

Analytical Chemistry

Titration, pH Systems, Density- & Refractometers

User Com

The art of senses: The motto of the Argeville company



Y. Tattevin

Argeville is a company rich in tradition that produces fragrances and aromas near Grasse in the heart of the French perfume region. To cope with the ever-increasing number of samples arriving in the quality control department, the company recently put an LiQC Multi-Parameter System into operation for the simultaneous determination of specific gravity, refractive index and color. The system has greatly simplified the measurement of samples and allowed the export of data to the AS/400 server to be automated.



For rather obvious reasons when it was founded in 1932, Argeville chose the Argeville estate (le Domaine d'Argeville) in the heart of the French perfume region near Grasse as its production site.

Initially, the company began to develop the small-scale production of high quality natural floral extracts in the traditional way from flowers and aromatic plants such as jasmine and roses. These were cultivated on the estate or on land rented in the surrounding neighborhood. In 1981, Jean-Jaques Ardizio reorganized the company to give it an industrial and international dimension. It soon became

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METTLER TOLEDO

clear that the traditional regional production capacity was no longer sufficient to meet needs and contacts were established with leading producers of flowers in India, China, Egypt, Madagascar, and elsewhere. In 1996, the Laboratoire Européen d'Extraction (CEVESO site) was founded. This subsidiary specializes in the production of extracts and essential oils from plants. It is situated in the heart of Drôme Provençal, a region that has long been famous for production of lavender and aromatic plants. The traditional site at Mougins produces essences from the plant extracts.

The quality of Argeville's products is based on traditional know-how and the rigorous selection of high quality natural raw materials that have always been cultivated on the company's estate. The development of new raw materials, the creation of fragrances for the perfumery and the cosmetic industries, and the formulation of aromas for the food industry are based on the same awareness for quality to which Argeville has always remained faithful.

The activities in research, development and quality control are rooted in a profound knowledge of the different markets

and customer needs. They are supported by modern development laboratories and computer-aided systems for the creation, formulation and production of compositions.

Quality

The quality control laboratories ensure that Argeville products are of consistently high quality. The different production steps, from the procurement of raw material through to the final packaged products are monitored by an effective control system. This includes a very thorough olfactory test, gas chromatographic analysis and different physical-chemical analyses. The analytical data from these analyses can be used to create electronic data sheets for every raw material on an AS400 system. This guarantees the complete traceability of data regarding the use and storage of raw materials and the quality of the resulting production mixtures.

Specific gravity, refractive index, and color determination are some of the most important but at the same time most laborious chemical-physical analyses. They were performed for many years using the following equipment:

- Specific gravity: DMA 35 density meter, not automated
- Refractive index: RE40 refractometer
- Color: Minolta CM-3500d spectrophotometer

The analyses were very time-consuming and required large samples. During the analysis, samples inevitably became contaminated and could not be used for other purposes. Furthermore, the manual transfer of results to the AS400 System was prone to errors. This situation made it almost impossible to react adequately to the constant increase in the number of analysis samples and the growing demands of customers.

At the end of 2008, the company decided to resolve the situation and invest in new equipment. Bernard Soulier was



Figure 1:
Administration
offices on the
Argeville estate.

Figure 2:
150 new samples
arrive daily.



appointed to manage a project carried out in collaboration with the information technology department. As a result, an automatic METTLER TOLEDO measurement system was installed toward the end of January 2009. The system consists of a DR40 combined meter, an SC30 autosampler equipped with an external air pump (PPU) and a LOVIBOND PFX880 colorimeter (Fig. 3). It is controlled by an LiQC Multi-Device software and the measurement data are automatically transferred to the AS/400 server.

The system was installed stepwise to allow Bernhard Soulier and his team to become fully familiar with all its different possibilities.

The measurement system operates from six o'clock in the morning until 9 o'clock in the evening. During the day, it analyses about 150 samples. The sample turntable is nearly always full with 25 samples. The system can just about cope with the number of incoming samples because a measurement now takes less than 5 minutes. To reduce measurement time to a minimum, automatic cleaning after each measurement is performed in a single rinsing cycle using ethanol and the measurement cell is quickly dried by an external air pump (PPU).

One of the most difficult parts of the installation was to set up the color measurement because the parameters of the Minolta CM-3500d spectrophotometer had to be converted to those used by the Lovibond Colorimeter. Measurements on the Minolta instrument are performed in transmission using a quartz cell with a path length of 1 cm; the cell is fragile and manual filling and cleaning is time-consuming. The light source is D65 6500°K (daylight) and the observer 10° CIE (1964). The measurement parameters of the Lovibond colorimeter were matched to those of the Minolta spectro-



Figure 3: After measurement, the measured samples are returned to the bottles and can be used for the aroma library.

photometer through a PFX995 upgrade. The same results are now obtained for measurements in the Lab color space (L: dark – transparent, a: green – red, b: blue – yellow) on both instruments.

All the results are recorded and automatically transmitted to the AS400 server. The AS/400 generates a report every two hours that clearly documents any deviations of the results from the permissible tolerances.

Bernhard Soulier quickly realized the advantages of the automatic measurement system. The main criterion for his decision to purchase the system was the fully automatic exchange of data between the LiQC software and the AS400-server.

Analyses have now become so easy that they no longer have to be performed by laboratory technicians but can be done directly by people in the production department. They only have to place the bottles with barcode labels attached on the autosampler and then start the measurements on the PC (Fig. 4). The automatic sample recovery system is also very advantageous because the intact, uncontaminated samples can be used for the aroma library after the measurements. Whereas before, 12 mL of sample was needed for a simple color measure-



Figure 4: Bernhard Soulier operating the METTLER TOLEDO LiQC multi-parameter measurement system.

ment with the Minolta spectrophotometer, all three analyses (specific gravity, refractive index and color) can now be measured in one run and afterward the sample is available for the sample library. Furthermore, the time-consuming manual cleaning of the spectrophotometer cell is no longer necessary.

The LiQC software has eliminated the possibility of errors due to the transfer of measured values. A keyboard lock as well as limited access rights prevents errors in the acquisition and interpretation of results. The measurement system is now installed in the production and packing area, far away from the quality control laboratory. This has resulted in a tremendous increase in efficiency and time; the system sets new standards for physical-chemical measurements.

Quick and easy analysis of results – by comparing titration curves



V. Tai

BASF Electronic Materials Taiwan Limited offers reliable chemical solutions for the electronics industry. The integrated production strategy, unique chemical expertise and extensive global presence form the basis of a strong and comprehensive product portfolio. How does the quality control department adapt methods and compare the titration results of difficult samples?

BASF supports its customers with a broad range of products and services. Its specialized knowledge, chemical expertise and leading position in production and analysis allows BASF to offer its customers chemicals or customized solutions and to co-develop products together with customers based on their specifications. Modern, state-of-the-art facilities for ultra-pure chemicals and precise chemical process control and management enables BASF to provide products and services of high quality and reliability.

The quality control laboratory processes a large number of samples and performs a wide variety of analyses. Some of the routine tests include acid/base titrations and titrations in non-aqueous media. One analysis is particularly interesting, namely the determination of hydrofluor-

ic acid (HF) concentration. This is one of the most important criteria in determining product quality. Here, very strict tolerance limits apply and limiting values must on no account be exceeded.

The laboratory was equipped with a METTLER TOLEDO Excellence titrator. There was however a need for automation to increase workload and to satisfy new requirements. BASF purchased a T70 Excellence titrator with four burettes, a Rondo 20 Sample Changer with CoverUp™ lid handling unit (Figs. 1 and 2), an SP250 peristaltic pump, and LabX titration software for data management.

The most important challenges

A major analytical problem is the wide variety of samples that have to be analyzed. Strict tolerance limits apply to

each sample. The results must be precise and the relative standard deviation very small. If the product does not satisfy the requirements, it fails the quality control check and is not released.

The system is used by five to ten members of staff whose qualifications range from engineer to laboratory technician. The laboratory is normally very busy. Each operator has to perform and complete a whole series of analytical tasks. The One Click analysis start via Shortcuts on the Touchscreen and the user-specific Homescreen saves time and improves security. It would, however, be very tedious and time-consuming to prepare reports manually. The data generated in the analyses must be processed as quickly as possible and methods are needed to analyze the results quickly and reliably.

Figure 1:
The Titration
Excellence T70
with Rondo 20
sample changer
and CoverUp™ lid
handling unit.



Since samples are very different, it is important to determine the most favorable conditions for each analysis. In both method development and in routine analysis, a large number of experimental results have to be compared in order to decide which are better. This can be easily done by overlaying curves using the LabX titration PC software.

LabX titration PC software – the perfect partner

It has never been easier to run a titration, store the data, and automatically generate a report after each analysis than with the METTLER TOLEDO LabX software. The operator can perform the analysis on the titrator and view the titration curve

in real time on the computer screen. This immediately shows whether the titration is running as expected (Fig. 3).

Once the results are obtained from the sample batch, the titration curves can be displayed in a single chart using the Overlay Curves function.

How do you do this? It's very easy:

1. In the Reports tree view, double-click a curve symbol. The titration curve appears in the working window.
2. Select View > Curve > Overlay Curves... on the menu bar.
3. From the tree view, select a curve to overlay on the main curve. Click the OK button to confirm the selection. Repeat the process for additional curves or press and hold the CTRL key when marking additional curves.

The curves are displayed in different colors (Fig. 4). To obtain information on the overlaid curves, just go to View > Curve > Overlay Curves... on the menu bar. Due to the flexibility of the software, there is virtually no limit to the number of curves that be overlaid.

Conclusions

The powerful combination of the T70 Excellence titrator with the Rondo 20 sample changer and the LabX titration PC software is a perfect solution for any titration analysis. It not only handles many samples per batch, but also makes it possible to analyze the results systematically and professionally.

Overlaying curves with LabX saves time because HF concentrations can be quickly analyzed with just a few mouse clicks. The optimum titration conditions are easily found by comparing curves. Method development is quick and easy. Furthermore, in routine analysis, it is always clear whether the titrations are reproducible or whether anything is influencing the titration curve.

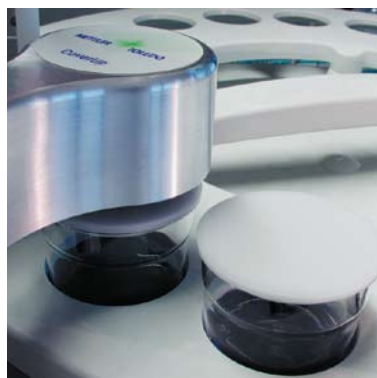


Figure 2: CoverUp™ allows the sample beaker to be automatically opened immediately before the titration.

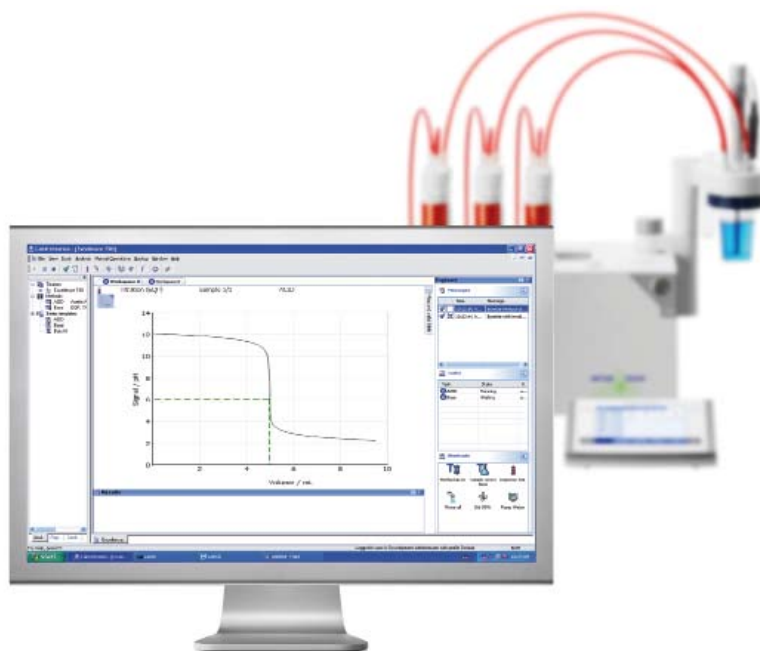


Figure 3: The LabX screen is easily adapted to the individual requirements of the user.

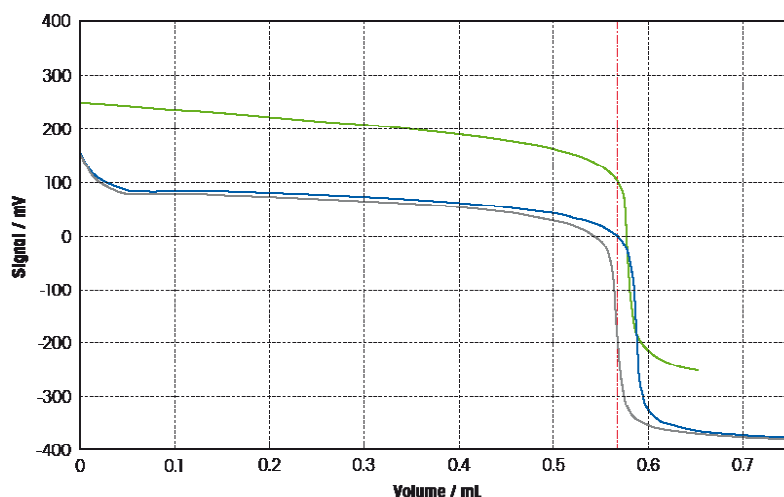


Figure 4: Titration curves overlaid using LabX. Sample: HF (hydrofluoric acid) solution under different reaction conditions. Titrant: 0.1 N NaOH (sodium hydroxide), sensor: DGi111-SC.

Versatile pH Meter – used in the cleanest room in the world!



K. Sägesser

A METTLER TOLEDO SevenMulti™ pH Meter has recently been installed at the Fraunhofer Institute for Manufacturing Engineering and Automation (IPA) in Stuttgart. The Fraunhofer IPA has the cleanest room in the world and the SevenMulti™ is used in it. A pH meter is of course seldom subjected to such extreme environmental conditions. But the SevenMulti™ easily mastered all the applications.



The Fraunhofer-Gesellschaft is one of the leading organizations for applied research in Europe. It undertakes application-oriented research of direct utility to private and public enterprise and of wide benefit to society but does not participate in basic research. The customers are industrial or service companies and the German federal and local government. The 57 Fraunhofer Institutes employ more than 15,000 staff at 40 different locations in Germany. The annual

research budget totals 1.4 billion Euros. There is very intense international cooperation through the research centers and representative offices in other European countries, the USA, Asia and in the Near East.

Fraunhofer Institute for Manufacturing Engineering and Automation IPA

The institute focuses on areas such as corporate logistics, automation and robotics as well as surface technology. Materials and equipment tested by the Fraunhofer IPA are awarded the “Fraunhofer IPA TESTED DEVICE” certificate. This certifies the clean room capability for the different classes of equipment. This can for example include robots, cables, chairs, linear axes and many other things.

Different physical and microbiological tests are performed in order to be able to provide exact information about each tested object or material and award the certificate. Our contact at the Fraunhofer IPA is Markus Keller of the Ultraclean Technology and Micro-Manufacturing Department.

Ultraclean and micro-manufacturing

The Ultraclean Technology and Micro-Manufacturing Department deals with technical questions concerning miniaturized production processes where contamination is a critical issue. These are encountered in branches such as the semiconductor industry, the automotive

field and the Life Sciences. The show-piece in this department is the “cleanest” cleanroom in the world: it is ten times cleaner than ISO Cleanroom Standard Class 1, which is officially the cleanest class. This “super cleanroom” operates at overpressure and with a laminar air flow of 0.45 m/s. The climatic conditions are 22 °C and 45% air/ relative humidity.

Markus Keller explains: “The SevenMulti™ S47 is used at the Fraunhofer IPA for different investigations at different places.” The most important tests are:

• Cleanability of surfaces

All surfaces used in hygienic production environments must according to the European Hygienic Engineering & Design Group (EHEDG) be especially easy to clean and disinfect. Polished stainless steel surfaces are considered ideal. More and more different materials and surfaces are being used whose easy cleanability has to be confirmed. To measure the effectiveness of the cleaning process, the microbiological bacteria count of the surfaces is measured before and after the cleaning using surface contact method (Figures 1 and 2). This is performed by pressing a Petri dish coated with nutrient agar against the surface with a defined force for 5 seconds.

In this test method, the SevenMulti™ and the InLab® Routine Pro pH electrode are used to prepare and set the exact pH of the nutrient agar.

Figure 1:
After successful cleaning, micro-organisms do not grow.

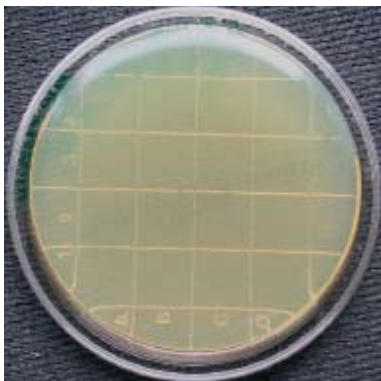


Figure 2:
If cleaning is not completely effective, numerous colonies grow on the nutrient agar after incubation.



- **Metabolization of materials**

Under certain climatic and environmental conditions, microorganisms can colonize and propagate on the surfaces of plastics. Their presence cannot only damage the plastic but also influence the proper functioning of the components that contain the plastics. To assess the action of microorganisms on materials, the Fraunhofer IPA uses the European EN ISO 846 test standard. The microbiological action on the plastic samples is investigated in a carbon-free nutrient medium. If no growth occurs in the culture medium, then the sample does not contain any nutrients for growth and metabolism can be excluded. The SevenMulti™ S47 two-channel instrument is used to set the pH of the mineral salt stock solution using a sterile 0.01 mol/L NaOH solution.

Other investigations in which the SevenMulti™ is used are listed below without going into any detail:

- Checking the acidification of rinsing solutions in tests for extractable metals.
- Checking the pH of solvents when washing out pH-unstable organic particles, e.g. precursors of pharmaceuticals, so that these are not dissolved, or to stabilize them.
- Monitoring purified water using the new InLab® 741 and the SevenMulti™ conductivity expansion unit.
- Adjusting buffer solutions, e.g. the potassium phosphate buffer.



Figure 3: Markus Keller adjusts the pH of a potassium phosphate buffer using the SevenMulti™ S47. To reduce contamination, protective clothing and facemasks must be worn in the cleanest room in the world.

The last two applications are usually performed in the cleanroom (Fig. 3). In this case, the SevenMulti™ has to be thoroughly cleaned. This includes cleaning with isopropanol and drying in a flow of pure air.

Markus Keller is happy about things: “Thanks to the dual-channel functionality of the SevenMulti™ S47, we can perform all the pH and conductivity measurements efficiently and very precisely with just one instrument.”

Simple and precise conductivity control measurements at MIELE Professional



A. Stütz

The MIELE company uses the capabilities of the InLab®741 conductivity sensor and the SevenMulti™ S70 as an ideal pair for the measurement of pure water. The instrument system has proven successful for control measurements of the built-in online conductivity sensors of large-capacity disinfectors.



MIELE was founded in 1899. Since then, the family company has established a reputation as a manufacturer of household equipment and professional cleaning equipment built for quality, long service lifetime and economic use of resources. Great importance is attached to regular and stringent quality control of the equipment. In the field of conductivity measurement of pure water, the METTLER TOLEDO SevenMulti™ S70 conductivity meter and the InLab®741 conductivity sensor have proven to be a reliable part-

ner. During a visit in Bielefeld, Germany, Mr. Balzer and Mr. Schartner showed us how the measurement system is used for quality control at MIELE and answered our questions in detail.

MIELE large-capacity disinfector – big brother of the dishwasher

Within the MIELE-Professional product line, the MIELE company manufactures large-capacity automatic disinfectors for professional cleaning and disinfection applications. In response to our enquiring looks, Mr. Balzer explained that a large-capacity disinfector is nothing other than a very large washing machine that not only cleans but also disinfects. The machines are mainly used in hospitals and clinics.

The risk of infection is particularly high in operating theaters; every piece of equipment and utensils must be absolutely sterile. Contaminated material is transported out of such sterile areas, but of course has to be replaced. This is done with the aid of a large-capacity disinfector which is built into the wall and functions as an air-lock between the outside environment and the sterile room (Fig. 1).

Thermal disinfection with pure water – online conductivity measurement as a purity indicator

A cleaning process can occur in several steps. Thermal disinfection is performed according to the German MPG law (Medizinproduktegesetz), which is the

German version of the EU Guidelines for Medical Devices. According to this, the medical material for use in a sterile room is rinsed with deionized water for at least ten minutes at a temperature of at least 90 °C. This kills 98–99% of all germs. The MIELE disinfectors operate at an even higher temperature of 93 °C. To monitor the cleaning performance, the purity of the waste rinsing water is continuously checked by means of a built-in online conductivity sensor.

Time saving and highest precision – InLab®741 and SevenMulti™ S70 an unbeatable pair

The functionality of the built-in online conductivity sensor is checked by MIELE staff in the final test department in production and during the annual service of disinfectors at customer sites or if repairs have to be made. Mr. Schartner demonstrated how the InLab®741 conductivity sensor is used. An InLab®741-5m is installed directly in the system right next to the built-in conductivity sensor by means of a bypass (Fig. 3).

Thanks to the five-meter cable, the direct control measurement can also be performed on machines that have already been installed. The InLab®741 as a two-pole sensor made of high quality stainless steel is ideally suited for the measurement of very low conductivities from 0.001 µS/cm up to maximum of 500 µS/cm. It also withstands temperatures of up to 100 °C, which is very important in this application. To measure the conductivity

Figure 1:
A MIELE-Professional large-capacity disinfector in the quality control department.



Figure 2:
Rinsing cycle with deionized water.



as accurately as possible, MIELE chose a SevenMulti™ S70 conductivity meter. This has an excellent performance for measurements in the low conductivity range. Mr. Balzer enters the absolute cell constant (given on the sensor certificate and the sensor cable to six decimal places) directly into the instrument and explains that a time-consuming calibration with corresponding calibration solutions is no longer necessary. Entry of the known temperature correction coefficient (α -coefficient) of the rinsing water then allows precise measurement results to be obtained without any loss of time.

The verdict of the InLab®741 sensor in the conductivity test

After installation of the InLab®741, Mr. Schartner starts a special test program on the disinfectant to check the built-in online conductivity sensor. Five to six successive rinsing cycles are performed to ensure sufficiently high reproducibility of the results (Fig. 2).

During each rinsing cycle, a salt solution is dispensed in predefined steps by means of a special dosing unit. In a next step the large-capacity disinfectant is rinsed until the conductivity reaches 1.5 $\mu\text{S}/\text{cm}$. The comparison measurement values of the InLab®741 are transferred to the disinfectant's control computer from the SevenMulti™ as an analog signal. The values can then be compared directly with the data from the online conductivity sensor (Fig. 4).

The suspense in the MIELE test laboratory increases as the two conductivity values on the monitor steadily decrease. Finally, the internal conductivity measurement



Figure 3: The InLab®741 is attached via a bypass next to the disinfectant's built-in online conductivity sensor.

display indicates 1 $\mu\text{S}/\text{cm}$ (no decimal places) and the InLab®741 conductivity sensor records a value of 1.142 $\mu\text{S}/\text{cm}$ (Fig. 5); the test run is terminated. If the internal conductivity measurement deviates by less than 2 $\mu\text{S}/\text{cm}$ from the comparison value then the verdict of the InLab®741 is positive and the machine passes the test and is released for use. Mr. Balzer is clearly pleased with the precision of the measurement: "You can really rely on this sensor".

Normally the entire test run takes one to one and a half hours. In the MIELE factory, it can be simultaneously performed on five or six machines. Quite likely other InLab®741 sensors will soon be used as experts for conductivity tests.



Figure 4: The comparison measurement values are transferred directly from the SevenMulti™ to the disinfectant's control computer.



Figure 5: The measured value display of the SevenMulti™.

Automatic determination of alpha acids in hop extracts using conductometric titration



M. Wild

The hop vine is a species of plant belonging to the hemp family (Fig. 1). The high content of alpha acids (bitter substances) in hops makes it an essential ingredient in beer brewing. Variation of the amount added has a decisive influence on the taste of the beer.



Figure 1:
Hop plants with the female flower cones.

Constant quality – for sure!

To brew beer that always has the same taste, it is important to determine the exact content of the alpha acids. The content of these bitter substances is also one of the main factors that influence the amount paid by breweries to farmers. The European Brewery Convention EBC develops standards and analytical methods to ensure that chemical analysis is standardized.

Figure 2:
Final product: Hop pellets as used in breweries.



The EBC 7.4 method describes the conductometric titration of hops and pellets (Fig. 2). Briefly, the sample material is extracted with toluene and an aliquot dissolved in methanol. This aliquot is then titrated conductometrically with lead acetate solution. The details are as follows:

The lead acetate titrant is prepared by dissolving 20 g $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ and 0.5 mL glacial acetic acid in 1 L methanol. This is titrated against a solution of 4 mL of a 0.05 mol/L sulfuric acid in 40 mL methanol. The consumption up to the equivalence point is used to calculate the concentration of the lead acetate solution. At the equivalence point, the entire sulfate from the sulfuric acid has been precipitated as lead sulfate and the conductivity reaches a minimum. Afterward, the conductivity increases due to the further addition of lead acetate (Fig. 3).

To determine the alpha acids, aliquots of the hop extracts are prepared depending on their sort, the extract and its expected content. These are then transferred to the titration beaker. The solvent mixture is added quickly and reliably by means of a peristaltic pump.

After a short conditioning time, the solution is titrated with lead acetate solution and the consumption up to the equivalence point calculated in percent content of alpha-acids (Fig. 4).

Short analysis times – high throughput – maximum accuracy

The Hallertau region in Germany is the largest hop-growing region in the world and produces 85% of German hops. In 2008, this represented a worldwide market share of over 30%. Hop-processing companies need to be able to analyze large numbers of samples in 24-hour shift operation. METTLER TOLEDO took up the challenge.

Our solution for hop analysis (Fig. 5) consists of:

- Excellence titrator with conductivity board
- InLab 718 sensor
- Rondo 20 for high sample throughput
- SP250 pump for rapid solvent addition
- LabX titration PC software for the control, evaluation and archiving of results
- Rainin pipettes for titer standard and sample addition.

This instrument system satisfies all the necessary requirements and ensures that the analysis is performed according to the EBC method.

The hops industry greatly appreciates the advantages of the system and is very pleased with the support from METTLER TOLEDO in application and service questions. The Excellence titrators are easy to use in routine operation but provide full flexibility for methods development. The results are more reliable than the previous manual evaluation of a recorder plot.

It is now possible to analyze 100 samples a day thanks to the ingenious automation of the METTLER TOLEDO system.

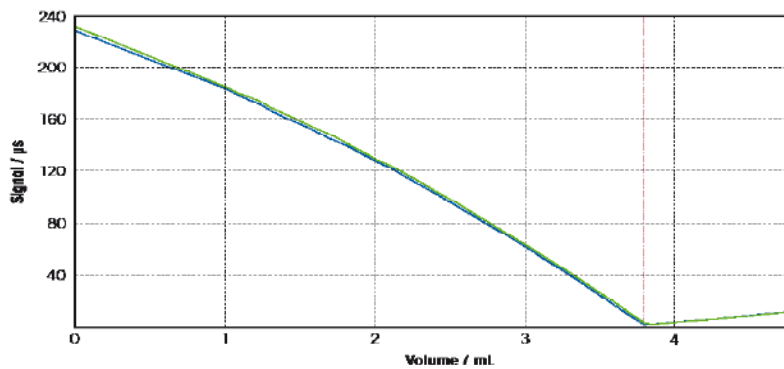


Figure 3: Titration curve of the titer determination using sulfuric acid.

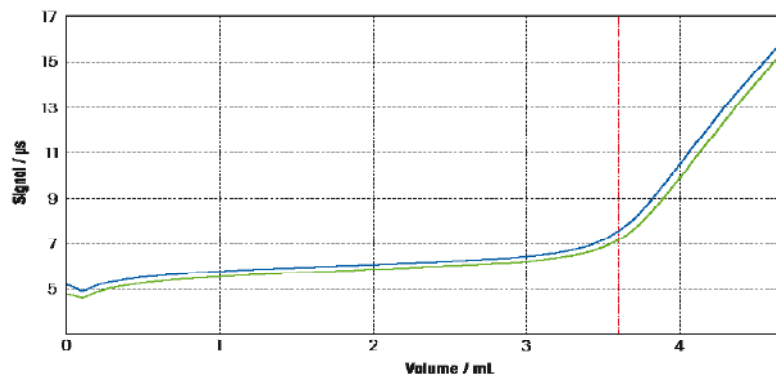


Figure 4: Typical titration curves of real samples.



Figure 5: Standard hops analysis using a METTLER TOLEDO Excellence titrator, Rondo 20, and LabX titration.

| Rx | Name | n | Mean | Unit | s | srel [%] |
|----|---------|---|-----------|------|----------|----------|
| R1 | Content | 7 | 19.968324 | g/L | 0.033124 | 0.166 |
| R4 | Titer | 7 | 0.99842 | | 0.001656 | 0.166 |

Table 1: The concentration determination takes only a few minutes and yields very reproducible values.

| No. | ID | Rx | Result |
|-----|-------------|--------------|--|
| 1 | Extract A 1 | R1 = R2 = | 3.456 mL Consumption 49.35% Content |
| 2 | Extract A 2 | R1 = R2 = | 3.450 mL Consumption 50.04% Content |
| 3 | Extract B 1 | R1 = R2 = | 3.595 mL Consumption 32.27% Content |
| 4 | Extract B 2 | R1 = R2 = | 3.651 mL Consumption 32.44% Content |
| 5 | Extract C 1 | R1 = R2 = | 3.305 mL Consumption 51.52% Content |
| 6 | Extract C 2 | R1 = R2 = | 3.378 mL Consumption 51.78% Content |
| 7 | Pellet A 1 | R1 = R2 = | 3.250 mL Consumption 18.05% Content |
| 8 | Pellet A 2 | R1 = R2 = | 3.245 mL Consumption 17.95% Content |

Table 2: The table shows the results for different hop extracts. Two determinations were performed in each case.

Bromine number and bromine index of petroleum products



T. Fossum

Petroleum products normally consist of a mixture of many different hydrocarbon molecules containing C=C double bonds. The number of double bonds corresponds to the degree of unsaturation. This is an important quality parameter for many raw materials and finished products such as hydrocarbon fuels and lubricants. How is it determined in practice?

Bromine number and bromine index are analytical procedures designed to determine the degree of unsaturation or content of reactive C=C double bonds (olefins) in a hydrocarbon. C=C double bonds can crosslink or react with oxygen to form epoxides, which are also highly reactive. The crosslinking causes the hydrocarbon to form long chain molecules (polymers) which are no longer liquid but solid and are termed gums or varnishes. These form deposits in a fuel system or in a carburetor and can clog up filters and the narrow tubing that supplies fuel to the internal combustion engine. The reduced fuel flow results in a reduction in engine power and might even prevent the engine from starting.

The titration uses a simple reaction

The main reaction in bromine number titration is the addition of one molecule of diatomic bromine to the C=C double bond. One bromine atom adds on each side, one to each carbon atom (Fig. 1). In the titration, bromine is steadily metered in while the level of bromine is detected by a polarized double-pin platinum sensor. When the bromine level is

low, more bromine is added. When no more double bonds are present to react, the level of bromine in the solution rises and the titration is terminated. The amount of bromine added corresponds to the amount of olefin originally present. The bromine number is the quantity of bromine in grams that reacts with 100 grams of sample under the test conditions. The bromine index is the number of milligrams of bromine that react with 100 grams of sample.

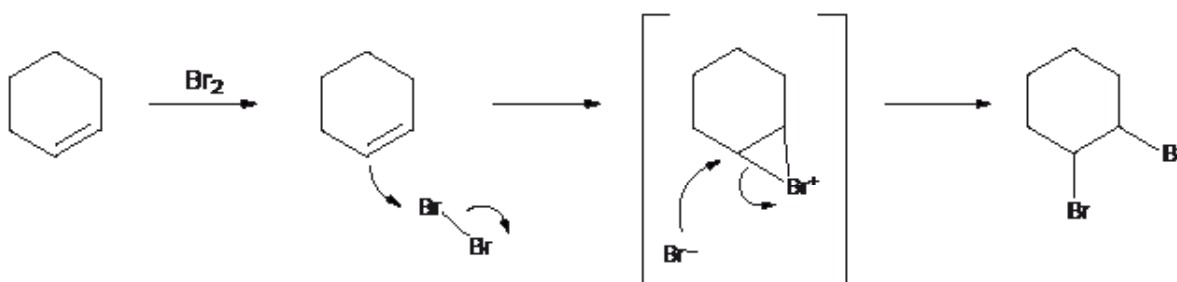
Other reactions in which bromine can participate are oxidation, substitution, and reactions with sulfur, nitrogen or oxygen-containing compounds. The oxidation and substitution reactions occur more slowly at low temperatures. For this reason, the ASTM D1159 (bromine number of petroleum distillates and olefins), ASTM D2710 (bromine index of hydrocarbons) and ASTM D5776 (bromine index of aromatic hydrocarbons by electrometric titration) standard test methods are all specified to be conducted at temperatures of 0 to 5 °C. In alpha-olefins, the double bond is between the end carbon and the adjacent carbon. These compounds do not react so readily with bromine and the reaction is incomplete.

Bromine number made easy

The conditions for the potentiometric (electrometric) determination of the bromine number or bromine index include an acidic polar solvent consisting of glacial acetic acid (714 mL), trichloroethane or dichloromethane (134 mL), methanol (134 mL) and sulfuric acid (16.7%, 18 mL). The mixture is held at 0 to 5 °C while a bromide-bromate titrant (KBrO₃ and KBr) is added in small increments. The titration is monitored by a double platinum pin electrode charged positively on one pin and negatively on the other by a constant current. The endpoint is reached when a significant change in potential occurs. A preset endpoint is defined in this region. The titration is terminated when the potential remains the same at this endpoint.

The Excellence titrators are ideal for determining bromine number and bromine index. The One Click shortcut for bromine number makes it easy to start the analysis. The Solvent Manager activates solvent exchange with One Click and so protects the user from contact with the chemicals. The thermostatable beaker keeps the solution between 0 and 5 °C. An external refrigerated circulating ther-

Figure 1: Reaction scheme for the addition of bromine to the double bond of cyclohexene.



mostat is needed for this low-temperature analysis. This applies to the bromine index as well. The method is changed to an EQP (equivalence point) titration for low bromine index levels.

Bromine index – clean and elegant ...

An especially clean, elegant and accurate way to determine the bromine index is to use coulometric titration. The bromine is generated directly in the titration vessel by a current supplied by a platinum-based electrolysis cell instead of through addition from a burette. Fewer chemicals need to be handled and the current generates bromine more accurately than it can be dispensed using a typical burette. The ASTM D1492 standard describes a test method for the coulometric determination of the bromine index at low concentrations. This is performed at room temperature using a fritless electrolysis cell. Typical samples from industry have bromine indices in the range of 2 to 50 for clean aromatic samples such as benzene, toluene, or xylene. The bromine index of raffinates, which are cracked hydrocarbons destined for gasoline production, can be much higher of the order several hundred to several thousand.

The METTLER TOLEDO C30X coulometer is a powerful instrument that can be used to determine the water content of a variety of samples according to Karl Fischer. It also offers a special method for the fast and accurate determination of the bro-

mine index. The control is fast for high values of the bromine index and cautious for small values. This allows accurate and reproducible determination of even low one-digit bromine indices using a mercury-free solvent. The simple method enables determinations to be made without having to develop a specific procedure because predefined method templates can be used. The solvent is blanked out and subsequent samples are all analyzed with the same method.

... and with One Click

The One Click user interface offers direct access to all routine tasks. One click is all it needs to start a method, run a sample or change the solvent. The ingenious design of the coulometric current-electrolysis cell makes cleaning easy and offers high accuracy. The titration vessel is emptied and refilled by activating the Solvent Manager from the titrator. This avoids contact with chemicals. Using the C30 coulometer, you can be sure that your samples meet the technical specifications.

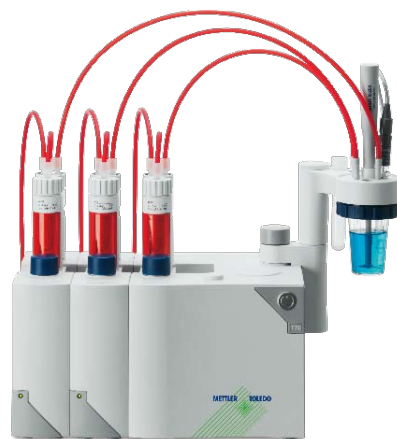


Figure 2: T70 titrator for bromine index and TAN/TBN determination.

| Theoretical value | n | Result | srel [%] |
|-------------------|---|--------|----------|
| 141 | 3 | 144,2 | 0,9 |
| 8,5 | 3 | 10,1 | 0,3 |
| 3,8 | 3 | 6,0 | 1,3 |
| 0,9 | 3 | 1,9 | 0,2 |
| Hexan | 3 | 1,4 | 0,3 |

Table 1: Results obtained using the C30 coulometer. Samples were cyclohexene diluted with toluene.

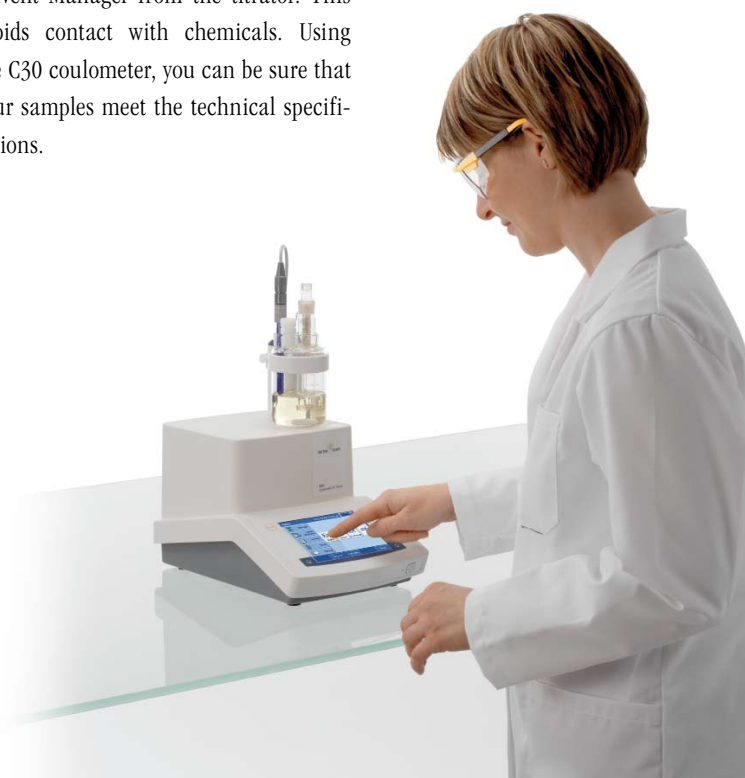


Figure 3: The C30X coulometer in routine use.

Assigning the correct equivalence point in the titration of mercaptans



S. Vincent

A well-established test in the petrochemical industry is the determination of the hydrogen sulfide and mercaptan sulfur content in petroleum distillates and other hydrocarbon products. The sulfur content of fuels is a key parameter in their quality control, and its limits are defined by strict quality standards.



Figure 1:
Acid rain can cause great damage to buildings and works of art.

A high content of sulfur in fuel leads to inefficient combustion and to the formation of corrosive, acidic deposits that damage the metal components of the engine.

Figure 2:
Entry of the correction factor, f , with the sample data.

| Sample 1/1 | |
|--------------------------------------|----------|
| Analysis = Sample list = Sample data | |
| Number | 1 |
| ID 1 | -- |
| Sample size | 0 g |
| Density | 1.0 g/ml |
| Comment | |
| Correction factor | 1.0 |

Figure 3:
The condition applied to the calculation function.

| Calculation | |
|--|-------------------------------------|
| Methods = Templates = Method = Calculation | |
| Result limits | <input type="checkbox"/> |
| Record statistics | <input type="checkbox"/> |
| Extra statistical functions | <input type="checkbox"/> |
| Send to buffer | <input type="checkbox"/> |
| Condition | <input checked="" type="checkbox"/> |
| Formula | nEQ=2*WDF=1 |

As well as damage to the engine, atmospheric emissions from sulfur-containing fuels have high levels of sulfur dioxide, which when dissolved in atmospheric moisture, falls as acid rain. This causes damage to the environment and building structures (Fig. 1), and has a negative economic impact.

The testing of petroleum distillates for their sulfur content is therefore mandatory. Many different test methods have appeared, but the ones that have proven to be most reliable are those based on titration. The UOP 163-05 laboratory test method outlines a simple titration with alcoholic silver nitrate solution that allows the sulfur compounds to be determined. However, things are seldom that simple...

The sulfur compounds most often found in petroleum distillates are hydrogen sulfide (H_2S) and alkyl mercaptans (RSH), although some distillates may also contain elemental sulfur. This reacts with mercaptans to form polysulfide compounds (RSSH).

In practice, most real-world samples contain mixtures of these substances, which will affect the resulting titration curve profile obtained. Any analytical technique used to analyze unknown samples must take account of this variation and yet still allow quick and easy calculation of the correct results.

The UOP163-05 test method (available from ASTM) describes how the differ-

ent curve types should be evaluated in practice. The first stage is to establish the presence or absence of hydrogen sulfide using the qualitative lead acetate strip or "Doctor Test" according to UOP 41 where a positive test result indicates the presence of H_2S . With this knowledge, there are then five possibilities to consider.

Interpreting the titration curve

The challenge for automating the procedure is to ensure that irrespective of the type of curve only the correct results are calculated. Two variables need to be taken account of:

- The number of equivalence points (EQP) on the curve.
- The result of the doctor test (positive or negative).

The first of these forms part of the raw data (nEQ) and is so easily accessible. The result of the doctor test result can be entered with the sample data using the correction factor and a binary format. We set $f=1$ for samples that give a positive test result and $f=0$ for those with a negative test (see Fig. 2.)

If the T90 Excellence titrator is used, we have the possibility of adding condition statements to the calculation functions in the method (see Fig. 3).

The full set of calculations needed in the method to cover all five possibilities given is shown in Table 1.

Ingenious calculations

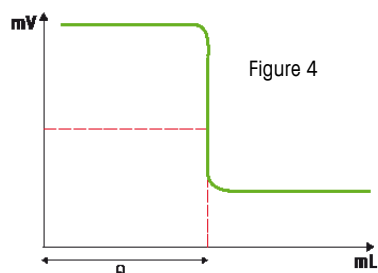
What can be done if a T90 is not available and we have to use a T50 or T70 for these tests?

The answer is more complex because we cannot use conditional statements to exclude incorrect calculation of results. The best we can hope to do is to render unhelpful results as either zero or NaN (not a number). The calculation formulae themselves need to be altered to allow this. The f or $(1-f)$ terms ensure that H_2S is only calculated when it is in fact present. (see Tab. 2).

The results of these calculations will allow the correct RSH value to be identified as can be seen from the table of outcomes (Tab. 3). The additional $(x-nEQ)$ elements of the second and third calculations (Tab. 2) prevent the calculation of multiple RSH results in the case of scenarios with two or three equivalence points (Figs. 5 and 6). There is only ever one non-zero result for the mercaptan content.

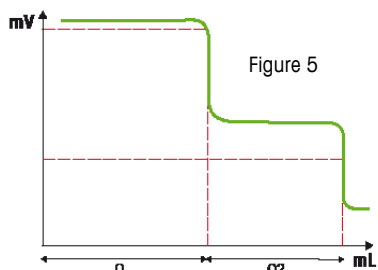
Conclusions

All the models in the Titration Excellence line allow the correct selection of calculation according to the UOP 163-05 standard test method, although the most convenient and best solution is available with the T90 model.



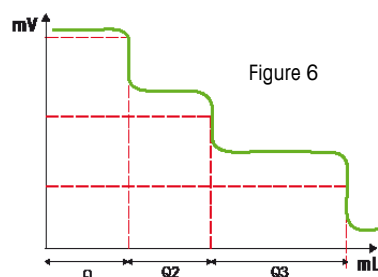
Curve with 1 EQP

- a) Positive doctor test
The EQP is caused by titration of the H_2S .
 $R = Q \cdot C / m$
- b) Negative doctor test
The EQP is caused by titration of the mercaptan RSH.



Curve with 2 EQPs

- a) Positive doctor test
There is elemental sulfur present. The first EQP is caused by the titration of the H_2S ($R = Q \cdot C / m$). The second EQP is caused by titration of mercaptan RSH. ($R = Q2 \cdot C / m$)
- b) Negative doctor test
There is elemental sulfur present, so we ignore the first EQP and take the total consumption to the second EQP as caused by the mercaptan.
 $(R = (Q + Q2) \cdot C / m)$



Curve with 3 EQPs

- a) Positive doctor test
The first EQP is caused by titration of the H_2S ($R = Q \cdot C / m$)
The second EQP is from the polysulfide formed when mercaptan-sulfur reacts with elemental sulfur. This EQP is ignored.
The third EQP is from the titration of the mercaptan, but the calculation must be based on the total titrant consumption from the first to the third EQP.
 $(R = (Q2 + Q3) \cdot C / m)$

| Result | Formula | Condition | Valid for n EQPs |
|------------|------------------------------|------------------------------|------------------|
| ppm H_2S | $R = Q \cdot C / m$ | $f = 1$ | 1, 2 or 3 |
| ppm RSH | $R2 = Q \cdot C / m$ | $nEQ = 1 \text{ AND } f = 0$ | 1 |
| ppm RSH | $R3 = Q2 \cdot C / m$ | $nEQ = 2 \text{ AND } f = 1$ | 2 |
| ppm RSH | $R4 = (Q + Q2) \cdot C / m$ | $nEQ = 2 \text{ AND } f = 0$ | 2 |
| ppm RSH | $R5 = (Q2 + Q3) \cdot C / m$ | $nEQ = 3 \text{ AND } f = 1$ | 3 |

Table 1: Calculations and conditions for the T90 method.

| Result | Formula |
|------------|--|
| ppm H_2S | $R = Q \cdot C \cdot f / m$ |
| ppm RSH | $R2 = Q \cdot C \cdot (1-f) \cdot (2-nEQ) / m$ |
| ppm RSH | $R3 = Q2 \cdot C \cdot f \cdot (3-nEQ) / m$ |
| ppm RSH | $R4 = (Q + Q2) \cdot (1-f) \cdot C / m$ |
| ppm RSH | $R5 = (Q2 + Q3) \cdot f \cdot C / m$ |

Table 2: Calculations for the T50/T70 method.

| nEQ/test | R1 | R2 | R3 | R4 | R5 |
|----------|-----|-----|-----|-----|-----|
| 1+ | xxx | 0 | NaN | NaN | NaN |
| 1- | 0 | xxx | NaN | NaN | NaN |
| 2+ | xxx | 0 | xxx | 0 | NaN |
| 2- | 0 | 0 | 0 | xxx | NaN |
| 3+ | xxx | 0 | 0 | 0 | xxx |

Table 3: Identification of the correct RSH value (xxx = result, NaN = not a number).

Determination of chromium and aluminum content using a base titration



Dr. D. Widmer

Electroplating baths must be continuously checked to ensure the constant quality of chromium coatings. In particular, the acid content and concentration of chromium(VI) as well as aluminum(III) formed in a side reaction are determined. This can be quickly and reliably done by means of a simple titration with sodium hydroxide in which the equivalence points of the curve are individually evaluated and calculated using empirically determined factors. The analyses can be easily automated using a T90/Rondo 20 titration system.



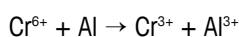
Undesired processes in the electroplating bath

Chromium is a corrosion-resistant, hard metal. In an electroplating bath, a chromium layer is deposited onto other metals to protect them from wear and corrosion.

This is done by immersing the metal parts in a sulfuric acid bath with a high concentration of chromium(VI) cations and applying a current between the bath and the metal parts. As an example, let us consider a company in England that coats aluminum components with chromium in this way.

To prepare a typical chromium bath, a tank is first half-filled with water. Concentrated sulfuric acid and solid chromium trioxide are then added. The solution is mixed and more water is added to make it up to the correct volume. The solution finally has a concentration of 270 g/L sulfuric acid and 55 g/L chromium and is dark orange in color. During the electrolysis, a thin layer of chromium is deposited on the aluminum

components immersed in the bath. At the same time the following undesired redox reaction occurs:

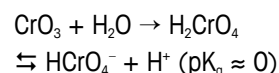


Small amounts of the metallic aluminum are oxidized to aluminum(III). At the same time, chromium(VI) is reduced to chromium(III). Chromium is therefore consumed without it making any contribution to the coating process. The more chromium(III) there is in the solution, the browner it becomes due to the green color of this ion. In a used bath, up to 14 g/L aluminum is present in dissolved form. In general, one can assume that the aluminum(III) concentration in the solution always corresponds to the chromium(III) concentration.

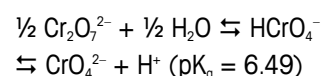
Chemical reactions during a base titration

Normally the acid content of a sample solution is titrated with sodium hydroxide while the aluminum and chromium content is determined complexometrically. Ethylenediaminetetraacetic acid (EDTA)

can be used as a complexing agent for chromium and for aluminum at higher temperatures. The intense natural color of the solution however makes photometric detection of the inflection point impossible. For this reason, a base titration is used to detect all the ions. The high acid content of the solution requires a titration with 1 M NaOH. When solid chromium trioxide (CrO_3) is added to water, the following reaction occurs in which chromic acid (H_2CrO_4) and the hydrogen chromate ion (HCrO_4^-) are formed:



The hydrogen chromate (HCrO_4^-) is in equilibrium with the orange dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and the yellow chromate (CrO_4^{2-}). Titration with NaOH shifts the equilibrium in the direction of chromate:

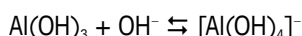


An additional mole of strongly acidic protons is present per mole CrO_3 in water. In the base titration, this together with the two protons of the sulfuric acid gives rise to just one equivalence point (EQP). The other proton from the formation of the chromic acid is titrated in a separate EQP.

If a solution containing aluminum(III) is titrated with NaOH, one expects two EQPs: one due to precipitation of aluminum hydroxide



and the other due to complex formation of aluminum hydroxide.



The ratio of the titrant consumption is however 3:1. During the addition of hydroxide ions, the aluminum cations form an Al-OH complex that reacts only slowly to further addition and which does not exhibit a definite stoichiometric ratio. This violates an important prerequisite for a titration and as a result, no clear jump can be detected in the titration curve. The same behavior is observed with chromium(III).

Interpretation of a titration curve with two to four equivalence points

A test solution prepared from the corresponding salts with sulfuric acid, chromium(VI), chromium(III) and aluminum(III) shows three equivalence points when titrated with sodium hydroxide (see Fig. 1):

- the first is from the two protons of the sulfuric acid and a proton of the chromic acid,
- the second is from chromium(III) and aluminum(III), and
- the third is from chromium(VI), that is, the second proton of the chromic acid.

The formation of a precipitate is observed during the second equivalence point and a color change from orange to yellow during the third. A fourth equivalence point can only be detected at higher aluminum concentrations. A large number of titrations with different concentrations of metal cations were performed. This allowed the dependence of titrant consumption of the three EQPs on the metal concentrations to be investigated. Surprisingly, the results showed that not only the position of the second EQP, but also that of the first and third EQPs depend on the chromium(III) concentration (see Fig. 2).

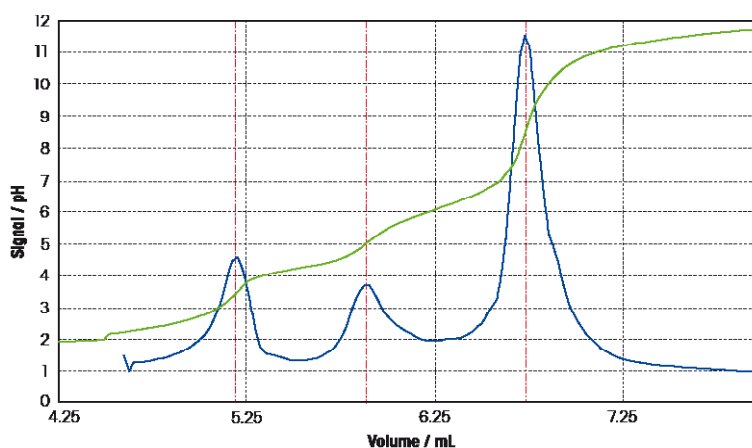


Figure 1: Titration curve of the test solution with sodium hydroxide.

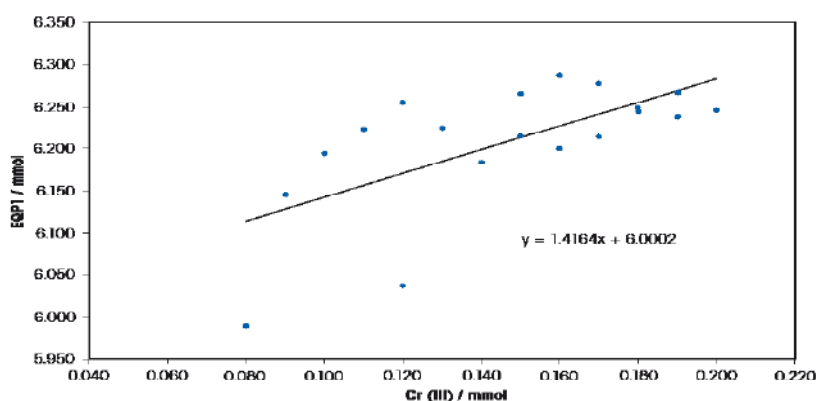
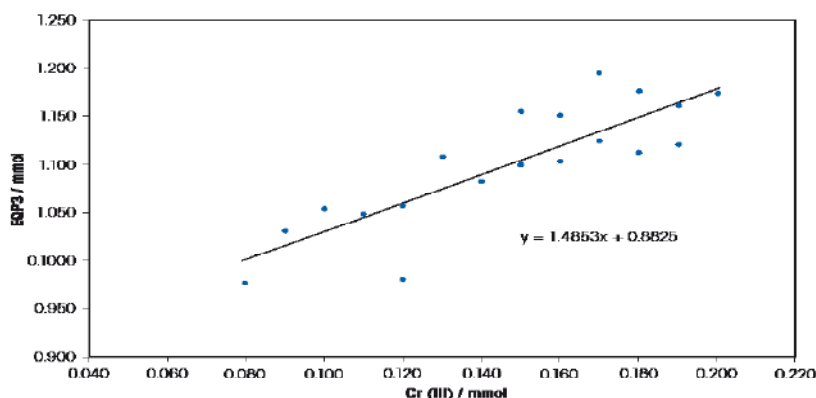
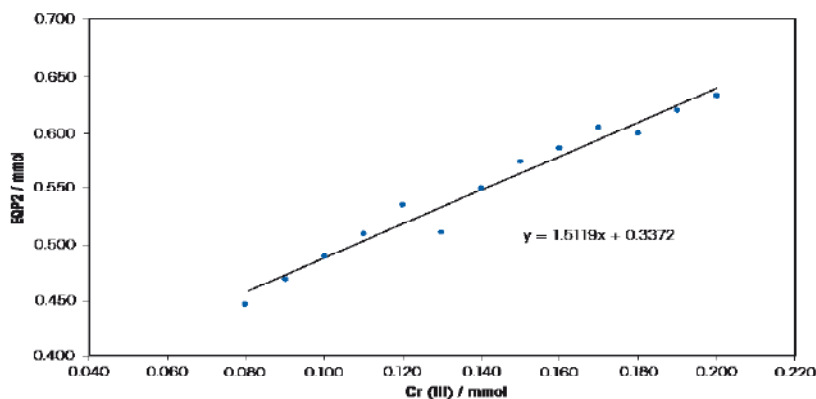


Figure 2: Dependence of the position of the EQP on the chromium(III) concentration.



However, since this is low compared with the concentration of sulfuric acid and chromium(VI), the influence is small. If we assume – as described above – that chromium(III) and aluminum(III)

are present in the solution in the same stoichiometric ratio, we do not need to distinguish between these two cations. We determined empirically that the amount of titrant of the second EQP cor-

responds to about 4.6 times the amount of chromium(III) or aluminum(III). In this way, accurate results can be obtained with concentrations greater than 4 g/L chromium(III) or 2 g/L aluminum(III) (Table 1): In a series of three samples the recovery deviates by less than 5% from the true value. With concentrations below 2 g/L chromium(III) or 1 g/L aluminum(III) the EQP is not detected because the titration curve is too flat. This represents the detection limit of the method.

The content of chromium(VI) is obtained directly from the third EQP. It must of course be taken into account that if the chromium(III)/aluminum(III) concentrations are too low, the second EQP is from chromium(VI). For this reason, the pH value of the second EQP is evaluated: If it is less than 8.5, the EQP is that of chromium(III)/aluminum(III). If the pH value is greater than 8.5, it is the EQP of chromium(VI). A condition in the titrator method allows the correct EQP to be determined. The titrant consumption for chromium(VI) is stored temporarily in an auxiliary value of the titrator.

By the way, one cannot necessarily assume that the last EQP of the titration always originates from chromium(VI). If the aluminum concentration is relatively high, a fourth EQP is observed.

The acid concentration is calculated by subtracting the titrant consumption of chromium(VI) from that of the first EQP in order to take into account the first acid proton of the chromic acid. This is done using the auxiliary value mentioned above.

Two-loop method for the individual analysis of all cations

If you cannot assume identical concentrations of aluminum(III) and chromium(III) and want to determine the content of all the individual cations, you have to perform two titrations. The first titration is performed in the same way as described above. For the second titration, an identical sample is first oxidized so that all the chromium(III) is present as chromium(VI). The sample is also titrated with 1 M NaOH, whereby three equivalence points are expected:

- the first is from strongly acidic protons (is not taken into account),

- the second is from aluminum(III), and
- the third is from chromium(VI) together with chromium(III) that has been oxidized to chromium(VI).

The oxidation is performed by adding 250 mg sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and 1 mL water to 1 mL of sample solution. The mixture is boiled for 10 to 15 min on a hot plate during which the brownish colored solution becomes orange due to oxidation of the green chromium(III) to orange-colored chromium(VI).

We developed a method that consisted of two sample loops, each with one EQP titration to pH 12. The calculation is performed at the end with conditions and auxiliary values. If the chromium(III)/aluminum(III) content is below the limit at which it can be determined, both titration curves appear the same with two EQPs; the second originates from chromium(VI) and the first from sulfuric acid and chromium(VI). Otherwise, the concentrations are determined as follows:

- Sulfuric acid: This is obtained from the first EQP of the first titration; the

Table 1:
Summary of results of titrated test solutions containing different metal cation concentrations (3 samples per series).

s = absolute standard deviation
srel = relative standard deviation (precision)

| | | Theoretical content | Mean | s | srel | Recovery |
|-------------------------|-------|---------------------|--------|-------|-------|----------|
| H_2SO_4 | mol/L | 2.508 | 2.546 | 0.010 | 0.37% | 101.5% |
| Cr(VI) | g/L | 49.971 | 49.825 | 0.551 | 1.11% | 99.7% |
| Cr(III) | g/L | 4.173 | 4.281 | 0.090 | 2.10% | 102.6% |
| Al(III) | g/L | 2.165 | 2.221 | 0.047 | 2.09% | 102.6% |
| H_2SO_4 | mol/L | 2.508 | 2.559 | 0.005 | 0.20% | 102.0% |
| Cr(VI) | g/L | 49.971 | 46.684 | 0.415 | 0.89% | 93.4% |
| Cr(III) | g/L | 2.086 | 2.306 | 0.041 | 1.79% | 110.5% |
| Al(III) | g/L | 1.083 | 1.197 | 0.022 | 1.80% | 110.5% |
| H_2SO_4 | mol/L | 2.006 | 2.039 | 0.008 | 0.39% | 101.6% |
| Cr(VI) | g/L | 39.977 | 38.980 | 0.340 | 0.87% | 97.5% |
| Cr(III) | g/L | 3.130 | 3.297 | 0.030 | 0.91% | 105.3% |
| Al(III) | g/L | 1.624 | 1.711 | 0.016 | 0.91% | 105.3% |
| H_2SO_4 | mol/L | 2.006 | 2.023 | 0.018 | 0.88% | 100.8% |
| Cr(VI) | g/L | 39.977 | 42.231 | 0.943 | 2.23% | 105.6% |
| Cr(III) | g/L | 5.216 | 5.375 | 0.168 | 3.13% | 103.1% |
| Al(III) | g/L | 2.707 | 2.790 | 0.087 | 3.12% | 103.1% |
| H_2SO_4 | mol/L | 1.755 | 1.764 | 0.005 | 0.29% | 100.5% |
| Cr(VI) | g/L | 34.980 | 36.365 | 0.665 | 1.83% | 104.0% |
| Cr(III) | g/L | 4.173 | 4.322 | 0.039 | 0.91% | 103.6% |
| Al(III) | g/L | 2.165 | 2.243 | 0.021 | 0.91% | 103.6% |

consumption for the chromium(VI) content must be subtracted.

- Chromium(VI): The most obvious way is by calculation from the consumption of the third EQP of the first titration. However, this value fluctuates strongly and depends on the aluminum(III) content. A better result is obtained by using the third EQP of the second titration and subtracting the chromium(III) content.
- Aluminum(III): Theoretically three hydroxide ions per aluminum cation are needed for the second EQP of the second titration (equivalent number $z = 3$). Detailed measurements in the corresponding concentration range followed by linear regression of the results showed that an approximation with decimal numbers leads to a better recovery.
- Chromium(III): The difference of the titrant consumption of each third EQP of the two titrations would mathematically yield the chromium(III) content. This value however fluctuates very strongly because the consumption to this EQP without chromium(III) produces results with a large scatter. The determination is more accurate if the second EQP of the first titration is used as the basis. In a calculation formula consisting of several terms and empirical values, the consumption for aluminum(III) is subtracted and a value for chromium(III) calculated.

Automation with Rondo 20

The method developed works with method functions that are only executed if defined conditions are fulfilled. This can be done using the T90 Excellence titrator. An automated system with a Rondo 20 sample changer is a good solution for dealing with the large number of incoming samples (Fig. 3). The PowerShower™ rinsing system prevents carryover of the titrated sample to the next sample beaker and can at the same time be used to dilute the sample volume to 50 mL.



Figure 3: T90 Excellence titrator with Rondo 20 sample changer and Excellence analytical balance.

Irrespective of whether a one or two loop method is used, only NaOH 1 mol/L titrant and the DGi111-SC pH sensor are required. Glass titration beakers were used to oxidize samples on the heating plate. The PC software LabX pro titration allows all the results to be stored and afterward be processed and transferred to a LIMS. Let us assume we want to determine all the cations individually using the two-loop method.

To achieve an exact result, four samples per series are needed. To do this, a series template is set up with four samples in the first and second loops and the Rondo start positions 1 and 5. Before the start, 1 mL of solution from the electroplating bath is added to each of the first four beakers. Positions 5 to 8 contain beakers in which 1 mL of the electroplating bath was diluted with 1 mL of water and oxidized with sodium persulfate on the hot plate (see above). The position after the last sample beaker is occupied by a beaker containing KCl solution in which the sensor is parked at the end for regeneration.

Furthermore, a second series template using the start positions 10 and 14 allows two series templates to be joined together to form a series sequence (see Fig. 4). In this way, the analysis of two electroplating bath samples can be started with one single click. The laboratory staff can go

home and the titration system works on into the night.

Conclusions

A base titration can be used to analyze both the high content of sulfuric acid and chromium and the relatively low content of aluminum in an electroplating bath. Recovery and precision under these conditions are very good. Due to mutual interdependencies, non-stoichiometric conditions arise which make analysis rather difficult. Knowledge of these factors and corresponding modification of the method allows a practical solution that can be efficiently automated with the T90/Rondo 20 Titration system.

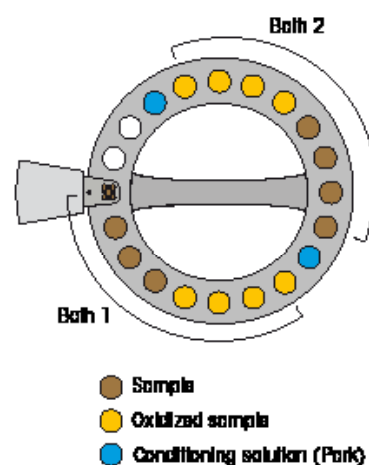


Figure 4: Schematic diagram of the Rondo 20 sample positions for the analysis of two baths in a two-loop method with four samples each.

Determination of the acid number (TAN) – tips and tricks



A. Aichert

The determination of the acid number (AN) in petroleum oils is a non-aqueous potentiometric titration that often causes problems. These include, for example, non-repeatable or incorrect results, non-recognition of the equivalence point, long titration times and so on. Experience shows that most problems can be solved if suitable measures are taken.



1. The Sensor

An accurate and reliable determination requires a good sensor. The DGi113-SC and DGi116-Solvent are ideal and were specially developed for non-aqueous titrations (Fig. 1).

The condition of the sensor can be assessed by the following tests:

- Calibration with pH 4 and pH 7 buffer. The zero point should be 0 mV \pm 30 mV and the slope s between -55 and -59.2 mV/pH.
- The potential difference between the pH 4 and pH 7 buffers should be at least 158 mV.

- The response time of the sensor can be determined using the following procedure in which the signal drift at pH 4, 7 and 11 are measured: Immerse the sensor in water for one minute, then dip it into the buffer pH 4, 7 or 11. Note the potential after 30 seconds in the buffer, and then again after another 30 seconds. The potential difference (drift) should not be more than 3 mV.

METTLER TOLEDO titrators of the latest generation provide a sensor test that takes the user interactively through the above steps and automatically yields the zero point, slope and response time (drift).



Figure 1: DGi113-SC and DGi116-Solvent, the special sensors for non-aqueous titrations.

Table 1 shows typical measurement values that were obtained in the tests.

2. Standardization of the titrant

The titrant is 0.1 mol/L KOH in 2-propanol. This is standardized with potassium hydrogen phthalate (KHP) in deionized water (CO₂ free).

The following factors are important for the standardization of the titrant:

- The titer stability of the 0.1 mol/L KOH in 2-propanol titrant is low. Standardization is required at least every two days.
- To accurately weigh the 70–110 mg KHP, it is essential to use a balance with adequate resolution, that is, with a resolution of at least four decimal places. A resolution of five decimal places is ideal.
- At least three determinations should be performed in order to obtain a reliable mean.
- It is better to use glass beakers. This reduces the influence of electrostatic effects, for example when weighing.

3. The determination of the buffer potential

According to the new ASTM D664-07 standard test method, the aqueous pH 4 and pH 11 buffers can be used. The buffer potentials are stored as auxiliary values in the titrator setup and serve as endpoint criteria for SAN (Strong Acid Number, pH 4) and TAN (Total Acid Number, pH 11) in the titration.

Procedure:

The buffer potential is measured after stirring for 5 minutes. The temperature should be the same as for the titration within 2 °C.

How often should the buffer values be determined?

- At least once a day
- Each time the sensor is changed.
- After each manual cleaning of the sensor
- After conditioning the sensor for a long period (>3 h)

The following factors are important for the determination of the buffer potential:

- a) The pH 11 buffer is not stable. In an open vessel, the potential changes by 0.1 mV/min. For this reason, fresh buffer should always be used for every buffer potential determination, and a buffer container that has been opened should be used within a week.
- b) Before measuring the buffer potential, the sensor should be conditioned for 3–5 minutes in deionized water at pH 5–5.5.

Under no circumstances should the sensor be conditioned in solvent (Solvent 664) before the buffer potential is measured. This would lead to dehydration of the gel layer of the pH-sensitive membrane and would result in a delay before the final potential is reached and unstable measurement values.

4. The determination of the blank value of the solvent

The blank value of the solvent must be determined. The solvent (Solvent 664) consists of 49.5% 2-propanol, 50% toluene and 0.5% water. The blank value is caused by acidic constituents and results in additional consumption of titrant. The blank value is normally in the range 0.01 to 0.002 mmol. The ASTM D664-07 standard test method stipulates that the same method parameters must be used for the determination of the blank value as for the sample.

| Sensor | diff. pH 4 to pH 7 | Drift at pH 11 | Drift at pH 4 |
|----------------|--------------------|----------------|---------------|
| DGi113-SC | 167.6 – 177.4 mV | 0.2 – 0.7 mV | 0.7 to 2.0 mV |
| DGi116-Solvent | 172.0 – 176.0 mV | 0.2 – 1.4 mV | 0.2 to 1.4 mV |

Table 1:
DGi113-SC and
DGi116-Solvent
values typically
obtained in the
sensor test.

The following control parameters are recommended for the determination of the blank value:

Titrant addition:

dE(set) = 8 mV

dV(min) = 0.002 mL

dV(max) = 0.02 mL

Measurement mode:

dE = 0.5 mV

dt = 6 s

t(min) = 30 s

t(max) = 60 s

The titration curve can be evaluated using the equivalence point or the buffer potential at pH 11.

The following factors are important for the determination of the blank value:

- a) Stir for at least 60 s before the blank determination so that the sensor has sufficient time reach the potential in the non-aqueous solvent.
- b) A blank value that is too high can be due to the sensor taking too long to reach the potential. Due to this, the potential lags behind between -100 and -200 mV despite further titrant addition. The buffer potential used as

the endpoint criterion is then reached at a titrant consumption that is too high. In such cases, the sensor must be cleaned and conditioned overnight in water at pH 5–5.5.

- c) An unstable potential can lead to poor repeatability of the blank value. In this situation, the following measures have proven useful:
 - Glass beakers instead of plastic minimize the influence of electrostatic effects.
 - Use a fixed increment = 0.02 mL for titrant addition and a fixed time = 40 s for the measured value acquisition.
- d) Before the blank value determination, the sensor should be dipped into the solvent (Solvent 664) for one minute after conditioning in deionized water.

5. Sample determination

Sample preparation:

If the sample is left to stand for longer periods, the aqueous constituents separate from the oil. The acid number in the upper part of the sample is higher than in the lower part. The sample must therefore be homogenized before taking a sample, for example by shaking.



Figure 2:
The updated titrant
data is stored on
the RFID chip. This
is completely en-
capsulated in the
burette housing and
reliably exchanges
data contact free
with the titrator.

The ASTM D664-07 standard test method recommends the following control parameters:

Titrant addition:

$dE(\text{set}) = 5\text{--}5.5 \text{ mV}$

$dV(\text{min}) = 0.05 \text{ mL}$

$dV(\text{max}) = 0.5 \text{ mL}$

Measurement mode:

$dE = 10 \text{ mV}$

$dt = 10 \text{ s}$

$t(\text{min}) = 15 \text{ s}$

$t(\text{max}) = 60 \text{ s}$

The titration curve can be evaluated using the equivalence point (EQP). If there is no EQP, the curve is evaluated using the buffer potential at pH 11 (Fig. 3).

Optimum control parameters for different samples

Tests of different oil samples have shown that the following control parameters are best for correct and repeatable results.

New and used oils with evaluation using the buffer potential:

Normal method:

Parameter: $dE_{\text{set}} = 12 \text{ mV}$

$dV_{\text{min}} = 0.05 \text{ mL}$

$dV_{\text{max}} = 0.3 \text{ mL}$

$dE = 1.0 \text{ mV}$

$dt = 6 \text{ s}$

$t_{\text{min}} = 15 \text{ s}$

$t_{\text{max}} = 60 \text{ s}$

Careful method:

Parameter: $dE_{\text{set}} = 8 \text{ mV}$

$dV_{\text{min}} = 0.05 \text{ mL}$

$dV_{\text{max}} = 0.3 \text{ mL}$

$dE = 0.5 \text{ mV}$

$dt = 6 \text{ s}$

$t_{\text{min}} = 15 \text{ s}$

$t_{\text{max}} = 60 \text{ s}$

New and used oils with evaluation using the EQP:

Parameter: $dV = 0.1 \text{ mL}$

$dt = 30 \text{ s}$

Figure 3: Typical shapes of TAN titration curves that can be evaluated using the EQP or the buffer potential.

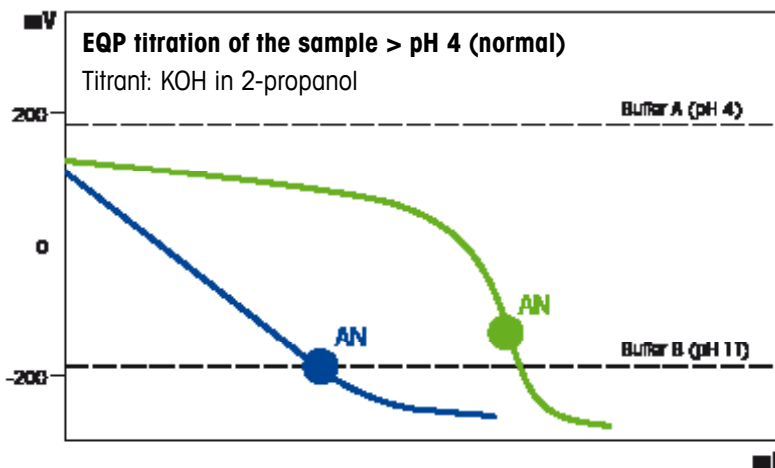
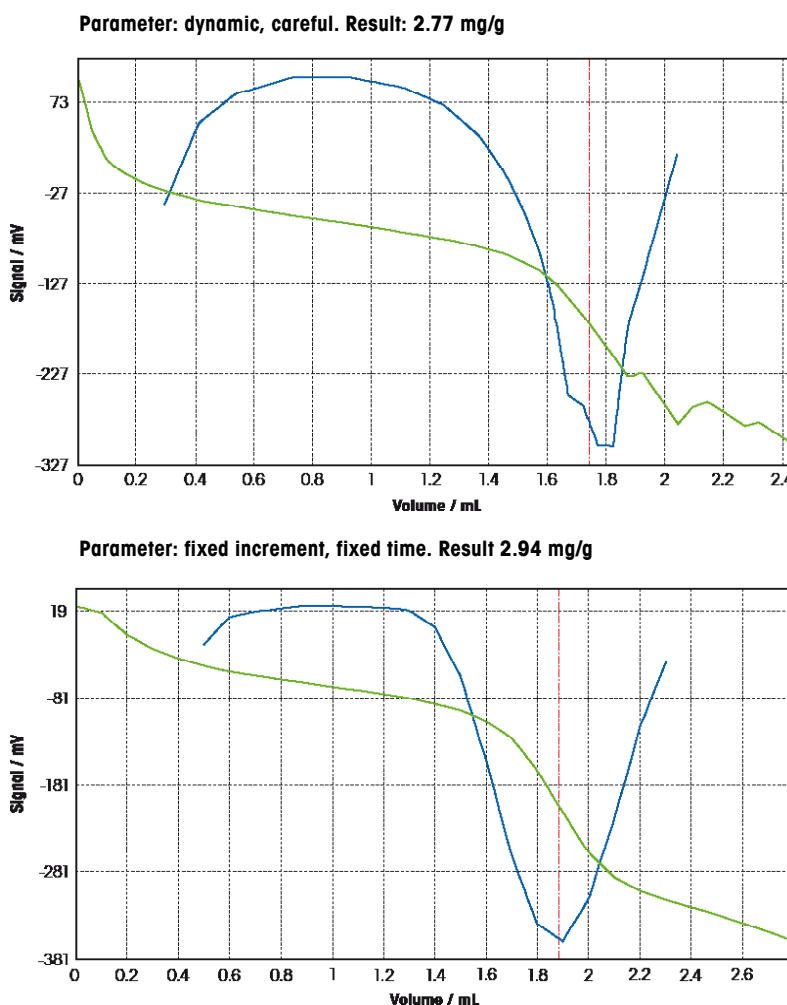


Figure 4: Titration curves of the TAN standard (TAN030, Paragon Scientific Ltd; set value = AN = 2.96 mg/g) measured using different control parameters. The curve in the region of the equivalence point measured using fixed titrant increments and fixed times for measured value acquisition is clearly smoother.



The tests showed that, using the EQP evaluation, the best repeatability and the most accurate results were obtained using the method with fixed titrant increments and fixed time for the measured value acquisition. Furthermore, small jumps at the EQP were more reliably evaluated with these parameters than with the dynamic titrant addition and equilibrium controlled measured value acquisition (Fig. 4).

The following factors are important for the titration:

- a) After each oil sample, the sensor must be conditioned for five minutes in water at pH 5–5.5. The pH of the conditioning solution is adjusted by mixing 40 mL deionized water and 10 mL pH 4 buffer.
- Tests with the DGi113-SC and DGi116-Solvent sensors showed that in a measurement in solvent (Solvent 664) with 5 mL 0.1 mol/L KOH, the potential had already changed by 30–40 mV (from -490 mV to -460 mV) after 20 minutes.



Figure 5:
T90 Titration
Excellence titrator
with two Rondo 20
autosamplers for
the automatic deter-
mination of 2 series
of 20 samples in
parallel operation.

The potential of -490 mV was reached again after conditioning in water for 10 minutes.

- b) Many oils contaminate the sensor to such a degree that special cleaning with chloroform or toluene is necessary after each sample. Without cleaning, the TAN value is 10–30% higher after each sample. We therefore recommend conditioning the sensor in chloroform, toluene or a mixture of chloroform and toluene for 3 minutes at a stirrer speed of 70–90%.
- c) The solution should be stirred for at least 60 seconds before the titration so that the sensor has sufficient time to reach the potential in the non-aqueous solvent. This measure prevents an additional, incorrect equivalence point at the beginning of the titration.
- d) Due to a reduction of electrostatic influences, a more stable mV signal is obtained through the use of glass beakers rather than plastic beakers. This improves EQP recognition and hence repeatability.

The following procedure cleaning procedure is recommended for the TAN determination:

After titrating the sample:

- Rinse with 15–20 mL solvent (Solvent 664).
- Condition in chloroform, toluene or a mixture of chloroform and toluene for 3 minutes at stirrer speed of 70–90%.

- Condition in deionized water at pH 5–5.5 for at least 5 minutes.

Before titrating the sample:

- Condition in 60 mL solvent (Solvent 664); 1 to 2 minutes.

To automate the cleaning procedure, we recommend the use of the Rondo 20 sample changer (Fig. 5).

This allows up to three conditioning beakers to be defined in addition to a rinsing beaker. The required conditioning steps can be then be performed in solvents of different polarity as well as intensive cleaning with the PowerShower™ rinsing unit.

6. Titrant TBAOH (Tetrabutylammoniumhydroxide)

TBAOH in 2-propanol/methanol can be used as titrant for the TAN titration instead of 0.1 mol/L KOH in 2-propanol. One should however note that this titrant is not proposed in the ASTM standard test procedure D664-07.

Advantages of TBAOH:

- A larger and steeper jump at the EQP (about two times larger than with KOH)
- A more stable measurement signal
- A more reliable and better evaluation of the EQP
- Better agreement of the AN values determined using the EQP and the buffer potential.

Disadvantages of TBAOH:

- Somewhat less stable than KOH in 2-propanol. Daily standardization is necessary.
- Significantly more expensive than KOH in 2-propanol.

Table 2 compares the titration curves obtained by titration of an oil sample with 0.1 mol/L KOH or 0.1 mol/L TBAOH. The titrator, sensor and sample were in both cases the same.

7. Conclusions

Reliable results for the TAN titration can be obtained by observing the following points:

- The DGi113-SC and the DGi116-Solvent are the ideal sensors. Their condition must be checked by performing periodic tests.
- The standardization of the titrant must be performed at least every two days. An analytical balance with 4–5 decimal places and glass beakers should be used.
- The buffer potential must be determined at least once a day using fresh pH 11 buffer. Before the determination, condition the sensor for 3–5 minutes in water at pH 5–5.5.
- Before the blank value determination, condition the sensor for 1 minute in solvent. Use glass beakers. The blank value should be in the range 0.01–0.002 mmol. If problems arise (values that are too high), perform

the titration with fixed increment (0.02 mL) and fixed time (40 s).

- After each oil sample, the sensor must be conditioned for at least 5 minutes in water at pH 5–5.5.
- With dirty oils, clean the sensor after each sample by conditioning in chloroform, toluene or a mixture of chloroform and toluene for 3 minutes using a stirrer speed of 70–90%.
- Before each titration of the oil sample, condition the sensor in 60 mL solvent (Solvent 664) for 1–2 minutes. Then stir for 60 seconds in the oil sample before the titration.

- Use the optimum control parameters for titration of the sample.
- A significant improvement can be reached using TBAOH instead of KOH as titrant for oil samples with a poor EQP that cannot be reliably evaluated.

The Excellence titrators support the user in a number of important ways:

- The monitoring systems of the titrant and the Plug & Play sensors request the user to perform the periodic standardization and the sensor test. These routines can be easily started using the Shortcut keys on the Excellence terminal.

- The monitoring systems can inform the user that he/she should perform the sensor test and standardize the titrant either by issuing a warning or by forcing him/her to do so by blocking the sample method.
- The user is provided with many different possibilities for method optimization so he/she can select and optimize the right parameters for the particular oil samples.
- Time-consuming conditioning and cleaning steps for sensor maintenance can be reliably automated with the Rondo sample changer.

Table 2:
Measured value table obtained by titration of an oil sample with two different titrants (KOH or TBAOH) using a DGi113-SC sensor and a T70 Excellence titrator.

| With KOH: AN = 1.71 mg/g | | | |
|--------------------------|---------------|----------------------------|-------------|
| Volume mL | Signal mV | 1 st Der. mV/mL | Time min:s |
| 0.0000 | 6.4 | | 0:30 |
| 0.1000 | -12.8 | -191.9 | 1:00 |
| 0.2000 | -37.6 | -248.1 | 1:30 |
| 0.3000 | -55.9 | -182.9 | 2:00 |
| 0.4000 | -70.2 | -143.5 | 2:30 |
| 0.5000 | -83.3 | -130.5 | 3:00 |
| 0.6000 | -98.5 | -151.9 | 3:30 |
| 0.7000 | -120.3 | -218.4 | 4:00 |
| 0.8000 | -153.6 | -332.8 | 4:30 |
| 0.9000 | -195.3 | -416.8 | 5:00 |
| 1.0000 | -236.1 | -408.4 | 5:30 |
| 1.1000 | -271.5 | -354.1 | 6:00 |

| Mit TBAOH: AN = 1.73 mg/g | | | |
|---------------------------|---------------|----------------------------|-------------|
| Volume mL | Signal mV | 1 st Der. mV/mL | Time min:s |
| 0.0000 | 14.9 | | 0:30 |
| 0.1000 | -39.7 | -545.4 | 1:00 |
| 0.2000 | -68.5 | -288.2 | 1:30 |
| 0.3000 | -87.0 | -184.8 | 2:00 |
| 0.4000 | -103.7 | -166.7 | 2:30 |
| 0.5000 | -127.5 | -238.4 | 3:00 |
| 0.6000 | -174.0 | -464.6 | 3:30 |
| 0.7000 | -264.8 | -908.6 | 4:00 |
| 0.8000 | -368.9 | -1040.4 | 4:30 |
| 0.9000 | -448.5 | -796.1 | 5:00 |
| 1.0000 | -495.8 | -473.7 | 5:30 |

Pipetting with the Liquid Handler: flexibly, accurately and automatically



Dr. H.-J. Muhr

Can we titrate a large number of oil samples every day to determine the acid number without weighing by simply placing the samples in beakers on the sample changer and leaving everything else to an automated pipetting and titration system? Can that possibly work in practice? Read how it is done!

Pipetting or weighing?

In sample preparation, this is often a crucial decision that many laboratory managers have to make in analytical quality control. The answer is obvious with solids, but not so clear with liquids. In this case, additional questions arise such as:

- Is the liquid suitable for pipetting due to its viscosity?
- Does the mass accuracy achieved through pipetting satisfy analytical quality requirements or is weighing unbeatable in this respect?
- Which of the two techniques can be most easily and economically automated?

To get a detailed answer to these questions, let us visit the quality control laboratory of a petrochemical company.

How can you measure out very many samples, accurately, reliably and efficiently?

This laboratory analyzes up to 115,000 used oil samples (marine diesel engine oils) every year. Of these, 55,000 samples are titrated to determine the acid or base number. Since this is a contract laboratory, particular attention has to be paid to the reliability of the analyses. To cope with the large number of incoming samples, there is no alternative but to use automated titration. The laboratory manager recently had to decide how the oil samples could be most efficiently measured out without risking the accuracy of the results. Weighing using an analytical balance seemed to her to be a good solu-

tion because of accuracy that could be achieved. However, she had doubts concerning the practicability and probability of errors. In addition to the unambiguous sample identification, the weight of the sample must also be transmitted to the titrator, which can lead to mistakes, especially when working under pressure. Weighing a sample is an additional step that is manually performed and is another possible source of error. An not least, the individual weighing steps for such a large number of samples add up to a significant amount of time.

For these reasons, the laboratory manager looked around for alternative solutions. Since the oil samples were all liquids, pipetting seemed an obvious choice. In this case, however, the following additional conditions must be satisfied:

- The laboratory assistant should only have to put an approximate amount of the sample into a beaker. The pipetting system must then automatically take the right amount of sample from the beaker without the laboratory assistant having to do anything.



Figure 1:
The automated
Titration system
T90, Sample
Handler and Liquid
Handler.

- The acid number of most oil samples varies from 0.05 to 1 mg KOH/g, but values between 5 to 8 mg KOH/g also have to be determined. This means that the pipetting system must be able to accurately and precisely measure out the optimum quantity of sample.
- The viscosity of the oil samples range from “watery/free flowing” (15 Cst at 40 °C) up to “bitumen-like/viscous” (1000 Cst at 40 °C). The pipetting system must be able to adapt to the individual rheological properties of the oil samples by using corresponding aspiration and discharge rates.
- The acid number of the oil sample is calculated from the sample weight and the titrant consumption up to the endpoint of the base titration. To calculate the sample weight, the pipetted sample volume has to be multiplied by the density of each oil sample. It turns out that the density of the oil samples hardly varies. This means a constant value of 0.89 g/cm³ can be used for all samples. Exceptions are particularly viscous used oils with acid numbers of less than 0.1 mg KOH/g. Such oils cannot however be pipetted, so that in these cases the classical weighing technique would be used.
- Up to 60 to 80 samples daily must be reliably, and in unattended operation, automatically titrated. The total analysis time per sample should not exceed 6 minutes.

Due to the diversity of the samples, the requirements outlined above are a major challenge for an automated system, both from the point of view of sample preparation and the titration.

The solution: The combination of the Liquid Handler and the Sample Handler

To meet the laboratory manager’s requirements, we proposed an automated titration system consisting of the following components:

- Pipetting: Liquid Handler
- Sample changer: direct 80 Sample Handler
- Titrator: T90 Excellence titrator
- Data processing: LabX pro titration PC software

In the following sections, we will briefly describe the automation sequences. The TAN titration is performed according to the ASTM 664 standard test method. For details on this and for additional tips on performing the TAN titration, we recommend reading the article “Determination of the acid number (TAN) – Tips and Tricks”, which appears in this issue of UserCom.

The sample changer

The TAN titration is performed using a direct 80 Sample Handler (see Fig. 1). A detailed description of the Sample Handler xyz-sample changer system can be found in UserCom 13. The rack on the Sample Handler holds a maximum of 80 titration beakers. Four beakers are placed at special positions (Fig. 2).

At three positions (C1, C2, C3) the beakers are filled with conditioning solutions of increasing polarity (toluene – isopropanol – water); the fourth (SR) is used for the preparation and cleaning of the pi-

pette, the sensor and inserts as well as for the titration.

This titration beaker itself is a masterpiece made of glass with a rather special construction (Fig. 3):

The beaker contains an integrated drainage system connected to an SP250 peristaltic pump. This pumps the titrated sample solution or rinsing liquid to waste without leaving any residues. The beaker is thus clean and ready for the next analysis after each titration and sample carryover is eliminated.

A total of 75 beakers is available for oil samples. These can be divided into individual or several different series and processed according to the particular titration method. The long DGi113-SCS sensor was developed for non-aqueous base-titration on the direct 80 Sample Handler and the Rondo 30 (see UserCom 13). In contrast to the otherwise identical DGi113-SC sensor, it has no ground-glass joint so it can easily be positioned and fixed on the titration head using a standard adapter.

Accurate measurement of the sample

The basic procedure is as follows: The laboratory assistant fills a small amount of the oil sample into a beaker up to fill-height of about 15 mm and places it at any position on the sample rack. The fill-height ensures that there is sufficient sample for taking a sample with the Liquid Handler and that the distance between the sample and the titration inserts (sensor, stirrer, dosing and drain tubing) is sufficiently large. This is necessary because the inserts are fixed to the titration head and have to be introduced into the beaker to take a sample. The pipette, however, dips into the sample because the sample has to be aspirated into pipette by the Liquid Handler without introducing air bubbles.

The Liquid Handler then takes a defined aliquot from the oil sample. The sample aliquot is transferred to the titration bea-

Figure 2:
The layout of the 80-position rack of the Sample Handlers with special beakers.

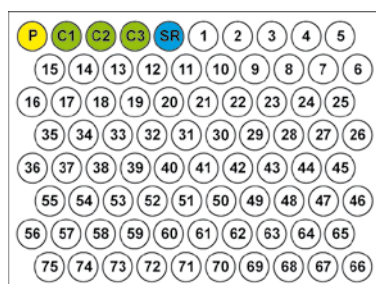
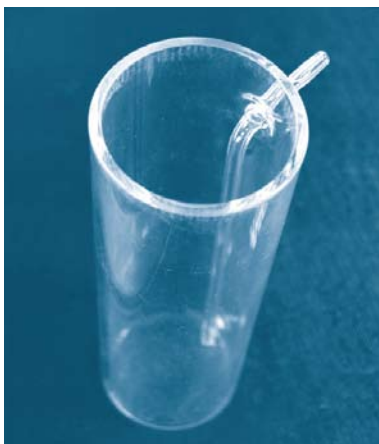


Figure 3:
The Sample Handler titration beaker with integrated drainage system.



ker at the fixed “SR” position containing the solvent mixture and simultaneously dissolves. Using this pipetting technique, the oil sample is only in the pipette and the aspiration tube. This eliminates possible contamination of the burette of the Liquid Handler by the oil sample. The pipetting process is shown in detail in the diagram in Figure 4. The oil sample is aspirated by means of a tube fixed to the titration head that serves as a pipette. The pipette is connected by a tube to the 6-way valve of the Liquid Handler.

The following section illustrates two features of the Liquid Handler, both of which are very important for the type of sample measurement required by the QC laboratory manager:

- Flexibility
- Accuracy and repeatability

Flexible pipetting

The sample volume to be pipetted is defined in the method as a formula, for example $f \cdot 2$. The factor f is a sample-specific factor. It allows the pipetted volume for each sample to be individually defined in the sample series editor of the Sample Handler Manager according to the expected acid number, without having to change the method.

The higher the viscosity of the sample, the slower should it be aspirated into the pipette or sample tube. This is achieved by setting the aspiration rate in the range 1.5 mL/min to 150 mL/min. In addition, especially with highly viscous samples, sufficient time should be allowed after aspirating the defined volume for the sample to flow completely into the volume in the dosing tip or tube defined by the burette. These two parameters can also be individually calculated for each sample using the factor f .

The relatively time-consuming pipetting process can be optimized to satisfy the requirement of 6 minutes analysis time per sample through an intelligent choice of the calculation functions. Further-

more, the method ensures that the optimum sample volume is pipetted for each acid number.

Accurate, repeatable pipetting

The dosing and pipetting accuracy of the Liquid Handler is excellent. Metrological measurements confirmed that the dosing accuracy always satisfied the requirements of the ISO 8655-3 standard for burette dosing systems independent of the aspirated dispensed liquid volume. The volume is always highly accurate irrespective of whether 10, 20, 100, 1000 or 50,000 μL is dosed or pipetted (see Tables 1 and 2).

The automated process

Prior to the titration, the DGi113-SCS sensor is calibrated with pH 4 and 11 buffers. The blank value of the solvent mixture (toluene/isopropanol/water 500/495/5) is then determined in a threefold determination by titration with 0.1M KOH in isopropanol and stored as an auxiliary value in the T90 Excellence titrator setup. An dosed volume of exactly 50 mL solvent mixture from the Liquid Handler

is used for the blank value and sample determination.

After the sample pipetting process described above, the titration is performed in the glass titration beaker. When the titration is completed, the titration beaker is drained, the titration inserts cleaned and the sensor immersed consecutively in the three conditioning solutions. The next sample is then measured. The process of calibration, blank value determination, and titration can be programmed with the Sample Handler Manager software as a sample series sequence and run automatically (see UserCom 13).

Measures for reliably running the sample series Cleaning and waste disposal

The titration is performed to an endpoint at pH 11, the acid number of the sample is calculated taking into account the blank value of the solvent mixture, and the titrated solution is drained to waste. Sensor and inserts are repeatedly cleaned with the solvent mixture using the PowerShower™ rinsing system and

| Nominal volume [mL] | Measured volume * [mL] | Absolute deviation [μL] | Standard deviation [μL] | Dosing accuracy [%] |
|---------------------|------------------------|--------------------------------------|--------------------------------------|---------------------|
| 0.05 | 0.05022 | 0.22844 | 0.28883 | 0.4569 |
| 0.20 | 0.20032 | 0.31897 | 0.92769 | 0.1595 |
| 0.50 | 0.50002 | 0.02156 | 0.70194 | 0.0043 |
| 1.00 | 0.99965 | -0.34705 | 1.26773 | -0.0347 |
| 5.00 | 4.9977 | -2.29599 | 3.81381 | -0.0459 |
| 10.00 | 9.99413 | -5.86388 | 6.20353 | -0.0587 |

Table 1: Values obtained for the dosing accuracy of the Liquid Handler based on a full burette, that is, filled with 50 mL deionized and degassed water. Dosing was repeated 10 times each time.

| Nominal volume [mL] | Measured volume * [mL] | Absolute deviation [μL] | Standard deviation [μL] | Dosing accuracy [%] |
|---------------------|------------------------|--------------------------------------|--------------------------------------|---------------------|
| 0.05 | 0.04979 | -0.20265 | 0.04763 | -0.4053 |
| 0.20 | 0.19919 | -0.80862 | 2.8103 | -0.4053 |
| 0.50 | 0.49936 | -0.63074 | 0.2746 | -0.1262 |
| 1.00 | 0.99841 | -1.59039 | 0.93667 | -0.1591 |
| 5.00 | 4.99677 | -3.22203 | 4.94846 | -0.0645 |
| 10.00 | 9.99239 | -7.60825 | 4.8697 | -0.0761 |
| 15.00 | 14.98728 | -12.71645 | 5.9108 | -0.0848 |
| 30.00 | 29.9774 | -22.51391 | 10.7234 | -0.0751 |
| 50.00 | 49.96175 | -38.24181 | 5.05866 | -0.0765 |

Table 2: The measured dosing accuracies based on an empty burette, that is, the aspirated volume was immediately dosed.

* Mean of ten measurements

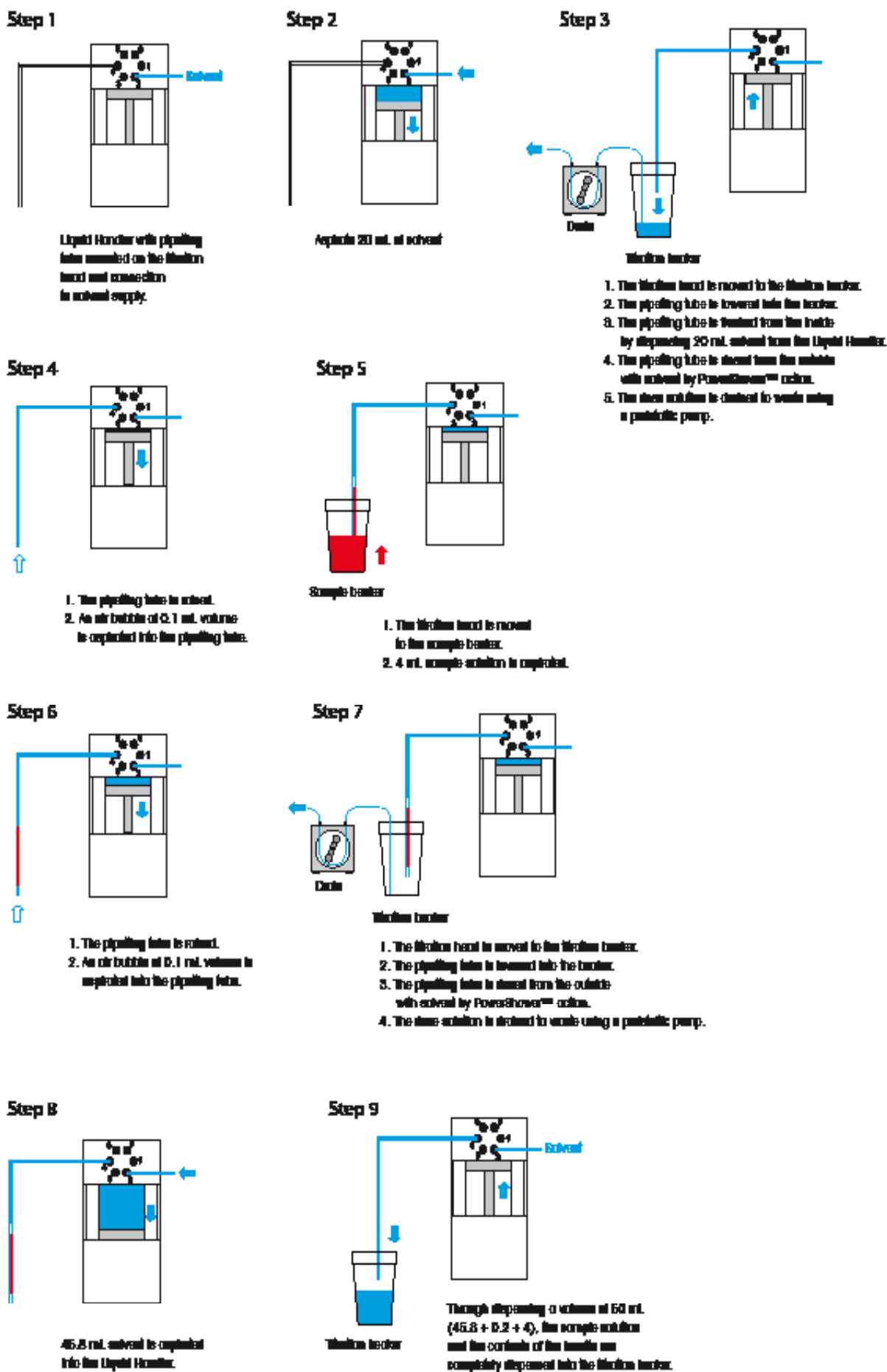


Figure 4: Schematic diagram of the pipetting process of the Sample Handler.

the rinsing solution is simultaneously drained to waste. This ensures that even sticky residues are completely removed and that no sample carryover or deterioration of the sensor performance occurs through a blocked diaphragm.

Since the solvent mixture is sent to a waste container under the fume hood after each titration and cleaning process, the sample rack of the Sample Handler is quasi “solvent free”. This prevents contamination of the laboratory environment. The beakers containing the oil samples are properly disposed of after aliquoting.

Sensor

After the titration, the sensor is conditioned for a certain time with stirring in the solvent mixture in conditioning beaker C1, in isopropanol in C2, and finally in water in C3. This provides additional cleaning and regeneration of the hydrated layer of the pH-sensitive membrane of the sensor. The sensor is therefore effectively maintained during the entire sample series. This increases the integrity of results and helps to lengthen sensor lifetime. Before pipetting the next sample, the titration beaker is rinsed with the solvent mixture to remove any adhering water.

Warnings

The conditional method functions of the T90 Excellence titrator offer possibilities that help to ensure that large sample series can be reliably and safely analysed. For example, the process can be in-

terrupted after a predefined number of samples by a warning message telling the user that the conditioning solutions should be replaced. This ensures the quality of the “integrated sensor maintenance” described above.

Securely fixed inserts

When so many samples as in this QC laboratory are analyzed in unattended operation, the individual processes must be completely safe. The dosing and drain tubes are fixed to the pipette as shown in Figure 5 to make sure that they are always safely guided to the beakers and do not get tangled up with the propeller stirrer or the sensor – a simple but very effective measure.

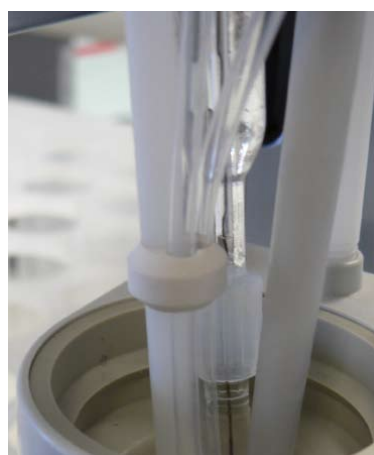
Conclusions

The automated Titration system consisting of the T90 – Sample Handler – Liquid Handler fully satisfies the requirements of the laboratory manager. Thanks to the great flexibility and accuracy of the Liquid Handler, she can have complete confidence and trust in the special type of sample dosing used for the oil samples. The robust construction of the system guarantees trouble-free operation even when large numbers of samples have to be processed. The design of the Sample Handler sample changer is very impressive due its great flexibility. Even oil samples that have to be weighed directly into the titration beaker because of their high viscosity can be titrated.

The large amount of incoming data is safely managed by the LabX titration



Figure 5:
The dosing and drain tubes fixed to the pipette.



software. In a later expansion stage, a LIMS system will be connected via LabX connect which is already used in the Sample Handler Manager. The aim here is to prepare the sample series on the LIMS and to transmit the results directly to it.

Since it was installed, the system operates reliably and is well-liked by laboratory staff because it is easy to operate. We can now answer the initial question: Clearly, pipetting with the Liquid Handler is very definitely a real alternative to weighing!

Good Titration Practice™ – innovative service solutions for correct titration analyses



Dr. H.-J. Muhr

METTLER TOLEDO has been supplying innovative products to industry and laboratories for more than 60 years. But we know it is not sufficient to just offer a product. Our commitment is to provide comprehensive, user-specific solutions, tailor-made for the particular application. That is why customer service and after-sales support are not just empty words. METTLER TOLEDO's high value services and service products help you maintain Good Titration Practice™ so that you can minimize risks and preserve the value of your investment.

Every measurement involves risks that can affect the quality of your products. When you use a titrator, you can avoid making measurement errors by following the Good Titration Practice™ guidelines. Remember, that only trained operators and properly maintained and calibrated titrators can guarantee that the results of a titration analysis are correct. The qualification packages and supplementary services such as calibration and preventive maintenance are professional solutions that METTLER TOLEDO offers to ensure correct measurements over the whole lifecycle of your titrator.

of product. The official regulations are not only mandatory for pharmaceutical and biotechnology companies operating in a regulated environment. Due to the increasing regulatory demands, all ISO certified manufacturers recognize the necessity for establishing and complying with quality management systems. Product quality is continuously monitored on a daily basis using analytical equipment. However, one of the major challenges is to fulfill the regulatory requirements. Precise and error-free measurements are absolutely essential. Errors leading to wrong results can affect product quality and in the worst case even endanger the safety of consumers. Let us analyze just two typical examples from titration.

The Karl Fischer titration is routinely used in laboratories for the determination of water content. A predefined water content in a product protects it against microbiological contamination and ensures that it has the right physical properties such as elasticity, softness, stability and resilience. Titration has even greater importance in the determination of concentration: an error here can result in the content of an active drug substance being too high or too low, which could endanger the health or even life of a patient.

Your needs

METTLER TOLEDO is continuously developing new service solutions that cover a broad range of needs. Do your regulatory

requirements demand full traceability supported by detailed documentation? Or do you just want a professional installation followed by immediate use of your titrator? A qualification by METTLER TOLEDO and the outstanding benefits of these services will cover all your various needs (see Tab. 1).

Why titrator qualification?

According to numerous quality standards and regulations, all manufacturing processes and analytical methods need to be validated. At the same time, the analytical equipment itself requires qualification (IQ/OQ). To help customers comply with these requirements, METTLER TOLEDO has created several different qualification packages for its titrators:

- EQPac and IPac packages for Excellence titrators
- EQPac and IPac packages for Compact KF titrators
- IPac packages for Compact G20 titrator and LabX PC software

The METTLER TOLEDO IPac and EQPac Qualification Packages offer professional solutions tailor-made for your needs and titrator model.

What are IPac and EQPac?

IPacs (Initial Qualification Packages) are the simplest and fastest solutions for a professional and regulatory compliant instrument qualification. The Installation and Operational Qualification (IQ/OQ) is performed by fully authorized, factory-trained service personnel who hand over

Figure 1: Karl Fischer Compact titrator with IPac documentation.



Quality assurance – a constant challenge

Manufacturers of goods for end-user consumption have to guarantee that their products are safe and of consistent quality. This can be ensured by complying with the specific quality management standards for the particular type

the qualification documentation at the end of the installation. Instrument start-up has never been easier thanks to IPac – after basic user familiarization the user can immediately start working with the titrator. And if no qualification was done before, IPac offers the possibility of requalification of an installed system.



The EQPac (Equipment Qualification Package) service solutions are specifically designed to address requirements for compliance in today's demanding regulatory environment. They include the qualification documentation for regulatory compliance, professional qualification, and the on-site calibration service. EQPac not only qualifies your titrator. You also get a detailed logbook that monitors all the events that occur in connection with the titrator and its use during its entire life cycle through to its disposal. This comprehensive qualification solution means you should not have any worries about not meeting compliance requirements (Fig. 2).

Only a calibrated titrator gives correct measurement results

The main benefit of using qualified calibrated instruments is the confidence you have that your titrator provides correct measurements over its entire life cycle. Regular verification of the instrument calibration is not only required by regulatory authorities. It is one of the

| User need | Service product |
|--|---|
| Regulatory compliance | Comprehensive services and documentation by professionally trained and fully authorized service specialists |
| Documentation relating to the requirements | Proven qualification protocols |
| Precise and reliable results | General system suitability test based on standards |
| Full traceability of results | Defined routine tests (PQ) |
| Constant high performance | Defined routine procedures for calibration |
| Qualified user and immediate operation of instrument | User training |
| Calibration and certification | Periodical calibration of the instrument (with certification) by authorized service specialists |
| Support and predictable maintenance costs | Defined service plan: trouble-free operation of the titrator and maintenance costs under control |

basic requirements of Good Titration Practice™ in which annual calibration and certification of titrators is recommended (Fig. 3).

After-sales support

Professional on-site training gives you the confidence and expertise you need to operate the titrator and prevent instrument failure through operating errors. However, there is a lot more that can be done to ensure error-free operation of the titrator. Preventive maintenance (preferably once a year) reduces the risk of instrument failure to a minimum. Authorized METTLER TOLEDO service specialists perform the preventive maintenance according to the requested schedule using a predefined maintenance checklist. The wide range of titrator services and support offered by METTLER TOLEDO ensures trouble-free titrator operation, maximum instrument uptime, correctness and traceability of results, and regulatory compliance.



Table 1: IQ/OQ solutions for titrators fulfill practically all requirements and offer important advantages.

Figure 2: Titration Excellence titrator with EQPac binder.



Figure 3: Calibration measurements on the compact Karl Fischer titrator.

New possibilities for titration automation – efficient and secure

Automation of sample analyses not only saves time but also increases security. Since the samples are automatically analyzed, the user can attend to other tasks. Security and repeatability increase because each sample is analyzed in exactly the same way and the influence of different operators is excluded. METTLER TOLEDO offers ingenious new possibilities to automate your titration analyses and further increase your efficiency and security.

Excellence further improved: Titration Excellence version 3.1

Version 3.1 of the successful T70 and T90 Excellence titrators offers a new dimension in flexible automation and at the same time unsurpassed ease of use:

- Full support of the new Liquid Handler. The T90 can even control two Liquid Handlers independently of one another. This allows two highly automated processes to run independently of one another or even be synchronized.
- Connection of other instruments such as density/refractive index- or turbidimeters via an intelligent RS interface. For example, results can be imported and exported, which means that the Excellence titrator is the center of a multi-parameter measurement system.

- The Continuous mode allows a sample series to run indefinitely. Samples are simply placed in the right position and the measurement automatically started. In combination with the Liquid Handler, automatic sample aliquoting can even be carried out, for example via an RS command or time dependent – without the user having to do anything.
- Many other intelligent improvements make the Excellence titrators even simpler, and more efficient and secure.

Existing Excellence titrators can be easily updated to Version 3.1 – METTLER TOLEDO will be pleased to help you.

Automatic sampling for titration: Liquid Handler

The automatic dosing system opens up new possibilities in automated titration because it solves an important problem in analysis, namely the repeatable accurate aliquoting of a liquid or sample solution:

- Flexible dosing or pipetting of samples occurs automatically under control of the titrator method.
- The robust Liquid Handler and the Excellence titrators allow the most varied automation applications to be easily realized.

Read the article “Pipetting with the Liquid Handler” in this issue of UserCom!

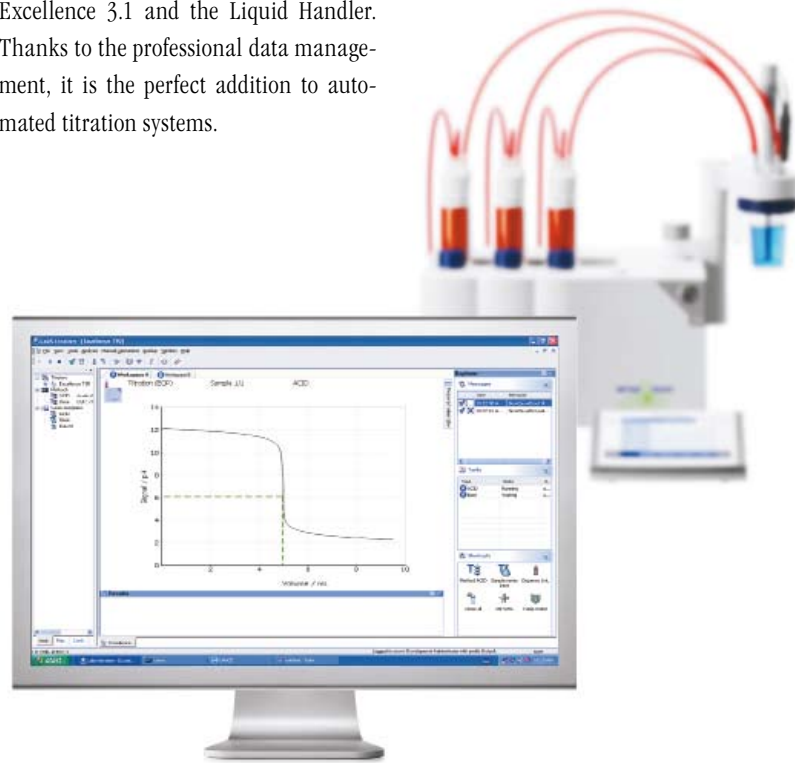


**Smart–Smarter–Smartcodes™:
LabX titration version 3.1**

The successful PC software controls all Excellence and Compact titrators and offers further benefits, for example with regard to automated systems:

- The samples labeled with Smartcodes™ can be simply placed on the Rondo sample changer. LabX pro automatically sorts out the Smartcodes™ and starts the right titration method. Mix-ups are prevented and security is further increased.
- LabX Instruction in combination with the T90 Excellence titrator allows different actions to be automatically performed on the PC of the titration. For example, if a result limit is exceeded, the PC can automatically send an e-mail.

LabX titration 3.1 fully supports Titration Excellence 3.1 and the Liquid Handler. Thanks to the professional data management, it is the perfect addition to automated titration systems.



The automatic titration system in action: T90 Excellence titrator, Rondo 20 sample changer, Liquid Handler and LabX pro titration.

One Click Titration – simple and dependable

The new G20 Compact titrator combines simplicity and dependability in one instrument. The G20 is especially designed for basic applications and is very easy to operate thanks to the unique One Click user interface and the Plug & Play concept of accessories. Up to nine samples can be automated using the Rondolino sample changer. The LabX light titration PC software offers secure database archiving and comprehensive result management possibilities.

One Click Titration

The large color touchscreen with the One Click user interface is easy to understand and you will be able to familiarize yourself in no time at all. Each user has his/her own homescreen with customized language selection and shortcut keys, which enable routine procedures to be executed with just one push of a button.

Reliable operation and fast installation

Both the titrant and the sensor are automatically detected upon connection to the titrator and all relevant data are stored on the burette or sensor chip. Errors occurring during installation of resources are now a thing of the past. Plug & Play – safe titration couldn't be simpler.

Compact and simple automation

The automatic Rondolino titration stand is easy to install and uses minimal bench space. Individual samples and series of up to nine samples are processed quickly and safely.

Working safely with chemicals

The Solvent Manager protects the user against contact with liquid chemicals. Fully controlled by the titrator, waste reagents can be pumped out completely after titration without intervention by the user.

Dependable results

thanks to the sensor test

The GLP-conform sensor test ensures that the sensor complies with applicable specifications prior to each titration. This increases the reliability and accuracy of analyses.

Data storage in PC Software

LabX light titration PC software offers full control of the G20, safe database archiving, efficient management of results with graphic monitoring and individual search filters. The convenient Windows-based user interface and the integrated online help system enable the user to operate the G20 via LabX light titration in a reliable and safe manner.



SevenGo Duo™ – safety and reliability thanks to intelligent multi-parameter instruments

The three new portable multi-parameter instruments offer functions for the determination of pH, conductivity, dissolved oxygen (DO) and selective ion concentrations (ISE). The intelligent sensor management system (ISM®) and the multi-language menu guidance offer the user a maximum level of security for more reliable results and optimum convenience in use. The robust, waterproof housing of the SevenGo Duo™ is suited for harsh working environments and can also be used in the laboratory.

Portfolio

- The SG23 is a robust dual-channel pH and conductivity instrument for routine tasks.
- The SG78 professional multi-parameter instrument combines all functions of pH and conductivity measurement with a complete mode for the determination of ion concentration.
- The SG68 professional multi-parameter instrument measures important parameters such as pH, ions and dissolved oxygen.

Powerful security functions and intuitive operation

- The full-text display of the SG68 and the SG78 with menu guidance in ten languages ensures user-friendly intuitive operation.
- Comprehensive security functions such as calibration reminder, PIN-protection, monitoring limit values as well as routine and expert modes.
- GLP functions for storing user ID, sample ID, sensor ID, date/time.

Avoid errors and save time with the Intelligent Sensor Management system (ISM®)

- Correct identification of the sensor: sensor type and serial number are automatically recognized and displayed.
- Calibration data including date and time are stored in the sensor. This function provides additional safety when the sensor is transferred to another instrument.

- You can view the last five calibration data records at any time and the maximum temperature to which the sensor was exposed in order to optimize the readiness of the instrument.
- The factory certificate can be checked and printed at any time.

Professional accessories for professional instruments

- All the important sensors for the measurement of pH, conductivity and dissolved oxygen are now available in ISM® versions.
- The practical rubber holster provides optimum impact protection.

- The robust and compact “Field Compact Case” protects your SevenGo Duo™ equipment during transport and provides space for all important accessories, cables and sensors.

Further information

Visit our 3D-simulator of the SevenGo Duo pro™ SG78 at

www.moreabout7.com



Publications

The application chemists of the Analytical Chemistry market support group have prepared several publications and a series of application brochures to support customers in their routine work in the laboratory. Each brochure is dedicated either to a particular branch of industry (such as paper, petroleum and beverages), a particular titrator or a specific analysis technique. The following list shows all the publications together with their order numbers. They are available from your local METTLER TOLEDO marketing organization.

| Publications, reprints and applications | German | English |
|---|----------|----------|
| Basics of Titration | 51725007 | 51725008 |
| Fundamentals of Titration | 704152 | 704153 |
| Applications Brochure KF Lebensmittel, Getränke, Kosmetika | 724477 | |
| Applications Brochure 2 Various Methods | 724556 | 724557 |
| Applications Brochure 5 Determination in Water | 51724633 | 51724634 |
| Applications Brochure 6 Direct measurement with ISE | 51724645 | 51724646 |
| Applications Brochure 7 Incremental Techniques with ISE | 51724647 | 51724648 |
| Applications Brochure 8 Standardization of titrants I | 51724649 | 51724650 |
| Applications Brochure 9 Standardization of titrants II | 51724651 | 51724652 |
| Applications Brochure 10 Selected METTLER TOLEDO methods for Specialty Chemicals Market Segment | | 51725073 |
| Applications Brochure 11 Gran evaluation DL7x | 51724676 | 51724677 |
| Applications Brochure 12 Selected Applications DL50 | 51724764 | 51724765 |
| Applications Brochure 13 Nitrogen Determination by Kjeldahl | 51724768 | 51724769 |
| Applications Brochure 14 GLP in the Titration Lab | 51724907 | 51724908 |
| Applications Brochure 15 Guidelines for Result Check | 51724909 | 51724910 |
| Applications Brochure 16 Validation of Titration Methods | 51724911 | 51724912 |
| Applications Brochure 17 Memory card "Pulp and paper" | | 51724915 |
| Applications Brochure 18 Memory card "Standardization of titrants" | 51724916 | 51724917 |
| Applications Brochure 19 Memory card "Determination in Beverages" | 51725012 | 51725013 |
| Applications Brochure 20 Petroleum | | 51725020 |
| Applications Brochure 22 Surfactant Titration | 51725014 | 51725015 |
| Applications Brochure 23 KF Titration with DL5x | | 51725023 |
| Applications Brochure 24 Edible oil and fat | | 51725054 |
| Applications Brochure 25 Pharmaceutical Industry | 51710070 | 51710071 |
| Applications Brochure 26 METTLER TOLEDO Titrators DL31/38 * | 51709854 | 51709855 |
| Applications Brochure 27 KF Titration with Homogenizer | | 51725053 |
| Applications Brochure 32 METTLER TOLEDO Titrators DL32/39 | 51725059 | 51725060 |
| Applications Brochure 33 METTLER methods for DL15, DL22 F&B and DL28 | | 51725065 |
| Applications Brochure 34 Selected METTLER TOLEDO Methods for Titration Excellence T50, T70, T90 | | 51725066 |
| Applications Brochure 36 Selected METTLER TOLEDO Methods for Biofuel Analysis | | 51725070 |
| Applications Brochure 37 Selected Water Analysis Methods for Titration Excellence line | | 51725072 |
| Applications Brochure 38 Karl Fischer methods for water content determination | | 51725075 |
| Applications Brochure 40 Automatic Pipetting and Dosing with Liquid Handler | | 51725111 |

* Also available in French (51709856), Spanish (51709857) and Italian (51709858)

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