Determination of Methanol:

Assessment of DMDC (Velcorin®) Cold Sterilization Using a Photometric Method

Objective

To determine the methanol concentration produced from the hydrolysis of dimethyl dicarbonate (DMDC) in soft drinks using a photometric method, and to evaluate the method's applicability to various beverage types.



Background

General Depending on national laws and regulations, dimethyl dicarbonate (DMDC, E242, INS 242) can be used for the cold sterilization of a variety of beverages. After it has been in a drink only a short time, DMDC breaks down completely (hydrolyses) into carbon dioxide and methanol (MeOH). From 250 parts DMDC, 120 parts MeOH are produced in this process (factor 0.48). This application describes the photometric determination of the methanol produced from DMDC in drinks. As part of this process, possible interferences with the test due to ingredients in the drinks (oxidation and reduction agents, e.g. ascorbic acid) are considered.

Method

Principle of Measurement

Determination of methanol concentration in soft drinks: The enzyme alcohol oxidase catalyses the reaction of alcohol with water and acid to produce acetaldehyde and hydrogen peroxide. The hydrogen peroxide produced combines with aminophenazone and a derivative of benzoic acid, catalyzed by a peroxidase, to form a red, quinoid colorant. This is measured in the photometer. The pH value of the sample must be between 2 and 6.

Equipment & Materials

- **Photometers:** DR1900, DR3900, or DR6000
- **Test Kits:** LCK300, Cuvette Test Alcohol
- **Standards:** Methanol parent solution, 6 g/L
- **Thermostat/Water bath:** Water bath or thermostat/temperature chamber to 20°C
- **Additional:** Membrane filtration set LCW916

Sample Requirements

- **Sample 1:** Beverage formulation without DMDC.
- **Sample 2:** Beverage after quarantine period post-DMDC addition.
- **Sample 3:** Sample 1 spiked with 120 mg/L methanol.



DR3900 Laboratory VIS and **DR6000** UV VIS Spectrophotometers

Sample Preparation

- Degas samples containing carbonic acid (for 1 minute, stirring continuously)
- Add 10 mL of sample 1 to 0.2 mL methanol parent solution (6 g/L) (= sample 3; formulation and testing of the parent solution, see appendix)
- Dilute samples 1. 2 and 3 at a ratio of 1:5 with distilled water
- (1 mL sample + 4 mL distilled water). The measuring range there is 10–150 mg/L methanol (originally produced from a dosage of 1.6–25 mL/hL DMDC).
- If the samples become turbid, filter 10 mL of each with membrane filtration set LCW916.

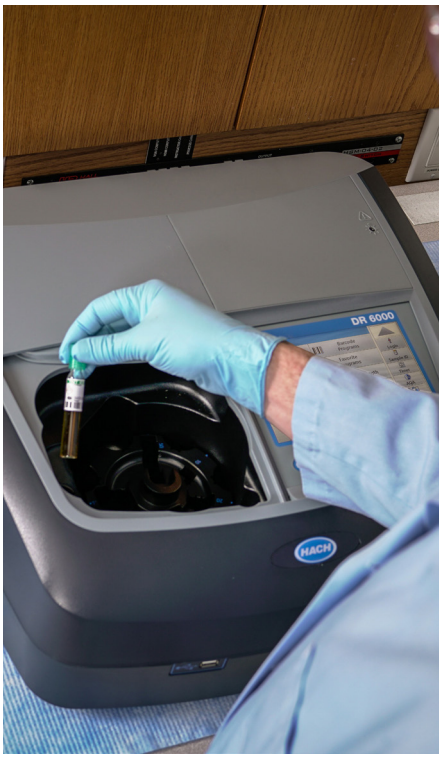


Analysis Procedure

- Set water bath or thermostat/temperature chamber to 20°C, switch on and leave running for approx. 30 minutes.
- Remove three cuvettes from LCK300 packaging, label them S1, S2 and S3
- Remove screw cap, discard and screw on Dosicap.
- Release the contents of the Dosicap by tipping it up and own 4–5 times. Do not shake it violently; the formulation foams up easily!
- Unscrew the Dosicap again and add 0.2 mL to each prepared sample using pipette. Close cuvette again using the Dosicap.
- Mix the contents of the cuvette by tipping it up and down 4–5 times. Again, do not shake; the formulation foams up easily!
- Immediately place the cuvettes in the water bath/thermostat/ temperature chamber.
- Set timer to 45 minutes and then start it.
- On the measurement instrument, select user test DMDC
- After 45 minutes, immediately before the measurement, set to zero with the zero cuvette from the packaging.
- Remove test cuvettes from the water bath/thermostats/ temperature chamber, clean thoroughly and measure in the order P1, P2, P3.

Data Evaluation

Following the measurement of P3 the results are shown immediately in mL/hL DMDC. The additional display % yield is only to be used for assessing the applicability of the process to the specific drink sample and should be between 80% and 120%.



Methanol parent solution, 6 g/L

A parent solution consisting of 99.8% methanol is created in distilled water.

- Fill a 100 mL volumetric flask with approx. 80 mL distilled water, place on weighting scales and tare to 0.
- Add exactly 0.600 g methanol (99.8%) using a pipette.
- Then fill the volumetric flask with distilled water to 100 mL.

Test of the methanol parent solution

- Add 0.200 mL of the methanol parent solution (6 g/L) to a 50 mL volumetric fl ask and fill up to the mark with distilled water.
- Carry out cuvette test LCK300 with the help of the work instructions, with 0.2 mL from the dilution as a sample.
- After the reaction time of 45 minutes (20°C), select the Methanol user test on the photometer.
- Set the instrument to zero with the zero cuvette and then measure the test cuvette with the diluted parent solution. The result must always be 24 ± 2 mg/L.

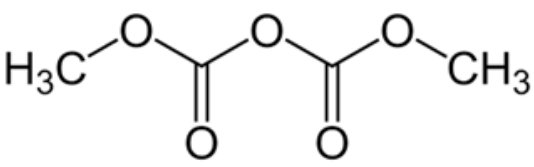
Results from Practical Application

Tested Beverages: Apple spritzer, forest fruits, health drink

Calculation DMDC MeOH	Apple Spritzer	Apple/Forest Fruits	Health Drink
Fruit juice content	60%	55%	3%
Additives	Lemon juice Carbonic acid Natural flavorings	Lemon juice Carbonic acid Natural flavorings	Lemon juice Carbonic acid Natural flavorings Various kinds of sugar Yerba mate extract Citric acid Ascorbic acid Green tea extract Vitamin Mix
Color	Yellow	Red	Light yellow
MeOH recovery	100.5%	93.7%	-1.4%
MeOH concentration in the sample determined by DMDC conditioned on	113.5 mg/L	113.3 mg/L	Not applicable
C additive for filling	20.6 mL/hL	20.34 mL/hL	22.55 mL/hL
Theoretical MeOH concentration in the sample determined by DMDC conditioned on	ca. 120 mg/L	ca. 120 mg/L	ca. 130 mg/L
Analyses comparable samples by means of headspace gas chromatography produced the following results: (MeOH mean value)	110 mg/L	99 mg/L	Not identified

Findings:

- Method is valid for fruit juice spritzers.
- Health drink additives caused interference - method unsuitable.
- Methanol results from spritzers matched gas chromatography within ±10%.
- Predicted vs. measured methanol from DMDC dosage also within ±10%.



Conclusion

- The photometric DMDC-methanol method is reliable for many fruit-based beverages.
- Drinks containing high levels of interfering substances (e.g., antioxidants in health drinks) are unsuitable for this method.
- When applicable, results are consistent with chromatographic reference methods.



Disposal

All waste must be disposed of in accordance with applicable regional and national regulations.