New approaches in density measurement

Dr Barbara Klug-Santner and Siegfried Hold, Anton Paar GmbH, www.anton-paar.com

As a leader in the development of digital density measurement, Anton Paar knows that new developments in density determination are of great importance in many industries. One major milestone is the patented 'Pulsed Excitation Method'.

Before digital density meters conquered the market, density was determined with hydrometers and pycnometers. Companies that could afford it would employ the pricier hydrostatic balances. Apart from the high required sample volume, density measurement was tedious and required extensive cleaning. Additionally, there was an ever-present risk of breaking the glassware. A new method was needed.

This was when the measuring cell of Anton Paar's density meters, a U-shaped glass tube came into the picture. The cell is electronically excited and the frequency of the cell's oscillation is measured. The oscillation depend on the filled-in liquid, gaseous, or paste-like sample, and correlate directly with the density of the respective sample. Thus, a fast, repeatable, and precise method was found that gets by with very small sample volumes of only a few millilitres. Today, this way of density measurement has become indispensable in the quality control in countless fields of application.

Digital density measurement enabled a measuring accuracy that could be increased to the fifth decimal place. In order to facilitate daily handling of the instruments numerous helpful developments were introduced. However, the technology itself remained largely unchanged until this way of density measurement no longer met contemporary requirements. The time had come to renew this technology according to present customer demands.

In 2015 Anton Paar set the tone for the future of digital density measurement.

A group of young and ambitious developers began to rethink this technology. The team recognised the weak points in the excitation electronics which were used to excite the U-tube and to measure its oscillating frequency and eventually created an entirely new measuring method: the patented 'Pulsed Excitation Method' (AT 514620 (B1), see *Figure 1*). It is now employed in the laboratory density meters DMA 501, DMA 1001, and the DMA M series (see *Figure 2*).

This novelty was a milestone in the development of density meters and enabled fundamental improvements of the entire measuring principle. Previously the commonly employed method was a forced oscillation that would be maintained during a measurement. If the measured frequency and the resonance frequency of the U-tube were different, the exciting frequency was readjusted until it was identical to the resonance frequency. Therefore, the system was never really in equilibrium, but in a constant state of alignment. This, in turn, represented an influencing factor that had to be compensated.

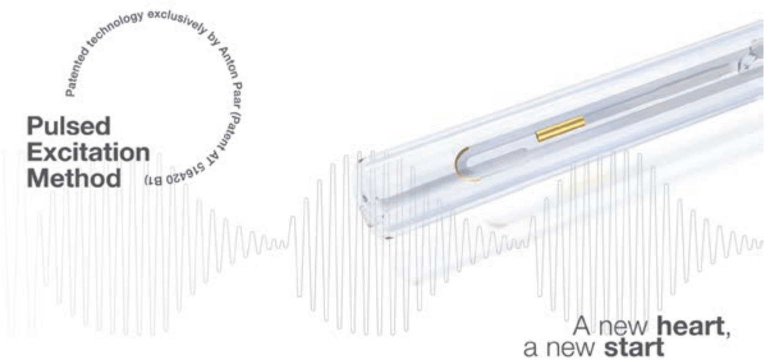

Figure 1. Excitation and fade-out with the 'Pulsed Excitation Method'.

With the new 'Pulsed Excitation Method', however, the U-tube is excited to oscillate with a series of impulses (*Figure 1*) until a constant amplitude is achieved. Then these impulses are stopped and the fade-out properties of the U-tube are monitored. During the fade-out period, the amplitude is measured precisely before the next excitation impulse is initiated. Both excitation and fade-out are repeated periodically.

The oscillation characteristics of the U-tube are influenced by the density, temperature, and viscosity of the filled-in sample. Therefore, this new method gathers much more raw data and leads to an even better way of describing the oscillation properties. Since the U-tube is no longer influenced in its resonance frequency and the fade-out oscillations are undisturbed this is the only correct way to determine the density accurately and precisely.

In order to convert the obtained raw data into understandable information new algorithms were developed, opening up new possibilities in the field of density measurement. They offer a twofold better viscosity correction when measuring highly viscous samples because the viscosity of a sample adds an extra damping effect to the oscillations of the measuring cell, creating an influencing factor that requires correction. Additionally, this new method can even determine the viscosity of Newtonian liquids with an accuracy of 5%. Simultaneous density and viscosity measurement in the range from 10 mPa.s to 3,000 mPa.s allows an improved recognition and compensation of the viscosity's influence on the density result. This is why density meters operating with the 'Pulsed Excitation Method' deliver more accurate results. Viscosity correction is now also applicable for density meters with a metallic U-tube like in DMA 4200 M.

Figure 2. Anton Paar's broad portfolio of digital density meters.

Correct sample filling for correct results

In order to obtain precise and accurate results the sample filling has to be done seamlessly. The FillingCheck function, a means of recognising inhomogeneities and gas bubbles in the measuring cell, has been noticeably improved over the years and is now able to react even more reliably thanks to the 'Pulsed Excitation Method'. The correct functioning and state of the glass measuring cell can now also be monitored continuously. Thus, on top of their robust and reliable construction and design, Anton Paar density meters score with a unique repeatability of better than $1*10^{-6}$ g/cm³.

The DMA 4200 M density meter with its measuring cell made of metal is especially suitable for petroleum measurements due to the fact that it works up to 200°C and 500 bar. It was developed to cope with samples like asphalt and waxes which are liquefied by high temperatures in order to be in a suitable aggregate state for density measurements. The 'Pulsed Excitation Method' makes it possible for the first time to also use the FillingCheck function for metallic measuring cells.

DMA 4200 M is factory-adjusted prior to delivery and ready for use as soon as the desired measuring temperature between 0°C and 150°C has been selected.

It's the oscillation that matters

Today, Anton Paar equips all new benchtop density meters with a so-called Y-oscillator (*Figure 3a*). This new design eliminates viscosity constraints over the entire measuring range, allows the reliable detection of particles and gas bubbles, and achieves an accuracy of up to 0.000007 g/cm³.

Some other density meters on the market have U-tubes that oscillate in the X-direction (*Figure 3b*). However, X-oscillators are proven to be subject to technical limitations such as limited accuracy in the case of viscous samples and a high error probability in the case of inhomogeneous samples or if there are particles and gas bubbles in the sample. This is why X-oscillators made from glass are limited to an accuracy of only 0.001 g/cm³.

Figure 3a. Working principle of a Y-oscillator.

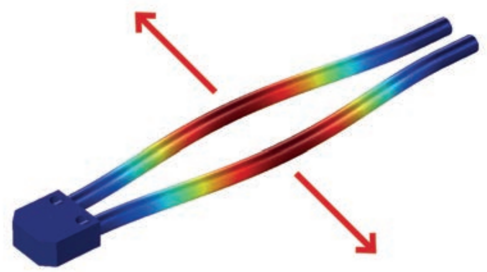

Figure 3b. Working principle of an X-oscillator.

However, the Anton Paar engineering team wanted to meet its customers halfway: In order to develop a measuring instrument that was accurate to the fourth decimal place and affordable at the same time, they developed the Y-oscillator for the DMA 1001 density meter. Thanks to this oscillator and its option for a one-point adjustment, the reference oscillator was rendered obsolete. The measured oscillation period of the water-filled measuring cell is compared to the obtained result of the prior adjustment and, based on the obtained data, a possible drift is compensated automatically. This means that the instrument is adjusted twice as fast and it takes only half the effort that other density meters require to reach full operational status. The density meters DMA 501 and DMA 1001 even indicate when there are suboptimal ambient conditions like humidity and temperature and give recommendations on how to achieve optimum life expectancy of the instrument.

The portable density meter DMA 35, the only density meter available in intrinsically safe versions suitable for use in hazardous areas (DMA 35 Ex and DMA 35 Ex Petrol), offers the patented feature of an exchangeable glass measuring cell (AT 516421 (B1)). Thus, a broken glass cell does not halt measurement processes anymore: The exchange of the measuring cell can be carried out by the user directly on-site. Additionally, the gesture control enables measurements to be initiated or stopped by defined movements of the instrument. This feature is especially useful as one hand remains free and represents an additional safety aspect if measurements are carried out in places that are difficult to access.

Table 1 indicates to what extent the technical configuration of Anton Paar's individual density meters meet the needs of a vast number of customer applications. The ISO 17025 accreditation certifies that Anton Paar density meters are not only produced according to the highest quality standards, they can also be traceably calibrated with certified reference materials.

Table 1. Anton Paar density meters and their characteristics.

Features	**DMA 35**	**DMA 501** **DMA 1001**	**DMA 4100 M** **DMA 4500 M** **DMA 5000 M**	**DMA 4200 M**
Portable	√			
Temperfect feature			√	√
FillingCheck feature		√	√	√
U-View feature		√	√	
Pulsed Excitation Method		√	√	√
Repeatability of the density result s. d.	0.0005 g/cm³	DMA 501: 0.0002 g/cm³ DMA 1001: 0.00005 g/cm³	DMA 4100 M: 0.00001 g/cm³ DMA 4500 M: 0.000005 g/cm³ DMA 5000 M: 0.000001 g/cm³	0.00005 g/cm³
Automatic filling		√	√	
System capability for multiparameter measurements			√	
Gesture control	√		√	√

In Anton Paar's patented 'Pulsed Excitation Method' the U-tube is excited by impulses to oscillate. Once a constant amplitude is achieved, the pulse sequence is stopped. The U-tube's oscillation is measured while it fades out freely and unaffected by any influences. Excitation and fade-out alternate periodically.

Its advantages are:

- More information for users compared to conventional density measuring methods
- Improved viscosity correction
- Improved repeatability and reproducibility

For more information see www.anton-paar.com/densityredefined

Please note: The name DMA for all Anton Paar density meters as well as the instrument features FillingCheck, U-View, and Temperfect are trademarks protected by Anton Paar. For better readability, the annex "TM" after the protected instrument features was omitted in the text.