The Use of Calcium-Selective Electrode to Determine Calcium in Mechanically Deboned Meat.

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SUMMARY: The material for examination was mechanically deboned chicken meat (MDCM). The determination of calcium was done in solutions obtained: 1) by soluting ash residues of MDCM, 2) in wet digestion procedure of MDCM. The calcium content of both variants of solutions were determined by: 1) the titration procedure according to the Association of Official Analytical Chemists method, 2) atomic absorption spectrophotometric method, 3) titrametric method using the calcium-selective electrode as an indicator of titration end point.

There was no significant difference between values obtained from the same sample of MDCM in different analytic procedure. On the basis of the obtained results it is evident, that to determine Ca-content the use of calcium-selective electrode as indicator of titration end point for a sample prepared in wet digestion procedure and titration with EDTA, is possible.

INTRODUCTION: Mechanically deboned meat (MDM) contains a certain amount of bone particles (from 0,14 to 4,00%) depending on the kind and technical state of a deboner, on the parametres of the process and on the kind and rate of musculature of deboned raw material. In Poland the maximum bone particles limit is 0,50%. The presence of bone particles results in the increase of mineral substances content including Ca and heavy metals. On account of this in some countries the admitted Ca content in MDM is 0,75%. The content of bone particles can be determined directly (according to the Polish standard BN/803505) or indirectly, calculating it according to the formula (AOAC 1984):

$$C_k = (\% \text{ Ca} - 0{,}015)F$$

where: C_k - the content of bone particles in MDM in %,
F - a factor with value depending on the kind of raw material.

Determination of bone particles content is simple but timetaking. It is more convenient to determine Ca and to carry out, on this basis, the evaluation of bone particles content. The condition is, however, the use of the quick Ca determination method, because MDM is an unstable product. If the control has to be reliable it must be carried out before taking the meat for processing or consumption,

To determine Ca in MDM the following methods are used incinerating of samples, the acid extraction of Ca, and Ca determination with flame photometre or with atomic absorption spectrophotometre (AAS). The latter method is regarded to be the standard one. Ashing samples is a long procedure and the use of the above equipment is expensive.

The method recommended by AOAC is the one based on the wet digestion and complexometric titration of calcium with EDTA. The method is quick but the results can be encumbered with an error resulting from visual subjective determination of the end point of titration by analytical chemists.

The ionometric methods with the use of an ion-selective electrode are treated as quick, simple, and objective methods of Ca determination in food. These methods have not already been used to analyse MDM. The procedures of direct measurement of calcium with the use of calcium-selective electrodes, in MDM samples, seem to be not precise enough. The ionometric titration, which is regarded to be the most precise analytic method with the use of ion-selective electrodes, can fulfil expectations. Conforming to the rules governing ionometry a titration error can not exceed 0,1% (Camman 1977).

The aim of this work was to examine possibilities of the use of a calcium-selective electrode to detect the complexometric titration end point to determine Ca content in MDM.

In order to compare results obtained by ionometric method with the results received by means of already applied methods calcium was determined in:
1) extracts of incinerated samples - with an atomic absorption spectrophotometre

- with a complexometric titration methods using the calcium-selective electrode or KALCES to detect the titration end point,

2) samples exposed to wet digestion - by a complexometric titration method using KALCES or calcium-selective electrode as an indicator of the end point.

MATERIALS AND METHODS: The material for experiments was MDCM with bone particles content 0,3% (sample 1) and 3,0% (sample 2).

Preparation of samples. A sample of total mass 1 kg was taken from different parts of 100 kg of MDM. It was mixed in a malaxer and divided into 4 equal parts. Out of each part 2 weighed portions were taken in order to examine them.

Incineration: a weighed portion of 20 g of meat was placed in a crucible and incinerated in temp. 450-500^{o}C in a muffle furnace. In the end of the incineration 1 cm^3 of concentrated nitric acid was added and it was incinerated till total evaportion and obtaining white powder (about 16 hours). Then the crucible with ashes was cooled in an exsiccator. After that calcium was extracted with 20 cm^3 of 1 M HCl, diluted with redestilled water to the volume of 500 cm^3.

Wet digestion was carried out in the way described in AOAC (AOAC 1984).

Calcium determination: 1) Atomic absorption spectrophotometric method - 1 cm^3 of a sample prepared by incineration was diluted in a 0.2% solution of La $(NO_3)_3$ up to the volume of 5 cm^3, and then the Ca content was determined with the spectrophotometre of atomic absorption ST9 TAYUNICAM. 2) Complexometric titration method: a) according to AOAC (AOAC 1984) with the distinction that for the determination of the titration end point, instead of hydroxy naphtol blue, KALCES was applied as an indicator (Wechler 1963); b) with the use of a calcium-selective electrode for a detection of the titration end point.

The calcium-selective electrode had a slope 25 mV per decade. In this last case the samples were titrated at ph 10-11 with constant magnetic stirring, measuring the potential 30-60 sec. after each addition of 0.02 M EDTA solution (0,1 cm^3 sample 1, and 0,5 cm^3 sample 2). The potential (E) was measured with the ph metre of N517 type. A calcium-selective electrode (with plastic membrane, on PCV basis) as an indicator electrode and a silver-silver chloride electrode (with double coating filled with 1 M KNO_3 as a reference electrode were used. Both electrodes were produced by the Ionoselective Electrode Works "Detector" in Warsaw.

Statistical analysis: The analysis of variance was used to compare the results obtained using different methods for the same sample.

RESULTS AND DISCUSSION: The ionometric titration curves were presented in fig. 1. Exact and reproducible results of determining the titration end point were obtained with the use of the second derivative method. The results of the Ca content in tested samples of MDCM were determined by different methods and presented in table 1.

No significant differences were found ($p = 0,05$) of Ca content caused by different preparation of samples or by the methods of the Ca maesurement. Scatter of results was lower in samples containing more bone particles. Thus the Ca content results obtained from MDCM by the ionometric titration method are comparable with those received by AAS method and recommended by AOAC. The error of precision in an ionometric method of the Ca determination does not exceed 5,5% like in the use of other methods. On the basis of the obtained results the following procedure was suggested in order to determine Ca in MDM by means of the ionometric titration.

Prepare the reagents and the wet digestion of MDM according to the way recommended by AOAC. Adjust the wet digestion solution to the ph 10-11 with KOH-KCN reagent. Titrate the samples (10 cm^3) with constant magnetic stirring with 0,02 M EDTA solution, using calcium-selective electrode as an indicator electrode and a silver-silver chloride electrode as a reference electrode. Construct titration curve - potential (E) vs. volume of EDTA (fig.1). Calculate the end point of titration (volume of titrant /A/) by the second derivative method. Calcutate the Ca content in tested samples of MDM according to the formula:

$$\%Ca = a\ M\ 10$$

where: A - volume of EDTA solution,
M - molarity of EDTA solution.

CONCLUSION: The ionometric determination of Ca in MDM is a simple and quick method (the time of carrying out a complete analysis is 2 hours). Taking into account the obtained results, accessibility of calcium-selective electrodes and their durability (can be used up to 6 months) it is possible to say that determination of Ca in MDM by the ionometric titration method should be widely used in the MDM control.

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Figure 1. Ionometric titration curves
(sample 2; wet digestion)

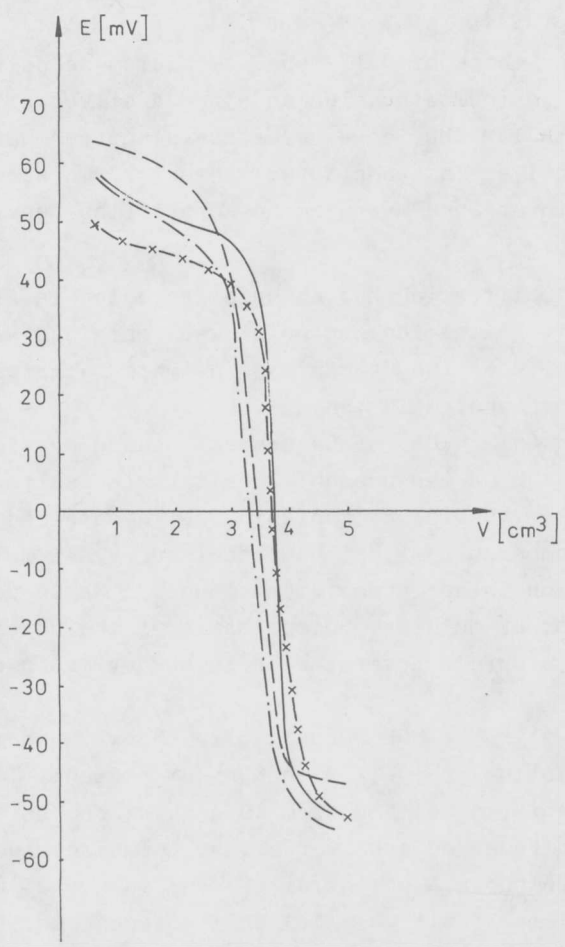

Table 1: Ca content in MDCM /%/

Method / Sample	Incineration			Wet digestion	
	AAS	Titration KALCES	Calcium-selective electrode	KALCES	Titration Calcium selective electrode
1	0,0605 s_x=0,0035	0,0634 s_x=0,0031	0,0590 s_x=0,0096	0,06656 s_x=0,0034	0,0672 s_x=0,0037
2	0,5885 s_x=0,00063	0,6403 s_x=0,0249	0,6475 s_x=0,0258	0,6597 s_x=0,0080	0,6422 s_x=0,0138

The data are the average values of 8 tests, s_x - standard deviation.