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Determination of chromium in cereals by electrothermal atomic absorption spectrometry

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A new method for chromium determination in cereals by electrothermal atomic absorption spectrometry is given. After dry decomposition and dissolution of the sample, chromium was extracted with diphenylcarbazide in *iso*butanol. The relative standard deviation for the concentration range of chromium in cereals from 0 to 0.1 μg g^{-1} is from 1.3 to 7.8%. The limit of chromium detection in cereals by this method is 0.002 μg g^{-1}.

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Chromium belongs to the group of essential elements for living organisms. It is known that chromium has several roles in the human organism: chromium is a co-factor of insulin, and it is involved in the metabolism of lipids, which has been associated with the prevention of atherosclerosis and other cardiovascular diseases. Cr(VI), in contrast to Cr(III), is very toxic. The largest sources of biologically active chromium are liver and cheese and, also unrefined sugar.

Consequently, it is very important to determine the concentration of chromium, especially in food, that may be introduced into the organism. Many methods and techniques are applied to chromium determination in food: spectrometry (1), flame atomic absorption spectrometry – FAAS (2 – 8), electrothermal atomic absorption spectrometry – ETAAS (9 – 13), spectrometry with inductively coupled plasma – ICP (4), *etc.*

In this work, a new method is presented for chromium determination in cereals, by ETAAS, with previous extraction of chromium with diphenylcarbazide in *iso*butanol.

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EXPERIMENTAL

Instrumental

A Perkin-Elmer Model 703 and 5000 atomic absorption spectrometers, equipped with a deuterium background corrector, HGA–400 graphite furnace, and Model 056 strip chart recorder were used. A chromium hollow cathode lamp was used as a source. Optimal conditions for chromium determination by ETAAS (temperature and time of drying, charing, atomizing, cleaning) are given in Table I.

Reagents and samples

All reagents and standards were of analytical grade. Chromium stock solution was prepared by dissolving Cr metal with 10 mL concentrated HCl and diluted with bidistilled water. Mass concentration of chromium was 1000 μg L^{-1} and from this solution other dilutions were prepared.

The samples of different types of cereals (wheat, corn, barley) were collected from Skopje region, Macedonia.

Table I. Instrumental parameters for chromium determination by ETAAS

Wavelength:	357.9 nm	Calibration mode:	peak height
Slit width:	0.7 nm	Background correction:	D_2-lamp
Lamp current:	10 mA	Gas:	argon

	Drying	Charing	Atomizing	Cleaning
Temperature (°C):	80	800	2300	2700
Time (s):	30	20	5	3
Ramp time (s):	2	1	0	

Procedure

10 g finely milled cereal was transferred to a porcelain crucible and it was 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 mL concentrated H_2SO_4. Then, 0.5 mL of 0.1 mol L^{-1} $KMnO_4$ were added and the solution was left on a hot plate at a temperature of 70 – 80 °C. After cooling, excess of $KMnO_4$ was eliminated by adding a few drops of 20% aqueous solution of hydroxylamine hydrochloride. After that, the solution was transferred to a separatory funnel and 2.5 mL of 0.1% solution of diphenylcarbazide and 10 mL saturated solution of NaCl were added. The mixture was shaken for one minute, 5 mL of *iso*butanol were added and this solution was shaken for 2 minutes. The organic layer was separated and a volume of 20 μL of this solution was introduced into a graphite furnace and chromium was determined.

RESULTS AND DISCUSSION

There are few data about chromium determination in cereal samples by ETAAS (9 – 13) but there is no information on the interferences with chromium absorbance. Elements of higher concentration in cereals, and possible interferents, are usually Ca, Mg, Na and K. Therefore, possible interferences of these elements with chromium determination were investigated. For this purpose, a series of samples with a constant concentration of chromium and varying concentrations of Ca, Mg, Na and K were prepared and chromium absorbance was determined by ETAAS. The mass ratios of Cr and Ca, Mg, Na and K were in the same range as in the cereal samples, and varied for Cr and Ca and K from 1:0 to 1:2000, and for Cr and Mg and Na from 1:0 to 1:200. The results of chromium absorbance in these samples are given in Table II.

Table II. Influence of Ca, Mg, Na and K on chromium absorbance (mass of chromium is 1 ng in 20 μL)

Sample No.	Mass ratio $m_{Cr} : m_{Me}$	Absorbance			
		Mg	K	Ca	Na
1	1 : 0	0.3335	0.3335	0.3335	0.3335
2	1 : 100	–	–	0.3335	0.3335
3	1 : 200	0.3335	0.3335	0.3261	0.3298
4	1 : 500	0.3298	0.3290	0.3261	0.3224
5	1 : 1000	0.3290	0.3290	–	–
6	1 : 2000	0.3272	0.3290	–	–

As it can be seen from the Table II, these elements interfere with chromium absorbance when the mass ratio is up to 1:200 for Ca and Na, and 1:500 for Mg and K. Because of these influences, on the one hand, and because of the very low concentration of chromium in the cereals, on the other, it was necessary, before determination by ETAAS, to separate and concentrate chromium from the matrix.

There are a few papers in the literature where extraction is suggested for chromium determination in food samples by AAS. Therefore, Jackson *et al.* (5) applied acetylacetone in MIBK for chromium determination by flame AAS. Baucelles *et al.* (8) used direct extraction of chromium by MIBK from acidic solutions of food samples. On the other hand, Cary and Allaway (3, 4) used APDC and 2,4-pentadione in chloroform in chromium determination in wheat samples.

Literature data for chromium determination by spectrometry (especially for water analysis), show that, in most cases, complexation with diphenylcarbazide, is applied. In these analyses some authors suggest extraction of this complex and spectrometric determination of chromium in MIBK (14) or in pentanol, n-butanol and cyclohexanol (15), or *iso*pentanol (16). In our investigations, we applied diphenylcarbazide for extraction of chromium from the solution obtained after dry decomposition and dissolution of mineralized samples of different cereals. We applied different organic solvents. It was shown that very good results can be obtained by using *iso*butanol.

It was necessary to establish the optimal concentration of sulphuric acid and the volume of saturated solution of NaCl in the procedure of extraction. For this purpose, a series of solutions of constant chromium concentration and different H_2SO_4 concentrations (0 – 8 mol L^{-1}) and a series with different volumes of NaCl solution (0 – 15 mL) were prepared, and extraction was applied. The obtained absorbances of chromium after ETAAS measurements are given in Tables III and IV. As it can be seen from Tables III and IV, due to maximal value of absorbance, the optimal concentration of sulphuric acid is 2 mol L^{-1} and the optimal volume of saturated solution of NaCl is 10 mL.

Table III. Influence of H_2SO_4 concentration on chromium extraction

$c_{H_2SO_4}$ / mol L^{-1}	A
0.0	0.0000
0.4	0.0833
1.0	0.0850
2.0	0.0862
4.0	0.0757
8.0	0.0737

Table IV. Influence of the volume of saturated NaCl solution on chromium extraction

Volume of saturated NaCl solution / mL	A
0	0.0177
5	0.0615
10	0.0860
15	0.0860

To verify this method, some cereal samples were dissolved and, after extraction, chromium was determined by ETAAS. Some of the samples were prepared with standard additions of chromium standard solutions and treated in the same manner. The results of chromium determination are given in Table V. It can be seen that the results obtained by the standard addition method are satisfactory (recovery from 95 to 102%).

Also, in two wheat samples, chromium was determined by inductive coupled plasma spectrometry (ICP). A comparison of the results obtained by this determination and by the proposed method is given in Table VI. As it can be seen, the results obtained by these two methods are very similar.

The results of chromium determination in different types of cereals from the Skopje region, Macedonia, are given in Table VII.

A calibration curve was constructed by a similar treatment of wheat samples by adding 0 – 0.1 μg chromium per gram of sample material. The standard deviation in this

Table V. Results of chromium determination by ETAAS in a wheat sample by the standard addition method (the results are in μg g^{-1})

Sample No.	Cr_{added}	$Cr_{calculated}$	Cr_{found}	RSD (%)	Recovery
1	–	–	0.12	–	–
	0.10	0.22	0.21	7.8	95.4
2	–	–	0.14	–	–
	0.20	0.34	0.33	2.3	97.1
3	–	–	0.10	–	–
	0.30	0.40	0.38	2.5	95.0
4	–	–	0.08	–	–
	0.40	0.48	0.49	1.3	102.1

Table VI. Comparison of the proposed method with ICP

Sample	Proposed method (μg g^{-1} Cr)	ICP (μg g^{-1} Cr)
1	0.11	0.10
2	0.20	0.18

Table VII. The results of chromium determination by ETAAS in different cereals from the Skopje region, Macedonia

Cereal	Cr (μg g^{-1})
Wheat	0.10 – 0.24
Corn	0.09 – 0.12
Barley	0.10 – 0.13
Rye flour	0.020 – 0.028
Wheat flour	0.010 – 0.035

region amounts to 0.0007 – 0.0016 μg g^{-1}. The limit of detection (as 3 standard deviations of a blank sample) is 0.002 μg g^{-1}.

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REFERENCES

1. R. Masironi, *WHO Bull.* 40 (1968) 305.
2. J. Jirovec and J. Adam, *Hutn. Listy* 29 (1974) 739.
3. E. E. Cary and W. H. Allaway, *J. Agr. Food Chem.* 19 (1971) 1159.
4. E. E. Cary and O. E. Olson, *J. Assoc. Off. Anal. Chem.* 58 (1975) 433.
5. F. J. Jackson, J. I. Read, and B. E. Lucas, *Analyst* 105 (1980) 359.
6. X. Zang, *Zhonghua Yufangyixue Zazhi* 16 (1982) 177; ref. *Chem. Abstr.* 97 (1983) 143199k.
7. R. Farre and M. J. Lagarda, *J. Micronutr. Anal.* 2 (1986) 201.
8. M. Baucells, G. Lacort, M. Roura, R. Farre, and J. Lagarda, *Nahrung* 33 (1989) 225.
9. E. G. Zook, F. E. Greene, and E. R. Morris, *Cereal Chem.* 47 (1970) 720.
10. W. J. Garcia, C. W. Blessin, and G. E. Inglett, *ibid.* 51 (1974) 779.
11. W. J. Garcia, C. W. Blessin, and G. E. Inglett, *ibid.* 51 (1974) 788.
12. J. J. Christensen, P. A. Hearty, and R. M. Izatt, *J. Agr. Food Chem.* 24 (1976) 811.
13. N. J. Miller-Ihli and F. E. Greene, *J. AOAC Int.* 75 (1992) 354.
14. P. D. Blundy, *Analyst* 83 (1958) 555.
15. D. I. Ryabichkov, A. I. Lazarev, and V. I. Lazareva, *Zh. Anal. Khim.* 19 (1964) 1110.
16. Zh. Paik, G. Berd, D. Devo, D. Kleinberg, and G. Kauen, *Radiokhimiya khroma, mishyaka, kadmiya i galogenidov*, Mir, Moskva 1964, 20.

SAŽETAK

Određivanje kroma u žitaricama elektrotermičkom atomsko-apsorpcijskom spektrometrijom

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Predložena je nova metoda za određivanje kroma u žitaricama elektrotermičkom atomsko-apsorpcijskom spektrometrijom. Nakon suhe dekompozicije i otapanja uzorka krom je ekstrahiran s difenilkarbazidom u *izo*butanolu. Za koncentracijsko područje kroma u žitaricama od 0 do 0,1 μg g^{-1} procijenjena je relativna standardna devijacija od 1,3 do 7,8%. Granica detekcije kroma ovom metodom iznosi 0,002 μg g^{-1}.