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INVESTIGATION OF THE POLYCONDENSATION REACTION OF WASTE CHEMICALS IN ORDER TO USE THEM TO PRODUCE ION-EXCHANGE POLYMERS

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Abstract: *In this article, we investigated the polycondensation reaction of cube wastes from the Shurtan gas-chemical complex with furfural as a function of reaction temperature, catalyst existence and concentration, starting substance ratio, and other factors. This research resulted in the creation of a new polymer that was used as a polymer matrix for the introduction of ionogenic groups. The composition of cubic waste (CW) from the Shurtan Gas Chemical Complex (SGCC) has been determined by chromatographic analysis. A mixture of CW-1 and CW-2 in equal weight ratios was used to produce the polymer (this mixture will hereinafter be referred to simply as CW). The effect of reaction temperature, catalyst type and concentration, and CW/furfural ratio on the polycondensation process was studied. The use of a polymer collected under ideal conditions as a polymer matrix for the introduction of ionogenic groups was possible. The effect of reaction temperature, concentration and nature of the catalyst and the ratio of the starting substances was investigated in order to establish the optimum conditions for polymer synthesis. The polycondensation reaction of furfural with CW was carried out at 70C, 80C, 90C, weight ratio of furfural to CW was 1÷1,5 in the presence of catalyst HCl in an amount of 5% by weight of starting substances. The optimum polycondensation temperature is 70-80C, at which a cationite with a high exchange capacity is obtained in a relatively short reaction time of polycondensation. Temperature 80C there is a linear increase in the reaction rate constant with the concentration of the catalyst HCl in the reaction mixture It is shown that the concentration of the catalyst accelerates the polycondensation process n leads to a polymer with high cross-linking density and low swell ability. The optimal concentration of HCl in the starting materials is 5% by weight. A uniform reaction is ensured at this HCl catalyst concentration, resulting in cationite with adequate physical and chemical properties.*

Key words: *ionite, furfural, polycondensation, ionogenic group, phosphorus cationite, cube residue, ion exchange, polymer matrix.*

INTRODUCTION. The Republic of Uzbekistan's rapid growth of different sectors of the national economy (chemical hydrometallurgical, water treatment, etc.) is largely dependent on the development and application of modern science and technology achievements. All of this is linked to one of the most pressing issues in contemporary high-molecular compound chemistry: the design and advancement of ion-exchange polymer systems, as well as further research into theoretical bases for controlling the efficiency properties of the resulting ion-exchangers [1].

While significant progress has been made in the production of ion-exchange materials in recent years, many of them, especially those of the polycondensation kind, do not meet the needs of industries such as hydrometallurgy, wastewater and industrial solutions treatment, water treatment, and so on in terms of availability, performance, sorption, and selectivity, necessitating the development of new ion-exchange materials. In addition, almost all of the ion exchangers used in manufacturing are still manufactured from CIS countries.

In the light of the above it is of practical and theoretical interest to find new ion-exchange polymers and effective methods of modification of existing ion-exchange resins. In this connection production of new ion-exchange polymers on the basis of waste chemicals and their further use in processes of industrial and waste water treatment will probably improve technical and economic performance of many industries, reducing environmental pollution in particular.

In this regard, research into the disposal of toxic waste and its eventual usage in the manufacture of modern ion exchangers, as well as their subsequent use in the treatment of different waters, is of considerable significance. The synthesis of ion-exchange polymers from chemical processing facilities, such as the Shurtan gas-chemical complex, is of functional, environmental, and economic importance. Another type of pentosan-containing raw materials for ion-exchange synthesis is the heterocyclic aldehyde-furfural, a secondary product of the hydrolysis industry for which there are vast stocks of pentosan-containing waste from the cotton-cleaning and agricultural industries in Uzbekistan.

Most polycondensation-type ion exchangers are known to be produced by the interaction of phenol, resorcinol, pyrogallol, ox benzoic acid with formaldehyde [2]. However, a common disadvantage of these ion exchangers is their low thermal, chemical resistance and mechanical strength [3]. By replacement of formaldehyde by furfural, obtained ion-exchange polymers with sufficiently high resistance to chemical, thermal, radiation and mechanical influences [4]. Based on the above, this work is devoted to obtaining ion-exchange polymers by interaction of cube wastes of Shurtan gas-chemical complex and furfural, the study and research of their performance properties, with a further search for specific objects of their practical application in the national economy [5].

RESEARCH METHODS. Chromotographic analysis of cubic waste from the Shurtan gas-chemical complex revealed that it primarily consists of cyclohexanone, cyclohexane, and linoleic acid, which has carboxyl groups in its structure (Fig. 1,2). We investigated two groups of cubic wastes (CW) using gas-liquid chromatography [5]. A GC/MS6890/5973 chromatograph with a mass selective detector was used to conduct the tests.

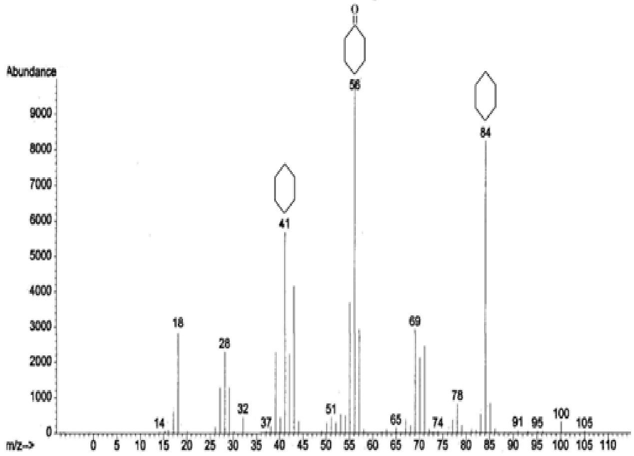


Figure 1. Chromatogram of cubic waste from the Shurtan gas-chemical complex (CW-1)

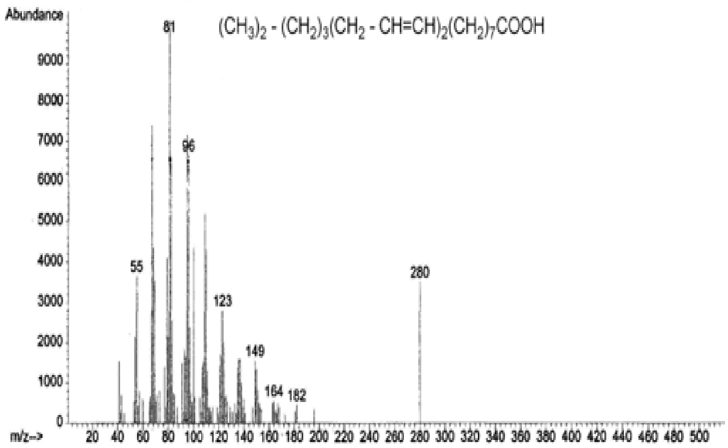


Figure 2. Chromatogram of cube waste from the Shurtan gas-chemical complex (CW-2)

Discussion of the results. The identification of the composition of KO was based on data we obtained from the technical laboratory of the Shurtan Gas Chemical Complex (SGCC), which are presented in Table 1. The cubic waste is a brown colored mass with a pungent stifling odor.

Table 1.
Physical and chemical characteristics of the waste composition of the Shurtan gas-chemical complex.

CW-1

Cyclohexanone	15,0 %
Cyclohexane	15,0 %
Density	800-900 kg/m^3
pH solution	10,5
Flashing temperature	180 ^{0}C

CW-2

Linoleic acid	8,7 %
Low molecular weight polyethylene	91,3 %
Density	638 kg/m^3

The pyrolysis preparation section of ethylene production in the cube of the DA-1201 cheloc column is represented by an aldehyde and ketone group condensation. These groups are formed in the pyrolysis stage called "yellow oil". The resulting "yellow oil" is periodically removed from the nearby alkaline washing section into special containers and taken out of the unit.

The copolymerisation of ethylene with butene-1 using Ziegler-Natta catalysts in cyclohexane solution produces a liquid residue which is a light yellow suspension with a pungent characteristic odour. On settling, it stratifies and a white sludge appears. This waste is produced at a rate of 100-120 kg/hour.

Thus, the present work is devoted to investigation of polycondensation reaction of CW and furfural followed by chemical transformation of synthesized polymer in order to obtain ion-exchange polymers. A mixture of CW-1 and CW-2 in equal weight proportions was used for polymer production (hereinafter this mixture will be simply called CW).

The effects of reaction temperature, concentration and nature of the catalyst and the ratio of the starting substances were investigated in order to establish the optimum conditions for polymer synthesis.

Influence of the reaction temperature on the polycondensation process of furfural with CW.

The polycondensation reaction of furfural with CW was carried out at 70□C, 80□C, 90□C, weight ratio of furfural to CW was 1÷1,5 in presence of catalyst HCl in an amount 5 % of initial substances weight. Fig.3 shows the dependence of conversion degree on reaction time at different temperatures.

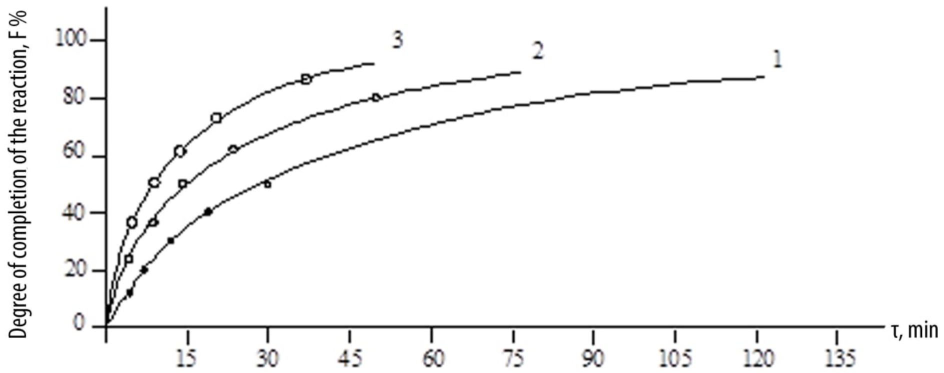


Figure 3. Degree of completion (F) of polycondensation of CW with furfural from reaction time at different temperatures, catalyst HCl, 5 %. 1-70□C; 2-80□C, 3-90□C.

Based on the results obtained using the second order equation, the reaction rate constant was calculated (Table 2).

Table 2.

Value of the rate constant for the reaction of polycondensation of CW with furfuryl at different temperatures, catalyst HCl, 5 %

Reaction time, min	Temperature, □C K-10^{-3} min¹		
	70 ^{0}C	80 ^{0}C	90 ^{0}C
10	1,264	2,25	4,25
20	0,143	1,95	4,08
30	0,853	1,76	3,12
40	0,685	1.58	2,42
50	0,567	1,35	2,43
60	0,478	0,96	2,17

As can be seen from Table 2, the rate constant is variable and decreases during the reaction. The decrease of rate constant in the process of polycondensation of furfural with CW is influenced by a sharp increase in viscosity of the system during the reaction, which leads to an increase in diffusion difficulties [6].

Table 3 shows the effect of the reaction temperature on the exchange capacity of the synthesized cationic exchange resins.

Table 3.

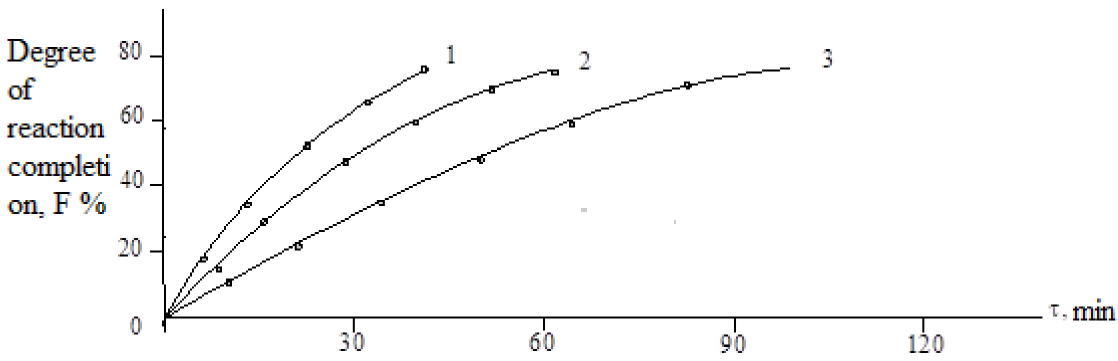
Influence of reaction temperature on physical-chemical properties of phosphorous cationic exchange resins based on polymer obtained by polycondensation of furfural and KO (weight ratio furfural to CW 1÷1,5)

Reaction temperature, □C	Polycondensation reaction time, min	Specific volume of swollen cationite, ml/gr	Exchange capacity for 0.1 N NaOH solution, mg-ekv/gr
60	300	2,2 – 2,4	5,8 – 5,6
70	180	2,4 – 2,7	5,6 – 7,0
80	120	2,8 – 3,1	6,1 – 6,0
90	60	2,2 – 2,3	5,8 – 6,0

As can be seen from Table 3, the optimum polycondensation temperature is 70-80 ^{0}C, at which a cationite with a high exchange capacity is obtained in a relatively short reaction time of polycondensation [7].

Influence of the ratio of starting substances in polymer synthesis based on polycondensation of CW and furfural on the properties of phosphorus cationic acid.

The polycondensation reaction of CW with furfural was carried out at different weight proportions of the starting substances and constant reaction temperature - 80□C, in the presence of a catalyst - HCl in an amount of 5% by weight of the starting substances.



1-1:1,5; 2-1:1,75; 3-1;2

Figure 4. Degree of completion (F) of polycondensation of furfural with CW from reaction time at a weight ratio of CW to furfural catalyst HCl, 5%.

Fig. 4 shows dependence of polymer conversion degree at different ratios of CW to furfural 1÷1,5, 1,75÷1, 1÷2.

The reaction rate constant calculated from the second order equation decreases its value during the polycondensation reaction. The value of the rate constant at different ratios is shown in Table 4. As the polycondensation reaction is completed, the reaction rate constant decreases. Variation of amount of furfural in reaction mixture leads to formation of cationite with different physicochemical and mechanical properties [8-10].

Table 4.

Value of the rate constant for the reaction of polycondensation of CW with furfuryl at different ratios of the starting components

Duration of reaction, min	Weight ratio of CW to furfural, $K*10^{-3}$ min^{-1}		
	1:1,5	1:1,75	1:2,0
10	1,5	2,14	4,8
20	1,05	1,90	4,05
30	0,92	1,67	3,87
40	0,75	1,42	2,94
50	0,41	1,26	2,09
60	0,37	0,96	2,00

The effect of the ratio of the starting substances on the properties of the cationic exchange resins is shown in table 5.

Table 5.

Influence of feedstock ratio on the properties of the obtained phosphate cationic acid (reaction temperature-80 ^{0}C)

Weight ratio of KO to furfural	Specific volume of swollen cationite, mg/gr	Static exchange capacity for 1 N NaOH solution, мг-ekv/gr	Mechanical strength, %
1,5:1	2,8	5,6-5,8	99.8
1,75:1	3,2	6,5-7,0	99,5
2,0:1	2,6	6,2-6,0	99,1

Table 5 shows that the exchange capacity and specific volume of the swollen cationite increases with decreasing amount of furfural. Increasing the amount of furfural increases the number of transverse bonds, which increases the mechanical strength. Based on the research results the optimum ratio of CW to furfural was taken as 1.5:1 weight ratio, which provides mechanical strength of cationite in combination with good exchange capacity and swell ability [11-13].

Influence of the nature and concentration of the catalyst in the production of the polymer matrix on the properties of the phosphorus cationic acid.

In the polycondensation reaction of CW and furfural we used different catalysts - zinc chloride, concentrated hydrochloric acid (Table 6).

Table 6.

Influence of the nature of the catalyst in the synthesis of a CW-based polymer in furfural on the properties of the phosphorus cationite (weight ratio furfural: CW 1:1.5; temperature-80 ^{0}C)

The nature of the catalyst	Duration of reaction, hour	Exchange capacity by 1 N NaOH solution, mg-ekv/gr	Specific volume of swollen cationite, mg/g	Mechanical strength, %
$ZnCl_2$ (crystalline anhydrous)	20	5,2-5,6	2,8-3,0	90-92
Hydrochloric acid concentrated	6	6,5-6,8	3,2-3,0	95-98

Table 6 shows that a cationite with sufficiently high mechanical strength is obtained when concentrated hydrochloric acid is used as a catalyst.

In order to study the influence of catalyst concentration on polycondensation of CW with furfural, the reaction was carried out in the presence of catalyst HCl (conc) with concentration 1.5; 2.5; 3.0; 5.0; 6.0 % of reaction mass weight [14-16]. The weight ratio of furfural to CW was 1:1.5 and the reaction temperature was 80 ^{0}C. A study of the effect of catalyst concentration on the polycondensation process showed that an increase in catalyst concentration led to an acceleration of the reaction (Figure 5).

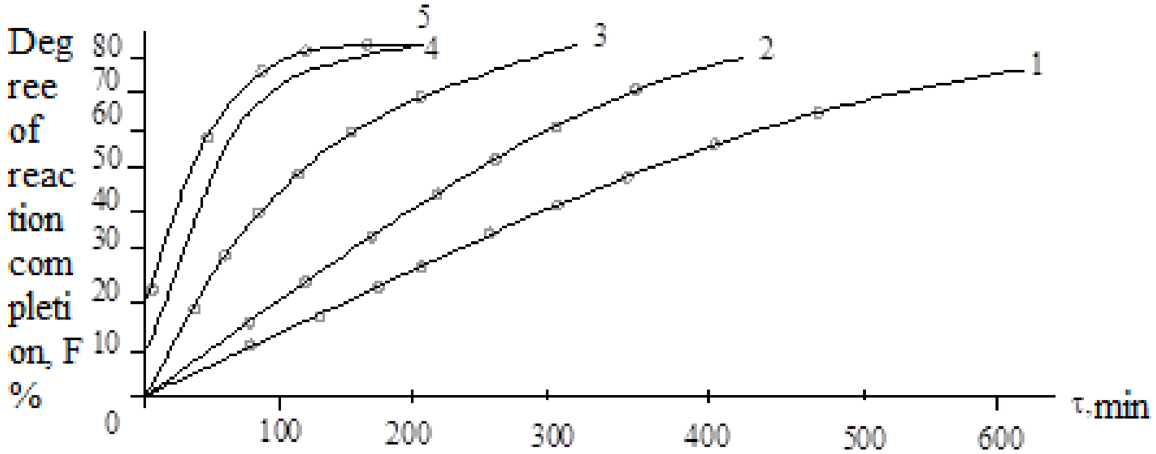


Figure 5. Degree of completion (F) of polycondensation of furfural with CW over time as a function of catalyst concentration.
1-1,5 %; 2-2,5 %; 3-3 %; 4-5 %; 5-6 %.

As can be seen from figure 6, the dependence of $\frac{1}{a-b} In \frac{(a-x)\cdot b}{(a-x)\cdot a}$ on τ (time) is straightforward, with a degree of polymerization of up to 40%.

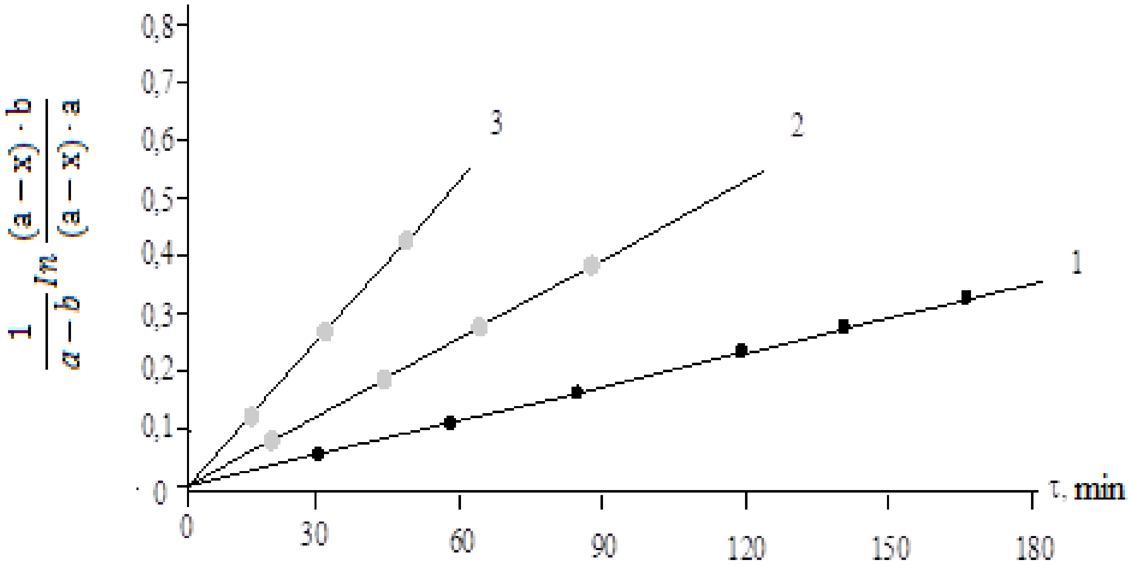


Figure 6. Change in the logarithm of reactant concentration with time as a function of catalyst concentration.

It should be noted that at 80 ^{0}C there is a linear increase in the reaction rate constant with the concentration of the catalyst HCl in the reaction mixture (figure 7).

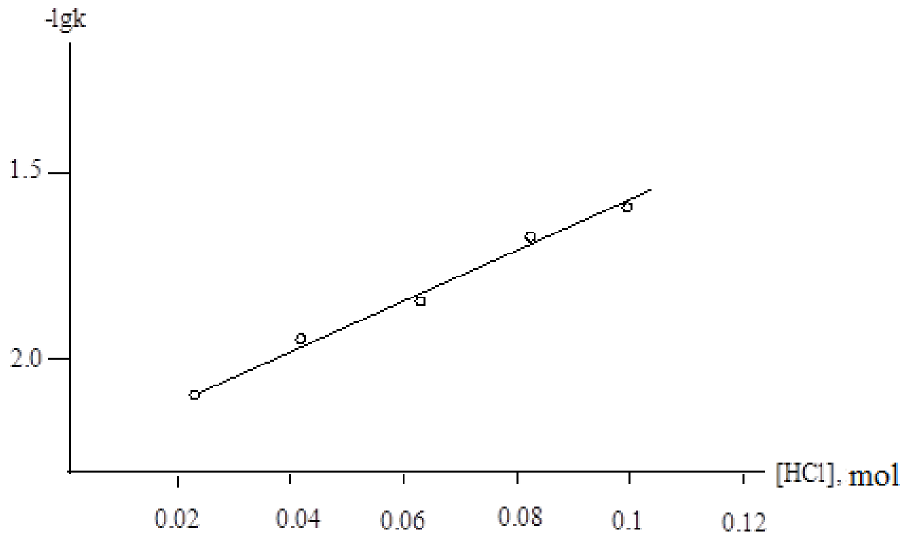


Fig.7. Dependence of the reaction rate constant on the concentration of HCl.

The results of a study on the effect of the catalyst concentration on the duration of the polycondensation reaction on the exchange capacity and swell ability of the cationic exchange resins are shown in Table 7.

Table 7.

Influence of HCl catalyst concentration on the properties of phosphate cationic exchange resins

Quantities of catalyst HCl by weight of starting substances, %	Duration of reaction, hour	Swell ability of cationic exchange resins in water, %	Exchange capacity of 1 N NaOH solution, mg-ekv/gr
1,5	10	128	5,0-5,6
2,5	7	132	5,0-5,1
3,0	7,5	158	5,2-5,6
5,0	5	152	6,5-7,0
6,0	5	150	6,3-6,5

Table 7 shows that the catalyst concentration accelerates the polycondensation process and results in a polymer with a high cross-linking density and low swelling.

The optimum concentration of HCl is 5 % by weight of the starting substances. At this concentration of HCl catalyst a homogeneous reaction is ensured, resulting in cationite with sufficiently high physical and chemical properties (Table 8).

Thus, on the basis of the carried-out researches we determined optimal conditions of polycondensation reaction of KO with furfural. The properties of phosphorus cationic exchange resin obtained from synthesized polymer are given in table 8.

Table 8.

Properties of phosphonic acid cationic exchange resins synthesized by the polycondensation of KO and furfural.

Indicators	
Humidity, %	25
Bulk weight, gr/ml	0,68
Specific volume of water-swollen cationite in H-form, ml/g	3,5
Static exchange capacity for 0.1N solution, mg-ekv/gr:	
NaOH	6,5-7,0
NaCl	1,1-1,2
$CaCl_2$	2,1-2,3
$CuSO_4$	1,3-1,4

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DETERMINATION OF MAIN INGREDIENTS IN MILK USING AKM-98 MILK ANALYZER

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Abstract: The aim of the research is a quick, easy, economical way to determine milk content. Nowadays, the production of cow's milk is dominant, but the original quality of non-bovine milk, such as camel's milk, is now better described and is experiencing growing interest. Camel's milk, goat's milk, ewe's milk and buffalo's milk have received special attention because