WALLIS

Zeta potential analyzer

User manual

CORDOUAN Technologies

V1.0 –November2013

WALLIS is an innovative **zeta potential analyzer** dedicated to the characterization of **nanoparticle suspensions**. It is based on a revisited and modern version of the **Laser Doppler Electrophoresis (LDE) technique** offering a unique and unequaled measurement resolution. It is complementary to the Cordouan's VASCO particle size analyzer to study colloidal solution stability and properties.

11, Avenue de Canteranne 33600 PESSAC – FRANCE
Phone: +33 (0) 556.158.045 Fax: +33 (0) 547.747.492

www.cordouan-tech.com

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Introduction

Scope of this guide

This manual intends to give an overview of the WALLIS™ product characteristics, installation and use in association with its full dedicated ZetaQ™ software. Information disclosed in this document is subject to change without notice and does not represent a commitment on behalf of CORDOUAN Technologies.

Warranty

WALLIS product is covered by a limited warranty. Using the equipment in a manner not specified in this manual may impair its performances and integrity. Never open the equipment without *CORDOUAN Technologies* written approval otherwise warranty will no longer apply. Unless otherwise stated notably according to local distributor conditions, standard warranty duration is 12 months starting at reception of the equipment.

Trademarks and property

All brands and products mentioned are trademarks or registered trademarks of their respective holders. The software described in this manual is provided under a license agreement and may be used or copied in agreement with the terms of the agreement.

Upgrades

ZetaQ™ software is under constant evolution. One year duration software upgrades will be available for free on *CORDOUAN Technologies* Web site at:

www.cordouan-tech.com

Certification and conformity

WALLIS is a CE marked product (2006/95/EC and 2004/108/EC directives). It is designed and assembled in compliance with electromagnetic compatibility and electrical safety standards (EN-61326/A1 and EN-61010-1). It is a class 1 laser equipment (EN-60825-1). It follows the standards ISO-13099-1 (Zeta potential - theory), ISO-13099-2 (Zeta potential – Optical methods) and CFR21 part.11 recommendations (Electronic records and signatures)

Please contact our customer support service for more information

service@cordouan-tech.com

Installation of the equipment

Important recommendations

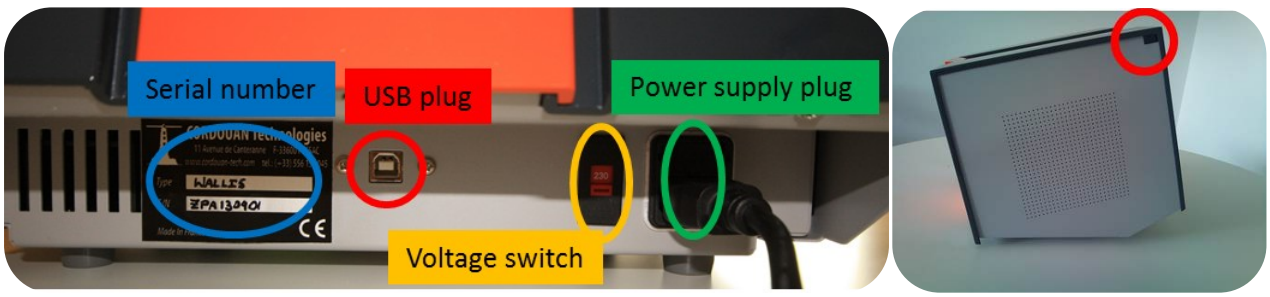
	The equipment is electrically configured to be operated either under 115V-60Hz or 230V-50Hz. Check if the voltage switch at the bottom of the back plane of the device is well positioned. If you have any doubt, please contact us before plugging the equipment, otherwise irreversible damage can occur if wrong voltage is applied. *Note: The equipment is protected by an electrical fuse located on the main power supply plug.*

WALLIS apparatus is designed to be operated in a temperature and humidity controlled environment. For the best performances, it is recommended to operate the module with an ambient temperature between 20 and 25°C.
When installing WALLIS make sure that air circulation on both the sides and beneath the apparatus is free.

If you don't have a PC with ZetaQ pre-installed, install it with the provided CD (refer to ZetaQ software installation chapter). ZetaQ is designed to be operated under Microsoft Windows operating system exclusively (XP, Vista, Seven, Eight). Make sure your computer processor is at least a Pentium III with a minimum RAM of 512Mo.

Installing and Starting WALLIS

1. Plug the power supply cable and the USB cable (provided with the equipment) to the device.
2. Plug the power supply cable to power socket
3. Switch on the computer with Zeta Q install on it
4. Plug the USB cable to the computer
5. Switch on the device



Back panel view (left) and main power supply ON/OFF switch (left) on the upper right side WALLIS

Measurement quick start guide

Note: If you are not familiar with Wallis equipment and Zeta potential measurements, we recommend you to read the detailed description in Wallis equipment section before starting measurement.

Measurement cell preparation

1. Inject your sample in a standard 10mm cuvette cell for around 1ml (~10mm height in the cell).
2. Dip completely the provided electrodes head in the cuvette cell
3. Check by a visual inspection that there is no bubbles in the electrodes area
4. Open the device lid
5. Insert the cuvette with its electrodes head in the cell holder of the device.
6. Close the device lid

Start measurement

1. Verify that the device is correctly installed
2. Switch on the device
3. Start the ZetaQ software
4. Enter the parameters corresponding to your measurement (refer to software explanations chapter for more details)
5. Click start button and wait until the software go to analysis screen

After measurement

1. Open the device lid
2. Remove gently the cuvette with its electrodes head from the cell holder
3. Remove the electrodes head from the cell and wash carefully the electrodes (refer to the cleaning of electrodes head chapter for more details)
4. Put the dried electrodes head in the provided dry and clean disposable cuvette cell, and put it back to its storage case
5. Get rid of the sample and cuvette cell as you wish in accordance to your laboratory practices and country regulations.

ZetaQ™ software: General overview

Introduction

ZetaQ™ is proprietary software designed by *CORDOUAN Technologies* specifically for the WALLIS zeta potential analyzer. With its user friendly interface, ZetaQ™ allows the user to:

- Set and optimise and store in a very simple manner the experimental parameters for the measurements.
- Create and load SOP to start routine experiments in a click
- Store and recall experimental results for data post treatment
- Generate a measurement report in order to keep track of the results

Starting with zetaQ™

To start the zetaQ software, double click on the desktop icon: 

A login window appears; in order to start zetaQ session , the user has to select its profile [Admin / Expert / Operator] and to enter his personal login and password. The tab below gives default values for each three profiles.

Default logins and passwords values		
Profil	**Login**	**Password**
Admin	Admin	
Expert	testExpert	
Operator	testOperator	

It is not possible to run two or more sessions of zetaQ® at the same time.

Notes :

1. At the very first zetaQ run, an error message appears pointing a ftdi installation issue. Actually the ftdi driver installation will be completed only when the instrument will be USB connected for the first time.
2. At the very first login, a message box invites you to change your password.
3. Each of the three user profiles has different access rights to the software functionalities. Please refer to the **logged profile rights table**.
4. When logged as an administrator, you have access to all user's accounts and profiles management system; please refer to the **AdminZetaQ utility** section.

Presentation of the zetaQ™ user interface:

Zeta Q user's interface is designed to be intuitive and easy to use, even for non expert users. It is built in a natural sequence of menus:

Mode Menu

The Mode menu (see below) is the starting point of ZetaQ; From this point you can start a measurement, make an analysis and display data, superimpose and combine results of stored measurements, adjust some settings (expert users), manage user data base (admin users only).

1. Choose your operation mode by clicking on the corresponding icon.
2. Advanced parameters menu (see details
3. Users management tool (accessible only in *Admin* log)
4. Logged user – Click to change the user
5. Instrument connection status
6. Current cuvette holder temperature (°C)

Measurement mode

This mode allows defining an experiment and launching measurement in a few clicks. (see below)

Analyze data mode

This mode allows users to select experiment measurement data, to sort the results, display corresponding graph, superpose measurements results, etc.
For more information, see Appendix 3

Parameters mode

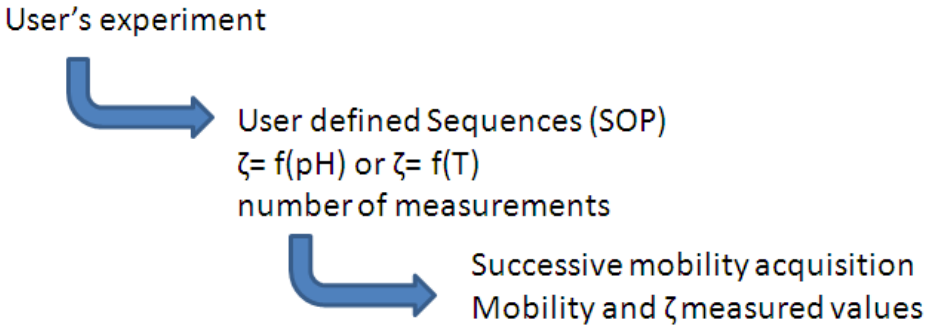
This mode allows Expert and Admin users to modify default parameters (laser power, report saving directories, data base selection, interface language, etc).
For more information see Appendix 4

Users management mode

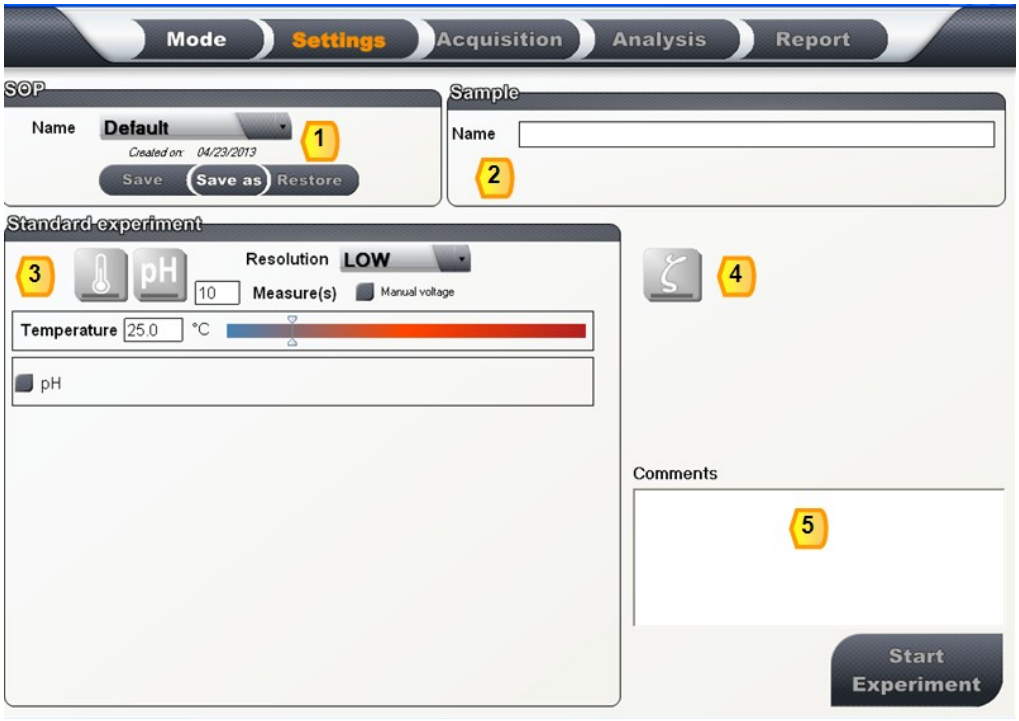
ZetaQ software integrates a User management data base utility. This utility allows **admin users** only to manage a data base of declared Wallis users (create login and password, delete, modify user profile, etc)
For more information see Appendix 5

Measurement mode

Thanks to its clever conception, ZetaQ allows a user to really launch experiments rather than single measurements only. Indeed, as defined, an experiment is associated to a given Standard Operating Procedure (SOP) made of a user defined measurement sequence. A sequence corresponds to different experimental settings (pH, Time, Temperature, concentration, number of measurements, etc). For each user defined sequence of a protocol, successive zeta potential/mobility acquisitions are achieved; the successive measurement results are stored and displayed, with averaged value. An experiment is thus the results of measurements according to a protocol. It is saved as such.



When you select **Measurement mode**, the **Settings** page opens.



1 Select an existing procedure (SOP); if you select default, measurement settings will be the one currently loaded at the start of ZetaQ.

2 Enter your sample name (auto complementation from previously operated measurements stored in database)

3 Define your experiment procedure (PH, Temperature, number of measurement, resolution, etc)

4 Activate or not the zeta potential calculus from electrophoretic mobility.

5 Write comments to describe your experiment

SOP Settings

Standard Operating Procedures (SOP) are user pre-defined settings associated to an experiment. A user can create, modify, restore, and download SOPs. Note that only Admin and Expert users have the rights to create/modify a SOP. Operators can only use existing SOP.

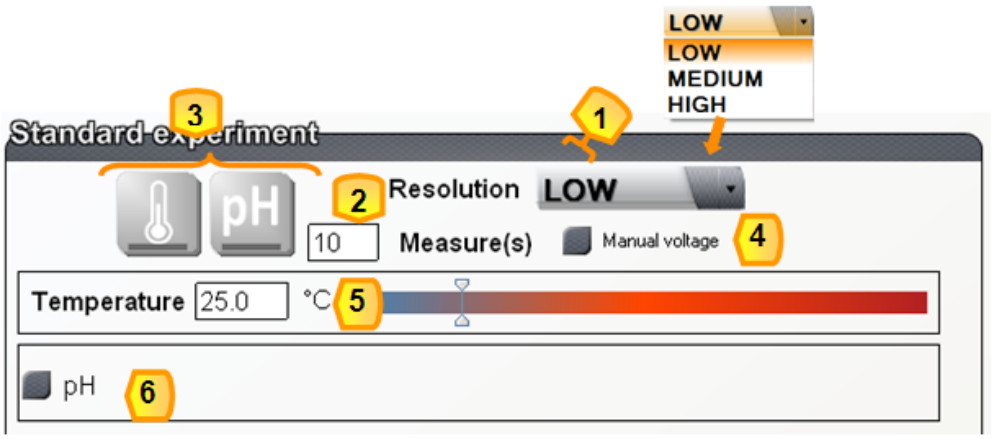
1 Select an existing procedure and configure all settings fields with predefined values. A listbox appears with all SOPs already saved in the dedicated data base. Only the sample name is not encompassed in a SOP.

2 As soon as a field is changed after having selected a procedure, the “Restore” button is enabled. By clicking on it, zetaQ restores all initial values of the first loaded SOP.

3 The “Save As” button allows the user to save its current configuration as a new SOP. The expert is able to replace an existing SOP with the current one.

Experiment definition

An experiment is associated to a given protocol (SOP) made of a user defined sequence of measurements. A sequence corresponds to different experimental settings which can be defined in the **Standard Experiment** window (see below): the user has the choice between several “dynamic/ kinetics” modes: zeta vs pH, zeta vs sample temperature. The user can also select some parameters like number of measurements and measurement resolution.



1 Select your resolution level. Equivalent Doppler frequency resolution is actualised according to the selected level (Low=5 Hz, Medium = 0.8 Hz, High =0.3 Hz) ; note that the higher the resolution, the longer the measurement.

2 Define the number of measure per run (i.e. per sequence)

3 Select one of the dynamic mode (pH, Temperature driven experience).

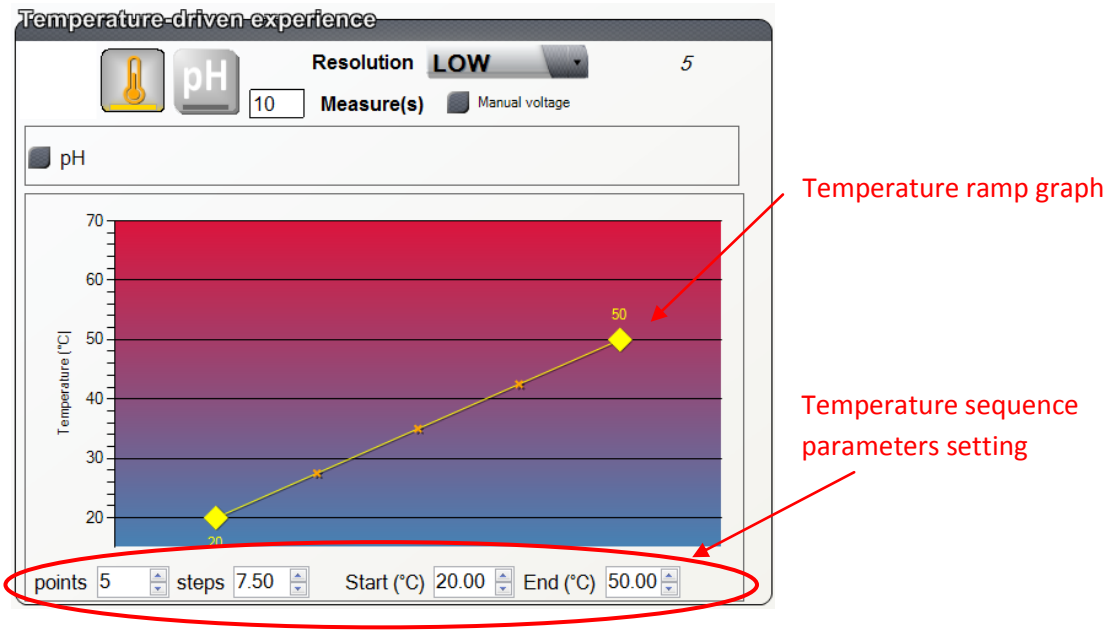
4 Unlock automatically set applied voltage and select it manually in the pre-defined list (High-conductivity measurement)

5 Define the sample regulation temperature for the whole experience

6 Add pH value as comment if known (not required)

Zeta vs Temperature experiment

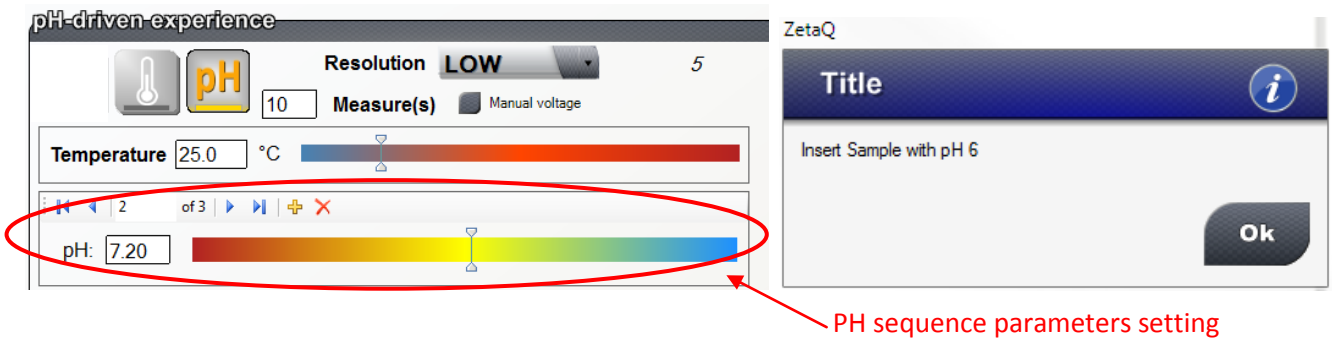
In this mode, the user can define a sequence of measurements by specifying a temperature ramp, with a start, an end temperature and the number of acquisition point or temperature increment. In this mode, the pH value is assumed to be constant during all the sequence.



NB: Never use disposable plastic sample cells for temperature higher than 50°C. For temperature higher than 50°C we recommend to use Quatrz Suprasil or BK7 cell (check sample cell specification from your supplier).

Zeta vs pH experiments

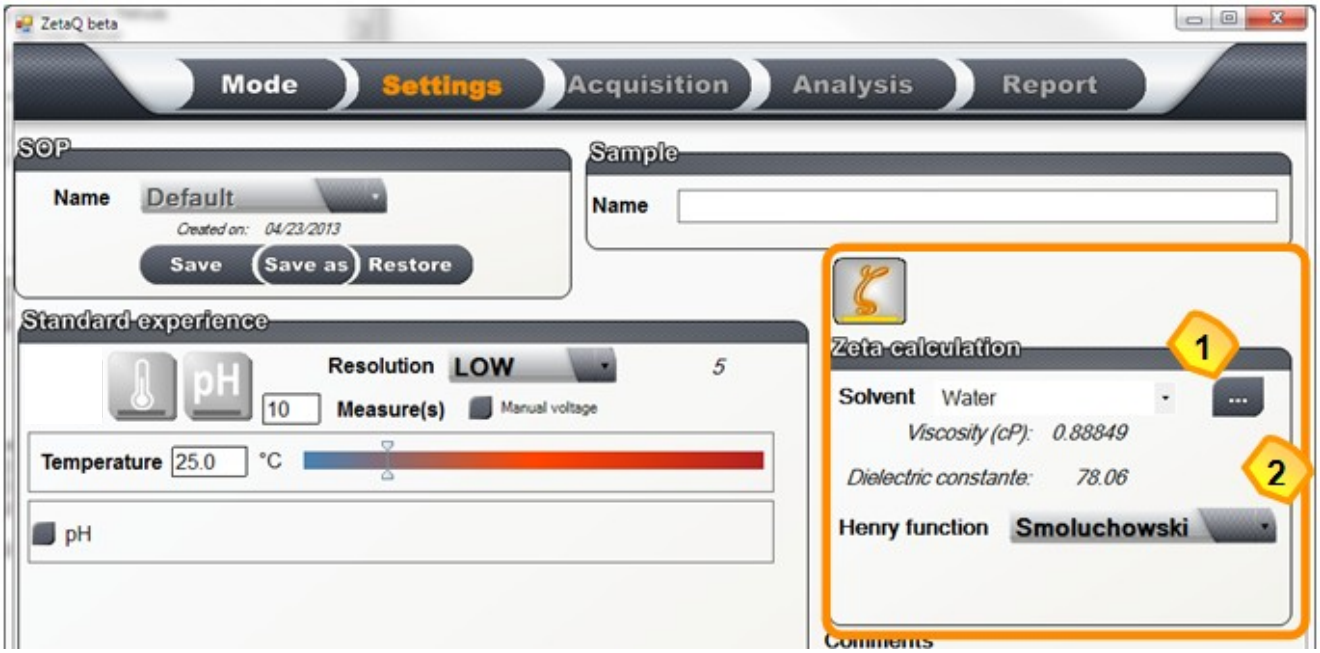
In this mode, the user can define a sequence of measurements by specifying total number of pH points of sequence and their respective values. In this mode, the Temperature setting is assumed to be constant during all the sequence. This semi automatic sequence is achieved step by step since the user needs to introduce the sample with the right pH before starting the measurement.



NB: in its current version, WALLIS is not provided with the Auto-titrator option; pH values need to be set manually by the user.

Zeta Potential calculation Settings

WALLIS primarily measures electrophoretic mobility of charged particles; Corresponding Zeta potential values are calculated from electrophoretic mobility measurement based on the solvent properties and on the double layer model selected (for more information , see Chapter Measurement principle). So to make zeta potential measurements you first need to give information about your solvent and about the double layer model you want to apply for the calculations.



ZetaQ is provided with its own solvent data base which contains the most common solvent (see Appendix 4 for a non exhaustive list of these solvents) with their physical properties namely Viscosity η, dielectric constant ε. The viscosity η and dielectric constant ε values are automatically updated according to the temperature setting of the experiment.

The double layer model is described by the Henry function: two extreme case are typically used depending on the assumption made on the double layer model: Smoluchowski and Huckel (see chapter Zeta potential : basics and principle p31-32) ; some intermediate custom value of the Henry function can be set by the user.

NB: In case you are only interested by mobility measurements you don't need to document the zeta potential menu.

When the apparatus is properly connected and all the mandatory settings properly documented, the Start experiment button is blinking, you can start the experiment by clicking on it and follow the running of the experiment in the Acquisition folder 

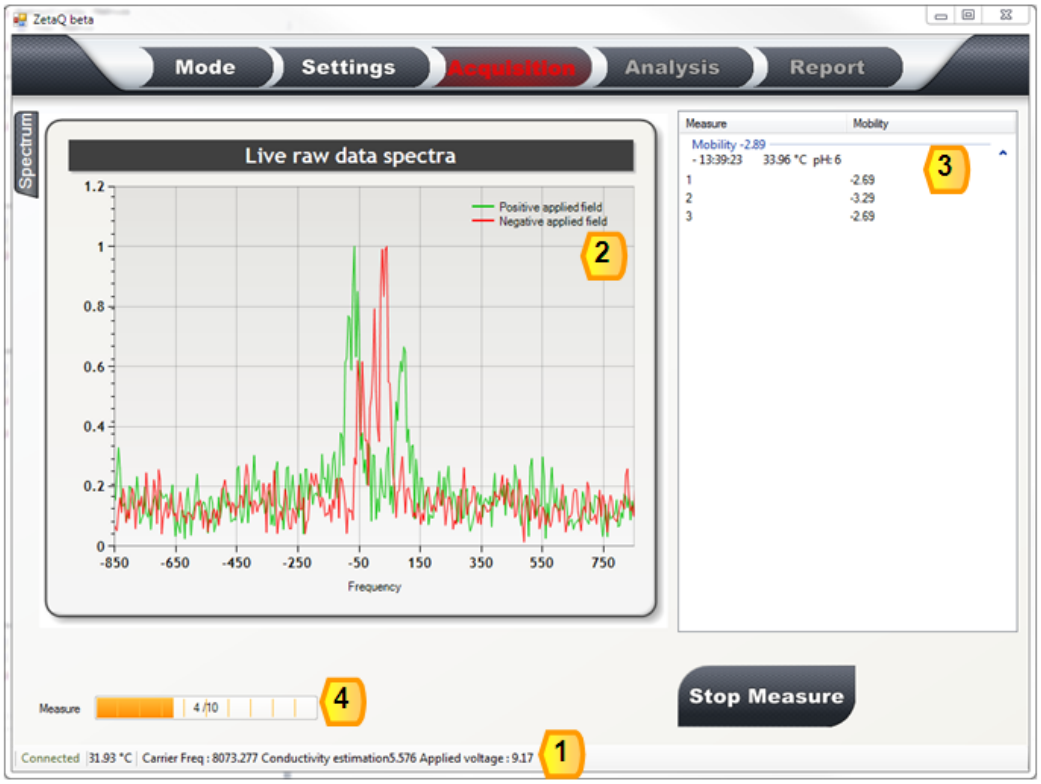
NB: The symbol  *indicates unfilled fields when the mouse pointer flies over the "Start measure" button.*

When starting an experiment, several steps are automatically followed by ZetaQ before launching the first sequence of measurements:

1. Scattering intensity level setting I_0 (measurement arm)
2. Reference Intensity level setting I_{ref} (Reference arm intensity balancing)
3. Carrier modulation frequency measurement f_0
4. Sample conductivity estimation σ
5. Electrodes Electric field adjustment E

The completion of these successive steps will typically take about one minute before the launching of the first measurement. The results of these settings are displayed in the **Acquisition** page (see tag 1 below)

Acquisition folder



1 Experiment settings for pre-run measurement: Intensity balance setting, carrier frequency measurement, voltage measured as conductivity and corresponding electrodes applied voltage. Units of displayed values are mentioned in Appendix 3: FAQ ; The scattering

intensity is automatically adjusted by ZetaQ in order to be set at an optimum value for good SNR. In some cases, depending on your sample scattering properties, the scattering intensity cannot be set to its optimum value; it could be either too high or either too low.

Setting Value ranges	Displayed message	Cause & consequences	recommendation
I_0<200 kcts	Too low scattering	sample concentration too low-> poor SNR	Increase laser power (see Appendix 7)
200 kcts < I_0<1000 kcts	Low scattering	sample concentration too low-> poor SNR	Increase number of measurements (see Appendix 7)
I_0 ≈1000 kcts	Normal	Optimum SNR condition of measurement	OK
1000 kcts < I_0<4000 kcts	High scattering	sample concentration too high with respect to normal setting	Dilute sample and/ or decrease laser power (see Appendix 7)
I_0>4000 kcts	Too high scattering	sample concentration too high-> risk of detector saturation	Dilute sample and/ or decrease laser power (see Appendix 7)

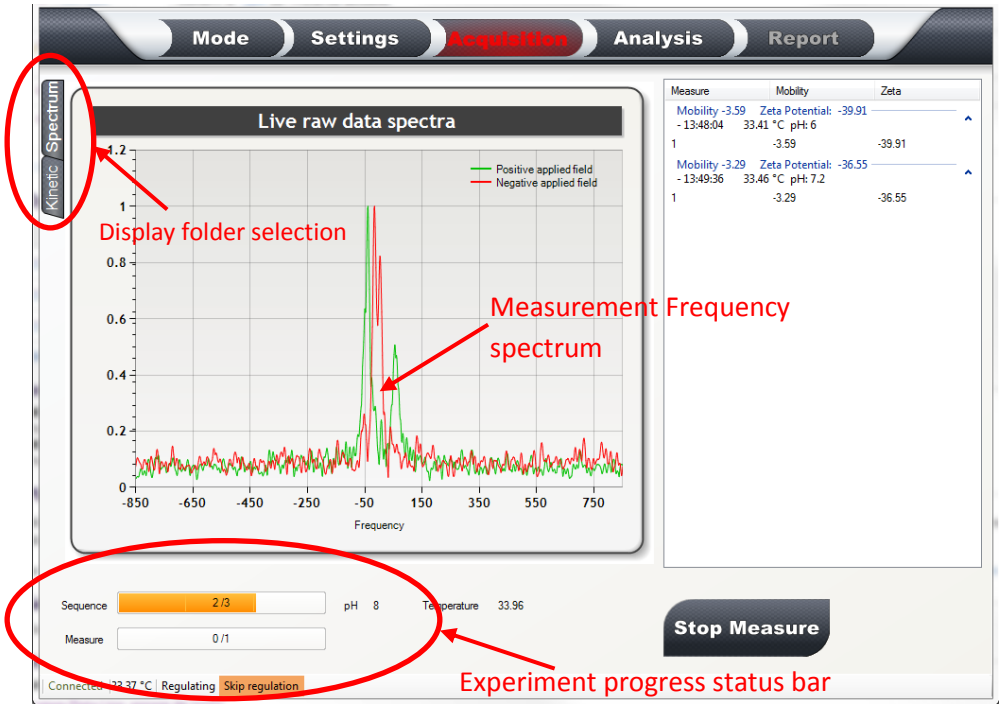
2 Real time Doppler frequency spectrum from both positive and negative applied electric field

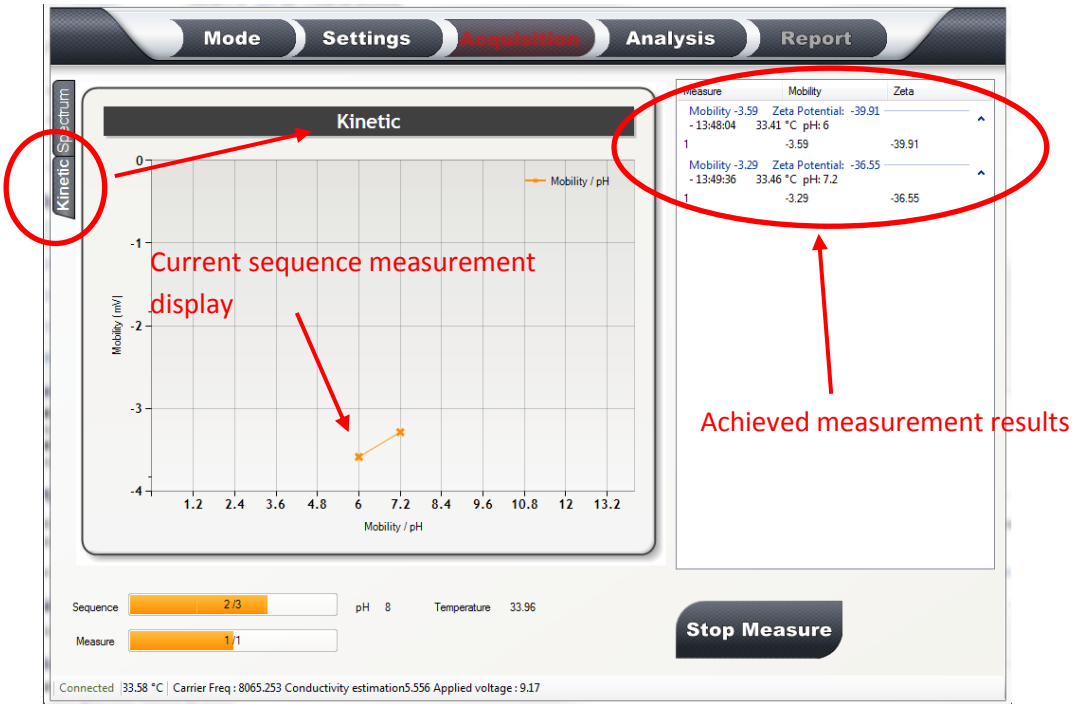
3 Display of already measured mobility values of the experiment; the averaged value is displayed in blue

4 Experiment progress status bar

Note that experiment can be stopped at any time by the user just by clicking on the button: 

During the acquisition, you can either display the real time frequency spectrum or current measurement results in the dynamic mode by selecting the corresponding folder (see figure below). By a right click on the mouse, you can select to display either mobility or zeta potential graph, copy data or graph/bitmap to clipboard for further post treatment. The progress status of the sequence and measurement of the experiment are also displayed below the graph.





Once all the sequences of the running experiment are completed, ZetaQ automatically switches to the **Analysis folder** which allows you to visualize all the results of the experiment.

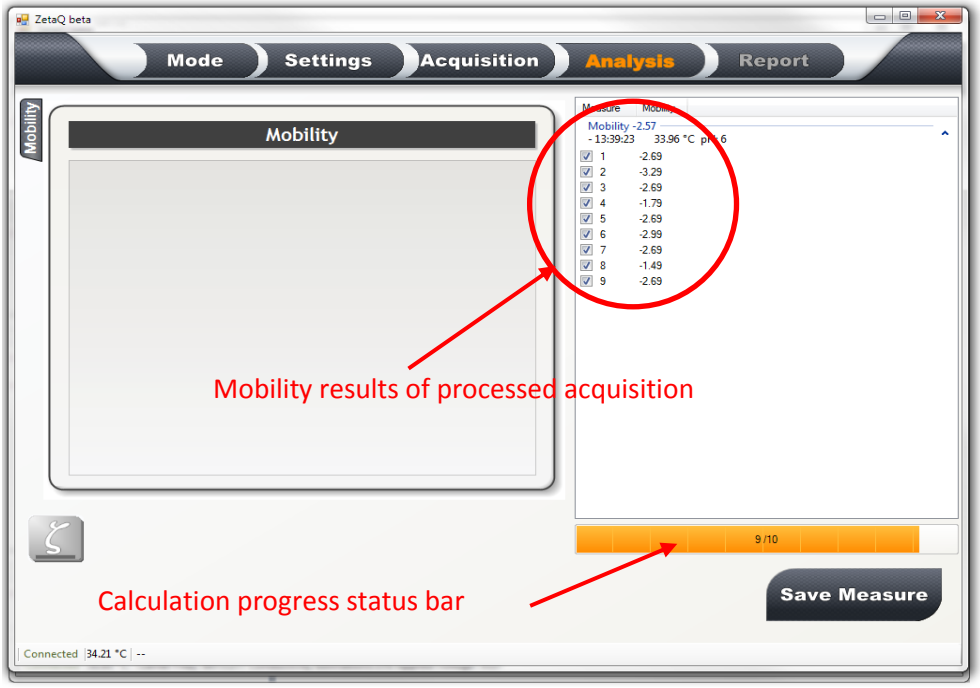
NB: you cannot access the Analysis folder before the running experiment is completed

Analysis Folder

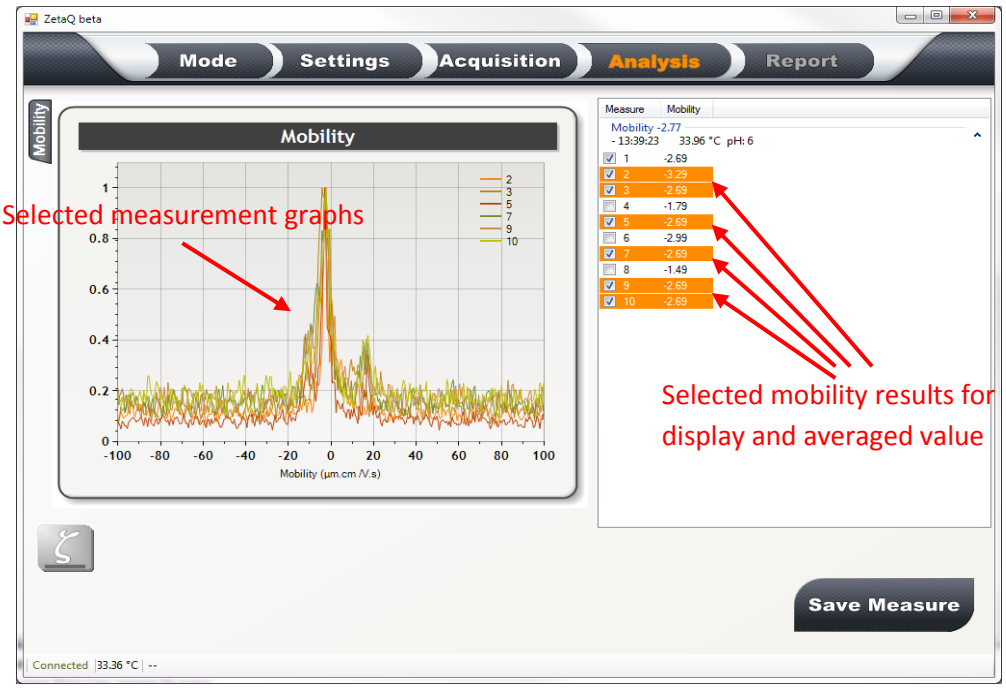
After completing the running experiment, ZetaQ switches to the analysis folder automatically and starts processing the results: zeta potential values for each mobility acquisition, averaged mobility

and zeta potential for each sequence, Lorentzian fit of mobility and zeta potential experimental curve, etc.

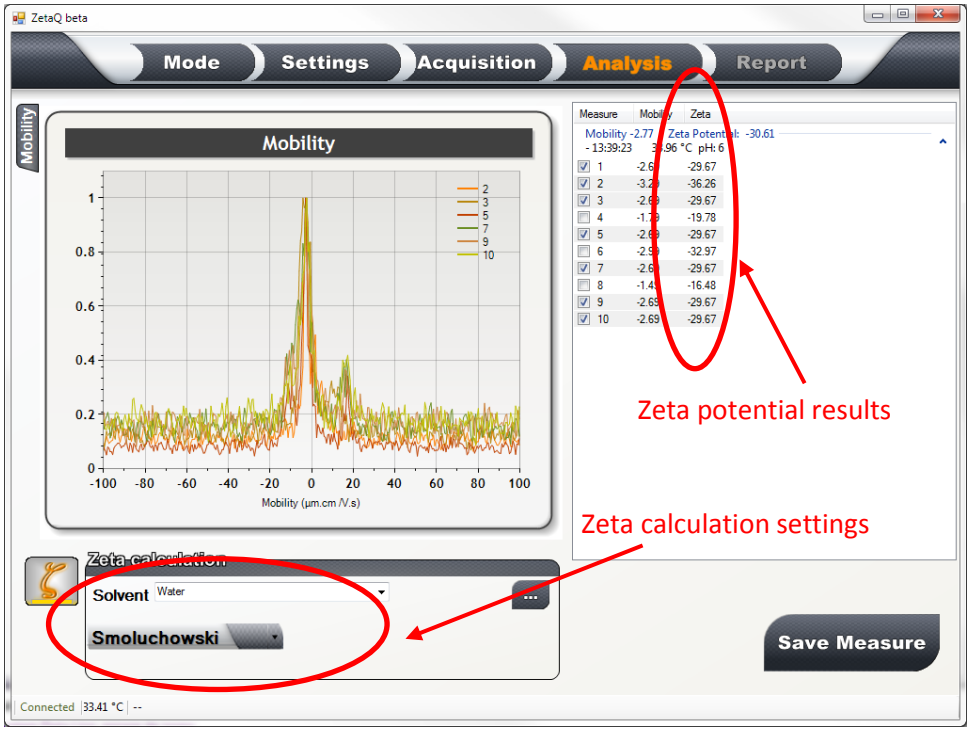
NB: No graph is displayed until the processing of all the measurements is completed.



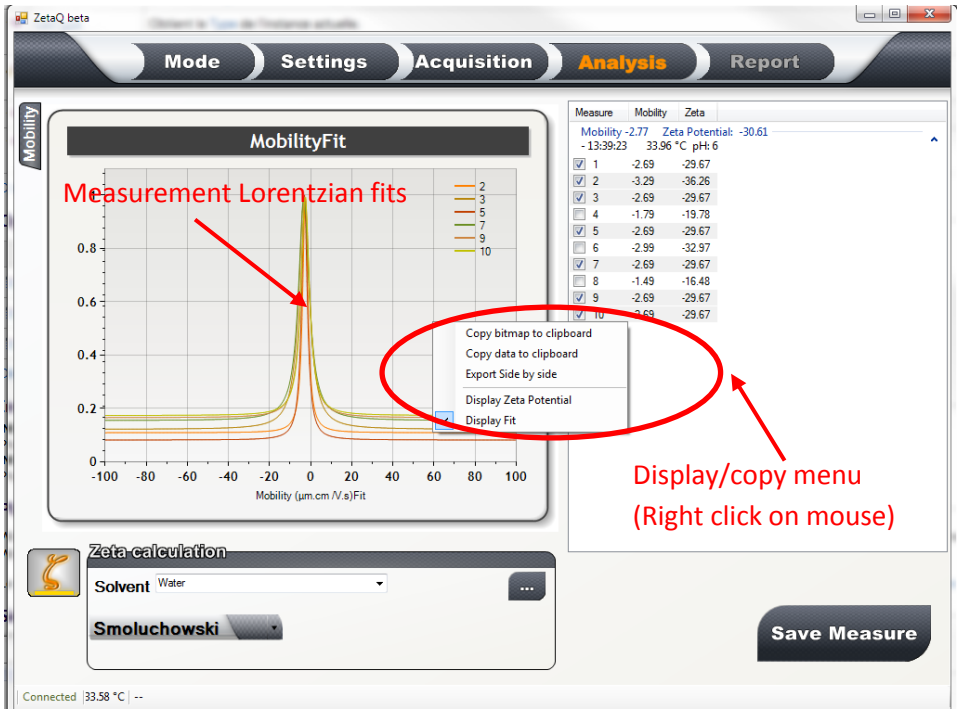
Once all the calculation of the analysis is completed, analysis results and corresponding graphs are displayed in the analysis folder. You can select the measurements results to be displayed in the graphs and accounted for in the averaged value calculation. The selected measurements are highlighted in orange. This allows the user to sort measurements results out a complete experiment without having to remake a full experiment.



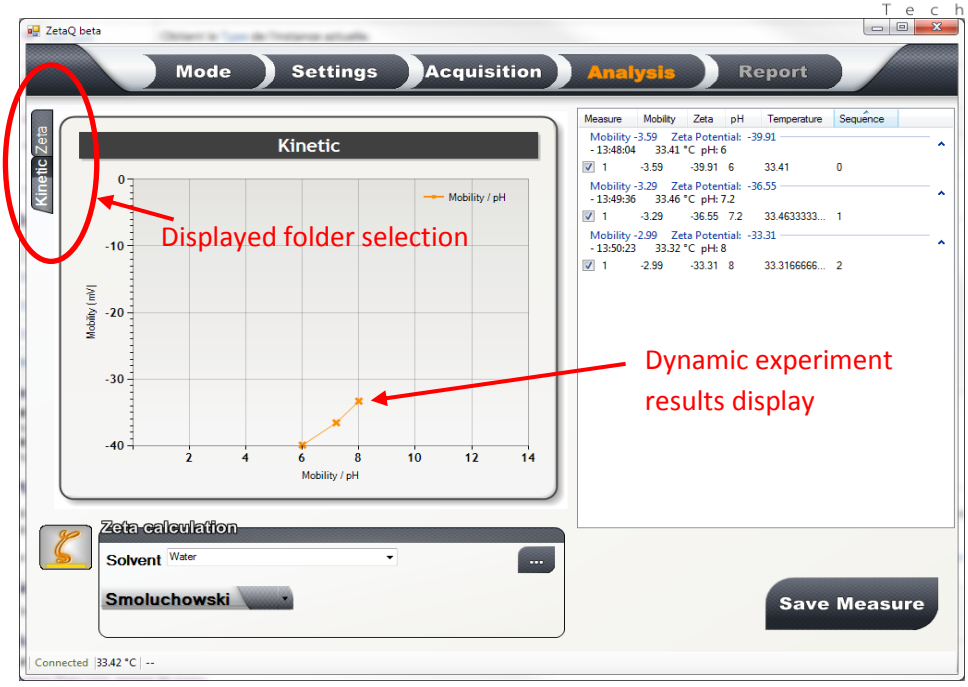
It is also possible to display corresponding zeta potential values and to re-process the calculation by changing the settings of zeta calculation (solvent properties, Henry function model). Note that ZetaQ will automatically update the results of zeta potential calculation with the new settings.



A right click on the mouse positioned over the graph will show up a display/copy menu; in this menu, you can select to display either mobility or zeta potential graph, copy data or graph/bitmap to clipboard, display the Lorentzian fit of each measurement.



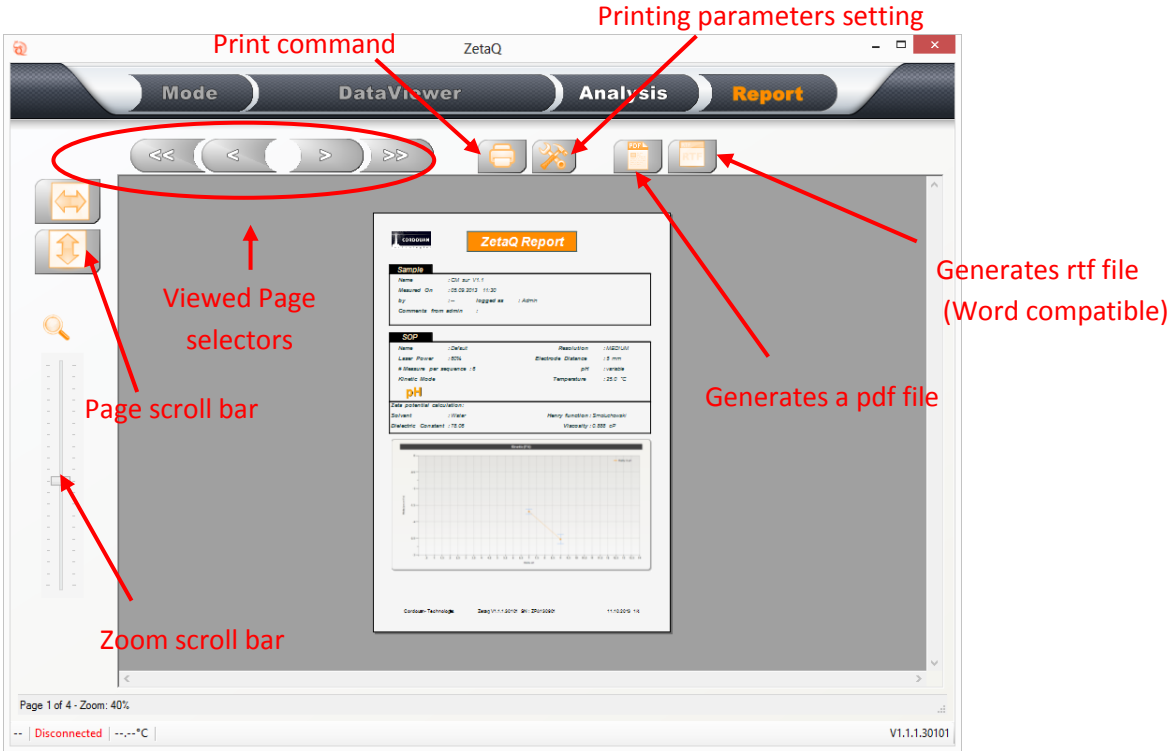
For a dynamic experiment, it is also possible to display the graph of the results by selecting the Dynamic folder on the right side of the graph display.

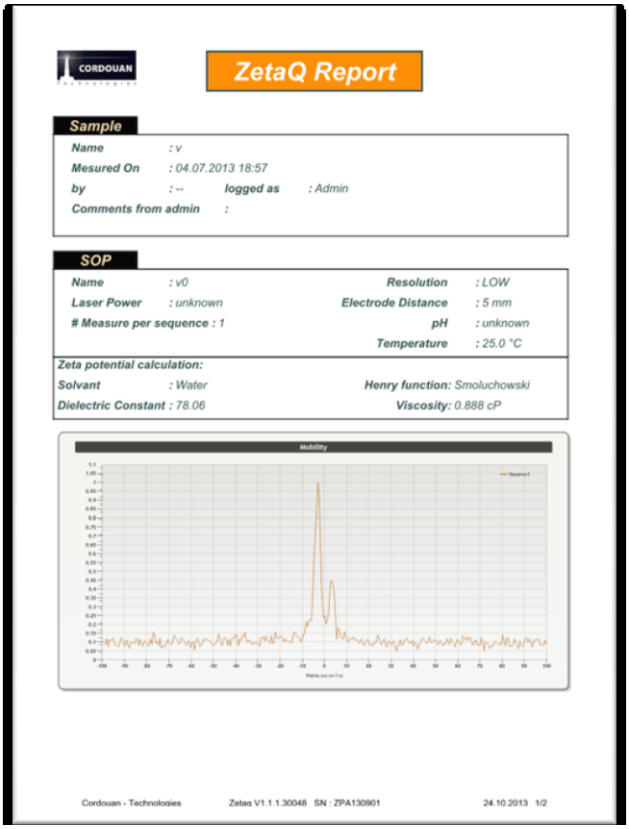


Once analysis is completed, you can gather all your results into a pdf report.

Report Folder

This folder allows the user to preview and edit in a very user-friendly way a measurement report in pdf or rtf file format and to select printing options.





ZetaQ Report

Sample

Name : v
Mesured On : 04.07.2013 18:57
by : -- logged as : Admin
Comments from admin :

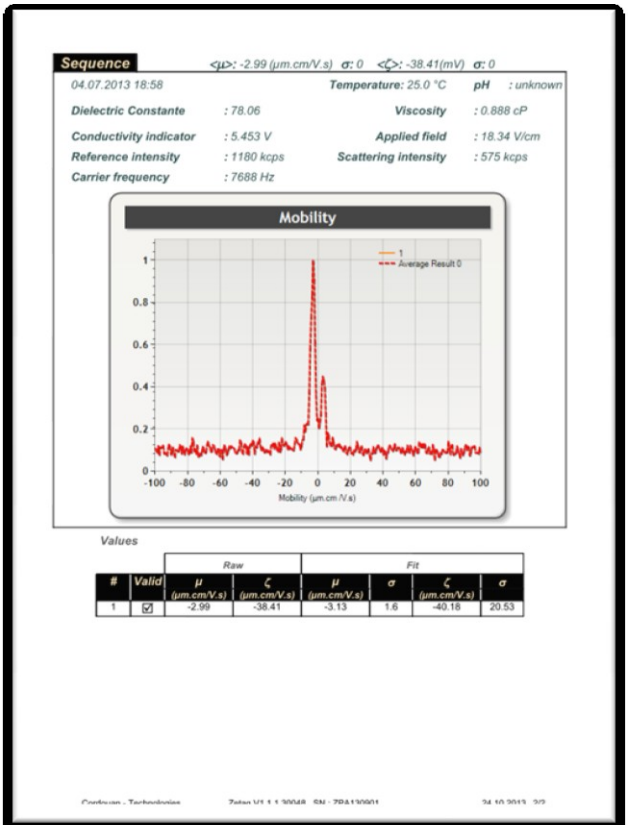
SOP

Name : v0 Resolution : LOW
Laser Power : unknown Electrode Distance : 5 mm
Measure per sequence : 1 pH : unknown
Temperature : 25.0 °C

Zeta potential calculation:
Solvant : Water Henry function: Smoluchowski
Dielectric Constant : 78.06 Viscosity: 0.888 cP

Mobility

Cordouan - Technologies Zetaq V1.1.1.30048 SN : ZPA130901 24.10.2013 1/2



Sequence <μ>: -2.99 (μm.cm/V.s) σ: 0 <ζ>: -38.41(mV) σ: 0

04.07.2013 18:58 Temperature: 25.0 °C pH : unknown
Dielectric Constante : 78.06 Viscosity : 0.888 cP
Conductivity indicator : 5.453 V Applied field : 18.34 V/cm
Reference intensity : 1180 kcps Scattering intensity : 575 kcps
Carrier frequency : 7688 Hz

Mobility

Values

		Raw		Fit			
#	Valid	μ (μm.cm/V.s)	ζ (μm.cm/V.s)	μ (μm.cm/V.s)	σ	ζ (μm.cm/V.s)	σ
1	☑	-2.99	-38.41	-3.13	1.6	-40.18	20.53

Example of generated pdf report format.

Wallis instrument and accessories

Overview

Wallis is composed of a main unit and its dedicated ZetaQ software to be installed and operated on a separate PC. Wallis uses standard cuvette cell with 10mm optical path; it is provided with one electrodes head.

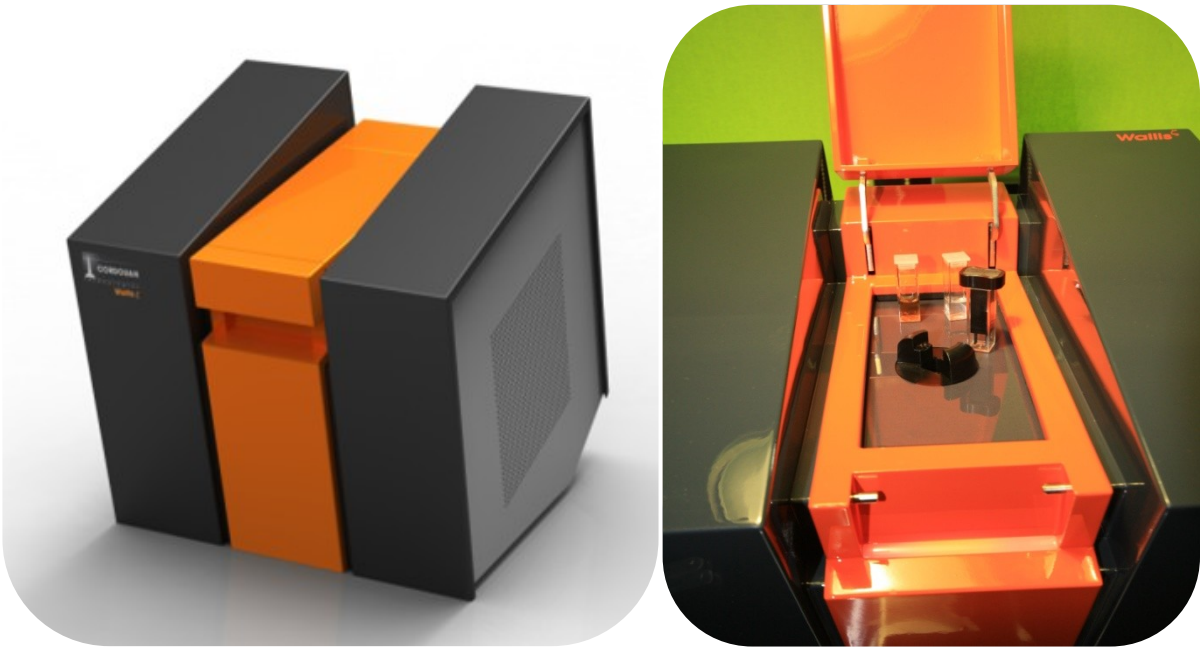


Figure 1: WALLIS overview

Wallis unit : main parts designation and precaution of use.

Lid: On the front panel, on the top of the orange colored part, there is the lid opening system. You can open it by pulling gently toward you the front part of the lid. The lid will open smoothly and give you access to the sample cell holder area. To close the lid, push down gently the main part of the lid until it resist and then push down the front part of the lid until it lock into place. Be sure nothing is left around the cell holder as it may damage the lid.

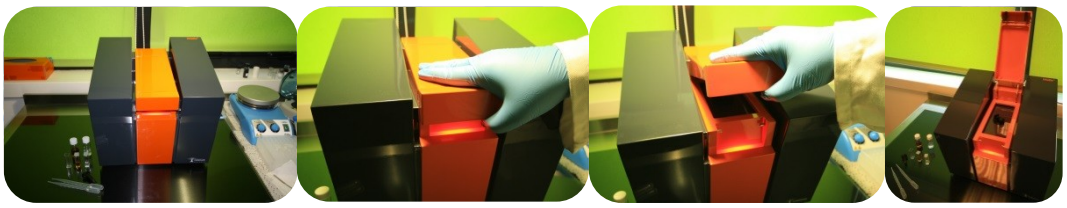


Figure 2: Lid opening

Cell holder area: The surrounding of the cell holder is made of a flat glass plate with good chemical resistance. Refrain to put sample cell, pipette or any other stuff in this area. If accidentally

some sample is spread on this area, clean it as soon as possible with soft towel moisten with water or soft detergent.

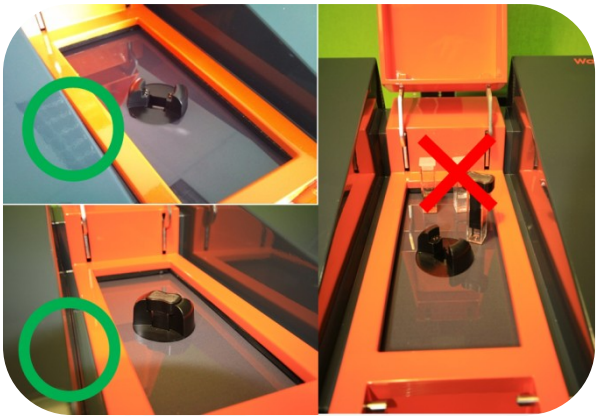


Figure 3: Cell holder area

Cell holder: When the lid is opened, you have access to cell holder. It is designed to hold standard square shape 4 ml cuvette cell.

Figure 4: Insertion of cell in cell holder

Cell holder electrical connectors: Two electrical connectors are located on each side of the square shape cell holder receptacle. These connectors allow applying an electrical field between the electrodes when immersed in the sample. Make sure that these connectors are always clean and dry. If not, irreversible damage may occur to the main unit.

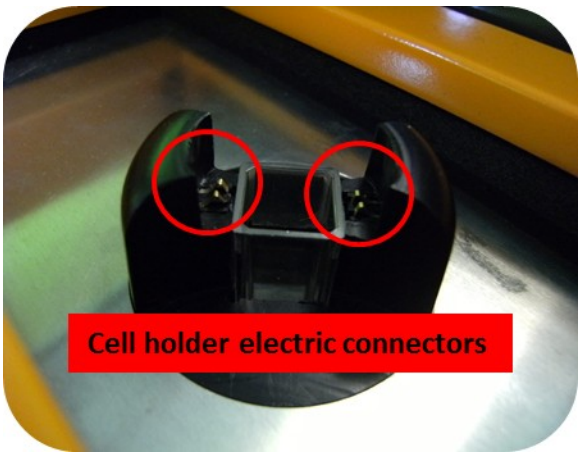


Figure 5: Cell holder electric connectors

Power switch: The main ON/OFF electrical switch is located on the right panel, in the back up corner. When WALLIS is switch ON, the front panel is illuminated, and the fans should be audible. Be sure that the unit is correctly plugged to a power supply before switch it ON.

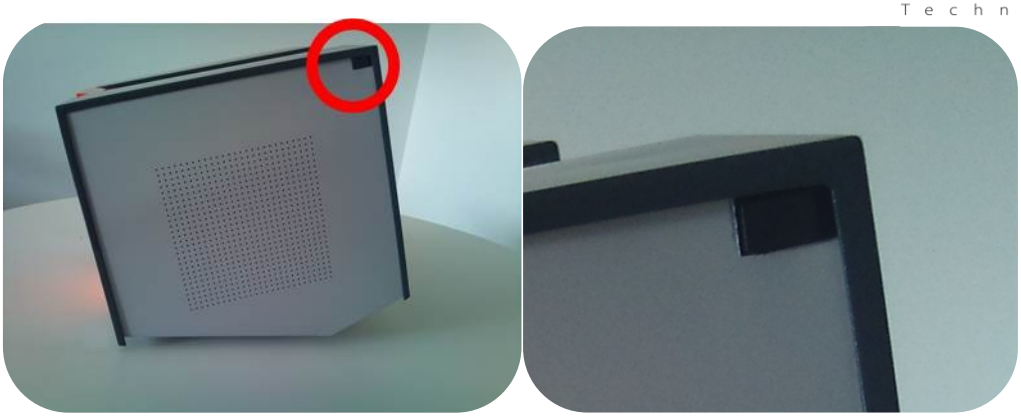


Figure 6: Power switch description

Serial number: On the rear panel, at the bottom left, there is a sticker with the unit serial number. Please do not forget to mention this serial number in case of communication with our customer support service.

USB plug: On the rear panel, at the bottom center, there is the USB plug. It should be used with the provided cable.

Voltage switch: On the rear panel, at the bottom right, there is the voltage selector. The unit can be operated either under 115V-60Hz or 230V-50Hz. The voltage selector must be switched in the requested configuration before switching ON the unit otherwise irreversible damage may occur to the main unit.

Power supply plug: On the rear panel, at the bottom right, there is the standard power supply plug. It should be used with the provided cable.

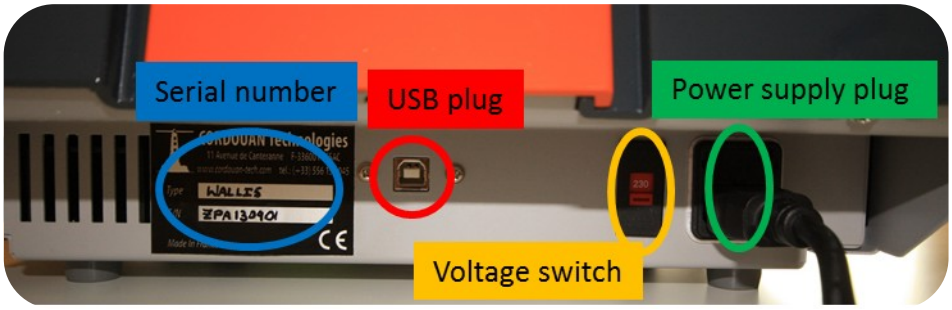


Figure 7: Rear panel description

Electrodes head

Electrodes head is necessary to perform a Zeta potential measurement with Wallis main unit. It is one system composed of three items.

Electrodes: The two 10mm long black sticks emerging from the main part are vitreous carbon electrodes. Refrain to touch them with bare hand, nor to put them directly In contact with hard matter (like a table) or to shock them as irreversible damage may occur.

Head electric connector: They are located on each side of the top of electrodes head. When installing the cell, please make sure that head is properly inserted into the cell holder in order to guaranty a good electrical contact between the head and the holder connectors.

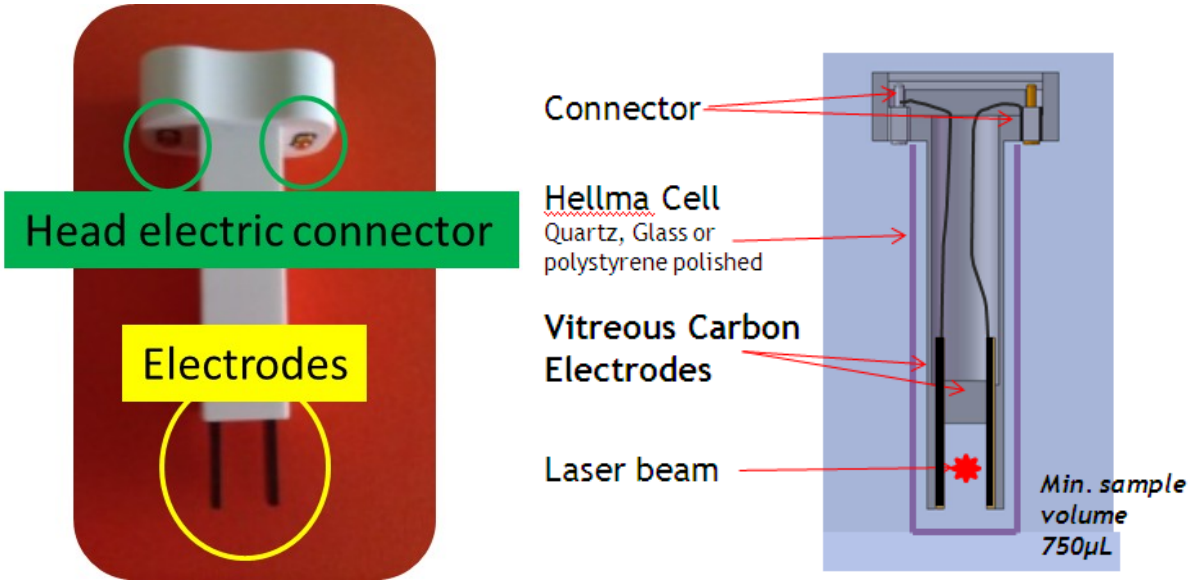


Figure 8: Electrodes head description

Top shape: The ergonomic shape of the top part of the electrodes head is designed to handle both electrodes head and cuvette cell with one hand. In addition, this shape gives the only obvious position for the right setting of the WALLIS system as shown on pictures below.

Figure 9: Insertion of electrodes head in cell holder

Cuvette cell

In order to do a measurement, a standard cuvette cell, 4ml, 10mm light path, square section is necessary. You can use either transparent disposable/plastic or glass material.

NB:For experiment at temperature higher than 50°C, recommend to use Quatrz Suprasil or BK7 cell (check sample cell specification from your supplier). Disposable cells are usually not design to be operated at temperature higher than 50°C.

Manipulation of electrodes head and cuvette cell

In order to proceed to a measurement, you should first input your sample inside the cuvette cell of your choice in accordance with WALLIS recommended cuvette cell. The minimum sample volume is 0.75mL and maximum is 1,2mL. Using lower sample volume will not provide correct measurement and putting more sample will results in overflow out of the cell and possibly damage the equipment. Once you have filled the cuvette cell with your sample, gently insert the electrodes

head inside the cuvette cell until the bottom ①Check that no bubbles are present between or on the electrodes. If so, pull up slightly the electrodes head and put it back to the bottom. Repeat this procedure each time some bubbles appear between the electrodes during filling. If you start a measurement with bubbles between the electrodes, the results will not be correct.

To put the system electrodes head and cuvette cell assembled, take the top part of the cuvette cell between index and thumb. Never touch the bottom part of cuvette cell to prevent dirt hampering the light pass. Handling this way, put the cuvette cell inside the cell holder/receptacle of the main unit after opening the lid as describe above. Insert completely the cuvette cell and then push down gently on the top of the electrodes head until it fits on the cell holder electric connectors.

To remove the system electrodes head and cuvette cell assembled from the cell holder, take the top part of the cuvette cell between index and thumb, and pull up gently to extract both parts together (1→2→3).

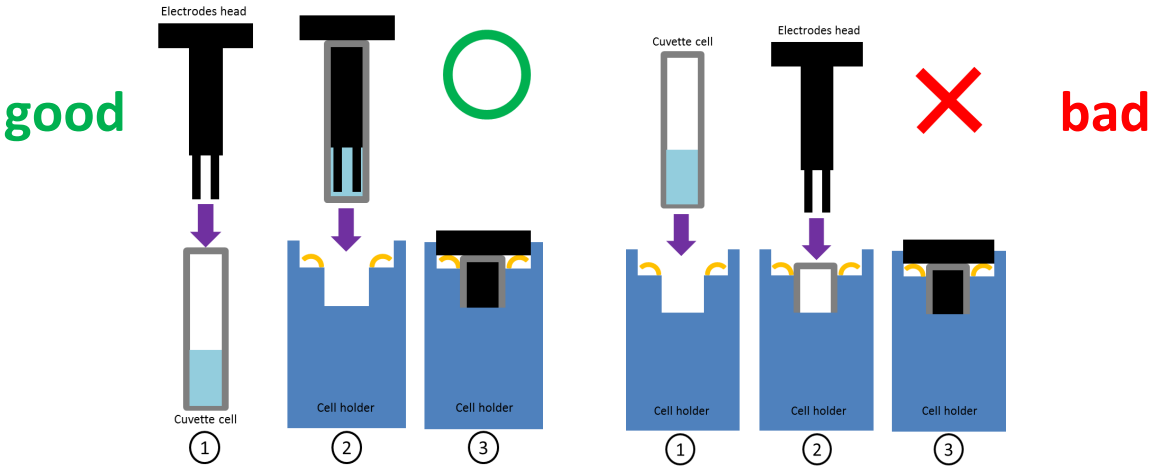


Figure 10: How to insert electrodes head and cell in cell holder (drawings)

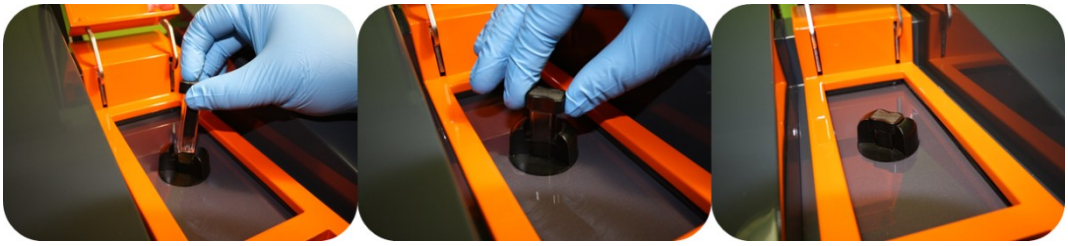


Figure 11: How to insert electrodes head and cell in cell holder (photos)

NB: we recommend not to start an experiment without the sample cell in place in its receptacle. Never put your finger on the cell holder electrical connectors while launching a measurement; electrical voltage and current are low so there is no risk of injuries bbut the device could be damaged.

Cleaning of electrodes head

After a measurement, you must clean as soon as possible the electrodes in order to prevent from contamination. Do not let dry up the sample droplets on the electrodes. To clean the electrodes, you can agitate gently the electrodes inside a Becker containing cleaning solvent like

water, alcohol or acetone. You can also rub very carefully and gently the surface of the electrodes with soft paper (or cotton bud) moistens with cleaning detergent. Do not rub the surface with hard tool or bare hand. You can also dip the electrodes in sonication bath for duration of less than one minute. Do not dip completely the electrodes head or let the full unit for long bathing (see Figure 12, Figure 13, and Figure 14).

Note: For all the manipulation describe below, be sure to respect the enforcing law of your country about disposability of your sample and solvents.

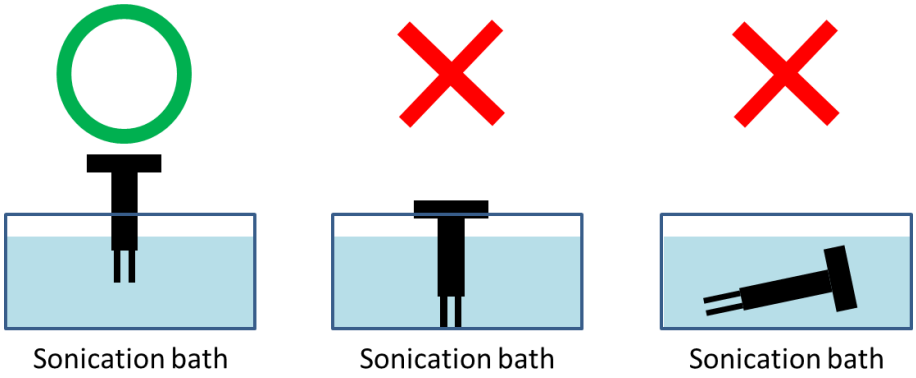


Figure 12: How to clean electrodes head with sonication bath

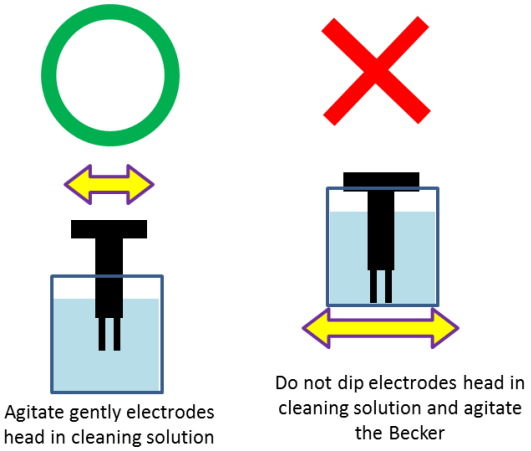


Figure 13: How to clean electrodes head with cleaning solution

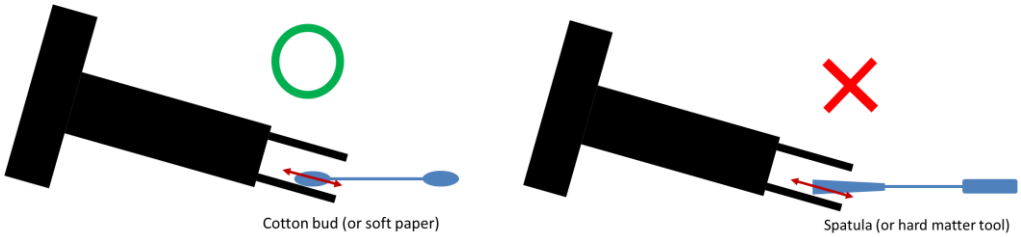


Figure 14: How to clean electrodes head with cleaning tools

Zeta potential: basics and principle

Introduction

Charged particles in liquid medium are complex systems being studied for quite a long time. The understanding and control of charge properties of colloids is subject for novel discovery as much as industrial process management. Unfortunately, complexity of models and real world of colloids make that charge of colloids often misinterpreted. After recalling how and what is really measured in Zeta potential measurement system, we then explain how these measurements relate to particle interactions and to colloids stability.

Electrophoresis physical principles

Electrophoresis phenomenon exists because particles in liquid are charged. The principle of measurement consists in applying a constant amplitude electric field ($\vec{E}$) to the colloidal solution. The resulting electrostatic force ($\overrightarrow{F_e}$) induces a motion of the particles with a charge q along the field direction. In addition, in a liquid media, the moving particles will undergo a friction force ($\overrightarrow{F_f}$) opposite and proportional (α) to their speed ($\vec{v}$) direction as illustrated on Figure 15. After an initial acceleration phase, the two forces canceled each other when the particles reach a stable, constant speed limit ($\vec{v}_{lim}$) given by:

$$\vec{v}_{lim} = \frac{q}{\alpha}\vec{E} \qquad (1)$$

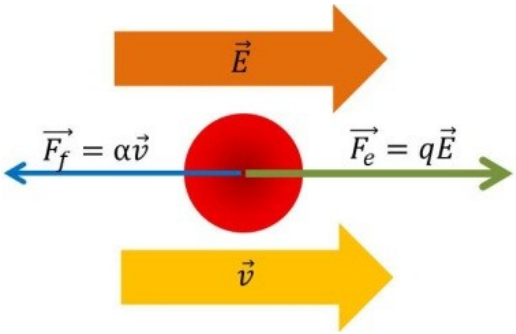


Figure 15: Forces on positively charged particle in a liquid, moving under electric field.

The factor q/α, called the electrophoretic mobility μ_e, is the capacity for a charged particle to move in a fluid under the action of an electric field. The electrophoresis measurement principle is, by optical means, to measure the Doppler frequency shift generated by the speed of the particle to get $\vec{v}_{lim}$ and thus, knowing the electric field $\vec{E}$, determine the electrophoretic mobility. This μ_e parameter is deeply meaningful to characterize particles because it doesn't need any particular assumption about the charge repartition of the particle nor specific knowledge of particle size or shape indebted in the α parameter.

Electrophoretic mobility to Zeta potential relationship

One question raises at this point: how does electrophoretic mobility relates to zeta potential and to particle-particle interaction. The simplest way to explain that is first to consider the electrostatic potential of a charged particle in space which fully determines the interaction with other particles. The electrostatic potential $V(r)$ associated to a charge q in space is defined by:

$$V(r) = \delta \frac{q}{\varepsilon r} \qquad (2)$$

Where r is the distance to the center of charge, δ is a constant and ε is the dielectric constant of the medium. The dielectric constant is define as :

$$\varepsilon = \varepsilon_0 \varepsilon_r \qquad (3)$$

Where ε_0 is the vacuum dielectric constant and its value is ε_0 = 8,854187.10^{-12} F.m^{-1}, and ε_r is the relative dielectric constant (See **Erreur ! Source du renvoi introuvable.**)
In vacuum δ = 1/4π and $\varepsilon = \varepsilon_0$ ($\varepsilon_r = 1$). This potential is represented in Figure 16. The shorter the distance to the charge the strongest the interaction (the potential) is. Keeping in mind this basic model let's continue with the measured quantity: the electrophoretic mobility μ_e.

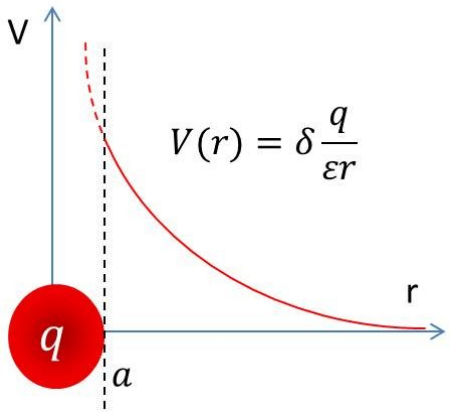


Figure 16: potential for one particle of radius a

If we assume that the particles are spheres immersed in a liquid of viscosity η and have a hydrodynamic radius R, the friction factor α (see ***Figure 15***) is given from the Stokes[1] relation:

$$\alpha = 6\pi\eta R \qquad (4)$$

From (1), the electrophoretic mobility is then given by:

$$\mu_e = \frac{q}{6\pi\eta R} \qquad (5)$$

According to relation (2) one can define a new potential ζ , given by the following relation:

$$\zeta = b\mu_e \frac{\eta}{\varepsilon} = B\frac{q}{\varepsilon R} \qquad (6)$$

where B and b are constant factors, η is solvent viscosity and ε is solvent dielectric constant. ζ has the dimension of an electrostatic potential like V for an equivalent charge Bq (see (2) and ***Figure 17***); it is called the Zeta potential. In fact, ζ represents the electrostatic potential measured at a distance R from the center of the particle. According to the Stokes model, the hydrodynamic radius R of the

[1] The α factor for spheres appears also in the particle size measurement by dynamic light scattering (DLS).

particles is the physical radius of the particles plus the surrounding ions/molecules environment "stuck" to the particle (see ***Figure 17***). Therefore, the potential of the particle at this *new* radius, determining the amplitude of interaction with the other particles, is a fundamental characteristic of the stability of solution. Indeed, the lower the zeta potential, the easier it is for two particles to approach each other and eventually to aggregate together, so the less stable is the colloidal suspension.

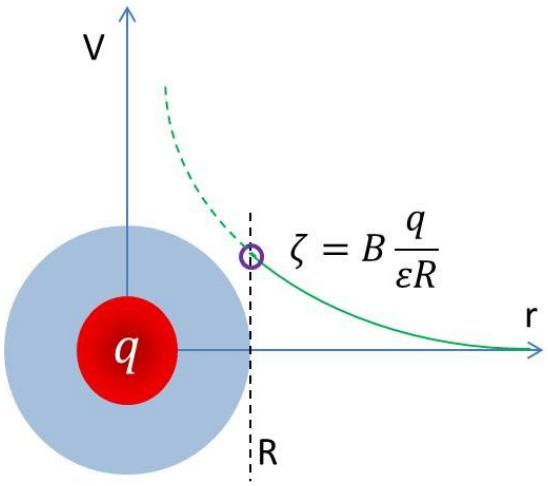


Figure 17: Zeta potential

The last point to understand in the definition of ζ is the signification of the parameter b. As one can see from (5), the determination of the Zeta potential requires to know the solvent viscosity and dielectric constant. This reflects that Zeta potential is a global property of the particle associated to its surrounding solvent counter ions layer thus representing the global free net charge of particles.

Net charge models

The global net charge of particle is defined by the Henry function $f(\kappa a)$ that is corresponding to the b factor. Thus, the full Zeta potential equation from Wallis measurement is:

$$\zeta = \mu_e \frac{\eta}{\varepsilon} f(\kappa a) \qquad (7)$$

κ^{-1} is the Debye length corresponding to the size of the charge layer that surrounds the particle and a is the physical radius (ie hard sphere radius) of the particle (***Figure 18***). Note that $\kappa^{-1} + a = R$. By limiting the Henry function to these two parameters, shape effects are neglected which is a realistic assumption for hard surfaces. The Debye length κ^{-1} is solvent dependent consequently is the Henry function.

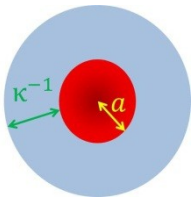


Figure 18: Debye length illustration

In fact, the Henry function varies between 1 and 1.5 depending on the κa factor value. In practice, there are two opposite situations that correspond to most of the real experimental case, See ***Figure 19***. First case: Smoluchowski approximation. Henry function equals 1, corresponding to a Debye length small compared to the particle physical radius. This case accurately described the aqueous type solution. Because of high polarizability of aqueous type solvent molecules, few will be enough to screen the particle potential thus, the surrounding layer of counter ions attracted and stuck to particles will be small. Second case: Hückel approximation. Henry function equals 1.5 corresponding to a Debye length large compared to particle size. This case accurately described organic like solvent. Because of low polarizability of organic like solvent molecules, a lot will be needed to screen the particle potential thus, the surrounding layer of counter ions attracted and stuck will be large.

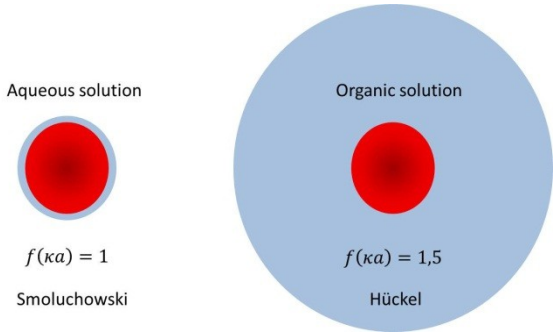


Figure 19: Henry function approximation

The hard step

The fine understanding of this complex world, opened by the measurement of Zeta potential, needs deeper explanation and further readings. In few words, the interaction of liquid's ions with solid surface like particle surface induces surface molecules dissociation or charge adsorption. It results an organization of charge near the solid surface depending of several properties of the surface and solvent (see ***Figure 20***). This structure has been named the Electrical Double Layer (EDL) and is generally described by the Gouy-Chapman-Stern model [1-2]. It characterizes particle-particle interaction thus determines the solution properties like stability, chemical activity, optical activity…etc. Such interactions are fully described by the DLVO theory, named after Derjaguin, Landau, Verwey and Overbeek whom developed it [3]. It modeled the electrostatic potential created around the particles so that the particle-particle interaction can be analyzed. Even though this theory is complex, the knowledge of the Zeta potential is a global key to understand stability of colloids solution.

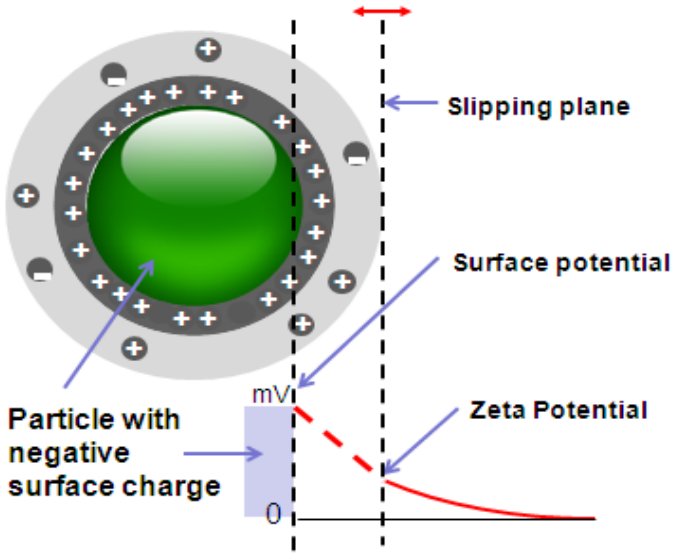


Figure 20: Electrical double layer

Conclusion

This chapter ought to introduce a basic understanding of Zeta potential with a simplified description of what happen at particle interface in liquid. It shows that Zeta potential reflects a particle-solvent interaction. It results that the knowledge of Zeta potential is a key factor for understanding stability of colloidal dispersion.

Measurement principle

Introduction

It has been shown in the previous section that, for most colloids, zeta potential can be related to the electrophoretic mobility in a very simple manner. Indeed, all zeta potential analyzers rely on the measurement of the electrophoretic mobility which is related to electrokinetic phenomena. This section describes how WALLIS measures with an improved accuracy the electrophoretic mobility using an optimized Laser Doppler Electrophoresis (LDE) technique.

Electro kinetic

The interaction of liquid's ions with solid surface like particle surface induces surface molecules dissociation or charge adsorption. It results an organization of charge near the solid surface depending of several properties of the surface and solvent. It has been named the Electrical Double Layer (EDL) and is generally described by the Gouy-Chapman-Stern model; its complete dynamic behavior is named electro kinetic phenomena [IUPAC]. Electrophoretic mobility (μ_e) is one of these phenomena. It determines the speed $\vec{v}$ of particles when an electric field $\vec{E}$ is applied to the liquid solution. It is define as:

$$\vec{v} = \mu_e . \vec{E} \qquad (8)$$

For more detailed explanation, read Zeta potential chapter.

Electro osmosis

The particles that have a charged surface as described by EDL move along the applied field direction. However, applying an electric field to a liquid can produce a parasitic effect named electro osmosis. Similarly as the surface of particles gets charged when immersed in liquids, the cell walls also get charged along their inner surfaces. If the applied electric field is close enough to the inner surface, like for example in capillary configuration, the charges at the surface will move inducing the liquid to flow at a speed $\vec{v}_{eo}$ along the inner surface. This will cause the liquid to flow back along the center of the cell at a speed $-\vec{v}_{eo}$ modifying the apparent electrophoretic speed $\vec{v}$. To correct for this bias several techniques are used; a mechanical adjustment along $\vec{v}_{eo}$ profile along the radius of the capillary to find the stationary layer or multiple cross measurement are generally performed but correction efficiency is limited due to confined space. Thanks to its optimized dip cell configuration WALLIS prevents from electro-osmotic flow to happen by applying the electric field far away enough from the inner surfaces of the cell.

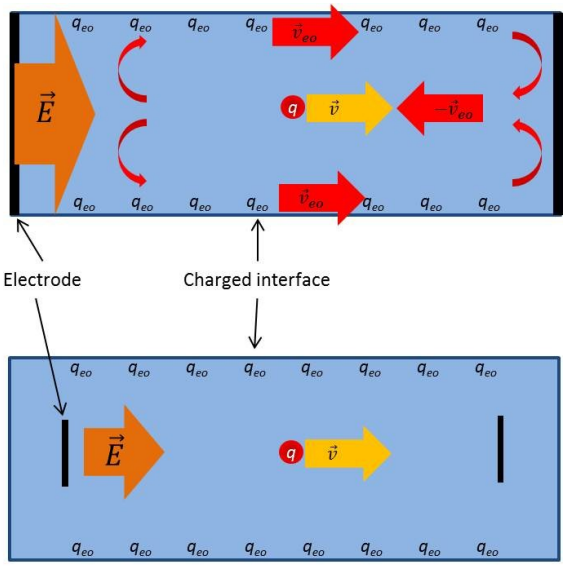


Figure 21: Electro osmosis effect illustration

Measurement principle

Now that the particles move in one direction without artifact, the particle speed/mobility can be measured by an optical method based on the measurement of Doppler frequency shift $f_{Doppler}$. This Doppler frequency shift is a well know phenomenon observed by a fixed observer when a signal at a fixed frequency is scattered/emitted by an object moving with respect to the observed /detector. The Doppler frequency shift for colloidal solution is usually of the order of several Hertz to compare to the original frequency of laser source (f_0) of 5.10^{14} Hertz. A very sensitive way to extract this small shift is the optical interferometry. The principle is to split a part of the laser source as reference light and mix it on the optical detector with the light scattered by the sample. The resultant frequency of the mixing is the difference between the frequencies of each beam cancelling the original frequency of the laser (present in each beam) and giving the Doppler shift as a result. In practice, only the absolute value of $f_{Doppler}$ is measured but the sign of $f_{Doppler}$ that is related to the sign of Zeta potential then the charge of particles is necessary. To get the sign of the charge, the reference light is phase modulated having an additional known frequency $f_{Modulation}$. In this case, the measured resultant frequency is $|f_{Doppler} + f_{Modulation}|$ giving directly the sign of $f_{Doppler}$. This technique is known as heterodyne measurement [ref ISO].

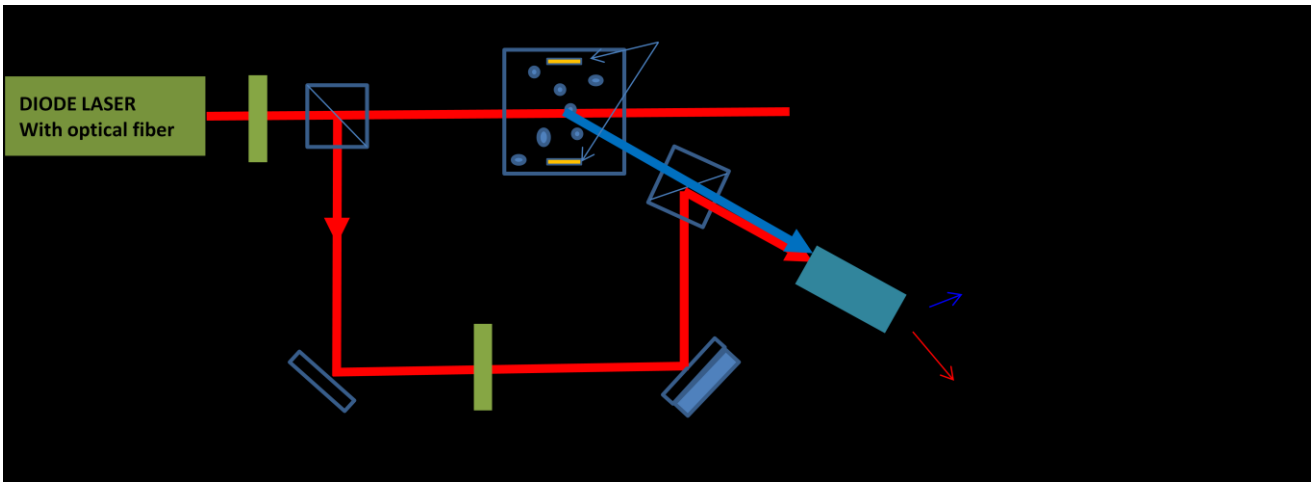


Figure 22: LDE measurement principle

Doppler frequency shift relation with electro-phoretic mobility

After measuring the Doppler frequency shift, the electrophoretic mobility can be calculated depending of the geometry of the experimental setup. As explained above, to probe the sample, the laser source (incident direction = $\overrightarrow{k_I}$) is focused on the sample where particles are moving. The scattered, frequency shifted, light is collected at a fix angle θ_d (scattered direction = $\overrightarrow{k_S}$).

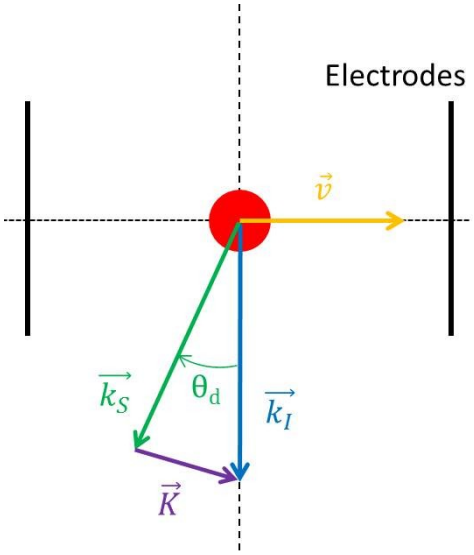


Figure 23: Geometric definition

The Doppler frequency shift $f_{Doppler}$ is related to the speed $\vec{v}$ of particles and the detection angle θ_d (through the scattering vector $\vec{K}$ define in Figure 23) by:

$$2\pi f_D = \vec{v}.\vec{K} = \vec{v}.\left(\overrightarrow{k_I} - \overrightarrow{k_S}\right) \qquad (9)$$

As Figure 23 represents the standard optical design for Zeta potential measurement device, and recalling eq (8), the following relation can be written:

$$\vec{v}.\overrightarrow{k_I} = 0 \qquad (10)$$

$$\vec{v}.\overrightarrow{k_S} = \mu_e E \frac{2\pi}{\lambda}\cos\left(\frac{\pi}{2} + \theta_d\right) \qquad (11)$$

Where $\left\|\overrightarrow{k_S}\right\| = 2\pi/\lambda$, with λ the wavelength of the incident light. It results for the electrophoretic mobility μ_e:

$$\mu_e = \frac{\lambda}{E \sin\theta_d} f_{Doppler} \qquad (12)$$

The electrophoretic mobility μ_e is directly proportional to Doppler frequency shift $f_{Doppler}$. In fine, Zeta potential, which is proportional to the electrophoretic mobility, is then also proportional to Doppler frequency shift. Obviously the better the quality of $f_{Doppler}$ measurement is the better the expected results will be.

The overall principal of the zeta potential measurement as described above and applied in the Wallis analyzer is depicted in the follow diagram:

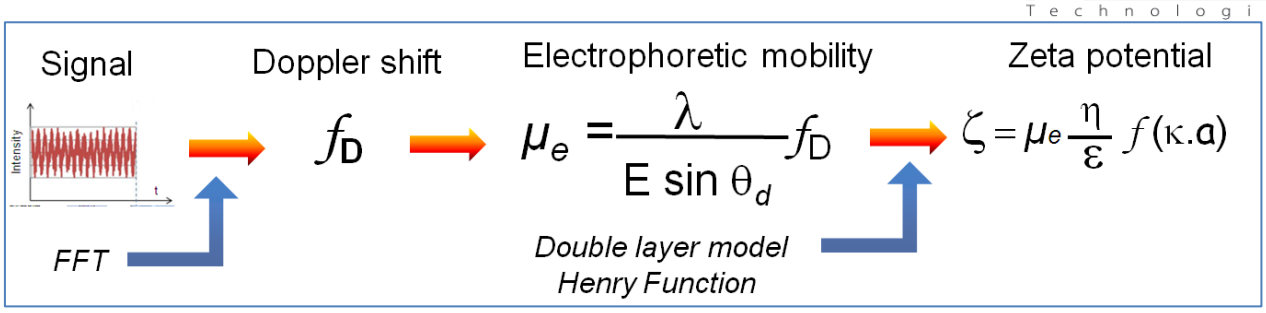


Figure 245: overall zeta potential measurement sequence principle

Discussion on frequency domain analysis

The physical output of the optical detector (APD) is the mixing amplitude versus time. This output signal contains a frequency that is the sum of the Doppler frequency shift and selected modulation frequency $|f_{Doppler} + f_{Modulation}|$. Usual data treatment uses a correlator to calculate the autocorrelation function. In this case, the autocorrelation function is a damp sine wave at the same frequency as the original intensity time series. Damping is an exponential decrease due to Brownian motion like in particle size measurement. Applying an FFT on the autocorrelation function gives the frequency. Historically, this method still used in all zeta potential analyzers is preferred for several reasons: it can manage large buffer size (long time series) and produce good Signal-Noise-Ratio (SNR). The use of a correlator also allows combining into one instrument Zeta potential and particle size measurements. Unfortunately, the price to pay in using a correlator with its powerful averaging capacity is the lack of time resolution and thus hampering the capacity of having high resolution on the FFT output.

To understand this point, let us remember the resolution δf of the Fourier transform:

$$\delta f = \frac{f_s}{N} \qquad (13)$$

Where f_s the sampling frequency and N is is the number of point in the sample. In the case of the autocorrelation function, the number of point is set by the number of channels. To increase the resolution, the only possibility is to decrease the sampling frequency. The sampling frequency should satisfy the Nyquist–Shannon sampling theorem:

$$f_s \geq 2f_c \qquad (14)$$

Where f_c is the maximum measured frequency (it means the maximum of $|f_{Doppler} + f_{Modulation}|$ + noise). Some typical numerical values are given in the Table 1. Considering that the measured Doppler frequency shifts are of a magnitude of several Hertz, it become obvious that for a good correlator (N~4000) the maximum measured frequency must be very low to get a descent resolution. As explained above, the modulation frequency is necessary to get the sign of Zeta potential, but also to get out of the low frequency noise band. A modulation frequency of 300Hz (f_c ~500Hz) is the minimum necessary to get out of the extremely noisy band under 100Hz in this case the best you can get is a resolution of 1Hz (in reality several Hertz). The best is to go above 2 kHz far away all the environmental noises but in this case the resolution is too high to get any results.

f_c (Hz)	f_s(Hz)	N	δf(Hz)
500	1000	4000	1
2000	4000	4000	4
10000	20000	4000	20

Table 1: Relation between measured frequency and resolution.

For Wallis, a different approach, dedicated to Zeta potential was used. Using recent development in rapid data acquisition hardware, the FFT is performed directly on the original time series. Averaging is made over several acquisitions. Using the high buffer capacities of modern hardware, the number N can be largely increased. It allows to both enhanced greatly the resolution and increase the modulation frequency to avoid all background frequencies noise. Typically, Wallis uses a modulation frequency of several kHz and being able to get a resolution of 0,1Hz.

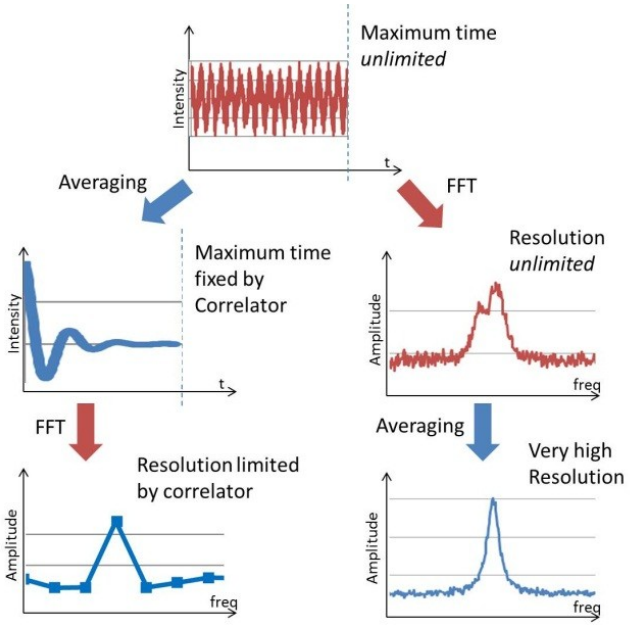


Figure 25: High resolution measurement

Conclusion

This note shows that thanks to its optimized acquisition chain purely dedicated to electro-phoretic/ Zeta potential measurement system improves Wallis greatly improves zeta potential measurements. Indeed, getting rid of the correlator commonly used in 2 in 1 DLS + Zeta device, allows optimizing the acquisition chain specifically for zeta potential measurement leading to a significant improvement of the resolution of the measurement.

Appendix 1: Specifications

Zeta potential range	-200 mV to 200 mV
Mobility range	10^{-10} to 10^{-7} $m^2/V.s$
Particle size	1 nm up to 100 µm
Sample concentration	0.0001% to 10% w/% (solvent dependent)
Temperature control range inside the cell	10°C to 70°C +/-0,1°C
Sample volume	Typically 750 µL
Maximum sample conductivity	300 mS/cm
Sample Type	Aqueous & organic solvents – pH: 1-14 (depending on cuvette cell material)
Measurement technology	Laser Doppler Electrophoresis (LDE)
Laser source	Highly reliable 20 mW diode @635 nm
Measurement angle	Single angle for zeta potential at 17°
Data processing algorithm	Fast Fourier Transform
Resolution	Mobility = 10^{-10} $m^2/V.s$ or Zeta = 0,1 mV (in water)
Detector	Avalanche PhotoDiode – APD
Computer interface	USB 2.0 – Windows XP, Seven
Dimensions	33 cm x 33 cm x 38 cm (HWD)
Weight	16 kg
Power	100-115/220-240 VAC, 50/60 Hz, 100 W max
CE certification	CE marked product - Class I laser product, EN 60825-1:2001, CDRH
ISO norm	ISO 13099-2 : 2012 – Colloidal system – methods for zeta-potential determination – Part 2 : Optical methods

Appendix 2: FAQ

1. **Does the electrodes head is symmetrical in use?**

   Yes. The symmetric shape of the connectors and electrodes give a symmetric use of the electrodes as long as you insert it correctly in the cell holder.

2. **Will the measurement proceed if the lid is open?**

   Yes. The lid must not be closed to proceed to measurement.

3. **How can I check that my electrodes are clean?**

   First make a visual inspection of the electrodes, in particular the inner surface; If it looks OK, make a measurement with pure de-ionised water. If the result is not zero, the electrodes are not clean.

4. **I don't have any more standard sample provided with the device. Where can I buy some?**

   You will need to contact our customer service to get a new bottle of sample.

5. **I would like to use a 2 transparent face cuvette cell for measurement. Is it OK?**

   It is possible to use a 2 transparent face cuvette cell for measurement as long as you use it properly. You must put the transparent faces perpendicular to the electrodes. For better reproducibility and accuracy, we recommend using Quartz Suprazil reusable cuvette.

6. **What are the units of the quantities used in ZetaQ?**

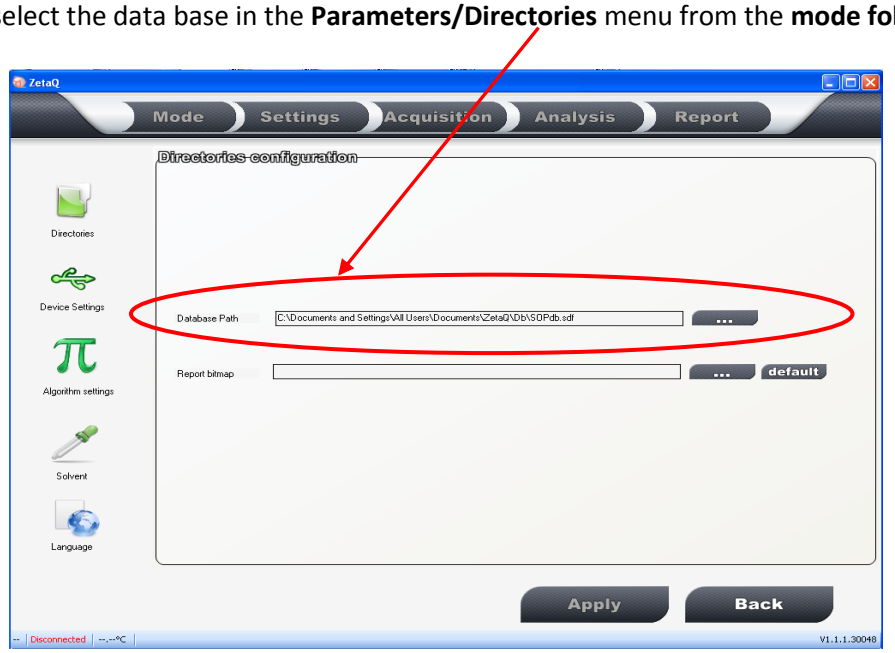
   Wallis units are defined according to the international MKS system:

designation	Symbol	SI units	ZetaQ units
Electro-phoretic mobility	μe	$m^2.V^{-1}.s^{-1}$	$\mu m.cm.V^{-1}.s^{-1}$
Zeta potential	ζ	V	mV
Electric field	E	$V.\ m^{-1}$	$V.\ cm^{-1}$
Conductivity	σ	$S.\ m^{-1}$	$mS.\ cm^{-1}$
Carrier frequency	f_m	Hz	Hz

Notations: m=meter, V=volt, s=second, S=Siemens, Hz=Hertz.

Appendix 3: Analyze data mode

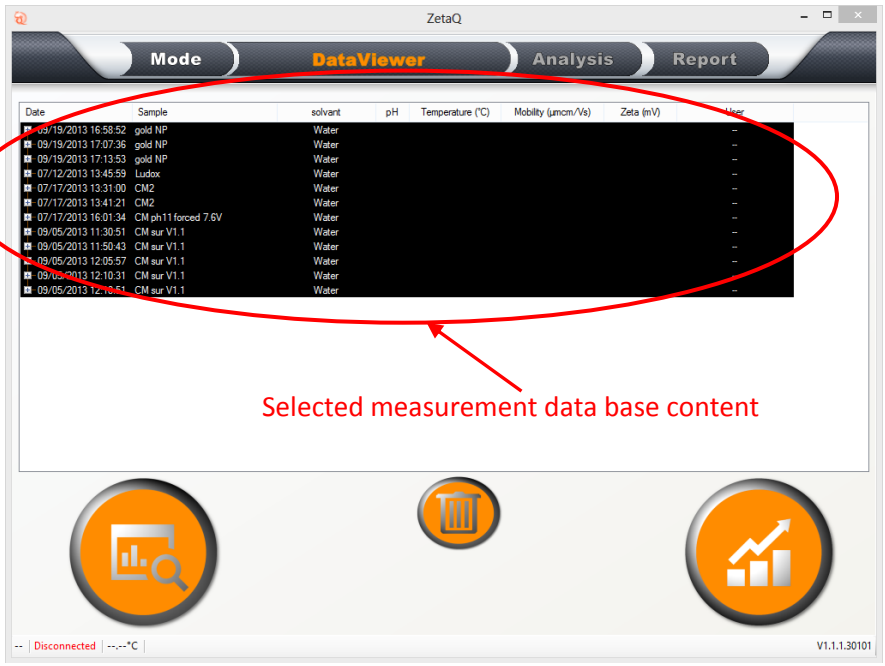
The Analyze data mode allows the user to perform measurement data post treatment and comparison on the measurement results saved into the data base;
First you need to select the data base in the **Parameters/Directories** menu from the **mode folder**:



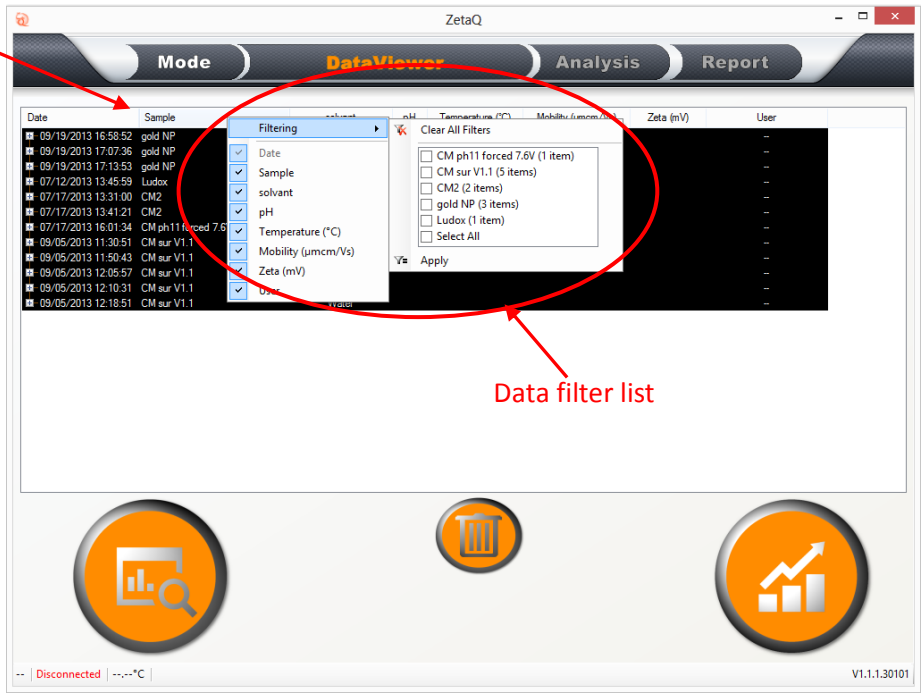
NB: only one data base at a time can be open with Zeta Q; it not possible to superimpose data from two different data bases.

In the **mode menu** of ZetaQ, clicking on the icon 

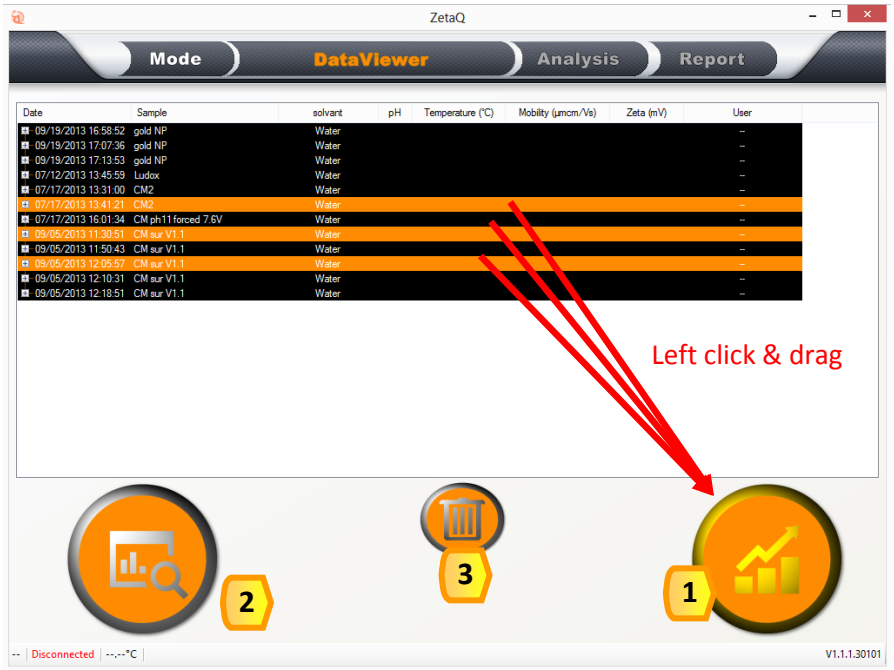
will open a new **Data Viewer** folder which will give you access to the content of the measurement data base.

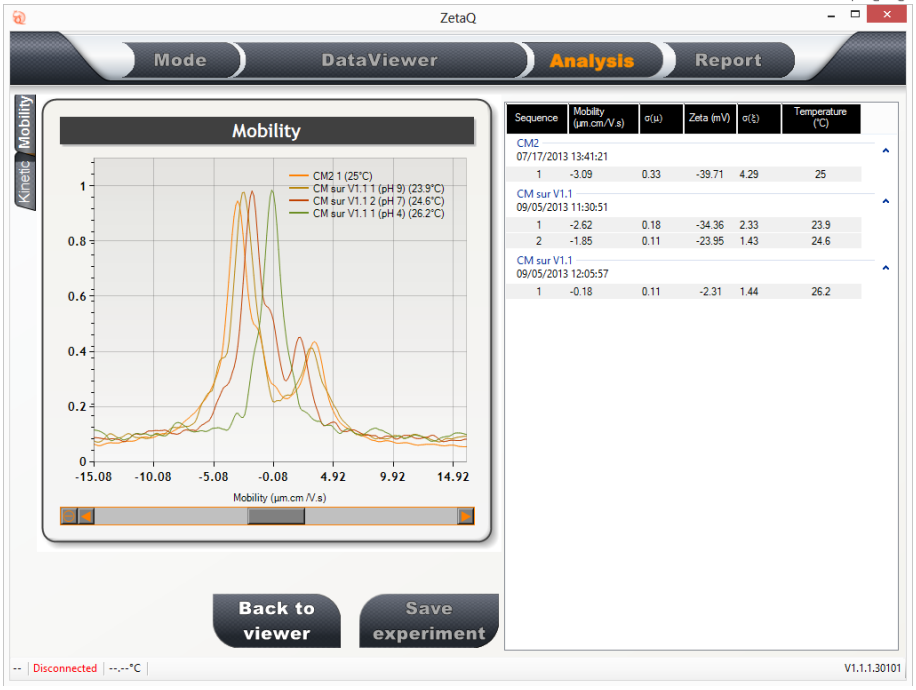


You can sort the measurements to be displayed in the list by using data filters (PH, solvent, user, etc.) These filters are similar to the ones used in excel files for examples. The filter list appears by a right click on the columns header.



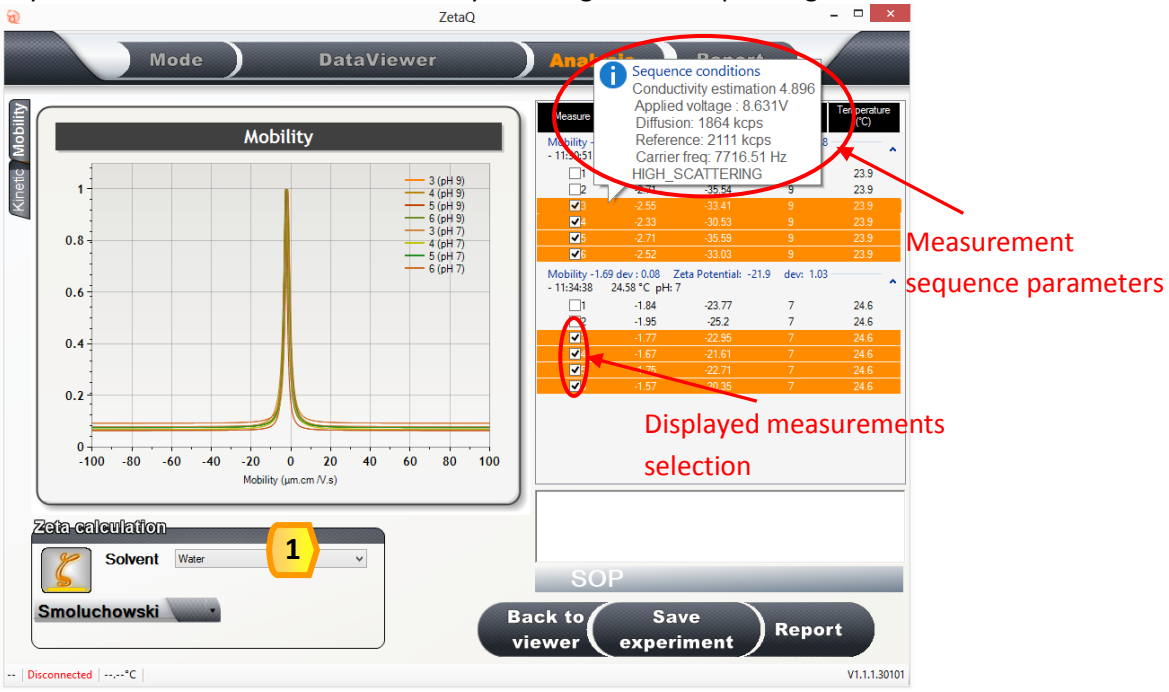
Select measurements to be displayed and analysed by a left click on the corresponding line and then drag the selected line with the mouse on the icon 1. If you want to visualize only one experiment, you can drag the selected line on icon 2. To remove the results of an experiment from the database, select its corresponding line with the mouse and drag it on the trash can icon 3.





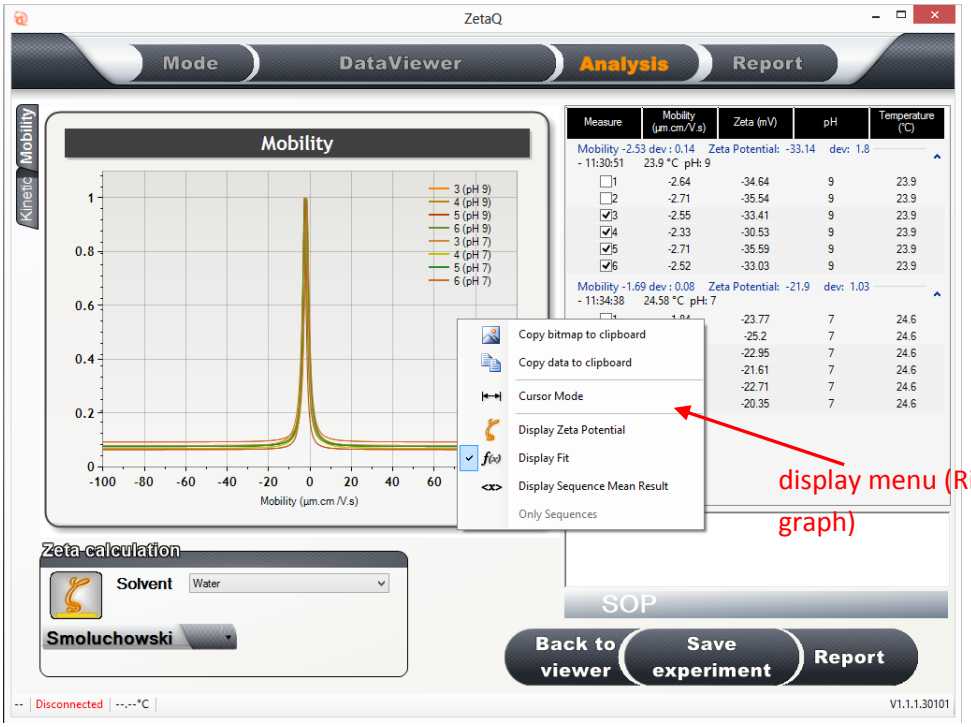
Example of experiment measurement results simultaneous display.

Measurement sequence parameters can be displayed by pressing the **CTRL key** and pointing the mouse to the selected line. Displayed measurements can be selected by checking the corresponding selection box.



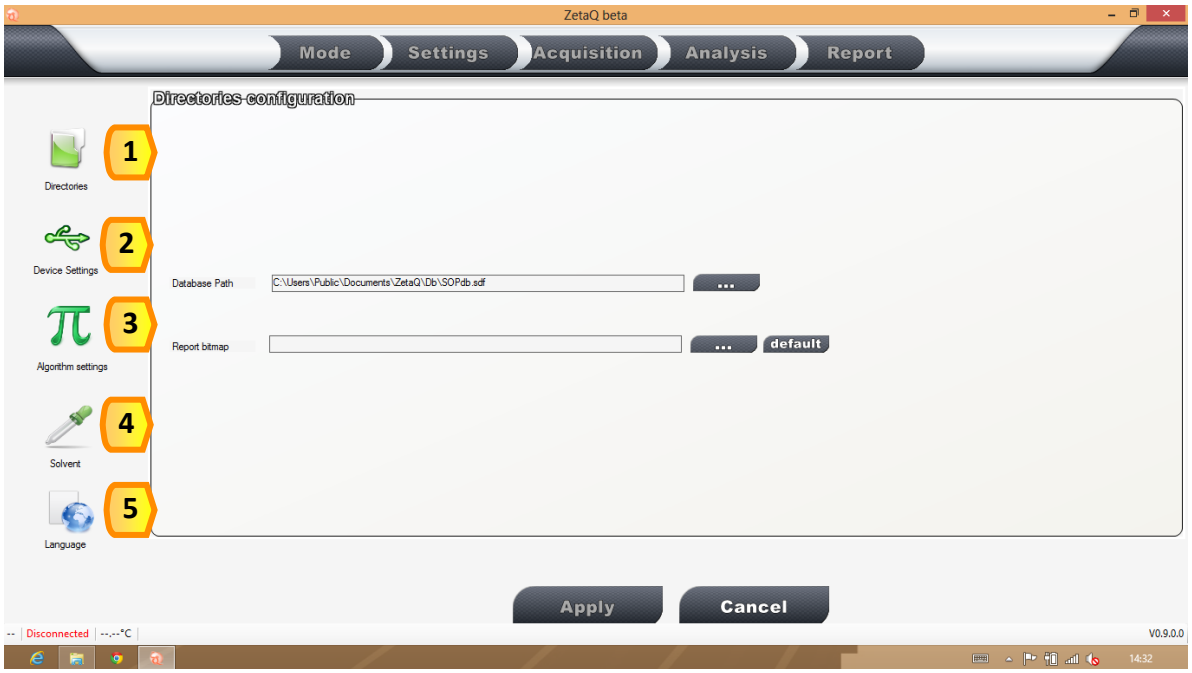
For each selected measurement you can change the zeta calculation model and solvent properties in Zeta calculation menu 1 .

By a right click on the graph (see below) , a selection menu appears which allows to copy data / bitmap (graph) to clip board, activate the cursor mode, display fit , display zeta potential graphs, etc.



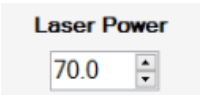
display menu (Right click on graph)

Appendix 4: Parameters mode and solvent data base



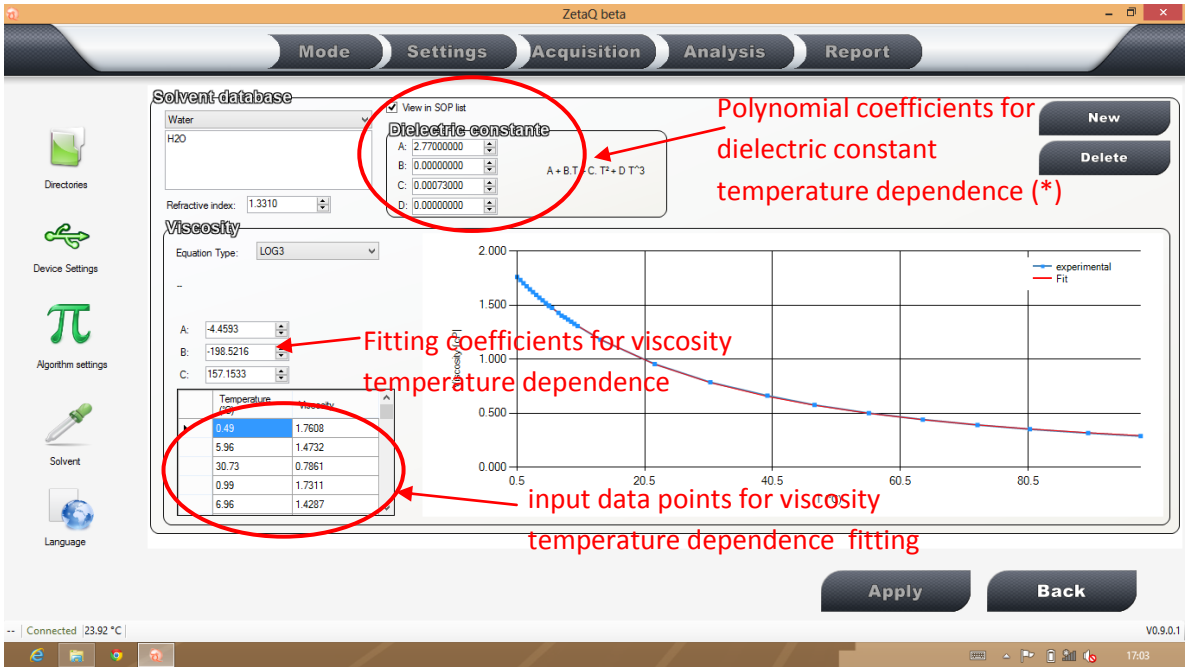
This menu allows the user to:

1. Define the measurement database and bitmap directory saving path
2. change the laser power default setting of the device (*)



3. access to the solvent data base and modify it (see screen capture below)
4. User defined settings for algorithm optimisation (not implemented yet)
5. Select the interface language (not implemented yet)

(*)*NB: This command is only accessible to administrator and expert users; changing the laser power away from its nominal operating point may have an impact on the measurement quality; if note required recommend to leave the laser power unchanged to its nominal value of 60%; laser power can be increased in some case of very low scattering samples.*



Solvent data base menu

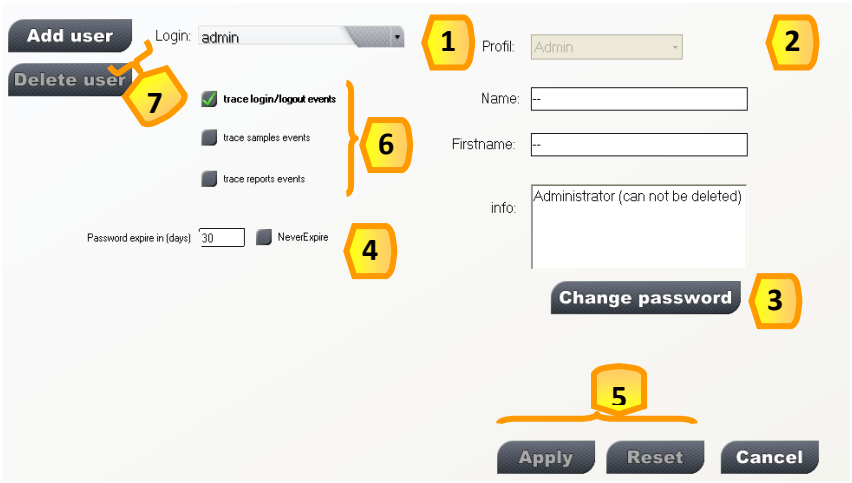
(*) Note: in this equation, T is the sample absolute temperature (in °K); if you know only the dielectric constant value at ambient temperature, you just have to enter this value as the A coefficient and set all other coefficient to 0;

Appendix 5: Users management utility

ZetaQ software integrates a User management data base utility. This utility allows **admin users** only to manage a data base of identified Wallis users (create login and password, delete, modify user profile, etc)

When logged as **admin** a supplementary button appears in the Mode folder.

Click on it to enter the AdminZetaQ simplified interface.



1 Select an existing user in the database list with its login

2 Change its profile as *Admin / Expert / Operator* in order to define its access rights restriction level. Then fill *Name* and *Firstname* field. If necessary. Additional information could be notified.

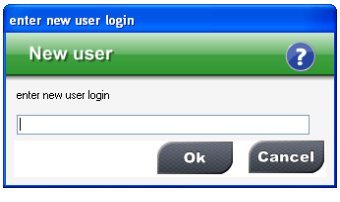
3 Modify the current password or create a new one.

4 Enable/disable password expiration and adjust time in days

5 Store modification by clicking on “Apply” or select “Reset” to initialize all fields.

6 CFR21 Compliance : login, samples or reports events could be stored in an encrypted file. Contact service@cordouan-tech.com to know how to access.

7 The “Add user” function creates a new login in the database. Fill all fields in the same way as a modification action. Admin could delete a wrong or no more usefull login from the user database.



Appendix 6: literature references

[1] ISO -13099B1, Colloidal systems—Methods for zeta potential determination—Part 1: Electro-acoustic and electrokinetic phenomena

[2] V.DELGADO *et al.*, Measurement and interpretation of electrokinetic phenomena (IUPAC Technical report) , *Pure Appl. Chem.*,Vol.77, No. 10, pp. 1753–1805, 2005.

[3] J. Lyklema, Fundamentals of Interface and Colloid Science, Academic Press, 1995

The solvent data base values are extracted from the CRC handbook and Viswanath book:

[4] W. M. Haynes (dir.), *CRC Handbook of Chemistry and Physics*, Boca Raton, FL, CRC Press

[5] DABIR S. VISWANATH, *Viscosity of liquids*, Springer, ISBN-10 1-4020-5481-5