

NOVA

Voltammetric Analysis Potentiometric Stripping Analysis Tutorial



1 – Voltammetric analysis and Potentiometric stripping analysis methods

This tutorial provides information on the voltammetric analysis techniques (see Section 2 and the Appendix 1 and 2) and the potentiometric stripping analysis (see Section 3) methods supported in NOVA.



Scope of the tutorial

The aim of this tutorial is to provide information about the voltammetric analysis and the potentiometric stripping analysis commands in NOVA and the measurement possibilities in the software. The control of the mercury drop electrode (MDE) is also explained.

2 – Voltammetric analysis methods

Originating historically with *DC Polarography*, the voltammetric analysis methods include various potential stepping and current sampling schemes, designed to discriminate between faradaic processes (related to electron transfer) and capacitive processes (related to charging and discharging of the electrochemical double layer). These methods are deeply rooted in the polarographic tradition and are still used in combination with polarographic electrodes.

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All voltammetric techniques have in common that a potential range is scanned. The potential range is defined by the initial-, end- and step- potential. At the end of each interval time, just prior to the next step, a data point will be collected. Therefore, the number of points is equal to the potential range divided by the step size. In this manner, the duration of the complete scan is determined by the number of sampled points multiplied by the interval time.

Since these methods are often used for polarography, the option to control a drop knocker at the end of each potential step is provided.



Note

The term *polarography* is used to describe the use of the voltammetric analysis methods in combination with a liquid working electrode whose surface is periodically renewed (Mercury Drop Electrode - MDE).

2.1 – Hardware setup

Although it is possible to use the voltammetric analysis methods on any type of electrode, this tutorial focuses on the use of the MDE. Three types of MDE stands can be controlled remotely by the Autolab:

- Metrohm 663 VA Stand¹
- Princeton Applied Research 303/303A Static Mercury Drop Electrode
- Dropping mercury electrode (DME)



Warning

The implementation of the pulsed methods (Differential pulse, Normal pulse, Differential Normal pulse and Square wave) is different than the implementation of these methods in the Autolab GPES software and the Metrohm Computrace software. Please refer to Appendix 2 for more information.

Remote control of these mercury electrode stands requires the IME663 (for the Metrohm 663 VA Stand, shown in Figure 1) or the IME303 (for the PAR303/303A and for the DME) interface². The IME can be connected to one of the DIO connectors on the rear of the PGSTAT or μ Autolab (Refer to the Appendix 1 of this tutorial for more information concerning the installation of a supported mercury drop electrode stand).



Figure 1 – The Metrohm 663 VA Stand and the Autolab IME663 interface

¹ <http://products.metrohm.com/prod-26630020.aspx>.

² In the rest of this tutorial, both interfaces will be referred to as IME.

NOVA Voltammetric and Potential Stripping analysis tutorial

In order to use the IME, the hardware setup in NOVA must be configured accordingly (see Figure 2).

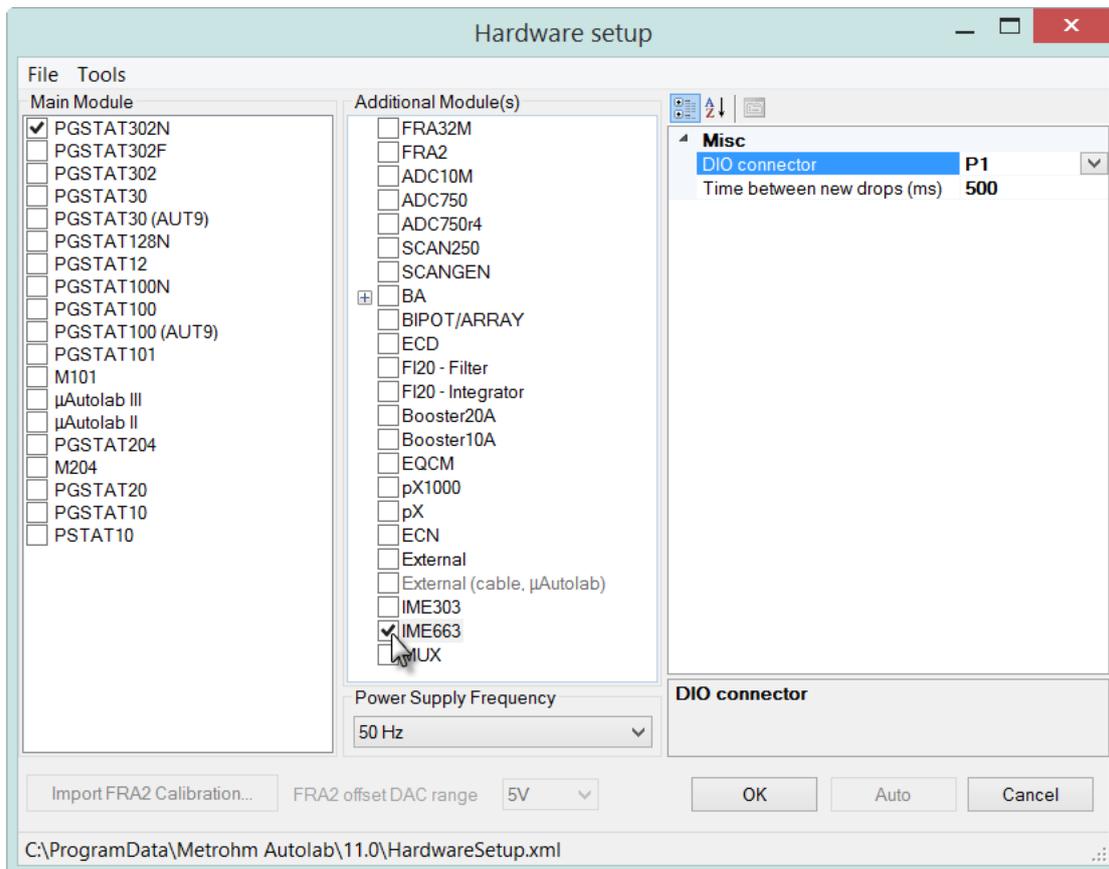


Figure 2 – Selecting the IME in the hardware setup

The DIO connector used to control the IME interface is defined on the right-hand side of the Hardware setup window, using the drop-down list, as shown in Figure 3 (the default connector is P1).

NOVA Voltammetric and Potential Stripping analysis tutorial

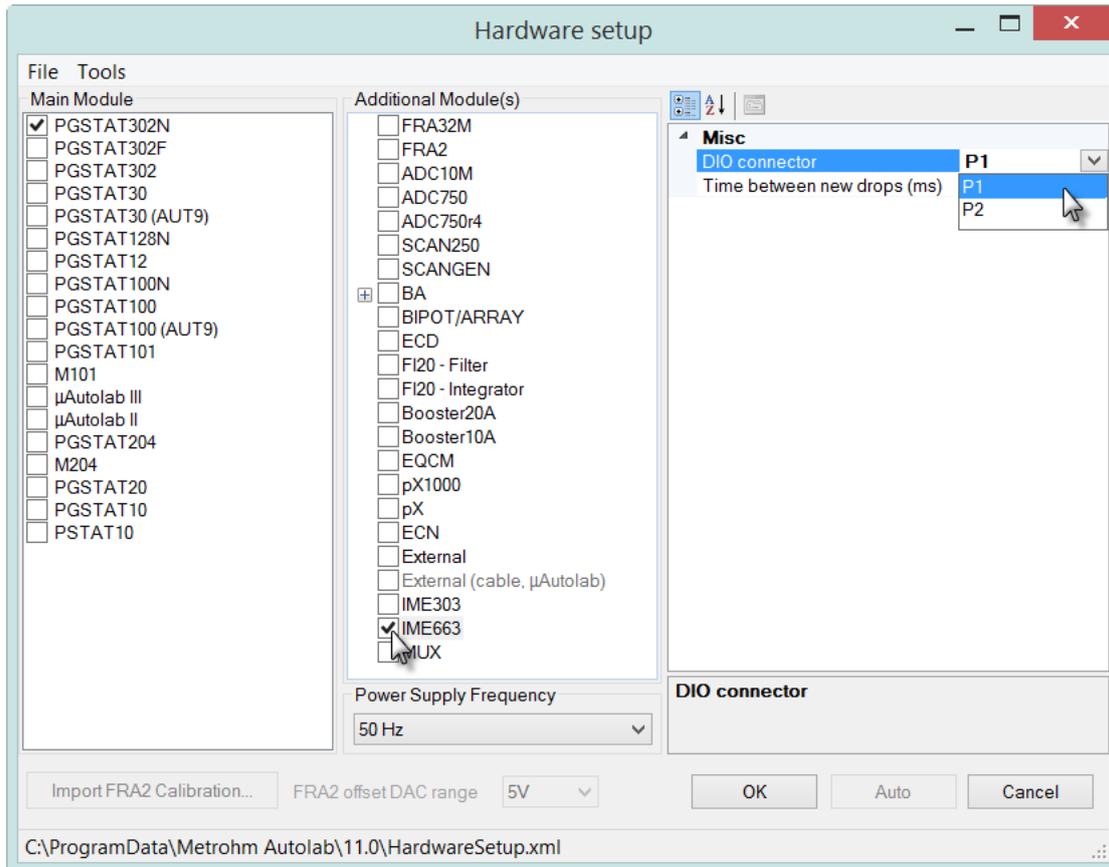


Figure 3 – Specifying the DIO port used to control the IME



Note

In the frame on the right-hand side it is also possible to define the time delay between two consecutive drops, in ms. The default value is 500 ms.



Warning

The 663 VA Stand only operates properly under computer control when it is switched in **SMDE** mode.

The settings of the Metrohm 663 VA Stand are defined using the knobs located on the top cover of the instrument (see Figure 4).

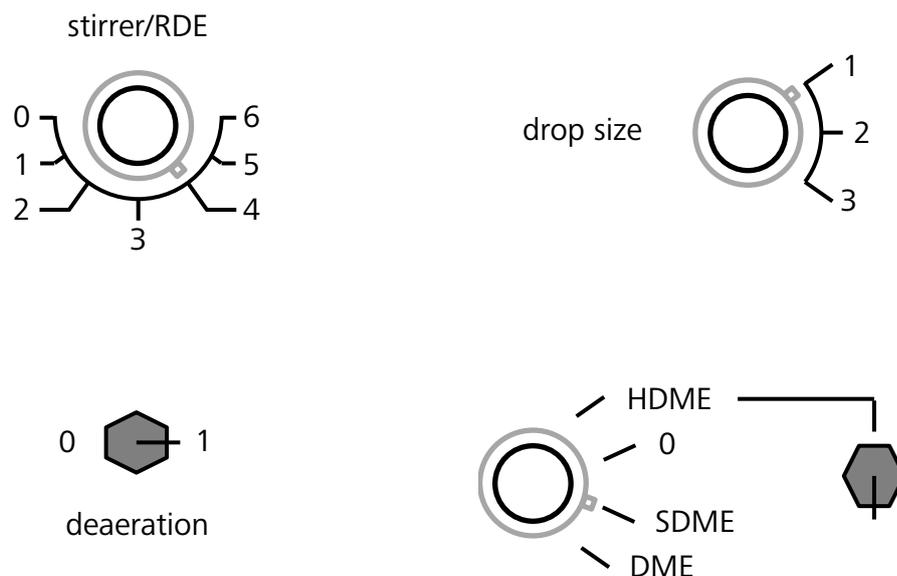


Figure 4 – Controls for the Metrohm 663 VA Stand are located on the top cover of the instrument (top left: stirrer control, top right: drop size control, bottom left: deaeration control, bottom right: MME mode and knocker control)

2.2 – Manual control of the MDE

The MDE module can be controlled manually at any time, using a dedicated panel of the Autolab display. To add the MDE manual control panel to the Autolab display, select the MDE manual control option from the View menu (see Figure 5).

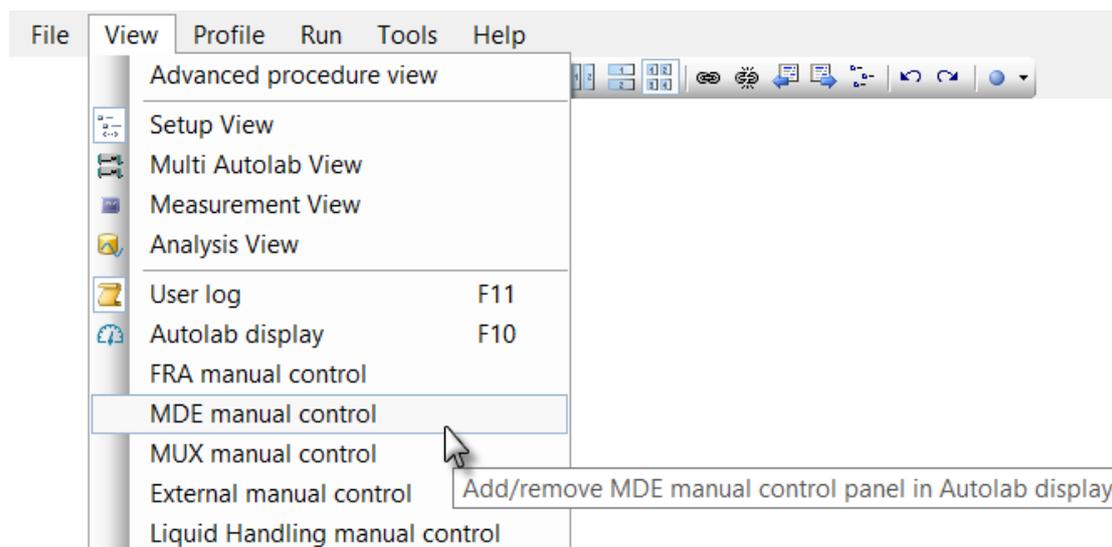


Figure 5 – Select the MDE manual control option from the View menu to add the MDE control panel to the Autolab display

The MDE manual control panel will be shown whenever the Autolab display is displayed (see Figure 6).



Note

Use the F10 shortcut key to quickly display the Autolab display.

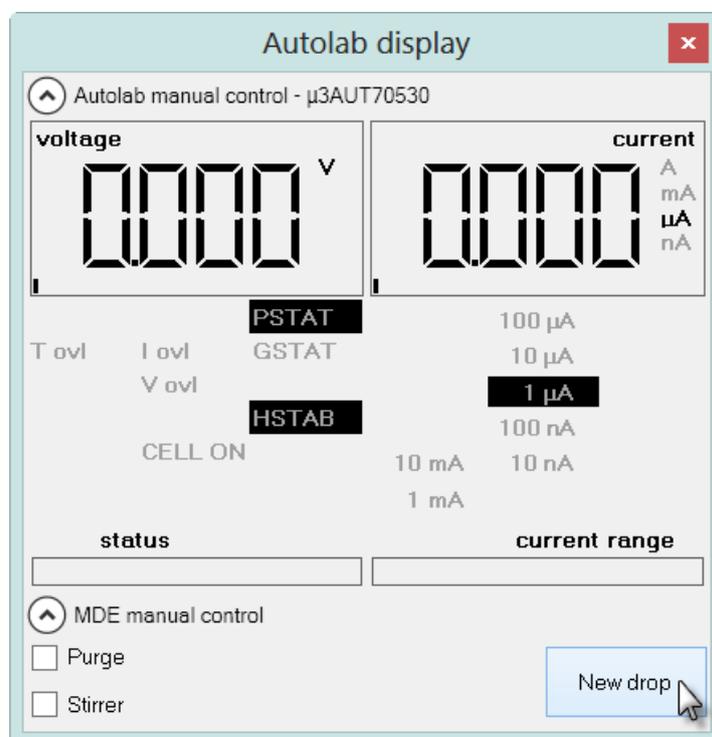


Figure 6 – The MDE manual control panel

The Electrode control interface can be used to switch the **stirrer** and the **purge** function on the MDE stand on or off. It also offers the possibility to create a new Hg drop by activating the drop knocker (see Figure 7).

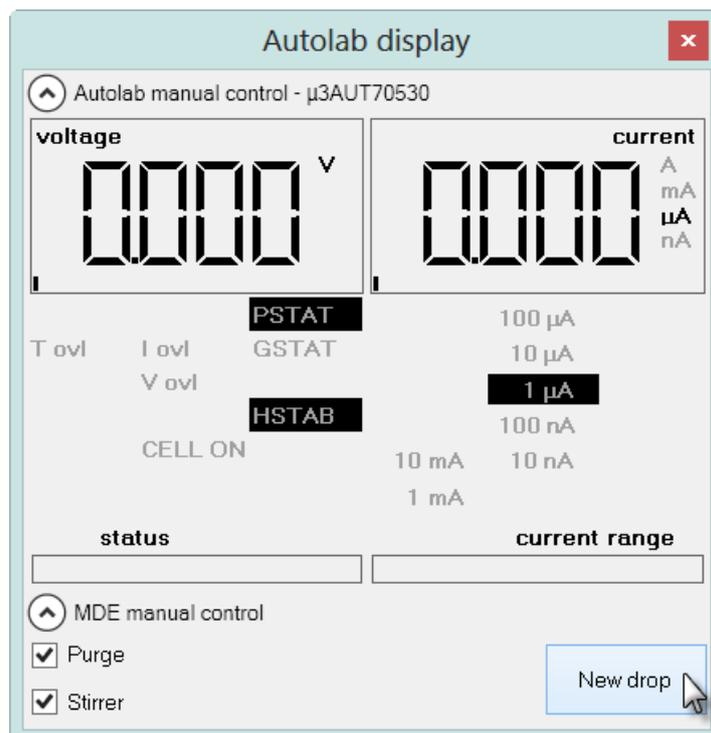


Figure 7 – Controlling the stirrer, purge and drop knocker through the MDE manual control panel

2.3 – Automatic control of the MDE

Control of the MDE during a measurement is also possible using the *Autolab control* command or three dedicated commands located in the Measurement – General group (see Figure 8).

The following commands are available:

- **Purge**: switches the Purge function of the MDE on for the specified duration, in seconds. During purging, the stirrer is automatically switched on.
- **Set stirrer (on/off)**: switches the stirrer on or off. The rotation rate is defined on the MDE.
- **Create new drop**: defines the number of new drops to create using the drop knocker function of the MDE. The creation of a new drop is always followed by a delay of 500 ms. The drop size is defined on the MDE.

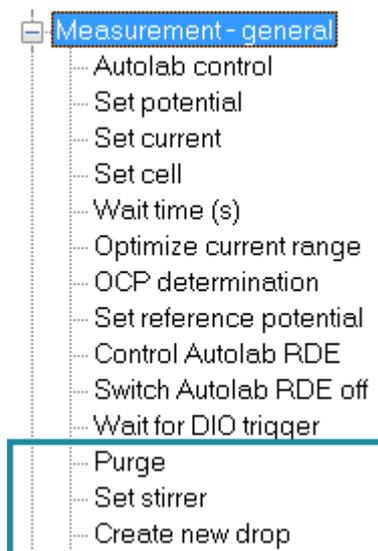


Figure 8 – Dedicated commands are available in the Measurement – General group³

These three commands are also directly available using the *Autolab control* command, in the IME663 or IME303 section (see Figure 9).

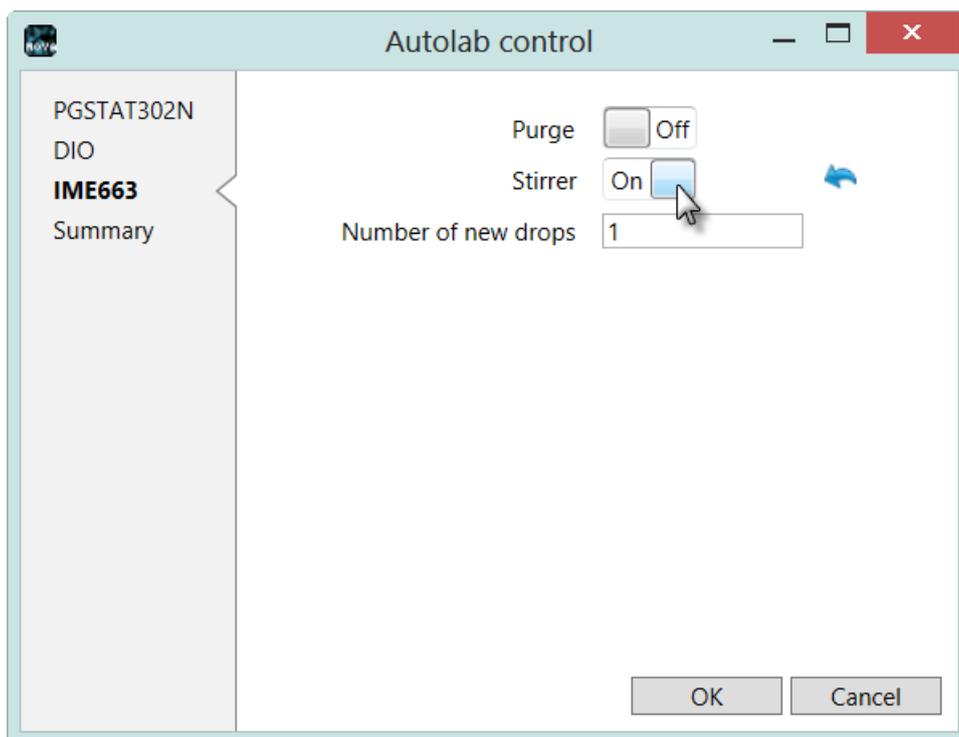


Figure 9 – The Autolab control window can be used to control the MDE

³ The commands listed in the Measurement – general group have been filtered using the Basic and Electroanalysis profile.

NOVA Voltammetric and Potential Stripping analysis tutorial

The Autolab control can be used at any time during a measurement to control the MDE. The properties changed in the *Autolab control* command will be displayed in the procedure editor, as command parameters (see Figure 10).

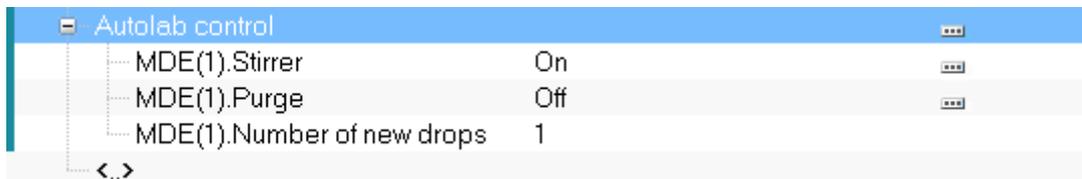


Figure 10 – The MDE settings defined in the Autolab control are displayed as command parameters

The MDE(1) parameters shown below the *Autolab control* command, in the procedure editor, can also be linked to other parameters, like an *Input box* command for example.

2.4 – MDE polarography option

Polarographic measurements involving the mercury drop electrode require a new drop to be created for each measurement point. To indicate that a new drop must be created at the beginning of each measurement step, the Options must be edited. To edit the options, click the  button next to the options item in the procedure editor or click the  button in the quick access toolbar (see Figure 11).

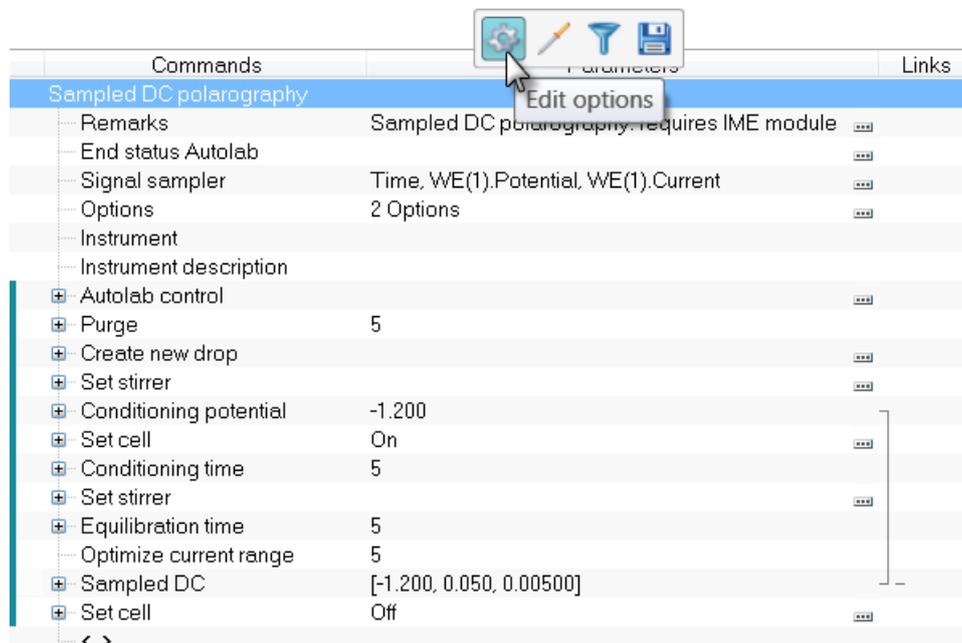


Figure 11 – Opening the options editor

The Edit Options dialog will be displayed (see Figure 12).

NOVA Voltammetric and Potential Stripping analysis tutorial

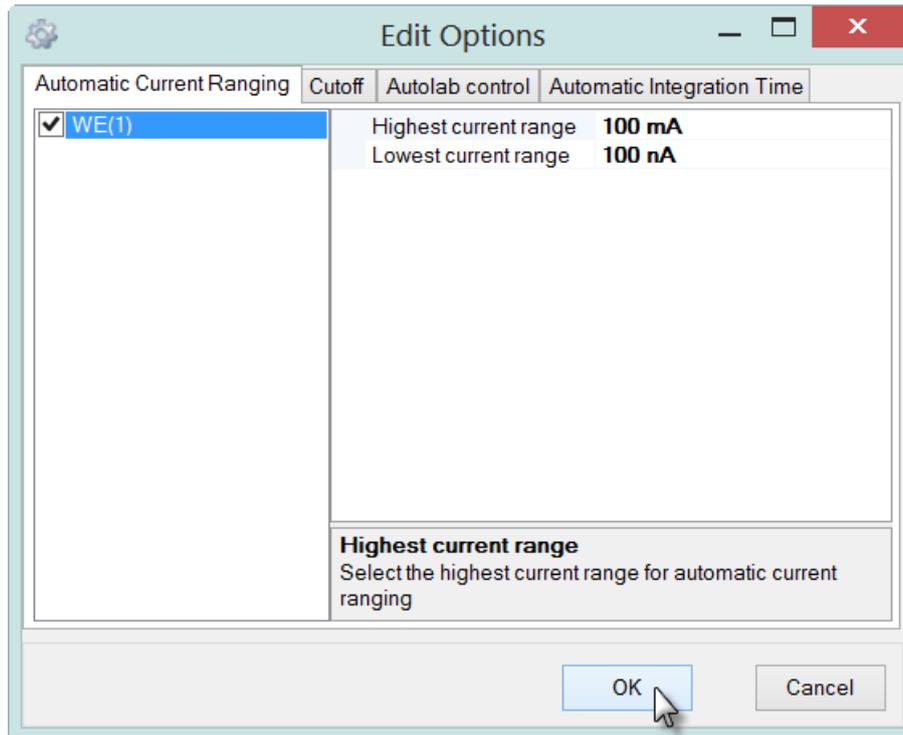


Figure 12 – The Edit Options dialog

The instrumental settings to modify at each data point are defined on the Autolab control tab of the Edit Options editor (see Figure 13).

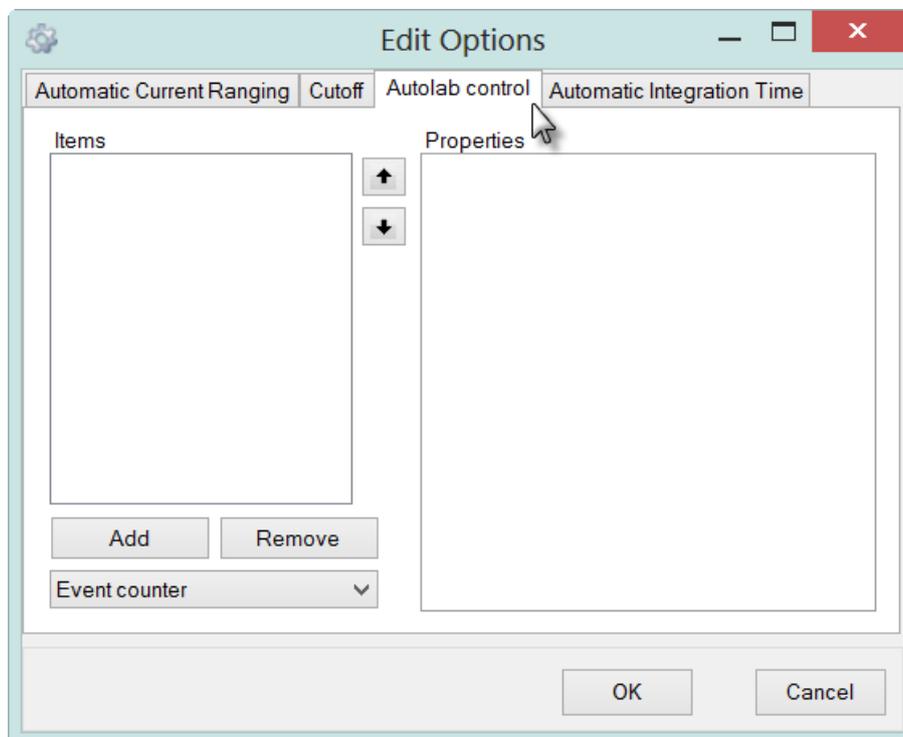


Figure 13 – The instrumental options are defined on the Autolab control tab

To indicate to the Autolab to create a new drop for each data point, select the Autolab control option from the drop-down list and click the button to add this option to the list of items displayed in the frame on the left-hand side (see Figure 14).

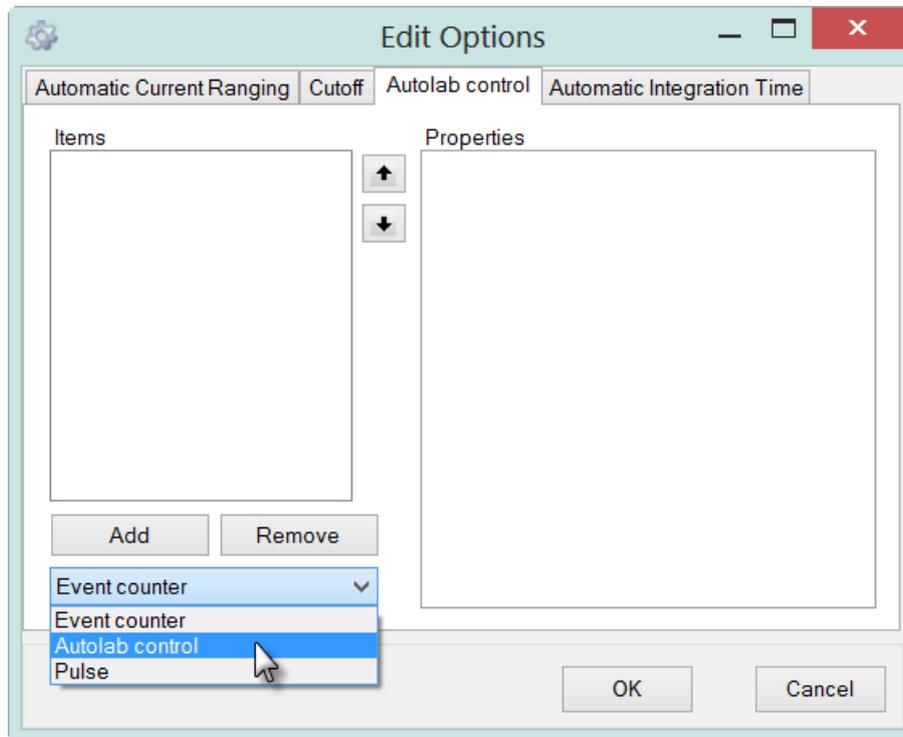


Figure 14 – Adding an Autolab control option

Once the Autolab control item is added to the list, click the button located in the properties frame (see Figure 15).

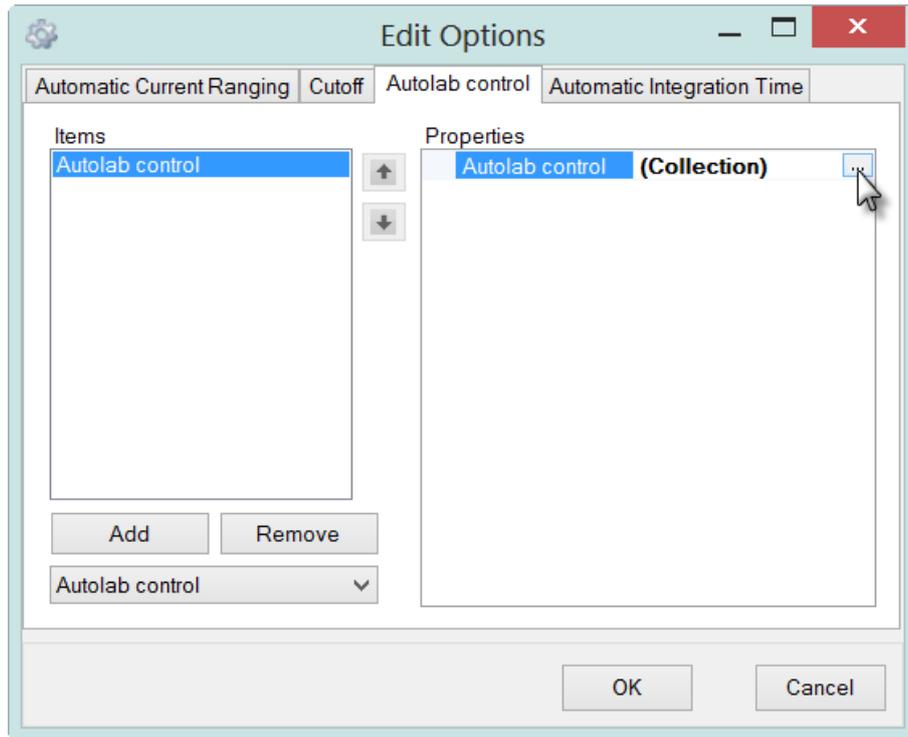


Figure 15 – Editing the settings of the Autolab control

The Autolab control editor will be displayed. Click the IME663 or IME303 section and set the *Number of new drops* to 1 using the provided editor (see Figure 16).

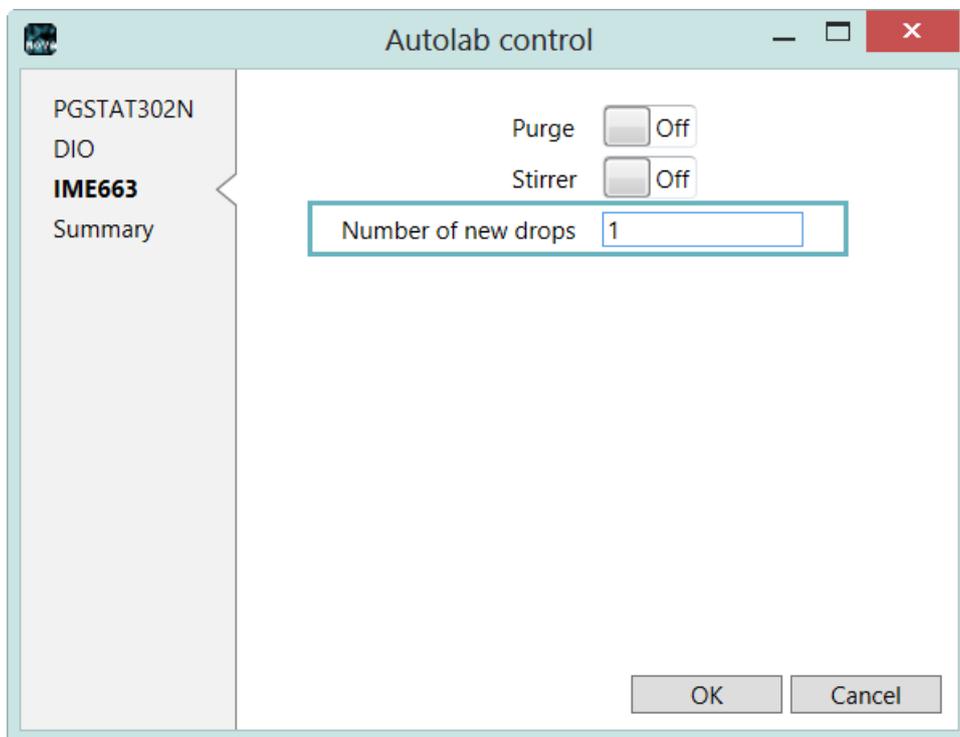


Figure 16 – Specifying the number of new drops

NOVA Voltammetric and Potential Stripping analysis tutorial

Click the OK button to close the Autolab control editor and then OK again in the Edit Options editor. Specify the measurement commands for which to apply these options in the Preview changes window (see Figure 17).

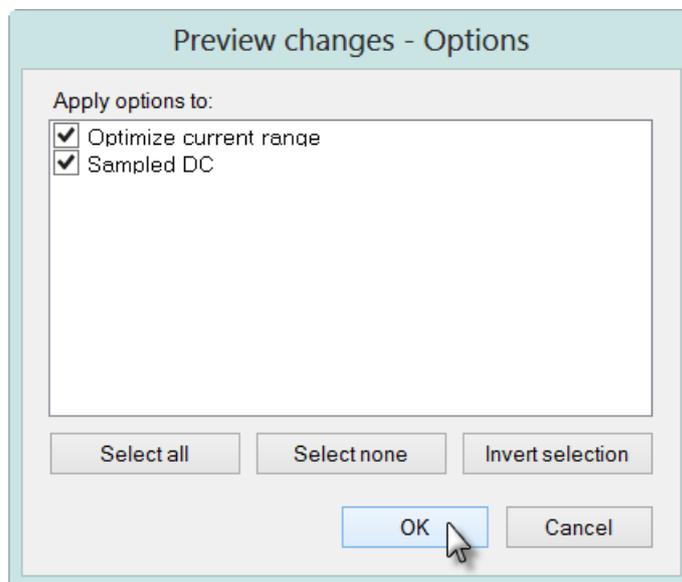


Figure 17 – Validating the new options



Note

The Sampled DC polarography procedure provided in the Autolab group is preconfigured to create a new drop at each new data point.

2.5 – Measurement commands

Nova provides a series of dedicated measurement commands for voltammetric analysis, located in the Measurement – Voltammetric analysis group of commands (see Figure 18).

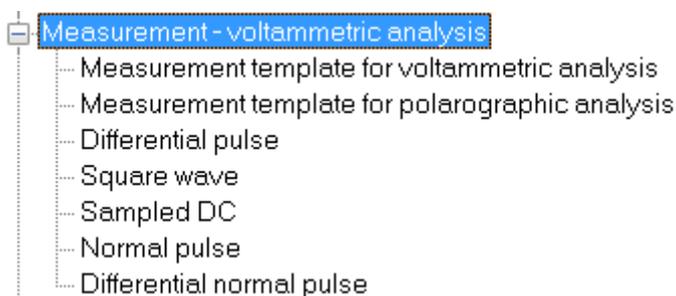


Figure 18 – Voltammetric analysis measurement commands are located in the Commands browser

To facilitate the procedure building process, two templates command has been added to the Measurement – Voltammetric analysis group of commands (*Measurement template for voltammetric analysis* and *Measurement template for*

NOVA Voltammetric and Potential Stripping analysis tutorial

polarographic analysis). These commands contain most of the instructions required to perform a typical voltammetry or polarography experiment, respectively (see Figure 19).

The figure shows two screenshots of a software interface for building measurement templates. Each screenshot displays a list of commands with their parameters and associated stages. The first screenshot is for voltammetric analysis, and the second is for polarographic analysis.

Command	Parameter	Stage
Autolab control		
Purge	5	
Create new drop		
Set stirrer		Preconditioning
Conditioning potential	0.000	
Set cell	On	
Conditioning time	5	
Deposition potential	0.000	Deposition
Deposition time	[5, 1]	
Set stirrer		
Equilibration time	5	
Optimize current range	5	Equilibration
Set cell	Off	

Command	Parameter	Stage
Autolab control		
Purge	5	
Create new drop		
Set stirrer		Preconditioning
Conditioning potential	0.000	
Set cell	On	
Conditioning time	5	
Set stirrer		
Equilibration time	5	
Optimize current range	5	Equilibration
Set cell	Off	

Figure 19 - The *Measurement template for voltammetric analysis* and the *Measurement template for polarographic analysis* can be used as templates in the procedure building process

The *Measurement template for voltammetric analysis* command includes the following stages:

- **Preconditioning:** purging is switched on after the *Autolab control* command is used to setup the Autolab. After the purge period, five new drops are created, the stirrer is switched on, the conditioning potential is defined and the cell is switched ON. The conditioning time defines the duration of this segment of the preconditioning stage.
- **Deposition:** a preconcentration stage is also included in the Timed procedure. For this stage a deposition potential and time are defined. At the end of the deposition time, the stirrer is switched off. An equilibration time is also defined in order to let the solution return to quiescent state.

NOVA Voltammetric and Potential Stripping analysis tutorial

- **Measurement:** the final stage is the measurement itself. The *Optimize current range* command is included in order to begin the measurement in the most suitable current range⁴. The measurement command itself is missing: the user can pick any one of the five measurement command of the Voltammetric analysis group and add it to the template, between the *Optimize current range* command and the *Set cell* command.

The *Measurement template for polarographic analysis* command includes the following stages:

- **Preconditioning:** purging is switched on after the *Autolab control* command is used to setup the Autolab. After the purge period, five new drops are created, the stirrer is switched on, the conditioning potential is defined and the cell is switched ON. The conditioning time defines the duration of this segment of the preconditioning stage.
- **Measurement:** the second stage is the measurement itself. The *Optimize current range* command is included in order to begin the measurement in the most suitable current range⁵. The measurement command itself is missing: the user can pick any one of the five measurement command of the Voltammetric analysis group and add it to the template, between the *Optimize current range* command and the *Set cell* command.

The *Measurement template for voltammetric analysis* and the *Measurement template for polarographic analysis* commands provided in the Measurement – voltammetric analysis group requires the IME declared in the Hardware setup (IME663 or IME303). If the IME is not selected in the Hardware setup, the following error message will be displayed (see Figure 20).

⁴ This requires the Automatic current ranging option to be used.

⁵ This requires the Automatic current ranging option to be used.

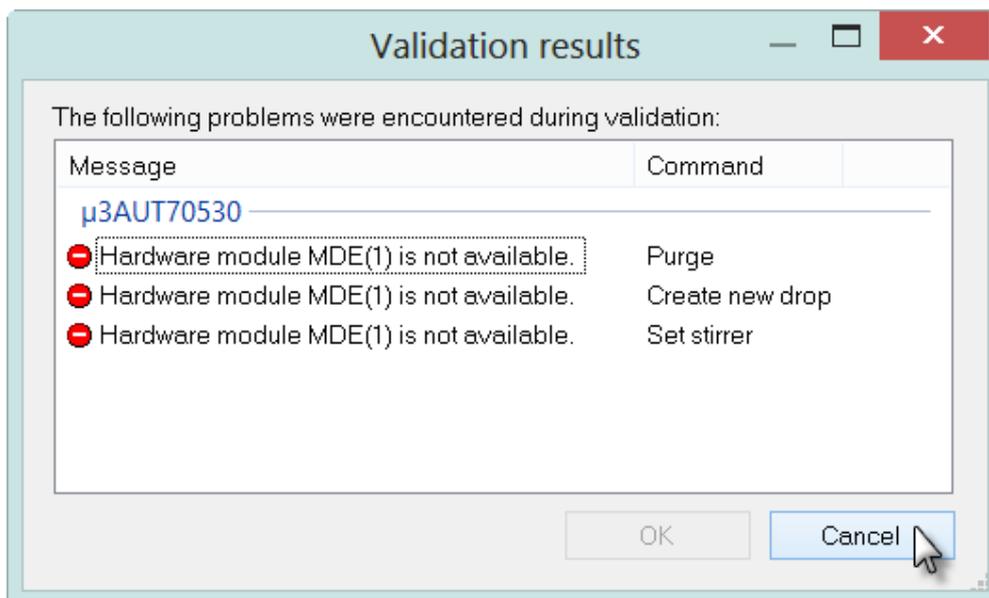


Figure 20 – A list of error messages are displayed when *Measurement template for voltammetric analysis* or the *Measurement template for polarographic analysis* command is used and the IME module is not specified in the Hardware setup



Note

The same errors will be displayed when one of the following Autolab procedures involving the IME module is executed without the IME specified in the Hardware setup (Differential pulse Voltammetry, Square wave Voltammetry and Sampled DC polarography). If these procedures need to be executed on a stationary electrode, the MDE specific commands (Purge, Stirrer, New drop) can be deleted from the procedure.

2.5.1 – Sampled DC

This technique is classically applied to mercury electrodes. In practice, interval times are in the range 0.5-6 seconds for polarography. On short time scales, there is relatively more interference due to the capacitive currents, while at longer time's noise problems increase since the total current will keep decreasing due to reactant depletion. In favourable circumstances, detection limits in the range of 10^{-6} M can be achieved.

This technique can also be used for non-polarographic applications at interval times lower than 0.5 seconds.

The implementation of this technique is fairly straightforward. The potential is scanned through the defined range. The current is sampled at the end of each potential step. Usual potential step heights are in the order of several millivolts. Choosing smaller steps will yield a finer resolution on the potential scale, but will increase the measurement duration. Figure 21 provides an overview of the potential profile and the parameters used in Sampled DC.

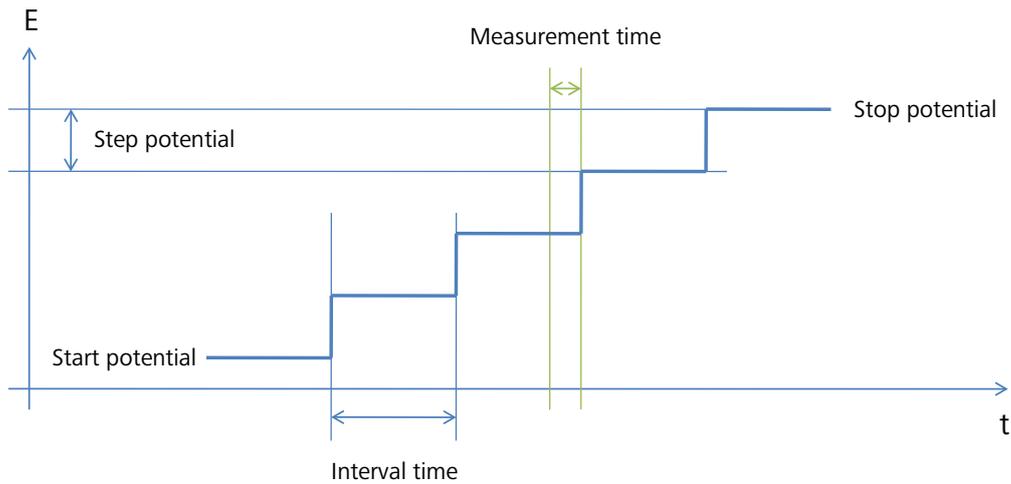


Figure 21 – Overview of the parameters of the Sampled DC method

Figure 22 shows the details of the *Sampled DC* command. The values of the initial and end potential define the scan direction and the sign of the step potential⁶.

Sampled DC		[-1.200, 0.050, 0.00500]
Initial potential (V)	-1.200	
End potential (V)	0.050	
Step potential (V)	0.00500	
Interval time (s)	0.500000	
Estimated number of points	260	
Scan rate (V/s)	0.01000	
Signal sampler	Time, WE(1).Current	...
Options	No Options	...
Potential applied	<..array.> (V)	}
Time	<..array.> (s)	
WE(1).Current	<..array.> (A)	
Index	<..array.>	
i vs E		...

Figure 22 – Overview of the *Sampled DC* command

The scan rate (\vec{v}) is defined by the step potential (E_{step}) and the interval time (Δt):

$$\vec{v} = \frac{E_{step}}{\Delta t}$$



Note

The scan rate value and the total number of points are shown in grey since these are calculated parameters.

⁶ The step potential is negative for a negative going scan.

2.5.2 – Normal pulse voltammetry

While applying sampled DC, the reactions are allowed to proceed during the whole interval time. As a result, the region near the electrode is depleted from reactant, lowering the faradaic current. Furthermore, the reaction product can accumulate on the electrode, poisoning its surface.

To decrease these detrimental effects, the Normal pulse voltammetry (NPV) technique was developed. Here, the electrode is kept at an inactive potential, the *Base potential*, for most of the interval time. Shortly before the end of the potential step, a pulse of increasing amplitude is applied. The current is then sampled at the end of the pulse. A short pulse leads to high currents but also increases the contribution from the capacitive current.

This technique is approximately one order of magnitude more sensitive than sampled DC. However, data analysis is more complicated. Furthermore, since the time scale employed is shorter, it is possible to experience effects due to irreversibility of the electrode reaction.

The parameters for this method are similar to those used in sampled DC, with the addition of a pulse time. Normally, a reasonable value for the pulse time would be about 50 ms. Figure 23 provides an overview of the potential profile and the parameters used in Normal pulse voltammetry.

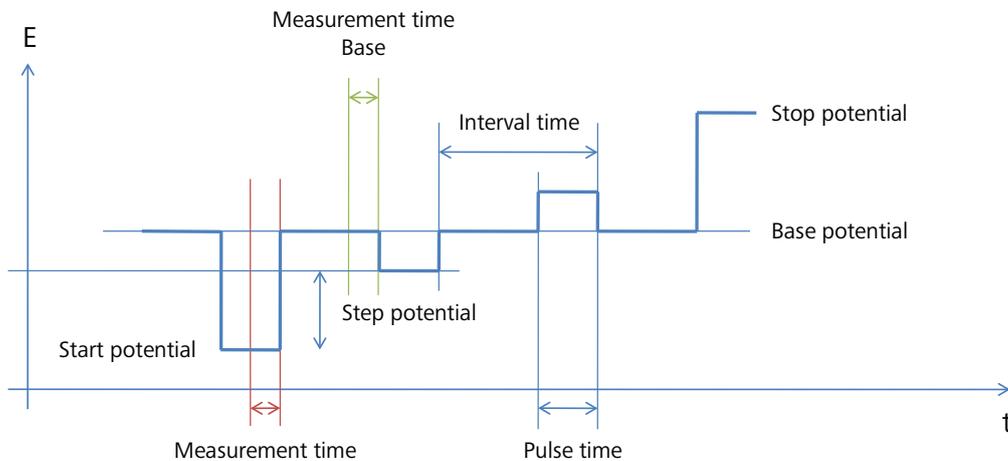


Figure 23 – Overview of the parameters of the Normal pulse method

The scan rate (\vec{v}) is defined by the step potential (E_{step}) and the interval time (Δt):

$$\vec{v} = \frac{E_{step}}{\Delta t}$$

The absolute amplitude of the pulse is given by the difference between the initial potential ($E_{initial}$) and the base potential (E_{base}), incremented during the scan by the value of the step potential (E_{step}):

$$(\Delta E_{pulse})_i = (E_{initial} - E_{base}) + \sum_{i=0}^{n-1} E_{step}$$

Figure 24 shows the details of the *Normal pulse* command. The values of the initial and end potential define the scan direction and the sign of the step potential⁷.

Normal pulse		[-1.200, 0.050, 0.00500, 0.000, 0.07000, 0.50000]
Initial potential (V)	-1.200	
End potential (V)	0.050	
Step potential (V)	0.00500	
Base potential (V)	0.000	
Pulse time (s)	0.07000	
Interval time (s)	0.50000	
Estimated number of points	260	
Scan rate (V/s)	0.01000	
Signal sampler	Time, WE(1).Current	...
Options	No Options	...
Potential applied	<..array.> (V)	}
Pulse.Time	<..array.> (s)	
WE(1).Pulse.Current	<..array.> (A)	
Index	<..array.>	
i vs E		...

Figure 24 – Overview of the *Normal pulse* command



Note

The scan rate value and the total number of points are shown in grey since these are calculated parameters.

2.5.3 – Differential pulse voltammetry (DPV)

This technique is similar to the sampled DC method with the addition of a pulse of constant amplitude at the end of each potential step. The current is sampled just before **and** at the end of the pulse, recording the difference as the result. Since the differential current is obtained during this type of experiment, peaks will be observed rather than regular waves obtained with sampled DC or normal pulse voltammetry.

This method further improves the detection limit. Compared to the NPV, faradaic waves can be discriminated from the background more easily due to the larger 2nd derivative of the current/potential relation for faradaic processes. Since the modulation amplitude is constant, capacitive current contributions will be expressed as a more or less constant baseline. Electro -oxidizable and -reducible substances on the other hand, will appear as recognizable peaks.

Detection limits of 10⁻⁸ M are possible, though one should be aware of the increasing probability to encounter irreversible phenomena. The latter can be

⁷ The step potential is negative for a negative going scan.

detected by a shift of the voltammetric peak to more negative (reduction) or positive (oxidation) potentials and by the lowering of the peak with decreasing modulation time.

When choosing the potential steps and interval time, the same rules apply as for NPV. The modulation amplitude should preferably be in the range 5-100 mV. Larger amplitudes will yield a stronger response, but will also broaden the peak, lowering potential resolution. Moreover, the peaks can be distorted due to non-linearity effects at larger amplitudes. Figure 25 provides an overview of the potential profile and the parameters used in Differential pulse voltammetry.

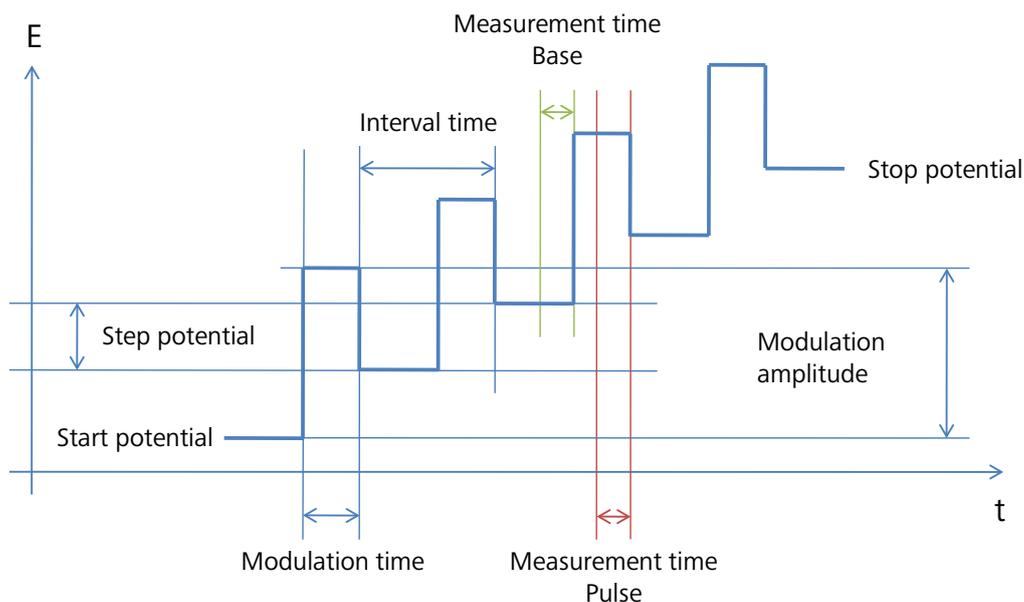


Figure 25 – Overview of the parameters of the Differential pulse method

Figure 26 shows the details of the *Differential pulse* command. The values of the initial and end potential define the scan direction and the sign of the step potential. The scan rate is defined by the step potential and the interval time. The modulation amplitude is defined independently of the scan direction.

Differential pulse		[-1.200, 0.050, 0.00500, 0.02500, 0.05000, 0.50000]
Initial potential (V)	-1.200	
End potential (V)	0.050	
Step potential (V)	0.00500	
Modulation amplitude (V)	0.02500	
Modulation time (s)	0.05000	
Interval time (s)	0.50000	
Estimated number of points	260	
Scan rate (V/s)	0.01000	
Signal sampler	Time, WE(1).Current	...
Options	No Options	...
Potential applied	<..array.> (V)	}
Base.Time	<..array.> (s)	
WE(1).Base.Current	<..array.> (A)	
WE(1).Pulse.Current	<..array.> (A)	
WE(1).Δ.Current	<..array.> (A)	
Index	<..array.>	}
Δi vs E		...

Figure 26 – Overview of the *Differential pulse* command

The scan rate (\vec{v}) is defined by the step potential (E_{step}) and the interval time (Δt):

$$\vec{v} = \frac{E_{step}}{\Delta t}$$



Note

The scan rate value and the total number of points are shown in grey since these are calculated parameters.



Warning

The sign of the modulation amplitude defines the direction of the pulse. Please refer to Appendix 2 for more information.

In a differential pulse measurement, two consecutive current samples are collected for each step. The current value measured in the first part of the step corresponds to the **WE(1).Base.Current** signal while the current value measured at the end of the pulse corresponds to the **WE(1).Pulse.Current** signal. The differential value, corresponding to the **WE(1).Δ.Current** signal is given by the difference of the pulse and the base current values.

Using the signal sampler, it is possible to record other electrochemical signals during this experiment. All additional signals, except *Current* signals will be measured in the base only. Current signals, like the **WE(2).Current** are sampled both in the base and in the pulse and the differential value is calculated. Figure 27 shows an example of such a sampling scheme. The **WE(2).Current** and the **External(1).ADC164 #1** signals have been added to the signal sampler.

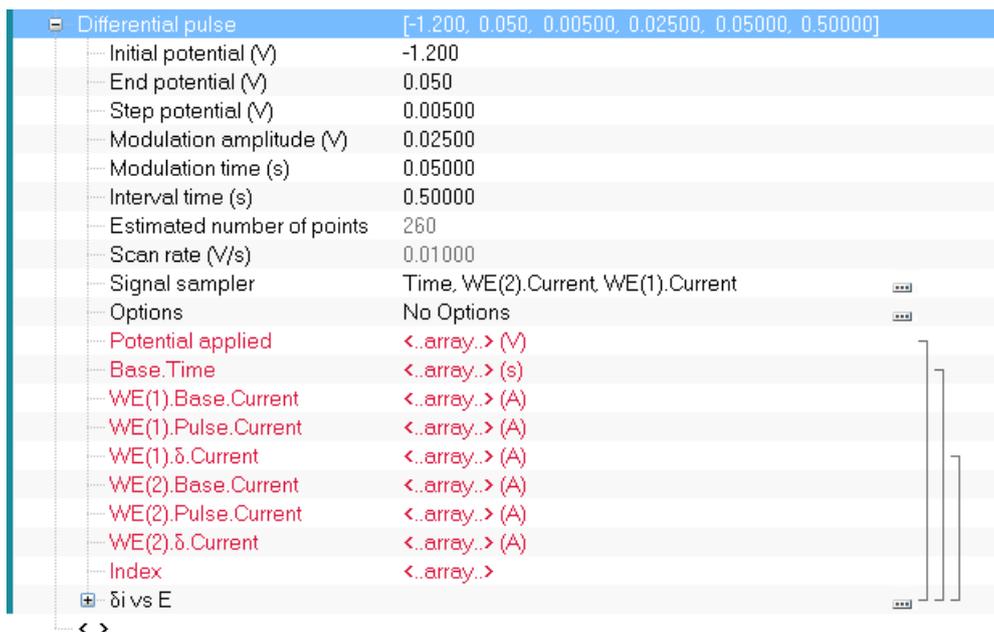


Figure 27 – Adding additional signal to the sampler

2.5.4 – Differential normal pulse voltammetry (DNPV)

This is a hybrid of DPV and NPV. Similar to the normal pulse method, a pulse will be superimposed on a base potential. On top of this pulse a modulation step with definable amplitude and duration is applied. The current will be sampled just before and at the end of the modulation step and the difference will be recorded. In this manner, the advantages of NPV (short electrolysis time) are combined with those of DPV (pronounced faraday currents).

The pulse time and modulation time are subject to similar considerations as in the case of NPV and DPV.

Since its waveform is rather complex, care should be taken not to confuse parameters. For instance, the step potential and interval time define the relationship between consecutive data points, and are not related to the properties of the pulses applied in a single measurement.

Figure 28 provides an overview of the potential profile and the parameters used in Differential normal pulse voltammetry.

Warning

This implementation of differential normal pulse voltammetry is different from the description in: "Electrochemistry" by C. M. A. Brett and A. M. Oliveira Brett, Oxford University Press 1993.

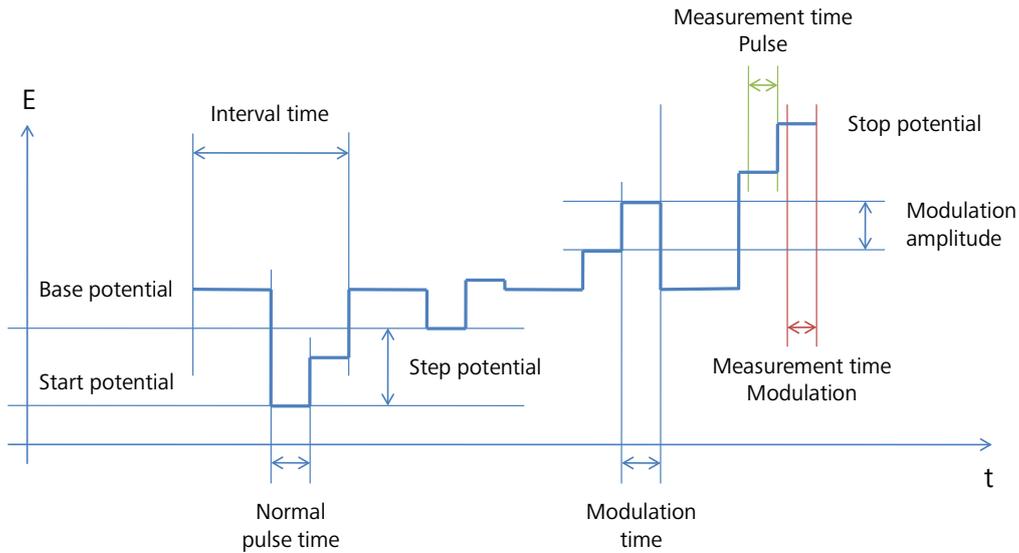


Figure 28 – Overview of the parameters of the Differential normal pulse method

Figure 29 shows the details of the *Differential normal pulse* command. The values of the initial and end potential define the scan direction and the sign of the step potential.

Differential normal pulse [-1.200, 0.050, 0.00500, 0.000, 0.02500, 0.02500, 0.50000, 0.02500]	
Initial potential (V)	-1.200
End potential (V)	0.050
Step potential (V)	0.00500
Base potential (V)	0.000
Modulation amplitude (V)	0.02500
Normal pulse time (s)	0.02500
Interval time (s)	0.50000
Modulation time (s)	0.02500
Estimated number of points	260
Scan rate (V/s)	0.01
Signal sampler	Time, WE(1).Current
Options	No Options
Potential applied	<..array.> (V)
Pulse.Time	<..array.> (s)
WE(1).Pulse.Current	<..array.> (A)
WE(1).Modulation.Current	<..array.> (A)
WE(1).δ.Current	<..array.> (A)
Index	<..array.>
δi vs E	

Figure 29 – Overview of the *Differential normal pulse* command

The scan rate (\vec{v}) is defined by the step potential (E_{step}) and the interval time (Δt):

$$\vec{v} = \frac{E_{step}}{\Delta t}$$

The absolute amplitude of the pulse is given by the difference between the initial potential ($E_{initial}$) and the base potential (E_{base}), incremented during the scan by the value of the step potential (E_{step}):

$$(\Delta E_{pulse})_i = (E_{initial} - E_{base}) + \sum_{i=0}^{n-1} E_{step}$$



Warning

The sign of the modulation amplitude defines the direction of the pulse. Please refer to Appendix 2 for more information.

In a differential normal pulse measurement, two consecutive current samples are collected for each step. The current value measured in pulse of the step corresponds to the **WE(1).Pulse.Current** signal while the current value measured at the end of the modulation corresponds to the **WE(1).Modulation.Current** signal. The difference between the modulation and the pulse current corresponds to the **WE(1).δ.Current** signal.

Using the signal sampler, it is possible to record other electrochemical signals during this experiment. All additional signals, except *Current* signals will be measured in the base only. Current signals, like the **WE(2).Current** are sampled both in the pulse and in the modulation and the differential value is calculated.

2.5.5 – Square wave voltammetry (SqW)

During square wave voltammetry the potential is scanned as in sampled DC, but an additional square wave is applied. The recorded curve is the difference between the average currents in the forward and the reverse pulse, sampled just before each flank. The main advantage of this technique over DPV is the increased number of samples, which allows for higher scan speeds while retaining a good resolution on the potential axis.

The implementation is somewhat different from the other voltammetric techniques. Now, the interval time is implicitly determined by the reciprocal square wave frequency. Thus the scan rate is proportional to the frequency.

Each data point corresponds to the measured current at the high level (forward sample), minus the current at the low level (backward sample). The duration or acquisition time of the measurements is determined by the previously explained rules, taking half the square wave period as the pulse duration.

Reasonable amplitudes are in the range of 5-25 mV. Larger amplitudes yield a larger response, but faradaic peaks will get broader and potential resolution will be lost at very large amplitudes. Note that the amplitude corresponds to half the peak-to-peak potential difference of the square wave.

A proper choice of frequency is of the utmost importance. Similar to using short pulse durations in pulse voltammetry, the influence of capacitive current is larger at high frequencies.

NOVA Voltammetric and Potential Stripping analysis tutorial

The bandwidth of the Autolab is lower at low current ranges as well. The properties of the low current range might not be suitable for the specified frequency. Normally, the useful frequency range is 8-250 Hz.

Figure 30 provides an overview of the potential profile and the parameters used in Square wave voltammetry.

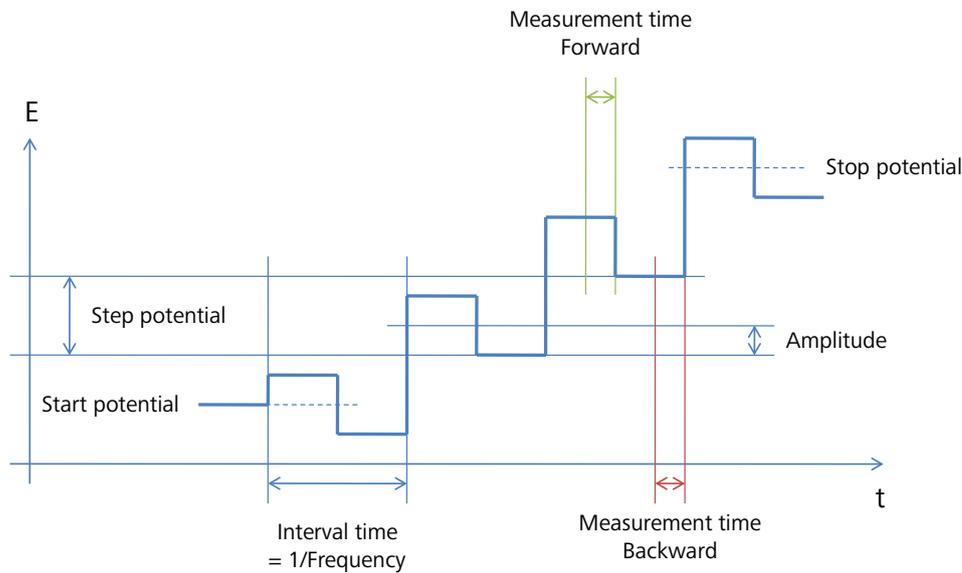


Figure 30 – Overview of the parameters of the square wave method

Figure 31 shows the details of the *Square wave* command. The values of the initial and end potential define the scan direction and the sign of the step potential.

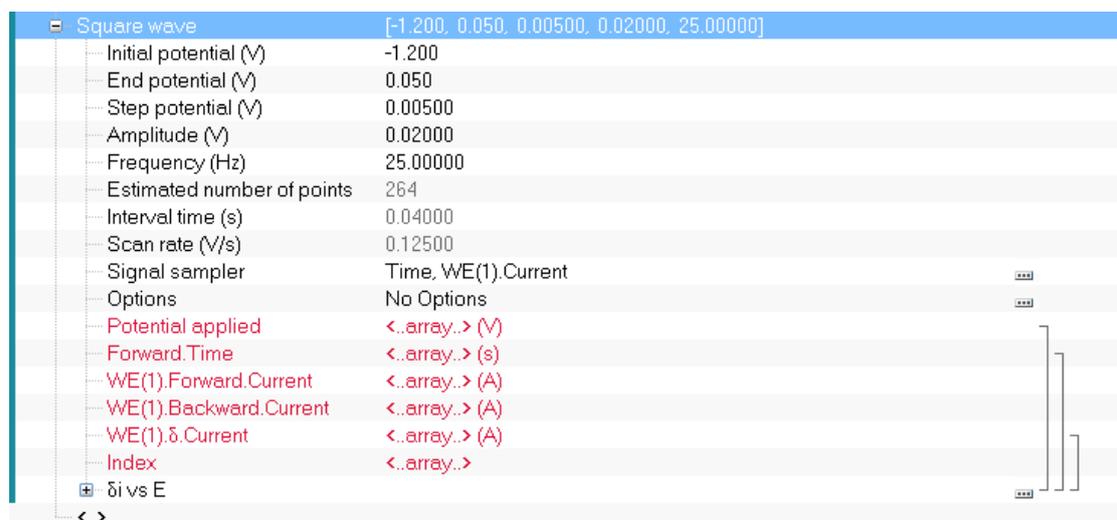


Figure 31 – Overview of the *Square wave* command

The scan rate (\vec{v}) is defined by the step potential (E_{step}) and the frequency (ω_{SQW}):

$$\vec{v} = E_{step} \cdot \omega_{SQW}$$



Warning

The sign of the modulation amplitude defines the direction of the pulse. Please refer to Appendix 2 for more information.

In a square wave measurement, two consecutive current samples are collected for each step. The current value measured in first half of the step corresponds to the **WE(1).Forward.Current** signal while the current value measured in the second half of the step corresponds to the **WE(1).Backward.Current** signal. The difference between the backward and forward currents corresponds to the **WE(1). δ .Current** signal.

Using the signal sampler, it is possible to record other electrochemical signals during this experiment. All additional signals, except *Current* signals will be measured in the base only. Current signals, like the **WE(2).Current** are sampled both as forward and backward values and the differential value is calculated.

3 – Potentiometric stripping analysis

The term Potentiometric stripping analysis (PSA) was introduced by Jagner and Granelli⁸ in 1976. This method is similar to the anodic stripping voltammetry method, which can be carried out using one of the measurement commands described in Section 2 of this tutorial, usually by differential pulse voltammetry. The difference with the electroanalytical methods is that in classic PSA, the oxidation of the preconcentrated analyte is carried out chemical rather than electrochemically. This means that the working electrode remains at open circuit during the stripping stage of the measurement.

The working electrode is usually a glassy carbon electrode covered with a thin film of mercury.

The chemical oxidation is usually carried out with Hg(II) or by dissolved oxygen and the working conditions are set in such a way that the rate of oxidation of the preconcentrated metals remains constant throughout the stripping stage. The rate is determined by the rate of diffusion of the oxidant from the solution bulk in **Potentiometric stripping analysis**.

The analytical signal is recorded by monitoring the potential of the working electrode as a function of time. As such, this method is the equivalent of a potentiometric titration, in which the titrant is added in situ at a constant rate. The measurement stops when the maximum time is reached (Time stop) or when the measured potential exceeds a user defined limit (Potential stop). Figure 32 shows a typical potentiometric stripping analysis potential profile.

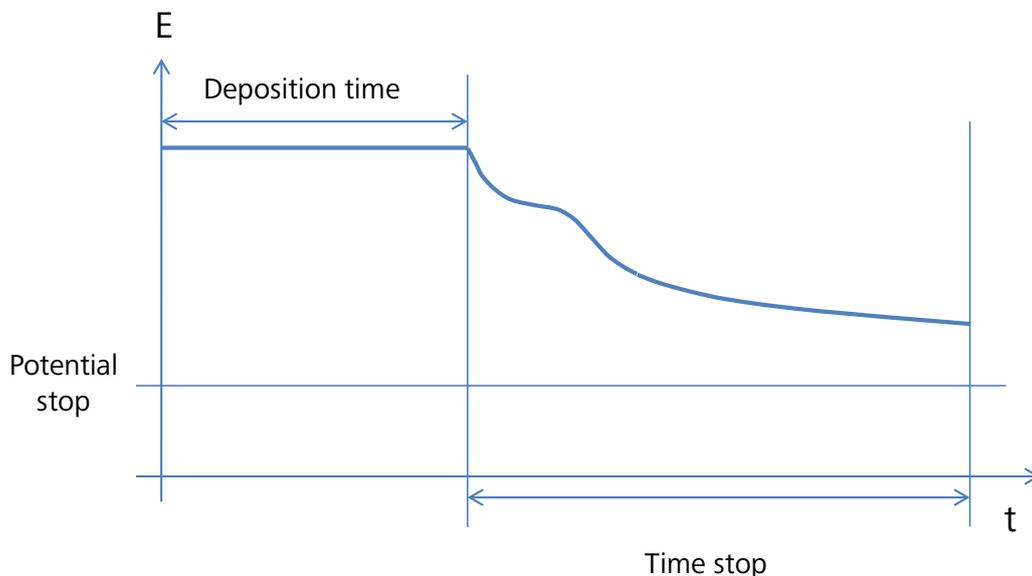


Figure 32 – A typical potentiometric stripping analysis measurement

⁸ D. Jagner, A. Granelli, Anal. Chem. Acta 83, 1976, 19-26.

The voltage measurement E vs t is used to calculate the retention times dt/dE vs E . Figure 33 show an example of the E vs t measurement and the resulting peak-shaped plot.

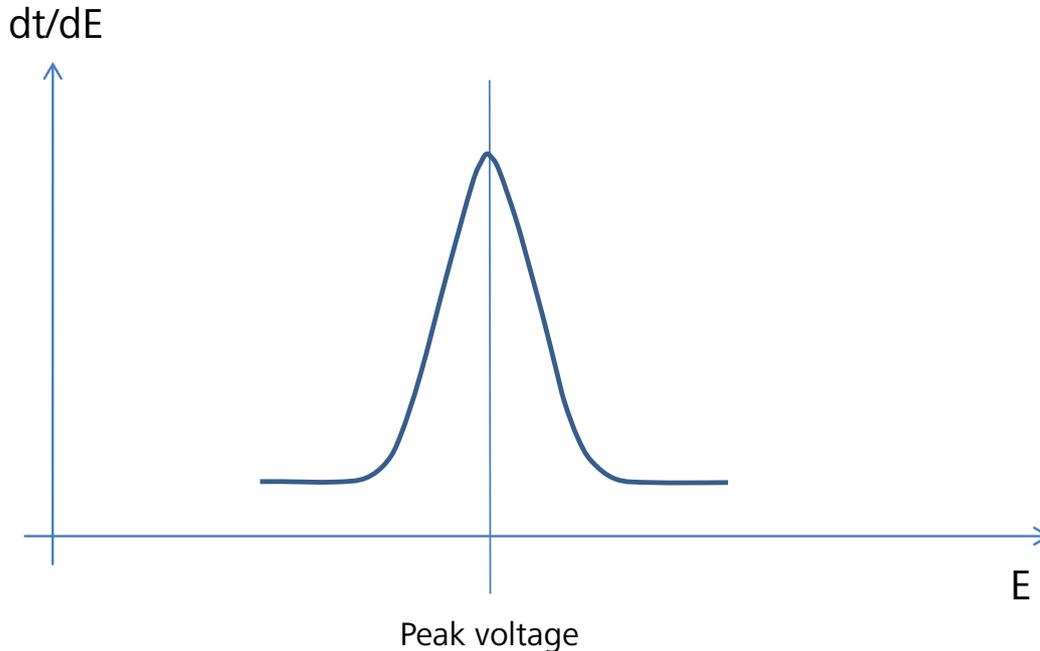


Figure 33 – Schematic overview of a PSA measurement (E vs t measurement, top and dt/dE vs E plot, bottom)

The Peak voltage position is characteristic of the substance, the Peak area is proportional to its concentration.

As an alternative, it is also possible to electrochemically oxidize the preconcentrated metals by applying a constant oxidation current. This method is used in **Potentiometric stripping analysis (Constant current)**.

3.1 – Measurement commands

Nova provides a series of dedicated measurement commands for potentiometric stripping analysis, located in the Measurement – potentiometric stripping analysis group of commands (see Figure 34).

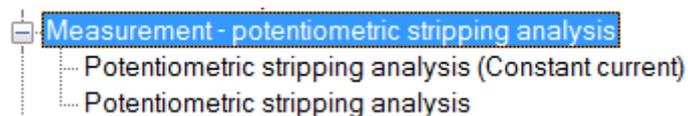


Figure 34 – Potentiometric stripping analysis measurement commands are located in the Commands browser

NOVA Voltammetric and Potential Stripping analysis tutorial

3.1.1 – Potentiometric stripping analysis (Constant current)

This command can be used to perform a constant current PSA measurement. In this measurement, the preconcentrated species are oxidized at a constant rate defined by the specified current.

A predefined procedure for this type of measurement is provided in the Autolab group of procedures (see Figure 35).

Commands	Parameters	Links
Potentiometric stripping analysis (Constant current)		
Remarks	Potentiometric stripping analysis...	...
End status Autolab		...
Signal sampler	No signals.	...
Options	No Options	...
Instrument	μ 3AUT70530	
Instrument description		
Autolab control		...
WE(1).Mode	Potentiostatic	
WE(1).Bandwidth	High stability	
WE(1).Current range	1 μ A	
Set potential	-0.800	
Set cell	On	...
Wait time (s)	5	
Potentiometric stripping analysis (Constant current)		
Stripping current (A)	1E-06	
Potential limit (V)	0.8	
Maximum time (s)	10	
Filter	On	...
Filter time (s)	0.02	
WE(1).Potential	<..empty..> (V)	
$\delta t/\delta E$	<..empty..> (s/V)	
t	<..array..> (s)	
$\delta t/\delta E$ vs E		...
Build E vs t plot		...]
Calculate signal	t-MIN(t)	...]
E vs t		...]
<..>		

Figure 35 – The default Autolab Potentiometric stripping analysis (Constant current) procedure



Note

The Set potential command located at the beginning of the procedure can be used to define the preconcentration conditions.



Note

The Potentiometric stripping analysis (Constant current) command automatically switches the instrument to Galvanostatic mode.

The details of this command are shown in Figure 36.

NOVA Voltammetric and Potential Stripping analysis tutorial

Potentiometric stripping analysis (Constant current)	
Stripping current (A)	1E-06
Potential limit (V)	0.8
Maximum time (s)	10
Filter	On
Filter time (s)	0.02
WE(1).Potential	<..empty..> (V)
$\delta t/\delta E$	<..empty..> (s/V)
t	<..array..> (s)
$\delta t/\delta E$ vs E	
Build E vs t plot	
Calculate signal	t-MIN(t)
E vs t	

Figure 36 – Details of the Potentiometric stripping analysis (Constant current) command

The following parameters are available:

- **Stripping current:** the current applied during the stripping stage, in A.
- **Potential limit:** the maximum potential of the working electrode, in V. The measurement stops when the potential of the working electrode exceeds the specified value.
- **Maximum time:** the maximum duration of the stripping stage, in s. The measurement stops when this limit is reached.
- **Filter (On/Off):** specifies if a filter must be applied on the measured potential signal. The implemented filter is based on a moving average over the specified Filter time parameter.
- **Filter time:** the filter time, in s, used if the filter is On. This parameter is automatically set to 20 ms or 16.66 ms depending on the line frequency specified in the hardware (50 Hz or 60 Hz, respectively).

The command measures the WE(1).Potential signal and the time and determines the derivative of time versus the measured potential.



Note

The current range needs to be adjusted in order to apply the stripping current properly. This can be done using the Autolab control command located at the beginning of the procedure.



Warning

No additional signals can be measured by the Potentiometric stripping analysis (Constant current) command. The sampling rate is set to the highest possible value during this type of measurement and the measured data cannot be displayed in real time. Options like cutoffs and counters cannot be used.

NOVA Voltammetric and Potential Stripping analysis tutorial

3.1.2 – Potentiometric stripping analysis

This command can be used to perform a PSA measurement. In this measurement, the preconcentrated species are oxidized at a constant rate defined by the diffusion rate of the oxidizing species located in the solution.

A predefined procedure for this type of measurement is provided in the Autolab group of procedures (see Figure 37).

Commands	Parameters	Links
Potentiometric stripping analysis		
Remarks	Potentiometric stripping analysis	...
End status Autolab		...
Signal sampler	No signals.	...
Options	No Options	...
Instrument	μ 3AUT70530	
Instrument description		
Autolab control		...
Set potential	-0.800	
Set cell	On	...
Wait time (s)	5	
Potentiometric stripping analysis		
Potential limit (V)	0.8	
Maximum time (s)	10	
Filter	On	...
Filter time (s)	0.02	
WE(1).Potential	<..empty..> (V)	
$\delta t/\delta E$	<..empty..> (s/V)	
t	<..array..> (s)	
$\delta t/\delta E$ vs E		...
Build E vs t plot		...]
Calculate signal	t-MIN(t)	...]
E vs t		...]
<..>		

Figure 37 – The default Autolab Potentiometric stripping analysis procedure



Note

The Set potential command located at the beginning of the procedure can be used to define the preconcentration conditions.

The details of this command are shown in Figure 38.

NOVA Voltammetric and Potential Stripping analysis tutorial

Potentiometric stripping analysis	
Potential limit (V)	0.8
Maximum time (s)	10
Filter	On
Filter time (s)	0.02
WE(1).Potential	<..empty..> (V)
$\delta t/\delta E$	<..empty..> (s/V)
t	<..array..> (s)
$\delta t/\delta E$ vs E	
Build E vs t plot	
Calculate signal	t-MIN(t)
E vs t	
<..>	

Figure 38 – Details of the Potentiometric stripping analysis command

The following parameters are available:

- **Potential limit:** the maximum potential of the working electrode, in V. The measurement stops when the potential of the working electrode exceeds the specified value.
- **Maximum time:** the maximum duration of the stripping stage, in s. The measurement stops when this limit is reached.
- **Filter (On/Off):** specifies if a filter must be applied on the measured potential signal. The implemented filter is based on a moving average over the specified Filter time parameter.
- **Filter time:** the filter time, in s, used if the filter is On. This parameter is automatically set to 20 ms or 16.66 ms depending on the line frequency specified in the hardware (50 Hz or 60 Hz, respectively).

The command measures the WE(1).Potential signal and the time and determines the derivative of time versus the measured potential.



Warning

No additional signals can be measured by the Potentiometric stripping analysis (Constant current) command. The sampling rate is set to the highest possible value during this type of measurement and the measured data cannot be displayed in real time. Options like cutoffs and counters cannot be used.

Appendix 1 – Metrohm 663 VA Stand

The 26-pole edge connector should be plugged into the rear side of the 663 VA Stand. The short green banana plug should be connected to the ground. The 9-pins D-connector on the other end of this cable must be plugged in the IME663 socket, marked 'VA Stand' (see Figure 39, overview for the μ Autolab).

The cable with the 25-pin D-connector or 15-pin D-connector (PGSTAT101/204 and M101/M204) (male) and the 15-pin D-connector (male) is used to connect the PGSTAT/ μ Autolab to the IME663.

For the μ Autolab the remaining DIN connector should be inserted in the cell cable socket of the Autolab, replacing the standard cell-cable.

For the PGSTAT the cell cables of the PGSTAT are connected directly to the electrodes of the electrochemical cell. Please, lift the hood of the 663 VA Stand and disconnect the original electrode cables. Replace them with the connectors of the special cable that is supplied by Autolab Instruments. This cable should be connected to the banana plugs of the original Autolab cell cable.

For stirrer control with the IME663, the cable with the 5-pin DIN connectors is used. One end of this cable must be plugged into the plug marked 'STIRRER' on the IME663. The other end is plugged into the male DIN-connector E at the rear side of the 663 VA Stand.



Warning

The 663 VA Stand only operates properly under computer control when it is switched in **SMDE** mode.

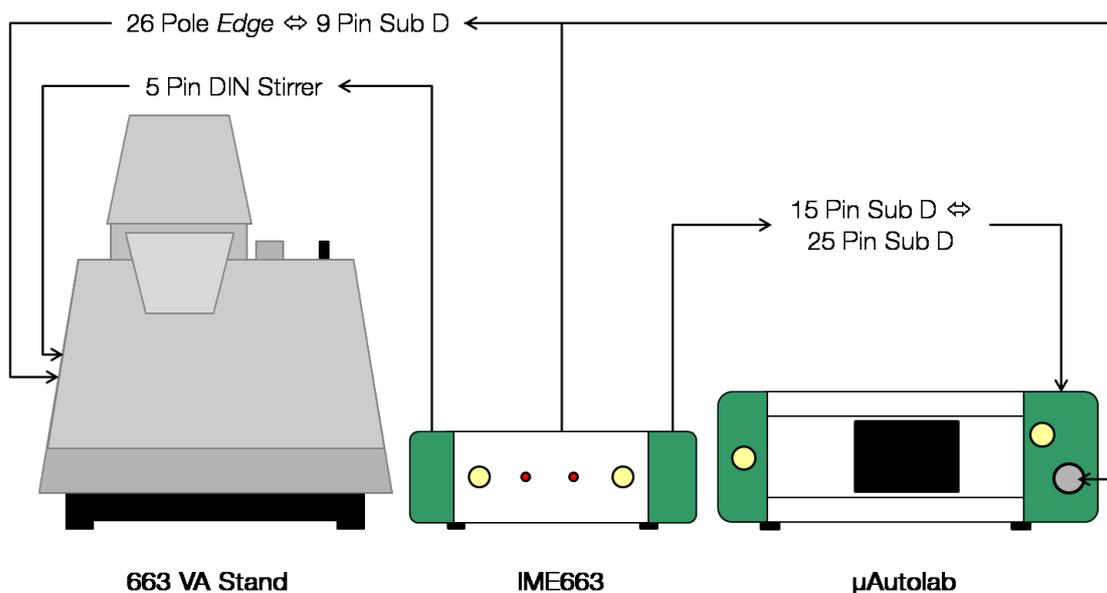


Figure 39 – Overview of the connections between the IME663, the μAutolab and the 663 VA stand (for the PGSTAT, connect the cell cables directly to the electrodes in the cell and the mercury electrode on the VA stand using the provided adaptors)

Princeton Applied Research 303/303A

The cable with the 25-pin D-connector or 15-pin D-connector (PGSTAT101) (male) and the 15-pin D-connector (female) is used to connect the Princeton Applied Research electrode to the IME303. Use the connector marked with 'PAR303' at the rear side of the IME303. The 25-pin D-connector, or 15-pin D-connector (PGSTAT101 and M101) must be plugged into the 'J1'-connector at the rear side of the PAR303/303A electrode. To connect the cell-cable, use the adapters delivered with the IME303. These connectors fit into the sockets at the rear side of the PAR303/303A.

DME

A drop knocker can be controlled with the IME303. Use the banana sockets at the rear marked: 'Solenoid'. Every time a 'New Drop' action takes place, either manually or using the *Create new drop* command or the *Autolab control* command, a 15 V pulse will be generated between the pins. The electrodes should be connected directly to the Autolab cell cable.

Appendix 2 – Implementation of pulsed methods

The implementation of the pulsed methods (Differential pulse, Normal pulse, Differential normal pulse and Square wave) is different in NOVA compared to the Autolab GPES software and the Metrohm Computrace software. To compare experimental data, the following differences need to be taken into account.

In Autolab GPES and Metrohm Computrace

The **amplitude** parameter in the GPES and Computrace software is automatically adjusted in order to have the same sign as the scan direction. This means that the amplitude will be defined as a positive value in a positive going scan and as a negative value in a negative going scan. Regardless of the scan direction, the amplitude is defined as a positive value (see Figure 40).

NOVA Voltammetric and Potential Stripping analysis tutorial

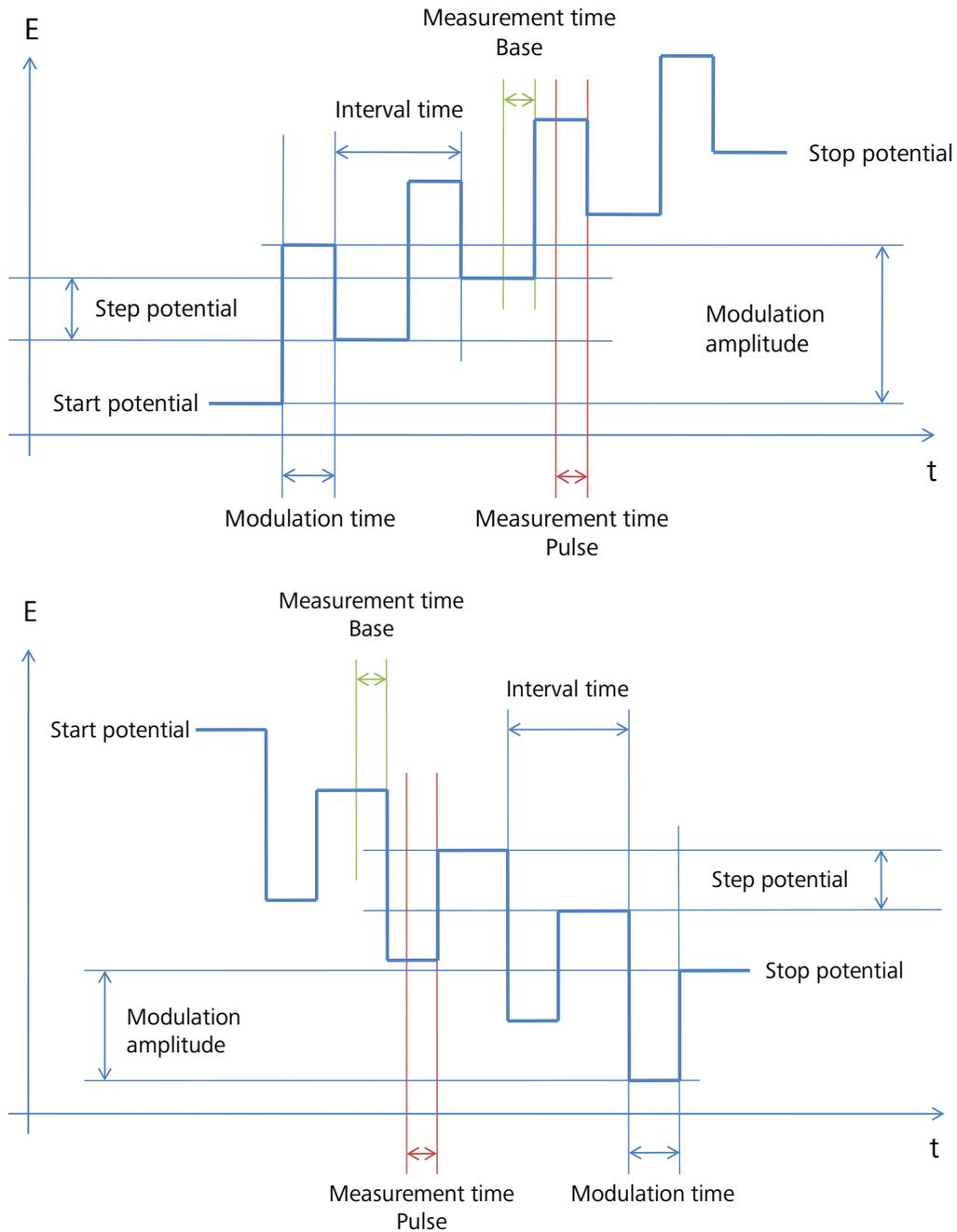


Figure 40 – Differential pulse implementation in GPES and Computrace with a positive amplitude (top: positive going scan, bottom: negative going scan)

When the sign of the amplitude is defined as a negative value, the pulse direction will be reversed. For a positive going scan, the pulse direction will be negative and for a negative going scan, the pulse direction will be positive (see Figure 41).

NOVA Voltammetric and Potential Stripping analysis tutorial

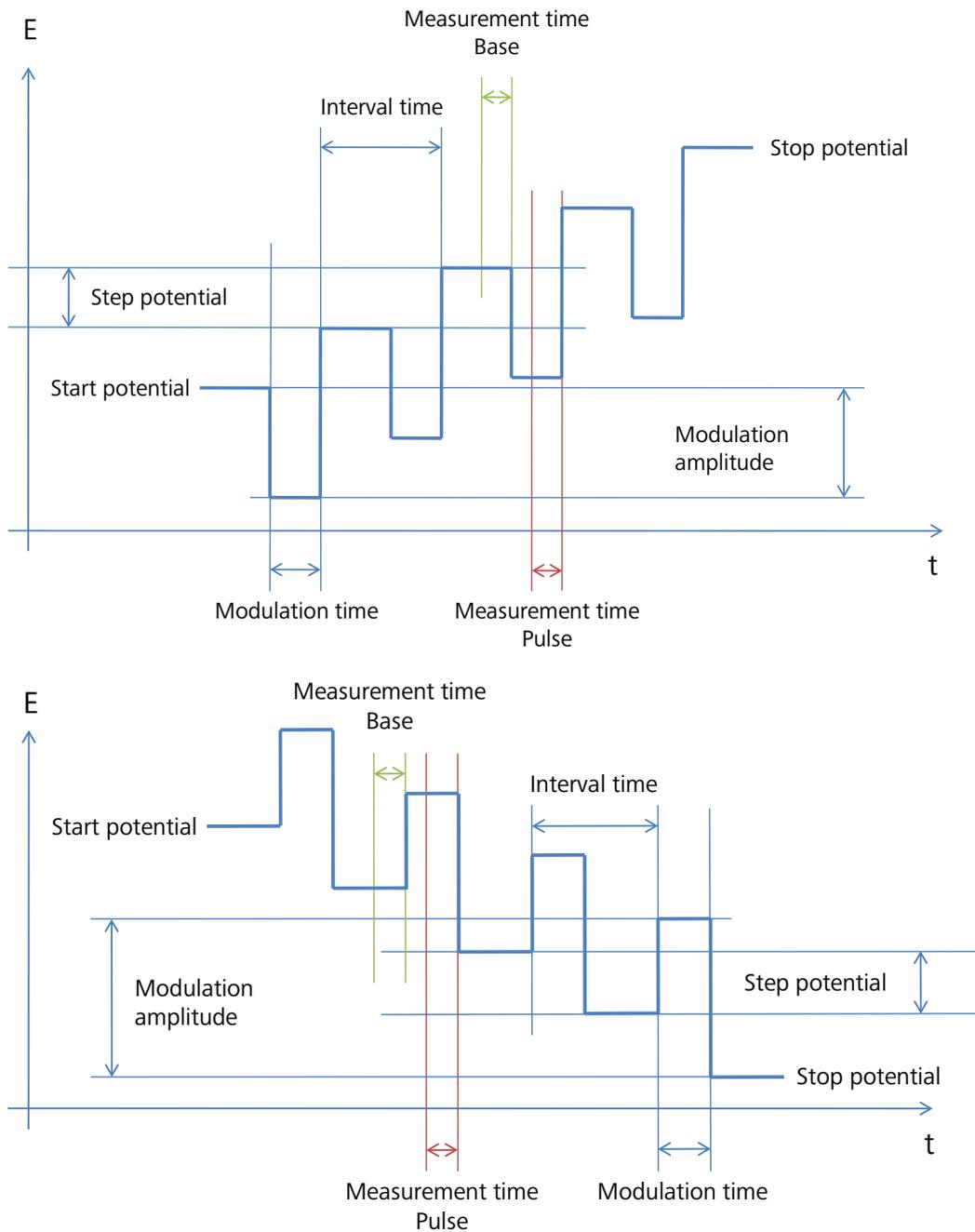


Figure 41 – Differential pulse implementation in GPES and Computrace with a negative amplitude (top: positive going scan, bottom: negative going scan)

In Autolab NOVA

The **amplitude** parameter in the NOVA software is defined as an independent parameter. This means that the amplitude can be specified independently from the scan direction. Regardless of the scan direction, a positive amplitude will be applied when the amplitude is specified as a positive value (see Figure 42).

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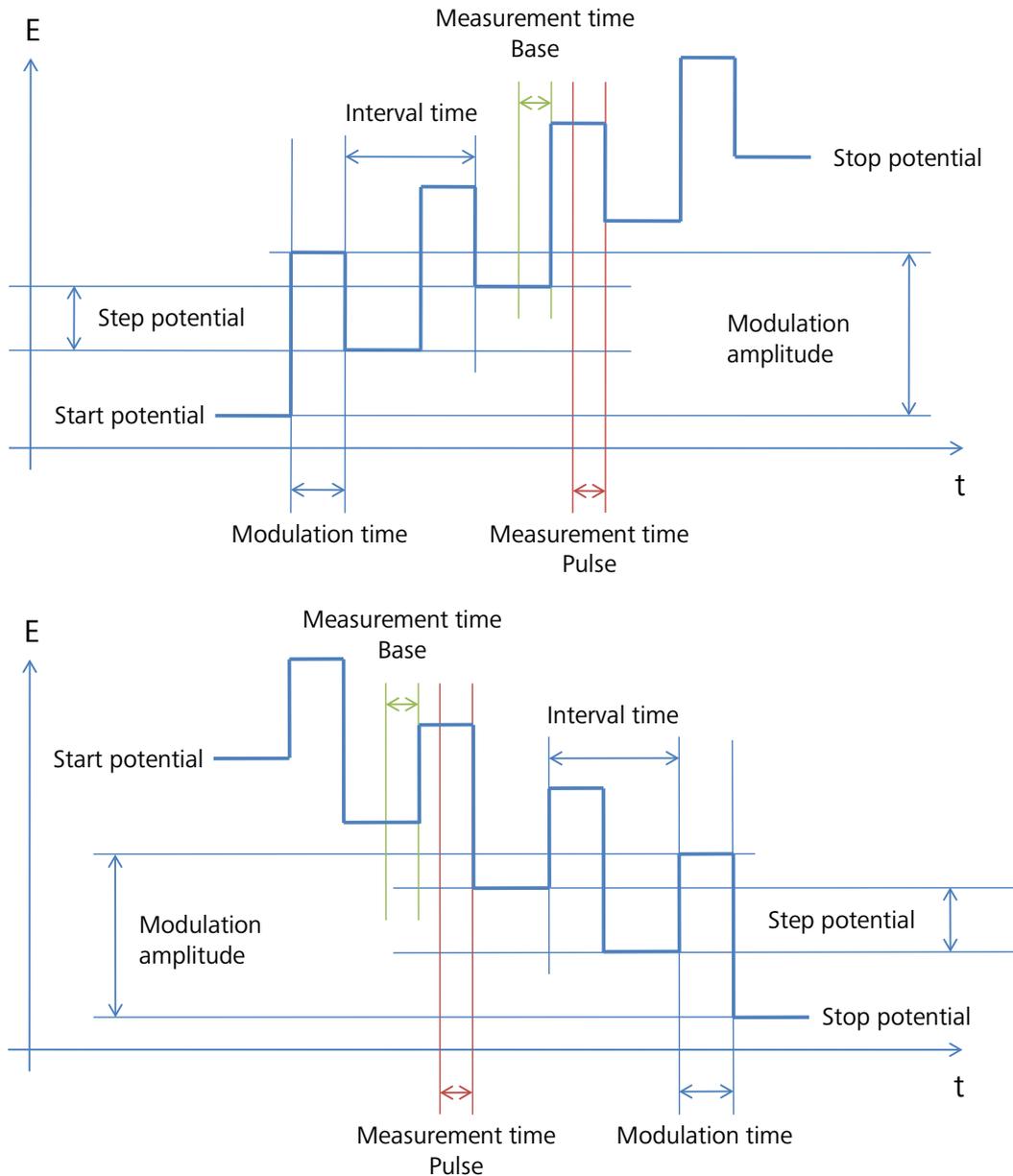


Figure 42 – Differential pulse implementation in NOVA with a positive amplitude (top: positive going scan, bottom: negative going scan)

When the sign of the amplitude is defined as a negative value, the pulse will be applied in the negative direction, regardless of the scan direction (see Figure 43).

NOVA Voltammetric and Potential Stripping analysis tutorial

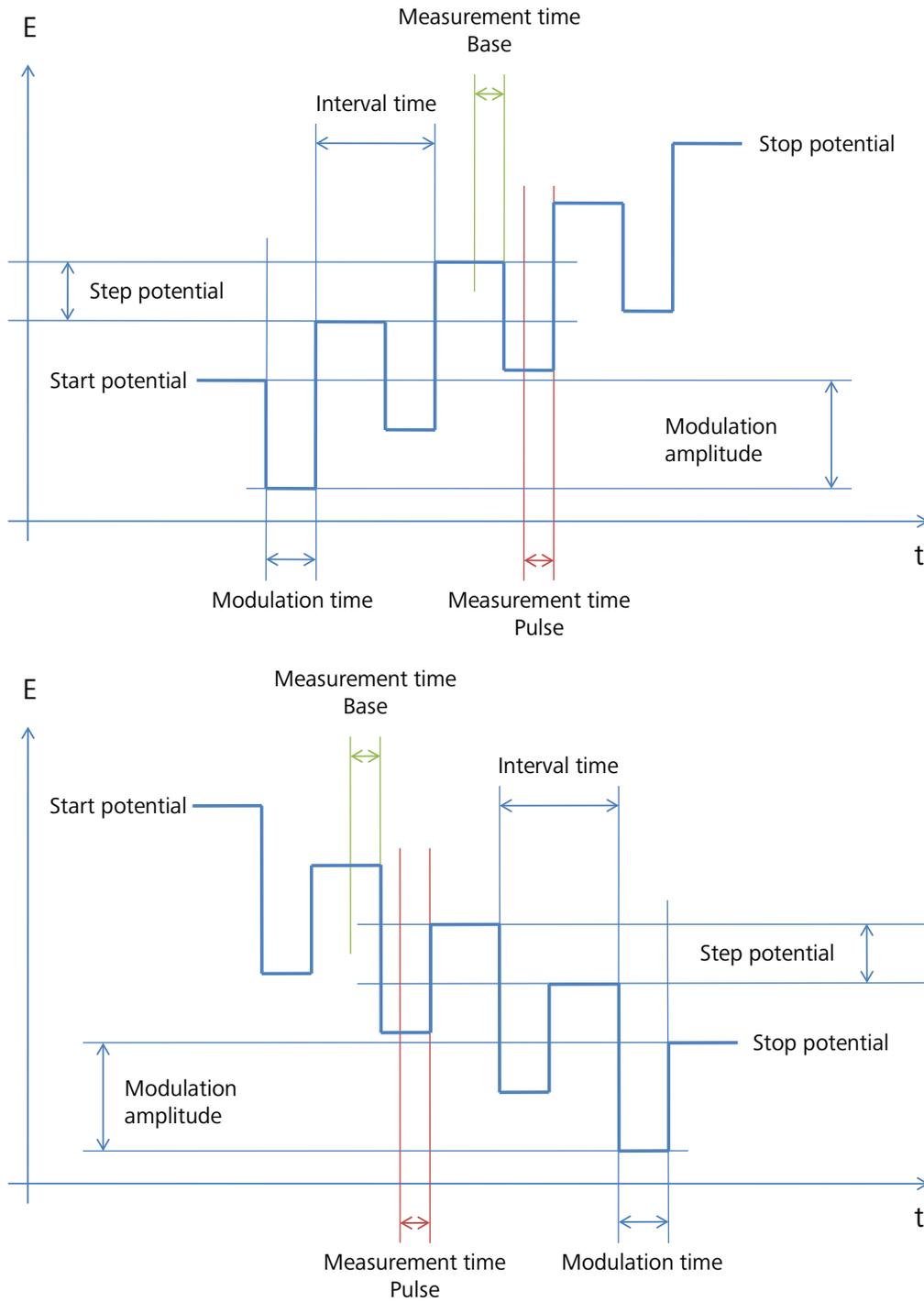


Figure 43 – Differential pulse implementation in NOVA with a negative amplitude (top: positive going scan, bottom: negative going scan)