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Determination of silver in cereals by electrothermal atomic absorption spectrometry

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A new procedure of silver determination in cereals by electrothermal atomic absorption spectrometry is presented. After the destruction and dissolution of the cereals sample, silver was extracted by diphenylthiocarbamate in methyl*iso*butyl ketone. The precision of the procedure, as a relative standard deviation, is from 1.8 to 11.0% for the range up to 0.1 $\mu g\ g^{-1}$ silver in cereal. The limit of detection of silver for this method is 0.002 $\mu g\ g^{-1}$. The results of determination of different cereal samples from the Skopje region, Macedonia, are given.

Keywords: silver determination, cereals, electrothermal atomic absorption spectrometry

Contrary to the elements which are normally present in food such as Fe, Zn, Ca, Mg, K, Na, Mn, Co, Cr, which are necessary for the unfolding of particular functions in the organisms, silver is a potential contaminant of food, without any major significance in physiological processes in human organism. Thus, the concentrations of silver that may appear in food are very low (from 0.002 to 0.07 $\mu g\ g^{-1}$) (1).

Among the works on silver determination in various types of food reported in the literature, different methods and techniques are presented, such as flame atomic absorption spectrometry – AAS (2, 3), electrothermal atomic absorption spectrometry – – ETAAS (4), spectrometry with inductively coupled plasma (5), neutron activation analysis (6) and others. Determination of silver is carried out directly from the solutions of the samples or after extraction of silver (1, 7, 8).

In this work, a new procedure for silver determination in cereals by electrothermal atomic absorption spectrometry is presented. After the destruction and dissolution of the sample, silver was extracted by diphenylthiocarbamate in methyl*iso*butylketone (MIBK).

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EXPERIMENTAL

Instrumental

Perkin-Elmer Models 303 and 5000 atomic absorption spectrophotometers equipped with deuterium background corrector, HGA–400 graphite furnace and Model 056 strip chart recorder were used. A silver hollow cathode lamp was used as source. Optimal conditions for silver determination (temperature and time of drying, charring, atomizing and cleaning) are given in Table I.

Reagents and samples

All reagents and standard substances were of analytical grade. Stock solution of silver was prepared by dissolving $AgNO_3$ in redistilled water. The mass concentration of silver was 1000 μg dm^{-3}, and from this solution the other dilutions were prepared.

Samples of different types of cereals (wheat, corn, barley) and wheat and rye flour were collected from the Skopje area, Macedonia.

Table I. Instrumental parameters for silver determination by electrothermal atomic absorption spectrometry

Wavelength	328.1 nm	Lamp current	10 mA
Spectral slit	0.7 nm	Background correction	D_2 lamp
Calibration mode	Peak height	Gas	Argon
	Temperature (°C)	Time (s)	Ramp time (s)
Drying	80	20	2
Charring	400	20	1
Atomizing	1600	5	0
Cleaning	2700	3	

Procedure

10 g of milled cereals was transferred to a porcelain crucible and heated in a muffle furnace at a temperature of 150 °C for 30 minutes, at 250 °C for 1 hour and at 550 °C for 8 hours. The obtained mineral residue, after cooling at room temperature, was dissolved in 10 cm^3 of 0.1 mol dm^{-3} HCl. This solution was transferred into a separatory funnel, and 1.5 cm^3 of diphenylthiocarbamate solution (1%) and 5 cm^3 of MIBK were added. The mixture was shaken for 5 minutes, the organic layer was filtered off and 20 mm^3 of this solution was introduced into a graphite furnace with Eppendorff pipette.

RESULTS AND DISCUSSION

There are few data about the matrix interferences during silver determination in food by ETAAS. Therefore, Jackson *et al.* (1) show that, during the determination of silver by flame AAS, the presence of Ca and Cu in concentrations higher than 2.8 mg cm^{-3} and 0.035 mg cm^{-3}, respectively, lead to an increase of silver absorbance. In contrast, the presence of Fe and Na in concentrations higher than 0.35 and 35 mg cm^{-3}, respectively, decrease silver absorbance. Our previous investigations (9) have shown a high negative interference on silver absorbance in the presence of Fe, Ca, Mg and Al.

To avoid these interferences, on the one hand, and because of very low concentrations of silver in cereals, on the other, it is necessary to separate and concentrate silver from the samples. There are a few papers in the literature where extraction is suggested for silver determination in food samples. Thus, Kacimi *et al.* (10) applied ditizone in MIKB, Subramanian *et al.* (11) ammonium pyrrolidone dithiocarbamate. In the determination of silver, Jackson *et al.* (1) suggested using diethylammonium diethyldithiocarbamate in MIBK for extraction of silver.

In our investigations we applied diphenylthiocarbamate which is used in silver extraction from geological samples, and it was shown that the best extraction medium is n-butyl acetate (12). We found that, for silver extraction with diphenylthiocarbamate from cereal samples, very good results in the recovery were obtained when MIBK was used as extraction medium. In the case of the destruction of cereal samples, it is possible to dissolve the mineral residue with different acids, usually HCl or HNO_3. To see which acid is better for the suggested extraction, a destructed sample of wheat flour was prepared and dissolved with HCl and HNO_3 solutions of different concentrations, and after that the suggested extraction was applied. The results are given in Table II. They show that higher absorbance was obtained with 1 mol cm^{-3} solution of HCl and HNO_3, but better results were obtained with HCl.

Table II. Values of silver absorbance in the organic phase in dependence on the concentration of HCl and HNO3

Concentration of HCl or HNO_3 (mol dm^{-3})	Absorbance in the presence of	
	HCl	HNO_3
0.0	0.3479	0.3479
0.1	0.3979	0.3565
0.2	0.3979	0.3670
0.5	0.3979	0.3809
1.0	0.4789	0.3851
2.0	0.4589	0.3732
5.0	0.4295	0.3410

Also, by determining the maximum value of the absorbance of silver in the organic phase, the volume ratio of the organic and inorganic phases was found to be 1:2.

To verify this procedure, some cereals were dissolved, and after the extraction, silver was determined by ETAAS. Some of these samples were prepared with standard additions of silver and treated in the same manner. The results are given in Table III. It can be seen that the results obtained by standard addition methods are satisfactory (relative standard deviation ranges from 1.8 to 11.0% and the recovery from 92.9 to 99.1 %).

Table III. Results of silver determination in wheat samples by a standard addition method (results are given in $\mu g\ g^{-1}$)

Sample No.	Ag_{added}	$Ag_{calcd.}$	Ag_{found}	RSD (%)	R (%)
1	–	–	0.016	–	–
2	0.012	0.028	0.026	8.82	92.86
3	0.050	0.068	0.066	10.98	97.06
4	0.075	0.093	0.091	1.78	97.85
5	0.100	0.116	0.115	1.75	99.14

Applying proposed procedure silver was determined in different cereals (wheat, corn, barley) from the Skopje region, Macedonia. It was found that the mass concentrations of silver in these samples range from 0.016 to 0.036 $\mu g\ g^{-1}$.

A calibration curve was constructed by a similar treatment of wheat samples by adding solution containing 0 to 0.1 $\mu g\ g^{-1}$ silver. Relative standard deviations are from 1.8 to 11.0% for this range of silver concentrations. The detection limit of silver, as a triple standard deviation of a blank sample, was found to be 0.002 $\mu g\ g^{-1}$.

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S A Ž E T A K

Određivanje srebra u žitaricama elektrotermičkom atomsko apsorpcijskom spektrometrijom

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Prikazan je novi postupak određivanja srebra u žitaricama elektrotermičkom atomsko apsorpcijskom spektrometrijom. Nakon razaranja i otapanja uzorka žitarice, srebro je ekstrahirano difeniltiokarbamatom u metil*izo*butil ketonu. Preciznost postupka izražena kao relativna standardna devijacija iznosi 1,8 do 11,0% za koncentracijsko područje srebra u žitaricama do 0,1 $\mu g\ g^{-1}$. Granica detekcije je 0,002 $\mu g\ g^{-1}$. Prikazani su rezultati analiza različitih uzoraka žitarica skopske regije (Makedonija).

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