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ION-SELECTIVE ELECTRODE METHOD FOR THE DETERMINATION OF SODIUM CHLORIDE IN AKAWI CHEESE AND IN BRINE

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Abstract

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A method is described for the determination of the chloride content in Akawi cheese and in brine used for the production and preservation of this cheese. Cheese and brine were prepared using 0.1 mol/l nitric acid. The chloride ion selective electrode was used for measuring the chloride content. The method is sufficiently precise reliable and rapid. The mean standard deviation of the determination of the chloride content in cheese was 2%, in the brine 3.0 to 3.8%. The duration of one determination, including the sample preparation, was about 15 and 10 minutes for cheese and brine, respectively.

Salt content, comparison of methods.

Cheese salting is one of the important procedures of cheese production. Salting improves the taste of cheese, its consistence, hardens its rind, reduces some of the whey, partly eliminates the undesirable microflora and favourably affects further ripening.

The majority of cheeses are salted in a salt solution whose concetration, acidity and temperature differ according to the type of cheese. The concentration of salt solutions is usually 160 - 230 $g.kg^{-1}$ of sodium chloride, the temperature 10 - 15°C, the duration of salting ranging from a few hours to 1 - 5 days. The exact values of concentrations of the salt solutions, temperature and duration of salting for the individual cheeses are given in the technologies. In the course of salting sodium chloride diffuses into the cheese and part of the whey from cheese passes into the salt solution. That is why the concentration of salt in the solution decreases.

The sodium chloride content in cheese is nowadays being determined argentometrically using Mohr's or Volhard's method. These methods are inexpensive but relatively laborious (pipetting, filtration, titration). Their disadvantage is the subjective assessment of the point of equivalence.

Among the currently used analytical methods in food industry the use of the ion-selective electrode (ISE) is increasing.

Muldon and Liska (1971), Fernandes et al. (1982)

and Šucman (1982) have already described the determination of the chloride content in milk, Randell and Linklater (1972), Olmos and Echevaria (1983), Collomb and Steiger (1984), Steinhauser (1984) and Horký et al. (1984) in milk and infant formulas.

The advantage of the ion-selective electrode system as compared with the classical titration methods is especially that the determination is rapid, simple and that it saves the expensive silver nitrate used for titration.

The aim of the present study was to elaborate a rapid and sufficiently precise method for the determination of chloride in Akawi cheese and in the brines used for its production and storing.

The present authors have not yet found a method for the determination of sodium chloride in brine used in the production of Akawi cheese using the ion-selective electrode.

Materials and Methods

Akawi cheese and salt brine used in the production of the cheese were used as samples.

De-ionized water was used for the preparation of the solutions. Standard sodium chloride solutions were used in a concentration of 0.1 mol/l and 0.01 mol/l. All readings were made by means of a ion-selective electrode using the Chloride Ion Meter OP-261 (Radelkis, Hungary) with a chloride ion-selective electrode of a flow-through type placed in a thermostated aluminium block. The reference electrode in this system is the calomel electrode with a liquid junction filled with potassium nitrate.

For comparison we used Votoček's method of sodium chloride determination because it is used as a rapid method in laboratories of the dairy industry (Černá and Mergl 1971).

Determination of sodium chloride using the ion-selective electrode:

Preparation of the cheese sample:

10 g of cheese was rubbed thoroughly in a mortar with 30 ml of 0.1 mol/l nitric acid and filled up to 200 ml with 0.1 mol/l nitric acid in a volumetric flask, then shaked and part of the solution was filtrated. The filtrate was used for the measurements.

Preparation of the brine sample:

About 50 ml of 0.1 mol/l nitric acid was added to 1 ml of 0.1 mol/l silver nitrate in a 100 ml volumetric flask. One ml of brine (the brine is shaked well before use) was pipetted into this volumetric flask, shaken and filled up to 100 ml with 0.1 mol/l nitric acid. This prepared sample was filtrated and measured.

Preparation of standard solutions:

for cheese: STD_1 ... $1.00 \cdot 10^{-1}$ mol/l sodium chloride in 0.1 mol/l of nitric acid

STD_2 ... $1.00 \cdot 10^{-2}$ mol/l sodium chloride in 0.1 mol/l of nitric acid

for brine: STD_1 ... 1 ml of 0.1 mol/l silver nitrate is filled up in a volumetric flask to 100 ml with a solution of 0.100 mol/l of sodium chloride in 0.1 mol/l of nitric acid

STD_2 ... 1 ml of 0.1 mol/l silver nitrate is filled up to 100 ml in a volumetric flask with a solution of $1.00 \cdot 10^{-2}$ mol/l of sodium chloride in 0.1 mol/l nitric acid

Measurements:

Samples were measured on a Chloride Ion Meter OP-261 keeping to the instructions given by the producer. One minute after the intake of the sample and setting of the apparatus in the measuring position, the concentration was read on the scale. Each sample solution was measured twice. The mean value was taken for the calculations. If the concentration on scale of the apparatus is c_x, then we can calculate the concentration of chlorides as sodium chloride in the

(a) cheese sample: g NaCl/kg = c_x . 11.69
(b) brine sample: g NaCl/kg = (c_x + 0.1) . 58.44

Notes: (1) The concentration of Cl^- ions in standard solutions has been chosen in such a way that the concentration of Cl^- ions in the samples measured would be within the range limited by these standard solutions.

(2) The standard solution of 0.1 mol/l of sodium chloride can be prepared by dissolving 5.8443 g of sodium chloride p.a. in de-ionized water and filling up to mark in a volumetric flask to 1000 ml with deionized water

(3) After each measurement the electrode of the apparatus was cleaned by suction of de-ionized water for 10 seconds after which air was drawn in for about 10 seconds. Then the next sample or standard could be measured.

Results and Discussion

For the determination of chlorides in Akawi cheese the average value of the relative standard deviation of the present method was s_r = 2.0% ranging from 1.2% to 3.3%.

The concentrations after repeated measurements of the sample were as follows:

Measurement	n	c_{NaCl} (g/kg)	s_r (%)
1	5	75.2	2.1
2	3	77.9	1.5
3	3	77.5	1.3
4	6	77.1	1.5

The accuracy of the method was confirmed by a recovery test, i.e. the known amount of sodium chloride was added to the cheese extract so as to increase the concentration of the solution by 0.02 mol/l and/or 0.05 mol/l. The results were documented as follows:

Table 1
Verification of the accuracy of the determination of the content of chlorides in cheese

sample	n	$c_{Cl^-} . 10^2$ (mol/l)	found
cheese	6	6.77	-
cheese + 0.02 mol/l Cl^-	6	8.73	99.5
cheese + 0.05 mol/l Cl^-	6	11.06	94.0

It was found that deviations of the yields from 100% are insignificant on the significance level of = 0.05.

The determination of chlorides in brine was complicated because the results obtained were loaded with a significant error. Several variants of the brine sample preparation were checked. Satisfactory results were obtained by adding a small amount (1 ml) of 0.1 mol/l silver nitrate solution to the standard and sample solutions.

Using this method, an average of 205 g NaCl/l with a relative standard deviation of s_r = 3.8% was determined in a brine sample indicated as 18%. In a 24% brine sample, an average of 225 g NaCl/l was found, the relative standard deviation being 3.0%. The same as in cheese samples, the accuracy of the determination was verified using the test of recovery. Such standard additions of Cl^- to the brine sample prepared for measurement were made so as to increase the concentration by 0.02 mol/l and/or 0.05 mol/l.

The following table shows the results

Table 2

Verification of the accuracy of the method of the determination of the chloride content in brines

sample	n	c_{Cl^-}(mol/l) .10^2	found (%)
24% brine	6	3.88	-
24% brine + 0.02 mol/l Cl^-	6	5.88	100.0
24% brine + 0.05 mol/l Cl^-	6	9.43	106.2
18% brine	6	3.46	-
18% brine + 0.02 mol/l Cl^-	6	5.41	99.1
18% brine + 0.05 mol/l Cl^-	6	9.23	109.1

Also in this case can the measurements be considered to be sufficiently accurate, because deviations from 100% were insignificant.

On the basis of repeated measurements a permissible difference of two parallel determinations was calculated according to E c k s c h l a g e r et al. (1980) with a significance level of 95%.

For the cheese sample: 4.0 g/kg
For the brine sample: 3.0 g/kg

At the same time, with two following measurements from the same sample prepared (cheese extract and diluted brine) the values read from the scale of the apparatus may differ maximally by 0.2 . 10^{-2} mol/l. If this deviation is higher a third measurement should be done. If this third value agrees with one of the former two, the remaining one is not taken into account for the calculation. If the third value is between the two former ones, then the average of all three measured concentrations is used. If the two measurements do not differ by more than was the value given, then the average of both measurements was used for further calculations.

The duration of one determination, including sample preparation, was as follows:

for cheese: about 15 minutes
for brine: about 10 minutes.

The method is reliable, sufficiently precise and rapid.

Metoda stanovení chloridu sodného v sýru Akawi a v nakládacích lácích pomocí iontově selektivní elektrody.

Metoda je určena pro stanovení obsahu chloridů v sýru Akawi a v nakládacích lácích používaných k výrobě a uchovávání tohoto sýru.

Vzorky sýru i láku se zpracují pomocí 0,1 mol/l kyseliny dusičné. Měření obsahu chloridů se provádí chloridovou iontově selektivní elektrodou.

Vypracovaná metodika je dostatečně přesná, spolehlivá, a rychlá. Průměrná směrodatná odchylka stanovení obsahu chloridů v sýru byla 2%, v lácích 3,0 až 3,8%. Doba trvání jednoho stanovení, včetně přípravy vzorku, je pro sýr asi 15 minut, pro lák asi 10 minut.

Метод определения хлорида натрия в сыре Акави и в рассолах с помощью ионо селективного электрода

Метод предназначен для определения содержания хлоридов в сыре Акави и в используемых в процессе производства и хранения данного сыра рассолах.

Образцы сыра и рассола обрабатывают с помощью 0,1 моль/л азотной кислоты. Измерение содержания хлоридов проводят хлоридным ионо селективным электродом.

Разработанная методика отличается достаточной точностью, надежностью и быстротой. Среднее стандартное отклонение в определении содержания хлоридов в сыре составляло 2%, в рассолах - 3,0 - 3,8%. Продолжительность одного определения, включая подготовку образца, у сыра достигала около 15 минут, у рассола - около 10 минут.

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