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BEER - beverage with the lowest content of heavy metals

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1 INTRODUCTION

There are two groups of analytical methods used for determination of trace amounts of heavy metals in samples, electrochemical and spectrometric. Last years with development of electronics became again an expansion of electrochemical methods, which were almost forced out by spectrometric methods. Dominant position in spectrometric methods takes atomic absorption spectrometry (AAS) with different ways of atomisation and introduction of sample into the atomisator (FAAS, GFAAS). Multielemental analysis is represented namely by inductively coupled plasma (ICP-AES, ICP-MS) emission and mass spectrometry.

Stripping determination of trace amounts of metals is based on deposition on the surface of electrode (so called preconcentration) using a constant potential. In next stage the deposit is stripped by application of constant current and measurement of time dependent potential (galvanostatic stripping chronopotentiometry-GSCP). This method is highly selective, the cost per one determination is low and it is possible to determine several metals simultaneously. An electrochemical flow-through cell with a porous working electrode made of vitreous carbon particles and plated with mercury was used for the determination of Zn, Cd, Pb and Cu using GSCP in a flow system.

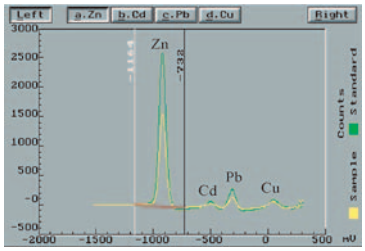

Figure 3 Chronopotentiometric curve for sample and standard solution

Figure 7 View of electrochemical analyser Istran EcaFlow GP 130

2 METHODS

2.1 Decomposition Technique

Wet ashing under elevated pressure with focussed microwave heating in 3 ml of 65% HNO_3. (Plazmatronika BM-1S, PL). Samples (solid samples - malt and hop - approximately 0.5 g , liquid samples - water, sweet wort, wort, degassed beer - approximately 10 g) were weighted accurately into polytetrafluoroethylene digestion bombs. Digestion was then completed using a microwave oven for 3 minutes at low power followed by 7 minutes at high power. After cooling for 10 minutes, the digests were transferred quantitatively into volumetric flasks (50 ml) and diluted to volume with deionized water.

2.2 Measurements

Determination of zinc, copper, cadmium and lead by GSCP

Electrochemical analyser Istran EcaFlow GP 130 produced by Istran (Bratislava, SK) which is suitable for laboratory research and also for monitoring of metals in aqueous solutions e.g. in beverage industry was used for electrochemical measurements. Scheme of electrochemical analyser is shown in figure 1. View of electrochemical analyser Istran EcaFlow GP 130 is shown in figure 7.

The evaluation (transformation) of sample chronopotentiometric curve is shown in figure 3. The analysis is carried out in full automatic mode. First, a given volume of sample solution is pumped through the cell with porous working electrode set to the deposition potential where the trace metals are collected. The heart of the system is the patented compact electrochemical cell. This cell is shown in figure 2. In the next step the deposit is stripped by constant current to the optimum electrolyte solution whereas the change of potential of the working electrode is monitored and evaluated. After the measurement of the sample, background signal is measured automatically in a similar way just by treating the electrolyte solution instead of the sample solution. The background signal is then substracted from the sample signal giving the background-corrected net signal. By integrating the stripping peaks, the concentration of the corresponding trace elements is calculated by making use by automatic standard addition. Example for simultaneous measurement of zinc, copper, cadmium and lead is shown in figure 4. Operating conditions for this measurement are summarised in Table 1.

Table 1 GSCP operating conditions

Electrode	Istran E 56-LMF
Electrolyte	sodium acetate 0.1 mol.l-1
Accumulation current	-5000 mA
Initial potential	-1600 mV
Final potential	350 mV
Stripping current	200 mA
Dwell time	10 s
Measurement time	30 s
Regeneration time	10 s
Regeneration potential	200 mV
Sample volume	***1 ml***
Standard adition volume	***0.1 ml***

Determination of zinc, copper, cadmium and lead by ICP-MS

Elan 6000 (Perkin Elmer Sciex) ICP mass spectrometer, with peristaltic pump Gilson 212, was used for determination of Cd, Cu, Pb and Zn in sample digests. The solutions were aspirated into nebulizer in 3 - 5 % v/v HNO_3. Operating conditions for this measurement are summarised in Table 1. The following isotopes were used for signal evaluation: Cd 112, Zn 66, Cu 65, Pb 208. In 115 and Bi 209 were applied as internal standards.

Table 2 ICP - MS operating conditions

Sweeps/Reading	5
Dwell time / ms	200
Gas flow rates/ l.min-1	
Coolant	17.0
Auxiliary	1.2
Nebulizer	0.8
Forward power /W	1000
Sample uptake rate/ ml.min-1	1.0

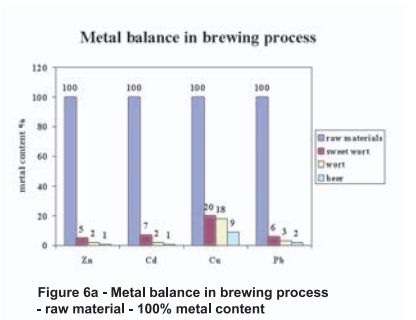

Figure 6a - Metal balance in brewing process - raw material - 100% metal content

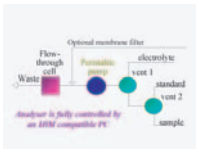

Figure 1 - Schema of electrochemical analyser Istran EcaFlow GP 130

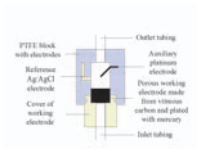

Figure 2 - Scheme of electrochemical flow-through cell

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A total of 200 bottles of different beers were analysed by GSCP for determination of zinc, copper, cadmium and lead. Resultant medians and maximum values are shown in figure 4. GSCP method was validated by ICP-MS method. As maximum and mean lead concentration was relatively high, soft-drink (50 samples) and wine (50 samples) samples were analysed for lead content. Median lead concentrations are shown in figure 5. Beer represents the purest beverage from point of view lead concentration. Metal balance for zinc, copper , cadmium and lead is shown in figure 6a,b. Only metal traces are transported from raw materials to final beer. Brewing process is a self-cleaning process from heavy metal content point of view.

5 CONCLUSION:

- **GSCP is suitable method for simultaneous metal determination in beers.**
- **Beer is very clean product from metal concentration point of view (namely lead).**
- **Brewing process is self-cleaning process. This process reduce amount of heavy metal in beer.**