User Manual

for

Electrochemical Methods for Windows
version 4.9

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1. Electrochemical experiments with Autolab

1.1 Introduction

In this overview, the electrochemical methods available with an Autolab instrument are discussed. Each technique will be explained in a concise manner, supplemented with detailed information about Autolab’s technical implementation.
It is the intention to help the operator in choosing the most appropriate technique and to reach an optimal configuration in each electrochemical environment.

One should keep in mind that it is not always possible to select the optimal settings beforehand. Occasionally it will be necessary to perform some "trial runs" using different parameters. However, the instructions in the following sections should be helpful to reach optimal performance readily.

1.2 The flow of events: pretreatment, measurement, and post treatment

In electrochemical experiments it is often desirable to reach a predefined state preceding the actual measurement. When required, the electrode can be put in a certain electrochemical state by applying a potential for a desired duration or by the removal of oxygen from the solution (purging).

Table 1: Flow of events

	pretreatment			measurement		post treatment
stage	purging period	conditioning period	deposition period	equilibrium period	scan execution	standby state
potential[1]	cell off	conditioning potential(s)	deposition potential	initial/start/ standby potential	scan potentials	cell off/ cell at standby potential
stirrer	off	on		off		

Be aware that not all these stages are always available. Automatic purging and stirring is related to the presence of dedicated hardware. Also, depending on their relevance for each technique and on requests made by electrochemists in the past, some stages are implemented for specific methods only. Furthermore, multiple potentials can be specified in a single stage. For instance, most techniques allow the application of 3 conditioning potentials (except for Voltammetric Analysis, Electro Chemical Detection, and Potential Stripping Analysis). In some cases an option is provided to limit the duration of a stage by a limiting condition, for example: stop the equilibrium process when a threshold current has been reached.

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[1] For galvanostatic operation, currents are applied instead of potentials.

Stages may be disabled by the operator by entering a duration of 0 seconds. In that case, the corresponding potential/current will not be applied.

Though the individual pretreatment stages have been named with a particular purpose in mind, it is the operator who determines which processes actually will take place in the electrochemical object by specifying the potential (or current) levels.

On completion of the measurement stage, consideration should be given to what is supposed to happen to the electrode. Especially when measurements have to be repeated with the same electrode, a choice must be made whether the electrode should be kept polarised (standby potential) or be disconnected (cell off after measurement).

1.3 Configuring the measurement parameters

After deciding on an electrochemical method, its procedure should be parameterised. Finding the optimum set of parameters is not always trivial and requires prior knowledge about the electrochemical properties of the subject under investigation. The objective of the measurement should be clear. For instance, if one is interested in the determination of a faradaic current, the capacitive current is unwanted and should be kept as small as possible. However, when adsorption or double layer properties are under study, the opposite might be true.
At an electrode surface, two fundamental electrochemical processes can be distinguished:

Capacitive process

Capacitive currents are caused by the (dis-)charge of the electrode surface as a result of changes in the area size (dropping mercury electrode) , by a potential variation, or by an adsorption process. There is no reaction involved here. Under potentiostatic conditions, this process tends to be very fast and the resulting current will expire in a short time (usually a few milliseconds). This current can thus be reduced by choosing slower scan rates or pulse widths of longer duration. It should be noted that in high resistance media, the capacitive current will need a substantially longer period to fall off: this time is proportional to the product of the resistance and the capacitance.

Faradaic processes

Faradaic currents are a result of electrochemical reactions at the electrode surface. From the determination of the magnitude of such a current, one can obtain useful parameters as concentration and diffusion coefficient of a species. Furthermore, from the position of the current peak (peak potential), the nature of the species can be deduced. Usually under potentiostatic conditions, faradaic currents are slower to diminish than capacitive currents. However, when reactant depletion occurs, a faradaic current will also decrease with time. The scan rate/pulse duration should therefore be chosen slow/long enough to reduce the charging current, without letting the magnitude of the faradaic current decline below noise level.
Another strategy must be followed when electrode kinetics are to be studied. Due to the limiting effect of mass transfer, the influence of reaction rate, or corrosion resistance will only be expressed on short time scales, making it necessary to employ short pulses, fast scan rates, or high frequencies. It will be clear that in such cases, there might be an overlap with the capacitive current. Usually in these cases, one will

employ a range of scan rates, pulse duration’s, or frequencies allowing for a detailed analysis of the electrochemical components and their impedance’s.

Autolab does provide a set of default values, which can be adjusted in accordance with the requirements of each situation. Entry of the procedure parameters is designed to be as flexible and interactive as possible. For instance, it is allowed to change some parameters while a measurement is in progress and changes can be put into effect immediately by means of the "send" button (changes must first be validated with the <enter> key).

Some parameters that are directly related to the hardware or configure advanced operational issues cannot be edited in the measurement software. These parameters are stored in the Hardware Configuration File, which is located in the Autolab root directory named as: <sysdef40.inp>. This file can be edited by means of the Hardware Setup Program: <hardware.exe>. One can edit this file by hand with any text editor as well. However, care should be exercised with this practice.
In the following chapters, additional information is listed for each specific technique.

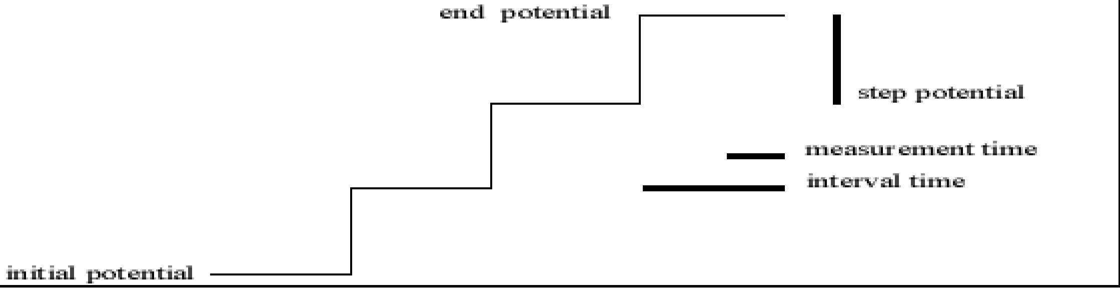
2. Voltammetric analysis

2.1 Overview of techniques

All voltammetric techniques have in common that a potential range is scanned, as defined by initial-, end- and step- potential. All potentials are rounded to the nearest discrete voltage level that is available. At the end of each interval time, just prior to the next step, a data point will be collected. Therefore, the number of samples 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 samples multiplied by the interval time. The actual details of data sampling are explained in the paragraph about sampling techniques. Usually, the measurement period (=acquisition time) is taken at the last quarter of the interval time, if possible rounded to a multiple of the line period, that is 20ms (50Hz) or 16.67ms(60Hz).
If during normal/differential pulse or square wave operation, the applied pulse is shorter than 40ms, the data acquisition is performed in the last half of the pulse period. It should be noted that noise levels can increase considerably when the measurement period is not a multiple of the line frequency.
In ac-voltammetry the current response is always acquired during the last half of the modulation time.
Since these methods are often used for polarography, the option to control a drop knocker is provided. When the interval time>0.5 s and the deposition time=0, the drops are knocked off after each data point and all measurements within the scan are performed on different drops.

2.2 Sampled DC

Fig. 1 Sampled DC

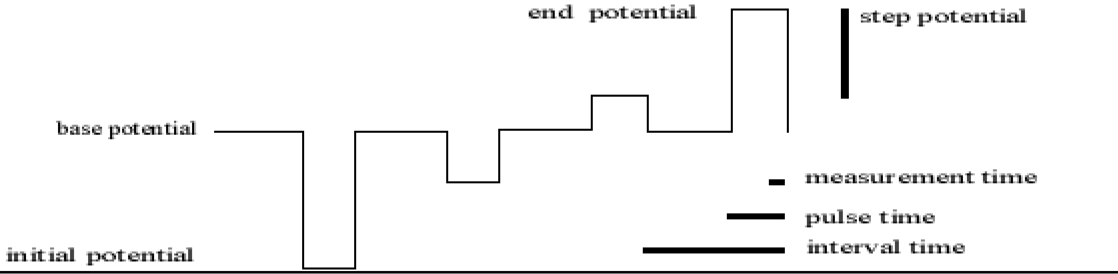


This technique is classically applied to mercury electrodes and is also called "tast polarography". In practice, interval times are in the range 0.5-6 seconds for polarography. On short time scales, there is relatively more interference due to the capacitive currents, while at longer times noise problems increase since the total current will keep falling off due to reactant depletion. In favourable circumstances, detection limits of ca 10^{-6} *M are obtainable.*
This technique can also be used for non-polarographic applications at interval times lower than 0.5 seconds. However, when fast scan speeds are required, the "linear sweep voltammetry" technique might be more appropriate.

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.
Usually 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 measurement duration.

2.3 Normal pulse voltammetry

Fig. 2 Normal pulse voltammetry

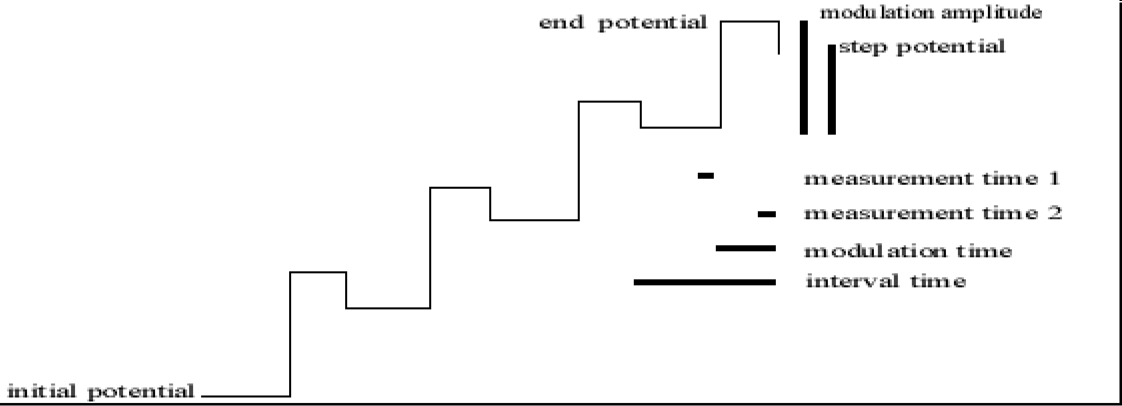


While applying sampled dc, the reactions are allowed to proceed during the whole interval time. As a result, the region near the electrode is depleted from reactant, lowering the faradaic current. Furthermore, reaction product can accumulate on the electrode, poisoning its surface.
To decrease these detrimental effects, the normal pulse technique was developed. Here, the electrode is kept at an inactive potential for most of the interval time: the base potential. Just prior to the measurement, the electrolysis potential is applied: the normal pulse. Concerning the duration of the pulse period, the familiar discussion applies here: a shorter pulse will yield response with a higher magnitude but the ratio of (unwanted) capacitive current will be higher as well.
This technique is approximately a factor 10 more sensitive than sampled dc. However, the 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. Then again, that might be just the objective.

The parameters for this method are chosen similarly to sampled dc, with the addition of a pulse time. Normally, a reasonable value for the pulse time would be about 50ms. Internally, the software will try to adopt a sampling period that complies the line period. When the pulse period is larger than 40ms, it will collect samples and average them during the last 20ms (for 50Hz line frequency).

2.4 Differential pulse voltammetry

Fig. 3 Differential pulse voltammetry

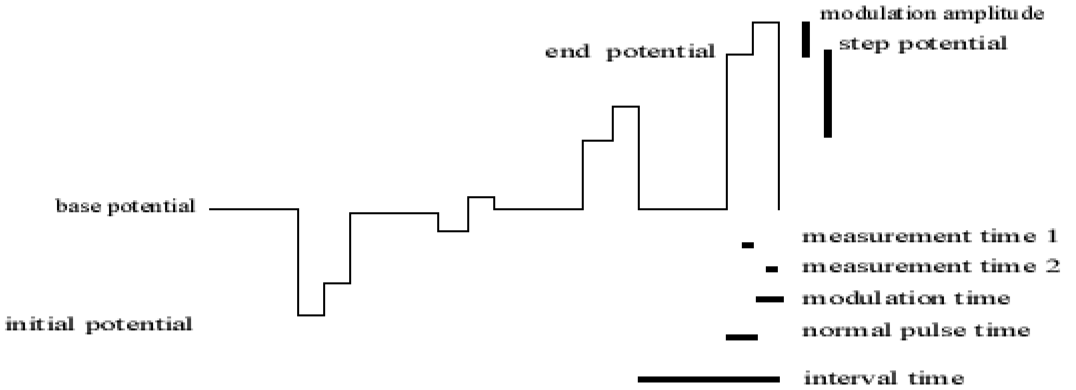


A pulse of constant amplitude is modulated on top of a potential scan not unlike sampled dc. Now, the current is sampled just before and at the end of the modulation pulse, recording the difference as the result. Obtained waves resemble the first derivative of a sampled dc scan, thus a peak.
Compared to the normal pulse technique, one can distinguish faradaic waves better from the background due to the larger 2nd derivative of the current/potential relation for faradaic processes. Since the modulation amplitude is constant, capacitive current will be expressed as a more or less constant baseline. Electro -oxidizable and -reducible substances on the other hand, will appear as recognisable 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 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 normal pulse voltammetry. 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.

2.5 Differential normal pulse voltammetry

Fig. 4 Differential normal pulse voltammetry

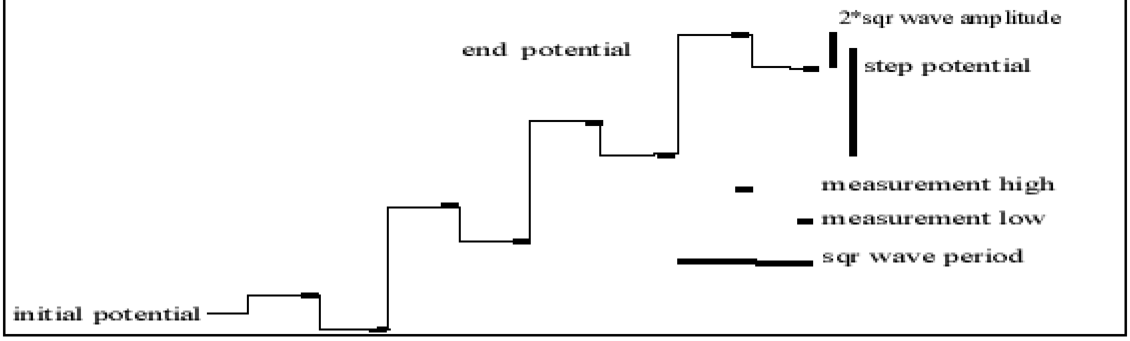


This is a hybrid of differential pulse and normal pulse voltammetry. Similar to the normal pulse method, a pulse will be superimposed on a base potential. On top of this pulse a modulation step with definable amplitude and duration is applied. The current just before and at the end of the modulation step will be measured and the difference will be stored. In this manner, the advantages of normal pulse (short electrolysis time) are combined with those of differential pulse (pronounced faraday currents).
The pulse time and modulation time are subject to similar considerations, and their magnitudes correspond with that in normal and differential pulse voltammetry.

Since its waveform is rather complex, care should be taken not to confuse parameters. For instance, the step potential and interval time define the relation between consecutive data points, and are **not** related to the properties of the pulses applied in a single measurement!
Please note that this implementation of differential normal pulse voltammetry is different from the description in: "Electrochemistry" by C.M.A.Brett and A.M.Oliviera Brett, Oxford University Press 1993.

2.6 Square wave voltammetry

Fig. 5 Square wave voltammetry



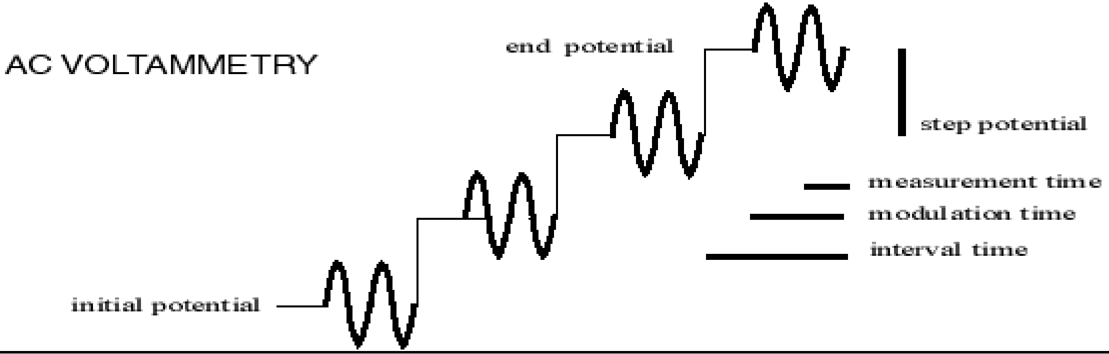
During square wave voltammetry the potential is scanned as in sampled dc, but an additional square wave is applied. The recorded curve is the difference between the *average currents in the forward and the reverse pulse, sampled just before each flank. The main advantage of this technique over differential pulse voltammetry is the increased number of samples, enabling 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, minus the current at the low level. 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. Please note that the amplitude corresponds with half the peak-peak potential difference of the square wave.
A proper choice of frequency is of the utmost importance. Similar to using short pulse duration’s in pulse voltammetry, the influence of capacitive current is larger at high frequencies.
The bandwidth of the Autolab potentiostat is lower at low current ranges as well. Therefore, the software will mark the lower current ranges red in cases where the current range is not suitable for the specified frequency. Of course the operator can choose to ignore such hints, but might be advised to be cautious. Normally, the useful frequency range is 8-250Hz.

2.7 AC voltammetry

Fig. 6 AC voltammetry



With ac voltammetry, a sine wave signal is superimposed on the voltage scan. For small amplitudes, the electrochemical interface can be treated as a linear electrical circuit, for which impedance’s admittance’s can be determined. These impedance’s are related to electrochemical parameters and can be used to obtain information about electrode kinetics, electrosorption, etc.
Usually, the results obtained with sine wave methods contain more capacitive current than square waves results. This might be considered a disadvantage. However, the mathematical analysis can be performed with more rigour. For instance, the

capability to separate inphase and outphase current components, greatly facilitates interpretation. Even more powerful is the frequency variation technique with the FRA module that will be discussed later.
The ac voltammetry implementation discussed in this paragraph, does ***not*** *require the FRA module.*

The basics of the potential scan are the same as for sampled dc and can be specified by initial-, end- and step-potential. Again 2 consecutive data points are separated by the interval time.
The ac amplitude is specified as the root mean square value. It will be applied only at the modulation period that is situated at the end of the interval period. The actual measurement is conducted in the last half of that modulation period.
The waveform of the perturbation waveform is constructed from a wave table and applied (after digital to analog conversion) to the potentiostat periodically, while sampling the currents at the same time.
Note that the number of points that are sampled within a waveform period are related to the frequency of the chosen perturbation and the maximum sampling rate of the Autolab.
The waveform of the perturbing potential is sampled once before the measurement starts. Its Fourier transform will be stored to be used as a reference to calculate the impedance’s. During the measurement periods, the current will be sampled and stored. When all samples have been collected, a Fast Fourier Transform is calculated. From the results at the principal frequency, the impedance will be calculated (phase+magnitude). Depending whether "Phase sensitive" is checked, the final result will be determined. If not set, the absolute value of impedance will be kept. When the option is set, the indicated phase will be used to calculate the response congruent to that phase: a phase setting of 0 degrees will lock on the inphase (ohmic) response, while a setting of -90 degrees will yield the capacitive signal.
When choosing the frequency, the familiar arguments arise. At higher frequencies, there will be more influence of the capacitive process and kinetic phenomena.

In the Autolab instruments containing a FRA module, the ac methods should be performed with the FRA program. The ac voltammetry method in the GPES software is **not** available for this combination.

2.8 AC second harmonic voltammetry

Most electrochemical objects have a non-linear relation with potential: usually an exponential dependence. Therefore, the impedance approach is only realistic at low amplitudes. At higher amplitudes, a sine wave perturbation will produce a whole range of harmonics. Sometimes it is useful to utilise this property of electrochemical objects and focus on the (2^{nd} order) quadratic response that will be expressed at the double frequency of the perturbation.
The 2^{nd} order wave somewhat resembles a second derivative of the sampled dc, though the exact mathematical description is rather complex. Please note that the second harmonic result cannot be called impedance in the classical sense. The definition of the phase is also unconventional.

The implementation of this technique is very similar to the one described in the previous paragraph. However, instead of focussing on the principal frequency, the second harmonic is extracted from the FFT spectrum.

A central parameter here is the perturbation amplitude that should be chosen rather large in order to obtain a substantial result. Keep in mind that the response will be proportional to the quadratic amplitude of the perturbing signal.

3. Cyclic and linear sweep voltammetry

3.1 Overview of techniques

Cyclic voltammetry is probably the most popular electrochemical technique for solid electrodes. The ability to obtain reproducible results, at least for subsequent cycles, is invaluable for relatively badly defined electrode surfaces. Also, the possibility to observe the reduction wave and the oxidation wave simultaneously is quite helpful in the investigation of electrode processes. Several electrode kinetic and electrosorption processes can be studied in detail from the analysis of cyclic voltammograms recorded at various scan rates.

Using these techniques, again a potential/ current scan is applied. However, the implementation is different. The principal parameter is the scan rate. Now the sample interval will be equal to scan rate/step potential. Here, the measurement period is defined by ¼ of the interval time and for reasons of noise reduction will be rounded to a multiple of the line period: 20ms (or 16.67ms) with a maximum of 1 second. Obviously, for intervals shorter than 80ms, this is not possible and a measurement period of exactly ¼ of the interval time will be used. For sample intervals from 25ms to 80ms this behaviour can be overridden by pressing the "Mean" button that will fix the measurement period to 1 line cycle, thus eliminating line noise maximally.

In cyclic voltammetry, it is often desirable to perform the measurement scan (cycle) repeatedly in sequence, as a part of the electrode conditioning process, or to monitor the electrochemical processes with time.
In principle, the number of data points that can be stored is only limited by the capacity of the PC, but for practical reasons the total limit is put to 30,000 points by default, with a 10,000 maximum for individual scans. If so desired, these limits can be adjusted by editing record [3,3] and record [3,4] of the hardware configuration file. One scan contains: "2*ABS(1st vertex potential – 2nd vertex potential)/step potential" data points. When during cycling the maximum number of scans has been reached, the eldest scan will be overwritten, thus the last scans will always be available in memory.
On screen, the most recent results will be shown. However, at fast sample rates, the computer lacks the time to plot all data points and only a few will be visible. All points will be replotted after the scan has finished.
The consecutive scans are stored in memory, in the sequence in which they were recorded. Each individual scan can be selected, analysed, and/or stored to disk.

When more than one scan is to be recorded in cyclic voltammetry, it is possible to save scans at regular intervals during the measurements. For this purpose, the parameter Save every nth cycle is introduced on page two of the Edit procedure window. If this parameter is zero, no scans will be saved during the measurements, otherwise every nth scan will be stored on disk. If, e.g. ‘5’ is specified, scan 1, 5, 10, 15 are saved. The path and the first three characters of the file name can be specified on page two of the Edit procedure window. ('Direct output filename'). The last five characters of the file name will be used as the scan number.

It is possible to record a second signal (or BIPOT signal) by selecting this option on page 2 of the Procedure window. Be aware that this option is not available when using an ADC750 module during the measurement.
When a Ring-Disk electrode is utilised and a BIPOT module is present, Iring versus Idisk plots can be constructed. In the Data presentation window, ‘WE2 vs. WE plot’ should be selected from the Analysis menu item.

The linear sweep method requires the same parameters as cyclic voltammetry and its implementation is nearly identical. The difference is that the sweep is in one direction while the cyclic method also includes a backward scan. For the linear sweep, one can only define start- and end-potential, whereas 2 vertex potentials are required for the cyclic technique.

3.2 Normal mode (staircase)

When using the normal staircase mode, the potential increases will be applied as steps at the end of each interval time. Usually, this is advantageous since it diminishes capacitive current in the same manner as pulse voltammetry. However, when one is interested in adsorption phenomena or UPD, this behaviour is unwanted. In the latter case, one should choose the linear scan mode utilising the SCAN-GEN module, or one should apply the current integration method discussed in one of the following paragraphs.

After the time for each step expires, the potential will be increased with the step potential. The current will be sampled at the end of each interval time, according to the previously explained rules.
An option is available to change the sample time position by means of the alpha parameter. Normally the current is sampled at the end of each interval time: alpha=1. By selecting a value of 0.5 the sampling would be performed halfway the interval, etc.

3.3 Stationary current

Stationary current cyclic voltammetry is intended for electrochemical objects that (after some time) yield a constant current, like batteries or hydrodynamically controlled systems. This method is also applied in corrosion studies.
While a voltammogram is being recorded, each newly measured data point will only be accepted when a stationary condition has been reached. In this mode, the scan rate will be dictated by the electrochemical object, since the scan will only proceed after the response is constant.

There are a number of criteria that can be applied to define the stationary condition. Every second, the current will be measured. If during 3 seconds, the current changes less than abs(di) per second, then the equilibrium is supposed to be reached. Alternatively, a relative change abs(di/i) can be specified. A maximum time interval can be entered as well. This will limit the waiting time at each potential, after which the steady state is supposed to be reached and the scan will be continued.

3.4 Scan averaging

Normally the scans are recorded and stored separately. In this mode, however, subsequent scans are averaged and displayed as a single scan. A "number of scans to reach equilibrium" can be entered that defines the scan number after which averaging should start. Note that the former scans are discarded and not included in the average. This technique is particularly useful for very noisy voltammograms. Of course, it would be preferable to eliminate noise at its source first.

3.5 Current integration

In some cases, the normal staircase potential scans are not desirable. For example, when studying fast electrode processes or UPD, the response is concentrated in a short time immediately after the pulse application and has disappeared when the actual measurement would start. In such cases, it is desirable to make a real linear scan. For those who do not have a SCAN-GEN module, there is an alternative approach that yields identical results: "The Current Integration" mode. The theoretical background is discussed in detail in the application note: "Appl-5".

The shape of the perturbation potential is the same as with the staircase mode, but the current is now determined by means of an analog integrator that collects the total charge that has passed during the whole interval time. This charge when divided by the interval time, is (mathematically) equivalent to the response to a real linear sweep. Because the operation and resetting of the analog integrator takes time, this method can only use every other sample time. Consequently, only half the number of samples are recorded as compared to normal operation.

3.6 Galvanostatic cyclic voltammetry

Although at first glance there are similarities with cyclic voltammetry, some distinct differences are present. The interpretation of the faraday current is simpler, but the behaviour of the charging process is more complex. Unlike with staircase voltammetry, the charging current will not decrease with increasing interval time. Separation of these components might therefore be more cumbersome.

This technique resembles the normal (staircase) voltammetric mode, except that the instrument will switch to galvanostatic operation. The scan will start with the "start current". After each sample interval, the potential is measured and stored, after which the current is increased with the step current. This process is repeated until the 1st vertex current is reached. Then, the scan proceeds to the 2nd vertex current and back again to the starting current.

3.7 Fast scan voltammetry

This mode is similar to the normal staircase method, but it is differently implemented enabling faster scan rates. For instance: automatic current ranging is not possible and user interaction while a scan is in progress is limited.

In fast operation, the instrument will only approximately realise the requested scan rate. After the scan has finished, it will determine its actual sweep rate and display this value.

3.8 Linear CV scans with the SCAN-GEN module

As discussed previously, it is sometimes desirable to produce a real linear potential scan. The SCAN-GEN module provides this option. This enables the study of fast discrete processes that would be difficult to study with a staircase scan. For instance, the capacitive current will expire very fast after the application of each voltage step and its determination is thus impossible with the staircase technique. On the other hand, when the capacitive current is unwanted, the use of the staircase scan method is more favourable.
The differences between the staircase method and the use of a linear scangenerator are discussed in the application note: "Appl-5".

The implementation of linear cyclic voltammetry is analogue to its staircase resulting in counterpart. However, the analog signal generator is less controllable, resulting in a vertex potential with less accuracy: +/-5mV instead of 0.15mV. Of course the actually realised vertex potentials will be recorded accurately.

3.9 Hydrodynamic linear sweep voltammetry with an RDE

When an RDE device is present, it is possible to do hydrodynamic linear sweep voltammetry. Multiple scans at different rotation speeds of the RDE can be recorded. The RDE should be connected to one of the BNC-connectors of the DAC module (preferably channel 3). Select the RDE control option in the Utilities menu, where the setup of the used RDE should be specified. During a measurement cycle, the rotation speed can be monitored in this window.

After finishing a measurement cycle, two additional parameters are present in the Analysis menu of the Data presentation window. It is possible to make the plots of i versus sqrt(ω) and 1/i vs 1/sqrt(ω), where ω equals (2*π/60)* rotation speed in r.p.m. These plots can be used to calculate the diffusion coefficient and kinetic parameters. For more information please refer to the textbook of A.J.Bard and L.R. Faulkner "Electrochemical methods: Fundamentals and Applications".
After selecting one of these plots, a potential must be selected.

The data should be saved as a so-called buffer file in order to perform the analysis afterwards. The Save data buffer As option of the file menu saves all scans and all rotation speed data.
An example for hydrodynamic linear sweep voltammetry is present in the TESTDATA directory, called: HYDRODYN.

4. Chrono methods

4.1 Scope of techniques

With chronoamperometry, the current is measured versus time as a response to a (sequence of) potential pulse(s). The potential perturbation can be defined in detail and the current response will be recorded continuously. The recorded current can be analysed and its nature can be identified from the variations with time. For example: at short times the capacitive current is dominant ($\mu\, e^{-t/RC}$ *; with R=solution resistance and C=capacity), while at longer time scales, the diffusion limited faradaic current might prevail (* $\mu\, t^{-1/2}$ *).*

*For chronopotentiometry, similarly to galvanostatic cyclic potentiometry, the mathematical description of faradaic currents is simpler than with chronoamperometry. Also any ohmic potential drop will be constant with time as well and will therefore not affect the shape of the response, except for an offset equal to R*I (solution resistance*current). On the other hand, the capacitive current is usually larger and its decay is related to the interfacial reaction impedance that is parallel to the double layer capacitance.*

4.2 Overview of techniques >0.1s

These techniques have in common that a response is recorded with time in a flexible manner. The measured quantity is sampled (at the end of) every interval time for the duration of one line cycle: 20ms or 16.67ms. The samples will be stored, depending on the definition of the interval time.

Sometimes it will be useful to increase sampling rates when the response changes rapidly with time. To this end, one can enter a maximum current/charge/potential change (di, dQ, dE) that will speed up sampling when necessary. For amperometry, one could specify a relatively long interval time with a small di, thus capturing the important features of the response with a minimum amount of data points. Keep in mind that the minimum interval is 0.1 s, so the maximum change between samples could be larger than specified.

The implementation of amperometry is straightforward. The potential levels are applied in the order in which they are specified, while the current samples are recorded at the end of each interval time.

Galvanostatic potentiometry is implemented in an analogue manner.

Zero current galvanostatic potentiometry is implemented as a separate method, since it involves the physical disconnection of the counter electrode. This method enables the user to measure the change in the Open Circuit Potential in time.

In chrono-coulometry, the current is measured and integrated numerically. Of course, the current variations between samples (0.1s) must be small enough, or in any case linear, to allow for accurate numerical integration. Otherwise, the method described in the next paragraph should be applied.

4.3 Overview of techniques <0.1s

More rapid sampling to about 35,000 samples/s can be accomplished using this mode. However, compared with the ">0.1s mode", some features are lost. In order to guarantee reliable time performance, automatic current ranging and the option to change sampling rate during a single scan, via "di", "dQ" or "dE", are not available. Faster sampling can be accomplished with the addition of the ADC750 module (maximum 750,000 samples/s).

The amperometric and potentiometric techniques work similar to the >0.1S methods, taking into account the remarks above.

The chrono-coulometric method requires the presence of an analog integrator. One of four integrator RC-times can be selected: 0.01, 0.1, 1, 10s.
Special attention should be directed to the combination of current range and integrator RC-time. At a too low range, the integrator will get into saturation yielding an incomplete result, while at unnecessary high values resolution will be lost. The saturation value is reached when the total charge is equal to approx. ±10*(Current Range * Integrator RC-time).
Unless one has a clear expectation about the magnitude of the response, some trial runs might be necessary. Perform a test measurement with chrono amperometry to determine maximum current and approximate charge. Choose a current range that is between 0.4 and 4 times the observed maximum. Evaluate the maximum charge with the "integrate" option in the <edit data> menu. Now select an integrator RC-time that corresponds to: maximum charge/ current range. In general a first choice for the integrator RC-time is the time which matches the pulse time or the total measurement time.
It is important to minimise the effects of integrator drift. Especially for the measurement of low charges at high current ranges, the drift may become dominant. In such cases, it would be advisable to place a resistor in the WE line, limiting the maximum current, thus enabling a more sensitive current range.

5. Multimode electrochemical detection

This method is intended for electrochemical detection as a function of time, for example in combination with HPLC or FIA.

When dc amperometry is selected, the current will be sampled at the end of every interval time until the run time expires. The measurement period is taken equal to one line period (20ms or 16.6ms).

Using multiple pulse amperometry, a sequence of potential levels can be specified that are applied during the transient. A number of objectives can be accomplished in this manner:

- Several current/time curves can be recorded at various potential levels within one scan.
- The electrode can be regenerated during the measurement.
- Electroactive species can be deposited.

Differential pulse amperometry can provide a higher sensitivity. Its response is defined by the difference of the current obtained at 2 potential levels (listed at page 2 of the procedure window).

6. Potentiometric stripping analysis

6.1 Overview and implementation

Just like stripping voltammetry, deposited reaction products or adsorbed substances are stripped from the electrode. The stripping itself can be done either by using a chemical reaction or by using an external current. During the stripping process, the potential is recorded and processed. From the response, recalculated to (dt/dE) vs E, the amount of stripped material can be determined from the peak size. The nature of the species can be deduced from the peak potential.

After starting the PSA measurement, the potential versus time is recorded at maximum speed (30-60kHz).
To facilitate interpretation, it is most descriptive to present the results as the inverse potential derivative with time (dt/dE), versus potential(E). The E vs t data are processed in the following manner:

- The voltage range is divided in a fixed number of steps with a so-called threshold level at the end of each step.
- Starting from the first recorded potential, the samples are counted, until the next threshold level is reached. The result will thus show the number of times that the measured potential lies between two threshold values.
- The obtained results are multiplied with a factor, equal to the sample time divided by the potential separation between threshold levels, yielding: (dt/dE).

When dt/dE is plotted against the potential, a peak shaped pattern is obtained, which allows for a detailed trace analysis.
Note that this method of data processing is only valid for continuously rising or monotonously decreasing stripping potential transient. Of course, this is usually a realistic assumption.

The value of parameter "Maximum time of measurement(s)" should be specified with some care. In case this value exceeds 3s, the resolution of the time measurements is lowered. In case an experiment takes less than 1/300 of the specified "Maximum time of measurement(s)", a warning message is given to specify a lower value.

6.2 Chemical stripping versus galvanostatic stripping

The substance under investigation is deposited by means of applying a "deposition potential" to the electrode, at which a substance will accumulate at the electrode surface.

When the chemical stripping technique is applied, the counter electrode will be disconnected at the stripping stage. The deposited material will be chemically removed (stripped), while the Open Circuit Potential (OCP) is being recorded.

On the other hand, during galvanostatic stripping, the potentiostat is transformed to a galvanostat at the stripping stage (see "advanced issues"). The deposited material is now stripped by electrochemical oxidation at constant current, while the potential is being recorded.

7. Steps and sweeps

With this option, the operator is able to define a free sequence of pulses and sweeps and to monitor the response with time. This enables the users to define their own waveforms.
In principle, the steps are implemented as in chrono amperometry and the sweeps as in linear sweep voltammetry. The implemented flexibility will reduce the maximum obtainable speed (maximum scan rate/minimum sample time).When a SCAN-GEN module is present, the staircase sweeps will become linear scans.

From the results, the separate stages can be selected by means of "select segment" in the <plot menu> of the data presentation window. In this way segments can be edited, analysed, and stored separately. Note that data manipulation is only possible when either the current or the potential data is selected, not both.

8. ElectroChemical Noise (ECN)

The potential- as well as the current-noise can be measured, stored, and analysed with this method. Using the Autolab there are two possibilities to measure the electrochemical noise, one using the normal cell cables. Therefore 3 identical electrodes should be placed in an electrochemical cell. One electrode is connected to the red WE-cable, another to the blue RE-cable, the remaining electrode to the green ground. The red S-cable should be connected together with WE, while the black CE-cable remains unconnected. In the described configuration, the potential noise is recorded with the RE-electrode that will be displayed as first signal (left axis in Data presentation). The current noise is recorded from the WE-electrode that is shown as second signal (right axis in Data presentation). The third grounded electrode enables the passing of the current.

The second option to measure electrochemical noise requires the optional ECN module. How the electrodes are connected and the date is processed can be seen in the chapter about the ECN module of the ‘Installation and Diagnostics guide’. If the ECN module is present the use of the module can be specified on the second page. The potential displayed as first signal during a measurement represents the potential at open circuit potential. If the option “show noise around zero volt” the potential displayed as first signal will only show the low frequent differential noise potential around the zero potential so in fact without the DC-component. The advantage of using the optional ECN module is that the DC component of the potential is compensated during measurement and therefore the noise potential can be measured with the highest sensitivity available.

8.1 Transient

The current and potential transients are recorded simultaneously. The minimum sampling time equals 0.002s. The duration of the transients is set to a power of 2 times the sampling interval, in order to enable proper FFT analysis (*). When starting a scan, the duration will be adjusted automatically to the next nearest power of 2, when necessary. If a running measurement is aborted prematurely, the dataset will be padded with zeros to the nearest power of 2 before FFT analysis is applied.
After recording the noise transients, a Spectral noise analysis option is present in the Data analysis window. A number of signal processing operations are available, like base line subtraction and several windowing functions. The result of the analysis is the power spectrum of the potential and current, or the magnitude of the impedance as a function of frequency. The impedance is defined as the Fourier transformed potential divided by the current at each frequency, both expressed in magnitudes.

(*) (duration time/interval time) $\equiv 2^n$ (= amount of data points)

9. Frequency Response Analysis with the FRA module

9.1 Principles of electrochemical frequency analysis

The ac impedance technique is commonly applied in investigations of electrode kinetics or corrosion. The reaction rate/corrosion rate will be related to a charge transfer/ corrosion resistance. When choosing the optimal frequency range, several aspects should be considered:
At very low frequencies, the mass transport (diffusion resistance) will dominate the impedance.
The electrical double layer capacitor will shortcut the Faradaic impedance at high frequencies.
At very high frequencies, the ohmic resistance will become dominant.
Thus, for a meaningful determination of the reaction rate/corrosion rate, one needs to find an optimal frequency range. For slow reactions, the useful frequencies will be located in the lower ranges, while fast reactions require higher frequencies. When the result is not a priori known, it will of course be useful to scan a wide frequency range for analysis.

The measurements can be done under potentiostatic as well as galvanostatic conditions.

The (potentiostatic) amplitude is generally put in the range: 5-25mV. In some situations, for instance in media with a low conductivity, it can be desirable to apply higher amplitudes. For impedance determinations, it does not matter whether the perturbation is applied as a potential or a current. In practice, the dc requirements will dictate which mode is selected.
Caution should be exercised when using galvanostatic perturbations: since the voltage applied on the electrochemical object is not controlled, it could exceed the advisable limits for linear behaviour, resulting in unexpected distortions by non-linearity effects. It is therefore recommended to verify afterwards whether the magnitude of the ac potential has remained within acceptable limits at that particular impedance. When in doubt, one could repeat the measurement applying a lower ac current amplitude and compare the result.

The Autolab instrument will determine the impedance of the object under test by performing a numerical Fourier analysis on the current/ potential samples that were recorded during the measurement period. This measurement period is defined by the integration time, which can be chosen by the operator. The integration time may be defined as a number of cycles. A longer integration time will yield a higher accuracy with better noise immunity, but will prolong the duration of the measurement. The latter might be a practical consideration at low frequencies.

The instrument employs an elaborate strategy to maximise dynamic performance and minimise effects of noise by utilising digitally controlled filters, variable amplifiers, and programmable offsets. Thus the resolutions of the internal ADC’s will be exploited optimally. From each Fourier transformed potential/ current result, it checks

whether the resolution is within a predefined range. When the software concludes that performance can be improved using another setting, adjustments will be made and the measurement is repeated. Thus it is possible that one can see measurements being repeated on the display, to a maximum of 4 times. For this reason, the total measurement duration can be longer than the estimation indicated in the "edit frequencies" dialog window.
This strategy yields a highly flexible performance, that allows for the accurate evaluation of a wide range of impedance’s.

A multiple sine wave mode is available. Simultaneously 5 or 15 sine waves can be applied, cutting down the duration of the frequency scan by factor 2-3. Especially for low frequencies this option can be profitable. Exploiting the characteristics of the Fourier analysis, the response of each frequency component can be determined separately, in principle without loss of accuracy. However, in practice, the accuracy will be somewhat less than with the single sine method, due to the loss of the dynamic performance: when multiple sine waves are mixed, a signal of higher amplitude must be processed, requiring a wider range that has lower resolution. The capability to reduce noise by filtering, is limited in the multiple sine mode.

9.2 Recording impedance’s at a single potential or current

For stationary electrochemical systems, most parameters are directly related to the dc electrode potential: double layer capacitance, reaction rates, etc. It may therefore be necessary to evaluate electrochemical parameters at fixed values of the potential. Most equivalent circuits are based on the constancy of each component during the scan. It is therefore desirable to eliminate time dependencies, or in any case, ensure that the "impedance drift" remains within limits.
Under galvanostatic conditions, the same considerations apply. Note that the variations of ac potential are not an issue. However, the dc potential should remain more or less constant during the scan.

The list of defined frequencies are applied in sequence. The duration of the measurement is determined by the integrator RC-time and the number of frequencies. The software will provide an estimation for the total duration. However, the actual duration of the scan might be larger, due to the autoranging process. When the instrument encounters an overload or finds that the current/potential gainsetting is not optimal, the measurement will be repeated, extending the total measurement time. When the total scan duration is found to be excessive, several strategies can be followed. First of all, the number of frequencies could be diminished, though the loss of data points is usually undesirable. Alternatively, one could lower the integration time, but that will diminish the accuracy of each data point. A third strategy would be to use the multi (5 or 15) sine method.
It is good practice to start a frequency scan at the highest frequency, ending with the lowest frequency. In this manner, the automatic ranging and automatic gaining will work most efficiently.

9.3 Recording impedance potential/current scans

More advanced analysis of the electrochemical processes requires the evaluation of electrochemical parameters as a function of potential. It would therefore be necessary to repeat the frequency scan at various potentials. The interesting range of potentials, depends of course on the electrochemical process under investigation.

This method is implemented similarly to dc voltammetry. A potential/current scan will be performed using the defined Start, End, and Step potentials. However, unlike dc voltammetry, the interval time is not available. Instead, the time duration between each measurement is defined by the duration of each frequency scan. The latter is determined according to the rules discussed in the first paragraph of this chapter.
It should be kept in mind that with changing dc potential, the dc current will vary as well. When the dc current gets into an overload condition, the ac results will also be invalid. Therefore, a proper range of current ranges should be chosen.

9.4 Recording impedance time scans

Most electrochemical phenomena are time variant. However, one often regards this as an undesirable effect and experiments are conducted within a short time window that ensures a fixed value for the electrochemical properties.
In other cases, one is interested in monitoring processes during a longer period, which requires the recording (variations) of electrochemical parameters with time. As can be expected, there is potential conflict here, since the measurement itself takes time. The variations within a frequency scan should be kept small, otherwise the analysis with an equivalent circuit will not be possible. The objective is to perform relatively fast frequency scans repeatedly at distant points in time, distributed over a long period.

The impedance/time scan is defined directly by 2 parameters: "interval time" and "duration of measurement". The interval time determines the time between the start of 2 consecutive measurements. Note that this time should therefore be larger than the duration of the frequency scan. If the latter requirement is not fulfilled, the next scan will start immediately, disregarding the listed "interval time". The "duration of measurement" parameter determines the duration of the total measurement.

9.5 Hydrodynamic Impedance Measurements

When an RDE is present, an Autolab equipped with FRA2 module can be used for hydrodynamic impedance measurements. The required external connections to the BNC connectors on the front panel of the FRA2 module are:
- 'signal out' to the input of the controller of the rotating disk electrode (RDE)
- 'Y' to the output of the controller of the RDE
- 'X' to the current output marked ‘Iout’ at the rear of Autolab

These connections have to be made, using shielded BNC cables.

The 'signal out' of the FRA2 module is used to modulate the rotation speed of the RDE.

The impedance analyser part of the FRA2 measures the signal from the RDE controller and the current intensity from the potentiostat/galvanostat.

When signals come from the X and Y, external inputs on the front panel have to be measured. This can be specified in the FRA manual control window. The check box 'Use external inputs' in this window must be checked.
The message 'External inputs are used!' appears after pressing the START button.

10. Advanced issues

10.1 Ohmic potential drop compensation

The PGSTAT12/20/30/100 models provide a facility to compensate for ohmic resistance on-line. The analog "current result signal" is fed back to the potential inputs of the potentiostat by means of a 12bit digitally controlled attenuator. In this manner, the potential is increased with an amount that is equal to the ohmic voltage drop (=i*R ; current* resistance) across the cell resistance, removing the effects of this resistance.

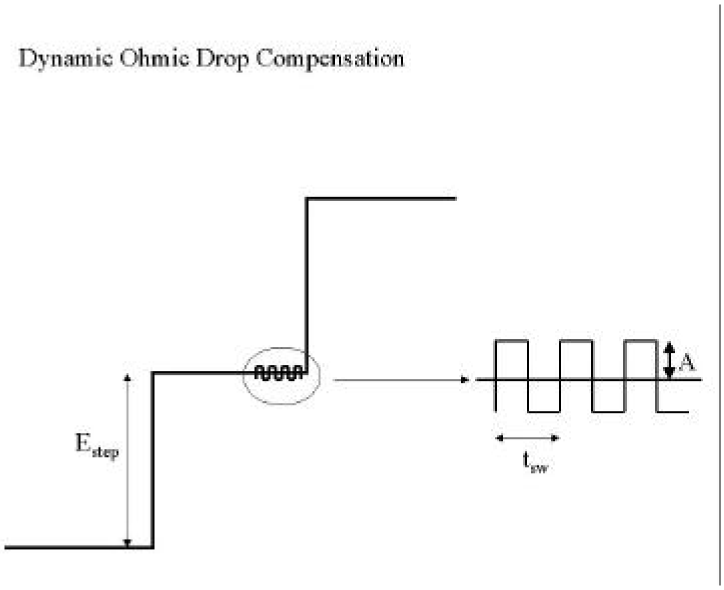
For proper operation it is necessary to set the feedback amplifier to a value that corresponds with the real ohmic resistance of the cell. Since the "current result signal" is inverse proportional to the current range setting, the limit and resolution of compensation are related. The maximum resistance (in ohm) that can be compensated is equal to 2Volt/current range (in A). The resolution is derived from the 12 bit attenuator, and is therefore 2^{-12} * maximum resistance. For example, at 1A range, the maximum resistance equals 2 ohm, with a resolution of 0.0005 ohm.

Initially, the actual ohmic resistance must be determined. A number of methods are available. Probably the most elegant strategy would be to analyse the equivalent circuit with the FRA technique (requires FRA module). Alternatively, one can apply the current interrupt technique or the positive feedback method.

10.2 Dynamic Ohmic drop compensation

In Cyclic Voltammetry and Chrono Methods this options offers the possibility to measure and compensate for the Ohmic Drop during the measurement. This is especially useful in systems where the Ohmic Drop changes during the experiment. At every potential level, either a step in staircase cyclic voltammetry or a step in chronoamperometry, a small amplitude high frequency square wave signal is added. By measuring the resulting current responses, the Ohmic Drop can be calculated.

Fig. 7 Dynamic Ohmic drop compensation



In the figure above a schematic description is given of the Dynamic Ohmic Drop method. E_{step} indicates a potential step in either cyclic voltammetry (staircase) or in chrono-amperometry/coulometry. The amplitude (A) of the square wave is user definable and can be 10 to 200mV, the t_{sw} in the picture indicates the period of the square wave. The standard value is 0.1 ms or a frequency for the square wave of 10 kHz. The current response to the square wave signal (I_{sw}) as well as the normal dc current (I_{dc}) are measured just before the setting of a new potential. The Ohmic Drop is then calculated from the I_{sw} value, and the potential in the next step is adjusted accordingly. The value of the measured ohmic drop will be shown in the data presentation window as a second signal.

Please keep in mind that the following limitations apply to this technique:

- It is only available for LSV and CV normal (staircase), and Chrono-amperometry/coulometry (Interval times >.1 s)
- The sweep rate in cyclic voltammetry is limited.
- The method cannot be used in combination with a Rotating Disk Electrode, an ARRAY, ADC750, BIPOT, pX or ECD module or any other device (EQCM, ESPR, etc.) that will result in an external signal.
- Hardware adjustments are necessary for this option, so the option cannot be used on an older instrument with new software only.
- The method only works in High Speed mode, meaning that it is not available on the old µAutolab.

10.3 Automatic dc current ranging

The Autolab instrument will choose the optimal dc current range automatically from the allowed list of current ranges. Prior to starting a method procedure, a short trial measurement will be performed from which result the most appropriate range will be evaluated. If during a measurement the current approaches a range limit, the

instrument will switch to a more suitable current range (either lower or higher). This is accomplished by comparing each sample with predefined threshold levels. When a result exceeds the upper threshold, a higher range is selected (when available). Likewise, when a measured current falls below the lower threshold repeatedly, a lower range is selected when available. By default, the threshold levels are defined as 0.04 and 4 times the current range.
If the current changes rapidly between two consecutive measurements, it might be possible that a data point will be outside reliable limits (5 times the current range), causing the overload indicator to be set. The point will be stored anyway and the scan will continue using a higher current range. The actual hardware limit is equal to 10 times the current range, thus those data points that are within 5-10 times the current range can still be used, ignoring the overload flag. However, their accuracy will be less, due to the non linear response characteristic for large signals.

Automatic ranging takes time: in the order of several milliseconds. Therefore this strategy can only be employed when the interval time is sufficiently large. For the "fast" techniques automatic ranging is not available. For other methods, this option is available, but its use will limit the maximum scan rate or the minimum interval time.

Note that this automatic ranging method is only available in the potentiostatic mode. For this reason, the potentiostatic methods have a broader dynamic range than their galvanostatic counterparts.

10.4 Sampling techniques

In order to exploit the resolution of the AD converters optimally and reduce noise maximally, the instrument employs automatic gaining and sample averaging. Each measured point, as it appears on screen and in the result file, is in fact the weighed average from several AD conversions that are collected at variable attenuation.

The ADC164 module has a programmable gain amplifier: 1x,10x, and 100x. Depending on the technique, the available time, and the settings in the Hardware Configuration File, a dedicated sampling strategy is applied:

- **SampleFast**: Only one AD conversion is performed and stored, using a preset fixed gain. This method is used for the fast techniques: "Cyclic Voltammetry Fast", "Chrono Methods (lowest possible sampling time)", and "Potential Stripping Analysis".
- **SampleOne** : First an ADC sample is taken at gain=10. The result is used to determine the optimal gain :1x/10x/100x, and the measurement is repeated. The result of the latter conversion is stored. This method is used in all techniques if the acquisition time is less than 157µs.
- **SampleMean**: First an ADC sample is taken at gain=10. The result is used to determine the optimal gain, which is selected. Subsequently, AD conversions are performed repeatedly until the available time has expired. The mean value is calculated and stored. This method is used for all techniques where SampleOne or SampleFast is not applied.
- **SampleGain**: First the input is sampled with a gain of 1. When it can be inferred that a higher gain is profitable, the gain is increased to 10, and the measurement is

repeated. If the high sensitivity option is enabled and the previous result indicates that the 100x gain is meaningful, the measurement is repeated at that higher gain. In this manner the input is sampled, continuously switching gains, until the measurement period expires. All samples are averaged, yielding a single data point that is stored. This technique can be applied instead of SampleMean.

The measurement period (=acquisition time) depends on the technique. To get rid of line noise, it is usually attempted to take exactly 1 line period or a multiple of this. If for some other reason sample averaging is not desirable, one can override it by changing record [21,4] in the Hardware Configuration File to 1. This will disable sample averaging and apply the "SampleOne" method for all (non fast) techniques.

The ‘fast techniques’ are : Cyclic & Linear sweep voltammetry/Fast scan, Chrono methods (<0.1s) and Potential stripping analysis. The Fast Cyclic/Linear voltammetric and Chrono techniques are performed with a fixed gain of 1, except when "Use high ADC resolution" is checked in the procedure window that puts the gain to 10. In the PSA method, the optimum gain is chosen automatically.

Gain variations introduce an uncertainty (jitter) in the time separation between consecutive samples. Therefore, when time synchronicity requirements are very stringent, like in ac-voltammetry, the current response is measured at a fixed gain.

The automatic gaining and averaging method is applied on voltammetric samples (current values) as well as on galvanostatic samples (potential values), unlike the autoranging described in the previous paragraph that is only applicable for current determinations.

10.5 Management of electrical connections to the electrodes

Cell on and cell off events

It is important to manage carefully how an electrode is electrically connected on a "cell on" or disconnected during a "cell off" event. Potentiostats operate by means of a feedback mechanism. If all the electrodes are not (yet) connected, it cannot work properly and the potentiostat will get into a state of saturation, applying the potential of the power supply to the electrode clamps. When such an open feedback loop is suddenly closed on "cell on", the electrodes will experience a potential spike that could spoil or damage them. Therefore, it is necessary to adopt a scheme that switches smoothly "On" and "Off". To this end, a programmable "dummy" feedback loop is introduced across the stage that controls the potential of the counter electrode. In this manner open feedback loops are avoided.

The reference and working electrode are always connected to the external connectors, also when cell is "Off". Note that it is therefore possible to measure the Open Circuit Potential (OCP) with "cell off".

Cell off situation:

The counter electrode is not connected, while the internal feedback loop is closed (=active)

Cell on event:

First the counter electrode is connected, 1 ms later the internal feedback loop is opened.

Cell off event:

First the counter electrode is disconnected, 1 ms later the internal feedback loop is closed again.

When the bipotentiostat is used, the second working electrode will be connected simultaneously with the counter electrode.

Switching from potentiostat to galvanostat

In the "Potentiometric Stripping Analysis, at constant current" the Autolab switches during the measurement from potentiostatic to galvanostatic operation. Since the implementation of this procedure is not trivial, it should be described in more detail.

- *Disconnect counter electrode, wait 3ms*
- *Close internal feedback loop*
- *Switch to galvanostat: open reference electrode feedback and close current follower feedback*
- *Set galvanostat to zero current, Connect counter electrode, wait 3ms*
- *Open internal feedback loop, wait 1ms*
- *Set desired current*

In case the zero current galvanostat (PSA chemical stripping) and zero current potentiometry is selected, the counter electrode is physically disconnected.

10.6 Recording Multiple Channels, BIPOT and second signals

The GPES package enables the simultaneous recording of several signals, either from multiple standard modules or user configurable external devices. On the 2nd page of the procedure window one can select:

- Bipotentiostat (when BIPOT module is present)
- Aux: any signal applied to selected ADC channel
- Charge: calculated charge
- Potential: measured potential
- Current: measured current
- ESPR: measured ESPR signal

Furthermore, multiple channels will be sampled when the multistat module is utilised. One should realise that all these measurements consume time. The lowest possible sampling time is therefore proportional to the number of signals that are to be recorded simultaneously.

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