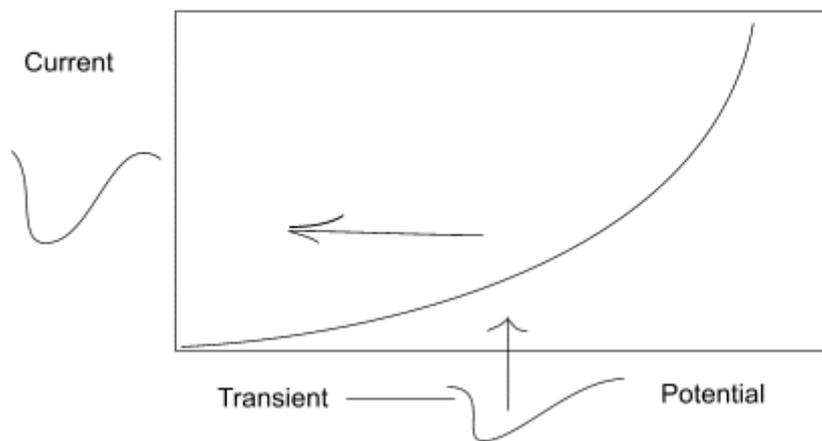


Localised Corrosion Monitoring (LCM™)

This analysis has the ability to supply information relating to Localised Corrosion Monitoring in the Initiation phase, both in terms of magnitude, an indication of the total depth of penetration and the General Corrosion Rate. Even in situations where localised corrosion is beyond the initiation stage, higher than expected values from the general corrosion rate will tell the user that something is not acceptable.

The LCM™ technique looks for negative going transients in the potential data caused by localised events such as a pitting initiation process. These are converted into a quantity of Coulombs via a calibrating polarisation and a V/I transient calibration curve.

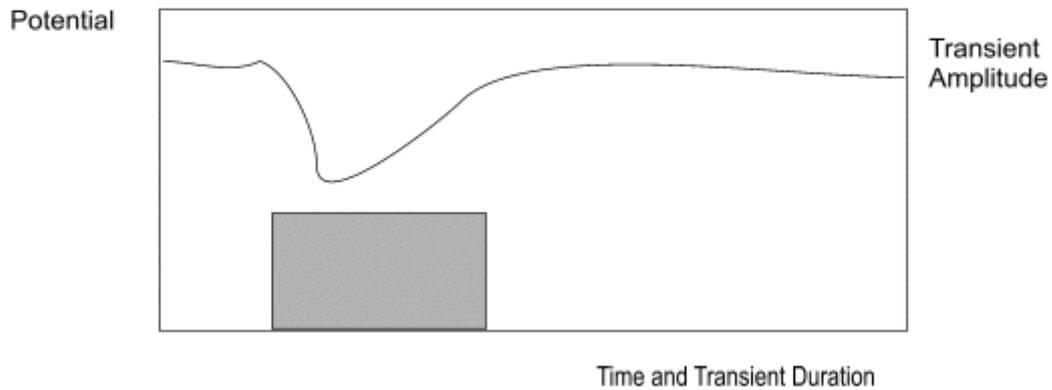


From the charge passed we can calculate the quantity of metal lost by a localised corrosion process necessary to produce the same quantity of charge by an Anodic reaction. For example $\text{Fe} = \text{Fe}^{2+} + 2\text{e}^-$. We assume all pits look like typical tin cans and the user can enter the ratio of width to depth. Thus it follows that if we know the charge passed by a single transient, we can calculate the penetration or depth of pit produced by such a transient. The calibrating polarisation is also used to measure the general corrosion rate via the LPR method.

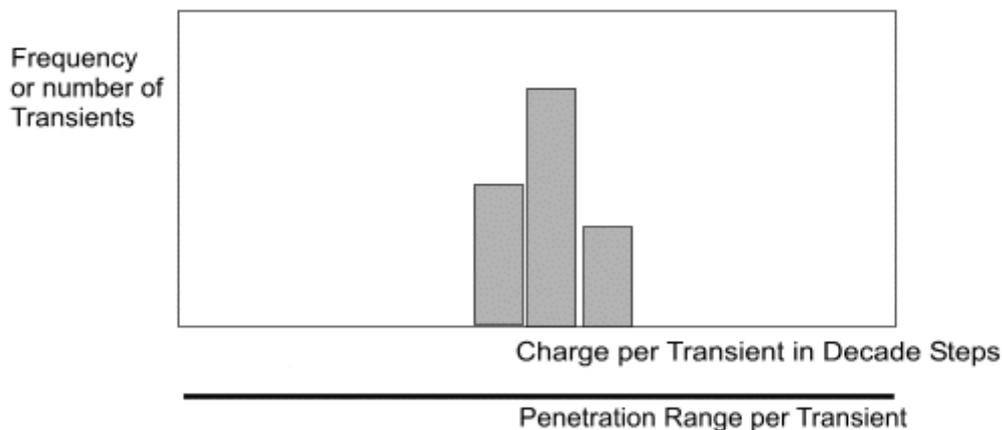
Interestingly, although all pits do not look like tin cans in shape, the difference in penetration for a hemispherical pit to a tin can shaped pit with equal aspect ratio, is only about 10% deeper, so in many cases it is good enough to assume all pits look like tin cans.

The job of this analysis software is to convert the raw data into something that is useful for the user. This is primarily done with a series of graphs.

The first of these graphs presents the raw potential data with respect to time. Blocks beneath transients detected in the data, indicate the magnitude and duration of the transients detected.

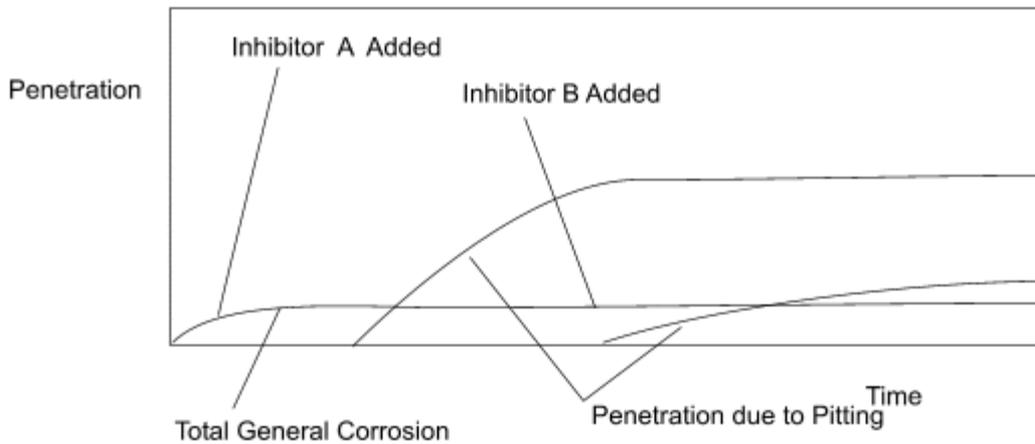


The second Graph Type presents the data in a form of a Histogram. The Histogram presents frequency on the Y axis, or the number of times a transient occurred, against one of two scales on the X axis. The X axis scales are either the quantity of charge passed by each transient in decade ranges, for instance $\times 10^{-5}$ to $\times 10^{-6}$, or allowing for the metal type and pit geometry, penetration range per transient. Interestingly the depth or width of a pit is proportional to the cube root of the charge passed. So a tenfold increase in charge passed increases the depth of a pit by a factor that is 2.15 x bigger or near enough double the depth or width.

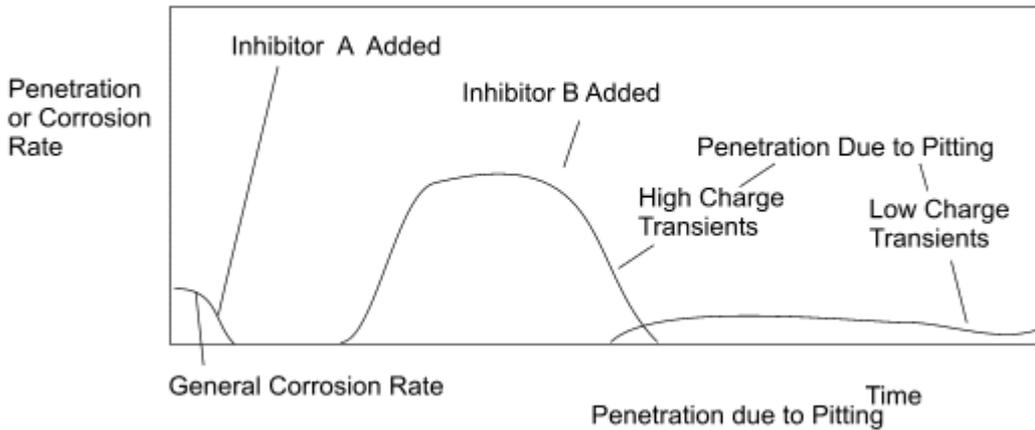


The third main graph type introduces the element of time into the data and present the data in terms of Total Penetration, Penetration Rate, and Penetration Acceleration. Most users will be familiar with the concept of Penetration Rate ν Time as this is the same type of graph as Corrosion Rate ν Time. Indeed General Corrosion Rate is presented on the same graph as Penetration Rate ν Time. Each graphic line that presents localised corrosion, takes its data from an individual bar in the above histogram.

Penetration v Time



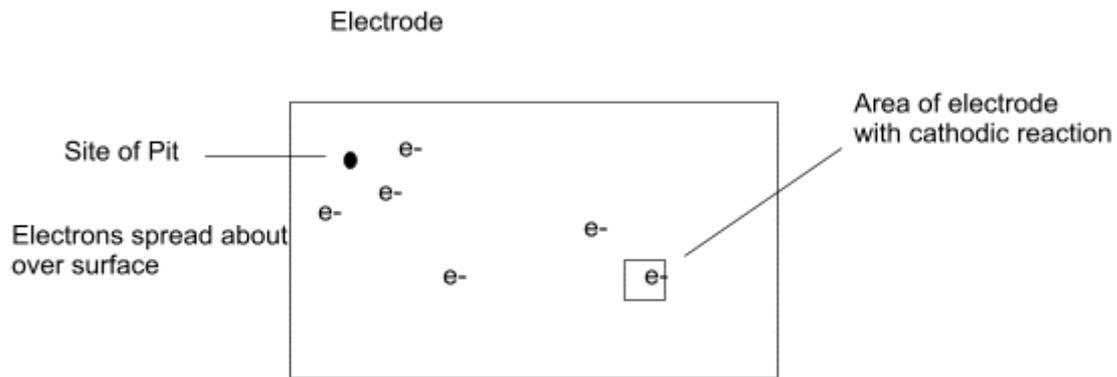
Penetration and Corrosion Rate v Time



Mechanism of a Transient

It is worthwhile to consider the mechanism of a localised event such as pitting initiation and consider its interrelation with the general corrosion rate. They are often seen as unrelated, however we intend to show you how they are very much related.

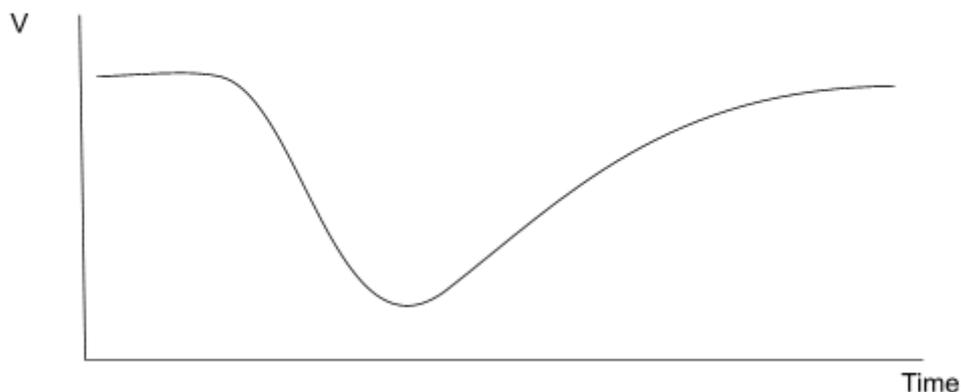
Consider a localised corrosion site. As the site starts to loose metal ions to solution, in some form of mass breakout, electrons are dissipated into the rest of the electrode. These electrons don't hang around, they rapidly spread about all over the surface of the electrode. This general excess of electrons leads to a dropping of the potential of the electrode.



If you consider yourself as part of the electrodes surface that is not corroding locally, you will experience a flow of electrons into your little patch. This extra supply of electrons will persuade you to up the rate of production of the Cathodic manufacturing process, where electrons and ions are combined. As the supply of electrons dwindles, this will encourage you to decrease the rate of production.

As an external observers with our voltmeter between a stable reference electrode and the electrode that is experiencing these localised events, we will see the localised event as a decrease in potential due to the excess of electrons, followed by an increase in potential as the area undergoing the localised event and the supply of electrons dries up. This effect is known as a transient. Transients can be quite short, perhaps just a few seconds, or last several hours.

Potential of a Transient



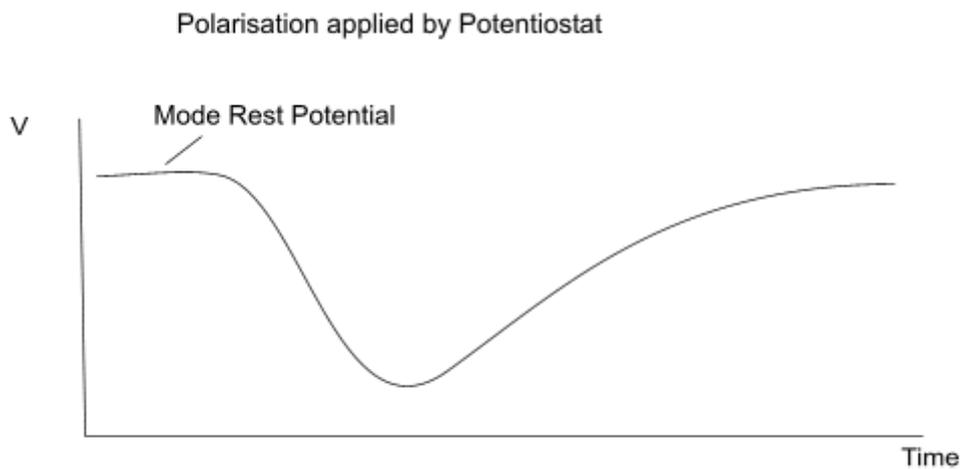
Consider now applying a polarisation to the electrode via a Potentiostat. The potential

polarisation is the same magnitude and time duration as that monitored during the natural pitting event. In this case electrons are supplied by a wire connected to the test electrode as opposed to a naturally occurring pit.

If as before, you consider yourself as part of the electrodes surface that is not corroding locally, you will experience a flow of electrons into your little patch. This extra supply of electrons will persuade you to up the rate of production of the Cathodic manufacturing process, where electrons and ions are combined. As the supply of electrons dwindles, this will encourage you to decrease the rate of production.

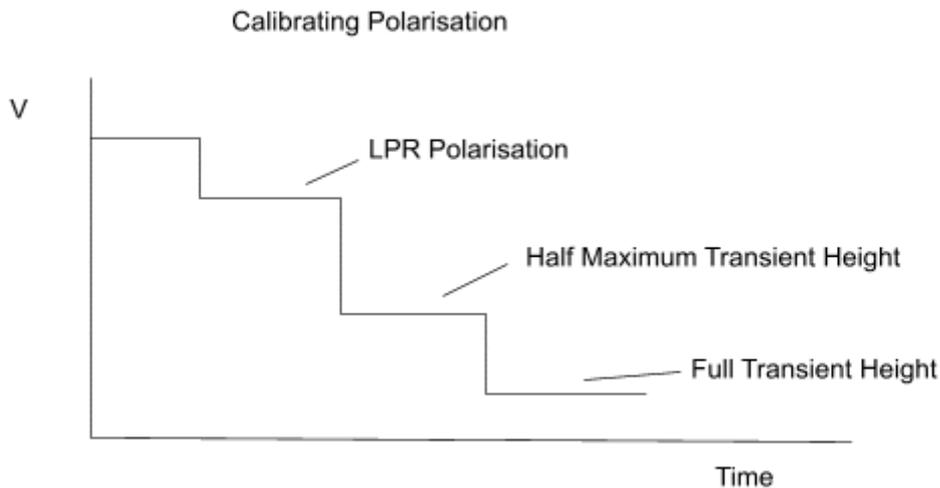
The point here being that with regards to the Cathodic reaction rate, it makes no difference where the electrons are supplied from. The Potentiostat or the Pit site, it makes no difference. Except with the Potentiostat we have the ability to monitor the amount of current associated with the pitting event.

Thus we have a means, by way of a polarisation, to convert naturally occurring potential v time transients into current v time transients and subsequently coulombs consumed by the Cathodic reaction.

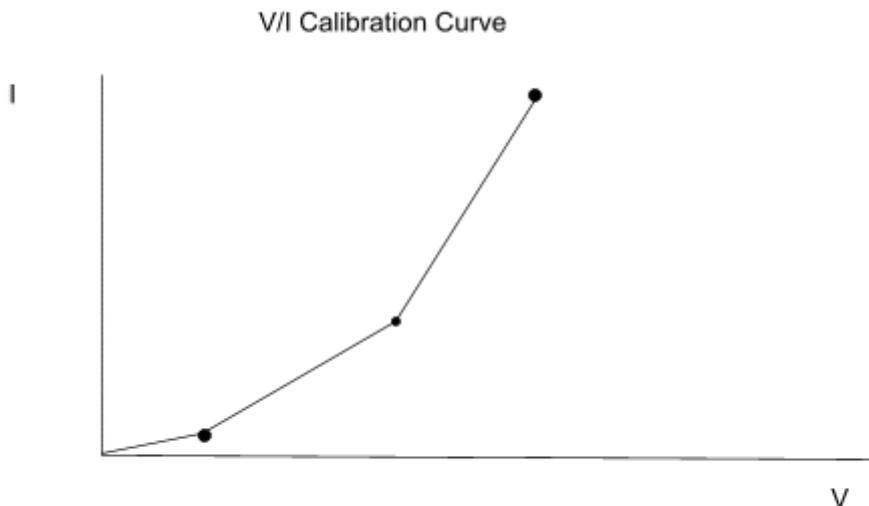


Interestingly if we apply the same polarisation as the naturally occurring transient and record current at the same time, we will produce the current transient produced by the naturally occurring pit site. This need not have the same appearance as the Potential Transient. It may appear like a much more pronounced burst of current in a passive metal system.

The technique involves taking potential measurements for a prolonged period of time during which time there may be transients of several different sizes. It would be nice to calibrate each transient using an identical polarisation as per each individual transient, however due to time constraints and the possibility of further natural pitting as the polarisation potential climbs back up to the Mode Rest Potential, a simpler method is used that involves three polarisations.

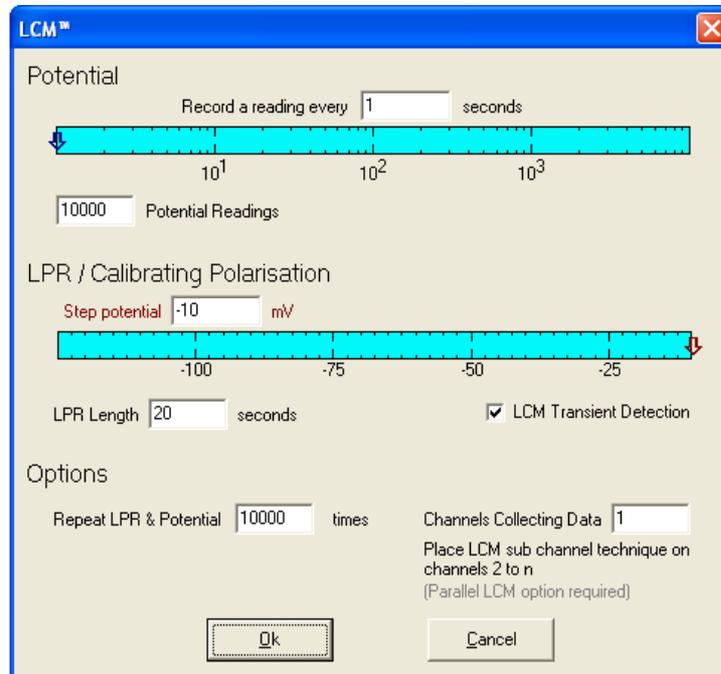


Three polarisations are applied, the first, a small one to measure the general corrosion rate around the Linear Region. The second at a point that represents half the maximum transient height and the third at a point that represents the full transient height. These parameters are presented on a V/I calibration graph which represents the rate of electron consumption by the Cathodic Reaction, given that a small delay in current measurement is allowed for charging of any double layer capacitance.



It is important that any calibrating polarisation needs to be as big as the naturally occurring transients due to the non linear nature of electrochemistry. A polarisation of 100mV may give 100 times more current response than a polarisation of 10mV. From the above diagram it can be seen that using three points gives a good approximation to the expected curve passing through the three points.

This LPR polarisation is only done in the negative direction, in an attempt to reduce the probability of any naturally occurring transients from occurring during this polarisation. Transients tend to occur close to the Mode Rest Potential. By polarising anodically we will be enhancing the probability of a naturally occurring transient from occurring. Naturally occurring transients during a LPR polarisation will, particularly with passive metals that have an oxide film, give misleading results for LPR.



The LCM™ technique is formed of two parts, potential monitoring and an LPR step. Potential monitoring is set by the read rate and number of potential measurements. The LPR step is set by the Step/Stop potential (which must be negative) and the length of the step.

Repeat LPR & Potential - decides how many times the potential measurements and LPR steps will be repeated.

Selecting the LCM™ Transient detection will enable two automated features. The first checks the potential data for transients (pitting events) and will not allow the potential measurement to end during a transient. The second feature finds the largest transient and changes the LPR step from one to either two or three steps between the step potential and the largest transient size, depending on how far away from the step potential the largest transient was.

Channels collecting data - is the total number of channels that will be recording at the same time. Each of these additional channels must use the LCM™ Sub channel technique. This option is for sequential instruments with the parallel LCM™ hardware, all other sequential and parallel instruments must have this set to 1.

 LCM™ Sub-channel

For instruments containing the parallel LCM™ hardware, it is possible for multiple sequential channel instruments to measure the potential measurements on all channels at the same time. Each channel will then queue to perform the LPR step, but will keep recording the potential measurements while they are waiting.

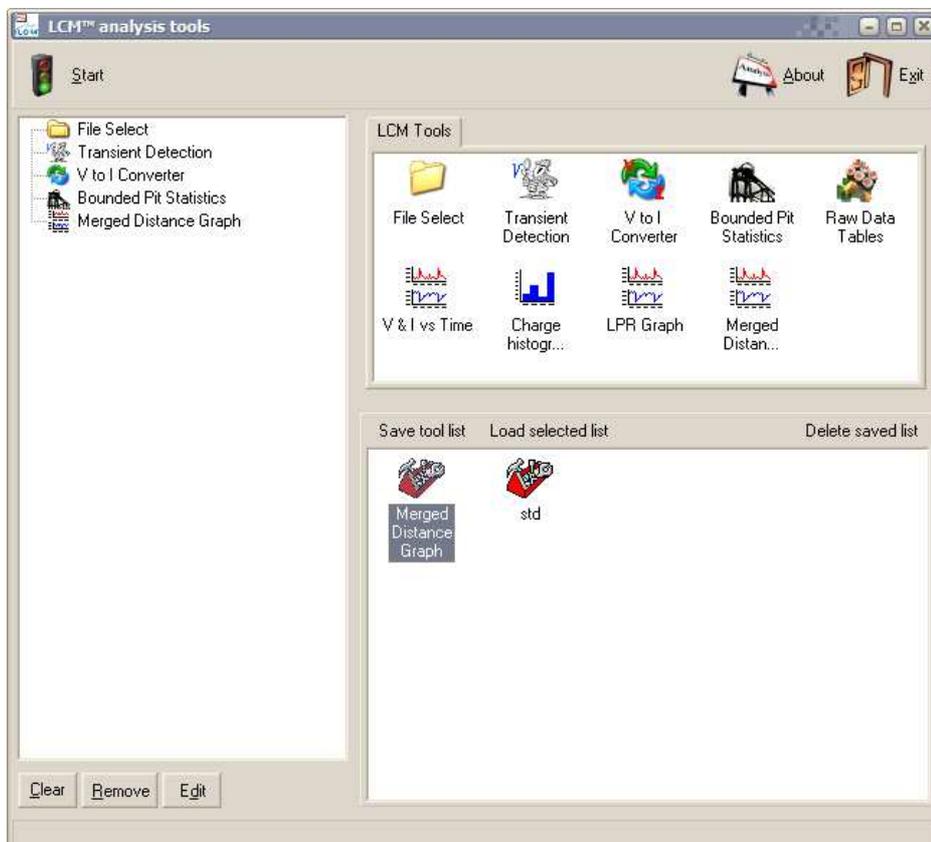
The LCM™ Sub-channel technique must be placed on the additional channels (i.e., channels 2 and above) with LCM™ technique on channel 1. The LCM™ technique must have the correct number of channels collecting data set.

LCM™ Analysis

The LCM™ Analysis software attempts to analyse and present the data using a series of tools in a sequential manner. In this respect it is rather like a production line for analysing data. The same data passing through the same set of tools will produce the same results every time. Within each tool it is possible to set parameters that are more suited to particular data sets. Having set up a series of tools and the parameters within those tools, they can be further stored off in the form of a tool kit. Thus to present data in a form that is easy to understand, the user simply feeds the raw data through the appropriate tool kit.



To enter the LCM™ Analysis Software select the following ICON.
This brings up the LCM™ analysis tools page shown.

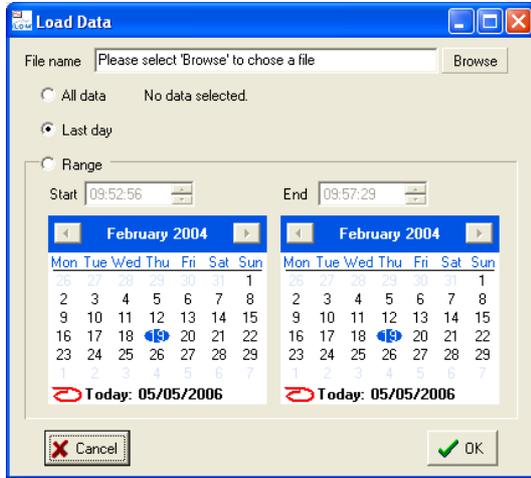


Above we have the tool selection page with the icon bar highlighted. On the left is the tool list and on the right a list of available tools. The bottom section shows where the tool kits are stored. Each tool kit contains a series of tools that have been previously selected. To add a tool to the list simply drag the tool to the required position in the list or double click to add to the end of the list. You can also drag the tools within the tool list to change their order. As a rule of thumb, add tool from left to right, top downwards. Most tools require other specific tools before them, e.g., Current transient calculation requires the Potential transient detection before it, because the current transients are calculated from the potential transients. Once the tool list is selected, select the “Start” option to begin running through the list of tools.



File Select. The first tool selected is the file select tool, without it no data is loaded, so no analysis can take place. To select a file add File Select to the tool list and either double click on File Select in the tool list to pre-select a file or select "Start" to run through the tool list.

File Select Options:



Select the Browse button to choose a file.

There are options to load "All data" in the chosen file, data recorded in the "Last day" (last 24 hours), or a "Range" of data.

The LCM™ technique can amass a large amount of data. Although we have developed the analysis with this in mind, older PC's may struggle. If this is the case, use the Range option to analyse the data in segments.

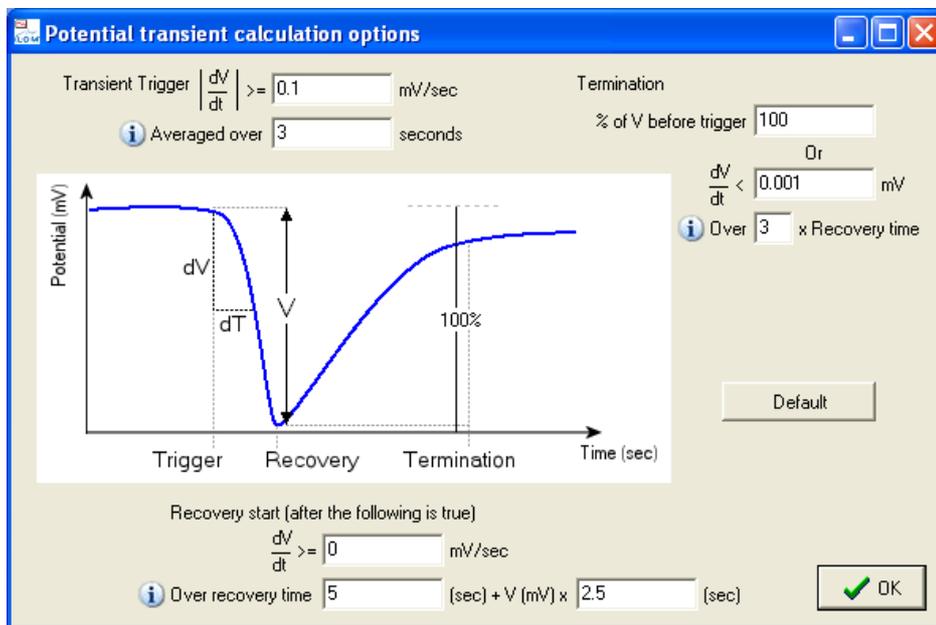
The LCM™ analysis can only analyse LCM™ data. If other techniques were logged to the same data file, their data will be ignored.



Potential Transient Detection

Potential transient detection. Probably the most important tool, this is where the transients are located within the potential data. Requires the file select tool. To select the parameters for detecting transients, add the potential transient detection tool to the Tool list double click on it.

Transient Detection options:



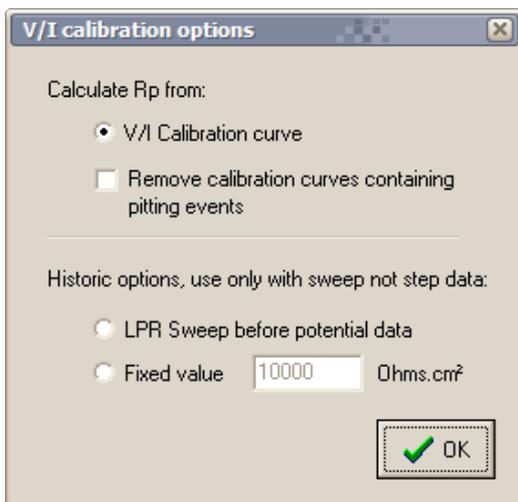
Transients are made of three sections, the trigger, the recovery and the termination. We detect the trigger, the recovery and the termination. To do this we calculate the slope of the data and see if it has passed a certain value.

In the settings above, for the trigger we take 3 seconds worth of data and calculate the slope. If the slope is greater or equal to 0.1 mV/seconds we mark this as the start of a transient. Using a larger value than 0.1 and increasing the time period will have the effect of ignoring small perturbations in the potential such that only more significant transients are detected.

For the recovery, we are looking for when the data changes gradient, typically from a negative to a positive slope. Here we have additional options that increase the length of time we calculate the slope over, depending on how large the transient is becoming. In the above example we have 5 seconds plus the present height of the transient in mV multiplied by 2.5 seconds. If the height of the transient is 10mV this gives us a time of 30 seconds which we calculate the slope over. The increase of time is to allow for better detection of larger transients and to reduce the affect smaller transients within lager transients have on the recovery detection. For the termination, we look at either the gradient, or if the potential comes within a percentage of the transients height. If the percentage was set to 100% the recovery would need to reach the same value of potential as when the transient started. Again, with the slope we have options which increase the time we calculate the slope over, depending on the size of the transient. This ensures that potential shifts, perhaps caused by another minor transient over a short time scale, do not interfere with the termination detection.



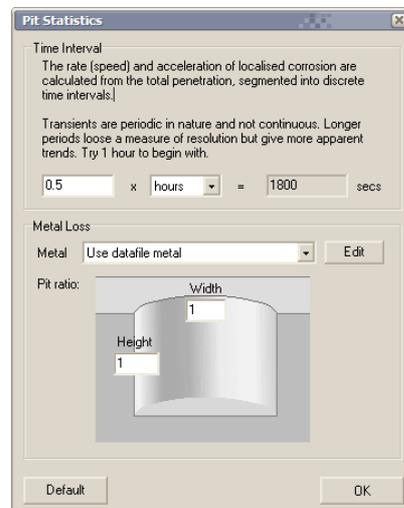
V to I Converter. Current data for a transient is obtained by converting Potential into Current using a Voltage v Current calibration curve. Such a curve is made by the calibrating polarisation which follows the potential monitoring cycle. This tool requires the Transient detection tool to be selected first. The software that controls the actual test gives the user the transient is obtained by converting Potential into Current using a Voltage v Current calibration curve. Such a curve is made by the calibrating polarisation which follows the potential monitoring cycle. This tool requires the Transient detection tool to be selected first. The software that controls the actual test gives the user the option to just apply a LPR type polarisation instead of a full V/I calibration curve. If only a LPR type polarisation has been applied, then the Voltage v Current calibration curve will be a straight line that ignores any non linearity caused by transient amplitudes that are significantly bigger than the LPR polarisation amplitude. An interesting option is Remove calibration curves containing pitting events. By only polarising Cathodically we try to inhibit any naturally occurring pitting events



By only polarising Cathodically we try to inhibit any naturally occurring pitting events during a polarisation, however on occasion such a pitting event can occur. This has the effect of giving a spurious LPR value and incorrect calibration data. By checking this box we look at the potential immediately after a calibration polarisation and if that potential is significantly lower than expected, this polarisation data is discarded and the next calibration polarisation used to calibrate two lots of potential data.



Pit Statistics. Different corrosion systems can produce pits with different geometries. Some can be narrow and deep whilst others are wide and shallow. We assume that all pits are cylindrical for mathematical ease. The user can enter the pit geometry. We suggest a ratio of one to one if you are unsure. The tool calculates the depth of metal lost by individual transients. This tool requires the transient area calculation tool. The tool has two additional functions. Firstly the metal type can be selected either from a list or the user can create their own alloy from a mix of metals. Secondly the user can set a time base. Transients tend to be periodic in nature and may not occur for several days followed by a huge event. If plotting a graph of Penetration v Time and we simply connected data points together, this would indicate a steady Penetration Rate for several days. However by inserting additional data points at discrete time intervals, the period of non activity is better presented as is the significant transient at the end of the period of inactivity.





Raw Data Tables

Raw data table. Original a tool to help debug the software, its usefulness was too great to leave out. The raw data table allows you to view all of the data stored in memory. This includes the original potential and LPR step data, as well as any data calculated from them, such as the transients, current data, current transients, etc.

DataSet	Unit time (sec)	Points	Real Data Points
0	1800	243	110
1	1800	243	110
2	1800	243	110
3	1800	243	110
4	1800	243	110
5	1800	243	110
6	1800	243	110
7	1800	243	110
8	1800	243	110
9	1800	243	110
10	1800	243	110

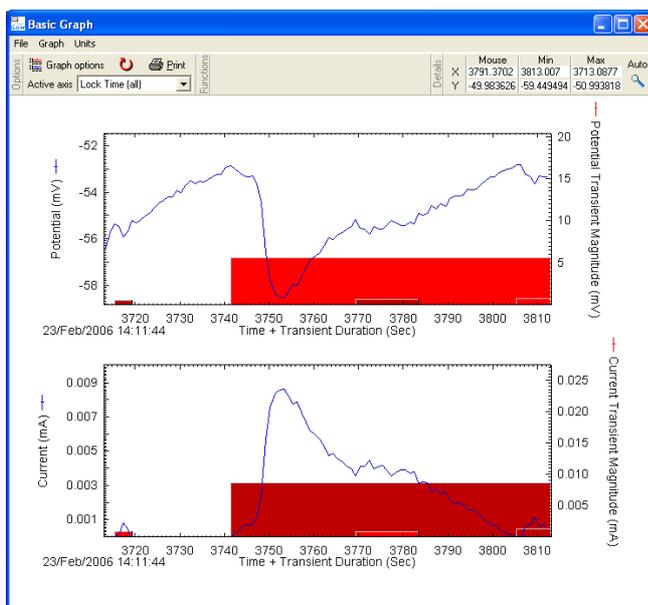
Time	Odometer	Speed	Acceleration
1800	0.0000949	5.274E-08	2.93E-11
3600	0.0001168	1.214E-08	-2.255E-11
5400	0.0001324	8.708E-09	-1.905E-12
7200	0.0001358	1.841E-09	-3.815E-12
9000	0.0001376	1.045E-09	-4.421E-13
10800	0.0001395	1.045E-09	0
12600	0.0001414	1.045E-09	0
14400	0.0001433	1.045E-09	-8.387E-12

Any of this data can be exported as an ASCII file by selecting the save selected to file option. You can select a range of data to save by dragging the mouse over a range of cells, or save all the data by choosing only a single cell.



V & I vs Time

V & I vs. Time allows the potential and constructed current data to be compared, along with transient magnitude and duration. The left hand axis shows the Potential recorded and the data is represented by the graphic line. The right hand axis shows the maximum magnitude of a transient. Magnitude and duration of transients are shown by the coloured blocks showing magnitude and duration.



On the V&I graph the mouse can be used to zoom into data. First select the active axis, i.e., the one you want to change. Select the active axis either by clicking on the axis label or from the drop down list. The list also gives the option to zoom on the time axis for both graphs at the same time. To zoom into data simply click with the left mouse button and drag a box around the required area. The right mouse button can be used to cancel the operation.

For mice with a thumb wheel, you can zoom into the beginning of the data and then use the mouse wheel to scroll through the data.

To restore the previous graph press Ctrl and Z, or select Undo from the graph menu. The file menu gives us the options to save the data (in various formats), print the data or exit (which takes us to the next tool in the list).

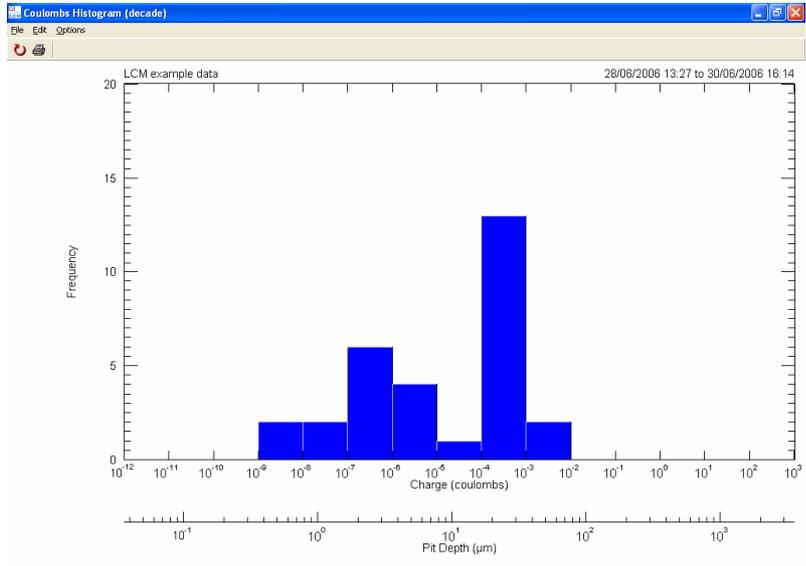


Graph options

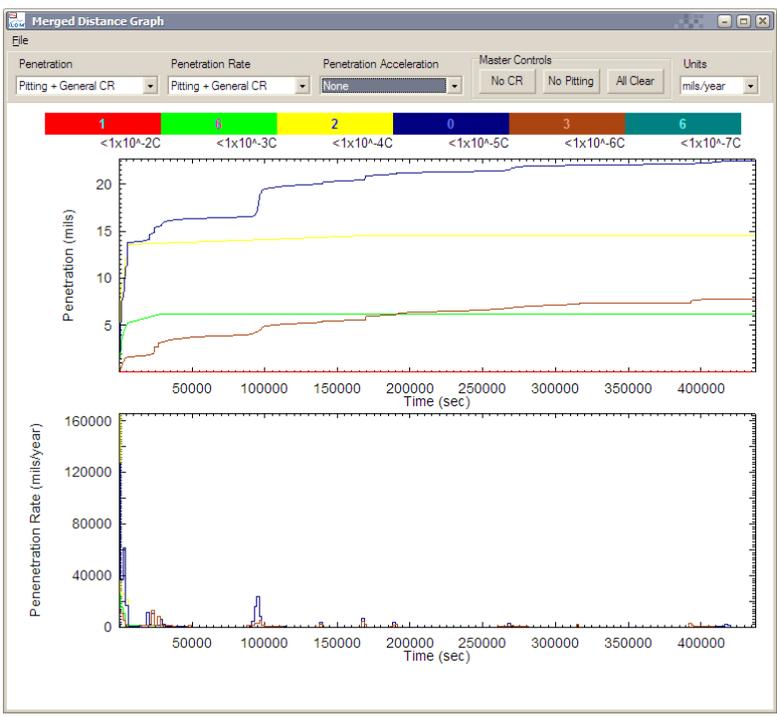
Gives the options to show Potential, Current, Potential transients or Current transients on the graph.



Charge histogram displays the Charge (coulombs), and Pit depth data in a bar graph/histogram format. Frequency indicates the number of times a transient within a certain range has occurred. As a rule of thumb, the penetration doubles for each decade increase in the charge of a transient. Options are also available to print the graphs. The charge axis remains the same, this is to make it easier to compare one data set with another. Options are also available to print the graphs.



The Histogram method of presenting data does not give an indication of time. The same information can be presented graphically with respect to time in the form of distance, speed and acceleration. In terms of Pitting, this can be termed as Penetration, Penetration Rate and Penetration Acceleration. The user is probably more familiar with Corrosion Rate as for General Corrosion Rate. An integration of Corrosion Rate will give total metal loss through corrosion which has the same units as Penetration, whereas the rate of change of Corrosion Rate has the same units as Penetration Acceleration. Thus the general corrosion rate and its related values are presented on the same graphs as for Penetration, Penetration Rate and Penetration Acceleration.



A graphical line is presented for each bar in the previous histogram, except the data is now presented with respect to time. If the user positions a mouse over a graphic line, the range of charge the data is obtained from is highlighted. The user can also enter the number of pits producing the data within a range of charge by entering a number in the coloured bar chart. For simplicity we suggest this is always one pit per decade of charge as this makes it easier to compare on set of data with another.