}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Pd}(\text{NO}_3)_2$ и смеше $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$. Најбоља стопа уклањања арсена концентрације 98,4 % за референтни материјал ERM-CE278k, је постигнута након додавања смеше $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$. Просечне концентрације арсена биле су $1,551 \pm 0,836$ и $1,298 \pm 0,410$, односно $2,794 \pm 0,958 \text{ mg kg}^{-1}$, за ракове, мекушце и главоношце, уз примену смеше $\text{Pd}(\text{NO}_3)_2 + \text{Mg}(\text{NO}_3)_2$ као модификатора матрице. Концентрације арсена у истом узорку мерене коришћењем различитих модификатора матрице су се веома разликовале, чак и преко изнад 70 %. Уз тренутну стопу потрошње производа од морских плодова, канцерогени и неканцерогени ризици повезани са изложеношћу арсену кроз морске плодове су веома ниски за становнике Босне и Херцеговине.

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REFERENCES

1. U.S. DA and U.S. HHS: *Dietary Guidelines for Americans 2020–2025*, 2020
2. E. B. Rimm, L. J. Appel, S. E. Chiuve, L. Djoussé, M. B. Engler, P. M. Kris-Etherton, D. Mozaffarian, D. S. Siscovick, A. H. Lichtenstein, *Circulation* **138** (2018) e35 (<https://doi.org/10.1161/CIR.0000000000000574>)
3. EFSA NDA PANEL: *Scientific Opinion on health benefits of seafood (fish and shellfish) consumption in relation to health risks associated with exposure to methylmercury*, 2014
4. D. J. H. Phillips, P. S. Rainbow, *Biomonitoring of Trace Aquatic Contaminants*, Elsevier, London, 1993
5. W. L. Schoolmeester, D. R. White, *South Med. J.* **73** (1980) 198 (<https://doi.org/10.1097/00007611-198002000-00021>)
6. P. B. Tchounwou, A. K. Patlolla, J. A. Centeno, *Toxicol. Pathol.* **31** (2003) 575 (<https://doi.org/10.1080/01926230390242007>)
7. C. R. Tyler, A. M. Allan, *Curr Environ. Health Rep.* **1** (2014) 132 (<https://doi.org/10.1007/s40572-014-0012-1>)
8. G. Chiocchetti, C. Jadán-Piedra, D. Vélez, V. Devesa, *Crit. Rev. Food Sci. Nutr.* **57** (2017) 3715 (<https://doi.org/10.1080/10408398.2016.1161596>)
9. S. Naess, I. Aakre, A. K. Lundebye, R. Ornsrud, M. Kjellevold, M. W. Markhus, L. Dahl, *Food Addit. Contam., B* **13** (2020) 99 <https://doi.org/10.1080/19393210.2020.1735533>)
10. IARC: *Arsenic and inorganic arsenic compounds*, 1973
11. B. C. Chen, W. C. Chou, W. Y. Chen, C. M. Liao, *J. Hazard. Mater.* **181** (2010) 161 (<https://doi.org/10.1016/j.jhazmat.2010.04.112>)
12. P. B. Tchounwou, C. G. Yedjou, A. K. Patlolla, D. J. Sutton, in *Molecular, Clinical and Environmental Toxicology. Experientia Supplementum*, Vol. 101A. Luch, Ed., Springer, Basel, 2012, p. 133 (https://doi.org/10.1007/978-3-7643-8340-4_6)
13. M. Molin, S. M. Ulven, H. M. Meltzer, J. Alexander, *J. Trace Elem. Med. Biol.* **31** (2015) 249 (<https://doi.org/10.1016/j.jtemb.2015.01.010>)
14. H. Amlund, J. J. Sloth, in *Encyclopedia of Environmental Health*, J. O. Nriagu, Ed., Elsevier, Burlington, 2011, p. 145 (<https://doi.org/10.1016/b978-0-444-52272-6.00344-5>)
15. M. Bonsignore, D. S. Manta, S. Mirto, E. M. Quinci, F. Ape, V. Montalto, M. Gristina, A. Traina, M. Sprovieri, *EcoToxicol. Environ. Saf.* **162** (2018) 554 (<https://doi.org/10.1016/j.ecoenv.2018.07.044>)
16. G. Falco, J. M. Llobet, A. Bocio, J. L. Domingo, *J. Agric. Food Chem.* **54** (2006) 6106 (<https://doi.org/10.1021/jf0610110>)
17. Dz. Hajric, M. Smajlovic, B. Antunovic, A. Smajlovic, D. Alagic, D. Tahirovic, D. Brenjo, E. Clanjak-Kudra, J. Djedjibegovic, A. Porobic, V. Poljak, *Food Control* **133** (2022) 108631 (<https://doi.org/10.1016/j.foodcont.2021.108631>)
18. O. Munoz, V. Devesa, M. A. Suner, D. Velez, R. Montoro, I. Urieta, M. L. Macho, M. Jalón, *J. Agric. Food Chem.* **48** (2000) 4369 (<https://doi.org/10.1021/jf000282m>)
19. F. Conte, C. Copat, S. Longo, G. O. Conti, A. Grasso, G. Arena, M. V. Brundo, M. Ferrante, *Food Chem. Toxicol.* **81** (2015) 143 (<https://doi.org/10.1016/j.fct.2015.04.020>)
20. R. M. Lorenzana, A. Y. Yeow, J. T. Colman, L. L. Chappell, H. Choudhury, *Hum. Ecol. Risk Assess* **15** (2009) 185 (<https://doi.org/10.1080/10807030802615949>)
21. F. Cubadda, B. P. Jackson, K. L. Cottingham, Y. O. Van Horne, M. Kurzius-Spencer, *Sci. Total Environ.* **579** (2017) 1228 (<https://doi.org/10.1016/j.scitotenv.2016.11.108>)
22. S. C. Wilschefski, M. R. Baxter, *Clin. BioChem. Rev.* **40** (2019) 115 (<https://doi.org/10.33176/AACB-19-00024>)

23. A. B. Volynskii, *J. Anal. Chem.* **58** (2003) 905 (<https://doi.org/10.1023/A:1026115330513>)
24. U.S. EPA Method 7010: *Graphite Furnace Atomic Absorption Spectrophotometry*, 2007
25. D. C. Manning, W. Slavin, *Appl. Spectrosc.* **37** (1983) 1 (<https://doi.org/10.1366/0003702834634262>)
26. A. B. Volynsky, *Spectrochim. Acta, B* **55** (2000) 103 ([https://doi.org/10.1016/S0584-8547\(99\)00175-5](https://doi.org/10.1016/S0584-8547(99)00175-5))
27. B. Welz, G. Schlemmer, J. R. Mudakavi, *J. Anal. At. Spectrom.* **7** (1992) 1257 (<https://doi.org/10.1039/JA9920701257>)
28. D. Juresa, M. Blanus, *Food Addit. Contam.* **20** (2003) 241 (<https://doi.org/10.1080/0265203021000055379>)
29. J. Djedjibegovic, A. Marjanovic, D. Tahirovic, K. Caklovica, A. Turalic, A. Lugusic, E. Omeragic, M. Sober, F. Caklovica, *Sci. Rep.* **10** (2020) 13238 (<https://doi.org/10.1038/s41598-020-70205-9>)
30. EPA: *EPA Region III risk-based concentration table*, 1995
31. FAOSTAT: *Food Balance Sheet*, 2018
32. U.S. EPA, CASRN 7440-38-2: *IRIS (Integrated Risk Information System) Assessment Summary Arsenic, inorganic*, 2002
33. Bosnia and Herzegovina: *Regulation on maximum levels for certain contaminants in food*, 2018
34. M. Ferrante, S. Napoli, A. Grasso, P. Zuccarello, A. Cristaldi, C. Copat, *Food Chem. Toxicol.* **126** (2019) 322 (<https://doi.org/10.1016/j.fct.2019.01.010>)
35. M. Yabanli, I. Sener, A. Yozukmaz, S. Öner, H. H. Yapıcı, *Environ. Sci. Pollut. Res.* **28** (2021) 53171 (<https://doi.org/10.1007/s11356-021-14569-z>)
36. U.S. EPA: *Risk Assessment Guidance for Superfund Volume I*, 2010
37. U.S. EPA: *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories Volume 2*, 2000
38. P. Olmedo, A. Pla, A. F. Hernández, F. Barbier, L. Ayouni, F. Gil, *Environ. Int.* **59** (2013) 63 (<https://doi.org/10.1016/j.envint.2013.05.005>)
39. X. Wu, M. Gao, L. Wang, Y. Luo, R. Bi, L. Li, L. Xie, *Ecotoxicol. Environ. Saf.* **102** (2014) 168 (<https://doi.org/10.1016/j.ecoenv.2014.01.028>)
40. D. Ramon, D. Morick, P. Croot, R. Berzak, A. Scheinin, D. Tchernov, N. Davidovich, M. Britzi, *J. Food Sci.* **86** (2021) 1153 (<https://doi.org/10.1111/1750-3841.15627>)
41. N. Bilandzic, M. Sedak, B. Calopek, N. Dzafic, D. Misetic Ostojic, D. Potocnjak, *Bull Environ. Contam. Toxicol.* **95** (2015) 611 (<https://doi.org/10.1007/s00128-015-1619-0>)
42. J. Markovic, D. Joksimovic, S. Stankovic, *Arch. Biol. Sci.* **64** (2012) 265 (<https://doi.org/10.2298/ABS1201265M>)
43. N. J. Novakov, B. D. Kartalovic, Z. A. Mihaljev, K. M. Mastanjevic, N. S. Stojanac, K. J. Habschied, *Food Addit. Contam., B* **14** (2021) 219 (<https://doi.org/10.1080/19393210.2021.1931475>).