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WORKING OUT PROCEDURES FOR ANALYZING TOXIC ELEMENTS CONTENT IN OIL PRODUCTS AND OIL RAW MATERIALS USING ATOMIC-EMISSION SPECTROMETRY WITH INDUCTIVE-BOUND PLASMA TO ASSESS PRODUCTS SAFETY

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Our goal was to work out a procedure aimed at determining low concentrations of toxic elements in oil products using atomic-emission spectrometry to assess products safety.

We performed a comparative examination of various mineralization techniques, studied extraction conditions impacts, as well as autoclave and microwave mineralization impacts on the results of toxic elements determination in oil raw materials and oil products. We detected that complete mineralization enabled achieving the least results inaccuracy in comparison with acid extraction.

We developed parameters for atomic-emission analysis of determining Fe, Cu, Ni, Pb, and Cd, in oil raw materials and oil products. We defined a wave length for each element and background correction; we also determined a device parameters (generator power, sample feeding speed, spraying speed), chose a cleft width and an analysis regime for data calculation.

Basing on the conducted research we created a high-precision procedure for determining low concentrations of such toxic elements, as Pb, Cd, As, Hg, Cu, Fe, and Ni, with atomic-emission spectrometry technique. Standard deviation in the procedure repeatability amounts to 1.4–4.3 %. Standard deviation in the procedure reproducibility amounts to 10.1–11.8 %. maximum expanded uncertainty in measuring concentrations of Cd, Pb, and As, amounts to 30.6 %; Hg, 23 %; Cu, Fe, ands Ni, 21 %; Pb, 33 %.

Application of the created procedure will help to enhance control over quality and safety of food products and to lower alimentary morbidity.

Key words: *toxic elements, atomic-emission spectrometry, oil raw materials, oil products, sample preparation, precision, food products safety.*

Emissions from industrial enterprises and city transport contaminate the environment and as a result toxic elements penetrate food products. Toxic elements can also get into food products during production processes or if storage conditions are unsafe. When they

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enter a human body in excessive quantities it exerts negative impacts on the immune system; it can also cause substantial metabolic and functional disorders.

According to the Customs Union's Technical Regulations No. 021/2011 "On food products safety", four most widely spread and most dangerous toxicants, namely Pb, As, Cd, and Hg, are determined in all kinds of food raw materials and food products, including oil and fat ones. Apart from these four elements, Cu and Fe contents in vegetable oils, spreads, and rendered animal fats, are to conform to fixed standards as these elements influence oxidative processes activation. Ni contents are standardized in products which are the result of vegetable oil and animal fats processing (margarines, cooking fats, and mayonnaise) as Ni is a part of a catalyst used in products hydrogenation.

Food safety assessment includes control over toxic elements contents. Occurrence of such elements as Pb, As, Cd, Hg, Fe, and Cu, in oil products and oil raw materials is always analyzed; these elements can get into finished products either from raw materials or during production processes. Colorimetric, polarographic, or spectrometric techniques are used to perform such analysis [1, 6, 7].

Atomic-emission spectrometry has a number of advantages over other techniques as it has low detection limits, and calibrating graphs linearity within a wide range of concentrations, and it allows to simultaneously determine a great number of elements.

Samples preparation has a great influence on the validity of the obtained results. Techniques applied in oil products samples preparation can be divided into two groups: acid extraction and complete mineralization. Nowadays there are several regulations which fix standards for oil products analysis and which envisage complete mineralization of samples; they are ISO 8294: 1994, ISO 15774: 2000, ISO 12193: 2004, ISO 10540-2: 2003. And there is a standard which fixes acid extraction, namely State Standard 26929-94. Literature sources [8, 11–14] state that results of mineral elements content examination in food products differ depending on a sample preparation technique. This difference is determined both by a chemical element essence, and its quantitative contents in food products.

Our research goal was to create a procedure for determining low concentrations of toxic elements in oil products using atomic-emission spectrometry with inductively bound plasma to assess food products safety.

To achieve the stated goal, we solved a number of tasks; we worked out atomic-emission analysis parameters and created samples preparation conditions for toxic elements analysis.

Data and methods. Our research objects were samples of refined and unrefined sunflower-seed oil, margarine, mayonnaise, sunflower seeds, poppy seeds, and fish oil.

Food products samples which were used in comparative examination of various mineralization techniques didn't contain any additives.

Native oil raw materials and oil products, and also products with known introduced toxic elements content were used as examination samples for metrological research. Toxic elements were introduced in quantities corresponding to their maximum permissible concentrations in food products. CONOSTAN oil standards (the USA) with the known toxic elements contents were used for sunflower-seed oil; standard Pb, Cd, As, Hg, Cu, Ni, and Fe solutions were used for other samples.

We used concentrated nitric acid (67%, «for trace analysis» class, Fluka), hydrogen peroxide (36%, puriss.), hydrochloric acid (36 %, puriss.), deionized water, which was received with the use of Direct-Q3 water deionizer (Millipore Corporation, the USA), and standard samples of Pb, Cd, As, Hg, Cu, Ni, and Fe solutions in our work.

Acid extraction techniques and complete mineralization techniques were applied in samples preparation.

We applied Horiba Jobin Yvon atomic-emission spectrometer (Japan-France) with radial vision of argon plasma and 1 meter focal distance to determine elements content in mineralized samples.

Results and discussion. Oil products mineralization techniques can be divided into two groups, namely acid extraction and complete mineralization; the latter means samples decomposition in mineral acids when analytical autoclaves are applied under thermal treatment or microwave radiation.

Extraction samples preparation has an advantage as it allows to obtained mineralized samples with high analyte content taking a substantial sample weight into account; it is also not necessary to use specialized equipment for mineralization.

We changed extraction time and solid and liquid phase ratio to study influence exerted by acid extraction conditions on the analysis results. Extraction was performed in a heatproof flask containing a sample, boiling centers and hydrochloric acid solution diluted 1:1 in volume. The flask content was boiled for 45 or 90 minutes. We applied the following ratios of a sample and acid-extractive mixture: 20 g and 40 ml (1:2); 8 g and 40 ml (1:5); 4 g and 40 ml (1:10).

As we can see in Figure 1, decrease in a ratio of a sample to an extracting agent volume leads to increase in extracted elements quantity. It becomes most apparent when Cu is extracted. Extracted Cu quantity varies 1.5-2.6 times depending on an examined sample and "sample - extracting agent" ratio. Fe quantity varies not so greatly, 1.1-1.5 times.

Increase in extraction time from 45 to 90 minutes also results in growing quantity of an element extracted out of a sample. Cu quantity grows by 10-40%; Fe quantity, by about 10%.

So, the obtained data allow us to conclude that decrease in a ratio of a sample weight to a sample volume and increase in extraction time leads to growth in the quantity of elements extracted out of a sample. We should note that decrease in a ratio of a sample weight to an extracting agent volume also results in greater errors in measurement. Maximum error for ratio 1:2 amounts to 3% for Cu and 8% for Fe; it is equal to 10 and 25% correspondingly when ratio is 1:10.

The performed examinations enables determining the most suitable conditions of extraction sample preparation which allow to extract maximum quantity of elements; these conditions include sample weight being equal to 4 g and acid extraction ratio being 1:10; optimal extraction time is 1.5 hours.

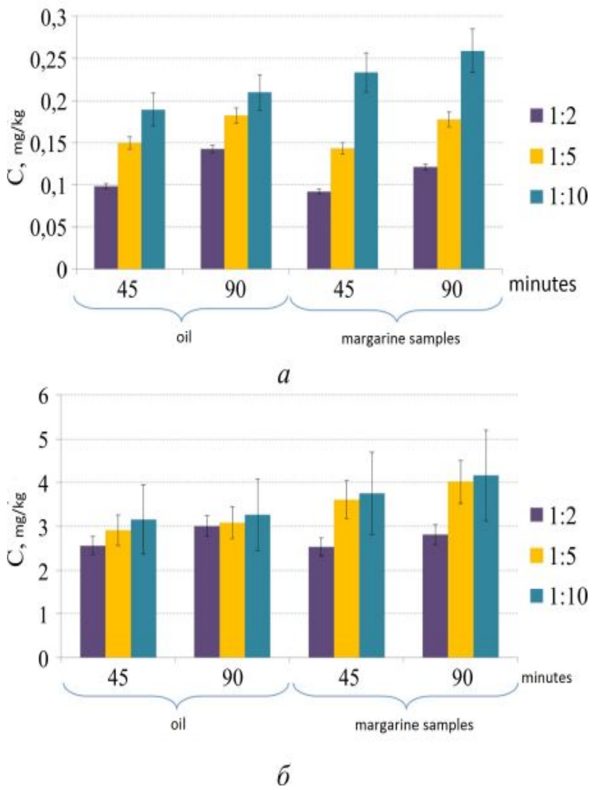

Figure 1. Influence exerted by acid extraction conditions
on the results of determining Cu (*a*) and Fe (*б*) in oil and margarine samples

Acid extraction can be applied only when treating vegetable oil, butter, food fats, and margarine. Besides, this sample preparation technique is not suitable for determining highly volatile elements, notably, Hg.

Complete decomposition performed in closed vessels allows to avoid possible losses of highly volatile elements.

When performing complete mineralization, we put a sample weighing 0.5-2 g into a fluoroplastic cup, embedded it with an oxidative mixture made of concentrated nitric acid and concentrated hydrogen peroxide, and then, after a preliminary exposure, we performed mineralization heating the mixture or treating it with microwave radiation. We obtained the control solution by performing mineralization without a sample. To examine conditions of autoclave sample preparation we applied two mineralization regimes with different time and temperature. The first regime which was a longer one was accomplished in three stages with a gradient reaction mixture temperature rise during 30 minutes and heating under a certain temperature: 160 °C for 1 hour, 180 °C for 1 hour, 200 °C for 2 hours. The second regime had two stages: 160 °C for 1 hour, 180 °C for 2 hours. The research revealed that mineralization regime had no influence on the results of mineral elements (Cu and Fe) determination in sunflower-seed oil. Difference between the results amounted to only 1-3%.

We performed microwave mineralization of oil products samples applying a multi-stage program under controlled growing pressure and temperature conditions for each product type. Microwave sample preparation examination enabled determining the most efficient microwave mineralization regime for all oil products samples.

We compared various mineralization techniques, including autoclave and microwave one, as well as acid extraction. When acid extraction was performed, we applied conditions which allowed to obtain the maximum quantities of extracted elements. We applied the following program for microwave decomposition: control over the process as per pressure, control pressure value P was equal to 160 psi (1,103 MPa), decomposition time was 25 minutes. Autoclave mineralization process included two stages: 160 °C for 1 hour, 180 °C for 2 hours.

Table 1 summarizes the comparative characteristics of influence exerted by various mineralization techniques on the results of determining Cu and Fe in oil products. Data comparison reveals that the created mineralization parameters allowed to obtain identical information on Fe quantity both at complete and incomplete samples mineralization. Cu content determined in the samples after extraction varies from 62 to 87% of the content obtained after complete mineralization. It can be related to low Cu concentrations in oil products, much lower than Fe concentrations; or it can be related to peculiarities which extraction of this element has.

In relation to that we considered a possibility to apply autoclave sample preparation or preparation in a microwave mineralizer to perform atomic-emission analysis of toxic elements.

The greatest sample volume was used in complete mineralization and it led to relatively low concentrations of an analyzed element in a mineralized solution. This problem can be solved either via mineralizing agent concentrating, or via application of analysis techniques and devices with low detection limits.

Choice of a wave length, sample feeding speed, spraying speed, data acquisition regime, as well as application of an ultra-sound sprayer instead of a pneumatic one allow to obtain a considerable growth in elements detection sensitivity.

Table 1

Cu and Fe content in oil products after different sample preparation techniques, mg/kg

Sample	Element	Mineralization regime		
		autoclave	microwave	extraction
Sunflower-seed oil	Cu	0,26 ± 0,04	0,19 ± 0,01	0,16 ± 0,02
	Fe	3,37 ± 0,05	2,29 ± 0,16	3,26 ± 0,39
Margarine	Cu	0,30 ± 0,02	0,41 ± 0,01	0,26 ± 0,04
	Fe	4,10 ± 0,56	4,40 ± 0,5	4,16 ± 0,37
Mayonnaise	Cu	0,26 ± 0,03	0,38 ± 0,04	–
	Fe	2,83 ± 0,05	3,56 ± 0,21	–
Sunflower seeds	Cu	21,86 ± 0,09	21,22 ± 0,55	–
	Fe	50,45 ± 0,19	52,80 ± 1,98	–

To obtain lower detection limits of an atomic-emission spectrometer, we used the following device parameters:

– generator capacity was 1000 – 1100 Wt;
– plasma gas flow rate was 12 l/min;
– gas flow rate in a sheath was 0.2 l/min;
– assist gas rate was 0 l/min;
– sprayer was 0.8 l/min at 2.8 bar;
– sample feeding speed, l/min, was 0.84 l/min;
– photomultiplier amplification was 100.

Measurements were performed at the following wave lengths, nm: Pb – 220.353; As – 193,.695; Cd – 228.802; Hg – 194.163; Cu – 324.754; Fe – 259.940; Ni – 221.647.

As a rule, detection limits for mineralized samples are much higher than for water solutions which is related to a matrix influence exerted by a mineralizing agent [4, 5]. Basic noises occur in plasma [9]. Changes occurring in a spraying system or a sample feeding system also contribute considerably into matrix noises. When acid concentrations or dissolved substance contents vary it leads to changes in spraying efficiency and, consequently, to changes in sensitivity. It is noted in the paper [8] that perchloric acid or hydrochloric acid are the best analytical media for atomic-emission measuring. However, food products mineralization or biological substrates mineralization is usually performed with nitric acid with its final concentration in a mineralized solution being equal to 25–30 %. It is also stated in the paper, that growth in nitric acid concentration to 30% results in 30% decrease in Mg and Al emission signal intensity in comparison with 5%-concentrated nitric acid.

We determined detection limits for each examined elements via its tenfold measuring in the control solution.

A conventional way to introduce a solution into inductively bound plasma is to apply a pneumatic sprayer. An ultra-sound sprayer allows to obtain significantly lower detection limits for a spectrometer. A liquid sample is pumped into a piezoelectric detector where it is transformed into a dense thick spray. Gas flow in a sprayer takes this spray through a heating tube where evaporation takes place and the liquid is further condensed with a thermoelectric cooler and is taken out via drainage. As a result, a dry highly concentrated spray is in a sprayer and it is sprayed in plasma. It allows to get 5-10 times better elements detection limits.

Detection limits for Pb and As were obtained with the use of an ultrasound sprayer; for Cu, Fe, Ni, and Cd, with a pneumatic sprayer.

Table 2 contains data on an approximate content of Pb, As, Cu, Cd, Fe, Ni, and Hg, in solutions after complete mineralization of samples containing toxic elements at the level set forth in the regulations, at a device detection level, and the obtained elements detection limits.

As we can see from Table 2, detection limits obtained under real life conditions differ from those declared by a manufacturer. Spectral and matrix influences which occurred when samples with a complicated structure were analyzed led to substantial rise of determined contents bottom boundary and made it more difficult to determine elements correctly in complex biological samples. Difference for Cu amounted to 2.45; for As and Cd, to 4.6-4.8. The greatest discrepancy between the measured detection limit and a declared one was revealed for Pb, and it makes it obvious that a device parameters need to be adjusted in case one performs separate measuring of this element.

If we compare device detection limits with a pneumatic sprayer for Hg and permissible Hg content in a solution (Table 2), we can see that to it is necessary to apply hydride generation to detect this element.

The technique is based on Hg recovery with Na borohydride as per reaction scheme

$$Hg^{2+} + BH_4^- + H^+ \rightarrow B_2H_6 + H_2 + Hg.$$

B_2H_6 is then hydrolyzed into boric acid.

Research on influence exerted by different acids on efficiency of determining hydride-forming elements revealed that 2M hydrochloric acid solution was the most suitable medium for Hg detecting [2, 3, 15].

When autoclave mineralization is performed, an analyte is in nitric acid. Its further transformation into a muriate solution is quite complicated as elimination of nitric acid remains under thermal treatment can cause Hg losses. In relation to that we studied a possibility to detect Hg in nitric acid solutions.

Table 2

Toxic elements content in a mineralized solution after acid extraction and detection limits

Element	Content in a mineralized solution*, µg/dm^3	Device detection limit, µg/dm^3			Detection limit, µg/dm^3
		Sprayer		Hydride add-on device	
		pneumatic	ultrasound		
Pb	4 – 40	1,5	0,2	–	1,91
As	4–40	1,5	0,2	0,2	0,92
Cu	4–16	0,2	0,05	–	0,49
Cd	1–20	0,15	0,02	–	0,72
Fe	60–200	0,2	0,05	–	5,11
Ni	28	0,3	0,06	–	1,78
Hg	0,1–12	0,4	–	0,03	–

Note: * sample weight is equal to 1 g and a mineralizing agent volume is equal to 25 ml.

We used 0.6% borohydride solution in 0.05 M NaOH as a borohydride solution.

Figure 2 shows dependence between energy emission (signal intensity) and Hg content in standard samples in 3н HCl and 3н HNO_3 medium. As we can see from Figure 2, Hg emission energy value in nitric acid solution is insignificantly higher than emission of this element in hydrochloric acid solution and it proves that it is quite possible to use nitric acid solutions directly for introducing into a hydride add-on device.

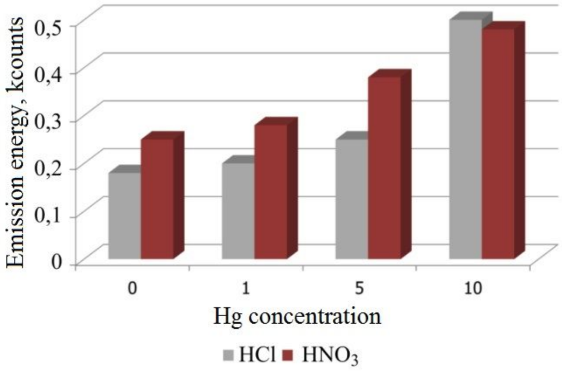

Figure 2. Emission energy dependence on Hg content in standard samples in 3н HCl and 3 н HNO_3 medium

Precision and correctness parameters were determined during metrological certification of the technique. Precision parameters (repeatability and laboratory reproducibility) were determined in conformity with STB ISO 5725-2, cl. 7. To assess correctness parameter, we used the results of checking significance of discrepancy from recovery rate unit (STB ISO 5725-4, cl. 4). Recovery rate for toxic elements as per this technique was studied in laboratories under repeatability conditions via analyzing samples with the known toxic elements admixture.

Metrologic calculations revealed that standard deviation in the repeatability for the examined toxic elements with the use of the created conditions amounts to 1-8%; standard deviation in the reproducibility for these elements lies within 2-22% range.

We detected dependence of maximum extended uncertainty (*U*) on concentrations of toxic elements in oil raw materials and oil products.

Maximum extended uncertainty within the range of the measured Pb, Cd, Hg, Cu, Fe, and Ni concentrations in oil raw materials and oil products is within 4-15%; it amounts to 33% in case of Pb.

Conclusions. So, basing on the results of the conducted research we worked out a high precision technique for determining low concentrations of toxic elements with the use of atomic-emission spectrometry.

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