

DETERMINATION OF LEAD IN CEREALS BY ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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A new method for lead determination in cereals by electrothermal atomic absorption spectrometry was given. After mineralization and dissolution of the samples, lead was extracted with sodium diethyldithiocarbamate in carbon tetrachloride. With this method it is possible to determine lead in cereals up to $0.0075 \mu\text{g g}^{-1}$. The relative standard deviation for the concentration region from 0.025 to $0.1 \mu\text{g g}^{-1}$ is from 1.42 to 12.05%.

Key words: lead determination, electrothermal atomic absorption spectrometry, cereals

INTRODUCTION

The presence of lead in plants and animals is particularly due to its relatively high natural abundance in soil, and partially to contamination by industry (smelteries of lead and zinc, production of batteries and dyes) and by traffic (vehicle exhausts). In the human body lead is accumulated in the bones, from which it is mobilized when changes in the organism occur, in which case it blocks the work of the enzymes which are taking part in the synthesis of hemoglobin [1]. Also, higher levels of lead in the body can cause other disorders such as disorders in heart functions, higher blood pressure, influence on CNS, etc. [2].

Because of the fact that lead can be absorbed into the body by consumption of lead-containing food-stuffs, it is a necessary to determine levels of lead in various types of food precisely and exactly. In the work reviewed in written studies many methods for lead determination in food are presented. Usually, a method of flame atomic absorption spectrometry (AAS) [3–5], electrothermal AAS [6–10], AAS with hydride system [11], spectrometry with inductively coupled plasma (ICP) [12] or amperometry [13] have been used. In this work, a method for lead determination in cereals by electrothermal atomic absorption spectrometry (ETAAS) with previous extraction of lead by sodium diethyldithiocarbamate in carbon tetrachloride is given.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer Models 703 and 5000 atomic absorption spectrophotometer equipped with a deuterium background corrector, HGA-400 graphite furnace and Model 056 strip chart recorder were used. A lead hollow cathode lamp was used as a source. Optimal instrumental conditions for lead determination (temperature and time) are: drying 120°C and 30 s; charring 550°C and 20 s; atomizing 2100°C and 5 s; cleaning 2700°C and 3 s.

Procedure

10 g milled cereals were transferred to a porcelain crucible and heated in a muffle furnace at a temperature of 150°C for 30 minutes, then at 250°C for an 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 1% (v/v) HNO_3 solution. Then, a 5 cm^3 of 50% solution of ammonium citrate was added and by the adding of a 20% solution of NaOH, the pH value was adjusted to about 11.5 (from 10.5 to 12.5). After that, 5 cm^3 of 5% KCN were added and the mixture was transferred to a separatory funnel. 5 cm^3 of 0.2% sodium diethyldithiocarbamate were added and the mixture was shaken for a minute. After 10 minutes, 5 cm^3 CCl_4 were added. The mixture was shaken for 1–2 minutes and after 10 minutes, the organic layer was filtered off and from this solution a volume of 20 mm^3 was introduced in the graphite furnace with an Eppendorf pipette, and lead was determined by ETAAS.

It is also necessary always to prepare the blank sample parallel with the cereals samples for the correction of the zero value.

RESULTS AND DISCUSSION

There are little data about the matrix interferences on lead determination in food by ETAAS. Therefore, Gherardi et al. [6] show that in the direct determination of lead in solution obtained by acid digestion, the highest problems are chemical interferences because of the presence of chlorides and phosphates of alkaline elements. This influence could not be eliminated even by background correction or by the method of standard additions. Kotani [14] found a high influence of chloride, especially in the presence of a high concentration of Mg.

Usually, the elements with a high concentration in the cereals, and the possible interferents, are Ca, Mg, Na and K. Therefore, the interferences of these elements on lead determination by ETAAS were investigated. For this purpose, a series of samples with a constant mass of lead and varying masses of Ca, Mg, Na and K were prepared and lead was determined by ETAAS. The mass ratios are in the same range as in the samples and varied for Pb and Mg and K from 1:0 to 1:2000, and for Pb and Ca and Na from 1:0 to 1:200. The results of lead determination by ETAAS in these samples are given in Table I.

Table I.

Influence of Ca, Mg, Na and K on lead absorbance (mass of lead is 1 ng in 20 mm³)

Sample No.	Mass ratios $m_{Pb} : m_M$	A b s o r b a n c e			
		Mg	K	Ca	Na
1	1 : 0	0.0381	0.0381	0.0381	0.0381
2	1 : 100	0.0381	0.0381	0.0381	0.0381
3	1 : 200	0.0381	0.0381	0.0414	0.0400
4	1 : 500	0.0414	0.0381	—	—
5	1 : 1000	0.0414	0.0400	—	—
6	1 : 2000	0.0420	0.0430	—	—

As can be seen from Table I, these elements interfere with the lead determination by changing the absorbance of lead, 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 lead in cereals, on the other, it was necessary, before the determination by ETAAS, to separate and concentrate lead from the matrix.

There are a few papers in the literature where extraction is suggested for lead determination in food samples by ETAAS. Therefore, Oelschalger et al. [15] applied dithizone in chloroform and Dabeka [7] suggested ammonium pyrrolidine dithiocarbamate in MIBK. Gherardi et al. used sodium diethyldithiocarbamate in methyl isobutylketone (MIBK) [6] for the preliminary extraction of lead after mineralization of the different food samples.

The written data showed that it is possible to extract lead with sodium diethyldithiocarbamate in CCl₄ in alkaline medium. Bode [16] found that by adding ammonium citrate and KCN, the extraction of lead with sodium diethyldithiocarbamate is the most effective in the pH range from 10.5 to 12.5, and that most of the other elements did not coextract. For cereal samples it is most important that the elements with a higher concentration did not coextract too, such as Ca, Mg, Na, K. For this reason, in our investigation this extraction was applied for the lead determination in different types of cereals. First, we prepare a series of samples with a constant concentration of lead and varying concentrations (the same ratios as it is shown in Table I) of Ca, Mg, Na and K and applied this procedure. We found no changes in lead absorbance. Certainly, this procedure, described in the experimental part, was adapted to lead determination in such type of samples (sample destruction and dissolution).

To verify this method, some cereal samples were mineralized and dissolved, and after the extraction, lead was determined by ETAAS. Some of these samples were prepared by standard addition of lead and treated in the same manner. The results of lead determination by ETAAS in these samples are given in Table II. It can be seen that the results obtained by the standard addition method are satisfactory (recovery is from 96.1 to 100.7%).

Table II.

Results from the lead determination in wheat samples by standard addition method (given results are in $\mu\text{g} \cdot \text{g}^{-1}$)

Sample No.	Pb _{added}	Pb _{calc.}	Pb _{found}	s_r (%)*	R %**
1	—	—	0.120	—	—
1'	0.025	0.145	0.142	12.05	97.9
2	—	—	0.080	—	—
2'	0.050	0.130	0.125	1.77	96.1
3	—	—	0.100	—	—
3'	0.075	0.0175	0.170	1.42	97.1
4	—	—	0.200	—	—
4'	0.100	0.300	0.302	5.50	100.7

* s_r — relative standard deviation and **R — recovery

Also, in 2 samples of wheat, lead was determined by inductively coupled plasma spectrometry (ICP). The results of a comparison of this determination and that given by the proposed method are shown in Table III. As can be seen from Table III the results obtained by these two methods are very similar.

Table III.

Comparison of proposed method
with ICP

Sample	Proposed method ($\mu\text{g/g Pb}$)	ICP ($\mu\text{g/g Pb}$)
1	0.08	0.09
2	0.20	0.19

The results from the lead determination in different types of cereals from the Skopje region, Macedonia, are given in Table IV. It can be seen that the lead content in wheat (from 15 samples) is from 0.08 to 0.36, in corn (for 10 samples) from 0.26 to 0.29, in barley (for 5 samples) from 0.01 to 0.013 and in one sample of rye flour about $0.02 \mu\text{g} \cdot \text{g}^{-1}$.

A calibration curve was constructed by similar treatment of samples of wheat by the adding of lead

Table IV.

The results of lead determination by ETAAS
in different cereals from Skopje region, Macedonia

Cereal	$w_{\text{Pb}}/\mu\text{g} \cdot \text{g}^{-1}$
Wheat	0.08 – 0.36
Corn	0.26 – 0.29
Barley	0.010 – 0.013
Rye flour	0.021

containing from 0 to $0.1 \mu\text{g} \cdot \text{g}^{-1}$ lead. The relative standard deviation in this region is from 1.42 to 12.05 %. The limit of detection (as 3 standard deviations of a blank sample) is $0.0075 \mu\text{g} \cdot \text{g}^{-1}$.

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ACKNOWLEDGMENT

We would like to thank Dr. P. Radošević from the Institute of Preventive Medicine, Belgrade, Yugoslavia, for the ICP analysis.

Резиме

ОПРЕДЕЛУВАЊЕ НА ОЛОВО ВО ЖИТАРИЦИ СО ЕЛЕКТРОТЕРМИЧКА АТОМСКА
АПСОРПЦИОНА СПЕКТРОМЕТРИЈА

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Клучни зборови: олово, житарици; атомска апсорпциона спектроскопија

Предложен е нов метод за определување на олово во житарици со електротермичка атомска апсорпциона спектрометрија. По растворувањето на обрасците, оловото се екстрахира со натриум диетилдитиокарбамат во јаглерод-

тетрахлорид. Границата на детекција на оловото во житарици со примена на овој метод е $0.0075 \mu\text{g} \cdot \text{g}^{-1}$. Релативната стандардна девијација за масениот удел на оловото до $0.1 \mu\text{g} \cdot \text{g}^{-1}$ се движи од 1.42 до 12.05%.