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# STABILITY OF COPPER, MOLYBDENUM AND SELENIUM IONS BINDING TO THE SURFACE OF DIETARY FIBRE PREPARATIONS IN SIMULATED CONDITIONS OF THE HUMAN GASTROINTESTINAL TRACT

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The release of copper, molybdenum, and selenium ions previously adsorbed on wheat bran and apple pomace was studied in vitro using human digestive enzymes. The highest desorption of copper was by gastric juice from wheat bran and apple pomace, while the largest quantities of molybdenum were desorbed by duodenal juice from wheat bran. The strongest binding during treatment with both digestive enzymes was found to be that of selenium to apple pomace.

The chemical structure of dietary fibre features several functional groups of various qualitative composition [5, 6, 11]. Their ion-exchange and complex-formation properties make it possible to permanently deposit on the fibre surface ions of various elements that are important for the human organism [1, 3, 6, 11].

The sorption capabilities of the system dietary fibre -ions of macro- or micronutrients are due to the possible presence on the system's surface of acceptor-donor centres having the character of Lewis acids and bases [8, 9, 12].

In Poland there have recently been appearing foodstuffs with a high dietary fibre content in combination with trace elements supplied by natural mined salt, e.g. wheat bran supplemented with trace elements. There thus arises the problem of availability of elements from such foodstuffs by the human organism.

The complex sorption process in the system dietary fibre-trace elements ions probably produces bindings of various stability which may be additionally affected by environmental conditions. In conditions of the human gastro-inte-stinal tract the various individual trace elements may be adsorbed and released from fiber in various degrees [4, 9, 10]. The aim of the research reported here was the study of the reversibility of the adsorption of copper, molybdenum, and selenium on dietary fibre of various origin in conditions of digestive enzymes treatment.

## MATERIAL AND METHODS

### MATERIAL

The starting point in this research was the obtaining of surface bonds of copper, molybdenum, and selenium ions previously sorbed on the surface of wheat bran and apple pomace in optimal conditions of this process determined earlier [13].

The following amounts of the studied trace elements were adsorbed on the surface of wheat bran: 890 $\mu$g Cu/g, 38.7 $\mu$g Mo/g and 23.16 $\mu$g Se/g of the dietary fibre preparation. The respective figures for apple pomace were as follows: 680 $\mu$g Cu/g, 90 $\mu$g Mo/g, and 40 $\mu$g Se/g of dietary fibre preparation.

The digestive enzymes used in the experiments were supplied by the Institute of Gastroenterology of the Medical Academy in Poznań. The secretions were taken from healthy individuals by means of stomach and duodenum probing. The duodenal secretion was taken after secretin stimulation (1 secretin unit per 1 kg of body weight). The pH of stomach secretion used in desorption was 2.09, and of duodenal secretion it was 6.8. The secretions did not contain copper, molybdenum, and selenium ions.

### METHODS

The process of copper, molybdenum, and selenium ions desorption from wheat bran and apple pomace induced by stomach juice and duodenal juice was studied according to the following procedure.

One-gram samples of wheat bran and apple pomace were promoted in turn by Cu, Mo, and Se ions in conditions of highest sorption. After separating the solid and liquid phases, the fiber preparations were dried at 343 K, and then transferred to dialytic sacks using 10 $cm^2$ of buffer with pH 2.09. Next, 0.7 $cm^2$ of gastric juice was added, and the sack placed in an Erlenmeyer flask on a thermostat shaker in 310 K temperature. The flask was filled with buffer (pH 2.09) to a level exceeding the level of fluid in the dialytic sack. After 30, 60, 90, 120, 150, and 180 min the buffer surrounding the dialytic sack was replaced with the same amount of fresh buffer. The contents of Cu, Mo, and Se ions were determined in the individual dialysates according to the method described and checked in an earlier research [13].

The desorption of Cu, Mo, and Se ions induced by duodenal digestive secretions was investigated analogously, using 1.5 $cm^3$ portions of these secretions in buffer of pH = 6.8.

The degree of desorption was expressed in per cent as the ratio of element content in the dialysate to the amount of this element adsorbed on the dietary fibre preparation. The results of the studies were analysed statistically using variance analysis for a completely randomized system with curvilinear effects taken into consideration [2].

## RESULTS AND DISCUSSION

Fig. 1 illustrates the desorption of Cu, Mo, and Se ions from wheat bran and apple pomace brought about by gastric juice while Fig. 2 shows the same process induced by duodenal secretions.

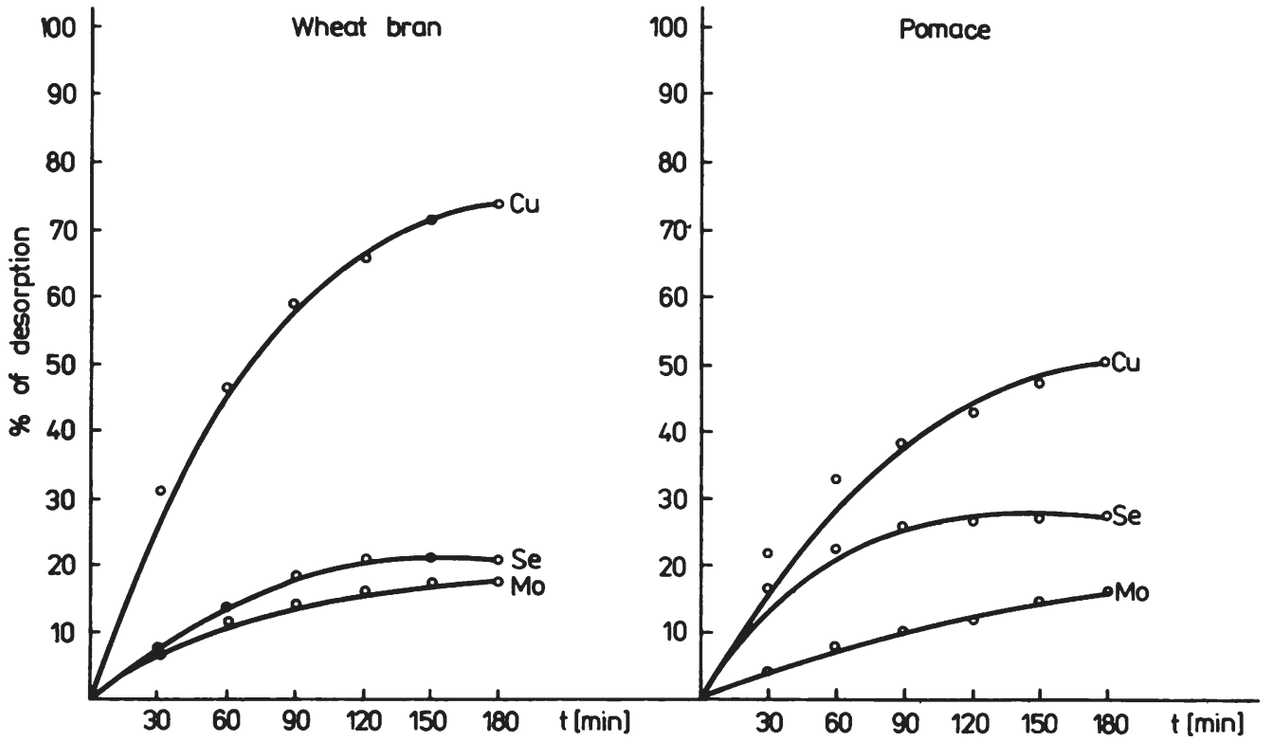


Fig. 1. Copper, molybdenum, and selenium desorption from wheat bran and apple pomace induced by human gastric juice

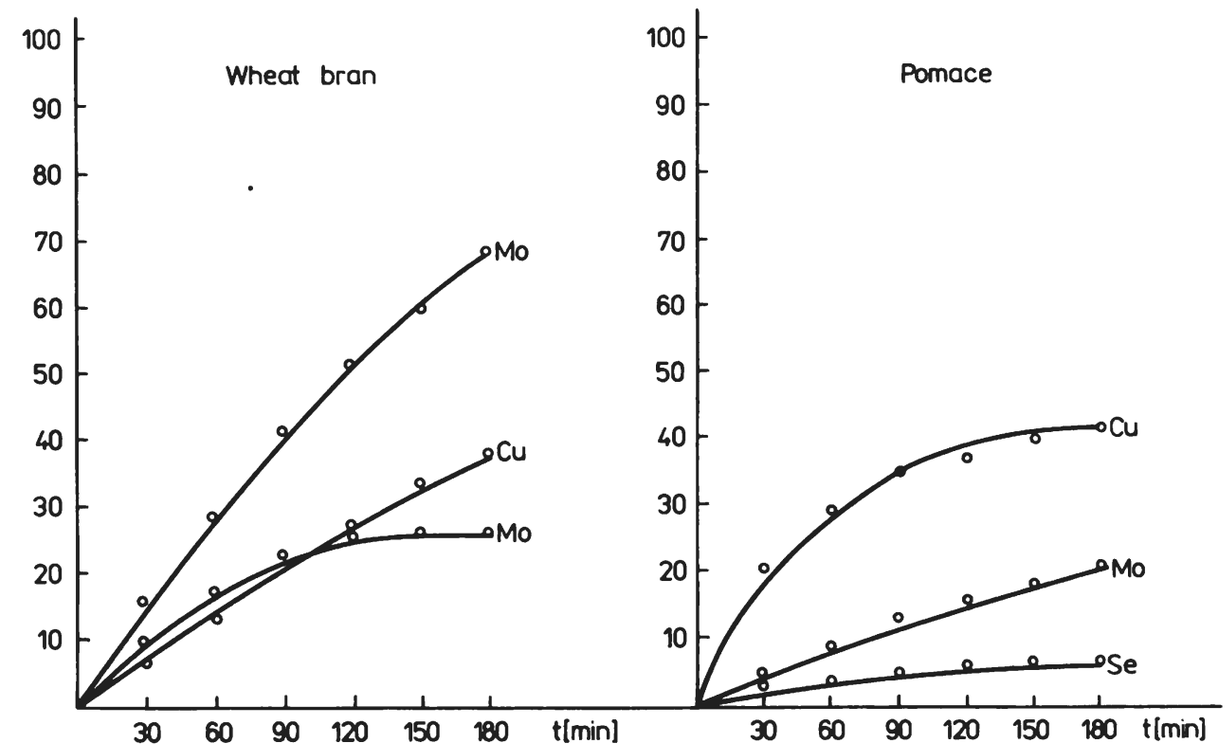


Fig. 2. Copper, molybdenum, and selenium desorption from wheat bran and apple pomace induced by human duodenal juice

The obtained results indicate that the amounts of desorbed ions depend on the element, the time of the process, and the kind of digestive juice. In the applied model conditions, gastric juice removed 74.2% of the copper ions previously adsorbed on the surface of wheat bran, the figures for molybdenum and selenium ions being 18.57 and 20.6%, respectively (Table 1). The large amounts of desorbed copper are indicative of the relative instability of the binding of this element (in the form of the $Cu^{2+}$ ions) to wheat bran surface. Bran, which may be regarded as a dietary fibre preparation rich in hemicelluloses, appears to bind molybdenum and selenium more strongly than copper. The process of promoting this fiber preparation with copper ions probably involves only acid groups which are subsequently unmasked by the acid gastric juice, whereas molybdenum and selenium ions form mainly chelate compounds which are more stable, in acid media.

In experiments with Cu, Mo, and Se ions desorption from apple pomace with the same digestive juice, the amount of desorbed copper ions was also considerable: on average 50.63% after 3 h. The degree of desorption in the case of selenium and molybdenum was much lower: 28.3 and 17.2%, respectively (Table 1).

Table 1. Desorption of Cu, Mo and Se from wheat bran and pomace after 3 hrs tratment of digestibile enzymes

| Element | Wheat bran | | Pomace | |
|---|---|---|---|---|
| | gastric juice | duodenal juice | gastric juice | duodenal juice |
| Cu | 74.20*) ± 0.19 | 38.20 ± 0.10 | 50.63 ± 0.25 | 42.40 ± 0.20 |
| Mo | 18.57 ± 0.14 | 68.60 ± 0.17 | 17.20 ± 0.26 | 20.97 ± 0.38 |
| Se | 20.60 ± 0.08 | 25.50 ± 0.20 | 28.30 ± 0.20 | 6.40 ± 0.20 |

*) Percentage of element adsorbed on particular material, which was relased by enzymes treatment.

The duodenal secretions used as electrolyte eluting trace elements from wheat bran caused the desorption of up to 38.9% of copper ions and 25.5% of selenium ions, but those desorbed most effectively were molybdenum ions, 68.8% of which were leased. In the case of apple pomace, duodenal juices desorbed 42.4% of copper ions, 20.9%of molybdenum ions, and about 6% of selenium ions.

As can be seen from these results, wheat bran is more susceptible to desorption induced by digestive juice than apple pomace. More than two thirds of the molybdenum and copper ions previously adsorbed on bran were released during desorption in simulated conditions of the gastrointestinal tract while apple pomace in the same conditions relased less than half of these elements. This suggests that the binding of the studied trace elements to apple pomace is more strong than the binding to wheat bran.

The desorption curves (Figs. 1 and 2) show that the kinetics of the process in the studied system is most intense during the first 60 min.

In all variants of the process, desorption depended closely on incubation time.

As can be seen from the quadratic regression equations (at significance level $\alpha = 0.01$) describing this dependence, the dynamics of copper and molybdenum ions desorption from apple pomace does not depend on the kind of digestive juices (similar values for parameters t and $t^2$), unlike in the case of wheat bran (Table 2). The relatively greater curvilinear effect for copper and selenium ions than for molybdenum indicates that in the case of the latter element the duration of desorption has a smaller effect of the kinetics of the process. In the experimental model applied here, the desorption of Cu, Mo, and Se ion from dietary fibre preparations was caused by the isolated effect of gastric and duodenal juices. In natural physiological conditions these preparations are exposed in succession to gastric juice ($H^+$ ions, pepsins) and to duodenal juices (bile acids salts, digestive enzymes of the pancreas, bicarbonate ions).

Table 2. Regression equations for desorption level of Cu, Mo and Se from dictory fiber, expressed as function of time

| Gastric juice | Element | Duodenal juice |
|---|---|---|
| | Pomace | |
| $D^* = 6.778 + 0.615\ t^* - 0.004\ t^2$ | Cu | $D = 6.711 + 0.556\ t - 0.004\ t^2$ |
| $D = -1.056 + 0.182\ t - 0.001\ t^2$ | Mo | $D = 0.533 + 0.162\ t - 0.001\ t^2$ |
| $D = 7.044 + 0.393\ t - 0.003\ t^2$ | Se | $D = 1.750 + 0.056\ t - 0.001\ t^2$ |
| | Wheat bran | |
| $D = 9.633 + 0.807\ t - 0.003\ t^2$ | Cu | $D = 1.211 + 0.181\ t + 0.001\ t^2$ |
| $D = 0.691 + 0.253\ t - 0.001\ t^2$ | Mo | $D = 0.780 + 0.513\ t + 0.001\ t^2$ |
| $D = -1.311 + 0.342\ t - 0.002\ t^2$ | Se | $D = -2.767 + 0.519\ t + 0.003\ t^2$ |

D — % of desorption
t — time min.

## CONCLUSIONS

1. The degree of desorption of copper, molybdenum, and selenium from dietary fibre preparations caused by in vitro exposure to human gastrio-intestinol juices varies, depending on the kind of preparation, gastrio-intestinol juice, and the element.

2. Gastric juice is responsible for the most intense desorption of copper from wheat bran and apple pomace, while duodenal juices have a similarly strong effect on molybdenum adsorbed on wheat bran.

3. The binding of copper ions to wheat bran and apple pomace is much weaker than similar bindings of selenium and molybdenum ions.

4. As the time of desorption increases, the intensity of the process decreases, with the phenomenon being most apparent in the cases of copper and selenium.

5. The trace elements adsorbed on dietary fibre may be accessible to the human organism to a limited and various degree.

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## BADANIA TRWAŁOŚCI POWIERZCHNIOWYCH POŁĄCZEŃ JONÓW MIEDZI, MOLIBDENU I SELENU Z PREPARATAMI BŁONNIKA W SYMULOWANYCH WARUNKACH PRZEWODU POKARMOWEGO CZŁOWIEKA

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S t r e s z c z e n i e

In vitro badano wpływ soków trawiennych człowieka na uwalnianie jonów miedzi, molibdenu i selenu z dwóch preparatów błonnika (otręby pszenne i wytłoki jabłkowe). Stwierdzono duże zróżnicowanie stopnia desorpcji wymienionych pierwiastków w zależności od użytego soku trawiennego i preparatu. Najłatwiej uwalniana przez sok żołądkowy była miedź związana z otrębami (w ok. 75%), natomiast przez sok dwunastnicy związany z otrębami molibden (w ok. 70%). W warunkach działania obu soków trawiennych najtrwalsze okazały się połączenia selenu, zwłaszcza z wytłokami jabłkowymi.

Przeprowadzone badania pozwalają sądzić, że spożycie preparatów błonnika pokarmowego może mieć istotny wpływ na dostępność dla organizmu człowieka niektórych pierwiastków śladowych.