Alcohol Measurement Using Anton Paar Density Meters

Relevant for: Alcoholic beverage industry (e.g. wine, spirits, brandy, whisky, etc.), tax and customs laboratories, pharmaceutical industry

The measurement of the alcohol content of alcoholic beverages is indispensable to ensure that the products conform to the label declaration of alcohol content, and to establish the basis for the payment of tax.

1 Density measurement is officially recognized

An officially recognized method for the determination of alcohol concentrations in alcohol/water mixtures either by weight (%w/w) or volume (%v/v; ABV = alcohol by volume) is the measurement of density followed by conversion into alcohol concentration using official alcohol tables.

Accepted instruments for alcohol determination include pycnometer, hydrometer and Anton Paar density meters.

Pycnometers provide good accuracy, but the method is time-consuming and requires trained personnel to obtain reproducible results.

Hydrometers usually provide less accuracy and require 300 mL to 500 mL of sample, but are easier to use. Careful calibration is necessary.

2 Common units of alcohol concentration

Alcohol %v/v: This unit is influenced by temperature changes, therefore temperature should always be quoted together with the alcohol concentration (example: 41.90 %v/v at 20 °C corresponds to 41.82 %v/v at 15 °C). Results obtained using different density/alcohol tables may be slightly different. Therefore it is advisable to mention the alcohol table together with the results.

Alcohol %w/w: This unit is not influenced by temperature (example: 40.82 %w/w at 20 °C is identical to 40.82 %w/w at 15 °C).

Grams per 100 mL or per L: The temperature must be quoted together with the results in g/mL (or g/L) as the results are influenced by the temperature.

°Proof: This unit is found in the US and several other countries. °Proof is the alcohol concentration in %v/v at 60 °F (15.56 °C) multiplied by two. Pure alcohol (100 %) therefore corresponds to an alcohol content of 200 °Proof (US °Proof = ABV * 2).

The unit °Proof in Great Britain (UK) is not as common as it is in the US and it is different from the American °Proof degrees (UK °Proof = ABV * 1.75).

3 Ideally suited: Anton Paar density meters

The Anton Paar density meters DMA 4100 M, DMA 4500 M and DMA 5000 M (compare **Figure 1**) provide a convenient means of determining density with excellent accuracy using very small amounts of sample (sample cell holds approx. 1 mL) in very short time (typically 1 minute to 4 minutes).

Figure 1: The Anton Paar density meters DMA 4100 M, DMA 4500 M and DMA 5000 M

Easy operation makes time-consuming training unnecessary. The temperature of the sample is held constant by a solid-state thermostat within the instrument. Direct display and/or printout of alcohol concentration in %v/v, %w/w, °Proof, specific gravity, and any other density-related unit is possible. The instruments offer password protection, routine operation is always possible.

Various alcohol tables are programmed into the instrument (OIML, AOAC, IUPAC, etc.). Special tables provided by the customer can be used as well.

Alcohol concentrations can be measured in the full range 0 % to 100 % using a single instrument.

4 Measurement of alcohol/water mixtures with DMA 4100/4500/5000 M

The alcohol concentrations of binary ethanol/water mixtures can be measured from 0 % to 100 % alcohol as %w/w or %v/v. Direct display of the concentration is achieved by programmed alcohol tables.

A variety of different alcohol tables is programmed, some of them differ considerably in the higher concentration range.

OIML Table (Organisation Internationale de Métrologie Légale): internationally the most frequently used table; it lists density versus **%v/v** or %**w/w alcohol**, temperature usually 20 °C.

AOAC Table (Association of Official Analytical Chemists): alcohol concentration %v/v at 60 °F.

IUPAC Table (International Union of Pure and Applied Chemistry): alcohol in %v/v or %w/w at 20 °C.

5 Determination of the alcohol concentration of alcoholic beverages

5.1 Beverages without extract

Alcoholic beverages produced directly by distillation and subsequent dilution with water (no addition of any other components, no storage in wood barrels, etc.) contain only alcohol and water. For fiscal purposes, traces of volatile by-products in the distillate are considered to contribute to the "strength" and the density values are referred to the alcohol/water density tables.

Typical examples are: vodka, fruit brandies and freshly distilled beverages before storage in wood barrels or addition of additives.

These liquids are officially considered pure alcohol/water mixtures, though small amounts of aroma substances, other alcohols, etc. can be present. Determination of the alcohol content is done directly by introducing the original beverage into the measuring cell using one of the techniques listed below.

For quality control (not for fiscal purposes!) some alcoholic beverages with very low and very constant extract content (e. g. some whisky brands) can be measured directly, too. But according to the extract content a correction must be applied to the alcohol concentration to compensate the influence of the extract on the density.

5.2 Beverages containing extract

Besides alcohol and water, many alcoholic beverages also contain various amounts of extract substances, aroma and color components, etc. All these substances influence the density of a liquid, therefore direct alcohol determination using density measurement is impossible.

Fortunately, the extract components are not volatile, whereas the alcohol is volatile. For this reason, the liquid can be separated into an alcohol and an extract fraction by performing a **distillation analysis**. Heating the alcoholic beverage causes the alcohol to evaporate, the vapors are condensed and collected in a separate flask. All the extract remains in the residue of the liquid.

A precisely measured volume (or weight) of the alcoholic beverage is filled into a suitable distillation apparatus. Then the distillation is performed, and the alcohol fraction is filled up to the original volume (or weight) with distilled water. This fluid now is of the identical alcoholic strength as the original sample, but it does not contain extract any more. Therefore the alcohol concentration can be determined with high precision using density measurement.

The distillation analysis is usually performed according to national or international standard methods.

6 Simultaneous determination of the extract concentration

The determination of the content of extract (or dry substance) is also frequently required for the characterization and quality control of alcoholic beverages. This value can easily be determined from the residue of the distillation.

Filling the distillation residue up to the original volume (or weight) results in a liquid of identical extract concentration as the original sample, but the alcohol is removed from this liquid. Internationally, the extract of most alcoholic beverages is dealt with as if it were a solution of pure sucrose in water (though there are other components present in various amounts).

The density of a sucrose solution in water can be converted into the sucrose concentration (= extract concentration) with high accuracy using a sucrose/density table. The sucrose table together with the alcohol table in the density meter makes the instrument an extremely useful tool in the alcoholic beverage industry.

7 What accuracy can be achieved?

Table 1, **Table 2** and **Table 3** list the accuracy (s.d.) in alcohol and extract determinations with DMA 4100/4500/5000 M density meters.

Table 1: Accuracy (s.d.) in alcohol determination

Instrument	Accuracy
DMA 4100 M	better **0.05 %v/v**
DMA 4500 M	better **0.03 %v/v**
DMA 5000 M	better **0.01 %v/v**

Table 2: Accuracy (s.d.) in extract determination

Instrument	Accuracy
DMA 4100 M	**0.025 %v/v**
DMA 4500 M	**0.013 %v/v**
DMA 5000 M	better **0.01 %v/v**

Table 3: Accuracy (s.d.) in density measurement

Instrument	Accuracy
DMA 4100 M	**0.0001 g/cm^3**
DMA 4500 M	**0.00005 g/cm^3**
DMA 5000 M	**0.000007 g/ cm^3**

8 Operating DMA M density meters

8.1 Routine operations and cleaning

The instruments are built for continuous operation. To ensure constant stability and best performance for long term operation, the instruments should not be turned off. The power consumption is very low (max. 50 VA).

If no measurements are performed for extended periods of time (overnight, over the weekend) the measuring cell should be cleaned and dried carefully to avoid contamination of the measuring cell (e.g. algae buildup).

The cleaning is best done by rinsing with distilled water immediately after the last sample. After rinsing with 96 % alcohol the measuring cell can be dried carefully using the built-in air pump.

Regular cleaning with a standard lab cleaner (e.g. Mucasol®) will help to prevent the formation of deposits in the measuring cell.

8.2 Sample preparation:

No sample preparation is required for samples containing no carbon dioxide.

If there are drops of alcohol condensate on the wall of the sample container above the fluid, this has to be re-introduced into the sample to establish its original concentration (see "Filling of the samples").

Gas bubbles in the sample influence the density and must be removed prior to introducing sample into the measuring cell. The FillingCheck™-feature of DMA M density meters will give a warning should bubbles remain in the sample – even if they are invisible to the eye. Dissolved carbon dioxide increases the density and results in apparently lower alcohol content of the sample. For this reason, samples containing carbon dioxide have to be degassed by shaking, stirring, and/or ultrasound. Generally special care must be taken at any step to prevent any evaporation of alcohol (**always cover sample vials!**).

Before filling, the temperature of the sample should always be **slightly above** the measuring temperature. If samples are filled at a temperature that lies below the measuring temperature, outgassing in the measuring cell may occur which results in the formation of tiny gas bubbles in the cell and may cause measurement errors.

8.3 Filling of the samples:

8.3.1 General remarks

Samples can be filled into the measuring cell

- Semi-automatically with the Xsample 320/330/340 sample filling and rinsing unit,
- fully automatically, using the Xsample 520/530 sample changer, or
- manually, using plastic or glass syringes.

The sample containers must always be covered. The loss of alcohol from uncovered containers can amount up to several hundredths of a percent **within a few minutes**.

The use of sample containers which are not filled completely (e.g. half empty bottles) can result in wrong results even if they have been covered. The alcohol tends to evaporate into the head space above the liquid, and the sample itself changes its composition. To restore the original composition, gently tilt the flask repeatedly (do not shake!) to dissolve all the alcohol in the sample again, and immediately perform the measurement.

Samples with alcohol concentrations of around 40 %v/v have to be filled especially slowly, because at this concentration bubbles form fairly easily during the filling. Sample temperatures slightly above the measuring temperature are of advantage.

8.3.2 Automatic filling using the Xsample 320/330 filling and rinsing unit

The Xsample 320/330 sample filling unit is easily built into a DMA 4100 M, DMA 4500 M or DMA 5000 M density meter via plug and play.

The sample is filled from a sealable vial. Xsample 320/330 uses a peristaltic pump to fill the sample. Xsample 330 additionally features a cleaning procedure: after the measurement, the measuring cell is automatically rinsed with up to two rinsing liquids and dried afterwards.

8.3.3 Automatic filling with the Xsample 340 filling and rinsing unit

The Xsample 340 filling and rinsing unit allows automatic filling of single samples into DMA M instruments from a syringe. Xsample 340 is designed to accommodate 2 mL, 5 mL, and 10 mL syringes as well as 5 mL glass syringes and it facilitates perfect filling and excellent precision due to the system's adjustable filling speed.

Xsample 340 with its cleaning module features rinsing and cleaning with up to two rinsing liquids and subsequently drying of the measuring cell. To save time, the cleaning module also supports drying with external compressed air of up to 2 bar pressure. Suitable cleaning agents provided, perfect measuring conditions regardless of the operator and sample are assured.

8.3.4 Automatic filling using the Xsample 520/530 sample changer

Xsample 520/530 can easily be built into a DMA 4100 M, DMA 4500 M or DMA 5000 M density meter.

The automated Xsample 520 sample changer in its standard version holds 24 vials of 50 mL. A customized version with 96 positions for 50 mL vials is also available. Unattended filling and measurement is possible even during the night and at weekends enabling operators to focus on other tasks.

The Xsample 530 sample changer for all DMA M instruments handles a wide range of liquid viscosities. Two standard versions of Xsample 530 are available: either 71 vials of 12 mL or 35 vials of 45 mL can be accommodated, custom options regarding positions and vial size are available upon request. After each measurement, the DMA M measuring cell can automatically be rinsed with up to three rinsing liquids and dried afterwards.

Thus, Xsample 530 is ready to measure a great diversity of samples within one run.

The tightly closed sample vials and the self-adapting filling procedure make it easy to measure volatile samples because evaporation to falsify the results is avoided. After each measurement, the measuring cell is automatically rinsed with up to two rinsing liquids and dried afterwards.

8.3.5 Manual filling by syringe:

Plastic syringes with a standard Luer tip and 5 mL or 10 mL volume can be used to fill the samples into the measuring cell. About two thirds of the sample should be pushed slowly through the measuring cell. The syringe must remain in the filling nozzle during the measurement.

9 Adjustment of DMA M density meters

The instruments are adjusted using air and bi-distilled, degassed water. One adjustment takes approx. 10 minutes.

The validity of the adjustment should be checked regularly by measuring bi-distilled, degassed water. The quality of the water shall meet the requirements of Type II as defined by ASTM D1193 or ISO 3696. If the measured density lies within the specifications of the instrument, samples can be measured immediately.

If the deviation of the measured density from the theoretical water density values exceeds the specifications of the instrument, a cleaning procedure has to be performed (water/alcohol or lab cleaner/water/alcohol), then the measuring cell has to be dried. Subsequently, bi-distilled, degassed water is measured again.

If the result is still not satisfactory, a new adjustment of the instrument has to be performed.

10 The numerous benefits of DMA M speak for themselves

- **Reliability**: measurements of highest precision with excellent reproducibility; robust instruments with exceptional life-span.
- **Simple operation**: Automatic calculation of alcohol concentration in %v/v or %w/w (no more printed tables!), direct display and/or printout of alcohol concentrations or other density-related units.
- **Speed**: 1 to 4 minutes for one result (depending on measurement temperature and required accuracy), automatic sample changer available.
- The **automatic viscosity correction** makes manual correction or adjustment with syrup standards obsolete.

- **Low** operating costs, and **small** sample volumes (minimum 1 mL) apply.
- All relevant data for operation according to **ISO 9000** or **GLP** routines can be printed with each measurement. Certified density standards for traceable calibrations are available.
- Optional combination with the **filling and rinsing unit Xsample 320/330/340** or **automatic sample changer Xsample 520/530** is possible.
- Standard **USB, CAN open and RS-232 interfaces** are built in.
- Connectors for PC keyboard and/or **bar code reader** are available.
- **Password protection** provides security.
- **Temperature control** of the sample is automatically performed in the instrument by solid state thermostats.

11 Official acknowledgements and certificates

Commission Regulation (CE) No. 2676/90 "Article 3 (2)". Laying Down Community Reference Methods for the Analysis of Wines.

Commission Regulation (EC) No 355/2005 Amending Regulation (EEC) No 2676/90: Community methods for the analysis of wines: Electronic densimetry has been validated in accordance with internationally recognized criteria and has been estimated as a simpler and more accurate means of checking the alcoholic strength by volume of wines. A repeatability of 0.067 (%v/v) for samples with an alcoholic strength between 4 %v/v and 18 %v/v is reported which is valid for DMA 4100 M, DMA 4500 M, and DMA 5000 M.

Commission Regulation (EC) No 128/2004 Amending Regulation (EEC) No 2676/90: Community methods for the analysis of wines: The results of determining the alcoholic strength (in %v/v) of a wide range of wines show the comparability of measurements carried out with the hydrostatic balance and the electronic density meter using a frequency oscillator and demonstrate that the values of the validation parameters are similar for both methods. A repeatability of 0.061 (%v/v) for electronic densimetry is reported which is valid for DMA 4100 M, DMA 4500 M, and DMA 5000 M.

Commission Regulation (CE) No. 2870/2000 "Method B", Laying Down Community Reference Methods for the Analysis of Spirits Drinks.

TTB (Alcohol and Tobacco Tax and Trade Bureau) certifies the use of Anton Paar density meter DMA 5000 in proofing alcohol for tax purposes.

HM Customs and Excise (Great Britain) approves the use of Anton Paar density meter DMA 5000 for the revenue accounting of spirits.

AOAC Official Method 982.10, Alcohol by volume in distilled liquors, Densitometric method for Anton Paar DMA 55 or equivalent.

Polish certificate (Polski Komitet Nomalizacyjny) allowing the use of Anton Paar Digital Density Meters for the determination of alcohol content in distilled products.

Automatic Methods for Analysis of Wine and Musts (by: O. I. V. Office International de al Vigne et du Vin): Alcohol Content in Volume Percent, Measurement with Digital Density Meter, required accuracy 0.00001 g/cm^3.

Automatic Methods for Analysis of Wine and Musts (by: O. I. V. Office International de al Vigne et du Vin): Density with Electronic Density Measurement, required accuracy for density measurement 0.0001 g/cm^3 or better.

12 References

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