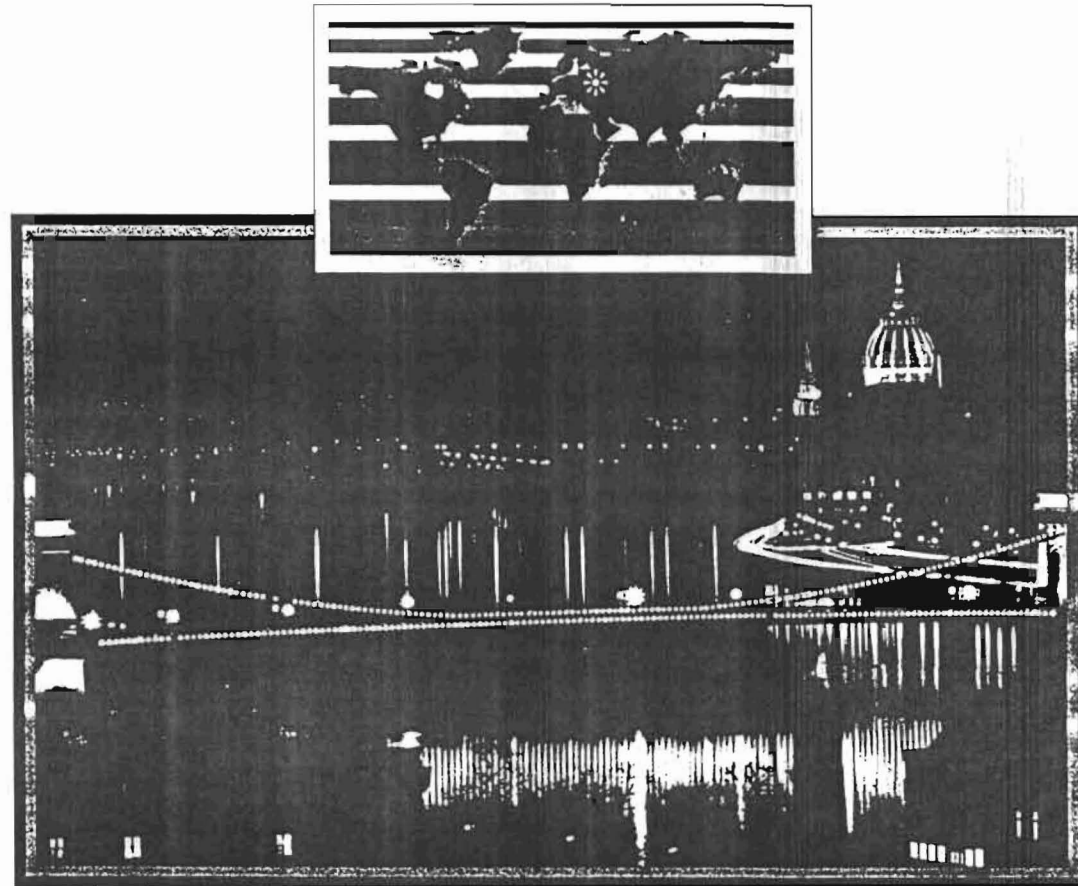


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SYMPOSIUM PROCEEDINGS

OCCURRENCE OF LEAD IN SOILS AND SOME BEVERAGE PRODUCTS IN THE AREA NEAR THE LEAD AND ZINC SMELTING PLANT IN TITOV VELES CITY, MACEDONIA

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Abstract

In this work an occurrence of lead in soils from different places near the lead and zinc smelting plant in Titov Veles city, Macedonia has been presented. The determination of lead was performed by atomic absorption spectrometry. The results pointed out that the content of lead in the surface soil samples is much higher than in those taken from deeper points. Also, the content of lead in some wine samples and food products (vegetables, fruits) has been determined. The content of lead in wine and food samples depends of the distance of place of production of grape or vegetable and fruit from the smelting factory.

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 (smelters 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 the changes in the organism occur in that case it blockades the work of the enzymes which are taking part in the synthesis of hemoglobin. Also, higher levels of lead in the body can cause some disorders as in heart functions, higher blood pressure, influence on central nervous system, etc.

Because of the fact that lead can be absorbed into the body by consumption of lead-containing food stuffs, there is a necessity of precise and exact determination of lead in various types of beverage and food. The survey of the literature has shown that there are many data on lead determination in food. It can be seen that usually the methods of flame

atomic absorption (AAS) [1, 2] and electrothermal atomic absorption spectrometry (ETAAS) [3-5], were used.

In this work determination of lead by atomic absorption spectrometry (AAS) in soils and in some beverage products (wines) or food products (vegetable, fruits) taken from different places near the lead and zinc smelting plant in Titov Veles city, Macedonia has been done.

Experimental

Instrumentation

A Perkin-Elmer models 303 and 703 atomic absorption spectrophotometer equipped with a deuterium background corrector, HGA-72 graphite furnace and model 056 strip chart recorder were used. A lead hollow cathode lamp was used as a source. Low concentration of lead were determined by ETAAS and for relatively higher by flame AAS. Optimal instrumental conditions for lead determination by ETAAS (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. Gas mixture of acetylene and air was used for flame AAS determinations.

Procedure for the lead determination in soils

1 g of fine milled soil sample was transferred in a glass beaker and 50 cm³ of acid mixture of HCl and HNO₃ (3+1) were added. A mixture was heated 3-4 hours on a hot plate to obtain a minimum volume. Then, 50 cm³ of deionized water were added and the solution was filtered off. The filtrate was collected in a volumetric flask of 100 cm³.

Procedure for the lead determination in wines

An aliquot of 50 cm³ of wine sample in an open silica crucible is evaporated in a sand bath to a viscous residue. It was added 2 cm³ of concentrated sulfuric acid and continued with the evaporation and finely on a electric plate until SO₂ fumes liberating. After that, the crucible was put in a furnace at about 500 °C for 2 hours. After cooling the residue was treated with 3 cm³ of concentrated HNO₃ and evaporated on a sand bath. Then, crucible was put in the furnace at 500 °C for 1 hour. The obtained white ash was solved with 3 cm³ concentrated HNO₃ and a few drops of water by heating. After cooling, the solution was filled with water up to 5 cm³, filtered off and the amount of lead was determined by flame atomic absorption spectrometry (FAAS) and electrothermal AAS (ETAAS).

Procedure for the lead determination in food samples

10 to 20 g of food samples were put in an erlenmeyer flask. 20 cm³ of hydrochloric acid solution (2:1 v(HCl)/v(H₂O)) was added, brought to a boil on a hot plate and simmered for 5 minutes. The solution was cooled, filtered and transferred to a 50-mL volumetric flask and made to volume with deionized water.

The results from the lead determination in soils from different places and different depths in the Titov Veles city area are given in Table I. It can be seen that in the soil samples which are near lead smelting plant (sample 1, 2, 4, 5) lead content is much more higher than in the samples 3 and 6 which are far-away from Pb-Zn smeltery. Also, it can be seen that lead content is much more higher in samples taken from the surface than those from deeper layers. Because of the accumulation of lead in the soil, lead content increases by time.

Table I.

Results from the lead determination in soil from different depths and different places in Titov Veles city area (results are given in %)

No	Place of taking the sample	Year	Depth of taking of samples		
			Surface	-10 cm	-50 cm
1	Factory Kiro Chuchuk raw field	1991	0.035	0.015	0.010
		1992	-	-	-
		1993	0.071	0.063	0.009
		1994	0.022	-	0.017
2	Near tunnel raw filed	1991	0.009	0.009	0.005
		1992	-	-	-
		1993	0.067	0.014	0.004
		1994	0.052	-	0.003
3	Factory Noncha Kamishova raw field	1991	0.013	0.009	0.007
		1992	-	-	-
		1993	0.031	0.012	0.004
4	Bavchi Dmjevica raw field	1991	0.111	0.080	0.006
		1992	-	-	-
		1993	0.094	0.084	0.004
		1994	0.058	-	0.007
5	Bavchi Rechani cultivated filed	1991	0.026	0.022	0.010
		1992	0.031	0.019	0.009
		1993	0.037	0.036	0.008
		1994	0.022	-	0.004
6	Dolno Kalaslari village raw filed	1991	0.007	0.002	0.001
		1992	-	-	-
		1993	0.008	0.007	0.002

From the results given in Table II it can be seen that the lead content in the most of the wine samples from Titov Veles region, occurs in concentration lower than those permitted by Macedonian government (maximum $0.3 \text{ mg} \cdot \text{dm}^{-3}$). But, in one sample of Smederevka white wine the content of lead is $0.325 \text{ mg} \cdot \text{dm}^{-3}$ and in other sample of home made red wine, produced from vineyard near lead smelting factory, the concentration of lead is very high - $1.03 \text{ mg} \cdot \text{dm}^{-3}$. It can be concluded that the lead concentration in wine samples depends from the distance of vineyard from the lead smelting factory.

Table II.

Results from the lead determination in different type of wine samples produced in 1993 from the region of Titov Veles city

Type of wine	Place of vineyard	$\gamma(\text{Pb})/\text{mg} \cdot \text{dm}^{-3}$
WHITE WINES		
Zhilavka	*	0.250
Zhilavka	Novichani	0.094
Smederevka	*	0.325
Smederevka	Bela Voda	0.169
Rizling	*	0.135
Rkaciteli	Babuna	0.152
Home made	Bojadjiska Cheshma	0.273
RED WINES		
Merlo	*	0.274
Merlo	Gumno	0.117
Vranec	*	0.255
Vranec	Ramnuk	0.140
Home made	Near Zn-Pb smelting factory	1.030

*Wine prepared from grapes from wide area of Titov Veles city

To cheque the content of lead in food produced in the region of Titov Veles city, a few samples of a different fruit (strawberries, cherries) and vegetable (cabbage, potatoes, onion) and propolis from bees are analyzed. From the results given in Table III it can be concluded that the lead content in the investigated samples of fruit and vegetable is in permitted limits (1 mg/kg). Also, it can be seen that the content of lead is evidently higher in unwashed samples than in those which are washed. This is a result of the precipitation of ore dust from the factory on the surface of fruits and vegetables. The content of lead in one sample of propolis obtained in this area is much more higher than in propolis produced from other regions in Macedonia [6].

Table III.
Results from the lead determination in different food samples taken in the region of
Titov Veles city

Type of food	w(Pb)/mg·kg ⁻¹
STRAWBERRIES	
Unwashed	0.74
Washed	0.10
CHERRIES	
Unwashed	0.20
Washed	0.10
CABBAGE	
Unwashed	0.20
Washed	0.10
POTATOES	0.20
ONION	0.20
PROPOLIS FROM BEES	19.50

Conclusions

The results pointed out that the content of lead in the surface soil samples is higher than in those taken from deeper points. The content of lead in some wine samples and food products (vegetable, fruit) is in permitted limits, except 2 samples of wine produced from vineyards near Pb-Zn smeltery. The content of lead is evidently higher in unwashed food samples than those which are washed, as a result of the precipitation of ore dust from the factory on the surface of fruits and vegetables.

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