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

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Abstract

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 min 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, sample weight 25 g, 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 correlation ($R = 0.999$) 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 in the German federal state of Baden-Württemberg had to be objected due to a faulty labelling of the alcoholic strength [2]. Exceeding the tolerated limits can have grave consequences for the manufacturers such as fines, high costs of recall and relabelling of a production lot. If, on the other hand, the alcoholic strength of the products is adjusted too high, an economical loss is the consequence. For spirit drink producing enterprises and distilleries, it is essential to have a method at hand for the determination of ethanol content 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 ecologically harmful reagents containing heavy metals, this method could not achieve acceptance. Automated methods such as GC, NIR, or HPLC could not replace pycnometry as a reference method because they are instrumentally complex and therefore more expen-

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sive. Furthermore, they required trained personnel for the handling and some methods did not have the required accuracy [4–10].

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 [11–14]. But it took till the year 2000 for the so-called oscillation-type density meters to be introduced into the European community's reference methods for the analysis of spirit drinks [15]. This is nowadays the state-of-the-art method preferred by the industry, because it is time- and cost-saving as well as simple to perform [14,16].

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 [15]. 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 a more suitable 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 [17]. 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 [18]. 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 an 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 that, for egg liqueur, eight times of rinsing the pipette to be necessary in order to remove all residues [3]. The same problem persists if graduated flasks are used to measure the volume. According to the official method [15] samples like liqueurs, for which it is very difficult to measure volume accurately, 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, the extensive and time-consuming pycnometric determination of density had to be used further on in the process for egg liqueurs. In this work, a newly designed oscillation-type density meter system, which allows for the reliable sampling of highly viscous samples using peristaltic pumping and is able to do n-fold measurements out of a vial to automatically detect the most frequent measuring errors, 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, Germany). The device is coupled to a tank filled with distilled water. 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 (maximum viscosity 600 mPa s) in comparison to the newly designed combined density and refractive index meter DR45 with sample delivery and cleaning unit SC1 (maximum 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 ($\rho_{20\,^\circ C} = 0.99820$). 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 [15]. 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 [15]. 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.