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CONTENTS

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METHODS FOR PREPARING RESEARCH SAMPLES IN ANALYTICAL CHEMISTRY

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Resume: Purpose: This study presents an effective technology for the preliminary preparation of test samples in analytical chemistry. It examines the influence of pH on the determination of organic compounds in aqueous solutions and acetonitrile through techniques such as extraction, freezing, and centrifugation. The technological capabilities and advantages of preparing samples for quantifying organic substances in aqueous media are demonstrated.

Gas chromatography, single-step extraction, and sample freezing combined with centrifugation were utilized in this process. The minimum detection limits in drinking water are as follows (in mg/l): aniline 0.1, diphenylamine 0.05, caffeine 0.015, and lindane 0.001. The developed technology is simple and can be executed in a single stage, with the total duration of sample preparation not exceeding 30 minutes.

Method: Chromatography was selected as the research method. This technique is utilized to identify organic compounds in water, food products, wine, and tea. Prior to conducting the research, it is essential to prepare the research sample. An alternative approach is cryoextraction of the research material. The proposed method is known as the extraction freezing method (EF). In this method, extraction occurs simultaneously with freezing: components are extracted at low temperatures from the liquid phase to the solid phase of ice. Freezing the extract can significantly enhance the concentration of analytes, streamline the procedure, and reduce both the time required for sample preparation and associated material costs.

Results: This study demonstrates the technological capabilities and advantages of sample preparation for measuring organic substances in aqueous media. Techniques such as gas chromatography, one-step extraction, and sample freezing combined with centrifugation are employed. The minimum detection limits in drinking water are as follows: aniline at 0.1 mg/l, diphenylamine at 0.05 mg/l, caffeine at 0.015 mg/l, and lindane at 0.001 mg/l. The technology developed is straightforward and can be carried out in a single step. The total duration for sample preparation does not exceed 30 minutes.

Conclusion: This study presents a novel method for separating organic substances from aqueous solutions, using several organic bases and lindane as examples. The method involves obtaining a sample through freezing under centrifugation conditions. It is characterized by its high efficiency, with results indicating that altering the pH of the environment significantly impacts extraction efficiency. This approach shows promise as an initial stage of sample preparation in chemical analysis. Furthermore, cryoextraction offers the advantage of being applicable in mobile laboratories for environmental pollution monitoring

Key words: aniline, diphenylamine, lindane, extraction using freezing and centrifugation, one-step sample preparation, chromatography, cryoextractor.

1. INTRODUCTION

Despite significant advancements in instrumental analytical methods, determining organic compounds dissolved in aqueous solutions often requires preliminary separation and concentration. This challenge is particularly pronounced when dealing with low concentrations of dissolved polar biogenic substances. Traditional extraction methods rely on transferring target substances from one phase to another, separated by a dividing boundary. These methods typically involve contact between water and the extractant, which can be a water-insoluble organic liquid, a sorbent, or a gas.

Cryoextraction presents a different approach. The extraction freezing method (EF) has been proposed, which combines extraction with freezing. In this method, components are extracted at low temperatures between a liquid phase (pre-treated with a water-soluble solvent) and the solid phase of ice. As ice forms in an initially homogeneous mixture, a boundary appears between the extractant and the aqueous solution. Additionally, freezing the extract under the influence of centrifugal force (CFF) can significantly enhance the concentration of analytes in the extract, streamlining the procedure and reducing both the duration of the sample preparation stage and material costs.

This method allows the use of hydrophilic, water-soluble extractants without requiring additional chemical modifications of the sample (such as salting out). Unlike solid-phase or liquid extraction techniques, it enables direct extraction of target substances from heavily contaminated dispersion systems without any intermediary steps (such as filtration). The resulting extracts contain very little water, allowing for immediate analysis by gas chromatography. The significant reduction in the chemical background from co-extracted substances during the preparation of biological samples improves the conditions for gas chromatographic (GC) identification with mass spectrometric detection, thereby decreasing contamination of the MS detector.

Moreover, the method enhances working conditions by minimizing the number of reagents and significantly reducing the variability associated with solvents and analytes. The advantages of the freeze-extraction method for determining various organic compounds are demonstrated through developed analysis schemes in biological and other samples.

Based on experimental results, theoretical foundations of the method have been established. The proposed model draws parallels between the extraction and adsorption processes. It is posited that when a mixture of an aqueous solution and an extractant is cooled, analyte molecules migrate to the surface of the forming ice crystals and are absorbed into the unfrozen volume of the organic liquid extractant. Simultaneously, the reverse process occurs, with analyte molecules sorbing onto the ice crystal surfaces.

The concentration of the analyte in the extract is linearly proportional to the volume of the extractant. The ratio mo/V, where mo represents the mass of the analyte in the original sample and V is the volume of the extractant, is derived from the extraction model. This relationship is supported by a substantial array of experimental results. The slope of the graph depicting this dependence serves as a parameter indicating individual adsorption of the analyte, which varies based on its physicochemical properties and the nature of the extractant. The value K characterizes the extraction efficiency of the analyte and effectively represents the distribution coefficient between the extractor (liquid phase) and the ice surface (solid phase), as it correlates with the adsorption-desorption equilibrium constant. This value is crucial for evaluating the method's efficiency.

In investigating a homologous series of carboxylic acids (C2–C8), it was found that the partition coefficient increases with the length of the acid molecule and its hydrophobicity. When acetonitrile is used as the extractant, the extraction efficiency of the test substance significantly improves. With water content in the extract not exceeding 4%, carboxylic acids C4–C8 can be fully separated from the aqueous solution, even at a volume ratio of water to acetonitrile of 10:0.4. The efficiency of the EF (extraction freezing) method can be selectively controlled by choosing appropriate extractants and study conditions, such as pH. In this work, we investigated the influence of pH on the efficiency of EF using several organic bases

2. MAIN PART

Reagents: The reagents used in this study include aniline, diphenylamine, lindane (gamma-1,2,3,4,5,6-hexachlorocyclohexane), and acetonitrile. All reagents were of chemically pure quality.

Equipment: For the preparation of model and standard solutions of organic substances, as well as for determining the mass of the obtained extract, we utilized an LV-210-A analytical balance with an error margin of no more than 0.5 mg. The obtained extracts and standard mixtures were analyzed using gas chromatography on Kristallyuks-4000M chromatographs, equipped with both ionizing flame (GC-FID) and electron capture (GC-ECD) detectors, along with a ZB-5 capillary column that is 30 m long and has an internal diameter of 0.32 mm.

Experimental Procedure: Extraction freezing was performed under centrifugation conditions. Standard solutions were prepared in glass test tubes by adding water and acetonitrile. The pH was adjusted using sulfuric acid and sodium hydroxide solutions. Each test tube was hermetically sealed with a screw cap, shaken, and then placed in the rotor of a cryoextractor to freeze the aqueous sample solution. The specific conditions for freezing were set to a temperature of -29 ± 2°C, with a rotor speed of 4000 rpm (resulting in a centrifugal acceleration of 1650 g) for a duration of 25 minutes. After completion of this process, the liquid acetonitrile layer was separated through decantation, weighed, and subjected to chromatographic analysis.

Results and Discussion

This study focused on carboxylic acids ranging from C2 to C8, revealing that extraction efficiency decreases as the medium shifts from acidic to alkaline. Specifically, when the pH increases from 3 to 10–12, the concentration of acetic acid during extraction decreases by a factor of 150. This decrease can be attributed to the heightened degree of ionization of carboxylic acids in an alkaline medium. According to our model, this increased ionization leads to greater adsorption on the surface of ice crystals that form in the organic liquid phase. Ice functions as a polar sorbent, aligning with the physical and chemical properties of water molecules. This phenomenon is consistent with adsorption theory and, by analogy, resembles liquid chromatography involving polar sorbents. It is also noteworthy that the ice surface becomes further modified by alkalis during the extraction process.

In contrast, when examining organic bases and amines, we observe an increase in the slope of the linear graphs representing the partition coefficient for aniline and diphenylamine. These two phases consist of the liquid extract and the ice phase formed during cryocentrifugation. As the environment transitions from acidic to alkaline, the partition coefficient (K) increases, leading to enhanced extraction efficiency. A similar pattern applies to liquid extraction from aqueous solutions of aniline and diphenylamine.

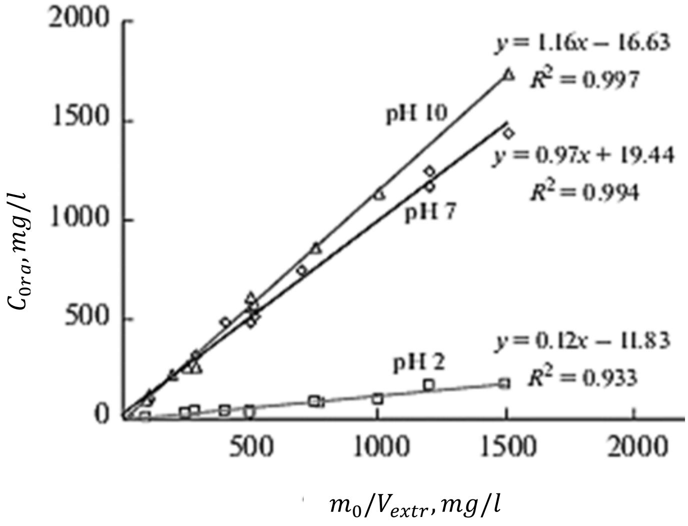

Fig. 1 Illustrates the relationship between the initial mass of aniline in water (mo) and the concentration of aniline in the extract following extraction and freezing at various pH levels. The molar fraction of acetonitrile in water is 0.027

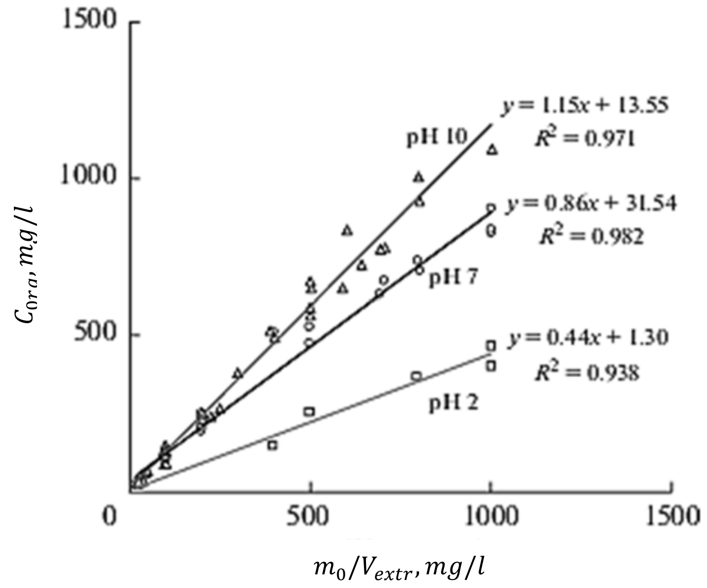

Fig. 2 Illustrates the relationship between the concentration of diphenylamine in the extract and its initial mass (mo) in water, as well as the volume of acetonitrile used during extraction and freezing, at varying pH values. The molar fraction of acetonitrile in the water is 0.027.

At pH 10, aniline and diphenylamine exhibit nearly identical partition coefficients, falling within the margin of experimental error. However, the efficiency of their extraction from an acidic medium using acetonitrile differs significantly. The partition coefficient of diphenylamine in acidic conditions is 0.44, which is notably higher than that of aniline, whose value is only 0.12. This suggests that diphenylamine is more effectively separated from water at pH 2 compared to aniline. This discrepancy can be attributed to the higher hydrophobicity and lower water solubility of diphenylamine relative to aniline.

The pH level can influence the extraction efficiency of an analyte from water. Caffeine, a basic compound containing three amine nitrogen atoms, reaches its maximum partition coefficient at pH 7. It is extracted less efficiently from both alkaline and acidic media than from neutral media. Similarly, the extraction efficiency of lindane from aqueous solutions is also greatest in neutral conditions.

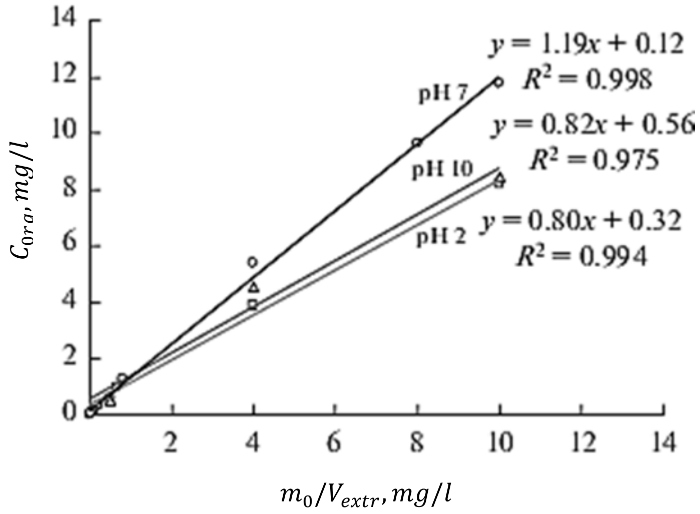

Fig.3 The relationship between the concentration of lindane in the extract and its initial mass mo in water, as well as the volume of acetonitrile, under extraction and freezing conditions at different pH values. The molar fraction of acetonitrile in water is 0.027

It is worth highlighting an interesting experimental observation. As shown in Fig. 3, the distribution coefficients K for lindane, unlike those for all other tested analytes, are nearly identical in both acidic and alkaline conditions. This phenomenon is likely due to the molecular structure of lindane, specifically its lack of acidic and basic properties.

$K \geq 1$ indicates complete extraction of the analyte (during extraction, freezing, and centrifugation) from water into acetonitrile, along with significant surface activity at the air-extract interface. From this, we can conclude that lindane at pH 7, as well as aniline and diphenylamine at pH 10, are fully separated from water during the extraction process when the volume ratio of water to extractant is 9.72:0.78 (with a molar fraction of acetonitrile in water of 0.027).

Table 1 shows the limits of detection for various analytes in tap water following a single extraction procedure. The data indicate that this method allows for rapid determination of analytes (sample preparation time does not exceed 25 minutes), requiring only a small sample volume of no more than 10 ml and an extract volume of 0.5 to 0.8 ml. Moreover, the one-step sample preparation eliminates the need for additional manipulations, which reduces the error in analyte determination. After 25 minutes, only the decanting of the extract from the ice surface is necessary. Given the method's advantages, it is reasonable to expect that it will be widely utilized in the near future for monitoring various organic substances in water, soil, sediments, and biological samples.

It is important to note that, unlike liquid-liquid extraction, the analysis of aqueous solutions using acetonitrile does not require thorough mixing of the aqueous solution with the extractant mixture during the sample preparation stage. This is because acetonitrile is infinitely soluble in water at room temperature.

Table 2 presents data on the limits of detection for analytes in aqueous tea solutions resulting from a single extraction procedure. The table indicates that this method allows for rapid determination of analytes while requiring only a small sample volume. The one-step sample preparation process, without additional manipulations, reduces the likelihood of error in analyte determination.

Given the advantages of this method, it is reasonable to expect that it will be increasingly utilized in the near future for monitoring various organic substances in biological samples.

Table 1

Determination of analytes in aqueous solutions by extraction and freezing, combined with centrifugation and gas chromatography

Substance	Gas Chromatography Detector	Water : Acetonitrile Ratio	Mass of Extract g.	The Limits of Detection in Water $c_{\text{H water}}$, mg/l	Consistancy
Aniline	Thermoionic	10 : 0.4 (pH 10)	0.024 ± 0.003	0.1	0.12
Diphenylamine	Flame Ionizer	10 : 0.5 (pH 10)	0.052 ± 0.004	0.05	0.052
Caffeine	Thermoionic	9.72 : 0.78 (pH 7)	0.07 ± 0.01	0.015	–
Lindane	Electroionic	9.72 : 0.78 (pH 7)	0.058 ± 0.005	0.001	0.03

Table 2

Determination of analytes in aqueous tea solutions through extraction and freezing under conditions of sample centrifugation, combined with gas chromatography

Substance	Gas Chromatography Detector	Water : Acetonitrile Ratio	Mass of Extract g.	The Limits of Detection in Water $c_{\text{H water}}$, mg/l	Consistancy
Aniline	Thermoionic	10 : 0.4 (pH 10)	0.030 ± 0.003	0.1	0.23
Diphenylamine	Flame Ionizer	10 : 0.5 (pH 10)	0.062 ± 0.004	0.05	0.15
Caffeine	Thermoionic	9.72 : 0.78 (pH 7)	0.15 ± 0.01	0.015	0.117
Lindane	Electroionic	9.72 : 0.78 (pH 7)	0.060 ± 0.005	0.001	0.012

3. CONCLUSION

This study demonstrates a new method for separating organic substances from aqueous solutions using the example of several organic bases and lindane. The method involves obtaining a sample by freezing under centrifugation conditions and is characterized by its high efficiency. It was found that changing the pH of the environment influences extraction efficiency. For relatively strong bases, efficiency increases when transitioning to an alkaline environment, consistent with established patterns in liquid extraction and sorption.

However, it was also experimentally established that for non-ionic analytes, such as lindane and weak bases, the efficiency of separation can be influenced by the formation of a solid ice phase. The separation of caffeine and lindane from aqueous solutions through freezing aligns with a previously proposed theoretical model.

This method's high extraction efficiency, coupled with a reduction in both the number of steps and the time required, as well as a decrease in the volume of reagents used, suggests that it is promising for implementation as a preliminary stage in chemical analysis. Additionally, the compact design of the cryoextractor makes it suitable for use in mobile laboratories, facilitating environmental contamination monitoring.

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საკვლევი ნიმუშების მომზადების ტექნოლოგია ანალიზურ ქიმიაში

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რეზიუმე: მიზანი. შემუშავებულია საკვლევი ნიმუშების წინასწარი მომზადების ეფექტური ტექნოლოგია ანალიზურ ქიმიაში. შესწავლილ იქნა pH-ის გავლენა ორგანული ნაერთების განსაზღვრაზე წყალხსნარებში და აცეტონიტრილში ექსტრაქციის ,გაყინვის და ცენტრიფუგირების გამოყენებით.. ნაჩვენებია ნიმუშების მომზადების ტექნოლოგიური შესაძლებლობები და უპირატესობები წყლის შემცველ გარემოში ორგანული ნივთიერებების რაოდენობის დასადგენად. გამოყენებულია აირ ქრომატოგრაფია, ერთსაფეხურიანი ექსტრაქცია, ნიმუშის გაყინვა ცენტრიფუგაციის რეჟიმთან ერთად. მინიმალური გამოვლენის ზღვრებია სასმელ წყალში მგ/ლ: ანილინი 0.1, დიფენილამინი 0.05, კოფეინი 0.015 და ლინდანი 0.001. შემუშავებული ტექნოლოგია მარტივია და შესრულებულია ერთ ეტაპად. ნიმუშის მომზადების ხანგრძლივობა არ აღემატება 30 წუთს.

მეთოდი: კვლევის მეთოდად შეირჩა ქრომატოგრაფია. ქრომატოგრაფიას იყენებენ ორგანული ნაერთების განსაზღვრისთვის წყალში , საკვებ პროდუქტებში, ღვინოსა და ჩაიში.კვლევის ჩატარებამდე საჭიროა საკვლევი ნიმუშის მომზადება.საკვლევი მასალის კრიოექსტრაქცია განსხვავებული მიდგომაა. შემოთავაზებულია ექსტრაქციის გაყინვის მეთოდი (EF) ამ მეთოდით ექსტრაქცია შერწყმულია გაყინვასთან: ხდება კომპონენტების დაბალ ტემპერატურაზე მოპოვება თხევადი ფაზას და ყინულის მყარ ფაზას შორის . ექსტრაქტის გაყინვამ შეიძლება მნიშვნელოვნად გაზარდოს ექსტრაქტში ანალიტების კონცენტრაცია. გაამარტივოს პროცედურა და შეამციროს ნიმუშის მომზადების ეტაპის ხანგრძლივობა და მასალის ხარჯები.

შედეგები: ნაჩვენებია ნიმუშების მომზადების ტექნოლოგიური შესაძლებლობები და უპირატესობები წყლის შემცველ გარემოში ორგანული ნივთიერებების რაოდენობის დასად-

გენად. გამოყენებულია აირ ქრომატოგრაფია, ერთსაფეხურიანი ექსტრაქცია, ნიმუშის გაყინვა ცენტრიფუგაციის რეჟიმთან ერთად. მინიმალური გამოვლენის ზღვრებია სასმელ წყალში მგ/ლ: ანილინი 0.1, დიფენილამინი 0.05, კოფეინი 0.015 და ლინდანი 0.001. შემუშავებული ტექნოლოგია მარტივია და შესრულებულია ერთ ეტაპად. ნიმუშის მომზადების ხანგრძლივობა არ აღემატება 30 წუთს.

დასკვნა: რამდენიმე ორგანული ფუძისა და ლინდანის მაგალითზე ნაჩვენებია, წყალხსნარებიდან ორგანული ნივთიერებების გამოყოფის ახალი მეთოდი: გაყინვით ნიმუშის ცენტრიფუგაციის პირობებში მიღება.. შემოთავაზებული მეთოდი გამოირჩევა მაღალი ეფექტურობით. ნაჩვენებია, რომ გარემოს pH-ის შეცვლა გავლენას ახდენს ექსტრაქციის ეფექტურობაზე. მოცემული მეთოდი პერსპექტიულია განსახორციელებლად, როგორც ნიმუშის მომზადების წინასწარი ეტაპი ქიმიურ ანალიზში. გარდა ამისა, კრიოექსტრაქცია საშუალებას მისცემს მკვლევარებს, გამოიყენონ ეს მეთოდი მობილურ ლაბორატორიებში გარემოს დაბინძურების მონიტორინგისთვის.

საკვანძო სიტყვები: ანილინი, დიფენილამინი, ლინდანი, ექსტრაქცია გაყინვით და ცენტრიფუგირებით, ნიმუშის ერთსაფეხურიანი მომზადება, ქრომატოგრაფია. კრიოექსტრაქტორი.

UDC 543.42

IMPACT OF METALS AND VOLATILE COMPOUNDS ON WINE'S ORGANOLEPTIC PROPERTIES

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Resume: Objective: The quality and organoleptic properties of wine significantly depend on its chemical composition. Key components, such as volatile compounds and metals, play a critical role in shaping the taste, aroma, and overall sensory attributes of wine. This study aims to identify the influence of these components on wine properties using data derived from sensory evaluations and chemical analysis.

The research focuses on examining the elemental and volatile organic compound content in samples of grape wines produced in Georgia. Using statistical methods, it assesses the potential to predict the organoleptic properties of wine based on the concentrations of these substances. The primary objective is to explore the effects of metals and volatile compounds on wine characteristics, with a focus on indigenous Georgian grape varieties.

Methodology:

The study utilized samples of red and white Georgian wines, including Saperavi, Rkatsiteli, Tsolikouri, Khikhvi, Ojaleshi, and Dzvelshavi. Sensory evaluation was conducted by five tasters tasked with assessing aroma, taste, color, and texture. Chemical analysis involved the measurement of volatile compounds using gas chromatography and quantification of metal concentrations via inductively coupled plasma mass spectrometry (ICP-MS).

Linear regression models were applied to establish correlations between sensory evaluations and the concentrations of chemical components. The statistical significance of the model was assessed through correlation coefficients and p-values.

Key words: Red and white wines, metals, volatile compounds, linear regression analysis

1. INTRODUCTION

Literature Review

Expert methods for assessing wine quality and modern approaches to chemical analysis have expanded significantly with advancements in science. Contemporary analytical chemistry methods greatly enhance the exploration of wine's sensory attributes, facilitating the identification of relationships between chemical composition and unique characteristics of different grape varieties. However, a clear and definitive connection between sensory evaluations and consumer preferences remains elusive.

Studies have demonstrated that volatile compounds influence the aroma and flavor of wine, while its taste attributes are largely determined by non-volatile components, such as titratable acids, amino acids, and mineral substances. These findings highlight the intricate interaction of wine's chemical profile with its sensory characteristics.

2. MAIN PART

The Correlation Between Metals and Wine's Sensory Properties

Metals in wine, such as iron, copper, and potassium, serve as markers for geographic origin and safety. This study examined the mineral composition, focusing on elements like Sr, Mn, Mg, and Li, which influence the stability of the wine's production processes and potentially its sensory characteristics.

Significance of Statistical Analysis

Statistical methods play a crucial role in evaluating wine quality, enabling the exploration of correlations between sensory evaluations and chemical composition, as well as differentiating wines by geographic origin. Techniques like linear regression, dispersion analysis, principal component analysis, and experimental design are widely applied. This study employed linear regression to identify relationships between sensory properties and chemical composition.

Experimental Methodology

The research focused on analyzing the elemental and volatile compound content of 50 wine samples produced in Georgia. Statistical methods were used to evaluate the ability to predict organoleptic properties based on chemical composition.

- **Participants and Sensory Analysis:**

Five participants (three men and two women) evaluated the samples, which were coded before testing. The assessment included transparency, color, aroma, flavor, and texture. Each sample (50 mL) was placed in closed containers covered with Petri dishes and left for 30 minutes before evaluation. The tests were conducted in a well-lit room at 16–22°C, with 2-minute intervals between tastings.

- **Chemical Analysis:**

Volatile compounds were measured using capillary gas chromatography with a flame ionization detector. Pre-treatment involved freeze-extraction and centrifugation. Samples were diluted in distilled water before analysis.

The research aimed to link the concentrations of chemical components, including volatile compounds and metals, to sensory evaluations, using linear regression models to establish significant correlations.

Statistical Analysis

The comparative analysis was conducted using **Statistica 10** software. Linear regression graphs were created to illustrate the dependence of sensory properties on the concentrations of metals and volatile compounds in the wines.

Results and Discussion

Table 2 summarizes the results of determining the concentrations of 12 volatile compounds and 15 metals, along with their correlations with the sensory properties of wines.

Observations:

Red Wines:

- Higher concentrations of metals such as **Ba, Co, Fe, K, Sr.**

- Higher levels of volatile compounds like **meso-2,3-butanediol, R-2,3-butanediol, acetic acid, isopentanol, and isobutanol**.

White Wines:

- Elevated concentrations of metals like **Al, Li, Na, Rb, Ti, Zn**.
- Prominent volatile compounds include **2-propanol and acetaldehyde**.

Commonalities in Red and White Wines:

- Similar concentrations of metals such as **Ca, Cr, Mg, Mn, Cu**.
- Shared volatile compounds include **1-butanol, 1-propanol, ethyl acetate, and furfural aldehyde**.

Table 1

Instrument Operating Parameters

Air chromatograph,crystal 2000M		(iCAP 7400)	
column	HP–FFAP (50 м × 0.32 mm, 0.52 mmk, Agilent, USA)	argon cooling flow rate l/min	12
injector temperature, °C	200	flow rate of argon carrying aerosol l/min	0.5
tempature °C	220	generator power wat	1150
nitrogen carrier gas flow ml/min	1.21	argon auxiliary flow rate l/min	0.5
Duration of analysis min	40	analytes	Zn 213.856 (I),
			Pb 220.353 (II),
			Co 238.892 (II),
			Mn 257.610 (II),
			Fe 259.940 (II),
			Cr 267.716 (II),
			Mg 280.270 (II),
			Cu 324.754 (I),
			Ti 334.941 (II),
			Al 396.152 (I),
			Sr 421.552 (II),
			Ca 422.673 (I),
			Ba 455.403 (II),
			Na 588.995 (I),
			Li 670.784 (I),
Injection volume мм^3	1		K 766.490 (I),
Hydrogen flow ml/min	20		Rb 780.023 (I).
Air flow ml/min	200		I – neutral atom
Temperature program	Initial oven temperature 70°C with izotherm 7 min, then 5°C/min to 140°C, plateau 10 min, then 10°C/min to 180°C and wait until the end of the analysis		II – ionized atom

Table 2

Concentrations of Metals and Volatile Compounds in White and Red Wines

component	red wines			white wines		
	Ojaleshi	Dzelshavi	Saperavi	Rkatsiteli	khikhvi	Tsolikouri
Al, mg/l	0.196–1.400	0.350–1.500	0.140–1.408	0.395–2.556	0.328–1.933	0.411–1.676
Ba, mg/l	0.050–0.340	0.131–0.320	0.085–0.390	0.041–0.190	0.054–0.220	0.065–0.400
Ca, mg/l	0.040–0.089	0.057–0.086	0.037–0.069	0.018–0.095	0.037–0.093	0.047–0.096
Comg/l	0.004–0.013	0.010–0.017	0.009–0.023	0.003–0.012	0.002–0.005	0.004–0.008
Cr, mg/l	0.008–0.023	0.015–0.032	0.008–0.015	0.007–0.021	0.020–0.042	0.012–0.021
Cu, mg/l	0.034–0.980	0.030–0.122	0.059–1.245	0.045–1.035	0.054–0.445	0.068–1.900
Fe, mg/l	1.268–6.700	1.400–8.400	0.600–4.219	0.421–6.337	0.630–6.456	0.660–6.634
K, mg/l	0.543–1.033	0.544–1.361	0.514–1.268	0.327–1.042	0.258–0.956	0.365–1.151
Li, mg/l	0.007–0.017	0.015–0.023	0.010–0.021	0.014–0.030	0.010–0.038	0.018–0.040
Mg mg/l	0.056–0.180	0.060–0.194	0.038–0.201	0.031–0.208	0.035–0.253	0.040–0.201
Mn, mg/l	0.827–2.480	1.000–2.590	0.580–1.682	0.454–3.962	0.549–2.354	0.470–2.731
Na, mg/l	0.008–0.063	0.020–0.100	0.019–0.072	0.010–0.097	0.024–0.140	0.014–0.081
Pb, mg/l	0.015–0.038	0.039–0.065	0.017–0.030	0.007–0.024	0.014–0.031	0.005–0.011
Rb,mg/l	0.732–1.776	1.029–1.811	0.878–1.704	1.520–1.997	1.935–2.361	2.115–2.974
Sr, mg/l	0.488–2.100	0.960–2.800	0.550–1.448	0.184–1.778	0.499–1.683	0.471–1.278
Ti,mg/l	0.006–0.017	0.007–0.018	0.009–0.020	0.017–0.034	0.014–0.035	0.012–0.028
Zn, mg/l	0.291–1.400	0.318–1.100	0.150–1.300	0.0804.600	0.222–2.300	0.210–5.138
1-butanol g/l	0.002–0.084	0.002–0.099	0.003–0.055	0.000–0.031	0.001–0.194	0.000–0.029
1- hexanol g/l	0.009–0.169	0.029–0.112	0.005–0.105	0.000–0.060	0.000–0.050	0.000–0.063
1-propanol g/l	0.019–0.075	0.000–0.069	0.015–0.108	0.010–0.088	0.018–0.084	0.000–0.069
meso-2,3,butanediol g/l	0.133–0.723	0.192–0.647	0.101–0.527	0.093–0.283	0.064–0.393	0.073–0.365
butanediol g/l	0.344–1.686	0.592–1.455	0.309–1.251	0.267–0.838	0.146–0.990	0.207–0.795
2- propanol g/l	0.000–0.014	0.000–0.005	0.000–0.005	0.000–0.006	0.000–0.178	0.000–0.015
acetaldehid g/l	0.025–0.129	0.015–0.088	0.025–0.085	0.019–0.132	0.032–0.167	0.028–0.126
acetic acid g/l	0.274–0.929	0.239–1.067	0.151–1.198	0.109–0.612	0.116–0.703	0.102–0.766
etilacetat g/l	0.044–0.170	0.063–0.164	0.049–0.115	0.028–0.148	0.031–0.136	0.039–0.122
furfural g/l	0.000–0.022	0.003–0.018	0.005–0.027	0.003–0.030	0.000–0.028	0.005–0.021
isopentanol g/l	0.210–0.705	0.192–0.567	0.226–0.574	0.112–0.448	0.000–0.564	0.097–0.366
isobutanol g/l	0.043–0.114	0.044–0.113	0.039–0.104	0.002–0.089	0.014–0.084	0.015–0.063
methanol g/l	0.062–0.956	0.086–0.841	0.158–0.508	0.042–0.505	0.020–0.226	0.036–0.246

Application of Linear Regression Models in Studying Wine Sensory Properties

The study utilized **linear regression models** to explore the relationship between wine sensory attributes and chemical compositions. Here, the sensory ratings provided by participants (evaluators) are treated as **dependent variables (responses)**, while the concentrations of substances, such as metals and volatile compounds, are the **independent variables (predictors)**.

Statistical Definitions and Methods:

- Yi: Individual ratings provided by evaluators.
- $\bar{Y}$ The average of the individual ratings.
- Y The average of the predictor values.

Residual and model errors were calculated using the following formulas:

- **Sum of Squares for Residuals (SS Residuals):**
- SSleftovers=$\sum_{i=1}^{n}(\overline{Y\iota}$-Yi)2

- **Sum of Squares for the Model (SS Model):**
- SSmodels=$\sum_{i=1}^{n}(\overline{Y\iota}$-Y)2

Key Analysis and Indicators:

The **comparative analysis** examined the influence of metal concentrations and volatile components on the development of organoleptic properties in wine. The linear regression model effectively described the functional relationships between the independent variables (chemical compositions) and dependent variables (sensory attributes).

A significant performance metric in this analysis is the **Coefficient of Determination** which measures the model's ability to explain the variability in the data. values range from **0 to 1**, where:**0** indicates that the model explains none of the variability **1** indicates a perfect model fit.

The formula for R This methodology provides insights into how chemical composition influences wine's sensory perception and establishes the predictive power of the linear regression models used.

$$R^2=1-\frac{SS_{leftovers}}{SS_{leftovers}-SS_{models}}$$

The adequacy of a regression model improves as the **sum of squares for residuals (SS Residuals)** becomes smaller, indicating that the observed data points are closer to the predicted regression line. A smaller SS Residuals reflects a model's higher precision in capturing the relationship between variables, leading to more accurate predictions.

In the context of wine sensory analysis, knowing the chemical composition allows for the **prediction of organoleptic properties** with greater confidence. The **coefficient of determination** plays a crucial role in evaluating the model's accuracy:

- When $R^2 \approx 1$ \approx the model is highly accurate.
- If $R^2 > 0{,}5$ the regression model is considered suitable for making predictions.

This approach underscores the potential to **predict sensory qualities** of wine based on its chemical makeup, helping winemakers optimize formulations and anticipate consumer perceptions.

The **multiple correlation coefficient** (R) quantifies the strength of the relationship between the dependent variable (response) and the set of independent variables (predictors). It is calculated as the **pairwise correlation coefficient** between the observed dependent variable values (YiY_iYi) and the predicted values ((Yi)ˉ(Y_i)\bar{}(Yi)ˉ) derived from the regression model.

In simpler terms:

- R measures how well the predicted outcomes from the regression model align with the actual observed data.
- A higher R value (closer to 1) indicates a stronger relationship, suggesting the model's predictions closely follow the observed values.

This measure is particularly useful in assessing the fit of the regression model, helping to determine how effectively the predictors explain the variability in the dependent variable.

A **regression model** was constructed using the **Forward Stepwise method**, an automated approach for selecting predictors. This method iteratively adds variables to the model, prioritizing those that significantly improve predictive accuracy while excluding less relevant ones.

Results for Red Wines

- **Dataset:** The regression model was developed using 30 wine samples.
- **Validation:** The predictive capacity of the model was tested on three randomly selected samples that were not part of the initial dataset.
- **Selected Variables:** Out of 30 possible predictors, 12 were included in the final model:
  - **Volatile Compounds:** Six components.
  - **Metals:** Seven components.

Summary Table (Table 3)

The parameters of the regression model, including coefficients for predictors, R2 values, and statistical significance indicators, are outlined in Table 3. These parameters provide insights into the influence of each variable on the sensory properties of red wines and the overall fit of the model.

Using **analysis of variance** , the sums of squares for residuals were calculated as follows:

- SSResiduals=91.89
- SSModel=190.232

Implications

These values contribute to the calculation of the **coefficient of determination**

$$R^2=1-\frac{91,89}{91,89+190,232}=0,674$$

R=0,821

This means that the regression model accounts for approximately 67% of the variance in the dependent variable compared to the mean values. The R-value being close to 1 indicates a robust model, suitable for predicting sensory evaluations based on the provided data.

Additionally, the regression equation is statistically significant because the **F-test** value (p-value) is less than 0.05. This demonstrates that the model reliably explains the variation in the dependent variable and is valid for predicting the sensory characteristics of wine based on the concentrations of metals and volatile compounds.

Table 3

Results of regression models in red wines

model predictors	**sensory error; R = 0.821, R^2 = 0.674. adjusted R^2= 0.490. F (13.23) = 3.662, $p < 0.003$. standard error of estimate: 0.198**						
	N	***b****	**standard error *b****	***b***	**standard error b**	***t* (23)**	***p-meaning***
free member		**–**	**–**	**77.319**	**2.997**	**25.8**	**0**
meso-2,3,butanediol g/l	**1**	**1.105**	**0.47**	**0.023**	**0.01**	**2.35**	**0.028**
methanol g/l	2	–0.613	0.326	–0.008	0.004	–1.878	0.073
1-butanol	**3**	**1.289**	**0.433**	**0.128**	**0.043**	**2.98**	**0.007**
isopentanol	4	–0.696	0.403	–0.012	0.007	–1.726	0.098
1-hexanol	5	–0.267	0.175	–0.022	0.015	–1.525	0.141
R-2,3-butanediol	6	–0.439	0.326	–0.004	0.003	–1.348	0.191
K	**7**	**0.614**	**0.186**	**0.008**	**0.002**	**3.31**	**0.003**
Al	**8**	**–0.708**	**0.231**	**–5.372**	**1.754**	**–3.062**	**0.006**
Mg	9	0.213	0.374	0.012	0.022	0.57	0.574
Mn	**10**	**0.424**	**0.201**	**2.599**	**1.23**	**2.11**	**0.046**
Sr	11	0.203	0.213	1.129	1.183	0.954	0.35
Na	12	0.085	0.208	0.012	0.03	0.407	0.688
Zn	13	–0.167	0.155	–1.436	1.333	–1.077	0.293

The regression coefficients of the equation for red wines are presented in the columns "b" and „b^*"· and are standardized by dividing the difference between the initial concentration and the mean value by the standard deviation S^2. The columns "t23" and "P-value" show the Student's t-test values and the statistical significance used to evaluate the regression coefficients. Statistically significant coefficients were those associated with the following metals: K, Al, and Mn, as well as the volatile compounds meso-2,3-butanediol and 1-butanol.

Table 4

Parameters of Combined Linear Models for Red Wines

model predictors	**parameter estimates** **sigma-constraind parametrerization**					
	predictors	N	***b***	***t***	***p***	***b****
free member			**77.848**	**23.977**	**0**	–
meso 2,3-butanediol		1	0.02	1.764	0.092	0.966
methanol		2	−0.007	−1.631	0.118	−0.570
1-butanol		**3**	**0.118**	**2.113**	**0.047**	**1.192**
isopentanol		4	−0.012	−1.398	0.177	−0.668
hexanol		5	−0.022	−1.469	0.157	−0.267
R-2,3-butandiol		6	−0.003	−0.825	0.419	−0.323
K		**7**	**0.008**	**2.966**	**0.007**	**0.628**
Al		**8**	**−5.248**	**−2.461**	**0.023**	**−0.692**
Mg		9	0.011	0.456	0.653	0.186
Mn		10	2.435	1.735	0.097	0.397
Zn		11	−1.410	−1.017	0.321	−0.164
Sr		12	0.829	0.581	0.568	0.149
Na		13	0.01	0.291	0.774	0.071
	ojaleshi		0.017	0.028	0.978	0.005
	sapheravi		−0.440	−0.597	0.557	−0.123

The "b" coefficients indicate that volatile compounds play a greater role in the formation of sensory attributes. For example:

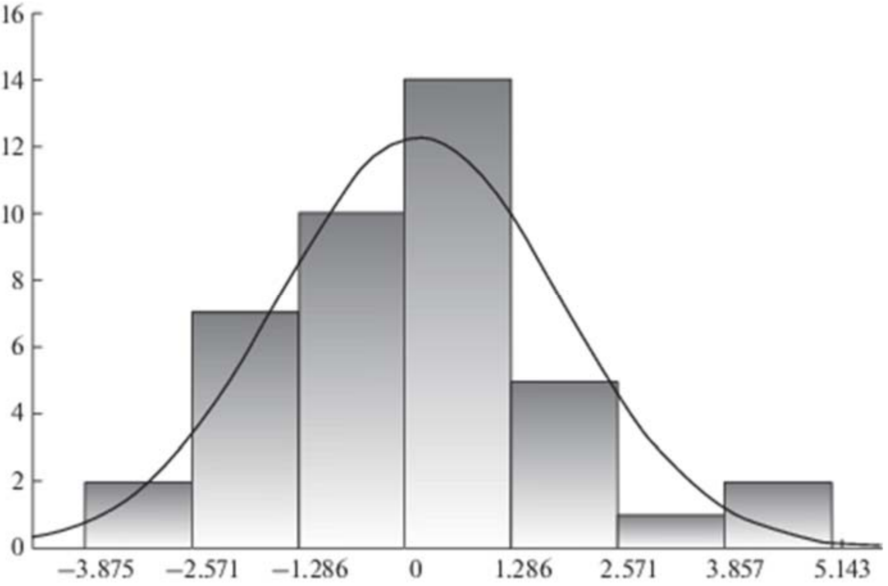
- 1-butanol b∗ = 1.192
- Meso-2,3-butanediol b∗=0.966b

The regression coefficients for metals are 0.326 and 0.664, respectively. This demonstrates that in red wines, the contribution of volatile organic compounds to sensory evaluation is twice as significant as that of metals. Using the coefficients provided in the "b" column, we constructed the linear model equations.

Y=77.319+0.023X1−−0.008X2+0.128X3−−−0.012X4 −−0.022X5−−0.004X6+0.008X7−−−5.372X8+0.012X 9+2.599X10+1.129X11++ 0.012X12−−1.436X13,

Where Y represents the response variable that determines the predicted values for sensory evaluation, and X1,X2,…,X13X_1, X_2, \ldots, X_{13}X1,X2,…,X13 are the model predictors, denoting the concentrations of components corresponding to their numbers in the "N" column.

Fig. 1. Histogram of Residuals Dispersion for Linear Models of Red Wines



Pic1. Y-number of observations, X-group

The histogram visually demonstrates that the distribution of residuals is close to a normal distribution. Additionally, the Pearson x^2 -test value presented on the graph is 0.249, which is greater than 0.05. This indicates that the hypothesis regarding the conformity of the residuals' distribution is justified.

Results

1. Impact of Volatile Compounds

The study found that 1-butanol and ethanol (volatile compounds) significantly influence the aromatic intensity and taste of wine. A strong correlation was observed between the concentrations of these compounds and sensory evaluation scores (R2=0.72R^2 = 0.72R2=0.72).

2. Impact of Metals

Potassium and magnesium were associated with wine's balance and sweetness. However, certain metals, such as iron and copper, negatively impacted the organoleptic properties of wine, emphasizing the need to control their concentration within specific thresholds.

3. Categorical Data

Variations in wine varieties had a significant influence on sensory evaluations. For instance, *Ojaleshi* demonstrated high aromatic intensity, whereas *Dzvelshavi* received lower scores.

4. Unique Profiles of Georgian Varieties

Georgian grape varieties exhibited distinctive aromatic characteristics. For example:

o *Saperavi*: Rich tannins and high concentrations of volatile compounds such as isobutanol and ethyl acetate.

o *Rkatsiteli*: High acidity and light aromas linked to potassium and magnesium content.

5. Impact of Volatile Compounds on Georgian Varieties

Ethanol and isobutanol were found to play a key role in enhancing aromatic intensity in Georgian wines. Varieties like *Khikhvi* and *Tsolikouri* were notable for their low levels of volatile esters, resulting in a light and harmonious profile.

6. Role of Metals

High concentrations of potassium and calcium were associated with balanced sensory evaluations in Georgian white wines (e.g., *Rkatsiteli* and *Khikhvi*). However, elevated levels of iron and copper negatively influenced wine aroma and promoted the development of amber coloration.

3. CONCLUSION

The results confirm that volatile compounds and metals play a critical role in sensory evaluations of wine. The impact of volatile compounds is nearly twice as significant as that of metals. However, certain metals can exert beneficial or adverse effects.

The unique profiles of Georgian grape varieties, shaped by the influence of volatile compounds and metals, underscore their distinctiveness in the global market. Based on these findings, Georgian wines can be positioned internationally as high-quality products with remarkable organoleptic diversity.

Future research should focus on the detailed interaction between metals and volatile compounds, which could be pivotal for enhancing wine quality.

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უაკ **543.42**

მეტალებისა და აქროლადი ნაერთების გავლენა ღვინის ორგანოლეპტიკურ თვისებებზე

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რეზიუმე: მიზანი: ღვინის ხარისხი და ორგანოლეპტიკური თვისებები მნიშვნელოვანად არის დამოკიდებული მის ქიმიურ შემადგენლობაზე. ძირითადი კომპონენტები, როგორიცაა აქროლადი ნაერთები და მეტალები, მნიშვნელოვნად განსაზღვრავენ ღვინის გემოს, არომატს და ზოგად სენსორულ თვისებებს. ეს კვლევა მიზნად ისახავს დადგინდეს ამ კომპონენტების გავლენა ღვინის თვისებებზე დეგუსტაციისა და ქიმიური ანალიზის მონაცემების დახმარებით.

მოცემული კვლევა წარმოადგენს საქართველოს ტერიტორიაზე წარმოებული ყურძნის ღვინოების ნიმუშების ელემენტური და აქროლადი ორგანული ნაერთების შემცველობის შესწავლას. სტატისტიკური მეთოდით შეფასდა ღვინის ორგანოლეპტიკური თვისებების პროგნოზირების შესაძლებლობა ნივთიერებების შემცველობის მიხედვით.

ამ კვლევის მიზანია შეისწავლოს მეტალებისა და აქროლადი ნაერთების გავლენა ღვინის თვისებებზე, ქართული ჯიშების მაგალითზე.

მეთოდი: კვლევისთვის გამოვიყენეთ წითელი და თეთრი ქართული ღვინოების ნიმუშები, მათ შორის საფერავი, რქაწითელი, ცოლიკოური, ხიხვი, ოჯალეში. ძელშავი. ღვინის სენსორული შეფასება განხორციელდა 5 დეგუსტატორის მიერ, რომელთაც ევალებოდათ არომატის, გემოს,ფერისა და ტექსტურის შეფასება. ქიმიური ანალიზი მოიცავდა აქროლადი ნაერთების კვლევას აირ-ქრომატოგრაფიით, მეტალების კონცენტრაციების გაზომვას ინდუქციური პლაზმის მას-სპექტრომეტრიით (ICP-MS). წრფივი რეგრესიის მოდელები გამოყენებულ იქნა სენსორულ შეფასებებსა და ქიმიური კომპონენტების კონცენტრაციებს შორის კორელაციის დასადგენად. მოდელის სტატისტიკური მნიშვნელობა შეფასდა კორელაციის კოეფიციენტით და p-მნიშვნელობებით.

შედეგები

1. აქროლადი ნაერთების გავლენა

კვლევის შედეგად აღმოჩნდა, რომ 1-ბუტანოლი და ეთანოლი (აქროლადი ნაერთები) მნიშვნელოვანად განსაზღვრავენ ღვინის არომატულ ინტენსივობას და გემოს. მაღალი კორელაცია დაფიქსირდა ამ ნაერთების კონცენტრაციასა და სენსორულ შეფასებას შორის ($R^2=0.72$). ქართული ჯიშებისთვის ასევე დადგინდა, რომ ეთანოლი და იზობუტანოლი მნიშვნელოვან გავლენას ახდენენ ღვინის არომატულ ინტენსივობაზე. ხიხვი და ცოლიკოური გამოირჩევა დაბალი ეთერული ნაერთებით, რაც ამ ღვინოებს მსუბუქ და ჰარმონიულ პროფილს ანიჭებს.

2. მეტალების გავლენა

კალიუმი და მაგნიუმი ღვინის ბალანსთან და სიტკბოსთან ასოცირდებოდა. თუმცა, ზოგიერთ მეტალს, როგორიცაა რკინა და სპილენძი, ჰქონდათ უარყოფითი გავლენა ღვინის ორგანოლეპტიკურ თვისებებზე, რაც მიუთითებს მათი კონცენტრაციების ზღვრული მნიშვნელობების აუცილებლობაზე.

ღვინის ჯიშის (სორტი) ვარიაციები სენსორულ შეფასებებზე, მნიშვნელოვანი აღმოჩნდა. მაგალითად, ოჯალეში გამოირჩეოდა მაღალი არომატული ინტენსივობით, მაშინ როცა ძელშავიმ უფრო დაბალი შეფასება მიიღო.

3. ქართული ჯიშების უნიკალური პროფილები

ქართული ჯიშები გამოირჩევა უნიკალური არომატული მახასიათებლებით. მაგალითად, საფერავს ახასიათებს მდიდარი ტანინები და მაღალი კონცენტრაციის აქროლადი ნაერთები,

როგორიცაა იზობუტანოლი და ეთილაცეტატი. რქაწითელი გამოირჩევა მაღალი მჟავიანობით და მსუბუქი არომატებით, რაც დაკავშირებულია კალიუმისა და მაგნიუმის შემცველობასთან.

4. მეტალების როლი

კალიუმისა და კალციუმის მაღალი კონცენტრაციები ქართული თეთრი ღვინოების (მაგალითად, რქაწითელი და ხიხვი) შემთხვევაში დამაკავშირებელი აღმოჩნდა სენსორული შეფასების ბალანსთან. თუმცა, რკინის და სპილენძის მაღალი დონე უარყოფით გავლენას ახდენს ღვინის არომატზე და ქარვისფერი შეფერილობის განვითარებას უწყობს ხელს.

დასკვნა

კვლევის შედეგები ადასტურებს, რომ აქროლადი ნაერთები და მეტალები მნიშვნელოვან როლს თამაშობენ ღვინის სენსორულ შეფასებებში. აქროლადი ნაერთების გავლენა თითქმის ორჯერ აღემატება მეტალებისას, თუმცა ზოგიერთი მეტალი სასარგებლო ან უარყოფით გავლენას ახდენს.

ქართული ჯიშების უნიკალური პროფილები, რომლებიც მეტალებისა და აქროლადი ნაერთების გავლენით ყალიბდება, ხაზს უსვამს მათ უნიკალურობას მსოფლიო ბაზარზე. ამ მონაცემებზე დაფუძნებით, შესაძლებელია ქართული ღვინოების საერთაშორისო ბაზარზე პოზიციონირება, როგორც მაღალხარისხიანი, ორგანოლეპტიკური მრავალფეროვნებით გამორჩეული პროდუქტი.

მომავალი კვლევები უნდა ფოკუსირდეს მეტალებისა და აქროლადი ნაერთების ურთიერთქმედების დეტალურ შესწავლაზე, რაც ღვინის ხარისხის გაუმჯობესებისთვის მნიშვნელოვანი იქნება.

საკვანძო სიტყვები: წითელი და თეთრი ღვინოები,მეტალები,აქროლადი ნაერთები,წრფივი რეგრესიული ანალიზი

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INVESTIGATION OF THE EFFECTIVENESS OF PERMEABLE POROUS COMPOSITES FOR SPHEROIDIZATION OF GRAPHITE INCLUSIONS AND DESULFURIZATION OF LIQUID CAST IRON

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Resume: Goal. A new technology for refining and modifying liquid metal using magnesium-containing penetrating porous composites has been studied. The influence of the sizes and quantities of the composite components on the spheroidization of graphite inclusions in high-strength cast iron and the concentration of sulfur during processing at various melting temperatures has been established. It has been shown that the technology in question is effective for processing small volumes of metal. The treatment of liquid metal with magnesium-containing penetrating porous composites is an effective technology for the modification and desulfurization of cast iron, which provides a high degree of magnesium absorption (up to 90-92%).

Methods: Experimental smelting and modification of cast iron weighing 50 kg was carried out. using an induction furnace of the MGP - 102 brand. To implement various variants of the technological process, 30 kg of liquid metal were harvested at each stage of the research. Penetrating porous composites were placed in the lower layers of the molten metal through a graphite cap. The temperature of liquid cast iron was measured using a platinum-platinum-rhodium thermocouple, the values of which were recorded on an OWON PC oscilloscope. The chemical composition of the alloys was determined using a Q8 MAGELLAN spectrometer. The structure of the obtained samples was studied by metallographic analysis using a Neophot-32 optical microscope.

Results: The effect of magnesium-containing composites with different morphology and porosity on the refining and modifying effect of liquid metal was studied. The efficiency of the spheroidized of this group was determined by the degree of desulfurization of cast iron and the shape of graphite inclusions. It is shown that the treatment of liquid metal with these composites does not lead to a pyroelectric effect and provides a high degree of magnesium absorption.

Conclusion.

- The treatment of liquid metal with magnesium-containing penetrating porous composites is an effective technology for the modification and refining of cast iron, which provides a high degree of magnesium absorption (up to 90-92%).
- For processing metal 30 kg. the optimal fraction of MgO is 2-2.5 mm.

- The optimal amount of magnesium in the composite for refining cast iron is 30-32%.
- Using this technology, it is possible to reduce the sulfur content in cast iron to an unprecedented value of <0.003%.
- The optimal temperature for refining and modification of liquid metal is 1350°C and does not require overheating of the metal.

Key words: High-strength cast iron, graphite inclusions, spheroidizer, modification, refining, desulfurization.

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1. INTRODUCTION

Improving the reliability and durability of machine installations significantly depends on the development of new construction alloys and the technology for their adoption. All this is also attributed to one of the most common materials in the technique, namely high-strength cast iron, the properties of which are determined to a greater extent by the concentration of harmful impurities in them and the degree of spheroidization of graphite inclusions.

Currently, it has been theoretically established and practically proven that one of the most effective technologies for slagging and refining liquid metal is the treatment of molten metal with magnesium. However, given that the boiling point of the specified metal is 1100^{0}C, and the saturated vapor pressure at 1400^{0}C reaches 10 atmospheres, the technology of processing with metallic magnesium is fraught with certain difficulties. Since a pyroelectric effect may occur and the liquid metal may flare up. Therefore, it is justified to supply magnesium in liquid form in the form of powdered mixtures using injection molding metallurgy methods. During these processes, dispersed magnesium particles are transported to the lower layers of the processed metal by an inert gas stream, but due to the high kinetic energy of the flow, the degree of absorption of the reagent is limited.

Therefore, the use of magnesium-containing porous composites to produce ingots of liquid metal and high-strength cast iron is of wide scientific and practical interest. The use of magnesium-containing composites allows you to adjust the intensity of the modifier supply during evaporation, simplifies the modification process and eliminates the pyroelectric effect.

The efficiency of using this technology depends on the ratio of the phase components of the composite, the degree of dispersibility and the melting point during processing.

Currently, various technologies for producing porous composites are known, for example, pressing powder mixtures and sintering. Composites obtained by sintering are characterized by a relatively uniform pore distribution and dimensional uniformity, which ensures targeted process control.

2. MAIN PART

In the presented work, the modifying effect of permeable porous composites was studied., For which magnesite of various fractions (1.6-4.3 mm), magnesium (0.2-2.3 mm) and 8-10% phenol-formaldehyde resin, in particular, PK-104 Table 1, were used. This is due to the fact that the granularity of the modifier components determines porosity the composite, which, in turn, determines the size of the bubbles formed and the dynamics of their interaction with the melt. To regulate the porosity of the composite, the sizes of the magnesite particles and their percentage in the mixture were changed.

It has been experimentally established that an increase in the average MgO fraction to 1.6-2.5 mm is accompanied by an increase in the degree of enrichment with metallic magnesium. A decrease in the above parameter leads to a decrease in the degree of magnesium absorption, since the cross-section of the channels for transporting evaporated magnesium decreases and the resistance to its displacement increases. As a result, the amount of steam supplied to the melt decreases dramatically. The process of formation of the gas phase and its transition to a liquid metal in coarse-pored composites proceeds much more intensively. At the same time, the rate of supply of magnesium vapor increases, due to which the degree of its assimilation is intensively reduced. The process described above is schematically shown in Fig. 1.

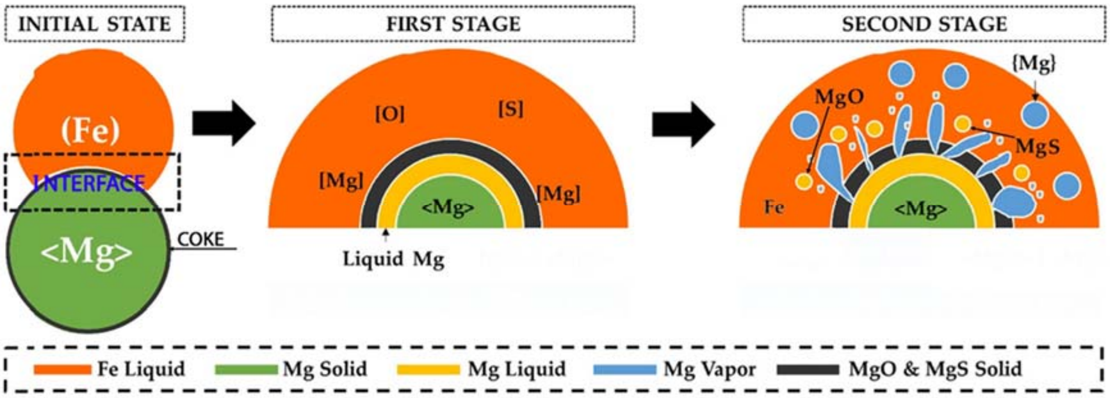


Figure 1. Schematic model of modification by permeable porous composites of liquid metal with Mg vapors

The use of phenol-formaldehyde resin in a porous composite ensures the formation of a coked film around magnesium particles during sintering, which reduces the kinetic energy of magnesium vapors formed during modification. The transportation of magnesium vapor through porous channels is facilitated by its metered supply at low speed to the liquid metal, which eliminates the pyroelectric effect and ensures a high degree of refining.

It was found that for processing 30-35 kg. of liquid metal, the optimal porosity of the composite is achieved using magnesite with a fraction of 2.0-2.5 mm.

Reactions of interaction of magnesium with harmful impurities occur with the release of thermal energy, and therefore the processing temperature of the liquid metal has a significant effect on the main parameters of the modification process (duration of the process, desulfurization and degassing of the alloy, as well as the degree of spheroidization of graphite inclusions). The experiments were carried out in stages at a temperature of 1300 -1450°C. After every 60 seconds of melt treatment, control samples were poured for intermediate chemical and metallographic analysis (Table.1).

Table 1

Influence of technological parameters of cast iron processing on the degree of magnesium assimilation

Melting #	*Composition of the composite*			*Particle size MgO, mm*	*Melt temperature, ^{0}C*	*Duration of modification, min.*	*The degree of assimilation of Mg*
	Mg	*ПК-104*	*MgO*				
1	2	3	4	5	6	7	8
The effect of MgO particle size							
21	*30*	*10*	*60*	*1.6*	*1350*	*5*	***82***
22	*30*	*10*	*60*	*2.0*	*1350*	*5*	***91***
24	*30*	*10*	*60*	*2.5*	*1350*	*5*	***87***
25	*30*	*10*	*60*	*3.4*	*1350*	*5*	***78***
26	*30*	*10*	*60*	*4.3*	*1350*	*5*	***74***
Influence of the modification temperature							
27	*30*	*10*	*10*	*2.5*	*1300*	*5*	***78***
28	*30*	*10*	*10*	*2.5*	*1350*	*5*	***91***
29	*30*	*10*	*10*	*2.5*	*1400*	*5*	***84***
30	*30*	*10*	*10*	*2.5*	*1450*	*5*	***77***

According to the results obtained, the best indicators are characterized by cast iron treated at a temperature of 1350°C fig.2.

Carrying out the process in a higher temperature range leads to an intensification of magnesium evaporation and a decrease in the duration of its contact with the liquid metal, which reduces the degree of assimilation of the modifier. Spheroidization of graphite inclusions and more complete refining of the melt during the experiment at a temperature of 1300°C requires an increase in the processing time.

Figure 2. Technological process of modification of Mg cast iron

The magnesium content in a porous composite is crucial, since this parameter determines the temperature of the technological process, the nature of modification and refining, the degree of assimilation of the modifier and the concentration of sulfur in the metal. To determine the ratio of the above parameters, various (30, 50 and 80%) composites with magnesium content were used. It was found that an increase in the Mg content in the composite leads to a decrease in the degree of assimilation of this component by the liquid metal in fig. 3.

For example, in composites containing 20-25% magnesium, the percentage of use of the spheroidized reaches 85-91%, and in 40-45% - 70-75%, and this depends on the modification temperature. The treatment of liquid metal with composites containing 75-80% magnesium is characterized by lower technological parameters. Figure 4 shows the effect of magnesium concentration on the degree of spheroidization of graphite inclusions in cast iron.

Based on the above, it can be concluded that the degree of Mg absorption by the melt is proportional to the ratio of MgO/Mg components and increases in accordance with this indicator. The high percentage of magnesium in composites leads to an intensification of the modification and refining process, which reduces the duration of interaction of magnesium vapors with liquid metal fig.5.

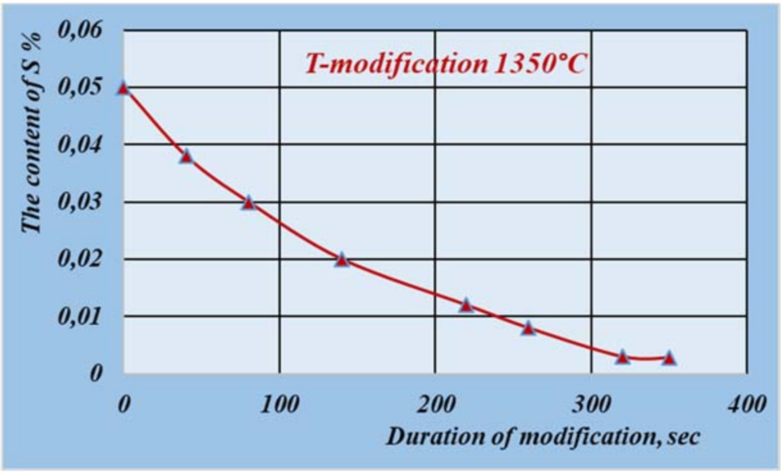
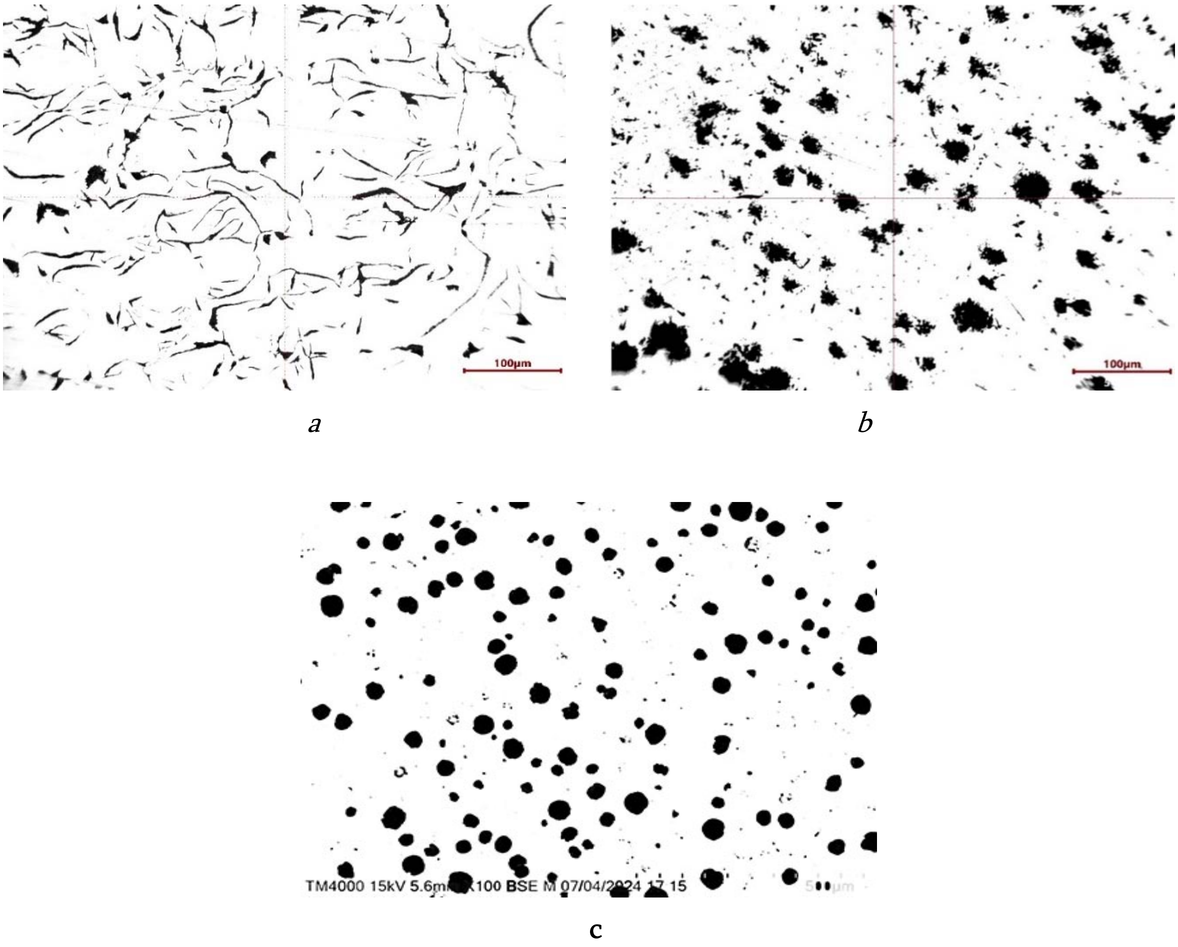


Figure 3. Effect of modification duration on the degree of desulfurization of liquid metal



a

b

c

Figure 4. The effect of magnesium concentration on the degree of spheroidization of graphite inclusions in cast iron: a - 0.015, b - 0.025 and c - 0.035

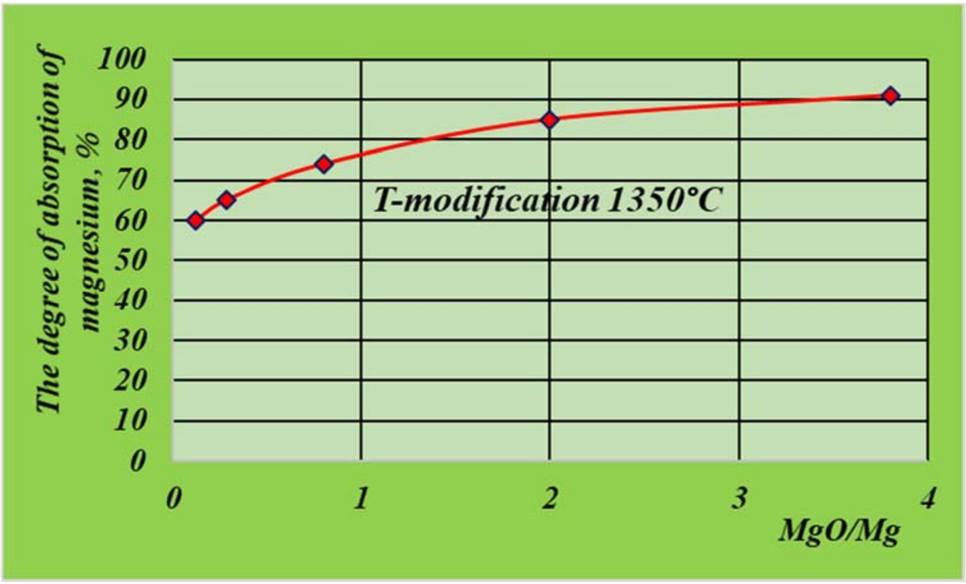


Figure 5. The effect of the ratio of modifying and refractory components in a porous composite on the degree of magnesium absorption by the metal.

According to the conducted research, the treatment of liquid metal with magnesium-containing permeable porous composites is an effective technology for modifying and refining cast iron. The selection of composite sizes, their optimal ratios and processing temperatures ensure a high degree of desulfurization and spheroidization of graphite inclusions. This technology can also be used to process small volumes of metal and reduces the sulfur content by less than 0.003%.

3. CONCLUSION

- The treatment of liquid metal with magnesium-containing penetrating porous composites is an effective technology for the modification and refining of cast iron, which provides a high degree of magnesium absorption (up to 90-92%).
- For processing metal 30 kg. the optimal fraction of MgO is 2-2.5 mm.
- The optimal amount of magnesium in the composite for refining cast iron is 30-32%.
- Using this technology, it is possible to reduce the sulfur content in cast iron to an unprecedented value of <0.003%.
- The optimal temperature for refining and modification of liquid metal is 1350°C and does not require overheating of the metal.

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გამჭოლი ფოროვანი კომპოზიტების ეფექტურობის კვლევა თხევადი თუჯის განგოგირდებისა და გრაფიტული ჩანართების სფეროიდიზაციის მიზნით

ს. გვაზავა

საქართველოს ტექნიკური უნივერსიტეტი. ბიონანოკერამიკისა და ნანოკომპოზიტების ტექნოლოგიის ინსტიტუტი. ბიონანოკერამიკული და ნანოკომპოზიტების სამეცნიერო ცენტრი

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რეზიუმე: ***მიზანი.*** თხევადი ლითონის რაფინირებისა და მოდიფიცირების ახალი ტექნოლოგია შესწავლა მაგნიუმ შემცველი გამჭოლი ფოროვანი კომპოზიტების გამოყენებით. დადგენილია კომპოზიტის კომპონენტების ზომებისა და რაოდენობის გავლენა მაღალმტკიცე თუჯში გრაფიტული ჩანართების სფეროიდიზაციაზე და გოგირდის კონცენტრაციაზე ნადნობის სხვადასხვა ტემპერატურაზე დამუშავებისას. ნაჩვენებია, რომ აღნიშნული ტექნოლოგია

ეფექტურია მცირე მოცულობის ლითონის დასამუშავებლად. მაგნიუმ შემცველი გამჭოლი ფოროვანი კომპოზიტებით თხევადი ლითონის დამუშავება წარმოადგენს თუჯების მოდიფიცირებისა და რამიფინირების ეფექტურ ტექნოლოგიას, რომელიც უზრუნველყოფს Mg-ის ათვისების მაღალ ხარისხს (90-92%-მდე).

მეთოდი: ექსპერიმენტალური თუჯების დნობა და მოდიფიცირებას განხორციელდა 50კგ. МГП-102 მარკის ინდუქციურ ღუმელში ტიგელი ფუძე ამონაგით. ტექნოლოგიური პროცესის სხვადასხვა ვარიანტების განხორციელების მიზნით კვლევის თითოეულ ეტაპზე მზადდებოდა 30კგ. თხევადი ლითონი. გამჭოლი ფოროვანი კომპოზიტები თავსდებოდა გამდნარი ლითონის ქვედა ფენებში გრაფიტის ზარის მეშვეობით. თხევადი თუჯის ტემპერატურა იზომებოდა პლატინო-პლატინოროდიუმის თერმოწყვილის გამოყენებით, რომლის მაჩვენებლები ფიქსირდებოდა OWON PC Oscilloscope-ზე. შენადნობების ქიმიური შედგენილობა განისაზღვრა სპექტრომეტრ Q-8 MAGELLAN-ზე. მიღებული ნიმუშების სტრუქტურის შესწავლა განხორციელდა მეტალოგრაფიული ანალიზით, ოპტიკურ მიკროსკოპზე Neophot-32.

შედეგები: შესწავლილი იქნა სხვადასხვა მორფოლოგიისა და ფორიანობის მქონე მაგნიუმ შემცველი კომპოზიტების გავლენა თხევადი ლითონის რაფინირებისა და მოდიფიცირების ეფექტზე. დადგენილი იქნა ამ ჯგუფის სფეროიდიზატორების ეფექტურობა თუჯების განგოგირდების ხარისხზე და გრაფიტული ჩანართების ფორმაზე. ნაჩვენებია, რომ თხევადი ლითონის დამუშავება აღნიშნული კომპოზიტებით არ იწვევს პიროეფექტს და უზრუნველყოფს მაგნიუმის მაღალ ათვისების ხარისხს.

დასკვნა.

- ✓ მაგნიუმ შემცველი გამჭოლი ფოროვანი კომპოზიტებით თხევადი ლითონის დამუშავება წარმოადგენს თუჯების მოდიფიცირებისა და რამიფინირების ეფექტურ ტექნოლოგიას, რომელიც უზრუნველყოფს Mg-ის ათვისების მაღალ ხარისხს (90-92%-მდე).
- ✓ 30კგ. ლითონის დასამუშავებლად MgO-ს ოპტიმალური ფრაქცია შეადგენს 2-2.5მმ.
- ✓ თუჯის რაფინირებისთვის კომპოზიტში მაგნიუმის ოპტიმალური რაოდენობა შეადგენს 30-32%-ს.
- ✓ აღნიშნული ტექნოლოგიის გამოყენებით შესაძლებელია თუჯში S-ის რაოდენობა შეიძლება შემცირებული იქნას უპრეცედენტო მნიშვნელობამდე - <0.003%.
- ✓ თხევადი ლითონის რაფინირებისა და მოდიფიცირების ოპტიმალური ტემპერატურა შეადგენს 1350°C და არ მოითხოვს ლითონის გადახურებას.

საკვანძო სიტყვები: მაღალმტკიცე თუჯი, გრაფიტული ჩანართები, სფეროიდიზაცია, მოდიფიცირება, რაფინირება, განგოგირდება.

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THE FORMULA OF THE RELATIONSHIP BETWEEN THE MATRIX PARAMETERS OF COMPOSITE MATERIALS AND THE COEFFICIENT OF RESISTANCE TO THE THERMOGRADIENT

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Resume: Goal: Formulation of empiric formula, which establishes relations between major matrix parameters of ceramic materials and composites and the coefficient of resistance to material thermogradient. **Method**: Harcort's method of cooling of water in boiling regime till disappearance of water. **Results**: It is proved that work-pieces reveal maximum thermal resistance and preservation of exploitation properties, when total closed porosity is within 2% - 8%, and pore sizes vary within 1 - 6 mcm. Besides, they are more or less of spherical form and are spread equally in the matrix. **Conclusion**: Thermogradient effect formula was defined for complex form work-pieces, when surfaces in the pieces are transacted several times by angles of various curvature radii.

Key words: Thermogradient Effect, Matrix Curvature Radius, Parameters, Temperature Field, Thermal Stress, Thermal Expansion.

1. INTRODUCTION

It is known that resistance to thermal- and air-thermal aggression and respectively to thermogradient of composite work-pieces made on ceramic matrix depends greatly not only on the value of the gradient at the mechanical stresses, which are mainly conditioned by the phases present in the material, thermal-processing regime and physical-chemical processes going on in the material during synthesis but also together with other factors, on their form [1] [2] [3] [4] .

If we take into consideration the fact that, when the nature of distribution of local mechanical stresses in solid bodies depends substantially on the form of a body, it is apparent that neglect of the form of a piece to thermogradient, will be associated with a big inaccuracy while determining the resistance of any specific work-piece [1] [2] . When we speak of the piece form, first of all, we have to imagine the curvilinear bodies with the surface of various curvature radii, which are mainly associated with the design of composite pieces. Composite materials are often characterized by rather complex profile relief, and in separate sections of its relief we often come across with very small radius curvature surfaces. It is namely pieces of such relief which are characterized by relatively high mechanical stresses, that is, static mechanical stresses [5] [6] [7]. When ceramic piece falls in the field of high thermal gradients the field efficiently acts on the section of a piece, in which mechanical stresses dominate, which is expressed in micro-efficiency, that is, in transformation of micro-cracks into macro-cracks and the final destruction of a piece [1] [2] [8] [9] [10] [11]. The fact is evident even without proving that in real conditions heat transmission is the last factor and temperature gradient between thermal emission and the piece at the border is bigger than the gradient formed in the piece, irrespective of the size of the piece.

2. MAIN PART

As far as it is known for us, in technical literature available up to now impact of the form of any work-piece on the resistance of thermogradient of pieces has not been elucidated yet. The known Weibull's formula [9] doesn't consider certain definite complex forms of ceramic work-pieces and their effect not only on thermogradient of pieces, but also on their thermal resistance, at large. Likewise, a form of a piece is not considered in Bio's [9] criterion, which characterizes value of temperature gradient between the piece surface and internal sphere. Fourier's [7] formula offers us only coordinates of a spot to be considered. Kingery [8] in his computations for non-stationary regime, when piece surface temperature suffers abrupt alteration from T1 to T2, while average temperature of a body remains almost unchanged (that is we deal with thermal shock) and at the same time heat transition tends to infinity—uses the so-called form factor, but physical content is not explained by interpretations. Kingery often introduces the form factor in the formula for thermal resistance.

In most cases these are spherical, cylinder and infinitely flat plates, that is, simple forms. We considered necessary to define formula of thermogradient effect for relatively complex forms, that is, when the piece surfaces are intersections by various curvature radius angle. For determination of a piece resistance to thermal aggression the value of this angle has determining significance. Although we will repeat that in the complex material structure, the composition, texture and many factors have important impact on thermal resistance. Besides, we have to take into consideration that selection of adequate parameter for evaluation of methodology of thermal resistance and its assessment is rather difficult [12]. We think that determination of thermal resistance [13] only by means of the values of mechanical strength at stretching, E-elasticity module and temperature conductivity—a, are not sufficient. Special literature [14] - [19] offers formulas, which are used for evaluation of heat stability of work-pieces. Apparently in those relations alongside with mechanical strength, porosity and thermal stability, we have to consider quantitative evaluation of the above referred parameters. Limit of strength [6] at bending of porcelain material, when it causes its destruction, approximately equals to 56 MPa [20] . If we consider Budworth's data [21] optimal volumetric quantity of pores in the matrix should not exceed 10%, and as a result, its mechanics suffers drastic worsening. At the same time Helga Gollisch-Szibov [22] offers optimal pore sizes—5 mcm. Kingery [8] offers insignificant porosity dependence on the factor of thermal resistance. According to the opinion of Strelov [23] at swift heating, porosity doesn't affect significantly crack formation process.

It is known from practice [3] that increase of porosity in most cases contributes to the elevation of thermal stability, but due to the fact that at this moment mechanical properties are decreased, it is complicated to determine optimal porosity. On the basis of experiments carried out by us by Harcourt [24] method and water cooling at boiling regime, it was proved that work-pieces reveal maximum thermal resistance, when total closed porosity in the matrix is within 0.5% - 8%, and sizes of pores vary within 1 - 6 mcm. At the same time, they are more or less of spherical form and are spread equally in the matrix. [24] , that is, the material is consolidated. We tried to offer explanation for this problem and by the provision of a series of experimental data we formulated empirical formula, which establishes relations between urgent matrix parameters for ceramic materials and composites and coefficient of resistance to thermal gradient of the material (for ceramic materials and composites). Temperature gradient created in the work-piece which is placed in temperature field should be characterized by the effect. Between the bottom of the work-piece and the heat source, there occurs the temperature difference, or the primary gradient. At the same time, temperature field created along the piece height, is parallel to the initial field, and is perpendicular to the secondary one, or on the heat, created on the bottom of the work-piece. Thus, we received secondary temperature difference between heat source and the heat, created on the height of the work piece. Vector direction of both heat sources is on the same side. Thermogradient effect should be conditioned by emission trajectory curvature in temperature field and should be characterized by the coefficient, which shows durability of a piece in thermo-gradient conditions and speed of temperature equalization in the environment. It is measured in cm/sec.

$$K=r\cdot\sigma_b(1-\mu)/a\cdot dT/dy\cdot d1/2\cdot E\cdot at$$

r - is for the work-piece curvature radius for selected surface element, σ_{bend} is mechanics at bending, MPa; μ - Poisson coefficient; a_t - temperature conductivity; E - Young's module; a - coefficient of linear expansion, dT/dy - thermal gradient for the selected y axis, along which thermogradient occurs, $d_{1/2}$ - half of piece wall thickness. It is necessary to allow some empiric assumptions, thus, e.g. that the piece from the side of heating should be flat, while the angle of joining of any two planes should be determined by curvature radius, which equals or exceeds

$$r\geq 0.3cm$$

Spot of joining of two planes of a piece is computed according to the design, empirically, at 30% maximum angle. As to the thermal expansion and thermal stress, it is considered that expansion of the work-piece is free, that is, mechanically unlimited, while the stress can be formed not only due to abrupt alteration but also at gradual changes, since at one and the same thermal gradient and at various curvature radii, various stresses will be formed in the piece.

In our case, to test the formula we used the properties of celsian electro-ceramic piece synthesized in $BaO\text{-}Al_2O_3\text{-}SiO_2$ system [25] and inserted the above listed properties in the formula by the succession of values given in the formula:

$$K=0.3\times69\times(1-0.282)/0.00354\times$$
$$\times75\times3\times10^{-6}\times140\times4=0.033325\ \text{cm/sec}$$

0.3-radius of curvature; 69-mechanics on bending; 0.18=1-μ; 0.00354-temperature conductivity; 140-temperature gradient; 4-half of the wall thickness of the product; 75-module of elasticity; 3-dimensional expansion coefficient.

Thus, if we determine universal connection between mechanical and thermal properties of the material, and alongside with it, we'll take into consideration the piece design and wall thickness, we'll be able to compute resistance of a piece to thermal gradient.

3. CONCLUSION

The formula enables us to determine numerical value, which will conform to the resistance of the given work-piece to thermogradient. This latter is computed by the provision of numerical values of the characteristics of the main ceramic materials (composites) used in practice which are given in the formula [26] . Designers of ceramic pieces will be able to use the data, first of all, with the view of selection of thermogradient, if threshold value of thermal resistance of the given material is known.

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კომპოზიციური მასალების მატრიცულ პარამეტრებსა და თერმოგრადიენტისადმი მედეგობის კოეფიციენტს შორის დამოკიდებულების ფორმულა

ზ. კოვზირიძე

საქართველოს ტექნიკური უნივერსიტეტი, ბიონანოკერამიკისა და ნანოკომპოზიტების ტექნოლოგიის ინსტიტუტი, ბიონანოკერამიკული და ნანოკომპოზიტური მასალების სამეცნიერო ცენტრი, თბილისი, კოსტავას ქ. 69, თბილისი 0175, საქართველო

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რეზიუმე: მიზანი: ემპირიული ფორმულის ფორმულირება, რომელიც ადგენს კავშირებს კერამიკული მასალებისა და კომპოზიტების ძირითად მატრიცულ პარამეტრებსა და მასალის თერმოგრადიენტისადმი მდეგობის კოეფიციენტს შორის. **მეთოდი**: ხარკორტის მეთოდი წყლის გაციების მდუღარე რეჟიმში წყლის გაქრობამდე. **შედეგები**: დადასტურებულია, რომ კერამიკა ავლენს მაქსიმალურ თერმორეზისტენტობას და ექსპლუატაციის თვისებების შენარჩუნებას, როდესაც ჯამური დახურული ფორიანობა 2%-8%-ის ფარგლებშია, ხოლო ფორების ზომები იცვლება 1-6 მკმ-ის ფარგლებში. გარდა ამისა, ისინი მეტ-ნაკლებად სფერული ფორმისაა და თანაბრად არიან განლაგებული მატრიცაში. **დასკვნა**: თერმოგრადიენტური ეფექტის ფორმულა განისაზღვრა რთული ფორმის სამუშაო ნაწილებისთვის, როდესაც ნაწილებში ზედაპირები რამდენჯერმე გადაიკვეთება სხვადასხვა მრუდის რადიუსების კუთხით.

საკვანძო სიტყვები: თერმოგრადიენტური ეფექტი, სიმრუდის რადიუსი, პარამეტრები, ტემპერატურული ველი, თერმული სტრესი, თერმული გაფართოება.

UDC 621.315.5/6

THE RECEIVING AND STUDY OF CELSIAN ELECTROTECHNICAL CERAMICS WITH INNOVATION ONE STAGE SIMPLIFIED TECHNOLOGIES IN THE $BAO-AL_2O_3-SIO_2$ SYSTEM

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Resume: Goal. Barite based celsian ceramics with phase composition accordingly (mass%): of celsian 93; Barium Aluminate and Barium Silicate-4; Glass phase - 3, has been synthesized on the bases of local raw materials with single stage innovation technology. **Method**. One burn at 1600^0C we have take out from standard technology in which barium carbonate is used. The material displays the best properties in conditions of synthesis at 1410-1460°C **Results**. Its properties have been studied in complex. The material shows high resistanse to heat shock. A completely new mechanism of ceramic production is proposed. Structure of celsian ceramics in $BaO-Al_2O_3-SiO_2$ system is studyd with electron microscope, X-ray, crystalline phase content, optical microscope. Water absorbtion, W%=O. Bending strength of non glazed, δ N/mm^2 – 69. CLTE, α_{20-700} 10^6C^{-1} temperature areas-3.7. Tanget of a dielectric loss angle at 50 Hz and 20°C and $tg\ \delta\ 10^{-4}$=107. HV GPa-18.0. Volume resistivity, ρ ohm/cm $20^0C-300^0C=10^{16}-10^{12}$. Elastic modulus, E N/mm^2-74.5.

The process of pores filling, full consolidation of material and hardness growth at comparatively high temperatures of baking interval are studied.

Conclusion. High refractoriness of celsian, (1740°C), low thermal coefficient of linear expansion of synthesized materials, high thermal resistivity enable this ceramics to be recommended for introduction in electronical and electrotechnical industry.

Key words: electron microscope, crystalline phase, transformation, reaction, celsian, silicate, aluminate

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1. INTRODUCTION

Technical progress needs the development of new innovation simple technologies. The scientists and technologists work on receiving high property modern materials by simplification of expensive technologies.

With one-stage technology instead of traditional two-stage technology ($BaC0_3$ and Geopolymer - kaolin composition, burnd two times at 1600^0C), for $BaO-Al_2O_3-SiO_2$ system in barite (Georgia), geopolymer - refractory clay (Ukraine) composition we obtained [1] composites B-1 with 93 mass% celsian phase content (Fig. 1). The rest consists of barium aluminates, barium silicates and glass phase. In composition of B-3 ceramics 12-14 mass% corundum is added at the expense of barite content decrease. The material displays the best properties in conditions of synthesis at 1410-1500°C (Table 1). Deformation temperature of ceramic materials is primarely determined by their phase composition, character of structure and mutual intergrowth of crystal formations, quantity and viscosity of vitreous phase. Material texture - character of its grain composition, number and arrangement of pores - is of certain significance. Dense items have a relatively high initial softening point and 4% compression, and final deformation temperature (20% and 40% compression) is mainly determined by chemical composition, rather than by material structure.

Deformation point of ceramics of pure oxides, containing small quantity of vitreous phase, approaches its melting point, i.e. is due to plastic deformation of crystal matter, making up ceramics. Deformation temperature would increase the more, the less are the vitreous easy-melting interlayers between grains closely adjoint at boundaries.

Ceramic materials, produced from the natural material contaminated with different raw admixtures, always contain a certain amount of vitreous phase. The greater the amount of vitreous phase, the greater the decrease of the item deformation point, as compared to their refractoriness. Deformation of ceramic materials under load at high temperatures determines the capacity to resist simultaneous effect of high temperatures and liquefying load

2. MAIN PART

Table 1

Properties of celsian ($BaO.Al_2O_3.2SiO_2$) materials

№	Denomination of parameters	T°C	Value of parameters	
			B-1	B-3
1	2	3	4	5
1	Firing temperature, T°C		1410-1500	1400-1450
2	Water absorption W%		0	0-0.1
3	Bending strength of non glazed, δ N/mm²	1350	33.0	42.5
		1410	66.4	72.6
		1450	68.7	56.0
		1500	59.3	-
4	Compression strength of non-glazed, δ N/mm²	1350	153.8	214.5
		1410	443.8	428.0

5	Density, ρ g/cm^3	1100	2.13	1.93
		1350	2.55	2.49
		1410	2.99	2.98
		1450	3.03	2.62
		1500	2.96	
6	Elastic modulus, E N/mm^{2}10^3	1410	71.32	69.35
		1450	74.53	79.22
		1500	78.50	-
7	Shear modulus, G N/mm^{2}10^3	1410	28.36	28.00
		1450	29.05	31.45
		1500	31.48	-
8	CLTE, α 10^{6}C^{-1} temperature areas	20-100	2.7	2.8
		20-600	3.7	4.4
		20-1000	4.1	4.9
9	Poisson's ratio, μ	1410	0.283	0.239
		1450	0.282	0.259
		1500	0.284	-
10	Heat capacity $C_{p\ 20\text{-}200}$ J/kg °K	1500	608	623
11	Heat conduction, λ WT/mK 20-200°C	1410	1.29	1.91
	fired at T°C	1500	2.32	-
12	Chemical stability after 1 hour boiling, %in water			
	in *NaOH* (35%)	1410	99.3	99.5
		1450	99.0	98.7
13	Volume resistivity, ρ ohm/cm	1450		
	20° C		10^{16}	10^{14}
	300°C		10^{12}	10^{10}
14	Tanget of a dielectric loss angle at 50 Hz		107	230
	and 20°C and *tg* δ 10^{-4}			-
15	HV, Gpa		18.00	24.00

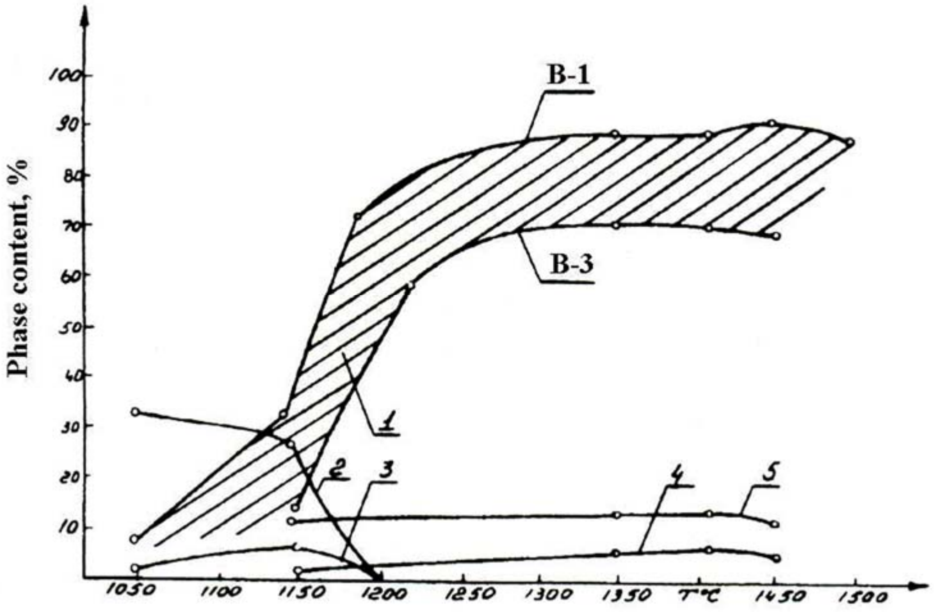


Fig. 1. Change of crystalline content phase depending on temperature in barite-bearing materials. 1. Celsian; 2. Barite in B-l; 3. Mullite in B-l; 4. Mullite in B-3; 5. Corundum in B-3

In scanning electron microscope tungsten cathode heated to 1800-2000°C in 10^{-5}-10^{-6} vacuum conditions is used as electron flux source.

Fig.2-5 show electron microscopy pictures of celsian ceramics in dynamics, in the whole 1410-1500°C temperature region of agglomeration interval.

The process of pores filling in material was studied.

In material B-1 synthesized at 1450°C (Fig.2-1) light colour restricted celsian formations are observed in dark colour basis of the sample. In Fig.2-2 and 2-3 the sample tends to pack. Here is clearly expressed sheetlike and in voids short prism-like structure of 0.5-3 μm of celsian crystals.

In Fig. 3 the main basis of B-l ceramics first sample synthesized at 1450°C is almost covered and limited with light colour celsian formation.

In samples 2,3 and 4 crystallization degree is mainly directed to structure packing resulting in gradual formation and growing in sample pores of small and homogeneous sheet-like celsian crystals. There happen filling and healing of pores. The process is clearly seen in case shown in Fig 4.

In Fig.4.1, the first sample of ceramics B-l synthesized at 1500°C is entirely covered with celsian crystals, their form apprehended as rounded in spite of the fact that at the mentioned temperature it crystallizes in monoclinic singony. We suppose that this happens because of a small increase x240.

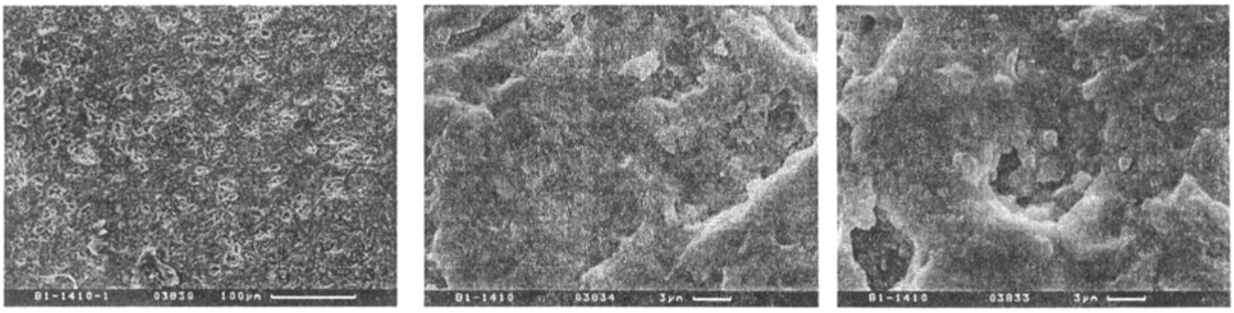
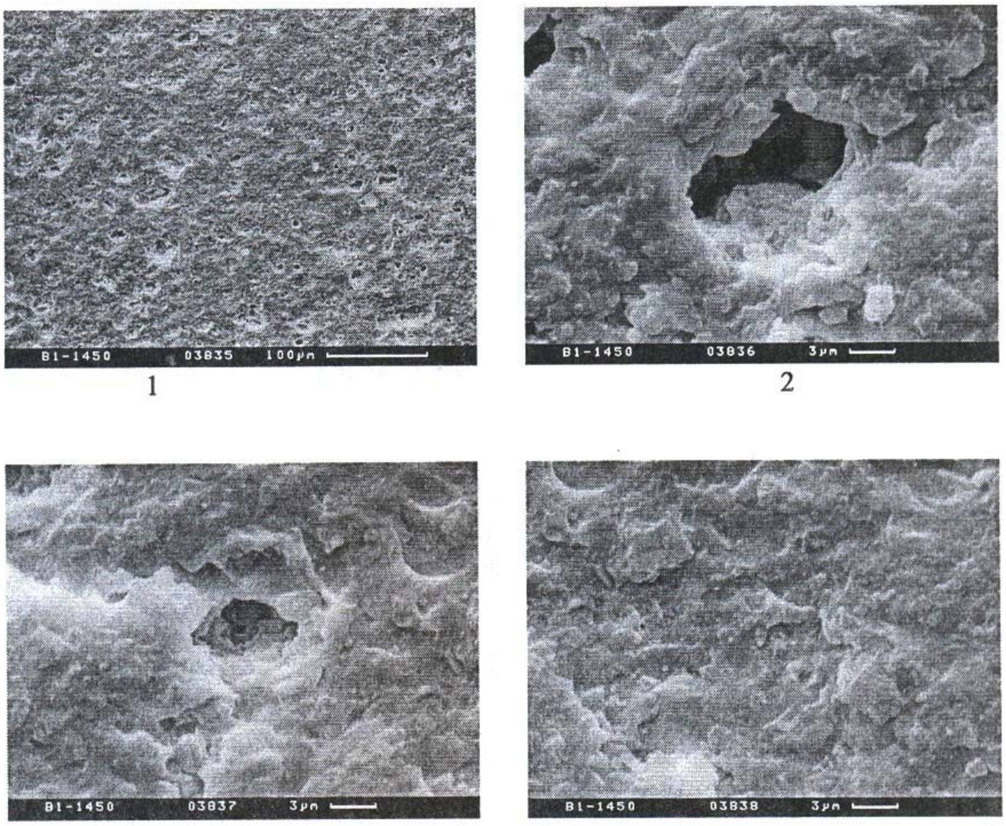


Fig. 2. Electron microscopy of B-I synthesized
at 1410°C, l-x240; 2-3 x4000



1

2

3

4

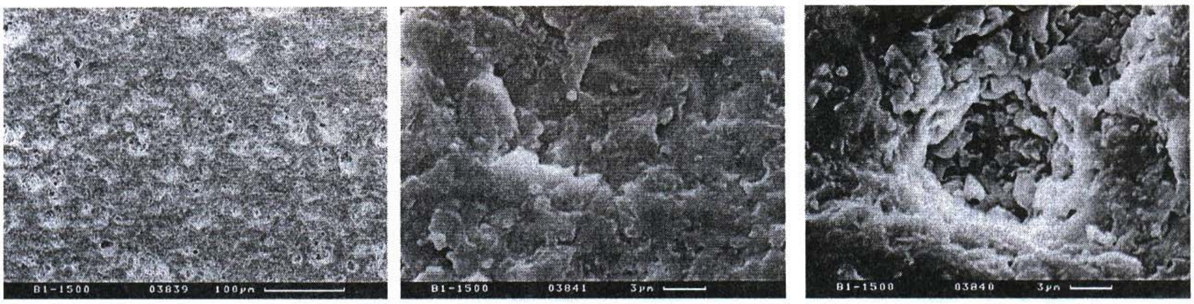
Fig. 3. Electron microscopy of B-l synthesized
at 1450°C. l-x240; 2-4 -x4000

In Fig. 4.3 celsian crystals in mass are characterized with sheet-like arrangement. The matrix is filled with short prism-like celsian of size 0.5-4 μm. In the Figure the process of pore filling is clearly seen. In Fig.4.2 we have regions where crystals have almost sheet-like form and make densely packed structure.

Ceramics B-3 x240 which is synthesized at 1450°C and has 12 mass % Al_2O_3 added in composition is characterized with dark colour main background. In this case celsian crystallization is observed only around corundum grains that do not take part in reaction.

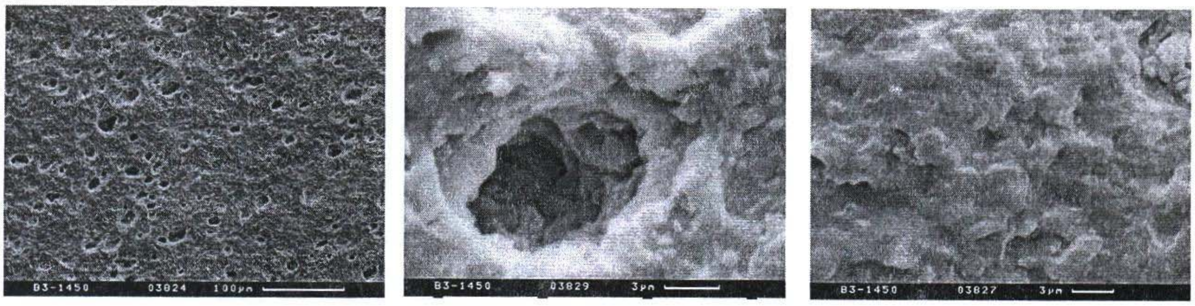
In case of samples 2 and 3 homogeneous densely packed sheet-like arrangement of celsian crystals is expressed.

It can be concluded that in $BaO\text{-}Al_2O_3\text{-}SiO_2$ system in composition of kaolin, refractory white burning clay and barite it is possible to obtain ceramics with high technical properties ceramics and with small enough crystals in matrix which are evenly distributed in the whole mass and make tight structure. Pores are successfully filled at the expense of crystallization. Of course in baking interval it is necessary to keep strict temperature regime in order to avoid the process of secondary crystallization that will lead to coarse grain structure and consequently to weakening of mechanics.



1 2 3

Fig. 4. Electron microscopy
of B-1 synthesized at 1500"C. 1-x240; 2,3 - x4000



1 2 3

Fig. 5. Electron microscopy
B-3 synthesized at 1450"C. 1-x240; 2,3 - x4000

Basing on the quantitative phase analysis, Fig. 6 shows the behaviour of a triple system of barite-celsian-barium silicates (BS) and barium aluminates (BA) phase, which are the main components of the mentioned system in the process of thermal treatment, depending on the fourth variable - temperature. As the Figure shows, the temperature is plotted as the vertical axis, the system of coordinates forming a right prism, each section of which being parallel to the base, represents the surface of constant temperature. It is clearly seen here that barite content in the system at 1200°C reaches zero and the point at the back side of the triangle expresses the composition of the binary system, while the first two points within the triangle express the composition of the triple system at 1050°C and 1150°C. After 1200°C the region of celsian abruptly rises up and at 1450°C attains its maximum with 93% content in the system. After this temperature partial melting of celsian takes place due to the presence of a small quantity of the vitreous phase in the composition and at 1500°C its content decreases to 89%, which is expressed by the point at this temperature. In Fig. 6 a projection is drawn on the base plane, corresponding to the back side of the triangle from the points at 1450°C and 1500°C reflecting the composition of the system. This enabled to show more clearly the development of triple system's composition in relation to temperature.

An interesting phenomenon has been observed during the analysis of the X-ray photographic pictures, namely, the presence of a crystalline phase, which in both materials is traced uniformly with interplane distances d_{hkl} = 2.18; 2.27; 2.56; 2.61; 3.27 Å at all used temperatures.

Diagram of condition of $Ba0-Al_20_3-Si0_2$ system according to Toropov and Galakhov [2] shows only one triple compound - celsian, occupying central position. Further, Planz and Muller-Hesse [3,4] having studied the triple system $Ba0-Al_20_3-Si0_2$ and parts of the system $Ba0-Al_20_3$, $Ba0-Si0_2$, $Al_20_3-Si0_2$ assertained the existance of one more triple compound $3Ba0-3AI_20_3-2Si0_2$ and in the left part of the system between B_2S_3 and B_2S the existance of B_3S_5 and B_5S_8.

On the left part of the constitution diagram intcrplanar distances of the phases undetermined by us, in most cases coincide with B_2S according to Levin and Ugrinic, [5] *(d_{hkl} =* 3.28; 2.61; 2.28; 2.04 Å); Roth and Levin [6] *(d_{hkl}=2.60;* 2.27; 2.18; 2.03 Å as well as with B_3S_5 *(d_{hKl}=* 3.27; 2.27; 2.18 Å and B_5S_8 with *(d_{hKl}=* 2.27; 2.18; 2.03 Å.

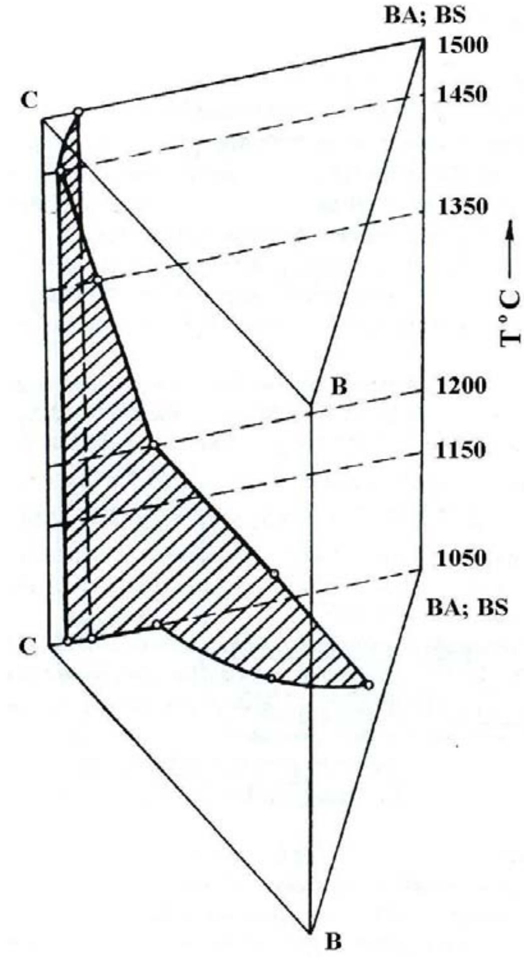


Fig. 6. Behaviour of the triple system:
C – celsian; B – barite; BS – barium silicate
BA – barium aluminate phase in dependence
to temperature

Material deformation point under load has been determined as per GOST Georgia at continuous heating with the set rate 4-5° per minute. Initial softening point (corresponding to the compression of the tested sample of 50 mm x 0.3 mm) at 4% and 40% compression was registered.

Cylinders, 36 mm in diameter and 50 mm in height served as samples. Load - 0.2 kg/cm^2 . Tests were carried out in a crypte kiln. Temperature up to 800-1000°C was measured with a thermocouple, from 800- 1000°C and higher with an optical pyrometer (the thermocouple is removed). Fig. 7 show time history of thermomechanical characteristics when ceramic materials B-1 were heated.

For complex analysis the figures show porosity curves for water absorption, for density and dilatometric tests at high temperatures, which allow to judge about the behaviour of items during thermal treatment, depending on physico-chemical processes taking place in the materials.

Caking interval and beginning of deformation could be determined by the change of linear sizes of mixture samples at heating. Investigations were carried out on optical dilatometer. Rate of temperature rise to 900°C is 6 degrees per minute, after 900°C - 3 degrees per minute. Allowance at finite temperature is 20 min. The samples - pencils for experiments were prepared by broaching on a screw hand press with inner diameter - 7.5 mm, length of the sample being 110 mm. Results of the experiments with masses are given in Table 2.

Table 2.

Behaviour of barite-containing ceramics at heating

Material index	Properties at heating under load	Temperature, C			Caking temper-ature, °C	Refractoriness, °C	Service temperature between IS and 4%, °C
		start of softening	4% compression	40% compression			
B-1		1400	1480	1640	1410	1650	1400- 1480
B-3		1380	1420	1520	1380	1620	1380- 1420
Material index	Dilatometric tests	Start of caking, °C	Beginning of intensive shrinkage, °C	Maximum compaction	Interval of finite caking temperatures, °C		Maximum firing shrinkage, %
B-1		1250	1320	1480	1400-1500		15,5
B-3		1220	1300	1410	1400-1440		15,0

Interesting results were obtained during dilatometric tests: compared to common feldspar behaviour of barium-bearing masses is somewhat different. Compaction begins at 1200°C and terminates in 1400-1450°C temperature range, while compaction of porcelain mass begins at 1100°C and ends in 1300-1350°C temperature range. According to the test data limiting firing temperature of B-1 and B-3 should be 1520 and 1450°C, respectively.

Shrinkage of barite-containing mass, as compared to production mass on feldspar basis, is higher, which is due to high content of sulphuric anhydride in barite. Caking interval of the prepared masses is greater than that of porcelain masses. Maximum interval is characteristic to masses B-1 and is about 200°C, which is explained by high viscosity of the compound in the 1200-1500°C temperature interval.

The fact, that the region of caking temperature is near maximum shrinkage temperature can be explained in the analysis of the processes taking place in ceramic masses during heating.

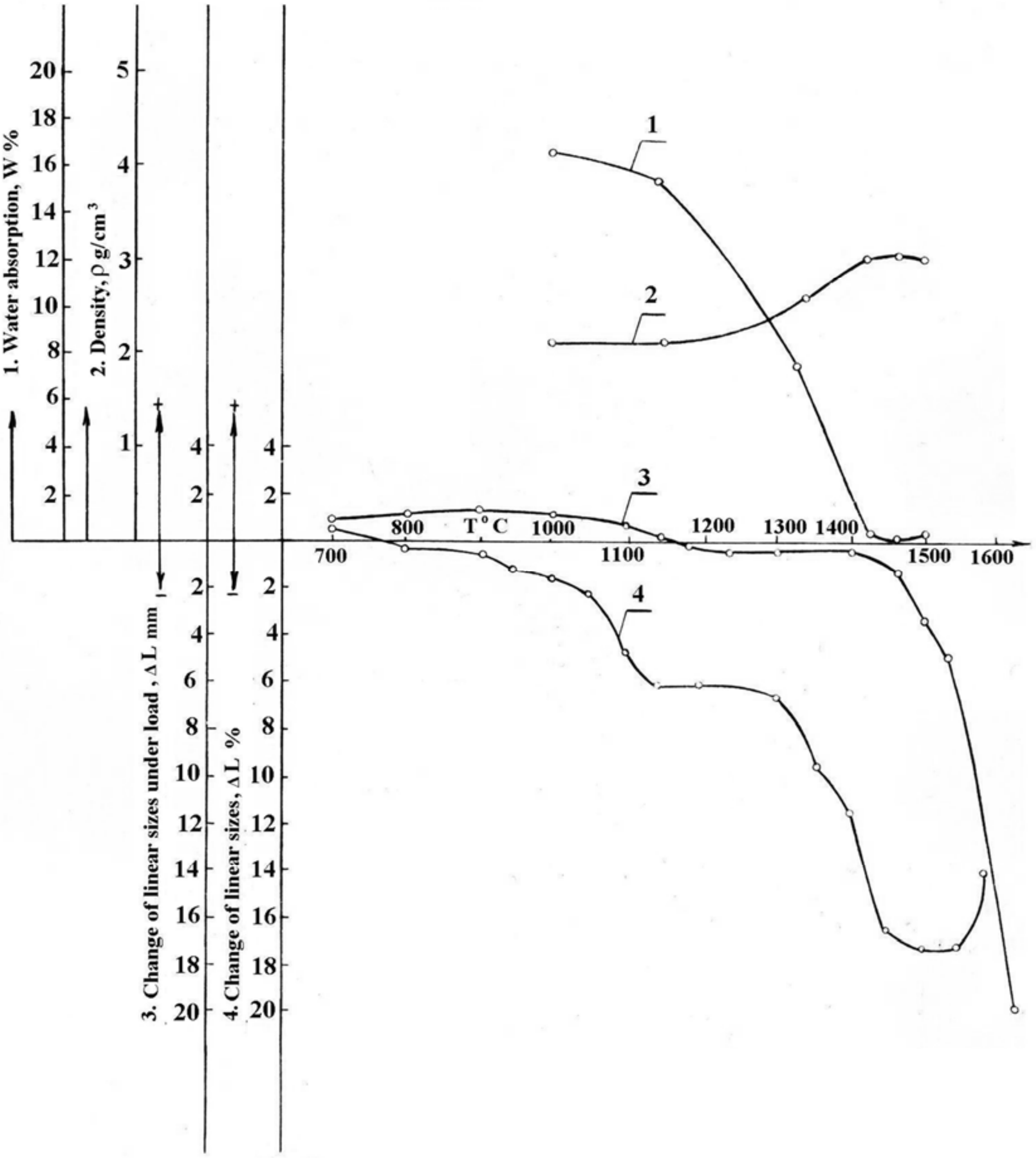


Fig.7. Time history of thermo-mechanical characteristics during heating of ceramic material B-1

Quantity of liquid phase increases and its viscosity changes (decreases) with the increase of temperature in the material, the pores of the crock gradually close, while the volume of gas contained in pores tends to expand with temperature increase. The resulting expansion of the crock is first slowed down by shrinkage phenomenon taking place in the mass, the maximum in which coincides with maximum caking temperature. With further increase of temperature the quantity of closed pores increases and expansion begins to prevail over shrinkage. This phenomenon corresponds to the point of shrinkage-to-expansion transition, i.e. to the beginning of swelling process development.

The number of closed pores in the process of caking will increase the more, the greater the remainder of unseparated gasses in the crock. Partial pressure of gasses in the closed pores will have greater effect on swelling of the material during heating. Such material, having reached the maximum value of caking, would sharply expand in the volume.

The greatest strain stability during deformation determination analysis at high temperatures was desplayed by material B-1.

The mass tendency to deformation during firing is manifested in the form of "horizontal area" on the deformation curve under load [7]. The more thickly melted is the glass phase in porcelain and the more intensive is crystal formation in it, the greater is the "horizontal area' and the more resistant the item is against deformation. In porcelain masses shrinkage increases within 1200-1230°C temperature range, and the area is widest from 1200 to 1600°C, while with B-1 masses it is 1150-1200°C, 1200-1450°C and 1200- 1400°C, respectively.

As Fig. 7 show, deformation is observed at 1000-1180°C when the process of celsian and mullite development can not yet resist the deformation. In this connection, masses at 1150-1400°C become more resistant in fire, when celsian and mullite begin to develop, and the crock matures and becomes dense.

A relatively great quantity of liquid is formed in perlite -containing mass B-3 and its viscosity at finite temperatures of firing is lower than that of material B-1. Therefore, the degree of deformation point decrease of B-3, compared to its refractoriness is higher than that of B-1.

Table 3 shows resistance criteria to thermal shocks for the materials fired at different temperatures.

Table 3

Values of resistance to thermal shocks of barium-containing composites

Material index	apparent porosity,	real porosity, W %	Density g/cm^3	δ bend. MPa	10^6 °C^{-1}	E, GPa	Poissons ratio, μ	R’ °C	R” WT/m	R’’’ 10^4 m^2/ kg
B^{1}1410	0,10	12,2	2,99	66,4	4,1	71,32	0,283	163	210,30	225,6
B^{1}1450	0,00	7,8	3,03	68,7	4,1	74,59	0,212	161	164,20	220,0
$B^3$1500	0,15	8,8	2,96	59,3	4,1	72,20	0,280	144	185,80	285,2
$B^3$1410	0,20	-	2,80	72,6	4,1	69,35	0,233	220	420,20	172,9
B^{3}1450	0,18	-	2,62	56,0	4,1	79,22	0,258	128	244,48	340,0

Analysis of Table 3 data and experimental data obtained from the study of the properties of thermal resistance of barium-containing composites enables to suggest that at a steady regime, celsian ceramics B-l fired at different temperatures and having zero open porosity is more stable, than B-3 having the highest value of thermal resistance - 480°C. It is apparently due to the presence of mainly one celsian phase having low expansion coefficient (TCLE) which predetermines high resistance to thermal shocks of the items made of composite materials on celsian basis. A somewhat low value of ceramics B-3 resistance to thermal shocks must be due to the fact that it is multiphase with different expansion coefficients contains: celsian, mullite, corundum and glass phase in the greater quantity than B-l, which has different CLTE, and which undoubtedly affects on its properties. However, introduction of additional alumina noticeably incerases resistance of corundum-celsian composites to thermal shocks [8-13], maintaining these values within temperature region of 400-420°C.

Basing on the above stated, the scheme of barite-argillaceous transformation reaction during thermal treatment can be presented in the form shown in Fig. 8.

Mechasnism of formation of celsian ceramics (B-I) is as follows:

At 1380-1410°C structure of materials becomes more compact, density increases. Change in density is caused by the increase of pressure in pores. General porosity decreases, open pores close, number of closed pores increases, mechanical strength increases insignificantly. At 1410°C open pores disappear. The material passes the inversion point.

In the range of 1410-1450°C density increases rapidly and the number of closed pores decreases as a result of merging of small ones; internal pressure in the pores decreases to zero. Mechanical strength increases. Values of ultra-sonic wave propagation rate and of elasticity and shear modulus attain maximum values.

At 1450-1500°C small pores unite as a result of continuous decrease in viscosity, pressure becomes stable and further compaction of the material takes place (3.03 g/cm ^{3}).

At temperature of 1500°C walls cannot stand internal pressure and the process of swelling begins. Material density decreases (2.88 g/cm^3). Pressure inside the pores increases to such an extent, that the pores lose round shape and become elongated.

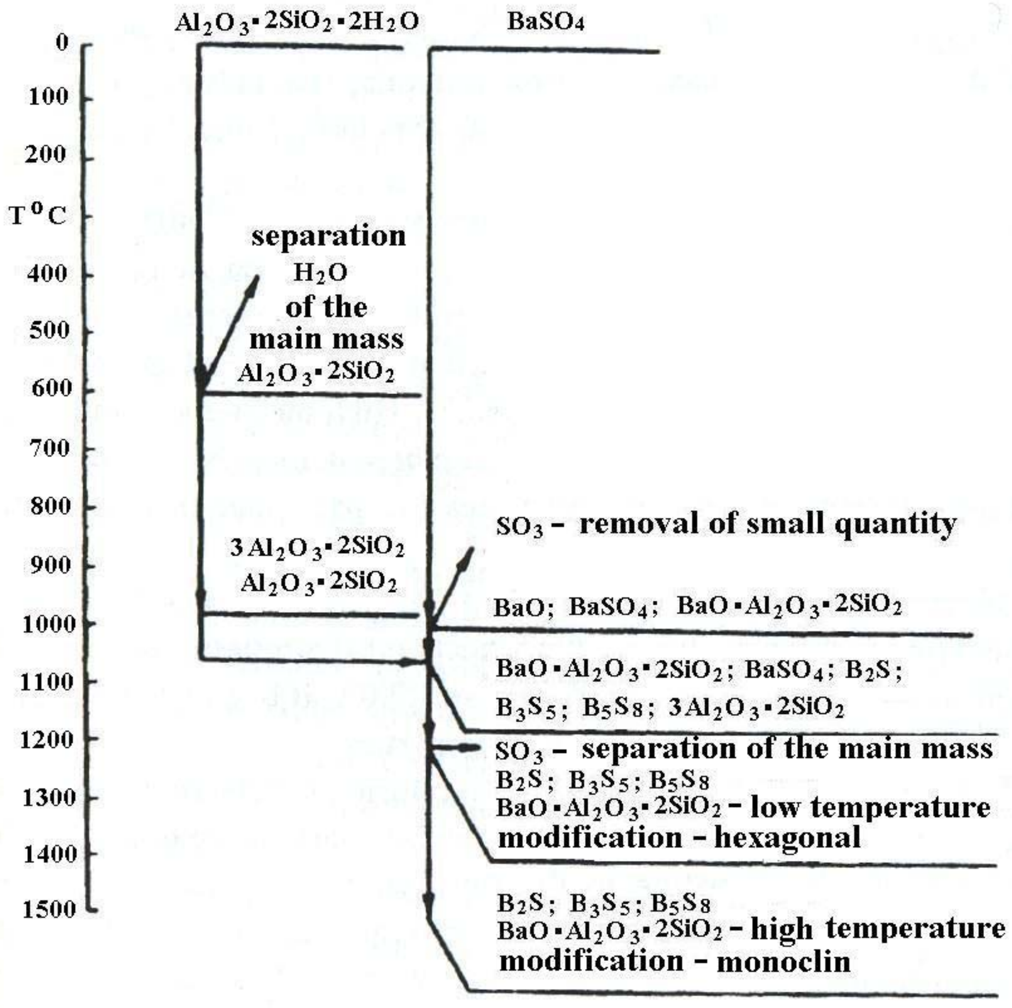


Fig. 8. Scheme of transformation reaction of geopolymer-barite mixture; 50:50.

3. CONCLUSION

Thus, in the process of investigation celsian composites with celsian content of up to 93% has been synthesized with innovation single stage simplified technology at 1450^{0}C and local raw material-barites (Georgia), instead of traditional two-stage technology $BaC0_3$ and Geopolymer - kaolin composition, burnd two times at 1600^{0}C. It is given the chemical kinetics and scheme of transformation reaction of geopolymer-barite mixture. High refractoriness of celsian, (1740°C), low thermal coefficient of linear expansion of synthesized materials, high thermal resistivity enable this ceramics to be recommended for introduction in electronical and electrotechnical industry.

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უაკ 621.315.5/6

ცელაზიანის ელექტროტექნიკური კერამიკის მიღება ინოვაციური ერთსაფეხურიანი ტექნოლოგიით BaO-Al_2O_3-SiO_2 სისტემაში

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რეზიუმე: მიზანი. ბარიტის ბაზაზე ცელზიანის კერამიკის მიღება ფაზური შედგენლობით (მასობრივი%): ცელზიანი 93; ბარიუმის ალუმინატი და ბარიუმის სილიკატი-4; მინისებური ფაზა - 3, სინთეზირებულია ადგილობრივი ნედლეულის ბაზაზე, ერთსაფეხურიანი ინოვაციური ტექნოლოგიით. **მეთოდი**. ერთი გამოწვა 1600^{0}C-ზე ამოღებული გვაქვს სტანდარტული ორსაფეხურიანი ტექნოლოგიიდან, რომელშიც გამოიყენება ბარიუმის კარბონატი. ჩვენს მიერ მიღებული მასალა ავლენს საუკეთესო საექსპლოატაციო თვისებებს 1410-1460°C-ზე სინთეზის შედეგად. **შედეგები**: მისი თვისებები შესწავლილია კომპლექსურად. მასალა ავლენს მაღალ მედეგობას თერმიული შოკების მიმართ. შემოთავაზებულია კერამიკული მასალების წარმოების სრულიად ახალი მექანიზმი. ცელზიანის კერამიკის სტრუქტურა BaO-Al_2O_3-SiO_2 სისტემაში შესწავლილია ელექტრონული მიკროსკოპით, რენტგენოსტრუქტურული, კრისტალური ფაზის შემცველობით, ოპტიკური მიკროსკოპიით. წყალშთანთქმა, W%=O. მექანიკა ღუნვაზე არამოჭიქული, δ N/mm^2 – 69. CLTE, $a_{20\text{-}700}$ 10^{-6} C-1-თვის-3.7. დიელექტრიკული დანაკარგების კუთხის ტანგენსი 50 ჰც და 20°C tg δ 10^{-4}=107. HV GPa-18.0. მოცულობითი წინაღობა, $\rho_{ohm/cm}$ 20-300^{0}C=10^{16}-10^{12}. დრეკადობის მოდული, E N/mm^2-74.5.

შესწავლილია ფორების შევსების პროცესი, მასალის სრული კონსოლიდაცია და სიხისტის ზრდა შეცხობის ინტერვალის შედარებით მაღალ ტემპერატურაზე. **დასკვნა**. ცელზიანის მაღალი ცეცხლგამძლეობა, (1740°C), სინთეზირებული მასალების ხაზოვანი გაფართოების დაბალი თერმული კოეფიციენტი, მაღალი თერმული წინაღობა საშუალებას იძლევა კერამიკა რეკომენდირებული იყოს ელექტრონულ და ელექტროტექნიკურ ინდუსტრიაში დანერგვისთვის. ტექნოლოგია დანერგილია თბილისის საშენ მასალათა კომბინატის საცდელ ქარხანაში. შვიდი დასახელების ელექტროტექნიკური ნაწარმი იგზავნებოდა რუსეთში.

საკვანძო სიტყვები: ელექტრონული მიკროსკოპია, კრისტალური ფაზა, ტრანსფორმაცია, რეაქცია, ცელზიანი, სილიკატი, ალუმინატი.

UDC 691.2

DEVICE FOR THE TREATMENT OF ONCOLOGICAL DISEASES BY THE METHOD OF CONTROLLED LOCAL HYPERTHERMIA

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Resume: Goal. Method. Results. The monotherapeutic effect of hyperthermia in oncological diseases was studied.To develop a method of controlled local hyperthermia based on experimental material, the Lezi 1 device, created at Bionanoceramic and Nanocomposite Materials Science Center of Georgian Technical University, was used. (Georgian National Center of Intellectual Property, "Sakpatenti". Deposit certificate No. 5054. "Controlled local hyperthermia and magnetic hyperthermia for the treatment of oncological diseases"). As a result, it was shown and established that all animals (albinos, 3-month-old mice) showed cancer stopped and developed intratumor necrosis. After 8-10 sessions, the tumor ulcerated, which indicates a positive result of the experiment (conclusion of the Patjeo pathological laboratory). Study #3119-12 and histopathological study #15272-13. Date of diagnosis: 14.01.2014. Tbilisi, Georgia).

The monotherapeutic effect of hyperthermia in proctologic cancer and cervical cancer was studied. To develop a method of controlled local hyperthermia based on experimental material, the "Lezi" device, created at the Bionanoceramic and Nanocomposite Materials Science Center of Georgian Technical University, was used. All animals (albino, 3-month-old mice) showed cancer stopped and development of intratumor necrosis. Georgian National Intellectual Property Center, "Sakpatenti". Certificate of Deposit 5054. "Controlled local hyperthermia and magnetic hyperthermia for the treatment of oncological diseases").

Conclusion. As a result, it was shown and established that after 7-10 sessions the tumor ulcerated, which indicates a positive result of the experiment (conclusion of the pathological laboratory "Patjeo").Study #3119-12 and histopathological study #15272-13. Date of diagnosis: 14.01.2014. Tbilisi, Georgia).

Key words: controlled local hyperthermia, necrosis, ulceration, metastasis.

1. INTRODUCTION

Relevance of the problem and novelty of the research

According to the World Health Organization, the incidence and mortality of malignant tumors are constantly growing worldwide. Today, the leading role in the treatment of cancer patients is assigned to:

1. Surgical methods;
2. Chemotherapy;
3. Radiotherapy.

Supportive methods include hormonal and immunotherapy.

However, in many cases, despite qualified intervention, the disease is fatal. In addition to multiple organ failure, this is due to immunosuppression caused by chemotherapy and radiotherapy, myelosuppression, leukopenia, cardio-, nephro-, hepato- and neurotoxicity, intercurrent microbial complications and others.All this makes it necessary to search for new ways to treat malignant tumors, which will be aimed at strengthening the antitumor strategy.

For the first time in Georgia, we have studied the antitumor effect of controlled local hyperthermia. Hyperthermia is a method that involves cytostatic action on tumor cells by increasing the temperature inside the cell, in our case by dissipating heat caused by the temperature field.

The number of people suffering from malignant tumors in Georgia reaches seven thousand every year. The total number of infected people is vourty-five thousand people.

It is known that malignant tumors consist of the body's own cells, which differ from the norm only in that they undergo uncontrolled, unlimited reproduction and growth. Therefore, the intensity of metabolic processes and, accordingly, the need for energy in malignant tumors is higher than in normal tissues. Taking this factor into account, it is promising to use such an effect on cancer patients and adjacent tissues, which over time will exhaust the energy potential of degenerated cells, cause denaturation (death) of their proteins, while maintaining the viability of healthy cells [1-3].

Such a biophysical effect can be local hyperthermia (+42 - +44°C).

Ceramic microspheres are known for their use in radiotherapy of cancer

Y_2O_3 –Al_2O_3 – SiO_2 Glass microspheres

In 1987, Hyatt and Dei [4] and Erbe and Dei [5] first confirmed that $17Y_2O_3$ –$19Al_2O_3$ – $64SiO_2$ (mol %) glass microspheres with a diameter of 20–30 μm could be used for in situ (on site) cancer irradiation.Yttrium-89 (^{89}Y) in this glass is a non-radioactive isotope that exists in nature in 100% abundance, but neutron irradiation activates ^{89}Y and produces the β-emitting ^{90}Y, which has a half-life of 64.1 hours. When these radioactive glass microspheres, 20-30 microns in diameter, are injected into an organ (for example, for liver cancer), they penetrate the small blood vessels of the tumor and block its nutrition, and also emit short-range, highly ionizing β-rays. β-rays do not affect other chemical elements and have a small penetration depth into living tissue - about 2.5 mm, therefore they do not pose a radiation hazard to surrounding healthy tissue. These microspheres are characterized by high chemical stability, due to which the radioactive ^{90}Y microsphere mainly remains inside the patient after placement and does not affect adjacent healthy tissue. The radioactivity of ^{90}Y upon neutron irradiation [6] decreases to negligible values within 21 days; therefore, the microspheres lose their activity soon after cancer treatment. They are already used in clinical practice for the treatment of liver cancer in Canada, the United States and China, and in clinical trials for the treatment of kidney and spleen disease, as well as for radiation synovectomy of arthritic joints [7-20].

Use of ceramic microspheres for cancer hyperthermia

Ferromagnetic glass-ceramic

Currently, glass ceramics containing lithium ferrite ($LiFe_5O_8$) in a biocompatible hematite matrix (α- F_2O_3) and a glassy phase SiO_2–P_2O_5 [21–27], magnetite (F_3O_4) in a β-wollastonite matrix (β-$CaSiO_3$) and a glassy phase CaO-SiO_2-B_2O_3–P_2O_5[28–35], α-Fe^x [36], a glassy phase CaO-SiO_2-P_2O_5 without F_3O_4 [37], and zinc iron ferrite in a glassy phase CaO-SiO_2[38] have been developed as thermal beads for cancer hyperthermia.For example, glass ceramics containing F_3O_4 in a β-$CaSiO_3$ matrix and a glass phase of CaO-SiO_2-B_2O_3–P_2O_5 are effective [29-31] in lysing cancer cells implanted in the femurs of rabbits when introduced into the brain canal in the form of a pin and placed in an alternating magnetic field [33]. However, such a glass-ceramic pin cannot be used in clinical conditions because tumor cells may be scattered around normal cells, and the introduction of a glass-ceramic pin into a tumor may cause tumor metastasis. It is possible to use ferromagnetic microspheres with a diameter of 20-30 μm for local heating of cancer cells due to the loss of hysteresis of ferromagnetic materials, without causing cancer metastasis; Microspheres can be introduced into the tumor through blood vessels [39] and then placed in an alternating magnetic field. However, microspheres with a diameter of 20–30 μm have not yet been created and have not demonstrated the ability to generate large amounts of heat..

Rates of morbidity and mortality from malignant tumors worldwide are constantly increasing and show no signs of abating.Early diagnosis is difficult, and a significant proportion of patients are hospitalized with advanced tumors (stages III–IV), which require combined and comprehensive treatment using surgical, radiation and drug components. The number of patients seeking oncology care with late clinical signs of tumor progression and various metabolic disorders has also increased.

The development of new methods of treating malignant tumors is an important task of oncology. The introduction into clinical practice of a drug or method of treatment, the positive effect of which is confirmed by experimental and clinical studies, is a step forward in the treatment of cancer patients.

The purpose and objectives of the hyperthermia study that we have developed.

The aim of the study is to improve short-term and long-term cancer treatment outcomes by applying hyperthermia to tumor lesions.

To achieve this goal the following objectives were set:

1) Study of the antitumor therapeutic effect of hyperthermia on experimental tumors.

2) Experimental determination of the antitumor adjuvant effect of hyperthermia in combination with poly chemotherapy.

Study of the influence of different hyperthermia regimens on the immediate and long-term effects of treatment.

Scientific novelty.

Based on experimental material, the antitumor mono therapeutic effect of hyperthermia and its adjuvant effect in poly chemotherapeutic treatment of tumors were proven for the first time in Georgia.

Object and objective of the study

The subjects of the study were 2-3 month old, 18-25 gram, non-stressed, non-linear white mice and their malignant tumor cells. Cancer cells usually die at temperatures around 42-44^{0}C because the oxygen supply through the blood vessels is insufficient, while normal cells are not damaged even at higher temperatures. In addition, tumors are more easily infected than the normal tissues surrounding them because the blood vessels and nervous system are less developed in tumors [1-3].

The experiment was conducted on twelve groups of animals. The results were equally positive for all groups. The results were published in Japan, the USA, Europe and Georgia. The reports were made at international conferences and world congresses [40-43].Based on these results and many years of experience, there was a motivation to create a clinical device for patient volunteers. Equipment for the treatment of superficial (skin and subcutaneous) oncological diseases using controlled local hyperthermia, created at the Bio nano ceramic and Nanocomposite Materials Science Center of Georgian Technical University.

Purpose of the work

The aim of the work is to create a clinical device designed by us for the treatment of superficial oncological diseases, which allows for controlled local hyperthermia and, through it, the targeted transport of a temperature field into a living organism for the treatment of superficial (cutaneous and subcutaneous) malignant tumors.

The essence of the work is that the temperature field is transported to the affected area of the body of a volunteer patient through a thermal pad (hyperthermic head) of the clinical device we created (Fig. 1).This headis placed at the tumor site for a certain period of time, which is determined empirically depending on how the patient responds to treatment and how the disease responds to treatment.Based on the above, the temperature range is 42-44^{0}C, and the time duration is empirically 20-40 minutes.

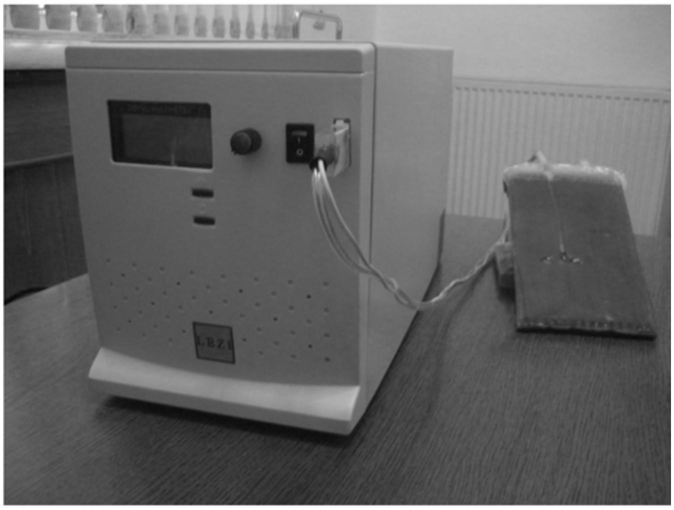
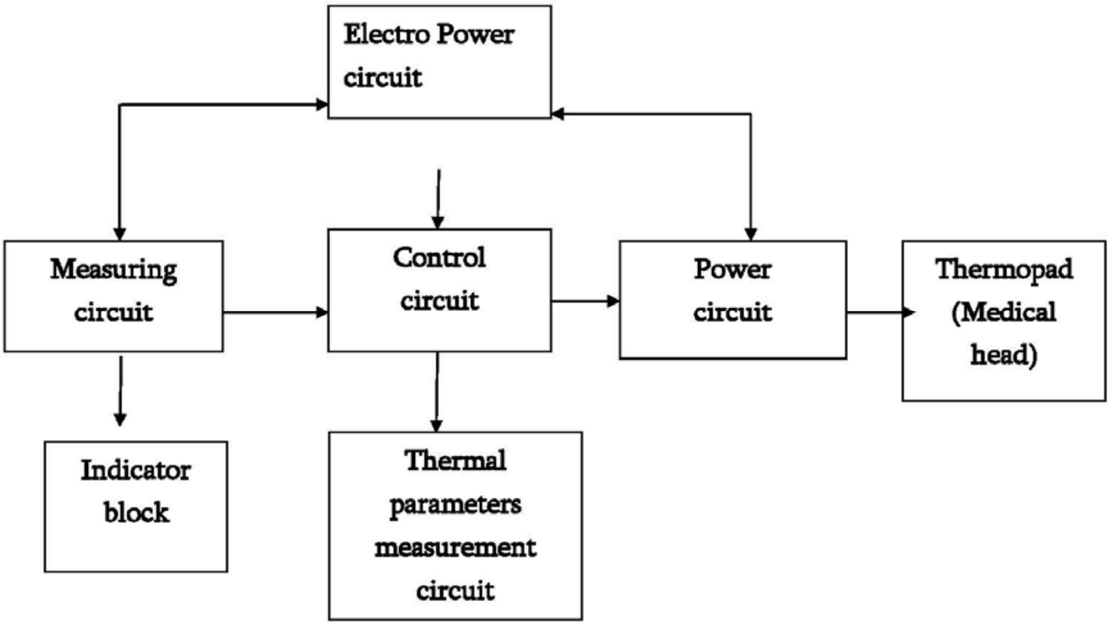


Fig. 1. Clinical medical device for the treatment of tumors of internal organs, skin and subcutaneous tissue "LEZI 1" for controlled local hyperthermia, created at the Bionanoceramic and Nanocomposite Materials Science Center of Georgian Technical University (manager: Prof. Z. Kovziridze)

Clinical therapeutic device "Lezi 1" created at the Bionanoceramic and Nanocomposite Materials Science Center (manager Prof. Z. Kovziridze) of Georgian Technical University for Treatment of skin and subcutaneous cancer diseases by controlled local hyperthermia.

The equipment diagram and description are provided below.



Basic parameters:

Adjustable temperature	41.5 –44.0 ^{0}C
Temperature adjustable pitch	0.1 ^{0}C
Voltage supplied to the thermal pad	32 volts

Power supply 220 volts

1. The thermal pad is made of poly dimethyl methylvinylsiloxane with dimensions LxWxH-200x115x5 mm, with an active heating grid built in before poly merization. The parameters of the heating network ensure uniform temperature distribution in the active zone of the thermal pad and sufficient heat transfer in the processing range of 42-44^{0}C. The non-working surface of the thermal pad is covered with thermal insulation.

2. The discrete power supply circuit ensures that the required power is supplied to the heating element at an intensity determined by the control circuit.

3. The control circuit determines the intensity of the power circuit operation based on signals received from the thermal parameter measurement and determination circuit.

4. The measuring circuit converts the temperature sensor signal to the level required by the indication and control circuit.

5. The thermal parameter detection circuit generates the required temperature signal level and switches the power supply circuit on and off.

6. The electric power supply circuit provides isolated power supply for signal and power circuits.

7. The indicator block provides indication of the temperature of the thermal pad and the heating intensity on a three and a half line liquid crystal display

CONCLUSION

For the first time in Georgia, the antitumor effect of controlled local hyperthermia has been studied, with the cytostatic effect on tumor cells being achieved by increasing the temperature in the cell, in our case, by dissipating heat caused by the temperature field.The temperature field is transported to the affected area of the patient's body through the thermal attachment of the clinical device (hyperthermic head), placing it on the tumor area for a certain period of time, which is determined experimentally. Temperature range 42-44^{0}C.

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უაკ **691.2**

მართვადი ლოკალური ჰიპერთერმიის მეთოდით სიმსივნური დაავადებების სამკურნალო აპარატი

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რეზიუმე: მიზანი. მეთოდი. შედეგი. შესწავლილია ჰიპერთერმიის მონო-თერაპიული ეფექტი კიბოს დაავადებების წინააღმდეგ. მართვადი ლოკალური ჰიპერთერმიის მეთოდის განვითარებისათვის, ექსპერიმენტულ მასალაზე დაყრდნობით, გამოყენებულ იქნა ხელსაწყო ”ლეზი 1”, რომელიც შეიქმნა, სტუ ბიონანოკერამიკისა და ნანოკომპოზიტების მასალათმცოდნეობის ცენტრში. (საქართველოს ინტელექტუალური საკუთრების ეროვნული ცენტრი, „საქპატენტი“. Dდეპონირების დამადასტურებელი მოწმობა 5054. “მართვადი ლოკალური ჰიპერთერმია და მაგნიტური ჰიპერთერმია კიბოს დაავადებების სამკურნალოდ”). შედეგად, ნაჩვენები იქნა და დადგენილია, რომ ყველა ცხოველში (ალბინოსი, 3 თვის თაგვები) დაფიქსირდა კიბოს დაავადების შეჩერება და განვითარდა ინტრატუმორული ნეკროზი. 8-10 სეანსის შემდეგ სიმსივნე დაწყლულდა, რაც ექსპერიმენტის დადებით შედეგზე მეტყველებს (პათოლოგიურ-ანატომიური ლაბორატორიის ”პათჯეო” დასკვნა. გამოკვლევის # 3119-12, და ჰისტო-პათოლოგიური გამოკვლევა N15272-13. დიაგნოზის გაცემის თარიღი 14.01.2014 წ. თბილისი, საქართველო).

შესწავლილია ჰიპერთერმიის მონო-თერაპიული ეფექტი კიბოს პროქტოლოგიური და საშვილოსნოს ყელის დაავადებების წინააღმდეგ. მართვადი ლოკალური ჰიპერთერმიის მეთოდის განვითარებისათვის, ექსპერიმენტულ მასალაზე დაყრდნობით, გამოყენებულ იქნა ხელსაწყო ”ლეზი”, რომელიც შეიქმნა, სტუ ბიონანოკერამიკისა და ნანოკომპოზიტების მასალათმცოდნეობის ცენტრში. ყველა ცხოველში (ალბინოსი, 3 თვის თაგვები) დაფიქსირდა კიბოს დაავადების შეჩერება და განვითარდა ინტრატუმორული ნეკროზი. საქართველოს ინტელექტუალური საკუთრების ეროვნული ცენტრი, „საქპატენტი“. დეპონირების დამადასტურებელი მოწმობა 5054. “მართვადი ლოკალური ჰიპერთერმია და მაგნიტური ჰიპერთერმია კიბოს დაავადებების სამკურნალოდ”).

დასკვნა. შედეგად, ნაჩვენები იქნა და დადგენილია, რომ 7-10 სეანსის შემდეგ სიმსივნე დაწყლულდა, რაც ექსპერიმენტის დადებით შედეგზე მეტყველებს (პათოლოგიურ-ანატომიური ლაბორატორიის ”პათჯეო” დასკვნა. გამოკვლევის N3119-12, და ჰისტოპათოლოგიური გამოკვლევა N15272-13. დიაგნოზის გაცემის თარიღი 14.01.2014 წ. თბილისი, საქართველო).

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