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EVALUATION OF METHODS FOR DETERMINATION OF ALCOHOL CONTENT IN EMULSION CREAMS

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Abstract. Alcoholic emulsion creams are characterized with high viscosity and density, which makes the alcohol content and other physical and chemical parameters determination of products significantly difficult. Analytical methods applied for the determination of ethanol, are labor-consuming, they are characterized with low precision, require the sample distillation and the achieved results are mostly underestimated. On a base of comparison of various distillation techniques and determination methods, it can be stated that ethanol concentration measurements in alcoholic creams using pycnometric and DMA-58 density-meter after previous sample distillation (100 cm^3 of cream + 200 cm^3 of water), are distinguished with relatively high precision and result repeatability. Also applying the SPME extraction in gaseous phase along with chromatographic analysis seems to be advantageous. The method based on the refractometric measurement of toluene and benzene extracts of egg emulsions is characterized with short performance time, sufficient precision and very low costs.

Key words: emulsion creams, alcohol content, determination methods

INTRODUCTION

Alcoholic emulsion creams (egg liqueurs) are characterized with specific sensor traits and belong to elegant and luxurious alcoholic beverages that satisfy a wide group of consumers.

Very high viscosity and density of creams (d = 1.132 – 1.138 g × cm^{-3}) makes the measurement of the extract content and other physical and chemical parameters of these products significantly difficult. The analytical methods applied up to date are quite labor-consuming and they are usually characterized with low precision, require sample distillation and moreover underestimate the ethanol concentration determination by about 1-2% vol.

The methods that are based on the density measurements (aerometer, pycnometer) are most commonly used for the strength (ethanol concentration) determination. Also

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vibration method [Brereton et al. 2003] and non-isosceles hydrostatic scales [Brose 1998 a, Brereton et al. 2003] are applied.

Refractometry is another technique for the strength determination of alcoholic solutions with no extract substances [Krełowska-Kułas 1993]. In order to omit the distillation phase, extraction with benzene may be used due to different refractive indices of benzene (1.5012) and ethanol (1.3614) [Wikiera 1982, Pizło 1993].

Also chemical method that consists in the oxidation of ethanol to acetic acid and iodometric titration of the $K_2Cr_2O_7$ excess is applied for determination of small quantities of ethanol [Sobczak 1975, Krełowska-Kułas 1993]. Rebelein [1979] applied the micromethod that was also based on the ethanol to acetic acid oxidation. Small sample amounts (2 cm^3) are distilled in a specialized kit directly into the flask with potassium dichromate. Similar dependence, but under different chemical conditions, is utilized in bubble method that consists in the passing of the neutral gas (argon, nitrogen) through the analyzed sample, and then ethanol concentration in the gas is proportional to its concentration in the liquid [Wikiera 1982].

The ethanol to aldehyde oxidation reaction using nicotine-adenine dinucleotide (NAD) and alcoholic oxidase (AO) is applied in enzymatic methods for determination of ethanol solutions strength [Steenbergen and Willems 1979], as well as in bio-sensors (analytical devices that contain biologically active material sensitive to specific chemical agents) designed for alcohol concentration determination [Tuszyński 2001].

The gas chromatography is one of the most common analytical techniques for ethanol determination. Elimination of labor-consuming distillation may be achieved by the use of Head Space system (taking the vapors from above the sample surface) or special fibers (SPME micro-extraction) along with Head Space system [Brose 1998 b, Sroka and Tuszyński 2002].

Some of the classical methods for strength determination (Mohr's scales, vibration method) were much modified by applying the new-generation measurement devices. A new densymetric scales Densimat equipped in computer system Alcosoft or oscillation density-meter DMA-58 may be the examples.

The aim of the present paper was to compare different distillation techniques and methods for ethanol content determination in emulsion creams.

MATERIAL AND METHODS

The experiments were carried out applying the commercial egg liqueur samples and standard emulsions (25% vol.) prepared according to the same procedure and reserved in Śląska Wytwórnia Wódek Gatunkowych "Polmos" in Bielsko-Biała. Particular variants of sample distillation and strength determination of achieved alcoholic solutions were made in 4-6 replications.

Distillation techniques

Industrial and standard cream samples for ethanol content determinations were subjected to distillation according to various techniques and variants.

1. Simple distillation
   – 50 g of cream + 100 g of water (according to PN-A-79529-6),

– 100 g of cream + 100 g of water,
– 100 g of cream + 200 g of water,
– 100 g of cream + 400 g of water.

2. Distillation with water vapor
   – 50 g of cream + 100 g of water.
3. Distillation under decreased pressure
   – 50 g of cream + 100 g of water.

   Each time, about 3 g of tannin was added into the samples prior to distillation in order to precipitate proteins and reduce the foaming of the liquid, then the solution was stirred and left for 20 minutes. Distillation was performed in a system combined with water pump and 100 cm^3 of liquid was achieved, in which ethanol content was determined by means of areometric (Tralles's areometer), refractometric (Zeiss's immersion refractometer), and pycnometric method as well as using oscillation densitymeter DMA-58. The cream and extract densities were determined according to PN-A-79529-6. The final ethanol concentration in cream was calculated taking into account the emulsion dilution or it was read from corresponding tables.

4. Distillation in system proposed by Rebelein [1979] with measurement of cream strength by chemical means
   – After sample dilution to 0.5% and 1.0% vol. of ethanol.

Extraction technique

Standard kits of emulsion creams with ethanol content from 5% to 34% vol. were prepared. The extraction of tested sample and standard solutions was performed in tubes (Vortex, 3 min), using toluene or benzene (5 cm^3/5 cm^3 of sample), adding each time 1 g of dehydrated potassium carbonate. After phase separation, the refractive indices (Abbe's refractometer) in ethanol-toluene and ethanol-benzene layers were evaluated and calibration curve for ethanol content readings was drawn.

Chromatographic technique

Standard egg emulsions with following ethanol contents were prepared: 10, 15, 20, 25 and 30% vol. The extraction of the tested samples and standard solutions was carried out by means of Head-Space SPME technique using fibers (polydimethylosilane 100 μm, temp. 40°C, 30 min). Determination of ethanol concentration was made by means of chromatographic technique (gas chromatograph HP 5880 series II with FID detector, temp. programmed from 50 to 120°C). The strength of the tested creams was read from the calibration curve made for standard solutions.

RESULTS AND DISCUSSION

Density of the tested creams was from 1.132 to 1.138 $g \times cm^{-3}$, which corresponded to norms. Table 1 presents mean values of ethanol content achieved using various methods.

Figures 1 and 2 present the calibration curves being the base for ethanol contents in egg liqueurs by means of refractometric as well as gas chromatographic techniques.

Table 1. Characteristic values of ethanol in emulsion cream
Tabela 1. Charakterystyka oznaczeń zawartości etanolu w kremach emulsyjnych

Ethanol recovery method Metoda odzysku etanolu	Cream/H_2O Krem/H_2O g	Determination method* Metoda oznaczania*	Number of replicates Liczba powtórzeń	Proof %vol. Moc %obj.	Standard deviation Odchylenie standardowe σ	Precision Dokładność %
Simple distillation Destylacja prosta	50/100	I	6	24.64	0.113	1.44
		II	6	24.64	0.151	1.44
		III	6	24.83	0.049	0.68
		IV	4	24.80	0.082	0.80
	100/100	I	6	24.69	0.171	1.24
		II	6	24.78	0.096	0.88
		III	6	24.90	0.081	0.40
		IV	4	24.88	0.096	0.48
	100/200	I	6	24.66	0.114	1.36
		II	6	24.88	0.130	0.48
		III	6	24.96	0.114	0.16
		IV	4	24.93	0.096	0.28
	100/400	I	6	24.63	0.151	1.48
		II	6	24.88	0.117	0.48
		III	6	25.03	0.197	0.12
Distillation with water vapor Destylacja z parą wodną	50/100	I	5	24.68	0.133	1.28
		II	5	24.82	0.096	0.72
		III	5	24.87	0.081	0.52
Distillation under decreased pressure Destylacja pod obniżonym ciśnieniem	50/100	I	4	20.23	1.079	19.08
		II	4	22.10	0.193	11.60
		III	4	22.00	1.473	12.00
Distillation by Rebelein Destylacja wg Rebeleina	to 0.5% vol. to 1.0% vol. do 0,5% obj. do 1.0% obj.	V	4	23.33	0.289	6.68
		V	4	24.17	0.144	3.32
Toluene extraction Ekstrakcja toluenem	–	I	4	24.86	0.020	0.56
Benzene extraction Ekstrakcja benzenem	–	I	5	24.83	0.064	0.68
SPME extraction Ekstrakcja SPME	–	VI	4	24.84	0.173	0.64

*refractometer (I), areometer (II), pycnometer (III), DMA density-meter (IV), chemical method (V), gas chromatography (VI).

*refraktometr (I), Areometr (II), piknometr (III), gęstościomerz DMA (IV), metoda chemiczna (V), chromatograf gazowy (VI)

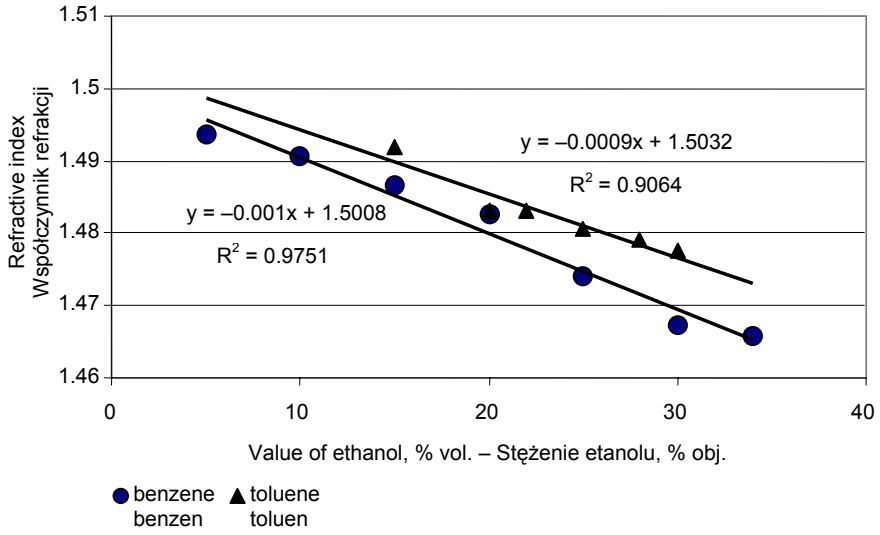

Fig. 1. Calibration curves obtained after benzene and toluene extraction (refractometric measurement)
Rys. 1. Krzywe kalibracyjne uzyskane po ekstrakcji benzenem i toluenem (pomiar refraktometryczny)

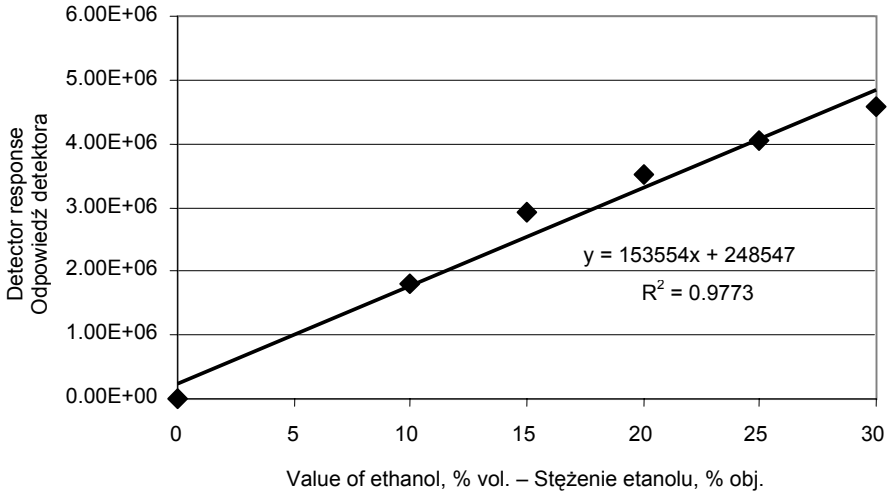

Fig. 2. Calibration curves obtained after HeadSpace-SPME extraction (chromatografic measurement)
Rys. 2. Krzywa kalibracyjna uzyskana po ekstrakcji techniką HeadSpace-SPME (pomiar chromatograficzny)

Table 2. Estimation costs and labor-consuming of ethanol determionation in creams
Tabela 2. Szacunkowe koszty i czasochłonność oznaczania stężenia etanolu w kremach

Ethanol recovery method Metoda odzysku etanolu	Cost Koszt	Labor-consuming Czasochłonność	Cost Koszt	Labor-consuming Czasochłonność
	one analysis jedna analiza		100 analysis 100 analiz	
	zł	min	zł	h
Simple distillation Destylacja prosta	38-66	45-80	3 800-6 600	75-133
Distillation with water vapor Destylacja z parą wodną	50-54	60	5 000-5 400	100-108
Distillation under decreased pressure Destylacja pod obnizonym ciśnieniem	25-29	30-35	2 500-2 900	50-58
Distillation by Rebelein Destylacja wg Rebeleina	60	40	3 380	67
Toluene extraction Ekstrakcja toluenem	80	60	1 530	30
Benzene extraction Ekstrakcja benzenem	80	60	1 530	30
SPME extraction Ekstrakcja SPME	550	180	5 500	100

Estimation of costs and labor-consuming of the applied methods for ethanol analysis in egg-liqueur-type creams was also made (Table 2). Inputs for measurement devices purchase were not included in calculations.

Regardless of the distillation way (Table 1), the lowest values of ethanol contents were achieved from refractometric determination. Areometer readings appeared to be between refractometric and pycnometric ones. Alcohol contents in creams determined from density measurements (pycnometer, DMA) were the closest to real concentration of the component (25% vol.) in tested emulsion samples. The experimental results confirm the usefulness of applying the pycnometric techniques as referential also for determination of the strength of alcoholic emulsion creams. During distillation, compounds with similar molecular weights but with different refractive indices are collected in receiver (e.g. $n = 1.35$ for ethanol and $n = 1.41$ for hexanol). Thus, slightly lower ethanol concentrations are achieved on a base of refractive determinations in reference to other methods. Measurements made with application of density-meter DMA-58 were characterized with relatively high repeatability ($\sigma = 0.082$-0.096). It may be supposed that application of instrumental analysis in this case made possible to eliminate, among others, manual errors that are the reason for lower repeatability of determinations performed using other methods [Brose 1998 a, Brereton et al. 2003].

Also the manner of the sample distillation, particularly dilution with water, exerted significant influence on a final result of determination. Determinations of ethanol con-

tent carried out in accordance with PN-A-79529-6 (50 g of cream and 100 g of water were used for distillation), did not allow for achieving credible results that were usually lower than real ones (25% vol.). Mean content of the alcohol ranged from 24.64% to 24.83% vol. Taking more sample for distillation (100 g of cream and 100 g of water) resulted in slightly higher values (by about 0.1% vol.), closer to a real concentration of the component in creams. Changing the amount of solutions for distillation (100 g of cream and 200 g of water) appeared to be more advantageous referring to previous determinations. Further increase of the sample dilution level (100 g of cream and 400 g of water), had not significant effect on quantitative separation of ethanol and final results.

Distillation of samples with water vapor did not significantly change the results of the strength of the tested egg liqueurs (Table 1); however, it was more energy and labor-consuming (Table 2). Complete elimination of emulsion burning and reduction of its adherence to distillation bulb walls, particularly at the end of the process, is no doubt the virtue of this way of distillation. Delay of sample adherence to vessel walls during liqueur distillation with water vapor was earlier observed by Krell [1997].

Pressure decrease during ethanol removing from egg creams appeared to be helpless due to relatively high losses of the determined component and finally strength determination results were significantly diminished ranging from 2% to 3% vol. (Table 1).

Chemical method, which is characterized with high sensitivity, is another way for alcohol concentration determination. However, samples have necessarily to be diluted (below 1% vol.). Applied method was characterized with low labor and time-consuming (Table 2), as well as slight reagent utilization [Wikiera 1982]. Rebelein [1979] proved that ethanol concentrations in vodkas and liqueurs, analyzed by means of both pycnometric and chemical methods, were comparable. Results referring to the strength of alcoholic emulsion creams, achieved in our experiments (Table 1) by means of Rebelein's micro-method, much differed from the real values. The result divergence in reference to similar results achieved using pycnometric method, was 1.2% vol., on average. Therefore, it may be supposed that multiple dilution of creams with high extract (over 430 g × dm^{-3}) and very small amounts of samples taken for the determination, had significant impact on final result and made impossible to apply this technique for evaluation of egg emulsion strength.

Ethanol extraction using toluene and benzene with further refractometric determination of the component concentration is also characterized with short performance time (15-20 min.) and extremely little utilization of reagents, which much decreases the costs (Table 2). No distillation stage is another reason for low costs. Results achieved using the technique (24.83% and 24.86% vol.) were comparable to those from pycnometric determination and previous distillation of egg liqueurs at optimum cream to water ratio 100:200. The performed extractions and determinations point out that such procedure may be useful for determination of egg emulsion strength. Earlier studies by Wikiera [1982] using model ethanol solutions (20-40% vol., 0-30% of sucrose) revealed that refractometric determinations guaranteed fast strength determination even in solutions with elevated extract content. Proportions of benzene and toluene in relation to ethanol applied in our experiments (5 cm^3/5 cm^3), which were previously proposed by Pizło [1993] for strength evaluation of vodkas and liqueurs with high extract content, appeared to be also optimum for extraction of egg creams.

Mean results of the strength of liqueurs subjected to extraction by means of SPME technique in gaseous phase (Head Space) and further chromatography analysis (Table 1) only slightly differed (24.83% vol.) from a real strength of emulsion creams (25.00% vol.). SPME extraction in Head Space system does not require any previous sample preparation, and it is characterized with relatively high precision making possible to simultaneous analysis of other volatile components of egg emulsion. This technique guarantees fast strength determination and eliminates labor-consuming distillation or extraction using organic solvents, but it requires a laboratory equipped in relatively expensive gas chromatograph. The application of SPME micro-extraction using special fibers and chromatography seems to be advantageous in laboratories that carry out ethanol concentration determinations at high frequency. High costs of a single analysis (Table 2) results first of all from relatively high prize of SPME fibers (intended for about 100 determinations), however, the cost of performing the series of the strength analyses is comparable to that involving distillation techniques.

CONCLUSIONS

1. Simple distillation of alcoholic egg cream with water in mass ratio of 1:2 is a credible technique for sample preparation to the strength determination. Results of the ethanol concentration determinations in the achieved samples using pycnometer or density-meter DMA-58 are comparable and they are characterized with relatively high repeatability, particularly in case of density-meter.

2. Refractometric determination of ethanol concentration in emulsion creams after previous extraction with toluene or benzene is characterized with short performance time (about 20 min), respectively high repeatability and credibility in comparison to pycnometric method.

3. Chromatographic determination of egg emulsion strength after SPME micro-extraction in Head Space system is distinguished with high precision and relatively short performance time (1 h) as well as opportunity for making simultaneous analysis of other volatile components of a sample.

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OCENA METOD OZNACZANIA ALKOHOLOWYCH KREMÓW EMULSYJNYCH

Streszczenie. Alkoholowe kremy emulsyjne charakteryzuje duża lepkość i gęstość, istotnie utrudniając oznaczanie zawartości alkoholu oraz innych parametrów fizycznych i chemicznych tych produktów. Metody analityczne stosowane do określania zawartości alkoholu etylowego są pracochłonne, odznaczają się zazwyczaj małą precyzją, wymagają oddestylowania próby, a ponadto uzyskane wyniki są przeważnie zaniżone. Na podstawie porównania różnych technik destylacji i metod oznaczania mocy można stwierdzić, że pomiary stężenia etanolu w kremach alkoholowych metodą piknometryczną oraz z użyciem gęstościomierza DMA – 58, po wcześniejszym oddestylowaniu prób (100 cm^3 kremu + 200 cm^3 wody), charakteryzują się stosunkowo dużą dokładnością i powtarzalnością wyników. Korzystne wydaje się również zastosowanie ekstrakcji SPME w fazie gazowej wraz z analizą chromatograficzną. Natomiast metoda oparta na pomiarze refraktometrycznym ekstraktów toluenowych i benzenowych emulsji jajowych odznacza się krótkim czasem wykonania, zadowalającą dokładnością oraz wyjątkowo niskimi kosztami.

Słowa kluczowe: kremy emulsyjne, zawartość alkoholu, ocena metod

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