Food and Beverage

Titration
pH & conductivity
Sugar (Brix, Oechsle)
Alcohol content
Wort determination
Workflow automation

# Alcoholic Beverage Solution Guide

## A Collection of Essential Analyses

METTLER TOLEDO

# Editorial

Dear Reader,

Working in alcoholic beverage manufacturing and production is challenging yet rewarding. Natural products of varying composition need to be manufactured into consumer goods of consistent high quality to meet consumer expectations. This requires consistent and stringent quality assurance measures. Strict hygienic specifications are prerequisite, thus requiring diligent execution of work tasks. Food safety trends and requirements further increase the demand for testing, error-free documentation and traceability.

This guide presents selected METTLER TOLEDO solutions that support your chemical analyses from incoming ingredients inspection, to production monitoring and final product quality control. The solutions describe routine tests, some of which are executed very frequently. Thus, automation can contribute to lab efficiency, results reliability and product quality.

Consumers appreciate genuine and appealing beers, wines and spirits that provide good taste and make drinking fun. Thorough and accurate testing is one of the major steps to achieving and maintaining consumer satisfaction.

Mettler-Toledo

Content

# 1. General Introduction

While the alcoholic beverage market's major categories – beer, wine and spirits – seem straightforward enough, the market itself is not. Consumer preferences in established and emerging markets differ, as do local regulations and attitudes towards consumption [1]. Thriving in this complex arena will require that producers innovate and streamline processes like never before.

Generally, in difficult economic times, alcoholic beverage consumption in established markets such as Europe and America goes down. This can impact profits for multi-nationals even with growth in emerging markets such as India, China and Brazil, in part because consumption is in these areas is mitigated by historic or religious prohibition, but also because drinks that are consumed tend to be entry-level or local. Health considerations are also challenging consumption in established markets [1].

**Say "cheers": Beer production**

The international beer market is still a highly profitable one, despite challenges from growing wine and spirit sales. Anheuser-Busch notes in a recent Beverage World article that 62 percent of growth in beer is coming from the top five worldwide producers, even with the burgeoning popularity of micro-breweries and craft beers [2].

Beer shoppers tend to be brand-loyal but willing to "trade up" to pricier brews when the occasion dictates. Craft, local and premium beers, considered an affordable luxury by many, saw continued growth in 2013. Craft beer is projected to keep growing fastest – up as much as 53.9 percent by 2017. At current rates, Beer Market Insights notes craft brewers will comprise 20 percent of the world market by 2020. So, despite relatively flat per-capita consumption-rate estimates through 2017, craft, local and premium segments are poised to flourish [3, 4].

In emerging markets where profit margins are currently quite thin such as China, a 2012 Accenture report notes that strategies such as bringing production of lower-cost beers to rural areas while offering a wider range of premium beers in urban ones could enhance margins and stimulate additional consumption [5].

As noted, beer, overall, has been increasingly challenged in the last decade or so by other alcoholic beverage choices. However, beer is still the largest category in the worldwide alcoholic beverage market, and it is expected to remain so for the foreseeable future [3].

**A sweet bouquet: Wine stats**

According to Organisation Internationale de la Vigne et du Vin (OIV) statistics, global wine production grew significantly in 2013 over 2012. As of October 2013, annual production levels were estimated at 281 million hectoliters (Mhl) - a volume not seen since 2006. Most wine-producing countries increased volume in 2013 as of the mid-year point with the exceptions of Hungary, Austria and Bulgaria [6, 7].

Europe has seen a slight decrease in land devoted to wine production since 1995, and it is the only world region to be experiencing this decline. However, Europe maintains top market positions worldwide with France, Italy and Spain as its frontrunners. Combined, these three countries produce more than a third of the world's wines [7].

While much of the world's beer is consumed near where it is produced, there is, of course, significant wine trade, particularly in bottled wines. The top 10 wine producing countries account for approximately 90 percent of the wine industry's exports. Consumption seems to have leveled off at about 254 Mhl, after significant gains made in the 1990s [7].

The president of OIV has noted that 2013 production is up despite a loss of vines since 2006 thanks to significant production enhancements [6]. As the world climate continues to shift, production enhancements will likely remain important to maintain supply and profit margins.

**Keeping spirits high: Liquor sales**

Whether it is cocktails in the UK or low-calorie ready-mix beverages in the U.S., like wines, spirits are seeing steady growth. Trends in this category include premiumisation and unique flavor profiles. These flavor profiles extend beyond vodka, too: Flavored rums and even whiskies are making a splash [8].

The upward trend in spirits consumption worldwide is expected to continue, with perhaps some softening in on-premise consumption in 2014, according to Beverage World's 2014 forecast. Craft spirits – locally produced, premium beverages – are continuing to grow in popularity, with many experts asserting that the U.S. market will house 1000 such distillers by 2020.

Comparing actual 2012 numbers in the spirits category to 2017 estimates shows a production volume growth of more than 12 percent and revenue growth of about 18 percent over the period. Bigger profit growth is being made possible by premiumisation. This trend is expected to continue with the millennial generation's appetite for boutique brands [9].

China is the largest market for spirits in the world, and it is expected to make up more than 50 percent of growth in this category in coming years with its own mix of premiumisation and local distillers, according to Brewer & Distiller International. And, while Russia has held its own as the number two market in the world, India may be set to overtake it in the next few years. The U.S. will likely be the fastest-growing geographic market for this segment through the end of 2015 at least [10].

Ready-to-drink cocktails, often with a focus on special nutrition profiles designed to promote a healthier physical appearance, are also making a mark in the spirits world. That trend is also expected to continue, as more people become concerned about health and weight worldwide.

**Health concerns**

Concerns about health will be an ever-present mitigating factor in the alcoholic beverage market. Recent attention has been paid in the European Union and the UK in particular to minors' alcohol consumption because of its neurotoxicity on the developing brain. Additionally, about one-in-four deaths of males between the ages of 15–24 in the UK is thought to be due to excessive alcohol consumption. Ready-to-mix and flavored beverages tend to be favored by young drinkers [11].

In addition to very real risk of accidental death either by traumatic injury while under the influence or over-drinking, excess alcohol consumption at any age also poses significant long-term health risk, according to the U.S. Centers for Disease Control and Prevention (CDC). Nearly 88 000 American deaths are attributed each year to alcohol consumption, with causes of death including risky sexual behavior, liver dysfunction, fetal injury, and cancer [12]. This number gets even more impressive when extrapolated to the global population. Better understanding of these risks may continue to cause per-capita consumption declines in major markets in particular.

**Regulatory considerations**

Because of the health risks associated with alcohol consumption, it is expected that the alcoholic beverage industry as a whole will continue to be one of the most heavily regulated. The sale, distribution and export of alcohol will remain closely monitored, requiring successful producers to have a clear understanding of their markets and the regulatory climates in which they operate. New public health campaigns about alcohol consumption risks are also likely [1].

However, even with its risks, for many people worldwide, alcoholic beverages remain either an occasional indulgence or regular part of a life well-lived. METTLER TOLEDO can help producers meet both consumers' expectations for consistency in their beverages of choice and regional/international regulatory standards with usable, robust, and accurate pH meters, titrators, pipettes, balances and other critical quality control/production equipment.

## 2. Alcoholic Beverages Included

This guide attempts to cover consumer products such as beer, wine and liquor. Despite the diverse range of consumer products being considered, from the point of chemical analysis, the same parameters need to be tested. Such analyses are performed along the entire production chain from raw ingredients to final product.

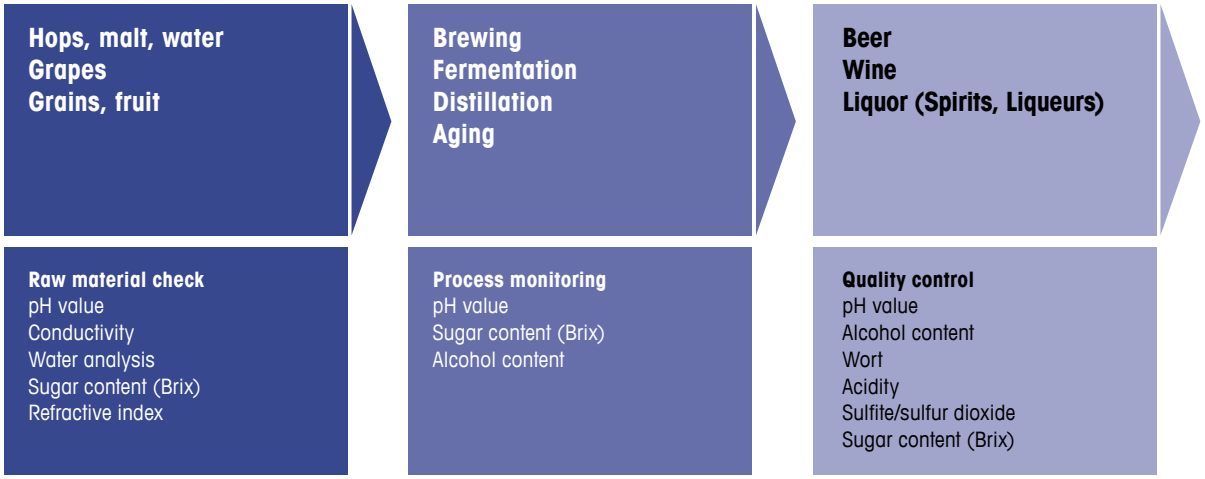



Figure 1: Alcoholic beverages overview

# 3. Analyses

In this chapter, we describe some general lab tasks and selected analytical parameters applied to analyze the aforementioned products. Some facts and explanations about the parameters, as well as some guidance on how to perform each task best, are presented.

| Analysis | Chapter | Analysis | Chapter |
|---|---|---|---|
| pH value | 3.1 | Acidity | 3.4 |
| Conductivity | 3.2 | Sugar content/Brix | 3.5 |
| Water analysis<br>total hardness (Ca, Mg)<br>alkalinity (p- & m-value)<br>chloride, fluoride, sulfate<br>sodium, potassium | 3.3 | Alcohol | 3.6 |
| | | Wort in beer | 3.7 |
| | | Multiparameter system based on density and refractive index measurement | 3.8 |
| | | Sulfite/sulfur dioxide | 3.9 |
| | | Workflow automation | 3.10 |

### 3.1 pH Value

The pH value indicates how much and how strong acids or leaches present in the sample are. Sample solutions with pH below 7 are acidic. If the pH is above 7, the solution is basic (also called alkaline). At pH 7.0 the solution is neutral. By definition, the pH value is related to the concentration of the hydronium ion $H_3O^+$ which is formed when an acid such as tartaric or citric acid is dissolved in water.

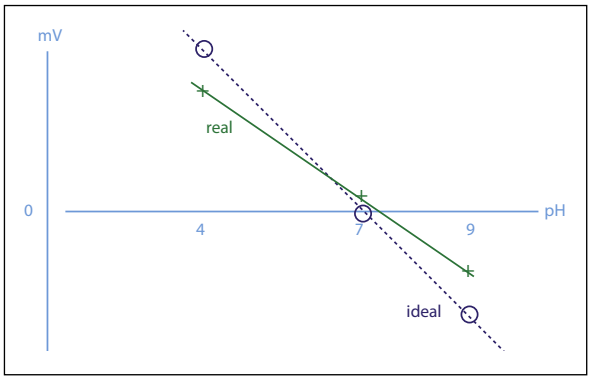



Figure 2: Schematic of a three-point pH calibration

The determination of the pH value requires a meter and a suitable electrode. Manufacturers usually offer a selection of models to cover the actual customer needs. Small meters for simple routine tasks or elaborate models with color display, touchscreen, high resolution, data storage and many more features are available. The user can also choose from a variety of electrodes. Shape of the glass membrane (round, flat, puncture, etc) and shaft material (glass, PEEK, polysulfone) are just two decisive factors.

Figure 3: Use of a portable pH meter with puncture electrode to check pH value of apples

In many beverage samples standard pH electrodes can be easily applied. However, the choice of pH electrode strongly depends on the application and the sample [13].

- Polymeric shaft materials such as PEEK or polysulfone provide virtually unbreakable electrodes.
- Samples containing proteins require electrodes with a reference system which avoids the leaking of silver ions to the electrolyte. When electrolyte containing silver ions flows through the junction into the sample, proteins are precipitated and clog the junction. Clogging the junction leads to slow electrode response and unstable readings. The ARGENTHAL™ reference system stops the silver ions from discharging into the electrolyte.
- If the reference electrolyte is a solid polymer, it can directly contact the sample via an open connection. This avoids any ceramic or sleeve junction. If there is no junction, then there is also no possibility of contamination or blockage. XEROLYT® is METTLER TOLEDO's solid polymer electrolyte. It is ideal for samples containing particles (suspensions).

For more information and electrode selection go to www.electrodes.net.

Because of the importance of the pH value, we recommend to apply a two or three point calibration. For water where pH is usually around 7, three calibration points at pH 4, 7 and 9 (or 10) are good practice. It ensures that pH values below and above 7 are measured correctly. If the samples are acidic, also a two point calibration between 4 and 7 is acceptable and yields reliable results.

### 3.2 Conductivity

Electrical conductivity is a non-specific sum parameter over all dissolved ionic species such as salts, acids and bases. This means that this technique is not able to differentiate between diverse kinds of ions. The reading is proportional to the combined effect of all ions in the sample and it gives a quick overview of the total dissolved solids in the water. Therefore, it is an important tool for monitoring and surveillance of a wide range of different types of waters (pure water, drinking water, process water...) and beverages. The higher the content of dissolved solids, the higher is the conductivity. Ultra-pure water has a conductivity of 0.055 µS/cm due to the self-ionization of water. Sea water containing about 35 g salt per liter reaches 55 mS/cm.

The determination of the electric conductivity requires a conductivity meter and a conductivity cell. It is fast, simple and reliable. One of the most important parameters for the selection of the conductivity cell is the cell constant. Figure 4 shows the recommended cell constant for different conductivity ranges. Whether the user opts for an epoxy, steel or glass shaft depends on the practical conditions of the conductivity measurement. Manufacturers also offer several conductivity meter models providing different levels of performance and operational excellence.

For instruments see chapter 5.4

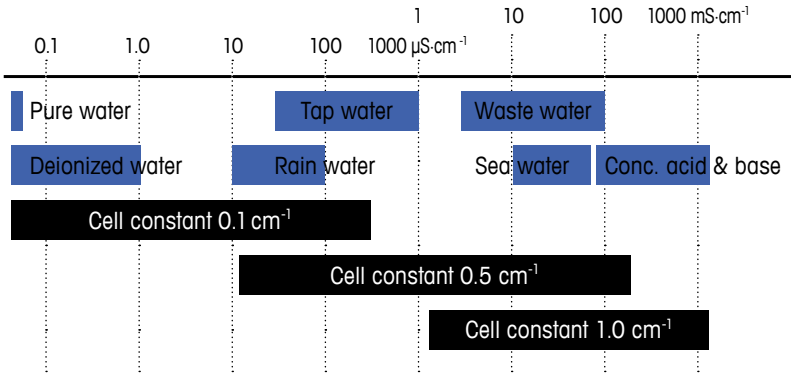



Figure 4: Set of samples and recommended cell constants

### 3.3 Water Analysis

Methods of classical water analysis include hardness (calcium, magnesium), p- and m-value, chlorides, fluorides, sulfates, sodium and potassium.

The m-value is also called alkalinity, total alkalinity, carbonate hardness or temporary hardness. The p-value is likewise referred to as phenolphthalein acidity or total acidity.

| Parameter | | Method | Hints |
|---|---|---|---|
| Hardness | total (Ca + Mg) | Complexometric titration at pH 10 (borate or ammonia buffer) using EDTA<br>Indication: Eriochrome Black T | Indicate equivalence point with a photometric sensor (e.g. Phototrode™ DP5) |
| | calcium (Ca) | Complexometric titration at pH 12 (NaOH solution) using EDTA<br>Indication: Murexide | Alternative titrant: EGTA<br>Alternative indication: by a calcium sensitive electrode |
| p- & m-value | acidity | p-value: Endpoint titration to pH 8.20 with NaOH<br>Indication: pH electrode | pH electrodes have replaced the phenolphthalein and methyl orange indicators. However, if these color indicators are still preferred, photometric sensors (e.g. Phototrode™ DP5) can be applied. |
| | alkalinity | m-value: Endpoint titration to pH 4.30 with HCl<br>Indication: pH electrode | |

| | | |
|---|---|---|
| Chlorides | Argentometric titration (precipitation of AgCl)<br>Indication: Silver ring electrode | Acidify sample to pH 4.5 before titration with diuted nictric acid. |
| Fluorides | Measurement with ion selective electrode | Add TISAB III solution |
| Sulfates | Precipitation titration with $BaCl_2$<br>Indication: Barium sensitive electrode | Adjust pH of sample with lithium acetate buffer to optimize the precipitation of $BaSO_4$ |
| Sodium | Measurement with ion selective electrode | Add ISA buffer solution<br>Preferably apply the standard addition method. |
| Potassium | Measurement with ion selective electrode | Add ISA buffer solution |

Table 1: Overview of classical water analysis parameters and methods

A detailed elucidation of these parameters exceeds the scope of this guide. We refer you to METTLER TOLEDO's application brochure 37 Selected Water Analysis Methods for a more thorough discussion [14].

For instruments see chapters 5.1 and 5.2

### 3.4 Acidity

Titration has been applied for centuries to determine the content of acids in various samples. Before the first electrode was invented, color indicators have been used to indicate the endpoint of the titration.

Figure 5: Example of a typical modern autotitrator

As such, acidity represents a classical parameter in quality control and routine analysis of water, beer, must, wines and other beverages. Grapes contain mainly tartaric, malic and citric acids which are carboxylic acids. In addition, other organic acids such as lactic, succinic and acetic are present in wines.

Generally, the titration of acids in beverages and water is rather straightforward: The acid content is determined by controlled addition of an alkaline titrant solution of known concentration (e.g. sodium hydroxide) until a specific endpoint is reached. Details of the acid content determination, however, are regulated by various national or international entities including standard owners such as the Association of Official Analytical Chemists (AOAC, USA), the Organisation International de la Vigne et du Vin (OIV, FR), the International Organization for Standardization (ISO) and regulatory bodies like the Food and Drug Adminstration (FDA, USA).

The endpoint of the reaction between the acid components present in the sample and the alkaline solution (titrant) can be indicated by the color change of the indicator solution (such as phenolphthalein). Nowadays, electrochemical sensors have replaced the classical color indicators in titration analysis.

In fact, the electrochemical potential can be monitored conveniently by means of a pH glass electrode connected to automated titration instruments. Based on the potential measured in the sample, the addition of titrant is

controlled. This means that larger or smaller portions (=increments) of alkaline titrant are added automatically by a motorized piston burette according to the signal change until the endpoint is reached.

From the titrant consumption and its concentration the acid content can be calculated. As an example, the acidity in wine is determined by direct titration with diluted sodium hydroxide solution to pH 8.20. The total acidity of wine is expressed in mmol/L or in g/100 mL of tartaric acid [15].

| Sample | Preparation | Result expressed for | Result | RSD |
|---|---|---|---|---|
| Cabernet Sauvignon | 5–10 mL diluted in 50 mL deion water | Tartaric acid | 0.57 g/100 mL | 2.1 |
| Red wine | 40 mL | Acids | 3.088 mmol/L | 0.46 |

Table 2: Selected acidity results. 5 or 6 samples titrated.

Among other parameters, a comprehensive equipment qualification including dedicated service and maintenance assures that instruments provide accurate, precise and reliable results.

An overview of automated titrators is given in chapter 5.1

### 3.5 Sugar Content

There are many different sugars, e.g. sucrose, malt sugar, glucose. Strictly speaking, in Brix only the sucrose content in a solution is meant. The unit Brix is defined as percentage by weight of sucrose in pure water solution. Therefore, the designation of Brix degrees is only valid for pure sucrose solutions in water. When determining the Brix degrees on malt sugar, glucose or other sugars, the obtained results are not true Brix degree but related values only.

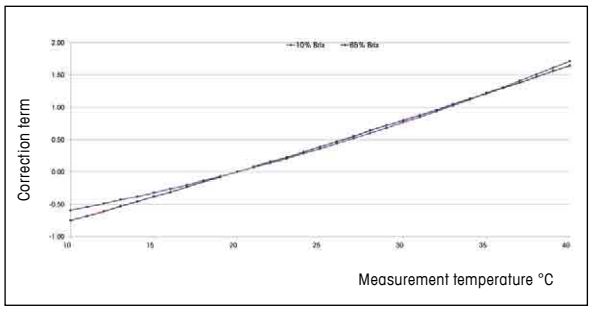



Figure 6: Temperature correction term to be applied to Brix value

Nevertheless, this popular and often used unit is widely applied to express concentration of sugars in different samples. Most commonly Brix is determined by density or refractive index. Manual density measurement methods include pycnometer and hydrometer. For refractometry, often Abbé-type refractometers are applied in either an easy-to-carry handheld or benchtop model. These manual methods, however, depend on operator readings which limit accuracy and precision of results.

Furthermore, very accurate results can only be obtained by thermostating the sample to the required temperature (e.g. 20°C). This takes a long time with pycnometers or hydrometers. Digital density and refractometers have a built-in Peltier thermostat which sets the temperature of the sample to ± 0.02°C of the target temperature within less than a minute.

More details about the sugar determination are explained in the Brix Application [16]

For very precise Brix measurements (e.g. concentrates, molasses) thermostated instruments are the best choice. The reading occurs at a user-defined target temperature (typically 20°C). Thus, any temperature compensation error is omitted. Modern digital benchtop meters have built-in solid state thermostats. This keeps the temperature of the measuring cell and the sample constant at the selected temperature precisely. Brix readings as precise as ±0.003 Brix are possible.

Raw refractive index and density values are converted into Brix degrees using official conversion tables issued by ICUMSA (International Commission for Uniform Methods of Sugar Analysis) and NBS (National Bureau of Standards), respectively. As the reading depends on temperature a temperature compensation is needed to get accurate results (Figure 6). For manual instruments, this implies adding a correction term to the reading. Digital handheld density and refractometers offer a built-in temperature correction, which obsoletes the manual error-prone compensation.

**Oechsle and other scales**

When measuring devices appeared, several scales to determine the sugar content of grape must were developed.

- The Oechsle scale is named after Ferdinand Oechsle and refers to the density of the must. 1 degree Oechsle (1°Oe) corresponds to 1 gram difference between the masses of 1L water and 1L must at 20°C temperature. Thus, 1°Oe compares roughly with 1 g sugar per liter must.
- KMW, Klosterneuburger Mostwaage, is another scale preferred in Austria. Introduced by August Wilhelm von Babo in 1861, the scale refers directly to the percent of sugar content in the must. In Italy, the scale is also applied but named Babo degrees.
- French pharmacist Antoine Baumé developed a general scale for density of liquids, where zero degree Baumé (= B°) is assigned to distilled water. Due to historical reasons, in France Baumé is also used for sugar in grape must.

Hydrometers and refractometers for the manual methods are often calibrated in one of these scales. Modern electronic and instruments have built-in capabilities to convert density or refractive index to the various historic units automatically.

For instruments see chapter 5.5 and 5.6

Figure 7: A digital benchtop refractometer

**3.6 Alcohol Content**

Alcohol determination in alcoholic beverages is stipulated by law and used for tax reasons. Alcohol content is also part of the product specification and often carefully considered by consumers.

One of the possible ways to determine alcohol (i.e. ethanol) content is by measuring density. In earlier days hydrometers were used for the determination. With this technique alcohol content was read off fast and directly but accuracy was rather low. Nowadays, digital density meters offer a much more reliable way to measure alcohol content with high accuracy. The measured density is converted into alcohol content in vol-% or wt-% using the official OIML tables R-22 (*). The alcohol content can be determined based on refractive index measurements as well. For this application, digital refractometers have replace the traditional Abbé apparatus.

Samples such as vodka, gin or brandy, being almost pure alcohol and water mixtures, can be directly applied after degassing to a density or refractometer. Density or refractive index respectively are converted to alcohol content with high accuracy. More details about density-based alcohol determination are explained in the Density Application [17].

Beer and wine, on the other hand, are multicomponent mixtures containing water, alcohol, sugars, acids, and further components. Hence, the straight OIML tables no longer apply. Traditionally, the alcohol content of such mixtures was determined using distillation for separating the alcohol fraction.

In this method, an exact volume of sample is distilled and the obtained alcohol fraction is filled up to the original volume with distilled water to obtain a binary mixture. Then, the density of this binary mixture is measured and

(*) OIML: Organisation Internationale de Métrologie Légale, International Organization of Legal Metrology

finally converted to alcohol content using the tables mentioned before. This procedure is very time consuming and prone to increased measurement uncertainty. However, it is still the official reference technique.

Therefore, formulas have been developed for multicomponent samples enabling direct alcohol content determination without distillation. Such formulas are highly useful in the beer and wine industry. The use of formulas requires at least two measured values determined by different independent measurement techniques, preferably such as density and refractive index (see chapter 3.8).

Documents and publications by MEBAK (**) explain how to obtain the alcohol concentration of beer. Likewise, formulas elaborated by Rebelein (***) are used to determine alcohol content in wine. For both sample types, it is necessary to combine density and refractive index measurements to obtain the correct alcohol content.

For instruments see chapter 5.5 and 5.6

Figure 8: A digital benchtop refractometer

### 3.7 Wort Determination

Wort and alcohol content are major quality parameters of beer. Wort is formed from malt through mashing when starch is converted to sugars by enzymes. Then, hops are added and wort is boiled. In the fermentation step, yeasts digest the wort's sugars to alcohol (i.e. ethanol) and carbon dioxide and beer is produced. Thus, wort or, more precisely its sugars, is frequently measured at several steps of beer brewing.

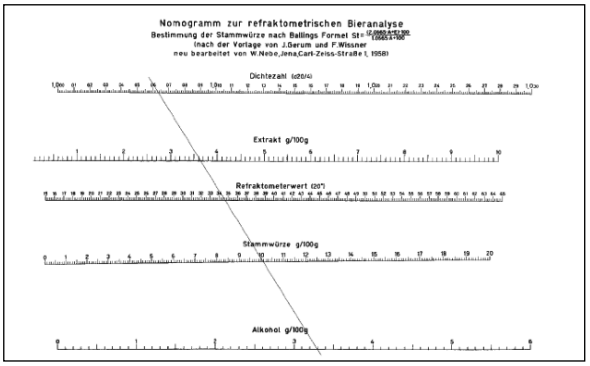



Figure 9: Nomogram used earlier to evaluate extract, wort and alcohol based on density and refractive index (Zeiss number) measurements [18].

Both wort and alcohol contents can be determined by density or refractive index measurements. The conventional, manual method applies density measurement by hydrometer or pycnometer. These manual methods, however, depend on operator readings which limits accuracy and precision of results. In addition, temperature has to be controlled exactly, because density of liquids depends on temperature.

Nowadays, digital instruments are typically used. They provide higher accuracy, ease of use, operator independent results and thermostating options which improve result reliability. Collected standards of the EBC (European Brewery Convention) or MEBAK explain the measurement procedures in detail. See also Beer Application [18] for Wort, extract and alcohol content determination.

The measured density values are converted to wort and alcohol content based on internationally accepted conversion tables. The unit used for wort (i.e. sugars) is Plato or °BRIX.

When refractive index is measured instead of density, conversion tables based on refractive index are applied. Compared to density measurement, refractometers are faster, easier to use and very simple to clean.

For instruments see chapter 5.5 and 5.6

Figure 10: A few drops of sample on the prism of the refractometer are sufficent.

(**) MEBAK: Mitteleuropäische Brautechnische Analysenkommision (middle European technical brewery analysis committee)
(***) Dr. Hans Rebelein (1916 – 1975)

### 3.8 Multiparameter Systems

Major advantages of multiparameter systems are workflow simplification and automation. This increases reliability, data safety and efficiency and can free lab operators for other tasks.

Many kinds of analytical multiparameter systems are possible. A few examples:

- The combination of potentiometric titrators and ion chromatographs for the complete ion analysis in water including alkalinity, pH and conductivity
  For more details: www.mt.com/titration-ic
- Thermogravimetry hyphenated with mass spectrometry for evolved gas analysis [19]
- Potentiometric titrators with several burettes connected to autosamplers and their peripherals for determining pH, acidity, and salt content or free and total sulfites or other parameters. See also chapter 3.10

In this chapter, we refer to density and refractive index based systems (see Fig. 10). Current density meters and refractometers tend to be highly reproducible and accurate thanks to built-in precise thermostating, operator independent result evaluation, automatic conversion to desired result unit, and automatic result documentation and data export. As such, they are ideally suited to multiparameter systems.

When applied to beer samples, such systems typically provide wort content, alcohol content and additional parameters such as pH value or color. Preferably, multiparameter systems are fed by autosamplers adding the most to reliability and efficiency.

After filling the entire sample loop, all measurements are performed simultaneously to assure reliable and reproducible results. After the measurements, the sample loop is thoroughly rinsed with deionized water and/or solvents and dried to avoid any carry-over or dilution.

For instruments see chapter 5.7

Figure 10: Multiparameter system with density meter, refractometer, pH meter, sample changer and LabX software

### 3.9 Sulfite, Sulfur Dioxide

Sulfites are naturally present in beverages such as wines since they result from alcoholic fermentation. However, sulfites are also added (e.g. as potassium metabisulphite) to the wine during the bottling process to form sulfur dioxide, $SO_2$. $SO_2$ is known to be an antioxidant protecting wines from oxidation. It also acts as antifermentation agent and inhibits the growth of yeast and other microorganisms.

The antiseptic and antioxidant activity of $SO_2$ is only achieved if the content of free sulfur dioxide reaches a certain value. Thus, its content has to be monitored. A second important reason to determine sulfur dioxide relates to the limits defined by standards and regulations. Moreover, too high an $SO_2$ concentration in wine has to be avoided. It leads to an unpleasant odor, and can cause headaches for wine drinkers.

Hence, reliable sulfite/sulfur dioxide determination techniques are needed. They allow winemakers to monitor $SO_2$ carefully during wine production, and intervene quickly if issues arise. Also testing labs need to be able to determine sulfite contents precisely.

Titrimetric analysis is an optimal choice. It meets the winemaker's needs for a fast and approximate method, and it serves testing labs with precision and accuracy as well. Titration of sulfur dioxide is straightforward. The sample, e.g. wine, is first acidified with sulfuric acid, and subsequently titrated with iodine. This direct titration determines **free** $SO_2$.

Then again, $SO_2$ is also bound to various components present in wine such as acetaldehyde, anthocyanins, and phenolic compounds. To determine **bound** $SO_2$, it must first be released from such components by addition of sodium hydroxide. After a fixed waiting time, the sample is then acidified and titrated with iodine similarly to the free sulfur dioxide.

Note: The sum of free and bound sulfur dioxide content is designated as the total $SO_2$.

For manual titrations, the endpoint is generally indicated by starch. In fact, starch is binding excess iodine titrant and thus turning to its characteristic violet color. Nowadays, electrochemical sensors have replaced the color indication with starch solution. The electrochemical potential can be monitored by a platinum metal ring or a platinum double pin redox electrode (see Fig. 11) connected to automated titration instruments.

Modern autotitrators perform titrations automatically including result calculation once a sample is started. Several models are available to meet different requirement levels from small to large-scale winemakers and wine testing labs. As an example, the total sulfur dioxide titration can be completely automated including the exact waiting time to hydrolyse bound $SO_2$. Autosamplers help manage sample series, providing various automation degrees and, thus, efficiency gains.

Figure 11: A platinum double pin electrode: DM143-SC

| Sample | Mean value mg/L | RSD % | Number n |
|---|---|---|---|
| Red wine | 10.07 | 1.00 | 5 |
| White wine I | 26.43 | 1.54 | 4 |
| White wine II | 21.19 | 0.32 | 6 |

Table 3: Free sulfur dioxide contents [15].

| Sample | Mean value mg/L | RSD % | Number n |
|---|---|---|---|
| California cabernet sauvignon | 31.89 | 1.15 | 3 |
| Spanish red wine | 135.28 | 2.34 | 5 |
| Swiss red wine | 73.34 | 0.60 | 4 |
| White wine | 86.42 | 1.44 | 3 |

Table 4: Total sulfur dioxide contents [15].

Among other parameters, comprehensive equipment qualification including dedicated service and maintenance helps achieve accurate, precise and reliable analysis results. Such types of equipment qualification is prerequisite to comply with standards and regulations.

An overview of automated titrators is given under chapter 5.1.

Figure 12: Wine bottling where sulfur dioxide is added for protection purposes

### 3.10 Workflow Automation

Automation can help labs process more samples in less time, which can be very desirable in a competitive manufacturing environment. However, effective automation of a titration process is often much more than just switching over samples. For the right decisions regarding automation one needs to consider the whole titration procedure from sampling,

identification and sample preparation to actual measurements, temperature control, result calculation and data gathering. Based on customer needs different degrees of automation then may be desired.

We differentiate the following automation degrees:
- Automated sample transport, dissolving and rinsing. See chapter 3.10.1
- Automatic identification and transfer of sample data. See chapter 3.10.2
- Automatic method detection. See chapter 3.10.3
- Automated liquid handling. See chapter 3.10.4

A brief description of each enabling technology and its benefits follows. In-beaker features are described in chapter 3.10.5

### 3.10.1 Flexible and Efficient Autosampling

A modern sample changer has to transport the samples to the titration stand. It also needs to add auxiliary reagents such as buffers or indicators, reactants, deionized water and solvents. It should stir the sample for a predefined time to dissolve it and mix it with other reactants if required. Such steps are carried out repetitively exactly according to method specifications and free QC staff to complete other tasks.

Figure 13: Titration Excellence titrator with InMotion™ Autosampler and LabX

**Innovation and modularity**

QC staff may still want to check the sampler visually to make sure all is okay. Current sample changer models offer status indicator lights. METTLER TOLEDO has put the status light of the InMotion™ autosampler atop the titration tower. Thus, one quick glance from all corners of the lab lets the operator know immediately if an analysis is still running, needs attention or is terminated.

Figure 14: Status light of InMotion™ autosampler

Modularity of the autosampler system adds other advantages.
- The automated system can be tailored to actual needs. Small or large sample racks, various sample beaker sizes or a second titration tower bring just the right solution to analyze different samples in a very efficient and optimized way.
- The system can also easily be extended and adapted to future needs.
- Accessories such as pumps can be added neatly to the sample changer while still maintaining the equipment's footprint to save bench space.

After completing a titration, a modern autosampler/titration system should wash and rinse stands, beakers, stirrers, electrodes and other equipment parts. All wash phases occur automatically without user intervention. METTLER TOLEDO's PowerShower™ option cleans thoroughly during a multi-angle rinse sequence to ensure no carry over distorts the following sample.

### 3.10.2 Secure Sample Data Transfer

Ensuring results are unquestionably allocated to the right sample can be difficult, particularly when a large number of various samples are being managed manually.

Keeping a sample's weight or volume, size and ID together without doubt is just one task. Avoiding transcription errors when recording sample weights is another. Remembering safely which sample is in which titration beaker is the third.

**Quantum of solace**

Modern automatic titrators and sample changers provide good solutions to such problems. The SmartSample™ workflow support, a recent innovation by METTLER TOLEDO, improves sample preparation and delivers secure sample handling and sample data transfer. No more beaker numbering, no more writing sample weights on beakers, papers or lab journals, no more confusing samples.

**How does SmartSample™ work?**

The RFID option of the new XPE and XSE Excellence balances sends (writes) sample ID and sample weight to the RFID tag of the titration beaker when weighing is complete. The InMotion™ sample changer then reads all sample data once the beaker passes InMotion's RFID option and forwards this information to the Excellence titrator. See Fig 15.

Because the RFID tag is uniquely attached to a beaker, beakers can be placed in any sequence on the InMotion™ sample changer with results still safely correlating to the appropriate sample data.

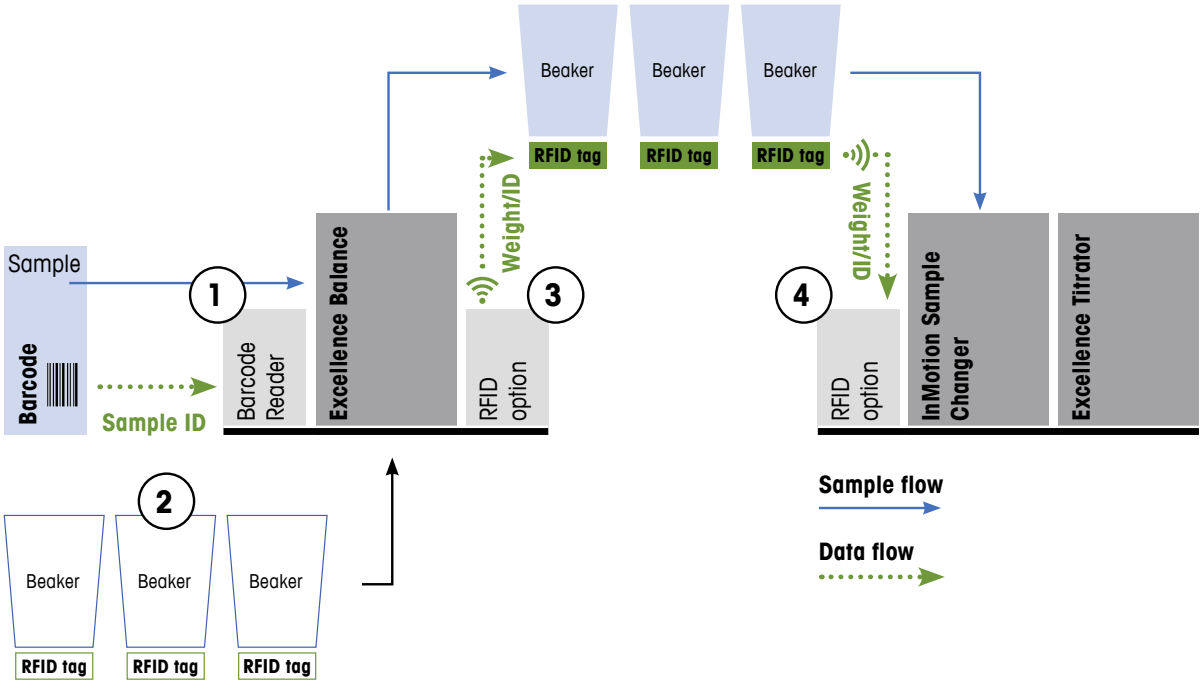



Figure 15: Secure sample weighing and data workflow with SmartSample™

### 3.10.3 Automated Method Assignment

When a QC lab or an at-line measurement station analyzes different samples, a dedicated method is applied for each sample to make sure samples are analyzed properly.

Up to now, the correct titration method needed to be selected at the titration instrument for each and every single sample or sample series. The method selection was entered manually strictly observing the sample sequence. Thus, running samples in mixed order had to be avoided by all means.

**A new way to assign methods**

With a new feature of the LabX 2014 Titration PC software called SmartCode™, the method is automatically assigned to the sample. Based on sample ID, the LabX 2014 software automatically chooses the correct method and lets the titrator execute it.

The required sample ID can be barcoded on the beakers or stored on a RFID tag (see chapter above). InMotion™ autosamplers with their respective accessories can read both barcoded and RFID tagged sample IDs on their own.

Assigning the correct method to a particular sample automatically avoids worries, eliminates wasted samples and can reduce rework.


Figure 16: The SmartCode™ principle

### 3.10.4 Versatile Automated Dosing

The Liquid Handler automated dosing system opens new horizons in titration automation: It automatically samples accurate and precise aliquots of sample solution. This avoids the error-prone step of manual pipetting and helps obtaining reliable results.

The Liquid Handler is fully integrated into the method concept of Excellence titrators. Tasks such as:

- Aspirating sample
- Rinsing tubes or
- Dosing solvent

are executed via straightforward programming of the Liquid Handler. Thus, the Liquid Handler provides unsurpassed flexibility in automated dosing and pipetting of samples.

Figure 17: Switching valve of Liquid Handler

### 3.10.5 In-Beaker Features for Carbonated Beverages and Fruit Juices

When analyzing beverages with multiple sample automation systems (see chapter 3.8), the pH value can be measured whilst the Brix determination is performed with the refractometer or density meter. The beaker for pH measurement is placed at the InMotion™ autosampler.

Sedimentation of the sample is prevented by uninterrupted stirring with the InMotion™ stirrer.

When measuring carbonated beverages, in-beaker degassing can be performed with a combination of air flow and stirrer before starting the measurement. This eliminates the need for prior degassing with an ultrasonic bath.

See chapter 5.2 for the InMotion™ Autosampler

# 4. Regulations and Standards

### 4.1 Regulations

Regulations regarding product safety become more and more demanding. An increasing number of regulations and stronger demands from retailers and finally consumers ask for extended testing and defining of critical control points.
A strong impetus comes from the US FDA's Food Safety Modernization Act (FSMA). FSMA was signed in to law in January 2011. Since then, this Act has influenced most other countries as well, due to the global food supply networks.

To assure the quality of food products from production to consumer, a chain of regulations is in place.

| Global food safety Initiative GFSI | | | |
|---|---|---|---|
| Hazard analysis<br><br>HACCP | Harmonized food quality systems<br><br>IFS, BRC, etc | Harmonized QC systems<br><br>ISO 22000 | Harmonized audits and certificates<br><br>FSSC 22000 |

Figure 18: Chain of regulations

### 4.2 Standards

**GFSI**

The Global Food Safety Initiative (GFSI) was launched in May 2000 and established as a non-profit foundation. Its mission is the continuous improvement in food safety management systems to ensure confidence in the delivery of safe food to consumers. GFSI includes all stakeholders of the food supply network, i.e. producers, manufacturers, distributors, retailers, standard owners, auditors, and governmental agencies.

GFSI maintains benchmarks accepted, approved and applied by the food supply stakeholders. It provides platforms for networking, knowledge exchange and sharing of information and best practice experience. One of these platforms is the annual Global Food Safety Conference.
GFSI is managed by the Consumer Goods Forum.

**HACCP**

Hazard Analysis Critical Control Point (HACCP) is a systematic preventive approach to safety of food and beverages. It was conceived in the 1960s for NASA's* first foods for space flights. HACCP addresses physical, chemical, and biological hazards from raw material production, procurement to manufacturing, distribution and final consumption. It focuses on identifying and preventing hazards rather than finished product inspection [16, 17].

1. Conduct a hazard analysis – Identify hazards, assess risk and list controls
2. Determine critical control points (CCP)
3. Establish critical limits – Specify criteria for each CCP
4. Establish a monitoring system – Define monitoring requirements for each CCP
5. Establish corrective action – Correct whenever monitoring indicates criteria are not met
6. Establish verification procedures – Ensure HACCP system is working as planned
7. Establish record keeping and documentation requirements – Recording keeping procedure

Table 4: The 7 principles of HACCP [20, 22]

* NASA = US National Aeronautics and Space Administration

Once CCPs have been defined, appropriate control measures are established. This may include at one point conductivity value measurements to monitor overall ionic concentration in water, titration of remaining caustic in bottle rinsing solutions, microbiological tests to prove absence of harmful bacteria and many more.

**METTLER TOLEDO support**
- Analytical instruments such as meters and sensors for pH, conductivity, dissolved oxygen, and carbon dioxide; potentiometric titrators
- Pipettes and sterile tips.

**Food quality systems**

These quality systems focus on process and product certification schemes. They ensure that companies deliver food products in line with safety and quality specifications defined by customers. They are risk-based and apply a scientific approach. Another task is the standardization of the applied quality, safety and operational criteria.

Two typical examples are BRC Global Standards and IFS International Featured Standards. Both BRC and IFS have been initiated by retail companies. Another example is SQF Safe Quality Food, designed to meet the needs of retailers and suppliers.

**Harmonized certification with FSSC 22000**

The Food Safety System Certification (FSSC) is a food certification scheme for ISO 22000-based certification of food safety management systems. FSSC 22000 is acknowledged by GFSI and compliant with GFSI's latest Guidance Document version 6. It includes well defined requirements for:
- Companies of the food chain requesting certification,
- Certification bodies (CB) and
- Accreditation bodies (AB).

Audits of a company following FSSC 22000 put the company's safety management system in the center. They stress commitment of the company's management, effectiveness of the safety management system, and continuous improvement processes. The audit cycle is typically 3 years.

The Foundation for Food Safety Certification, an independently managed, non-profit organization which owns the FSSC 22000, sees a growing demand for certifications throughout the supply chain [23].

**METTLER TOLEDO support**
- Certified buffer and standard materials traceable to international references
- LabX software based solutions for audit trails, user management and automatic data transfer and storage
- Complete documentation of methods, calibrations and results either via printer or data network

**ISO Standards 17025 and 9001**

The ISO standard 17025 is a measure of quality and competence of a lab. It assesses if the lab is technically competent to perform certain tests with respect to accuracy, reproducibility, measurement uncertainty and other result quality aspects. It also assesses if good lab management practice is applied, i.e. sustainable operations, effective quality management system, suitable testing equipment and environment.

ISO 17025 directly applies primarily to testing and calibration labs. However, quality control labs perform tests and calibrations as well and thus, are included in the scope of ISO 17025. The application of ISO 17025 minimizes the risk of inaccurate results and avoids expensive and time consuming retesting. It can also improve the acceptance of results by third parties.

ISO 17025 is also the basis for an accreditation. The accreditation, executed by technical assessors or subject matter experts, recognizes:

a) Specific technical competences of the lab, e.g. to carry out specific tests or types of tests,
b) People skills and knowledge; and
c) Procedures for calibration and maintenance of test equipment and for quality assurance of test and calibration data.

The ISO 9001 standard is, however, a rather generic standard for quality management systems. It applies to all organizations and recognizes the organization's ability to provide products according to preset specifications, customer requirements and regulatory requirements.

Certification against ISO 9001 considers the entire business and recognizes compliance with standards or specifications. The certification is executed by management system auditors [24].

**METTLER TOLEDO support**

- Webinar Evaluation of Measurement Uncertainty in Titration. Got to **www.mt.com/webinars**
- MuPac, a service offered by METTLER TOLEDO to evaluate measurement uncertainty of titration methods. Go to **www.mt.com/gtp-mupac** for more details.
- VPac Performance Verification for EasyPlus Titrators. See **www.mt.com/easyplustitration**

### 4.3 Test Methods

In the past, a "prescriptive approach" was taken which specified a certain method and its defined application. However, currently any suitable method is selected provided a defined set of criteria is fulfilled such as accuracy, specificity, precision, limit of detection, sensitivity etc. This freedom of methods selection, named "criteria approach", also takes into account developments in analytical sciences. From there, new methods and refinements of current methods flow into daily practice [25].

#### Reference method vs routine methods

Often in alcoholic beverage products, the parameter to be determined by the chemical analysis is not a chemical substance of known identity, but a mixture of substances captured by the method. Thus, many methods in food and beverage production are "defining methods". Usually they are tedious and time-consuming to carry out.

In addition, many reference methods in food and beverage are "defining methods" as well. Reference methods are applied for official control and legal reasons.

However, sample frequency and cost of analysis require fast, cheap and automated routine methods. Routine methods need careful examination to prove suitability. Extended result comparisons with the reference method explain and document result variability and potential systematic differences.

### 4.4 Sampling Plans

In order to make acceptance/rejection decisions based on statistical and uncertainty evaluations, sample plans for multiple tests by routine methods have been specified and implemented in quality control labs. This best practice has replaced the former testing of a few samples only by a reference method.

Sampling plans also take into account involved risks derived from raw materials and processing to the consumer product. Risks can be classified, for instance, from negligible to intolerable, indicating how measures and frequency of control have to be geared.

| | | | | | |
|---|---|---|---|---|---|
| **Probability** | most likely | 3 | moderate | high | intolerable |
| | likely | 2 | tolerable | moderate | high |
| | unlikely | 1 | negligible | tolerable | moderate |
| | | 0 | 1 | 2 | 3 |
| | | | mild | remarkable | extremely severe |
| | | | **Severity level of non-conformity** | | |

Table 5: Classification of risks [25]

### 4.5 Support by Analytical Instruments

In general, regulations ask for more and more elaborate testing to make sure that quality and safety targets for food and beverages are met at all times. The documentation of such testing tasks including all data and results has to be error-free and without gaps.

Modern instruments help to achieve both targets.

- Extended automation possibilities based on autosamplers, accessories and method structures keep or even increase the efficiency in spite of increased sample numbers and manage sample throughput.
  A typical example is the InMotion™ autosampler and its paraphernalia providing automatic sample changing for up to 303 samples and many more helpful features.
  InMotion™ samplers can be used with titrators, density and refractometers.
- Balances and analytical instruments communicate via external software (e.g. LabX software) or directly via various communication ports (e.g. USB, RS232). This safe and secure automatic data transfer avoids transcription errors, saves time and provides traceabilty.

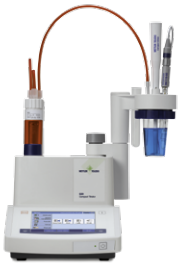
In either case, customers can decide on the automation level to match requirements. Thanks to METTLER TOELDO's modular solutions, future needs can be met easily as well.

# 5. METTLER TOLEDO Solutions

Some selected solutions are highlighted and summarized in this chapter. The complete offering is presented in the homepage and the Laboratory Catalog.

Homepage: www.mt.com
Lab catalog: www.mt.com/lab-catalog

## 5.1 Potentiometric Titrators

| Product line | Solution | Example |
|---|---|---|
| **Excellence Line** | T90 Titrator, T70 Titrator<br>• Intuitive user interface<br>• Personal home screen<br>• Flexible user management<br>• Automatic burette recognition<br>• Plug & Play sensors<br>• Hot Plug & Play concept<br>• Modular: tailored exactly to your needs<br>• Automation options: Rondolino, InMotion Autosampler<br>• PC software options: LabX express, LabX server, Regulation option (21CFR11)<br>• Full qualification services available |  |
| **Compact Titrators** | G20 Compact Titrators<br>• Intuitive OneClick™ user Interface<br>• Personal home screen<br>• Automatic burette recognition<br>• Plug & Play sensors<br>• Automation options: Rondolino<br>• PC software option: LabX express<br>• Installation qualification service available |  |
| **EasyPlus** | Easy pH Titrator, Easy Cl Titrator<br>• Affordable entry level titrator<br>• Quick start and intuitive operation with app based iTitrate™ user interface<br>• Only a few parameters to be set thanks to iTitrate™ intelligence<br>• Internet support for easy self installation and application database<br>• Unique VPac performance qualification service available |  |

## 5.2 Workflow Automation

| Product line | Solution | Example |
|---|---|---|
| **Autosampler** | InMotion™ – Maximum productivity in minimal space<br>• The models Flex, Pro and Mac and various racks accommodate different sample volumes and up to 300 samples<br>Options to improve your workflow:<br>• Protect your samples with the CoverUp™ Lid Handling system<br>• Ensure the right sample temperature with a water bath rack<br>• Secure sample data transfer with SmartSample™ technology<br>• Automate method assignments with Barcode reader and SmartCode™ of LabX |  |
| | Rondolino<br>Carroussel-type automated titration stand<br>• Can be loaded with up to 9 sample beakers<br>• One conditioning beaker in a unique position<br>• Dip rinsing (standard) or PowerShower (option) |  |
| **Sample dosing** | Liquid Handler<br>Controlled by the titrator, the robust Liquid Handler automatically doses and pipettes samples with the highest degree of accuracy. This enables the most demanding of automation processes to be implemented |  |

## 5.3 pH Meters and Electrodes

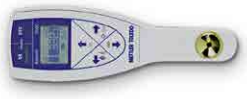
| Product line | Solution | Example |
|---|---|---|
| **Benchtop meter** | S220 SevenCompact<br>Universal instrument for measurements of pH, mV/ORP and ions |  |
| **Portable meter** | SG8 SevenGo pro pH/ion<br>Professional IP67 meter for pH, ion concentration, mV/ORP and rel. mV measurements<br>(New products to be introduced shortly) |  |

| Product line | Solution | Example |
|---|---|---|
| | SG2 SevenGo pH<br>Routine IP67 meter for pH, mV/ORP and rel. mV measurements<br>(New products to be introduced shortly) |  |
| **pH Electrodes** | InLab Routine Pro<br>Refillable pH sensor, precise and fast<br>(Find your sensor: www.electrodes.net) |  |
| | InLab Expert Pro / InLab 413 SG<br>Robust, maintenance-free pH sensors<br>(Find your sensor: www.electrodes.net) |  |

### 5.4 Conductivity Meters and Sensors

| Product line | Solution | Example |
|---|---|---|
| **Benchtop meter** | S230 SevenCompact<br>Universal instrument for measurements of conductivity, salinity, TDS, resistivity and conductivity ash |  |
| **Portable meter** | SG7 SevenGo pro Conductivity<br>Professional IP67 meter for conductivity, salinity, TDS and resistivity measurements<br>(New products to be introduced shortly) |  |
| | SG3 SevenGo Conductivity<br>Routine IP67 meter for conductivity, salinity, TDS and resistivity measurements<br>(New products to be introduced shortly) |  |
| **pH Electrodes** | InLab 731 / InLab 738<br>Robust allround sensors for average to high conductivity<br>(Find your sensor: www.electrodes.net) |  |
| | InLab 740 / InLab 742<br>Precision sensors for low conductivity and ultra-pure water<br>(Find your sensor: www.electrodes.net) |  |

### 5.5 Refractometers

| Product line | Solution | Example |
|---|---|---|
| **LiquiPhysics Line (benchtop models)** | Refractometers RM40, RM50<br>METTLER TOLEDO digital refractometers are the perfect solution for Brix measurements and refractive index determinations. Our refractometers can also be expanded to measure density, pH, conductivity, color or optical rotation. |  |
| **Portable models** | Refracto 30PX<br>Hand held refractometers allow you to determine the refractive index, Brix, Baume or specific gravity (SG) of a sample in the field or on-site |  |

### 5.6 Density Meters

| Product line | Solution | Example |
|---|---|---|
| **LiquiPhysics Line (benchtop models)** | Density Meters DM40, DM45, DM50<br>METTLER TOLEDO digital density meters are the perfect solution for Brix measurements and density determinations. Our density meters can also be expanded to measure refractive index, pH, conductivity, color or optical rotation. |  |
| **Portable models** | Refracto 30PX<br>Hand held refractometers allow you to determine the density, specific gravity (SG), Brix or Baume of a sample in the field or on-site |  |

### 5.7 Multiparameter System

| Product line | Solution | Example |
|---|---|---|
| **LiquiPhysics Line (benchtop models)** | Multiple parameter automation for beer and wine<br>• Refractometer RM40 or RM50<br>• Density meter DM40, DM45 or DM50<br>• Sample changer SC1 or SC30<br>• Additional analytical instrument e.g. pH meter, colormeter<br>• LabX software |  |

# 6. Conclusions

We have presented several essential analyses and tasks pertaining to laboratories in beer, wine and liquor manufacturing companies. When performing these analyses, accuracy and precision are absolutely non-negotiable. Any variation in the composition of a product could violate the product declaration, requiring, for example, batches of the product to be discarded. Any variation in taste could lead to disappointed consumers and future revenue losses.

Analytical instruments, balances and further solutions from METTLER TOLEDO empower you to perform these tasks with the confidence that your results will be accurate. Thanks to a unified and easy to understand interface concept, operation of instruments and balances is simple and straightforward. Depending on your needs, processes can also be automated to varying degrees, leading up to fully automated systems.

METTLER TOLEDO experts have contributed tips and hints to this guide advising you on best practices and ensuring you get the most out of your instruments and equipment. It's important to us that you achieve your target to manufacture quality beer, wine and liquors to satisfy your consumers.

# 7. Selected Application Methods

### 7.1 Total Hardness of Tap Water by Photometric Titration

(Mettler-Toledo Method M405 from Application Brochure 37 [14])

The total hardness of water, expressed as $CaCO_3$ content of water is determined by complexometric titration of calcium and magnesium at pH 10 using EDTA. The color change of the Erio T indicator (violet to blue) at the equivalence point is sensed by a DP5 Phototrode™

| | |
|---|---|
| **Sample** | Tap or surface water, 50 mL |
| **Substance** | Magnesium and calcium as $CaCO_3$, M = 100.09 g/mol, z = 1 |
| **Chemicals** | 10 mL 5% $NH_3$-solution<br>1 mL 0.1% Eriochrome Black T |
| **Titrant** | EDTA, c(EDTA) = 0.1 mol/L |
| **Standard** | $ZnSO_4$, c($ZnSO_4$)=0.1 mol/L, 5 mL |
| **Instruments** | Titration Excellence T50/T70/T90<br>2 additional dosing units |
| **Accessories** | 3 DV1010 glass burettes<br>Titration beaker ME-101974<br>Olivetti Printer JobJet 210 |
| **Indication** | DP5 Phototrode™, 660 nm |
| **Chemistry** | $Ca^{2+} + EDTA\text{-}H_2^{2-} = Ca\text{-}EDTA^{2-} + 2H^+$<br>$Mg^{2+} + EDTA\text{-}H_2^{2-} = Mg\text{-}EDTA^{2-} + 2H^+$ |
| **Calculation** | R1: Content (ppm)<br><br>R1 = Q*C/m,<br>C = M*1000/z |
| **Waste disposal** | Neutralization with hydrochloric acid before final disposal. |
| **Author** | Melanie Nijman |

**Preparation and Procedures**

1) The titer determination is first performed using 0.1 mol/L zinc sulfate ($ZnSO_4$) standard solution: 5 mL $ZnSO_4$ are added into a titration beaker and diluted with 50 mL deion. water.

2) 50 mL tap water are added into a beaker with a pipette.

3) 1 mL 0.1% Eriochrome Black T ethanolic solution is added to the sample beaker.

4) The pH of the sample solution is adjusted by adding 10 mL 5% $NH_3$-solution. Important: Add ammonia solution immediately before titration and after the ErioT indicator solution. Note: Instead of ammonia solution it is possible to use borate buffer pH10. Preparation: Dissolve 40 g sodium hydroxide (NaOH) in 500 mL water (Caution: solution gets hot!), add 65 g boric acid ($H_3BO_3$) and fill up to 1000 mL with deion. water.

4) This method allows a fully automated analysis procedure by using two additional burette drives. Nevertheless, the method can be modified for the manual addition of required reagents.

5) Before starting the subsequent sample, electrode and stirrer are cleaned and dried with a soft tissue.

**Remarks**

1) After turning on the phototrode, wait for 15-10 minutes before starting analysis to achieve a stable light intensity.

2) Subsequently, first check the transmission signal of the phototrode in deionised water and set it to 1000 mV by turning the knob on the top of it.

3) Avoid the formation of air bubbles during titration since they disturb the photometric indication. Thus, select the appropriate stirring speed.

4) The wavelength can be also set to 555 nm instead of 660 nm. In this case, the method parameter "Tendency" has to be set to "Positive".

5) The method parameters have been developed and optimised for the tap water samples used in this application. It may be necessary to slightly adapt the method to your specific sample.

6) The method can be easily modified for automated operation. Select the appropriate sample changer in the method function "Titration stand".

## Results

**All results**

| | | |
|---|---|---|
| Method-ID | M405 | |
| Sample | Tap water | (1/1) |
| R1 (Content) | 144.574 ppm | |
| Sample | Tap water | (1/2) |
| R1 (Content) | 144.462 ppm | |
| Sample | Tap water | (1/3) |
| R1 (Content) | 144.356 ppm | |
| Sample | Tap water | (1/4) |
| R1 (Content) | 144.216 ppm | |
| Sample | Tap water | (1/5) |
| R1 (Content) | 144.368 ppm | |
| Sample | Tap water | (1/6) |
| R1 (Content) | 144.550 ppm | |

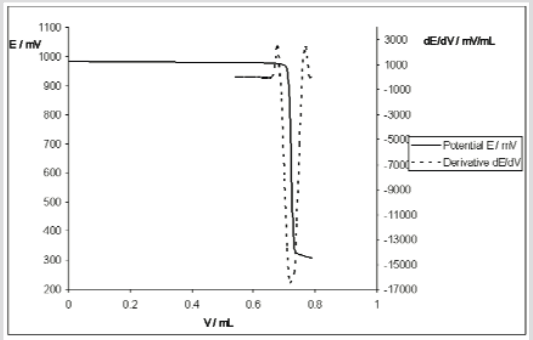
**Statistics**

| | | |
|---|---|---|
| Method-ID | M405 | |
| R1 | Content | |
| Samples | 6 | |
| Mean | 144.421 | ppm |
| s | 0.135 | ppm |
| srel | 0.093 | % |

## Table of measured values

| Consumption V / mL | Potential E / mV | Derivative dE/dV | Time / s |
|---|---|---|---|
| 0 | 982.8 | NaN | 0 |
| 0.5 | 977.5 | NaN | 3.9 |
| 0.51 | 979.2 | NaN | 12.2 |
| 0.52 | 978.5 | NaN | 15.3 |
| 0.53 | 979.4 | NaN | 18.3 |
| 0.54 | 979.3 | 7.79 | 21.3 |
| 0.55 | 979.1 | -19.15 | 24.4 |
| 0.56 | 979 | -19.83 | 27.4 |
| 0.57 | 978.7 | -28.22 | 30.5 |
| 0.58 | 978.2 | -19.32 | 33.5 |
| 0.59 | 978.4 | -13.4 | 36.6 |
| 0.6 | 978 | -17.18 | 39.6 |
| 0.61 | 978.1 | -14.72 | 42.7 |
| 0.62 | 977.8 | -30.46 | 45.7 |
| 0.63 | 977.5 | -42.16 | 48.7 |
| 0.64 | 976.7 | -47.26 | 51.8 |
| 0.65 | 976.7 | -50.9 | 54.8 |
| 0.66 | 975.2 | -27.34 | 57.9 |
| 0.67 | 975.2 | 732.92 | 60.9 |
| 0.68 | 973.9 | 2496.75 | 63.9 |
| 0.69 | 972.2 | -1736.72 | 67 |
| 0.7 | 968.7 | -8134.9 | 70 |
| 0.71 | 958.3 | -13710.18 | 73.8 |
| 0.72 | 810.2 | -16507.97 | 78 |
| 0.73 | 339.4 | -15699.94 | 96.5 |
| 0.74 | 324.1 | -11526.92 | 102.2 |
| 0.75 | 318.9 | -5341.16 | 105.2 |
| 0.76 | 315 | 439.68 | 108.3 |
| 0.77 | 312.3 | 2462.73 | 111.3 |
| 0.78 | 310.4 | NaN | 114.4 |
| 0.79 | 309 | NaN | 117.4 |
| 0.8 | 308.2 | NaN | 120.4 |
| 0.81 | 307.5 | NaN | 123.5 |
| 0.82 | 307 | NaN | 126.5 |

## Titration curve



## Method

**Method** M405 Total hardness of tap water 02.08.2006
**Author** METTLER TOLEDO

**001 Title**

| | |
|---|---|
| Type | General titration |
| Compatible with | T50 / T70 / T90 |
| ID | M405 |
| Title | Total hardness of tap water |
| Author | METTLER TOLEDO |
| Date/Time | 02.08.2006 |
| Modified | -- |
| Modified by | -- |
| Protect | No |
| SOP | None |

**002 Sample**

| | |
|---|---|
| Number of IDs | 1 |
| ID 1 | Water |
| Entry type | Fixed volume |
| Volume | 50.0 mL |
| Density | 1.0 g/mL |
| Correction factor | 1.0 |
| Temperature | 25.0°C |

**003 Titration stand (Manual stand)**

| | |
|---|---|
| Type | Manual stand |
| Titration stand | Manual stand 1 |

**004 Dispense**

| | |
|---|---|
| Titrant | ErioT |
| Concentration | 0.1 mol/L |
| Volume | 1.0 mL |
| Dosing rate | 60.0 mL/min |

**005 Stir**

| | |
|---|---|
| Speed | 35% |
| Duration | 6 s |

**006 Dispense**

| | |
|---|---|
| Titrant | 5% $NH_3$ |
| Concentration | 0.1 mol/L |
| Volume | 10.0 ml |
| Dosing rate | 60.0 mL/min |

**007 Stir**

| | |
|---|---|
| Speed | 35% |
| Duration | 6 s |

**008 Titration (EQP) [1]**

**Titrant**

| | |
|---|---|
| Titrant | EDTA |
| Concentration | 0.1 mol/L |

**Sensor**

| | |
|---|---|
| Type | Phototrode |
| Sensor | DP5 |
| Unit | mV |

**Temperature acquisition**

| | |
|---|---|
| Temperature acquisition | No |

**Stir**

| | |
|---|---|
| Speed | 35% |

**Predispense**

| | |
|---|---|
| Mode | Volume |
| Volume | 0.5 ml |
| Wait time | 5 s |

**Control**

| | |
|---|---|
| Control | User |
| Titrant addition | Incremental |
| dV | 0.01 mL |
| Meas. val. acquisition | Equilibrium controlled |
| dE | 2.0 mV |
| dt | 1.0 s |
| t(min) | 3.0 s |
| t(max) | 20.0 s |

**Evaluation and Recognition**

| | |
|---|---|
| Procedure | Standard |
| Threshold | 1000 mV/mL |
| Tendency | Negative |
| Ranges | 0 |
| Add. EQP criteria | No |

**Termination**

| | |
|---|---|
| At Vmax | 10.0 mL |
| At potential | No |
| At slope | No |
| After number of recognized EQPs | Yes |
| Number of EQPs | 1 |
| Combined termination | |

**009 Calculation R1**

| | |
|---|---|
| Result | Content |
| Result unit | ppm |
| Formula | R1=Q*C/m |
| Constant | C=M*1000/z |
| M | M[Calcium carbonate] |
| z | z[Calcium carbonate] |
| Decimal places | 3 |
| Result limits | No |
| Add. statistics functionalities | No |

**010 Record**

| | |
|---|---|
| Results | Per series |
| Raw results | Per series |
| Table of measured values | Last titration function |
| Sample data | Per series |
| Resource data | No |
| E - V | Last titration function |
| dE/dV - V | Last titration function |
| log dE/dV - V | No |
| d2E/dV2 - V | No |
| E - t | No |
| V - t | No |
| dV/dt - t | No |
| T - t | No |
| E - V & dE/dV - V | No |
| V - t & dV/dt - t | No |
| Calibration curve | No |
| Method | No |
| Series data | No |
| Condition | No |

**011 End of sample**

### 7.2 m-Value of Tap Water

(Mettler-Toledo Method M415 from Application Brochure 37 [14])

The m value of water is determined by an endpoint titration to pH 4.30 with hydrochloric acid.

| | |
|---|---|
| **Sample** | 100 mL tap water |
| **Substance** | -- |
| **Chemicals** | -- |
| **Titrant** | Hydrochloric acid, HCl<br>c(HCl) = 0.1 mol/L |
| **Standard** | Tris(hydroxymethyl)-aminomethane, 50-100 mg |
| **Instruments** | Titration Excellence T50/T70/T90<br>Rondolino Sample Changer |
| **Accessories** | 1 DV1010 burette<br>Titration beakers ME-101974<br>XS205 Balance<br>Olivetti JobJet 210 Printer |
| **Indication** | DG115-SC |
| **Chemistry** | $HCl + NaOH = NaCl + H_2O$<br>$HCl + CO_3^{2-} = HCO_3^- + Cl^-$<br>$HCl + HCO_3^- = CO_2 + H_2O + Cl^-$ |
| **Calculation** | Total alkalinity or methyl orange alkalinity (m-value) is expressed as mmol/L or mg/L $CaCO_3$ |
| **Waste disposal** | Neutralize the slightly acid waste before disposal. |
| **Author** | Madeleine Biber |

#### Preparation and Procedures

Note: This method allows a fully automated analysis procedure by using a Rondolinos sample changer. The method can be easily modified for manual operation. Select "Manual stand" in the method function "Titration stand".

1) Before the analysis, an electrode calibration was performed using METTLER TOLEDO buffers of pH 4.01, 7.00 and 9.21.

2) Fill a (preferably) PE bottle to the brim with the water to be analyzed. Keep it closed and at sampling temperature.

3) Pipette 100 mL into the beaker shortly before titration.

4) For best results, if the initial pH lies close to the end potential, use a lower concentration of the corresponding titrant.

5) The samples were analysed using a Rondolino sample changer. The electrode was rinsed during 2 s and conditioned during 10 s (Rondolino settings: 6). In this way, the electrode is cleaned with deionised water before starting the subsequent sample.

#### Remarks

1) The method parameters have been optimised for the sample used in this application. It may be necessary to slightly adapt the method to your specific sample.

2) The acid capacity allows surface waters to resist sudden pH changes due to e.g. organic acid waste, groundwater discharge or industrial waste, or due to sources such as bacteria, $Fe^{3+}$, hydrated $Al^{3+}$, $H_2S$, fatty acids, proteins, $CO_2$.

3) The acid capacity depends on the equilibrium of free $CO_2$, bicarbonate $HCO_3^-$, and carbonate $CO_3^{2-}$ in the corresponding water and on its temperature.
Mineral weathering buffers groundwaters, e.g. limestone rock
$CaCO_3$ (s) + $CO_2$ (g) = $Ca^{2+}$ (aq) + 2 $HCO_3^-$ (aq)
The bicarbonate ion then acts as a base to neutralize acids:
$HCO_3^-$ (aq) + $H^+$ (aq) = $CO_2$ (g) + $H_2O$ (l)

4) The m-value (total alkalinity) represents the acid neutralizing capacity and is determined in e.g. drinking water. Acidity can affect corrosion, soil leaching and aquatic life in general. The name originates from the methyl orange color indicator (red to yellow-orange at pH 4.3) formerly used.
References:
DIN 38409-H7

## Results

**All results**

| | | |
|---|---|---|
| Method-ID | M416 | |
| Sample | Tap water | (1/1) |
| R1 (Content) | 0.229 | mmol/L |
| Sample | Tap water | (1/2) |
| R1 (Content) | 0.220 | mmol/L |
| Sample | Tap water | (1/3) |
| R1 (Content) | 0.234 | mmol/L |
| Sample | Tap water | (1/4) |
| R1 (Content) | 0.217 | mmol/L |
| Sample | Tap water | (1/5) |
| R1 (Content) | 0.237 | mmol/L |
| Sample | Tap water | (1/6) |
| R1 (Content) | 0.214 | mmol/L |

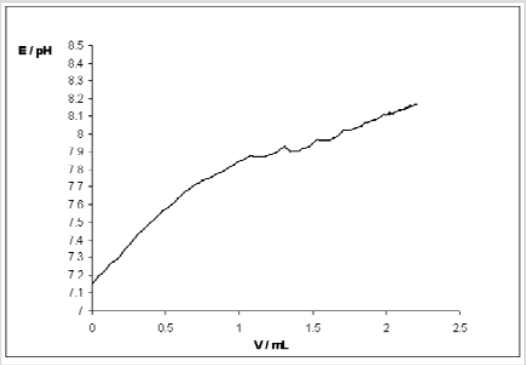
**Statistics**

| | | |
|---|---|---|
| Method-ID | M416 | |
| R1 | Content | |
| Samples | 6 | |
| Mean | 0.225 | mmol/L |
| s | 0.019 | mmol/L |
| srel | 4.190 | % |

## Table of measured values

| Consumption V / mL | Potential E / pH | Time / s |
|---|---|---|
| 0 | 7.092 | 0 |
| 0 | 7.15 | 1.3 |
| 0.01 | 7.16 | 2.3 |
| 0.025 | 7.172 | 3.3 |
| 0.045 | 7.194 | 4.3 |
| 0.07 | 7.214 | 5.3 |
| 0.101 | 7.24 | 6.3 |
| 0.136 | 7.27 | 7.2 |
| 0.174 | 7.296 | 8.2 |
| 0.216 | 7.339 | 9.3 |
| 0.26 | 7.383 | 10.3 |
| 0.306 | 7.424 | 11.3 |
| 0.354 | 7.463 | 12.3 |
| 0.404 | 7.501 | |
| 0.456 | 7.54 | |
| 0.508 | 7.58 | |
| 0.56 | | 92.2 |
| 0.61 | | 93.2 |
| 0.65 | | 94.2 |
| | .82 | 95.3 |
| | 8.163 | 96.3 |
| | 8.168 | 97.3 |
| | 8.173 | 98.3 |
| 2.216 | 8.171 | 99.3 |
| 2.221 | 8.177 | 100.3 |
| 2.222 | 8.174 | 101.2 |
| 2.227 | 8.17 | 102.2 |
| 2.228 | 8.175 | 103.3 |
| 2.23 | 8.173 | 104.3 |
| 2.24 | 8.172 | 105.3 |
| 2.246 | 8.176 | 106.3 |
| 2.247 | 8.179 | 107.3 |
| 2.25 | 8.175 | 108.3 |
| 2.252 | 8.178 | 109.2 |
| 2.255 | 8.179 | 110.2 |
| 2.264 | 8.186 | 111.2 |
| 2.27 | 8.18 | 112.3 |
| 2.272 | 8.186 | 113.3 |
| 2.276 | 8.187 | 114.3 |
| 2.281 | 8.198 | 115.3 |
| 2.281 | 8.198 | 116.3 |
| 2.29 | 8.197 | 117.2 |
| 2.295 | 8.2 | 117.6 |

## Titration curve



## Method

**Method** M416 p-Value of tap water (EP) 02.08.2006
**Author** METTLER TOLEDO

**001 Title**

| | |
|---|---|
| Type | General titration |
| Compatible with | T50 / T70 / T90 |
| ID | M416 |
| Title | p-Value of tap water (EP) |
| Author | METTLER TOLEDO |
| Date/Time | 02.08.2006 15:00:00 |
| Modified | -- |
| Modified by | -- |
| Protect | No |
| SOP | None |

**002 Sample**

| | |
|---|---|
| Number of IDs | 1 |
| ID 1 | Tap water |
| Entry type | Fixed volume |
| Volume | 100 mL |
| Density | 1.0 g/mL |
| Correction factor | 1.0 |
| Temperature | 25.0°C |

**003 Titration stand (Rondolino TTL)**

| | |
|---|---|
| Type | Rondolino TTL |
| Titration stand | Rondolino TTL 1 |

**004 Stir**

| | |
|---|---|
| Speed | 50 % |
| Duration | 15 s |

**005 Titration (EP) [1]**

**Titrant**

| | |
|---|---|
| Titrant | NaOH |
| Concentration | 0.01 mol/L |

**Sensor**

| | |
|---|---|
| Type | pH |
| Sensor | DG115 |
| Unit | pH |

**Temperature acquisition**

| | |
|---|---|
| Temperature acquisition | No |

**Stir**

| | |
|---|---|
| Speed | 50 % |

**Predispense**

| | |
|---|---|
| Mode | None |
| Wait time | 0 s |

**Control**

| | |
|---|---|
| Control | User |
| End point type | Absolute |
| Tendency | Positive |
| Endpoint value | 8.20 pH |
| Control band | 3.0 pH |
| Dosing rate (max) | 10 mL/min |
| Dosing rate (min) | 10 µL/min |

**Termination**

| | |
|---|---|
| At EP | Yes |
| Termination delay | 0 s |
| At Vmax | 10.0 mL |
| Max. time | Infinity |

**006 Calculation R1**

| | |
|---|---|
| Result | Content |
| Result unit | mmol/L |
| Formula | R1=Q*C/m |
| Constant | C=1000 |
| M | M[None] |
| z | z[None] |
| Decimal places | 3 |
| Result limits | No |
| Add. statistics functionalities | No |

**007 Record**

| | |
|---|---|
| Results | Per series |
| Raw results | Per series |
| Table of measured values | Last titration function |
| Sample data | Per series |
| Resource data | No |
| E - V | Last titration function |
| dE/dV - V | No |
| log dE/dV - V | No |
| d2E/dV2 - V | No |
| E - t | No |
| V - t | No |
| dV/dt - t | No |
| T - t | No |
| E - V & dE/dV - V | No |
| V - t & dV/dt - t | No |
| Calibration curve | No |
| Method | No |
| Series data | No |

**008 End of sample**

### 7.3 Acid Content in Wines and Fruit Juices

(Mettler-Toledo Method M561 from Application Brochure 19 [26])

**Sample:** Wines and juices, 10 mL

**Substances:** Malic acid
(M = 134.09 g/mol, z = 2)
Citric acid
(M = 192.13 g/mol, z = 3)
Tartaric acid
(M = 150.09 g/mol, z = 2)

**Preparation:** Deion. $H_2O$ (40 mL), boiled for 1 minute.
For substances: see remarks

**Titrant:** Sodium hydroxide
c(NaOH) = 0.1 mol/L

**Standard:** Potassium hydrogen phthalate

**Instruments:** METTLER TOLEDO DL55
Sample Changer ST20A
Printer HP Deskjet 500

**Method:** MT061

**Accessories:** Titration beaker ME-101974

**Indication:** DG111
DT1000

**Results:**

```
METTLER TOLEDO DL55   Titrator  V2.0     Mettler-Toledo GmbH
                      Jim 4              Market Support Laboratory

Method      MT061  acid content of beverages  28-May-1996  14:26
Measured    28-May-1996  17:38
User

ALL RESULTS

 No.  ID           Sample size and results
  1   apple juice       10.0      mL
                  R1 =  9.741     mL         titr. consum.
                  R2 =  6.391     g/L        acid content
  2   apple juice       10.0      mL
                  R1 =  9.729     mL         titr. consum.
                  R2 =  6.383     g/L        acid content
  3   apple juice       10.0      mL
                  R1 =  9.702     mL         titr. consum.
                  R2 =  6.366     g/L        acid content
  4   apple juice       10.0      mL
                  R1 =  9.713     mL         titr. consum.
                  R2 =  6.373     g/L        acid content
  5   apple juice       10.0      mL
                  R1 =  9.715     mL         titr. consum.
                  R2 =  6.374     g/L        acid content
  6   apple juice       10.0      mL
                  R1 =  9.743     mL         titr. consum.
                  R2 =  6.392     g/L        acid content

STATISTICS
  Number of results    R2       n = 6
  Mean value                    x̄ = 6.380    g/L    acid content
  Standard deviation            s = 0.01076  g/L    acid content
  Rel. standard deviation    srel = 0.169    %
```

## Method

```
Method    MT061     acid content of beverages
          Version   28-May-1996   14:26

Title
   Method ID  . . . . . . . . . . MT061
   Title  . . . . . . . . . . . . acid content of
                                  beverages
   Date/time  . . . . . . . . . . 28-May-1996  14:26
Sample
   Sample ID  . . . . . . . . . . apple juice
   Entry type . . . . . . . . . . Fixed volume
      Volume [mL] . . . . . . . . 10.0
   Molar mass M . . . . . . . . . 134.09
   Equivalent number z  . . . . . 2
   Titration stand  . . . . . . . ST20A
      Pump  . . . . . . . . . . . No
      Pump  . . . . . . . . . . . No
      Rinse . . . . . . . . . . . Yes
         Solvent  . . . . . . . . H2O
         Volume [mL]  . . . . . . 10.0
      Conditioning  . . . . . . . No
   Temperature sensor . . . . . . TEMP A
Stir
   Speed [%]  . . . . . . . . . . 50
   Time [s] . . . . . . . . . . . 60
EP titration
   Titrant/Sensor
      Titrant . . . . . . . . . . NaOH
      Concentration [mol/L] . . . 0.1
      Sensor  . . . . . . . . . . DG111
      Unit of meas. . . . . . . . pH
   Predispensing  . . . . . . . . to volume
      Volume [mL] . . . . . . . . 3
      wait time [s] . . . . . . . 0
   Titrant addition . . . . . . . Dynamic
      dE(set) [mV]  . . . . . . . 8.0
      dV(min) [mL]  . . . . . . . 0.02
      dV(max) [mL]  . . . . . . . 0.2
      dE [mV] . . . . . . . . . . 0.5
      dt [s]  . . . . . . . . . . 1.0
      t(min) [s]  . . . . . . . . 2.0
      t(max) [s]  . . . . . . . . 20.0
   End point  . . . . . . . . . . EP absolute
      Potential [mV,pH,..]  . . . 8.1
   Tendency
      Tendency  . . . . . . . . . Positive
   Termination
      Maximum volume [mL] . . . . 20.0
      Delay [s] . . . . . . . . . 0
Calculation
   Formula  . . . . . . . . . . . R1=VEQ
   Constant . . . . . . . . . . . C1=1
   Decimal places . . . . . . . . 3
   Result unit  . . . . . . . . . mL
   Result name  . . . . . . . . . titr. consum.
   Statistics . . . . . . . . . . No
Calculation
   Formula  . . . . . . . . . . . R2=Q*C2/m
   Constant . . . . . . . . . . . C2=M/z
   Decimal places . . . . . . . . 3
   Result unit  . . . . . . . . . g/L
   Result name  . . . . . . . . . acid content
   Statistics . . . . . . . . . . Yes
Calculation
   Formula  . . . . . . . . . . .
   Constant . . . . . . . . . . .
   Decimal places . . . . . . . . 0
   Result unit  . . . . . . . . .
   Result name  . . . . . . . . .
   Statistics . . . . . . . . . . No
Report
   Output unit  . . . . . . . . . Printer
   Results  . . . . . . . . . . . No
   All results  . . . . . . . . . Yes
   Raw results  . . . . . . . . . No
   Table of measured values . . . No
   Sample data  . . . . . . . . . No
   E - V curve  . . . . . . . . . No
   dE/dV - V curve  . . . . . . . No
   d2E/dV2 - V curve  . . . . . . No
   log dE/dV - V curve  . . . . . No
   E - t curve  . . . . . . . . . No
   V - t curve  . . . . . . . . . No
   dV/dt - t curve  . . . . . . . No
```

## Remarks

### Method

For the acid content determination the standard method EP TITRATION was used.
While the wine samples were titrated to the endpoint of pH 7.0, the endpoint for the juices was pH 8.1. These values are chosen for historical reasons (colour change potential of indicators).

### Calculation

To express the acid content in g/L in these beverages the predominantly present acids were chosen, such as:

- in red and white wine: *tartaric acid*
- in orange juice: *citric acid*
- in apple juice: *malic acid*

### Preparation

The samples were degassed in an ultrasonic bath for five minutes, to get rid of $CO_2$. This was sufficient for all samples except for apple juice, which had to be boiled for complete degassing. 10 mL sample was diluted with 40 mL deionised, boiled $H_2O$. Temperature was measured before the titration and the endpoint values were automatically corrected accordingly.

### Automation

A sample changer ST20A was used in this method for a fully automatic procedure. The method can easily be modified for manual operation. Enter STAND 1 as titration stand in the function SAMPLE.

### Observation

Precision of the white wine analysis was lower than for the other samples. Most likely the reason for that lies in the insufficient degassing. Attempts to degas the samples by boiling failed due to partial oxidation of some components.

### Table

| sample | n | mean [g/L] | RSD [%] | reference [*1] [g/L] |
|---|---|---|---|---|
| red wine | 6 | 5.277 | 0.238 | 4.2 - 6.5 |
| white wine | 6 | 4.350 | 1.032 | 4.2 - 6.5 |
| apple juice | 6 | 6.380 | 0.169 | 5.0 - 9.0 |
| orange juice | 6 | 6.965 | 0.135 | 8.0 - 12.0 |

[*1] Swiss Food Manual [5]

Authors: A. Aichert, N. Spiru

Remark: Since the establishment of this application, instruments and accessories have been renewed and replaced. The current models are:

| | |
|---|---|
| Titrator | Titration Excellence T50 |
| Sample changer | In Motion Flex |
| Electrode | DGi111-SC |

### 7.4 Free Sulfur Dioxide Content Determination in Wine

(Mettler-Toledo Method M419 from Application Brochure 31 [15])

The content of free sulphur dioxide ($SO_2$) in wine is determined by redox titration with iodine as a titrant. The titration is monitored using a Pt double pin electrode DM143 at a fixed polarization current (voltametric indication).

| | |
|---|---|
| **Sample** | 50 mL white wine |
| **Compound** | Sulphur dioxide, $SO_2$<br>M = 64.06 g/mol, z = 2 |
| **Chemicals** | 5 mL 10% potassium iodide, KI<br>5 mL 20% sulfuric acid, $H_2SO_4$ |
| **Titrant** | Iodine, $I_2$<br>c(1/2 $I_2$) = 0.02 mol/L |
| **Standard** | Ascorbic acid, $C_6H_8O_6$,<br>M=176.13 g/mol |
| **Indication** | DM143-SC |
| **Chemistry** | $SO_2 + I_2 + 2\ H_2O \rightarrow H_2SO_4 + 2\ HI$ |
| **Calculation** | R1: Content (mg/L)<br>R1=Q*C/m, C=M*1000/z |
| **Waste disposal** | Neutralize the acid waste before final disposal. |
| **Author, Version** | Claudia Schreiner, July 2006<br>Market Support Group Anachem |

#### Preparation and Procedures

Note:

This method allows a fully automated analysis procedure by using two additional burette drives.

1) The titer determination is performed using pure ascorbic acid as a primary standard.
2) Sample determination:
   50 mL wine is transferred into a titration beaker with a pipette.
3) 5 mL 10% potassium iodide solution are added. This step has been performed using an additional dosing unit. It can be performed manually using a pipette.
4) 5 mL 20% sulfuric acid is added to the titration beaker. This step has been performed using an additional dosing unit. If this is not possible, this step can be done manually with a pipette.

Note:

Sodium metabisulfite ($Na_2S_2O_5$, M = 222.32 g/mol) can be used as a $SO_2$-standard:
1 $Na_2S_2O_5 \rightarrow 2\ SO_2$

#### Remarks

1) The method parameters have been optimized for the above mentioned sample. It may be necessary to slightly adapt the method to your specific sample.
2) In order to avoid loss of $SO_2$, the samples must be taken from a freshly opened bottle. After opening the bottle, free $SO_2$ can evaporate with $CO_2$ or be oxidized while in contact with air resulting in too low results.
3) Working with the sample changer leads to $SO_2$ losses from the sample beakers already prepared on the rack. Therefore it is recommended to work without a sample changer to achieve a higher accuracy.

| | |
|---|---|
| **Instruments** | - T50/T70/T90 Titration Excellence<br>- 2 additional dosing units<br>- G20 Compact Titrator ( max. 1 dosing unit; with major changes in titration method)<br>- XS205 Balance |
| **Accessories** | - 3 x 10 mL DV1010 burettes<br>- Titration beaker ME-101974<br>- Olivetti Printer JobJet 210 |

## Results

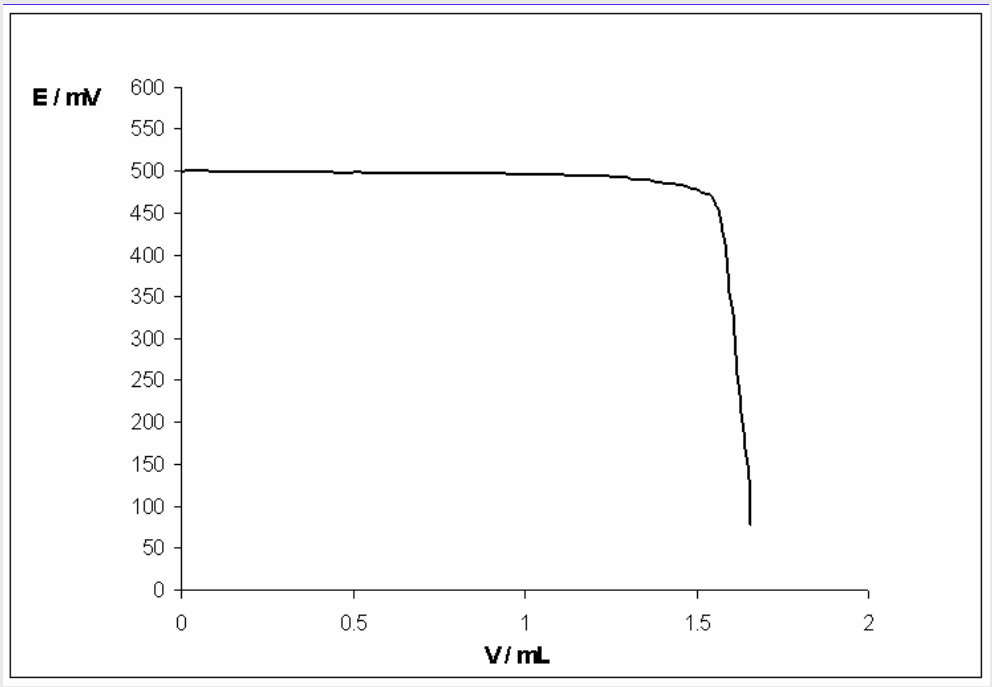
**All results**

| | | |
|---|---|---|
| Method-ID | M419 | |
| Sample | White wine | (1/1) |
| R1 (Content) | 21.222 mg/L | |
| Sample | White wine | (1/2) |
| R1 (Content) | 21.294 mg/L | |
| Sample | White wine | (1/3) |
| R1 (Content) | 21.160 mg/L | |
| Sample | White wine | (1/4) |
| R1 (Content) | 21.114 mg/L | |
| Sample | White wine | (1/5) |
| R1 (Content) | 21.190 mg/L | |
| Sample | White wine | (1/6) |
| R1 (Content) | 21.127 mg/L | |

**Statistics**

| | |
|---|---|
| Method-ID | M419 |
| R1 | Content |
| Samples | 6 |
| Mean | 21.185 mg/L |
| s | 0.067 mg/L |
| srel | 0.315 % |

## Titration curve



## Table of measured values

| Consumption V / mL | Potential E / mV | Time / s |
|---|---|---|
| 0 | 497.9 | 0 |
| 0 | 499.5 | 10.2 |
| 0 | 499.5 | 11.3 |
| 0 | 499.5 | 12.3 |
| 0 | 499.4 | 13.3 |
| 0.002 | 499.8 | 14.3 |
| 0.006 | 499.6 | 15.3 |
| 0.011 | 499.8 | 16.2 |
| 0.02 | 499.9 | 17.2 |
| 0.033 | 499.8 | 18.3 |
| 0.052 | 500 | 19.3 |
| 0.074 | 499.8 | 20.3 |
| 0.095 | 499.5 | 21.3 |
| 0.116 | 499.5 | [illegible] |
| 0.137 | 499.5 | [illegible] |
| 0.158 | 499.2 | [illegible] |
| 0.179 | 499.4 | [illegible] |
| 0.2 | [illegible] | [illegible] |
| 0.221 | [illegible] | 76.3 |
| 0.242 | [illegible] | 77.3 |
| 0.263 | [illegible] | 78.3 |
| 0.284 | 490.4 | 79.3 |
| 0.3[illegible] | 489.5 | 80.2 |
| [illegible] | 489.1 | 81.2 |
| 1.378 | 488.7 | 82.3 |
| 1.399 | 487.2 | 83.3 |
| 1.42 | 485.3 | 84.3 |
| 1.441 | 484.4 | 85.3 |
| 1.462 | 482.4 | 86.3 |
| 1.483 | 479.2 | 87.3 |
| 1.504 | 477.1 | 88.3 |
| 1.525 | 473.7 | 89.2 |
| 1.546 | 466.2 | 90.2 |
| 1.567 | 447.7 | 91.3 |
| 1.588 | 398.3 | 92.3 |
| 1.61 | 306.2 | 93.3 |
| 1.63 | 211.7 | 94.3 |
| 1.652 | 132.4 | 95.3 |
| 1.658 | 88 | 96.3 |
| 1.658 | 78.8 | 97.2 |
| 1.658 | 79 | 98.2 |
| 1.658 | 80.7 | 99.2 |
| 1.658 | 80.9 | 100.2 |
| 1.658 | 82.3 | 100.8 |

## Comments

- Iodine is also reduced by other wine components. These competing reactions can partly be delayed by the addition of 5 mL 10% potassium iodide solution.
- The reaction only takes place in acidic medium. Therefore, 5 mL 20% $H_2SO_4$ must be added immediately before titration.
- If the sample contains ascorbic acid the amount of $SO_2$ will be higher, because of the reaction from ascorbic acid with iodine.

## Method

**001 Title**

| | |
|---|---|
| Type | General titration |
| Compatible with | T50 / T70 / T90 |
| ID | M419 |
| Title | Free $SO_2$ content in wine |
| Author | METTLER TOLEDO |
| Date/Time | 02.08.2006 15:00:00 |
| Modified at | -- |
| Modified by | -- |
| Protect | No |
| SOP | None |

**002 Sample**

| | |
|---|---|
| Number of IDs | 1 |
| ID 1 | White wine |
| Entry type | Fixed volume |
| Volume | 50.0 mL |
| Density | 1.0 g/mL |
| Correction factor | 1.0 |
| Temperature | 25.0°C |

**003 Titration stand (Manual stand)**

| | |
|---|---|
| Type | Manual stand |
| Titration stand | Manual stand 1 |

**004 Dispense (normal) [1]**

| | |
|---|---|
| Titrant | 10% KI |
| Concentration | 1 mol/L |
| Volume | 5.0 mL |
| Dosing rate | 60.0 mL/min |

**005 Dispense (normal) [2]**

| | |
|---|---|
| Titrant | 20% $H_2SO_4$ |
| Concentration | 1 mol/L |
| Volume | 5.0 mL |
| Dosing rate | 60.0 mL/min |

**006 Stir**

| | |
|---|---|
| Speed | 50% |
| Duration | 10 s |
| Condition | No |

**007 Titration (EP) [1]**

**Titrant**

| | |
|---|---|
| Titrant | ½ $I_2$ |
| Concentration | 0.02 mol/L |

**Sensor**

| | |
|---|---|
| Type | Polarized |
| Sensor | DM143 |
| Unit | mV |
| Indication | Voltametric |
| Ipol | 10 µA |

**Temperature acquisition**

| | |
|---|---|
| Temperature acquisition | No |

**Stir**

| | |
|---|---|
| Speed | 50% |

**Predispense**

| | |
|---|---|
| Mode | None |
| Wait time | 10 s |

**Control**

| | |
|---|---|
| Control | User |
| End point type | Absolute |
| Tendency | Negative |
| Endpoint value | 100 mV |
| Control band | 30 mV |
| Dosing rate (max) | 1.25 mL/min |
| Dosing rate (min) | 100 µL/min |

**Termination**

| | |
|---|---|
| At EP | Yes |
| Termination delay | 5 s |
| At Vmax | 10.0 mL |
| Max. time | 600 s |

**008 Calculation R1**

| | |
|---|---|
| Result | Content |
| Result unit | mg/L |
| Formula | R1=Q*C/m |
| Constant | C=M*1000/z |
| M | M[Sulfur dioxide] |
| z | z[Sulfur dioxide] |
| Decimal places | 3 |
| Result limits | No |
| Record statistics | Yes |
| Extra statistical func. | No |
| Send to buffer | No |
| Condition | No |

**009 Record**

| | |
|---|---|
| Results | Per series |
| Raw results | Per series |
| Table of meas. values | Last titration function |
| Sample data | Per series |
| Resource data | No |
| E - V | Last titration function |
| dE/dV - V | Last titration function |
| log dE/dV - V | No |
| $d^2E/dV^2$ - V | No |
| E - t | No |
| V - t | No |
| dV/dt - t | No |
| T - t | No |
| E - V & dE/dV - V | No |
| V - t & dV/dt - t | No |
| Calibration curve | No |
| Method | No |
| Series data | No |
| Condition | No |

**010 End of sample**

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G20 Compact Titrator Method:

The G20 method includes slightly modifications:

...

**008 Calculation R1**

| | |
|---|---|
| Result type | Predefined |
| Calculation type | Direct titration |
| Formula | R1=Q*C/m |
| Result | Content |
| Result unit | mg/L |
| Constant C | M*1000/z |
| M | M[Sulfur dioxide] |
| z | z[Sulfur dioxide] |
| Decimal places | 3 |
| Result limits | No |
| Record statistics | Yes |

....

# 8. Information

## 8.1 Literature


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## 8.3 Applications and UserComs

We offer comprehensive application support for titration and many other analytical methods.

| | |
|---|---|
| Titration applications | www.mt.com/titration_applications |
| Titration UserCom | www.mt.com/anachem-usercom |
| Density data | www.density.com |
| Refractive index data | www.refractometry.com |

# Good Measuring Practices

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