Rapid determination of alcoholic strength of egg liqueur using steam distillation and oscillation-type densimetry with peristaltic pumping

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Abstract (max. 250 Wörter)

This paper introduces a new method of determining alcoholic strength in highly viscous samples like egg liqueurs. The method relies on fully automated steam distillation in combination with oscillation-type densimetry and peristaltic pumping. The procedure is much faster (taking less than 8 minutes per sample) and easier than the conventional reference method (distillation, pycnometry). This makes it possible to determine alcohol content efficiently and economically, both in official food control and in spirit production. In addition, the total dry extract of the liqueur can be indirectly calculated from the density of the sample and the density of the alcoholic distillate.

The parameters for the automatic steam distillation were optimised for the analysis of egg liqueur samples (100% steam power, 25 g weighed portion, 130 s distillation time, 50 ml receiver). Validation has proved the method robust and precise. The relative standard deviation was below 0.56% in all cases. By analysing spirit samples under routine conditions, a high correspondence (R=0.999) with the reference method was achieved.

Keywords: Ethanol, alcoholic strength, steam distillation, pycnometry, oscillation-type densimetry, peristaltic pumping, egg liqueur

1. Introduction

Within the work of official food control, the alcoholic strength by volume is one of the most important parameters in spirit drink analysis. In comparison with other countries, in the European Union only a marginal tolerance of ± 0,3%vol is allowed in respect of the indication of the actual alcoholic strength by volume in the labelling [1]. Well above 10% of all analysed samples of liqueurs and fruit spirits had to be objected to a faulty labelling of the alcoholic strength [2]. The exceedance of the tolerated limits can have grave consequences for the manufacturers such as fines,

high costs of recall and relabelling of a whole charge of products. If on the other hand, the alcoholic strength is adjusted too high in the products an economical loss is the consequence. For spirit drink producing enterprises and distilleries it is essential to have a method for the determination of ethanol at hand that assures the adherence to formulations and manufacturing prescripts. Concerning the market in ethyl alcohol of agricultural origin, the determination of the alcoholic strength is used as a basis for the fixation of the tax on spirits.

Until recently the distillation with subsequent pycnometric determination of the density has been the reference method for the determination of alcoholic strength in spirit drinks. Rebelein developed a screening method for the determination of alcoholic strength in liqueurs and spirits in 1975, which is based upon iodometric titration [3]. Because of difficulties in the handling and the use of heavy metal containing and ecologically harmful reagents, this method could not achieve acceptance. The automated methods such as GC, NIR or HPLC could not replace pycnometry as reference method because they are instrumentally complex and therefore more expensive. Furthermore they needed trained personnel for the handling and some methods did not have the required accuracy [4-8].

In the eighties another method, electronic densimetry, which is based on the electromagnetically induced oscillation of a U-shaped glass tube, was found to be superior above other methods of determination of alcoholic strength especially in terms of accuracy [9-12]. But it took till the year 2000 for the so called oscillation-type density meters to be introduced in the European community reference methods for the analysis of spirit drinks [13]. This is nowadays the state-of-the-art method preferred by industry, because it is time and cost-saving as well as simple to perform [12;14].

Besides the determination of density, in all cases a conventional distillation step is commanded in the reference methods. This distillation step is time-consuming and requires high personnel expenses. The distillation of emulsion liqueurs and especially egg liqueurs (Advocaat) has to be handled with great care in order to avoid entrainment of the sample [13]. Especially a slow heating process is necessary in order to prevent scorching and charring. These pyrolytic reactions could be responsible for faulty results in the determination of alcoholic strength. It is therefore mandatory to find an alternate method, which is fast and easy to handle in such a way as to enable the official food control and manufacturing enterprises to efficiently control the alcoholic strength.

A promising alternative is steam distillation, which is applied in this work. Early procedures using steam injection were inadequate, because small amounts of alcohol were not recovered so that it was necessary to apply correction factors to obtain correct results [15]. However, recently automated steam distillation devices are at hand which were originally developed for the Kjeldahl principle and have also been found to be applicable for the alcoholic strength determination in spirits [16]. Steam distillation is the most prominent example for a carrier vapour distillation. With the carrier vapour, the distillable part of a mixture is separated from the non-volatile residue.

Simultaneously a boiling point depression occurs and a thermally mild treatment is achieved. By passing steam into the sample, the alcohol is expelled and significantly shorter times of distillation are reached in comparison to conventional distillation.

For the highly difficult matrix of egg liqueur this method is restricted, because the high viscosity of these products does not permit an exact pipetting of the sample. As the viscosity of the products differs highly from the viscosity of water, the use of water-calibrated graduated pipettes is not advisable. Rebelein showed for egg liqueur eight times of rinsing the pipette to be necessary in order to remove all residue [3]. The same problem persists if graduated flasks are used to measure the volume. As the official method states [13], for liqueurs for which it is very difficult to measure volume accurately the sample must be weighed. The alcoholic strength by volume has then to be calculated using the density of the product. Unfortunately for emulsion liqueurs, this parameter cannot be automatically obtained with conventional oscillation-type density meters and manual injection can only be used with low accuracy due to air bubble formation.

As a consequence, for egg liqueurs the extensive and time-consuming pycnometric determination of density had to be used further on. In this work a new designed oscillation-type density meter system, which allows the reliable sampling of highly viscous samples using peristaltic pumping, is used for the first time for the analysis of alcoholic strength in highly viscous liqueurs. The results obtained with the new system are compared to conventional electronic densimetric and pycnometric reference methods. The parameters for the automatic steam distillation were optimised for the analysis of egg liqueur samples.

2. Experimental

2.1. Instrumentation

The automated steam distillation was accomplished with the Vapodest 30 (C. Gerhardt, Fabrik und Lager chemischer Apparate, Bonn). The device is coupled to a tank filled with distilled water and before every start-up the steam generator is pre-heated for 3 min with a water sample at full steam power (according to the manufacturers' instruction). For the tempering of the sample the heating circulator bath DC10-W26 (Haake, Karlsruhe, Germany) was used. The determination of density was accomplished with the conventional density meter DE51 with sample pump ASU-DE (max. viscosity 600 mPa·s) in comparison to the newly designed combined density and refractive index meter DR45 with sample delivery and cleaning unit SC1 (max. viscosity 30,000 mPa·s), both by Mettler-Toledo (Giessen, Germany). Both instruments were adjusted with air and water according to the manufacturer. The adjustment was checked daily using certified water standards

($\rho_{20°C}$=0.99820). The sample temperature in all measurements was adjusted to 20°C. The pycnometers and the distillation apparatus were purchased at Paris, Technische Glasbläserei (Karlsruhe, Germany) after specifications of the reference method [13]. The used chemicals were obtained from Merck (Darmstadt, Germany).

2.2. Reference method (distillation and pycnometry)

The reference method for determination of the alcoholic strength in spirit drinks was applied without modification as prescribed in the Commission Regulation (EC) No 2870/2000 laying down Community reference methods for the analysis of spirit drinks [13]. Besides the pycnometric determination of the density of the original sample (ρ_S), the samples were distilled and the alcoholic strength afterwards determined by pycnometric analysis of the distillate (ρ_A). The distillation takes up to 30 min for egg liqueurs.

2.3. Conventional oscillation-type density meter procedure with manual sample injection

The earlier systems used a membrane pump to deliver the samples to the oscillation-type density meter. The problem proved to be that the aspiration of the egg liqueur into the measure cell was not possible at all or only with lots of air bubbles. To solve this problem, the samples were directly injected with a 5 ml plastic syringe manually while the alcoholic distillates were pumped semi-automatically by the installed membrane pump. Between measurements the connecting tubes were purged with air and cleaned with water. Before shutdown of the system the hoses were purged with acetone and air until they were dry.

2.4. Density meter with peristaltic pumping procedure

The high pressure built up by the peristaltic pump allowed to move all egg liqueur samples automatically into the measuring cell. In contrast to conventional membrane pumping, samples are pushed and not aspirated. The instrument was set to autodetect when the cell is filled with sample and automatically switched off the pump. After each measurement the sample was drained (60 s). After that, sampling nozzle and the tubes were completely cleaned using water (30 s) and acetone (20 s) and dried inside using air (60 sec). The samples were stored in septum sealed sample vials in order to avoid evaporation or contamination. The sampling nozzle penetrates the septum to start the sampling process.

Air bubbles, inhomogeneous samples as well as solvent residues in the total system were automatically recognized by the system using repeated measurement and such measurements were discarded.

2.5. Determination of alcoholic strength using steam distillation

The sample is temperated in a water bath at 20°C. Following this, 25 g of the sample were weighed into a 400 ml Kjeldatherm digestion tube. After the addition of one drop of silicon defoamer, rests of the sample sticking to the edge of the tube were rinsed down with distilled water. Subsequently the tube is clamped in the distillation device. After that a 50 ml graduated flask is placed under the distillate outlet tubing, the distillation power is regulated to 100% (1500 W), which means that vapour with a temperature of 116°C is injected into the sample with 0.25 bar of overpressure. The distillation time is usually elected in such a way that the flask is filled up to the base of the flask neck (for egg liqueurs 120-140 sec). After starting the program, the distillation is automatically performed. After termination, the receiver and the tube are replaced and the hoses are rinsed with distilled water to be ready for the next sample.

The graduated flask with the distillate is temperated and filled up to the calibration mark. The density is determined with the oscillation-type density meters. With the density, the apparent alcoholic strength (AAS) is calculated by the density meters by using the stored official alcohol table data (measuring time approximately 2 min). The real alcoholic strength (RAS) has to be calculated with the following formula:

RAS [%vol] = 50 [ml] · ρ_S [g/ml] · AAS [%vol] / weighed portion [g]

2.6. Determination of the total dry extract

For the determination of the total dry extract according to Commission regulation (EEC) No 2676/90 determining Community methods for the analysis of wine [17], the density of the original sample (ρ_S) and of the alcoholic distillate (ρ_A) have to be determined. The specific gravity of the distillation residue has to be calculated by the following formula:

$d_r = 1.00180 (\rho_S - \rho_A) + 1.00000$

The total dry extract expressed in g/L is looked up in the table for the calculation of the content total dry extract. Using steam distillation, the necessary density of the alcoholic distillate is not directly available because the distillate is diluted and the weight portion varies. Therefore, the density (ρ_A) that corresponds to the previously calculated RAS was looked up in the official alcohol table.

2.7. Validation

For the determination of the most favourable parameters of the steam distillation and to test the ruggedness of the method under varying experimental conditions, the influence of steam power (40-100%, equivalent to 600-1500 W), distillation time (10-140 s) and sample volume (5-45 ml) were inspected. To check the method for linearity, 9 ethanolic solutions were prepared and analysed,

which varied in the area of 2%vol to 80%vol. To determine the accuracy of method, precision (expressed as RSD) and trueness (expressed as bias, which is the difference between the analysis result and the pycnometric reference value in percent (bias = (mean densimetry - mean pycnometry)/mean pycnometry*100)) of three authentic egg liqueur samples were determined under repeatability conditions (same operator, short time intervals) and under within-laboratory reproducibility conditions (different operators, 6 different days). To further check the trueness, 8 samples from the study stack of the CVUA Karlsruhe were measured with both densimetry following steam distillation and the pycnometric reference method.

The statistical evaluation was performed with standard programs. A statistical significance was assumed below the 0.05 probability level. The linearity was checked with Pearson's test.

3. Results and discussion

3.1. Optimisation of steam distillation

In order to optimise the method, the influence of the basic operation parameters of the steam distillation device (such as steam power of the steam generator, time of distillation and sample volume) was examined.

At a constant time of distillation (130 s) and with a weighed portion of 25 g, the increase of steam power at first showed a rising alcoholic strength. At a steam power of 80% the distillation was complete (Fig. 1). With the increase of the steam power an improvement of the reproducibility of the results was visible (decrease of standard deviation). As a consequence, all further experiments were performed with 100% of steam power.

The examination of the influence of the distillation time showed that the alcohol was completely separated from the sample after 120 s (Fig. 2). However, as the reference method's description shows, the steam distillation is also continued until the flask is filled up to the base of the flask neck. This is done to further improve the reproducibility.

The variation of the weighed portion revealed deviances in the range of 5-10 g (Fig. 3) due to higher weighing errors and higher dilution errors. Weighed portions between 20 g and 40 g showed only minor deviances (<0.1%). However, above 40 g of sample a decrease in yield of alcohol was observable because of incomplete distillation under the given conditions. Therefore, for all further determinations a weighed portion of 25 g was used.

Altogether, the method proved to be very rugged because the optima of the method are independent in a wide range of the varying influences of the parameters. The steam distillation device is programmed with the prescribed parameters, which are monitored during the operation. If deviations occur in the process (e.g. shortfall of the steam power) warnings are displayed.

3.2. Validation results

Steam distillation in combination with oscillation-type density meters shows an excellent linearity in the examined range between 2 and 80%vol ($y = 0.987\ x + 0.138$; $R=0.99997$; $p<0.0001$). This makes the method as well suitable for the analysis of mixed spirit drinks with only minor alcoholic strength as for high-proof spirit drinks, e.g. absinthe. However, the real advantages of the method are in the field of spirit drinks with high contents of total dry extract like egg liqueur.

For this complex sample matrix, analysis results of density of the original sample and apparent alcoholic strength of the steam distillateusing manual sample injection and peristaltic pumping were compared by linear regression (Table 1). A good agreement of analysis results between the two methods was achieved only for alcoholic strength ($R>0.999$). For density, an inferior correlation ($R=0.998$) with a broader confidence interval was determined, even if no constant or proportional difference between the two procedures could be proven besides random errors. The differences between the two methods were attributed to the error prone manual sampling.The results of the method validation for density, alcoholic strength and total dry extract are shown in Tables 2-4. For all analysed products, the methods show very high precision and trueness, indicating excellent assay accuracy. Using oscillation-type densimetry in combination with peristaltic pumping, the relative standard deviation of all cases was below 0.06% (density), 0.56% (RAS) or 0.14% (TDE), while the systematic deviation of results (bias) was lower than 0,18% (density), 0.88% (RAS) or 0.81% (TDE). On the other hand, conventional oscillation-type densimetry with manual injection, especially under within-laboratory reproducibility conditions, showed inferior relative standard deviations and systematic deviations (Table 2), as was likewise expected by the influence of the manual sampling.

The validation data showed a very good correspondence to those of the reference method with standard distillation [13]. The very high reproducibility of the results can be explained by the full automation of the steam distillation process and in the cases using peristaltic pumping by the likewise full automation of density measurement. The error sources are significantly reduced in comparison to conventional manual procedures. Oscillation-type density meters are more reliable than pycnometry, resulting in a higher accuracy.

By analysis of eight egg liqueurs under routine conditions, the applicability was assured. In Table 5, the labelled alcoholic strength as well as the results of the pycnometric method and oscillation-type densimetry and the systematic deviations between both are given. The linear correlation of both methods is excellent with correlation coefficients higher than 0.999 for the measurement of density, alcoholic strength as well as total dry extract (Table 6). Since slope and intercept encompass the

theoretical values, no constant or proportional differences between the two procedures could be proven besides random errors. The slightly lower correlation of the parameter densiy was attributed to the tedious procedure of figuratively struggling egg liqueur into a pycnometer. The deviation of the results obtained by oscillation-type densimetry in comparison to pycnometry were on the average only 0.08% (density), 0.34% (RAS), 0.45% (TDE). Using peristaltic pumping the deviations were significantly enhanced in comparison to earlier studies, which described deviations for alcoholic strength up to 2% between densimetry and pycnometry for egg liqueurs [16].

Apart from one sample (egg liqueur no 8), which was outside the labelling tolerance of 0.3%vol using the reference method as well as steam distillation and densimetry, an excellent agreement was also achieved between both methods and the labelling of the manufacturers.

3.3. Advantages of steam distillation

In accordance to the reference method, the distillation remains the basis even for this new, time-saving analysis. During method optimisation, it proved to be advantageous to distil 25 g of sample into a 50 ml graduated flask as a receiver. In contrast to the reference method, the distillate is diluted during steam distillation. However, the validation data showed that the calculation error is neglectable. The use of steam for the distillation of alcohol is fast, cost-saving and requires only a minimum of special knowledge of the laboratory personnel. Therefore, it could be the method of choice for governmental laboratories as well as for spirit manufacturers and distilleries. A further advantage is the fact that it can be used in the analysis of fluids that possess a high viscosity and boiling point and which usually tend to scorching and spattering in conventional distillation (e.g. emulsion liqueurs). Through the simultaneous heating and mixing effect of the steam injection, a good intermixture is assured, while at the same time a scorching of the sample is nearly impossible and was never observed. Of course, the cleaning of the used glass devices is made considerably easier with this method.

Furthermore, the shortened time of distillation (approx. 2 min) is a significant advantage over the classic distillation (approx. 30 min). Less than 7 min per sample are needed for the complete analysis including steam distillation and densimetry, which means that a high sample throughput of 9 samples per hour is possible. Furthermore, a complete automation of both steam-distillation and densimetry is possible using autosamplers, so that any operator dependent influences would be totally eliminated and the efficiency further enhanced. Both the possibility of high-throughput and the marginal cleaning effort lead to a cost reduction in personnel and therefore further proves this method to be superior to others.

3.4. Advantages of oscillation-type densimeter with peristaltic pump

With the membrane pump equipped oscillation-type densimeter, the determination of density was only possible of samples with low viscosity. The present egg liqueurs, which possess a high viscosity, were either impossible to pump into the U-shaped measuring cell or not air bubble-free. The manual injection with a plastic syringe, which was applied instead, showed only dissatisfactory accuracy. By using a peristaltic pump, it was for the first time possible to directly transfer and fully automatically measure egg liqueur with oscillation-type densimeters. The automated measuring systems reduced the work involved in the determination of density, they also help to prevent measurement errors and eliminate sample carry-over by automatic sampling and cleaning.

Pycnometers were generally considered to provide the greatest accuracy, but the method is time-consuming and requires special training of personnel if reproducible results are to be obtained. In our experience during this study, accurate pycnometric results were only possible by experienced laboratory technicians, especially for complicated matrices like egg liqueur. Trainees or students only yielded results, which were a priori out of the tolerance of the labelling. This confirms previous results of a collaborative study, in which pycnometry demonstrated greater variability in terms of precision than oscillation-type densimetry, because of the greater opportunity for experimental error in making the weight measurements necessary for pycnometry [12]. However using steam-distillation with densimetry, untrained personnel could easily achieve accurate results, which were included in the within-laboratory reproducibility studies.

3.5. Screening of total dry extract

The non-volatile content of drinks is commonly referred to as total dry extract [17]. In the case of liqueurs, the total dry extract can be used to estimate the sugar content. For the determination of the total dry extract, this screening method can easily be used to confirm the minimum sugar or honey content of 150 g/l demanded for the European specialties egg liqueur or Advocaat [18]. Therefore in many cases with high total dry extracts, the complex enzymatic or high-performance liquid chromatographic characterization of the saccharides is obsolete.

The calculation of the total dry extract is performed by using the conversion tables given in Commission regulation (EEC) No 2676/90 [17] requiring the density of the distillation residue, which is not available after steam distillation. Therefore, the total dry extract has to be indirectly calculated from the density of the sample and the density of the alcoholic distillate.

The validation data showed that the accuracy of the determination of the total dry extract was not as good as of density and alcoholic strength, which was expected because the indirect calculation of two measurements resulted in error propagation. However, the accuracy is completely satisfactory in the context of a screening method.

3.6. Conclusion

Steam distillation in combination with oscillation-type densimetry with peristaltic pumping showed such good accordance with the reference method that in the routine analysis of liqueurs the complex and time-consuming pycnometric reference method is omitted. Only after deviations from the tolerance in the determination of alcoholic strength are detected, the reference method is used to assure the results before a product is officially objected.

Further enhancements of the method could lead to an application on further complicated food matrices, e.g. for the determination of alcoholic strength in Black Forrest Cherry Cake.

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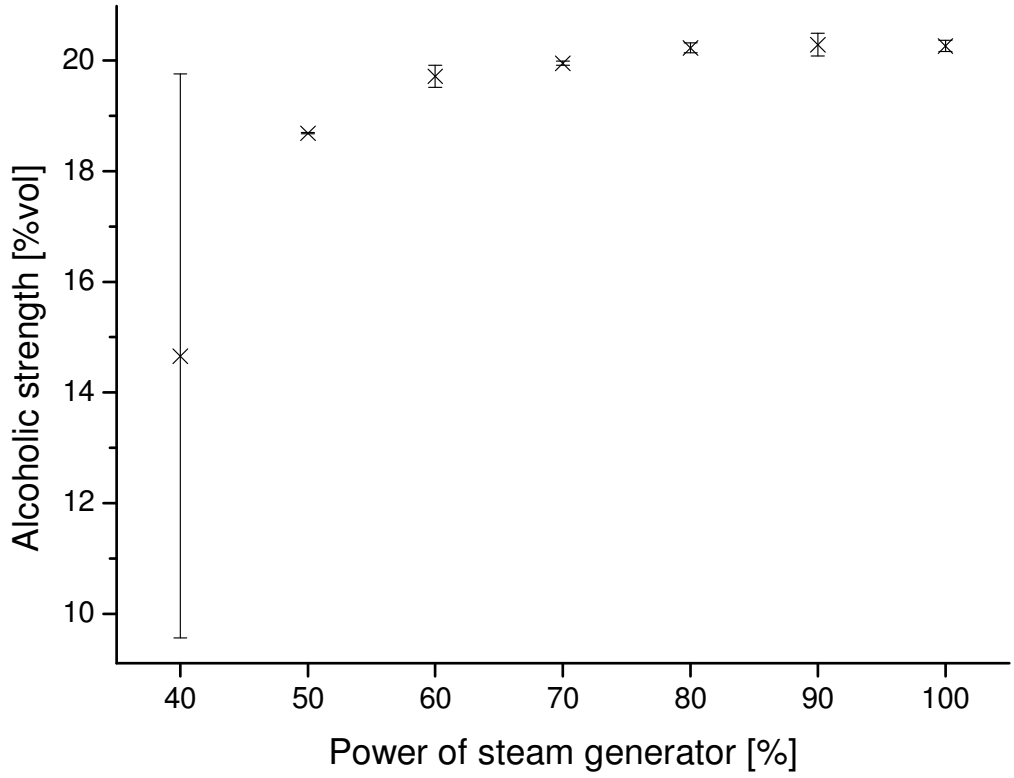


Fig. 1. Influence of the steam power on the determined alcoholic strength of the distillate using oscillation-type densimetry (mean ± standard deviation, n=4, sample: egg liqueur 20%vol, distillation time 130 s, weighed portion 25 g).

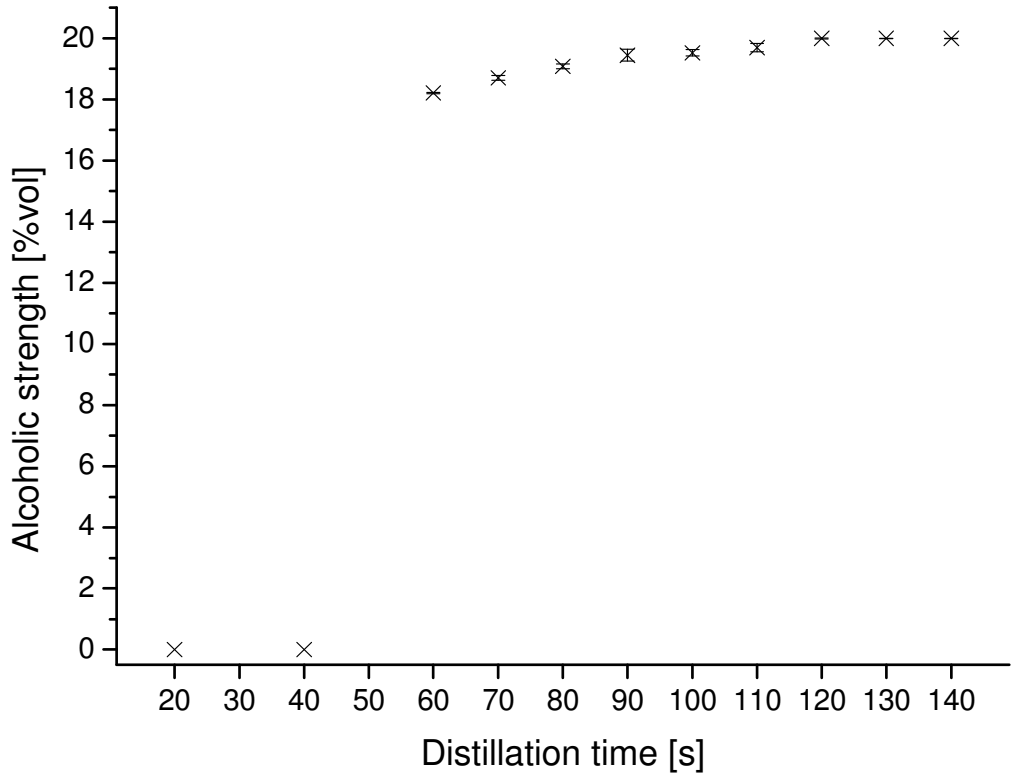


Fig. 2. Influence of the distillation time on the determined alcoholic strength of the distillate using oscillation-type densimetry (mean ± standard deviation, n=4, sample: egg liqueur 20%vol, steam power 100%, weighed portion 25 g).

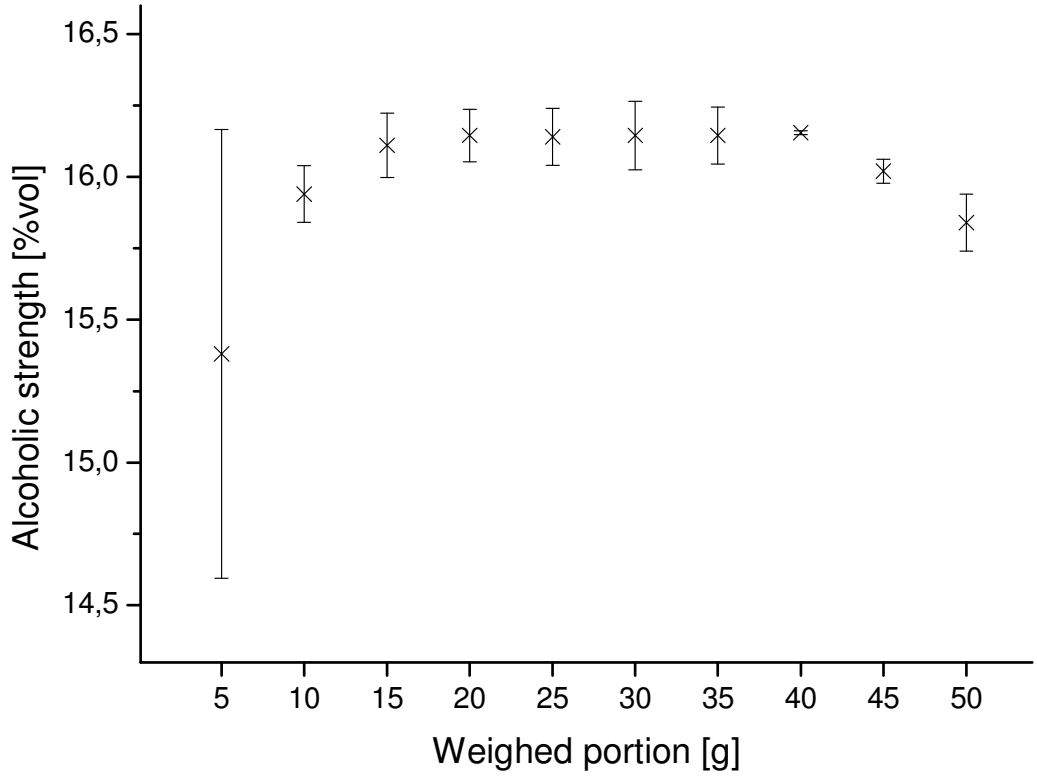


Fig. 3. Influence of the weighed portion on the determined alcoholic strength of the distillate using oscillation-type densimetry (mean ± standard deviation, n=4, sample: egg liqueur 16%vol, steam power 100%, distillation time 100 s).

Table 1. Linear correlation between analysis results using manual sample injection and peristaltic pumping before oscillation-type densimetry (n=70)

	Slope (LCI, UCI)	Intercept (LCI, UCI)	Correlation coefficient	Probability
Density [g/mL]	1.003 (0.987, 1.019)	-0.003 (-0.020. 0.014)	0.99821	<0.0001
AAS [%vol]	0.998 (0.992, 1.003)	-0.052 (-0.101. -0.003)	0.99975	<0.0001

Table 2. Validation results for the oscillation-type densimetric determination of density comparing manual sampling with automatic sampling using peristaltic pumping

	repeatability conditions	**within-laboratory reproducibility conditions**

	(n=5)					(n=9)			
	Sampling	**x [g/cm^3]**	**S [g/cm^3]**	**RSD [%]**	**Bias [%]**	**x [g/cm3]**	**S [g/cm3]**	**RSD [%]**	**Bias [%]**
Egg liqueur 1	Manual	1.0503	0.0003	0.0276	-0.1331	1.0497	0.0011	0.1061	-0.1902
	Automatic	1.0512	0.0001	0.0124	-0.0475	1.0514	0.0004	0.0337	-0.0285
Egg liqueur 2	Manual	1.0809	0.0008	0.0764	-0.0093	1.0808	0.0006	0.0554	-0.0185
	Automatic	1.0830	0.0006	0.0596	0.1850	1.0807	0.0004	0.0330	-0.0278
Egg liqueur 3	Manual	1.0825	0.0005	0.0452	0.0092	1.0824	0.0007	0.0677	0.0000
	Automatic	1.0830	0.0006	0.0596	0.0554	1.0828	0.0006	0.0599	0.0370
RFS	Manual	0.9494	0.0000	0.0032	0.0090	0.9494	0.0001	0.0058	0.0080
	Automatic	0.9492	0.0000	0.0047	-0.0055	0.9492	0.0001	0.0131	-0.0104

Table 3. Validation results for the determination of alcoholic strength using oscillation-type densimetry with peristaltic pumping

	repeatability conditions (n=5)				within-laboratory reproducibility conditions (n=9)			
	x [% vol]	**S [% vol]**	**RSD [%]**	**Bias [%]**	**x [% vol]**	**S [% vol]**	**RSD [%]**	**Bias [%]**
Egg liqueur 1	13.80	0.034	0.24	-0.65	13.77	0.077	0.56	-0.88
Egg liqueur 2	20.11	0.079	0.39	-0.13	20.14	0.093	0.47	-0.01
Egg liqueur 3	19.96	0.046	0.23	-0.09	19.97	0.053	0.27	-0.05

Table 4. Validation results for the determination of total dry extract using oscillation-type densimetry with peristaltic pumping

	repeatability conditions (n=5)				within-laboratory reproducibility conditions (n=9)			
	x [g/L]	**S [g/L]**	**RSD [%]**	**Bias [%]**	**x [g/L]**	**S [g/L]**	**RSD [%]**	**Bias [%]**
Egg liqueur 1	183.1	0.103	0.05	-0.81	183.2	0.258	0.14	-0.76
Egg liqueur 2	277.5	0.258	0.09	-0.57	277.6	0.320	0.11	-0.54
Egg liqueur 3	285.3	0.168	0.06	-0.42	285.3	0.152	0.05	-0.42

Table 5. Comparison between the pycnometric reference method and oscillation-type densimetry with peristaltic pumping

Egg liqueur No.		1	2	3	4	5	6	7	8
AS labelling [%vol]		14	20	20	20	20	20	20	20
Pycnometry	ρ [g/cm^3]	1.0517	1.0810	1.0824	1.0860	1.0827	1.0814	1.1124	1.0812
	RAS [%vol]	13.89	20.14	19.98	19.90	19.79	20.11	20.11	19.27
	TDE [g/L]	184.6	279.1	286.5	298.3	286.9	283.1	373.6	278.1
Density meter	ρ [g/cm^3]	1.0512	1.0830	1.0830	1.0872	1.0827	1.082	1.1135	1.0816
	RAS [%vol]	13.80	20.11	19.96	19.82	19.72	20.01	20.08	19.18
	TDE [g/L]	183.1	277.5	285.3	297.1	288.8	284.1	372.9	277.6
Bias	ρ [%]	-0.05	0.19	0.05	0.11	0.00	0.06	0.10	0.04
	RAS [%]	-0.65	-0.13	-0.09	-0.40	-0.35	-0.50	-0.15	-0.47
	TDE [%]	-0.80	-0.57	-0.42	-0.40	0.66	0.35	-0.19	-0.18

Table 6. Linear correlation between analysis results using the pycnometric reference method and oscillation-type densimetry (data from Table 5).

	Slope (LCI, UCI)	Intercept (LCI, UCI)	Correlation coefficient	Probability
Density [g/mL]	1.026 (0.987, 1.065)	-0.028 (-0.070, 0.014)	0.99928	<0.0001
RAS [%vol]	1.006 (0.992, 1.020)	-0.175 (-0.440, 0.091)	0.99991	<0.0001
Total dry extract [g/L]	1.004 (0.980, 1.029)	-1.685 (-8.703, 5.333)	0.99970	<0.0001