COMPARISON OF DIFFERENT METHODS FOR DETERMINATION OF SODIUM CHLORIDE IN CHEESE

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Abstract: The content of NaCl (weight fraction of Cl⁻ ions, in %) was analysed in different cheeses, which were bought in supermarkets, and made by domestic manufacturers. Sodium chloride in cheese samples was analysed after the extraction of chloride by nitric acid solution. Concentration of chloride ions was potentiometricly determined, with the chloride selective electrode and titrimetricly by Volhard method. According to the results in the analysis of the content of NaCl in %, by different methods it was determined that the share of NaCl in % ranged from 0.66 to 4.43% (determined by potentiometric route) that is from 0.97 to 4.72% (determined by titrimetric route by Volhard method). The difference in received results in different methods is less if the share of NaCl, in % is higher than 3%. If the share is less than 3%, the difference in results rapidly increases, and the biggest difference is when the share is less than 1%. This analysis was done according to the results received by Volhard method, which is accepted as a standard method. As Volhard method is in connection with cheese resolving by intense oxidation means, azotic acid and potassium permanganate, obligatory in fume board (hood), it is not a practical method. On the other hand, the potentiometric method with usage of the chloride-selective electrode is very simple and gives reliable and reproductive results. In case of a small content of NaCl, in %, higher precision and accuracy of determination by chloride-selective electrode can be obtained by indirect measurement of chloride-ions (by standard addition method).

Key words: cheese, chloride ion-selective electrode (ISE), Volhard method, pickle.

Introduction

Salting is the last operation in the cheese making process. The salting process represents the significant way of food preserving, besides dehydration and

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fermentation (Fox, 2000). Such way of food preservation was used even in prehistory. In a way it is surprising that men discovered preserving effect of salt so early, having in mind that, unlike fermentation and dehydration, salting is not a spontaneous process. The presence of NaCl in food is expressed by increasing the osmotic pressure of water phase, as well as decreasing the water activity. These features, together with other preserving factors, influence minimizing the growth of pathogenic bacteria in cheese (Guinee and Fox, 2007).

The presence of table salt in cheese significantly contributes to its sensor features. However, besides its influence to the taste, salt presence in cheese directly or indirectly influences numerable processes which happen during its ripening. It can be said that salt influences almost all quality elements of cheese. The influence of salt on cheese ripening includes the following aspects (Puđa, 2009):
   - Sensor and nutritive features of cheese
   - Influence on development and activity of cheese micro flora
     (stimulating and inhibited effects)
   - Inhibition of activity of certain enzymes in cheese
   - Regulation of water content in cheese
   - Influence on protein status (phenomenon of structure and hydration).

On the other hand, certain technological operations have influence on salt content in cheese. Because of that, it is necessary to control this parameter in the final product, especially in making new kinds of cheese (Holsinger et al., 1967).

In human diet one of the basic roles of table salt is providing the necessary amounts of sodium which is essential for undisturbed development of metabolic processes in an organism. However, numerous health problems such as hypertension, osteoporosis and kidney stone emerge as the result of excessive salt consumption. The minimum of necessary daily consumption is usually estimated at 0.5 g of NaCl, while average daily consumption in developed countries reaches 10-12 g, which is considered to be exaggerated and dangerous dosage. The recommended adequate and safe dose for adults is from 2.8 to 8.3 g of NaCl per day (Katsiari et al., 2000). Salt content in different kinds of cheese can be found in a very wide interval (Table 1).

The reason for such wide interval of salt content is in the expressed variety of cheese in general. The most important influences that lead to the expressed variety of cheese can be explained by geographic factors, people's habits, agriculture organisation, especially cattle production (Puđa, 2009). The Mediterranean kinds of cheese are products which very often contain a large amount of salt. Increased presence of salt is partially justified by technological condemns, which are mainly adopted from the traditional production of brine curd cheese, and partially from the traditional cheese diet so characteristic for warm areas which are used to higher daily salt consumption.

Table 1. Average content of salt and water in certain kinds of cheese (Puđa, 2009).

Kind of cheese	NaCl (%)	Water (%)	Kind of cheese	NaCl (%)	Water (%)
Kamamber	2.5	52.5	Munster	1.8	41.8
Gorgonzola	3.5	44.0	Provolone	2.2	43.0
Gauda	1.6	41.5	Mocarela	1.0	48.0
Edam	1.6	41.4	Ementaler	0.7	37.2
Čedar	1.4	38.0	Romano	3.0	34.0
Parmezan	3.0	28.0	Mančego	1.5	38.0
Kačkavalj	2.2	42.0	Trapist	1.7	42.0
Sjenički sir	2.9	53.5	Travnički sir	3.2	51.0
Livanjski sir	1.9	36.5	Njeguški sir	2.5	42.0

The recommendation for the reduction of table salt consumption, especially in the sensitive groups of consumers, made some countries impose the obligation for classification of food according to sodium content, which must be written on a declaration (high, medium and low content of sodium) (Personal communication).

The obligation of declaring % NaCl raises the need for finding more practical, accurate, quicker and cheaper chemical method in the system of quality control, which would allow manufacturers to cope with these demands easily (Kindtstedt et al., 1983).

Because of this the analysis of salt content in cheese and usage of appropriate methods of analysis is very significant in process of cheese making. The choice of the adequate method is very important in order to establish the accurate salt content in cheese.

Potentiometry

Potentiometric titration is a volumetric method which measures the potential between two electrodes (the referent and the indicator electrode, in this paper - chloride-selective electrode) as a function of additional reagents volume. The basic principle of potentiometric titration is the determination of unknown concentration of analysed solution by titration with some standard solution where jumping (quick) change of indicator electrode potentials shows and determines the equivalence point of titration.

Instrumental determination of the final point has several advantages over the usage of visual detection-indicator. The visual determination of the final point of titration is influenced by subjective factors, and cannot be used in stirred and coloured solutions. Potentiometric methods of determination of the equivalence point of titration can be used not only with acid-basis titrations but in precipitation, oxidation-reduction and other titrations.

Titration curve has characteristic sigmoid shape (Figure 1). The part of curve with a maximal change of potential is the equivalence point of titration. The

equivalence point of titration can be determined more accurately from differential curve ΔE/ΔV where curve jump determines the equivalence point of titration (Rajković, 2007).
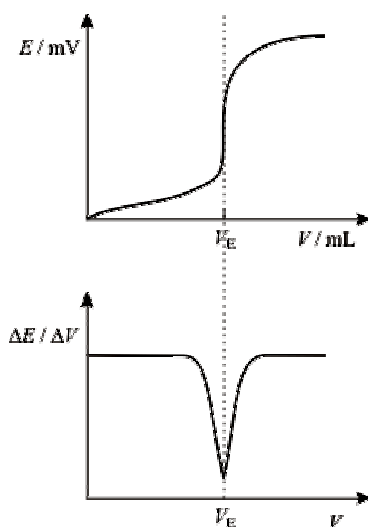

Figure 1. Potentiometric titration curve.

The aim of this work was to determine sodium chloride in cheese by different methods, classical, used for cheese analysis (Službeni list SFRJ, 1983; Crawford and Coppe, 1990) and method with the usage of chloride-selective electrode (Rajković and Novaković, 2007; Rajković and Sredović, 2009), as well as to compare the received results in order to suggest the referent method for cheese analysis.

Materials and Methods

The content of sodium-chloride is analysed in the following samples of cheese: sample 1. White cow cheese in brine (Dairy Mladost); sample 2. White cow semi fat cheese in brine (ZZ Stubal); sample 3. Sombor feta (Dairy Sombor); sample 4. Zlatar cheese (independent manufacturer); sample 5. White cow cheese in brine (Perkom doo), and sample 6. Sjenica cheese (independent manufacturer).

Characteristics of individual cheese: shape, size, look, cut view, taste, odour and consistency are given on manufacturer's declaration.

Sodium chloride in samples of cheese was determined after the extraction of chloride by potentiometer, with chloride-selective electrode and in titrimetric way, by classical Volhard method.

Reagents

- Primary standard solution of sodium chloride: 100 cm^3 of solution of 0.1 mol/dm^3 concentration was prepared by measuring the necessary mass of solid substance and dissolving it in appropriate measuring dish;
- Solution of silver nitrate: about 8.5 g of silver nitrate was measured on technical scale and dissolved in 500 cm^3 of distilled water; prepared solution was standardised with NaCl solution;
- Solution of potassium thiocyanate: about 6 g of substance was measured on technical scale and dissolved in 500 cm^3 of distilled water; prepared solution was standardised with silver nitrate solution;
- Solution of potassium permanganate: 7.5% solution was prepared by measuring 18.75 g of substance and dissolving it in 250 cm^3 of water;
- Solution of nitric acid: 60 cm^3 of nitric acid solution was measured in measuring cylinder, mass part (in %, 66% and 1.84 g/cm^3 density) and dissolved in 250 cm^3 of distilled water. Approximate concentration of prepared solution was 4 mol/dm^3;
- Concentrated solution of nitric acid.

Construction of calibration curve

Calibrating plot is mostly used for the determination of unknown concentration of analysed substance by the method of direct potentiometry. In this paper, the basic aim was to determine the limit concentration of usage of instrumental (potentiometric) method for determination of chloride ion content in analysed solution.

In order to construct calibrating plot, standard solutions of Cl$^-$ ions were prepared. First the working standard solution R_o of 1 mol/dm^3 concentration was prepared by dissolving the necessary amount of sodium chloride. Before measuring, sodium chloride was burnt until constant mass at 270°C. Solution of 0.10, 0.01 and 0.001 mol/dm^3 concentration of Cl$^-$ ion was prepared by dilution of the working standard solution. From such prepared standard solutions, solutions were prepared for making the calibrating plot in the following way: 5 cm^3 of standard solution of 1 mol/dm^3 of chloride ion was put by a pipette in a 100 cm^3 measurement dish, 10 cm^3 of 1 mol/dm^3 of nitric acid solution was added and solution was diluted by distilled water until measurement line. Nitric acid is added in order to regulate ion intensity of a solution. In the same way the other three standard solutions of chloride ion were diluted.

The potential in standard solutions and in samples was measured in the same way. 25 cm^3 of standard solution (sample) was put by a pipette to 50 cm^3 glasses, a magnetic nucleus was put inside and mixture speed was determined. The electrode was put into the solution and after five minutes the potential was read. In order to avoid the transfer of ions from one standard solution to the other (that is, from

sample to sample), measurements were done first in diluted solutions. Between measurements, electrodes were washed by distilled water, and drops which remained on electrodes were collected with cotton paper. Then the potential of standard solutions was measured, and the calibrating plot was constructed according to this result (Nenadović and Giljen, 2008; Barušić and Gluhović, 2009).

Preparation of samples for:

a) *potentiometric determinations*: (IDF Standard-88A, 1988) : between 2 and 3 g of samples were measured on analytical scale in 100 cm^3 glass and 30 cm^3 of distilled water, heated to 55ºC, was added. Pieces of cheese were resolved with a glass stick and the suspension was stirred. Then 3 cm^3 of 4 mol/dm^3 of nitric acid solution was added. Nitric acid besides adjusting ionic intensity simultaneously influences sedimentation of proteins from a sample. The glass stick was washed with 20 cm^3 of warm distilled water and the magnetic nucleus was put into it. Received suspension was stirred with magnetic whisk with magnetic nucleus, until it cooled at room temperature.

All potentiometric measurements were done on an ion-meter type C863 (Consort, Belgium). The combined chloride-selective electrode (type ISE24B) was used as the sensor electrode.

The results of potentiometric measurement were compared with classical titrimetric method, determination of chloride ion with Volhard method. Volhard method has been chosen because it allows titration of chloride ions in acid environment, which was obtained during the preparation of analysed samples.

b) *determination by Volhard method*: (Rajković and Sredović, 2009; Rajaković et al., 2000) results of potentiometric measurement were compared with classical titrimetric method, determination of chloride ion, by Volhard method.

About 2.0000 g of samples were measured on analytical scale in a 250 cm^3 Erlenmeyer, and 25.00 cm^3 of $AgNO_3$ solution and 25.00 cm^3 of concentrated nitric acid solution were added. The content in the Erlenmeyer was heated untill boiling, and then the solution of potassium permanganate was added. The solution of permanganate was added in small aliquots, until the content in the Erlenmeyer obtained permanently brown colour. Then glucose was added in order to decolour solution and 100 cm^3 of distilled water. The solution in the Erlenmeyer was cooled, 5.00 cm^3 of saturated solution of indicator $FeNH_4(SO_4)_2$ was added as well as surplus of silver nitrate re-titrated by solution of potassium thiocyanate till reddish brown colour.

Standard solutions of silver nitrate and potassium thiocyanate as well as standardization of these solutions were done according to familiar procedure (Rajković and Sredović, 2009; Rajaković et al., 2000). Samples were titrated in a way to put 25.00 cm^3 of solution by pipette in a 250 cm^3 Erlenmeyer, 5.00 cm^3 of

HNO_3 of 6 mol/dm^3 concentration was added and 15.00 cm^3 of standard solution of silver nitrate was added from burette. Solution was left for five minutes, and formed sediment of silver chloride was filtered through filter paper (black band) in a 250 cm^3 Erlenmeyer, 2.00 cm^3 of saturated solution of $FeNH_4(SO_4)_2$ was added and surplus of silver nitrate was re-titrated by solution of potassium thiocyanate.

In order to evaluate precision (accuracy) and reproductivity of suggested methods for samples preparation, five tests of analysed cheese were measured. The results of statistic processing of data are shown through standard deviation (σ), medium deviation (σ_m) and relative mistake of average values (Lacroix, 1978; Rajković, 2007) and relative error. For accurate value of measurement was conditionally taken value received by Volhard method, which is recommended for determination of chloride in cheese (Službeni list SFRJ, 1983).

Results and Discussion

The received calibrating plot for the determination of the content of chloride ions in samples of cheese of different manufacturers is shown in Figure 2. From the calibrating plot can be seen that the curve starts at concentration under 10^{-3} mol/dm^3, so in lower concentrations of chloride ions in low concentration samples, the unreliable results of analysis can be received.
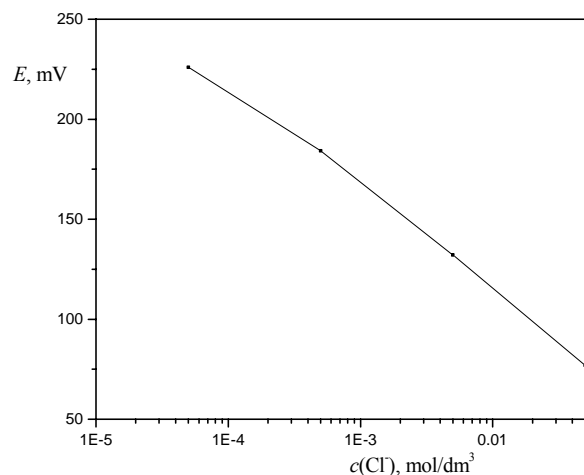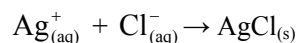

Figure 2. Calibration curve for chloride ion.

The determination of chloride in cheese by potentiometric titration, is based on the reaction between extracted chloride ion and silver(I)-ion (Ag$^+$) from silver nitrate ($AgNO_3$):

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$

During the titration, the concentration of chloride ion in solution decreases due to forming of hardly dissolving silver chloride. Because of that the potential of electrode gradually increases, until the moment when it is fully titrated with chloride ion, which starts sudden increasing of the electrode potential. Further adding of silver nitrate solution makes the potential of electrode, which is sensitive towards ions of silver (I) whose concentration in solution slowly rise, slowly increase again. The titration curve is received when the change in potential of ion-selective electrode shows, depending on volume of added $AgNO_3$. The volume $AgNO_3$ at the equivalence point of titration can be calculated from the jump on titration curve by the graphical method.

As this is very complicated, titration curves, shown in Figure 3, are made by computer programme Origine 6.1.

sample 1   sample 2

sample 3   sample 4

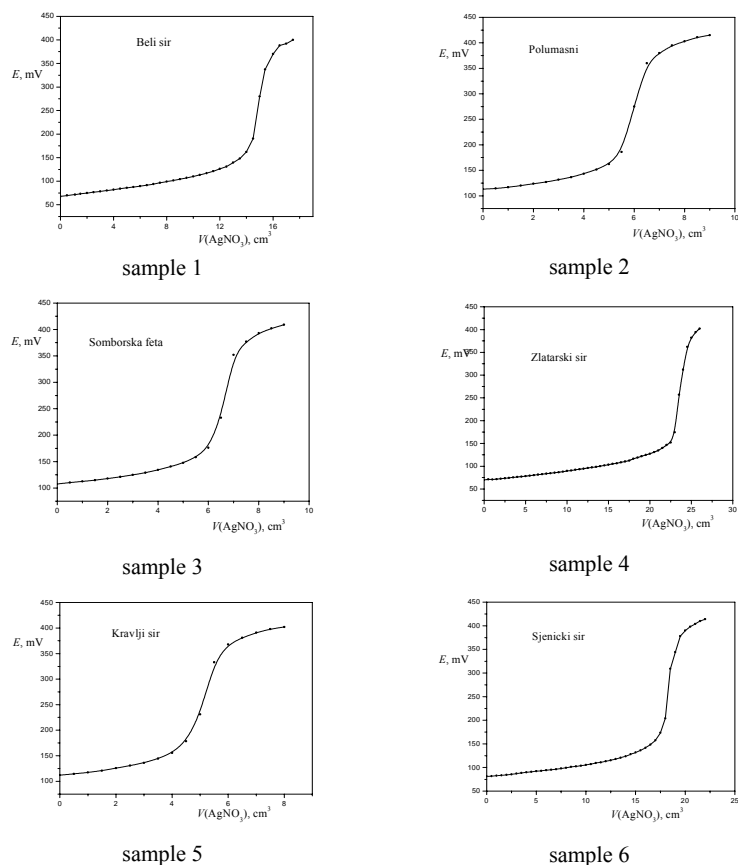sample 5   sample 6

Figure 3. Potentiometric titration curves for chloride
ion in cheese determination.

Curves shown in Figure 4 are made by the differentiation of received titration curves. They have a distinctive jump which corresponds to spent volume of silver nitrate at the equivalence point of titration.

sample 1

sample 2
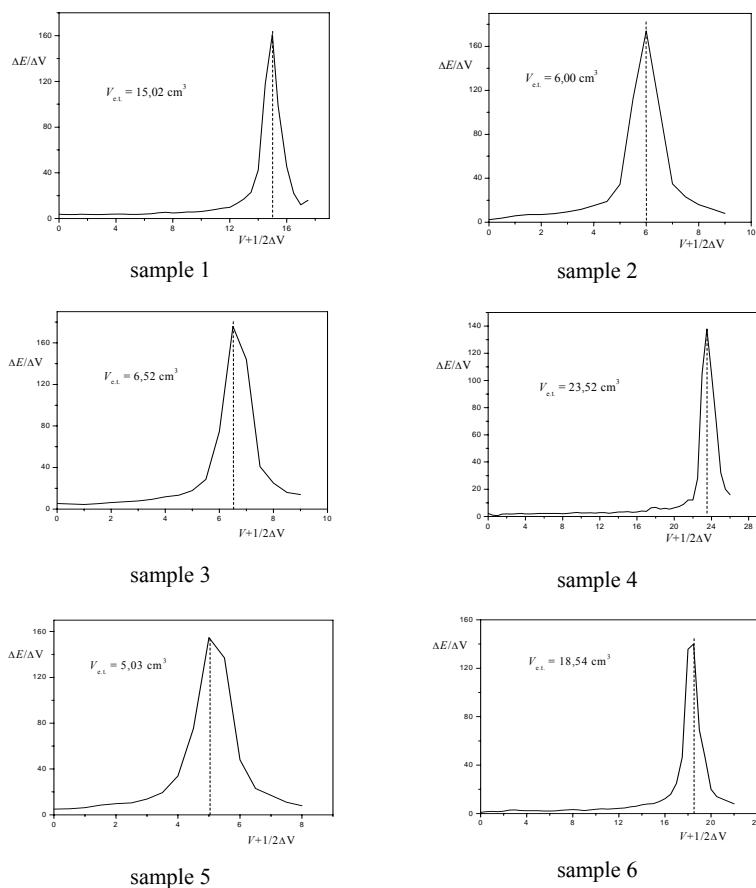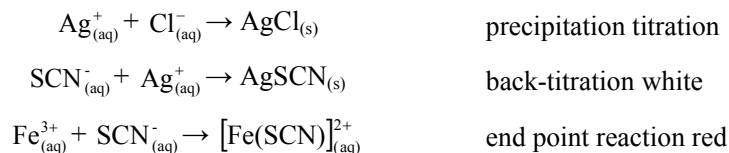

sample 3

sample 4

sample 5

sample 6

Figure 4. Differential potentiometric titration curve.

Mass share of sodium chloride (in %) is calculated in the following way:

$$\omega(\text{NaCl}) = \frac{c(\text{AgNO}_3) \cdot V_{et}(\text{AgNO}_3) \cdot M(\text{NaCl})}{m_{uz}} \cdot 100\,\%$$

and the results are shown in Table 2. And the results of sodium chloride determination by Volhard method are shown in Table 2.

The reaction during titration can be shown in the following way:

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)} \qquad \text{precipitation titration}$$

$$SCN^-_{(aq)} + Ag^+_{(aq)} \rightarrow AgSCN_{(s)} \qquad \text{back-titration white}$$

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightarrow \left[Fe(SCN)\right]^{2+}_{(aq)} \qquad \text{end point reaction red}$$

According to shown reactions, the mass of sodium chloride, in measured mass of samples, can be calculated as:

$$m(Cl) = [c(AgNO_3) \cdot V(AgNO_3) - c(KSCN)\, V(KSCN)] \cdot M(NaCl)$$

and fraction of sodium chloride, in percents is:

$$\omega(NaCl) = \frac{m(Cl)}{m_{uz}} \cdot 100\,\%$$

Table 2. Statistical processing determination of content of NaCl using different methods in different samples of cheese.

Sample	Number of measurements	Found value ω(NaCl), using ISE, in %	Standard deviation, in %	Relative mean deviation, in %	Found value ω(NaCl), according to Volhard method, in %	Error (in %)
White cow cheese in brine (sample 1)	5	3.31	0.051	3.86	3.36	1.49
White cow semi fat cheese in brine (sample 2)	5	1.24	0.035	6.94	1.47	15.65
Sombor feta (sample 3)	5	1.86	0.036	4.82	2.11	11.85
Zlatar cheese (sample 4)	5	4.43	0.026	1.48	4.72	6.14
White cow cheese in brine (sample 5)	5	0.66	0.062	23.51	0.97	31.96
Sjenica cheese (sample 6)	5	3.73	0.044	2.90	3.82	2.35

[*] The value received by Volhard method, which is recommended for determination of chloride in cheese, was conditionally used as an accurate value of measurement.

According to the results in analysis of sodium chloride content in %, by different methods, it was determined that the share of sodium chloride in % ranged from 0.66 to 4.43% (determined by potentiometric route), that is, from 0.97 to 4.72% (determined by titrimetric route by Volhard method).

Difference in received results in different methods is less if the fraction of sodium chloride, in % is higher than 3%. If the share is less than 3%, the difference in results rapidly increases (over 10%), and the biggest difference is when the share is less than 1% (even 30%).

Conclusion

The content of NaCl (weight fraction of Cl^- ions, in %) was analysed in different cheeses, which were bought in supermarkets, and made by domestic manufacturers. Sodium chloride in cheese samples was analysed after the extraction of chloride by azotic acid solution.

Concentration of chloride ions was potentiometricly determined, with the chloride selective electrode and titrimetricly by Volhard method. The results of statistic processing of data are shown through standard deviation (σ), medium deviation (σ_m) and relative mistake of average values and relative error, in %.

According to the results in the analysis of the content of NaCl in %, by different methods it was determined that the share of NaCl in % ranged from 0.66 to 4.43% (determined by potentiometric route) that is from 0.97 to 4.72% (determined by titrimetric route by Volhard method).

Difference in received results in different methods is less if the share of NaCl, in % is higher than 3%. If the share is less than 3%, the difference in results rapidly increases (over 10%), and the biggest difference is when the share is less than 1% (even 30%).

This analysis was done according to the results received by Volhard method, which is accepted as standard method. As Volhard method is in connection with cheese resolving by intense oxidation means, nitric acid and potassium permanganate, obligatory in fume board (hood), it is not a practical method.

On the other hand, the potentiometric method with usage of the chloride-selective electrode is very simple and gives reliable and reproductive results. In case of a small content of NaCl, in %, higher precision and accuracy of determination by chloride-selective electrode can be obtained by indirect measurement of chloride-ions (by standard addition method).

Acknowledgements

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POREĐENJE RAZLIČITIH METODA ODREĐIVANJA NATRIJUM-HLORIDA U SIRU

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R e z i m e

Sadržaj NaCl (udeo Cl⁻-jona, u %) analiziran je u sirevima domaćih proizvođača. Natrijum-hlorid u uzorcima sireva određivan je nakon ekstrakcije hlorida rastvorom azotne kiseline. Koncentracija hlorid-jona je određivana potenciometrijski, pomoću hlorid-selektivne elektrode i titrimetrijski klasičnom Folhardovom metodom. Prema rezultatima određivanju sadržaja NaCl, u %, različitim metodama utvrđeno je da se udeo NaCl, u %, kreće u oblasti od 0,66 do 4,43% (određeno potenciometrijskim putem) odnosno od 0,97 do 4,72% (određeno titrimetrijskim putem Folhardovom metodom). Odstupanja u dobijenim rezultatima različitim metodama su utoliko manja ukoliko je udeo NaCl, u %, veći od 3%. Ukoliko je udeo ispod 3%, razlika u rezultatima se rapidno povećava, dok je najveća razlika ukoliko je udeo manji od 1%. Ova analiza sprovedena je na osnovu rezultata koji su dobijeni Folhardovom metodom, koja je prihvaćena kao standardna metoda. Kako je Folhardova metoda povezana sa razaranjem sira u jakim oksidacionim sredstvima, azotnom kiselinom i kalijum-permanganatom, obavezno u digestoru, nije praktična metoda. Sa druge strane, potenciometrijska metoda uz upotrebu hlorid-selektivne elektrode je veoma jednostavna i daje pouzdane i reproduktivne rezultate. U slučaju malog sadržaja NaCl, u %, veća preciznost i tačnost određivanja hlorid-selektivnom elektrodom može se postići indirektnim merenjem hlorid-jona (metodom standardnog dodatka).

Ključne reči: sir, hlorid jon-selektivne elektode (ISE), Folhardov metod, salamura.

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