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**DETERMINATION OF TRACE QUANTITIES OF HEAVY METALS  
IN FOOD BY ANODIC VOLTAMMETRY. DETERMINATION  
OF CADMIUM, LEAD AND COPPER IN BEER**

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The optimum conditions for the determination of Cd, Pb, and Cu in beer were sought by the factorial design and the simplex method approaches. Two methods of sample treatment were used, *viz.* mineralization and mineralization combined with ashing. The values obtained,  $0.32 \mu\text{g} \cdot \text{l}^{-1}$  for Cd,  $15.6 \mu\text{g} \cdot \text{l}^{-1}$  for Pb, and  $64.7 \mu\text{g} \cdot \text{l}^{-1}$  for Cu, were compared with those obtained by atomic absorption spectrophotometry.

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The determination of trace quantities of heavy metals in beer by differential pulse anodic stripping voltammetry (DPASV) requires sample decomposition pretreatment. As compared with ashing, wet mineralization is advantageous by the smaller loss of inorganic substances; on the other hand, the chemicals used for the mineralization contribute to the contamination of the sample. Mineralization with acids such as nitric acid<sup>1</sup> or combinations of nitric and sulphuric acids<sup>2</sup> or perchloric, nitric, and sulphuric acids<sup>3</sup> resulted in ill-reproducible Cu contents in beer determined by DPASV on a thin mercury film electrode (TMFE); the solution was too acid and hydrogen was created and its desorption hindered an accurate determination of copper. This is due to the fact that the hydrogen overvoltage obtained on the TMFE is not so high as on the mercury dropping electrode because a fraction of the glassy carbon is uncoated by the mercury film. For 1M-HCl and HNO<sub>3</sub>, glassy carbon potentials from  $-0.7$  to  $+1.0$  V are of use<sup>4,5</sup>. At more negative potentials, requisite for the determination of cadmium, hydrogen is evolved and partly adsorbed on the uncoated electrode surface, and its desorption during the anodic stripping leads to an increase in the residual current over the potential region from  $-0.3$  to  $+0.2$  V (hydrogen wave). As a result, the limit of determination lowers particularly for copper. The only wet mineralization procedure that satisfied for the determination of Cd, Pb, and Cu by DPASV on TMFE was the decomposition with hydrogen peroxide in the presence of small amounts of nitric acid.

Mineralization by ashing was used for the determination of Pb and Cu in beer by anodic stripping voltammetry<sup>6</sup> (ASV). A drawback of this method is the high

loss of metal ions, particularly As, Hg, and Cd, during the ashing at a high temperature<sup>7</sup>. Ashing of organic substances containing lead is associated with some problems; for instance,  $\text{PbO}_2$  reacts readily with silicate at low temperatures and some lead compounds reduce as far as lead metal, which forms an alloy with the platinum of the crucible<sup>8</sup>. Therefore, anions affect appreciably the loss of lead during the ashing.

## EXPERIMENTAL

The conditions of the experiment were optimized as described previously<sup>9,10</sup>. The measurements were performed with a PA-2 polarographic analyzer and an EZ-7 recorder (Laboratorní přístroje, Prague). Pulse amplitude  $\Delta E = 100$  mV, pulse period 1 s, scanning rate  $5 \text{ mV s}^{-1}$ , chart speed  $2 \text{ cm min}^{-1}$ . The rotating disc electrode made of glassy carbon 0.3 cm in diameter, rotating at 1 500 rpm, was combined with a reference calomel electrode and an auxiliary platinum electrode.

### Procedure

Acetate buffer pH 5.8 as the supporting electrolyte and 1 ml of  $10^{-3} \text{ M}$  mercuric nitrate solution were added to sample, and the whole was diluted to 25 ml with purified water. The solution was electrolyzed for 6 min at  $-1.0$  V. After the electrolysis, before the anodic stripping current was recorded, the solution analyzed was replaced by supporting electrolyte solution.

## RESULTS AND DISCUSSION

### *Determination of Cadmium, Lead, and Copper in Beer After its Mineralization with Hydrogen Peroxide and Nitric Acid*

It is an advantage of this procedure that the products of hydrogen peroxide decomposition are oxygen, which can readily be removed from the solution, and water. The remaining  $\text{H}_2\text{O}_2$  decomposes partly during the heating. Also, the oxidation by hydrogen peroxide is catalyzed by small quantities of  $\text{Cu}^{2+}$  ions which are present in beer<sup>11</sup>.

To 50 ml of beer (12° Kozel, Velké Popovice) were added 2 ml of purified nitric acid and 3 ml of 32% hydrogen peroxide, the whole was heated to boil under reflux, and 3 ml portions of  $\text{H}_2\text{O}_2$  were added in 15 min intervals until decolouration of the solution. The boiling was continued for additional 30 min. The total takeup of hydrogen peroxide per 50 ml of beer was 15 ml and the mineralization took 60 min. After cooling down, the solution was diluted to 100 ml. A 10 ml aliquot (corresponding to 5 ml of beer) was added to the polarographic vessel and further proceeded as given in the Experimental. The record obtained is shown in Fig. 1. Cadmium, lead, and copper were determined by linear regression analysis using the standard additions method. The data (Table I) give the regression linear relations between the metal con-

tents  $X_i$  (in  $\mu\text{g}$ ) and the response current  $Y_i$  (in  $\mu\text{A}$ )

$$Y_i = 0.0364 + 22.97X_i \quad (1)$$

for cadmium,

$$Y_i = 1.491 + 19.15X_i \quad (2)$$

for lead, and

$$Y_i = 28.22 + 87.18X_i \quad (3)$$

for copper. The calculated  $X_0$  values for additions of 0.000  $\mu\text{g}$  characterize the Cd, Pb, and Cu contents of 10 ml of mineralized solution, which correspond to the amounts present in 5 ml of beer plus those introduced with the chemicals used. A multiplica-

TABLE I  
Determination of Cd, Pb, and Cu in beer after its mineralization; standard additions method

Standard addition <sup>a</sup> $\mu\text{g}$	$I, \mu\text{A}$						$I_{\text{average}}$ $\mu\text{A}$
Cadmium							
0.000	0.05	0.05	0.06	0.03	0.06	0.05	0.05
0.014	0.30	0.40	0.20	0.30	0.50	0.34	0.34
0.020	0.50	0.50	0.60	0.30	0.40	0.48	0.48
0.028	0.70	0.80	0.70	0.70	0.60	0.70	0.70
Lead							
0.00	1.5	1.6	1.7	1.2	1.5	1.5	1.5
0.25	6.0	6.1	5.9	6.0	6.5	6.1	6.1
0.38	9.0	9.2	9.0	9.0	9.3	9.1	9.1
0.50	11.0	11.2	10.8	10.5	11.0	10.9	10.9
Copper							
0.00	30.0	31.0	31.5	30.0	32.0	30.9	30.9
0.25	47.0	49.0	46.5	46.0	47.0	47.1	47.1
0.50	70.0	73.0	68.0	70.0	69.0	70.0	70.0
0.80	100.0	98.0	98.0	100.0	100.0	100.0	100.0

<sup>a</sup> Added to 10 ml of analyte solution, corresponding to 5 ml of beer.

tion factor of 200 was applied to obtain the values for 1 000 ml of beer; the  $200X_0$  values are 0.32, 15.58, and  $64.74 \mu\text{g l}^{-1}$  for Cd, Pb, and Cu, respectively.

The results obtained by the linear regression treatment using the standard additions method was compared with those derived from the calibration curve, and the latter were found lower than the former by 6% for lead and 2% for copper. This is probably due to the presence of partly decomposed organic substances in the analyte solution, which increase its viscosity and thereby slow down the mass transport to the electrode during the electrolysis.

Since no sample free from cadmium, lead, and copper was available, purified water was used instead of beer in the blank experiment; the whole treatment including the addition of nitric acid and hydrogen peroxide, heating, cooling down, dilution, and analysis of an aliquot was performed as with the actual beer sample. The DPASV trace is also shown in Fig. 1.

The accuracy of the method was tested by adding  $1.0 \mu\text{g}$  of cadmium,  $15 \mu\text{g}$  of lead, and  $60 \mu\text{g}$  of copper in the nitrate form to 1 litre of beer. The solution was mineralized as described and the metal content was determined. The results, documenting the accuracy of the method, are given in Table II.

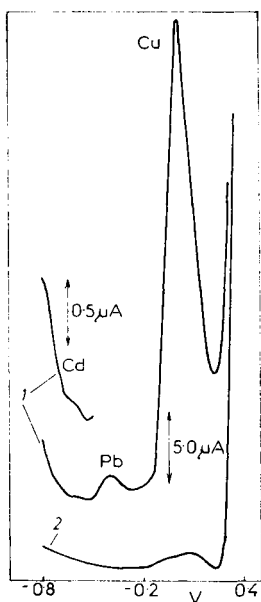


FIG. 1

DPASV record for the determination of Cd, Pb, and Cu in beer 1 and for the blank 2. Mineralization with  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$

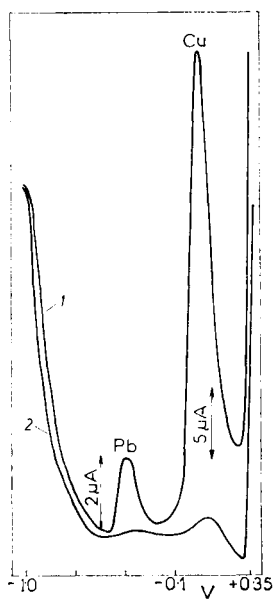


FIG. 2

DPAV record for the determination of Cd, Pb, and Cu in beer 1 and for the blank 2. Mineralization and ashing

The results obtained by the DPASV method were compared with those obtained by flameless atomic absorption spectrophotometry under the same conditions of sample mineralization. The data presented in Table III document a good agreement of the results.

TABLE II

Test of the accuracy of determination of Cd, Pb, and Cu in beer by the DPASV method after mineralization

Metal	Content $\mu\text{g l}^{-1}$	Added $\mu\text{g l}^{-1}$	Total $\mu\text{g l}^{-1}$	Found $\mu\text{g, l}^{-1}$	Recovery %
Cd	0.32	1.00	1.32	1.20	91
Pb	15.58	15.00	30.58	28.80	94
Cu	64.74	60.00	124.74	120.0	96

TABLE III

Comparison of the results of determination of Cd, Pb, and Cu in beer by DPASV with those obtained by flameless atomic absorption spectrophotometry

Metal	Found, $\mu\text{g l}^{-1}$	
	DPASV	AAS
Cd	0.32	1.00
Pb	15.58	13.20
Cu	64.74	68.10

TABLE IV

Test of the accuracy of determination of Cd, Pb, and Cu in beer after the sample ashing

Metal	Content $\mu\text{g l}^{-1}$	Added $\mu\text{g l}^{-1}$	Total $\mu\text{g l}^{-1}$	Found $\mu\text{g l}^{-1}$	Recovery %
Cd	—	1.0	1.0	0.52	50
Pb	14.2	15.0	29.2	28.0	96
Cu	63.6	60.0	123.6	120.0	97

*Determination of Cadmium, Lead, and Copper in Beer After Its Mineralization and Ashing*

25 ml of beer was added to a platinum crucible and heated slowly in a furnace at 30°C until the volume reduced to 5 ml. One ml of 98% H<sub>2</sub>SO<sub>4</sub> and 1 ml of purified HNO<sub>3</sub> were added and the temperature was raised slowly to 400°C. The sample was ashed at this temperature for 6 h, then the temperature was increased to 500°C at which the sample was held for another 6 h. After a slow cooling, 1 ml of HNO<sub>3</sub> was added and the contents of the crucible were transferred to a 50 ml flask and diluted to volume with purified water. A 10 ml aliquot was taken to the DPASV analysis. Insoluble silicates and calcium salts present in the ashed sample did not interfere with the analysis.

Lead and copper were determined by the standard additions method; the results agree well with those read from the calibration curve. Cadmium could not be determined in sample worked up in this manner. The record for lead and copper is shown in Fig. 2.

The blank experiment was performed with 1 ml of H<sub>2</sub>SO<sub>4</sub> and 1 ml of purified HNO<sub>3</sub>, placed in the platinum crucible and treated as described. The record of the blank experiment (Fig. 2) demonstrates that the sulphuric acid used contained lead and copper impurities.

The accuracy of the method was tested by adding 0.025 µg of cadmium, 0.375 µg of lead, and 1.50 µg of copper to 25 ml of beer and working the sample up as above. The results (Table IV) show that lead and copper can be determined accurately, whereas cadmium does not lend itself to analysis by this method.

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