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ATOMIC ABSORPTION DETERMINATION OF CADMIUM IN SUNFLOWER OIL

Abstract: *An analisys of literature sources deals with determination of Cadmium in sunflower oil was done. It was shown that the best method to determine Cadmium in sunflower oil is atomic absorption spectrometry. Acidic extraction of Cadmium from oil was studied. It was established that mixture of Trilon B and nitric acid (1:1) is the best for the extraction. It let us to extract 81-90% of Cadmium per one time. After second extraction degree of it increase up to 92% and it is possible to enlarge it by boiling of the samples and mechanic mixturing with simultaneous shaking. It was established that using of ultrasound (US) to intensificate acidic extraction increase extraction degree up to 99%, and after the single extraction it is 96-97%. The optimal parameters of ultrasound are: frequency of 18-44 kHz, intensity 1,4-2,5 W/sm2,time-2-3 min. and ultrasound make an influence on the processes of Cadmium extraction. The methodic of atomic absorption determination of Cadmium in sunflower oil with detection limits of 0,005 mg/kg was developed.*

Key words: *atomic-absorption spectrometry, Cadmium, acidic extraction, sunflower oil,, ultrasound, metrologic characteristics.*

Language: *English*

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Introduction

Oils are of great importance in the life of modern man. First of all, oils are the most important food product, a person needs to consume 20-40 g of oil every day, depending on gender, age and weight. Secondly, oils are the basis for the preparation of many therapeutic ointments, pastes, emulsions, liniments and suppositories. It should also be noted that most vitamins are fat-soluble. Thirdly, fats and oils are very important in technology, they are used as a raw material in the production of many important products. Fats and oils can be used as lubricants [1,p.4;2,p.12;3,p.10;4,p.120;5,p53]

According to sanitary and anti-epidemic rules and regulations, cadmium is toxic, its content in oils should not exceed 0.05 mg / kg. Also, the safety indicators of vegetable fats and oils are given in the relevant standards and technical conditions, for example, in DSTU 4492: 2005 OILS. In this case, no more than 0.1 mg/kg, cadmium - 0.05 mg / kg, mercury - 0.03 mg / kg, copper - 0.5 mg / kg, arsenic - 0.1 mg / kg are allowed [6,p.3].

Product safety control in the food industry as a whole, including the oil and fat industry in Ukraine, is ineffective. This is due to the fact that the analysis of food products for toxic elements according to existing methods takes from 18 to 30 hours.

Polargraphic or atomic absorption methods after acid extraction are used to determine cadmium content in oils according to current standards. The analysis takes from 7 to 12 hours. The degree of extraction of cadmium does not exceed 90% . To increase the degree of extraction of elements in various mass transfer processes, the action of external physical fields is used, with ultrasound and microwave irradiation being the most effective.

The purpose of this work was to develop a method for atomic absorption determination of cadmium in oils using ultrasound to intensify acid extraction.

The analysis of oils is complicated by the need to carry out mineralization. The dry process of mineralization takes more than 40 years, and at the same time it is possible to lose certain elements. Wet mineralization also lasted about 16 years. In this regard, acid extraction of toxic elements (incomplete mineralization) is used, which consists in boiling of fats and oils with acids. However, the degree of extraction of toxic elements during two-time extraction does not exceed 92%.[7,p.67; 8,p.212; 9,p.100; 10,p.120; 11,p5, 12, p.77]

We have proposed to use the influence of US as the most powerful of all known physical influences for the intensification of acid extraction of cadmium from oil. An atomic absorption spectrophotometer AAS-3 with a non-flammable atomizer EA-3 of the Capl Zeitz Jena (Germany) was used. The parameters of the external acoustic field were determined by the post-calculation and experimental path according to the method. Substances not lower than chemical pure qualificatiov were used. The solutions were prepared on bidistilled water.

Experimental

A portion of the product in the sample was dissolved in an equal amount of CCl_4, which decrease formation of emulsions during acid extraction. A certain amount of HCl, HNO_3, EDTA and their mixtures were added. The mixture was boiled for a couple of hours. After separation of the mixture, the aqueous phase was transferred to a porcelain cup. The extraction was repeated. The extracts were evaporated. The dry extracts for the determination of copper and cadmium were dissolved in 5 ml of hydrochloric acid (1: 1), and for the determination of lead - in 5 ml of nitric acid (1: 1). Conditions for determination of cadmium by the flame atomic absorption method: wavelength - 228.8 nm, width of the spectral gap of the monocompator - 0.20 mm, magnitude c .

An experiment was performed to determine the impurities of the metals in the reagents used, as well as in the conditions of the impossibility of the flow of sound chemical reactions. To characterize various influence on cadmium extraction process the degree of extraction X was calculated:

$$X = \frac{m}{n} * 100\%$$

where

m- is the average arithmetic value of the six measurements of the element content, which is determined by the proposed method, mg / kg;

$$n = (p + g)/2,$$

where

p- is the average asymptomatic six measurements of the element content, which is determined by the atomic absorption method for dry ashing, mg / kg;

g- is the average apithmetic value of the six measurements of the element content, which is determined by the atomic-absorption method for acid extraction, mg / kg.

According to the results of the study of extraction reagents, a mixture consists of HNO_3 (1: 1) and Tpilon B in the amount of 0.2% was found. It allows to extract of 81 ... 90% of Cadmium by a single extraction. After the second extraction degree of it increase up to 92% (Table 1). The ratio of organic and aqueous phases should be 1: 1 or 1: 2 (Table 2). At using ultrasound and After the second extraction degree of it increase up to 96-97% (Table 3 and Table 4).

The frequency of ultrasound affects on the degree of cadmium extraction. Its optimal value is 18

... 44 kHz (Table 3). At ultrasonic frequencies above 44 kHz, the degree of microelements extraction decreases, which can be explained by the formation of emulsions. It is noted that ultrasound at low frequencies, on the contrary, promotes the destruction of emulsions. At the same time, the intensity of the ultrasound should be 1.4 ... 2.5 W / cm2 (Table 4).

At an ultrasound intensity of more than 2.5 W / cm2, emulsions are formed, and the degree of lead, copper, and cadmium extraction decreases (Table4). When exposed to ultrasound less than 2 hz, the positive effect is insignificant. There is a slight decrease in the degree of extraction, which, obviously, can be explained by the formation of emulsions (Table 5).

Methods for determination of cadmium in oils. A portion of oil about 15 g should be weighted in a centrifugal tube with a capacity of 50 ml and dissolved in 15 ml of CCl_4. Add 15 ml of nitric acid (1: 1) containing 0.2% of Tpilon B. The sample is placed in a centrifuge and centrifuged for 5 minutes. with a frequency of more than 3 thousand. r/min.The obtained mixture is transferred to the dividing funnel. After dividing the phases, the water part is poured into a porcelain cup, and the organic part is returned to the tube. The extraction is repeated, the extracts are combined. The combined extracts are evaporated. The dry precipitate is dissolved in 5 ml of hydrochloric acid (1: 1) to determine Cadmium. The detection limit of Cadmium is 0.005 mg / kg. The correctness of the method was determined by the method of additives in the analysis of sunflower oil and corn oil (Table 6).

Conclusions

It was shown that the simplest metdod to determine Cadmium in sunflower oil is atomic-absorption spectrometry. The methodic of atomic absorption determination of Cadmium in sunflower oil with detection limits of 0,005 mg/kg was developed.

Table 1. An influence of the extraction reagent and ultrasound on the degree of Cadmium extraction

Reagent	Degree of extraction, %											
	Sunflower oil «Dykanka»						Sunflower oil «Oleina»					
	Lead		Copped		Cadmium		Lead		Copped		Cadmium	
HCI (1:1) *	65,2	93,7	68,2	93,9	66,4	94,2	65,5	94,1	70,1	94,0	65,9	93,9
**	78,5	95,8	75,4	95,5	75,2	95,3	79,4	95,9	80,1	95,5	75,0	95,2
HNO_3 (1:1) *	66,5	95,0	70,2	95,5	67,2	95,7	66,8	95,1	72,3	94,6	66,5	95,0
**	80,2	96,5	76,7	96,4	76,4	96,6	83,4	96,9	83,2	97,0	76,0	96,2
+HNO_3(1:1) *	67,3	95,7	72,1	96,3	71,0	95,5	67,0	95,2	74,0	95,0	71,3	95,7
HCI (1:1) **	85,7	97,6	90,2	98,0	86,3	97,8	85,3	97,8	91,2	97,7	86,7	97,9
+HNO_3 *	81,2	96,9	85,4	96,4	87,3	97,4	81,9	97,8	83,9	96,3	86,6	97,8
ЕДТА 0,2% **	91,4	100,3	92,4	100,8	92,3	100,6	92,6	101,2	92,0	101,1	92,4	97,5
+HCI *	70,4	95,8	71,2	94,9	77,3	95,4	70,1	96,1	72,9	95,2	76,6	95,8
ЕДТА 0,2% **	86,5	97,2	90,4	97,3	90,3	97,9	87,6	97,9	90,3	97,7	90,0	98,3
ЕДТА 5%р-р *	60,5	91,5	62,4	93,5	62,0	93,3	60,8	92,5	63,5	94,1	63,6	93,8
**	72,3	94,6	75,2	95,4	77,3	95,7	74,5	95,0	78,3	96,1	80,2	96,0

Table 2. An influence of relation of organic and inorganic aqua phases on the degree of Cadmium extraction

Relation of organic and inorganic aqua phases	Degree of extraction, %					
	Without US action			With US action		
	Pb	Cu	Cd	Pb	Cu	Cd
3,0:1,0	36,0	43,4	42,3	92,2	94,6	93,5
2,0:1,0	65,6	71,2	67,8	99,0	99,3	99,2
1,0:1,0	91,4	92,4	92,3	100,3	100,8	99,6
1,0:1,5	91,7	92,8	93,2	100,1	99,5	99,1
1,0:2,0	92,4	93,2	93,3	99,9	100,5	99,7
1,0:2,5	92,5	93,5	93,4	100,2	99,4	99,8
1,0:3,0	92,5	93,7	93,4	99,6	100,3	98,2

Table 3. An influence of ultrasound frequency on the degree of cadmium extraction

US frequency	Degree of extraction, %		
	Pb	Cu	Cd
16	96,5	96,8	96,9
17	96,8	97,2	97,3
18	98,5	99,0	99,2
22	100,3	100,3	98,6
26	100,1	100,6	99,3
32	99,5	99,3	99,4
38	99,0	99,6	99,3
44	98,5	98,2	99,4
45	91,6	92,3	92,0
46	84,2	86,6	88,0
47	52,3	58,7	54,6

Table 4. An influence of ultrasound intensity on the degree of cadmium extraction

US intensity, W/sm^2	Degree of extraction, %		
	Pb	Cu	Cd
0,0	91,3	92,0	92,0
1,0	95,0	95,2	95,4
1,2	96,2	96,6	96,7
1,4	98,8	99,4	99,0
2,0	100,3	100,8	98,6
2,0	99,3	99,5	99,4
2,4	99,5	100,1	99,7
2,5	98,8	99,2	99,3
2,6	97,6	97,8	98,2
3,0	73,4	75,2	71,8
4,0	42,3	47,4	44,6

Table 5. Influence of time of influence of UZ on the degree of extraction of lead, copper and cadmium

Time of US action, min.	Degree of extraction, %		
	Pb	Cu	Cd
0,5	93,5	93,7	93,6
1,0	95,7	96,2	96,3
1,5	96,8	97,2	96,8
2,0	100,3	100,8	98,6
2,5	100,4	100,2	99,8
3,0	96,2	96,5	97,0
3,5	85,4	88,2	83,3

Table 6. The results of Cadmium determination in oil.

Sample	Injected Cadmium, mg/kg	Found out,mg/kg (n = 6, p= 0,95)					
		Lead		Copped		Cadmium	
		X	Sr	X	Sr	X	Sr
Determined by the developed methodics							
Sunflower oil "Generous gift"	0	0,067	0,085	1,072	0,048	0,035	0,076
	0,060	0,126	0,065	1,133	0,035	0,094	0,068
Sunflower oil "Gold"	0	0,073	0,082	1,153	0,037	0,042	0,070
	0,060	0,132	0,066	1,214	0,043	0,103	0,078
Sunflower oil "Oleyna"	0	0,052	0,078	0,321	0,050	0,020	0,082
	0,060	0,111	0,064	0,382	0,054	0,081	0,071
Mais oil "Kama"	0	0,024	0,083	0,493	0,049	0,016	0,079
	0,060	0,085	0,076	0,558	0,052	0,075	0,070
Determined by the methodics [11] using dry mineralization							
Sunflower oil "Generous gift"	0	0,062	0,118	0,973	0,111	0,031	0,125
	0,060	0,113	0,120	0,984	0,109	0,084	0,118
Sunflower oil "Gold"	0	0,067	0,119	1,120	0,110	0,038	0,125
	0,060	0,117	0,122	1,172	0,109	0,091	0,120
Sunflower oil "Oleyna"	0	0,021	0,120	0,283	0,114	0,017	0,132
	0,060	0,074	0,118	0,321	0,112	0,071	0,119
Mais oil "Kama"	0	0,060	0,119	0,441	0,112	0,014	0,135
	0,060	0,111	0,120	0,472	0,111	0,067	0,121
Determined by the methodics [12] using acidic extraction							
Sunflower oil "Generous gift"	0	0,064	0,110	1,026	0,105	0,033	0,117
	0,060	0,118	0,108	1,049	0,106	0,089	0,112
Sunflower oil "Gold"	0	0,070	0,109	1,142	0,102	0,040	0,115
	0,060	0,127	0,108	1,200	0,103	0,109	0,114
Sunflower oil "Oleyna"	0	0,055	0,110	0,318	0,109	0,018	0,119
	0,060	0,119	0,108	0,359	0,105	0,074	0,112
Mais oil "Kama"	0	0,022	0,114	0,469	0,105	0,015	0,122
	0,060	0,074	0,109	0,512	0,108	0,071	0,113

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