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Kurzberichte

Determination of carbon dioxide in alcoholic beverages by a modified EBC method

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Carbon dioxide of a sample is bound with sodium hydroxide. An Erlenmeyer flask with a side arm is connected to a manometer, and the carbon dioxide is released from the prepared sample with sulphuric acid. The resultant increase in pressure is measured. The method is applicable for the determination of the carbon dioxide content of wine, cider, sparkling wine, beer and long-drink types of beverages. The method is simple, rapid and very accurate. The expanded measurement uncertainty (95 % confidence) is 3.8 %.
Key words: *carbon dioxide, determination, wine, cider, sparkling wine, beer*

Bestimmung von Kohlendioxid in alkoholischen Getränken mit Hilfe einer modifizierten EBC-Methode. *In einer Probe vorliegendes Kohlendioxid wird mit Natriumhydroxid gebunden. Ein Erlenmeyerkolben mit Seitenarm wird an ein Manometer angeschlossen und das Kohlendioxid aus der vorbereiteten Probe mit Schwefelsäure freigesetzt. Danach erfolgt die Messung der resultierenden Druckzunahme. Diese Methode eignet sich für die Bestimmung des Kohlendioxidgehaltes von Wein, Apfelwein, Schaumwein, Bier und Longdrink-Getränketypen und ist einfach, schnell und sehr genau. Die erweiterte Messunsicherheit (95 % Konfidenzniveau) beträgt 3,8 %.*
Schlagwörter: Kohlendioxid, Bestimmung, Wein, Apfelwein, Schaumwein, Bier, alkoholische Getränke

Dosage du dioxyde de carbone dans les boissons alcoolisées par une méthode EBC modifiée. *Le dioxyde de carbone présent dans l'échantillon est lié par de l'hydroxyde de sodium. Une fiole Erlenmeyer à tubulure latérale est raccordée à un manomètre, et le dioxyde de carbone est libéré de l'échantillon préparé avec de l' acide sulfurique. On mesure la surpression qui en résulte. La méthode s' applique au dosage du taux de dioxyde de carbone dans le vin, le cidre, le vin pétillant et mousseux, la bière et les boissons de type „long-drink". La méthode est simple, rapide et très précise. L'incertitude de mesure élargie (à un niveau de confiance de 95%) est de 3,8%.*
Mots clés: dioxyde de carbone, dosage, vin, cidre, vin pétillant et mousseux, bière, boissons alcoolisées

Fermentation produces carbon dioxide in alcoholic beverages. The quantity of carbon dioxide in wine, for instance, depends primarily on the alcohol concentration of the finished wine and the storage temperature. In the production of sparkling wines, carbon dioxide is one of the most essential products. Carbon dioxide can also be added to certain alcoholic beverages. Carbon dioxide affects the taste and aroma and is a preserving agent in alcoholic beverages (Boulton et al., 1996).

The international wine organisation 'Office International de la Vigne et du Vin' (O.I.V., 1990) has a reference method for determination of carbon dioxide. According to this method, the carbon dioxide in the sample is bound with sodium hydroxide whereafter the sample is titrated in the presence of carbonic anhydrase. The carbon dioxide content is calculated from the volume of acid needed to change the pH-value from 8.6 (bicarbonate form) to 4.0 (carbonic acid).

Based on a large number of experiments, we have found the reference method unsatisfactory because of a wide variation in results.
To improve the accuracy, we modified the European Brewery Convention (EBC, 1987) method for determination of carbon dioxide. In the modified method, the sample is cooled, and the carbon dioxide is bound with 10 M sodium hydroxide instead of monoethanolamine. The exact amount of sample is determined by weighing. Results of these methods are presented in this paper.

Materials and methods

Freshly boiled deionised water
10 M NaOH: Dissolve 100 g NaOH in 200 ml water and make up to 250 ml in a volumetric flask.
H_2SO_4, about 50 % (v/v): Cautiously add concentrated H_2SO_4 (95 to 97 %) to an equal volume of water. Mix well by stirring. Cool to room temperature.
CO_2 standard solution, 10 g/l: Dry Na_2CO_3 in an oven at 260 to 270 °C overnight, and cool it to room temperature in a desiccator. Dissolve 6.021 g of the dried Na_2CO_3 in water and make up to 250 ml in a volumetric flask.
CO_2 calibration solutions, 0.4, 1, 2, 4 and 6 g/l: Place 2, 5, 10, 20 and 30 ml of the standard solution in separate 50 ml volumetric flasks and make up to 50 ml with water.
Analytical balance with an accuracy of +/- 0.1 mg
Water-ethylene glycol bath, -4 °C
Electronic density meter or pycnometer (and thermostatic water bath, 20 °C)
Pipettes 2, 3, 5, 10, 20 and 30 ml
100 ml Erlenmeyer flasks, large ground-glass mouth
Manometer, e.g. Thyracont VD 81 vacuum meter
Reaction flask, e.g. 25 ml Erlenmeyer flask with a 3 ml side arm and a three-way valve
Water suction pump

Sample preparation

Prepare the sample in duplicate. Cool the sample in a refrigerator overnight or in a -4 °C water-ethylene glycol bath for 40 min. Put 3 ml of 10 M sodium hydroxide solution in a 100 ml Erlenmeyer flask. Weigh the flask with contents at an accuracy of 0.1 mg. Pour approximately 75 ml of the cooled sample into the Erlenmeyer flask. Weigh the flask with contents at an accuracy of 0.1 mg. Mix and temper to room temperature.

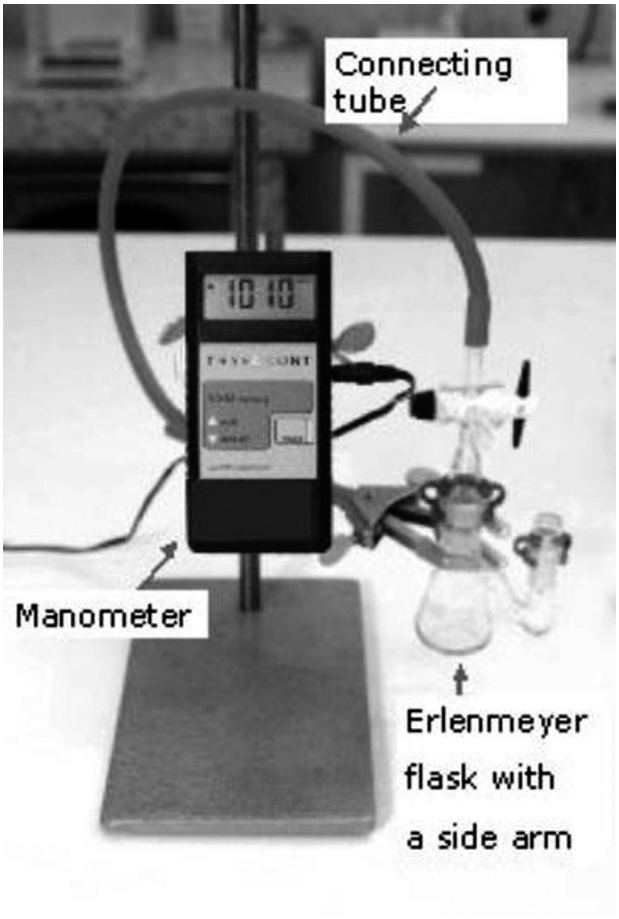

Fig. 1. Apparatus

Measurement of carbon dioxide content

The calibration must be carried out at the same temperature as the analysis of the samples and using the same reaction flask. Before analysing a new sample rinse the flask five times with tap water and once with deionised water. The rinsing water must be at room temperature.
Transfer 2 ml of prepared sample into the reaction flask (Fig. 1).
Connect the flask to the manometer via the open three-way valve. Pipette 0.5 ml of 50 % sulphuric acid into the side arm and stopper the side arm. Secure the three-way valve and the side arm stopper with clips. Note the air pressure. Close the three-way valve. Mix the contents by tilting and shaking vigorously. Note the pressure. The prepared sample can be diluted with water if necessary.

Table 1:
Example of the calculation of the content of carbon dioxide

Sample	Density d (kg/m^3)	Flask + NaOH m1 (g)	Flask + NaOH + sample m2 (g)	Air pressure p_{ap} (mbar)	Sample pressure p_s (mbar)	p_s - p_{ap}	Sample V (ml)	CO_2 g/l	Mean CO_2 g/l
Sparkling wine 1	1027.2	84.6287	156.162	1021	1112	91	69.64	4.77	
Sparkling wine 1	1027.2	84.6287	156.162	1021	1113	92	69.64	4.83	4.80
Sparkling wine 2	1025.3	86.1066	153.4407	1021	1118	97	69.67	5.13	
Sparkling wine 2	1025.3	86.1066	153.4407	1021	1118	97	69.67	5.13	5.13

Calibration

Proceeding as described above, three such calibration solutions should be measured that are within the expected concentration range of the sample. The calibration solutions are measured in duplicate.

Measurement of the density of the sample

Remove carbon dioxide from the sample by shaking the sample first in a separation funnel and then in a vacuum generated by a water suction pump for 3 min. Measure the density of the sample either by an electronic density meter or a pycnometer.

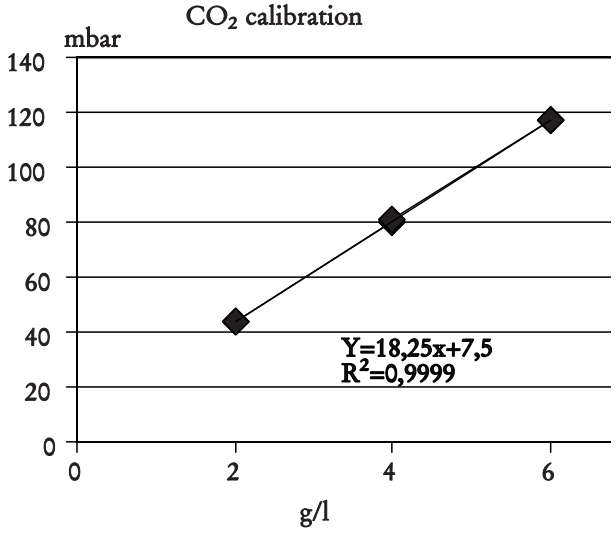

Figure 1: CO_2 calibration graph

Calculation of results

The carbon dioxide content is expressed in g/l. Calculate the pressure increase caused by the carbon dioxide released from each calibration solution and construct a calibration graph. Calculate the slope and intercept of the calibration graph.

Volume V (ml) of the prepared sample:

$$V = [(m2-m1) \times 1000]/d \quad (1)$$

where

m1 (g)= weight of flask + 3 ml NaOH
m2 (g) = weight of flask + 3 ml NaOH + sample
d (kg/m3) = density of sample

Pressure increase p_i (mbar) caused by the carbon dioxide released from the prepared sample:

$$p_i = p_s - p_{ap} \quad (2)$$

where

p_s = manometer reading after releasing the carbon dioxide from the sample
p_{ap} = manometer reading before addition of H_2SO_4 (i.e. air pressure)

Concentration C (g/l) of carbon dioxide in the sample:

$$C = [(p_i - \text{intercept})/\text{slope}] \times [(V + 3)/V] \times L \quad (3)$$

where

slope = slope of calibration graph
intercept = intercept of calibration graph
L = dilution factor in case the sample is diluted after sample preparation

Content of carbon dioxide in % by weight:

$$CO_2\ \%\ (w/w) = C \times 100/d \quad (4)$$

Validation

- Standard deviation estimated from duplicates, s_o = 0.07 g/l
- Relative standard deviation, RSD = 1.9 %
- Repeatability, r = 5.6 %
- Expanded measurement uncertainty (95 % confidence), U = 3.8 %

The proposed method is simple, rapid and accurate and does not need sophisticated instrumentation. It is therefore well suited for routine determination of the carbon dioxide content of alcoholic beverages.

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