

Adsorption of Zinc Contained in the Poultry Feedstuff onto Clinoptilolite

E. ŠUCMAN¹, J. PÁČ¹, K. BRZOSKOVÁ², M. VÁVROVÁ², P. KETTISCH³

¹Department of Biochemistry and Biophysics, Faculty of Veterinary Hygiene and Technology
University of Veterinary and Pharmaceutical Sciences Brno, Brno, Czech Republic

²Faculty of Chemistry, Brno University of Technology, Brno, Czech Republic

³Anton Paar GmbH, Graz, Austria

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Abstract

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The aim of this work was to find whether an adsorbent used as an additive in the feed mixtures could influence the concentration of free available zinc. The feed supplement ZeoFeed, which often constitutes a part of animal feed mixtures, mainly for poultry, was used as adsorbent in the amount of 10 g·kg⁻¹ of the feed mixture. A substantial part of ZeoFeed is clinoptilolite, a natural form of zeolite.

Two sample preparation methods were used for the determination of zinc. The microwave-assisted wet digestion method was used to achieve a complete decomposition of the feed mixture in order to determine the total zinc concentration. The extraction method represented a simplified model of the processes in the digestive fluid tract. The extraction was done under laboratory temperature for 30, 60 and 120 min. Concentrations of zinc both in digests and extracts were determined by the method of the differential pulse anodic stripping voltammetry.

The total zinc concentration (mean ± 95% confidence interval) in the feed mixture without addition of clinoptilolite was found to be 145 ± 32.0 mg·kg⁻¹ and in the feed mixture with added clinoptilolite 146 ± 11.5 mg·kg⁻¹.

The concentrations of free available zinc were approximately ten times lesser than the total amount. The analysis of extracts showed that no statistically significant differences between concentrations of zinc in extracts without clinoptilolite and with clinoptilolite addition have been found. The extraction time did not affect the extracted amount of zinc significantly.

In addition to zinc, also other three trace elements, namely the essential trace element copper and the toxic trace elements cadmium and lead, were measured. However, these data have only preliminary value and need further verification.

Adsorbents, microwave-assisted digestion, stripping voltammetry, trace elements

It is well known that the feeding of farm animals is one of the most important factors deciding the quality and/or safety of produced foods. The quality of feedstuffs and rational set up of feed rations are basic presumptions for high efficiency, production health and economic prosperity in the breeding.

Important constituents of feedstuffs today are various kinds of additives, among them also adsorbents. These are added to feed mixtures in order to improve the health conditions of animals and/or to improve the conditions of their environment. One of the adsorption substances, used very often nowadays is clinoptilolite. It is hydrated aluminosilicate of calcium, potassium, sodium and magnesium. Its crystal lattice is formed by tetrahedrons of (SiO₄)⁴⁻ mutually connected by atoms of oxygen. Additionally, atoms of aluminium may substitute some silicon atoms and consequently (AlO₄)⁵⁻ groups are formed. Dimensions of channels existing under such structure are large enough to be able to accept molecules having the size of up to a few tenths of nanometers. The effective diameter was found to be 0.4 nm. The volume of such channels forms 24 – 30% of the total volume (Zeoceem 2006).

Principally, there are at least two important reasons why adsorbents are used. The first one

Address for correspondence:

Prof. RNDr. E. Šucman, CSc.
University of Veterinary and Pharmaceutical Sciences Brno
Palackého 1-3, 612 42 Brno, Czech Republic

Phone: +420 541 562 603
E-mail: sucmane@vfu.cz
<http://www.vfu.cz/acta-vet/actavet.htm>

is based upon their ability to adsorb some harmful substances, e.g. mycotoxins. The second one is their favourable effect on the stable environment, where especially concentrations of ammonia can be substantially reduced. Consequently, better production results can be achieved (Olver 1997; Huwig 2001; Tomašević-Čanovic et al. 2001; Melenová et al. 2003; Cabuk et al. 2004; Suchý et al. 2006).

On the other hand, one must be sure, that at the same time when the above-mentioned desirable effects of adsorbents are occurring, adsorption processes connected with decreases in concentration of nutritionally important substances do not occur. As an example of such substances, trace elements may be named. Among essential trace elements, zinc plays an important role due to its participation in many enzyme and/or hormone processes (Karlson 1994). The possible consequences of zinc deficiencies have been described e.g. by Jantošovič (1995) and Jurajda (2003).

The aim of this work was to realise a model experiment in order to prove the possibility of zinc adsorption from feedstuffs containing clinoptilolite.

Materials and Methods

Instruments

The high pressure microwave-assisted digestion of samples was done using the Multiwave 3000 (Anton Paar, Austria), provided with two rotors. The 8SFX digestion rotor equipped with thick wall quartz vessels and the 8EVAP evaporation rotor.

The shaking machine LT 2 (Sklo union, Czech Republic) was used for extractions.

The voltammetric determinations of zinc concentrations were done by the ETP 30 polarographic equipment (Polaro-Sensors, Czech Republic) with control software Polar 5.1 (Polaro-Sensors, Czech Republic) The three-electrode mode was used, the hanging mercury drop electrode (HMDE) being the working electrode.

Chemicals

Both samples and standard solutions were prepared using the ultra pure water (NANOpur Barnstead, USA) having the specific conductivity less than $1 \mu\text{S}\cdot\text{m}^{-1}$. All chemicals were of Suprapur grade (Merck, FRG). Compressed argon 4.6 UN 1006, GA 260 (Linde Technoplyn, Czech Republic) was used.

Furthermore, the HMDE was filled up with Mercury for Polarography (Merck, FRG) and the solution of $3 \text{ mol}\cdot\text{l}^{-1}$ KCl (ORION Research, USA) was used in the reference electrode.

Analytical standards were prepared daily fresh from the $1.000 \text{ g}\cdot\text{l}^{-1}$ store solutions Astasol (Analytika, Czech Republic)

Samples

Feed mixture 301-N1-Bovans Goldline (Agrokonzulta, Czech Republic) and the adsorbent additive ZeoFeed (ZEOCEM, Slovak Republic) in the amount of $10 \text{ g}\cdot\text{kg}^{-1}$ of the feed mixture were used.

Microwave-assisted digestion

The 0.5 g of the sample was mixed with 6 ml of the digestion mixture in the digestion vessel. The mixture contained concentrated HNO_3 , H_2O_2 and HCl (12+12+1). The sample was digested for 85 min at $280 \text{ }^\circ\text{C}$ using the digestion parameters given in the Table 1. The digestion vessels were then transferred into the evaporation rotor and the liquid was evaporated to dryness. The appropriate parameters are also given in the Table 1. The residue after evaporation was dissolved in 10 ml of ultra pure water containing $40 \mu\text{l}$ of HNO_3 ($6 \text{ mol}\cdot\text{l}^{-1}$).

Table 1. Digestion and evaporation parameters used for Multiwave 3000

Step	Power [W]	Ramp time [min]	Hold time [min]	Cooling level
Digestion				
1	400	5	5	1
2	800	5	50	1
3	0	0	30	3
Evaporation				
1	900	0	25	1
2	0	0	30	3

Extraction

The simplified model for extraction using $0.01 \text{ mol}\cdot\text{l}^{-1}$ HCl was used. Under laboratory temperature ($22 \pm 2 \text{ }^\circ\text{C}$) 2 g of the feed mixture both without and with the adsorbent in the 250 ml Erlenmeyer flask have been extracted by

100 ml of HCl for 30, 60 and 120 min particularly. After each elapsed extraction time the aliquot volume of 0.1 ml was taken away, which was further analysed for the trace elements content.

Using both digestion and extraction procedures, at least five independent samples have been prepared.

Voltammetric measurements

The voltammetric trace elements determination was done by differential pulse anodic stripping voltammetry (DPASV) using the technique of standard addition. An aliquot of 100 μ l of extract or 50 μ l of dissolved evaporation residue was mixed with 10 ml of the acetate buffer (pH = 5.6) and measured. The following instrumental parameters were applied: deposition potential -1.1 V, final potential 0.15 V, scan rate 20 mV/s, drop time 0.2 s, pulse width 100 ms, pulse height 50 mV, deposition time 180 s, rest time 15 s.

At least two determinations in the voltammetric cell have been done. For subsequent calculations the mean of these parallel measurements was taken.

There is not any certified reference material available for such samples. Therefore, the accuracy of results was checked by the method of standard addition. The amount of the standard added, exceed the amount of the analyte in the sample approximately two times.

The statistical evaluation of results was done according to Eckschlager et al. (1992).

Results and Discussion

The examples of measured voltammetric curves are given in Fig. 1 for a digested sample and in Fig. 2 for an extracted sample. It should be mentioned that no effect of the adsorbent addition was found upon the shape of the voltammetric curves both in the case of the digestion and extraction.

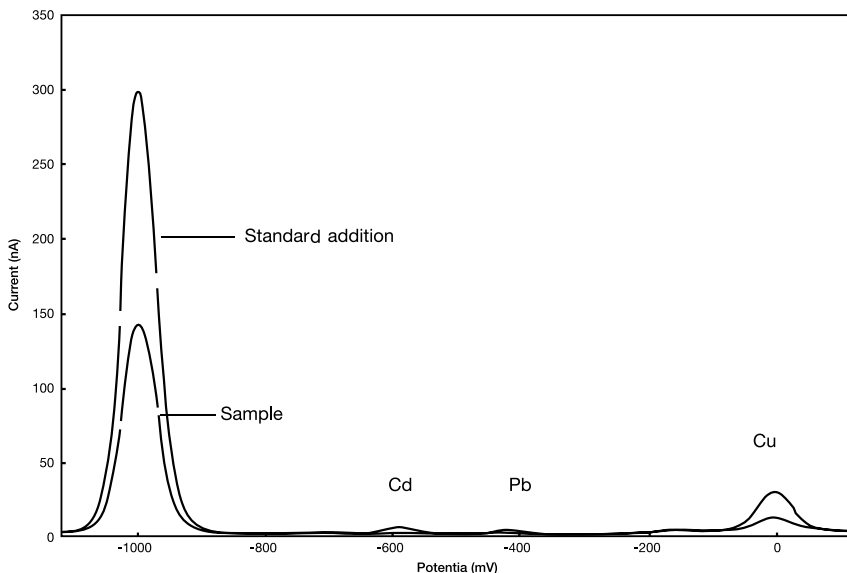


Fig. 1. Voltammetric curves for digested feedstuff sample without addition of adsorbent

As seen both in Fig. 1 and Fig. 2, the applied measurement procedure also enabled the determination of three other trace elements, namely copper, cadmium and lead. Nevertheless, the measurement conditions for these elements have not been optimized yet. Therefore, these results had only approximate value and are not included in this work.

In all determinations both in case of digested and extracted samples more than 90% of the added amount of zinc standard was found. Therefore, under experimental conditions used in this work the accuracy of results may be assumed to be satisfactory. The relatively higher variability may be explained by the inhomogeneity of the feed mixture. In future work an improvement in the field of sample homogeneity will be required.

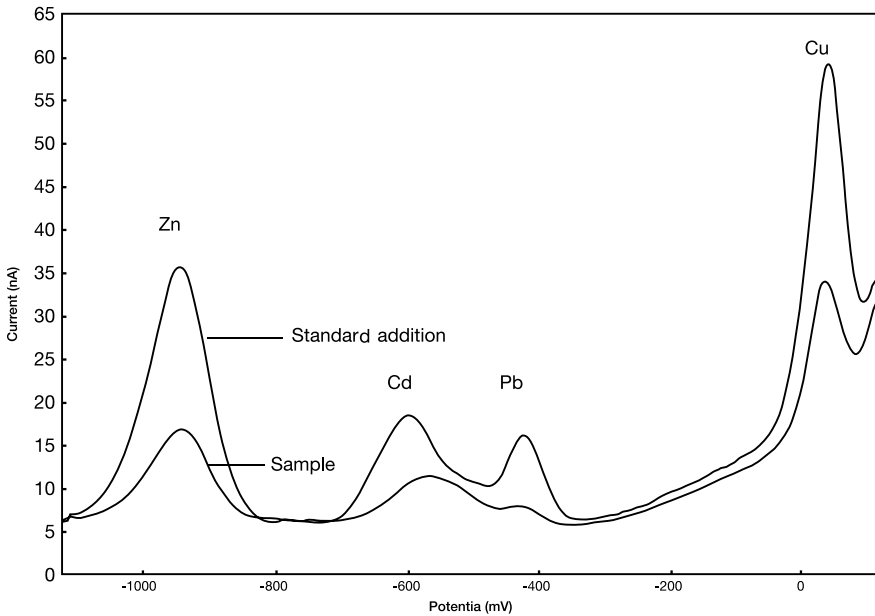


Fig. 2. Voltammetric curves for extracted feedstuff sample with adsorbent addition (extraction time 30 min)

First, concentrations of zinc in samples of feed mixtures without addition of the clinoptilolite were measured. Within the model situation used here, concentration of zinc in the digested samples represented the total concentration of zinc in the feed mixture, whereas concentrations found in extracts represented the available amount of free zinc in the digestive fluid tract.

The 95% confidence interval (95%CI) for the concentration of zinc in the digest was found to be $(145 \pm 32.0) \text{ mg}\cdot\text{kg}^{-1}$. Variability of the results expressed as the relative standard deviation (RSD) was 26.9%. These results can be compared with the extraction data given in Table 2a. Two conclusions could be drawn from the data given in Table 2a. First, the amount of zinc extracted under experimental model conditions is much lower (nearly ten times) than the total zinc concentration found in the feed mixture. This means at same time, that the available amount of zinc is relatively low. Secondly, the effect of the extraction time on the concentration of zinc in extracts is not statistically significant.

Table 2. Zinc concentrations in extracts of feed mixtures without and with the addition of clinoptilolite after various extraction time

Extraction time [s]	Number of extracts	95% CI [mg/kg]	RSD [%]
(a) Samples without clinoptilolite addition			
30	5	18.9 ± 3.69	19.5
60	5	16.8 ± 8.57	43.4
120	8	15.6 ± 3.91	24.8
(b) Samples with clinoptilolite addition			
30	5	19.1 ± 6.24	27.7
60	5	21.7 ± 4.41	17.2
120	8	17.6 ± 3.48	24.1

After the addition of 10 g·kg⁻¹ of ZeoFeed into the feed mixture (which is the usual concentration used in practice) the following results were obtained. The 95% CI for the total zinc concentration after the digestion of the sample was (146 ± 11.5) g·kg⁻¹, the calculated RSD was 9.6%. It follows from the results that the addition of adsorbent did not affect the total zinc concentration in the feedstuff. The concentrations found in samples with added adsorbent found under the same conditions given above are presented in Table 2b. The same conclusions as before may be drawn from the results given in Table 2b. The available zinc concentrations were approximately ten times lower than the total concentration of the analyte in the feed mixture and there was no statistically significant evidence that the extraction time could affect the concentration of extracted free zinc.

The most important message based upon the simplified model of zinc extraction is that the addition of the adsorbent on the basis of clinoptilolite does not affect the concentration of free zinc in the extracts that may be considered as the available amount of zinc in the stomach of chicken.

Adsorpce zinku obsaženého v krmivu pro drůbež na klinoptilolit

Cílem práce bylo zjistit, zda adsorbent použitý v krmné směsi jako aditivum může ovlivnit koncentraci využitelného zinku. ZeoFeed, používaný často jako aditivum s adsorptivními účinky, zejména v krmných směsích pro drůbež, byl použit v koncentraci 10 g·kg⁻¹. Podstatnou účinnou část ZeoFeedu tvoří minerál klinoptilolit. Pro analýzu zinku byly aplikovány dvě metody přípravy vzorků. Při stanovení celkové koncentrace byl použit mikrovlnami podporovaný vysokotlaký rozklad na mokré cestě směsi minerálních kyselin. Vedle toho pak extrakce krmiva za laboratorní teploty po dobu 30, 60 a 120 minut zředěnou kyselinou chlorovodíkovou představovala zjednodušený model procesu probíhajícího v trávicím traktu. Koncentrace zinku byly měřeny metodou diferenční pulsní anodické rozpouštěcí voltametrie. Celková koncentrace zinku (průměr a meze 95% intervalu spolehlivosti) stanovená v krmivu bez přídavku klinoptilolitu byla 145 ± 32,0 mg·kg⁻¹, s přídavkem klinoptilolitu pak 146 ± 11,5 mg·kg⁻¹. Stanovené koncentrace využitelného volného zinku byly asi o jeden řád nižší. Rozdíly mezi množství zinku nalezeným v krmivu bez a s přídavkem klinoptilolitu byly, na hladině významnosti $\alpha = 0,05$ statisticky nevýznamné. Také doba extrakce prakticky neovlivňovala množství volného zinku. Kromě zinku byly ve vzorcích krmiva dále stanoveny ještě měď (esenciální prvek), kadmium a olovo (toxické prvky). Tyto hodnoty jsou předběžné a vyžadují ještě další verifikaci.

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