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DEVELOPMENTS OF THE ELECTROCHEMICAL NOISE METHOD (ENM) FOR MORE PRACTICAL ASSESSMENT OF ANTI-CORROSION COATINGS

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ABSTRACT

The Electrochemical Noise Method (ENM) has particular attractions because of its non-intrusive nature, quickness in gathering data and ease of interpretation. The electrode arrangement for the standard ("Bridge") method of conducting ENM requires two separate working electrodes e.g. two painted Q panels and a reference electrode. Although satisfactory for laboratory use, it is not so suitable for monitoring or quality control. An improved experimental configuration is the Single Substrate (SS) method but this still requires the metal to be connected to the measuring instrument. This is avoided in the most recent development which needs No Connection to Substrate (NOCS). Results will be given for immersed low VOC samples monitored using the ENM NOCS arrangement and compared with the standard ("Bridge") method and DC resistance. Results will also be presented for work done using several different electrodes (platinum, calomel and silver/silver chloride). It is accepted that, because of the very small voltages and currents involved, ENM data can sometimes be affected by extraneous signals (although normally the results are changed by only a factor of two or less) and it may be that NOCS is more sensitive to interference of this type than the standard bridge arrangement. A simple data analysis package checking on the Gaussian nature of data enables the operator to have confidence in the R_n value. This has been applied to NOCS data. Further work is required to make ENM attractive enough to be employed as the electrochemical method of choice by users, specifiers and producers of organic anti-corrosive paints.

Keywords
Anti-Corrosive Coatings, Electrochemical Noise Method, Novel Configurations, Field application

INTRODUCTION

The pressure on industry due to increasingly stringent legislation to produce products with lower volatile organic content (VOC) has led to increased development and production of coatings that use water-based solvent. Market pressures combined with this mean that a new or modified coating needs to be tested and proven as rapidly as possible before it can be marketed with the guarantees expected of today's high performance products. Traditionally accelerated cabinet tests have been used such as ISO 11997 (cyclic – prohesion) which determines resistance to cyclic wet / dry / humidity and ultra-violet light conditions. Other cabinet tests use only salt spray or alternate wet dry cycles [1,2], but the aim of the tests is essentially the same in that they attempt to accelerate the ageing mechanism of the coating under test. The assessment of coated panels from these tests is usually by eye, assessed against a standard or measured in the case of coating under-cut at a scribe and it is here that electrochemical techniques can be of great assistance. Not only is a numerical value obtained which can be directly related to expected corrosion protection, but also by monitoring the performance of the coating with time, different coatings / formulations can be compared. Some workers claim to be able to predict life times by extrapolation of electrochemical data [3], and good correlation has been seen between immersion testing (using ENM to monitor) and Cyclic Prohesion testing with the less aggressive Harrison's Solution [4].

There are numerous electrochemical techniques in use for measurement of corrosion activity and some of these have been adapted to coatings applications with great success. Each has its advantages and disadvantages and as such in isolation one method can be viewed as part of a toolbox of available techniques. The choice of which "tool" depends much on the particular requirements at the time. Some common electrochemical techniques used for coating assessment are D.C resistance, impedance measurement, impedance spectroscopy (EIS), electrochemical noise monitoring (ENM) [5,6,7] and the DC transient (current interruptor) method [8]. This paper concentrates on electrochemical noise monitoring (ENM), which at one level can be used as a fast indicator of coating condition and used by a low skilled operator, but by contrast has many complex mathematical treatments available that can satisfy the most ardent theoretical electrochemist [9].

In particular this work concentrates on how the ENM technique has been adapted to enable a more practical application both as an assessment / screening tool in the laboratory. In this it builds on previous work conducted by two of the authors [10,11] and ultimately as a technique than can be applied in the field for condition monitoring. Some previous attempts have been made using ENM or EIS looking at coatings on ships [12], on bridges [13], and on transmission leg towers [14], Electrochemical Noise has also been applied to monitoring uncoated Chemical plant [15] and the adaptions described in this paper could have application to that type of situation as well.

ELECTROCHEMICAL NOISE MONITORING BACKGROUND

ENM requires three electrodes to establish a parameter known as the noise resistance (R_n). Two of these are working electrodes and current is measured between them at

regular intervals. Fluctuations in the current (typically in the μA or nA range) are called current noise and this is calculated as the standard deviation of the data set. Simultaneously, as the current data is obtained, the potential difference is measured between the working electrode couple and a third electrode (the reference). The fluctuations in potential are also calculated as the standard deviation and by using the two standard deviation values in an Ohm's law relationship (Equation 1.) the parameter R_n is obtained:

$$R_n = \sigma_v / \sigma_i \qquad \textit{Equation 1.}$$

R_n is a useful parameter which has been shown to be proportional to polarisation resistance in certain circumstances where corrosion rate is relatively slow [16]. More useful with regards to coated substrates is that a good correlation has been shown between R_n and D.C. resistance when measured through the coating. Bacon, Smith and Rugg [17], did extensive D.C. measurements with organic coatings on steel in simulated sea water and found a relationship between the resistance value and the corrosion protection afforded to the substrate. Less than 1 Mohm-cm^2 indicated poor corrosion protection, higher than 100 Mohm-cm^2 indicated good corrosion protection, and a value in between these two limits demonstrated an intermediate level of corrosion protection. The advantage of R_n over D.C. resistance measurement methods is that ENM only uses the small naturally occurring fluctuations in potential (and hence current) between the electrodes whereas D.C. and other electrochemical techniques impose sometimes quite high voltages across the coating to obtain a reading. This is potentially damaging to the coating physically and can disrupt the dynamics of a delicate corrosion cell. However, despite this considerable advantage, ENM has suffered from one considerable disadvantage in that the technique in its traditional form requires three electrically isolated electrodes to perform the measurement. These three electrodes consist of two nominally identical substrate elements which act as working electrodes and a standard laboratory electrode, such as saturated calomel or silver / silver chloride, as a reference electrode. It can be appreciated that to carry out this technique in the field it is very difficult to obtain two electrically isolated substrate elements in a structure and even then to make hard-wire connections to them.

The traditional method of obtaining electrochemical noise data is shown in Figure 1. In addition to the three electrodes a salt bridge is required as a path of ionic conduction between the electrolyte cells. The data logger and zero resistance ammeter (ZRA) are controlled by a standard personal computer. The ZRA is a specialist instrument which allows very small current measurements to be obtained without disturbing the corrosion cell circuit.

ADVANCES IN THE ENM TECHNIQUE

In an attempt to make ENM more applicable to field applications and for faster laboratory use a development of the technique by one of the authors was devised as part of his PhD research. The new set-up was called the Single Substrate (SS) technique and involved a re-configuration of the electrical connections and use of different electrodes. As shown in

Figure 2, the substrate is one complete unit carrying the two electrolyte cells attached to the coating. The reference electrode lead from the ZRA is attached to the substrate, and as such even in a field application an electrical connection would be required. The substrate in this configuration acts as a reference and replaces the salt bridge. In the two separate cells of electrolyte, standard laboratory electrodes act as working electrode 1 and working electrode 2 and as such are connected to the ZRA. Much work has been done using this technique on a range of coating resistances and even bare metal [18] and good agreement has been seen with both the standard (bridge method) of obtaining noise data and the D.C. resistance method.
The work presented here demonstrates a further development of the experimental set-up which has been called the No Connection to the Substrate (NOCS) technique. As the name implies this set-up does not require any electrical connection to the substrate and hence the advantage to field application becomes immediately obvious.

EXPERIMENTAL

Specimen Preparation
Coatings were applied to standard low carbon steel Q panels. Sets of samples were prepared, one for ENM to rank the coatings and other sets for cyclic cabinet test and external exposure. The Q panels were degreased in solvent and the coatings were then applied using a 150µm K-bar. This produced a dry film thickness (DFT) of 75µm which was attained for each system. The samples were then air dried for 7 days before exposure.

Coatings and Electrolyte
The coatings used in this work were waterborne and solvent based, comprising of:

- Acrylic
- Modified water thinneable alkyd
- Modified short oil alkyd
- vinyl-chloride acetate co-polymer

These were the same group of coatings which had been investigated earlier – other results can be found [10,11].
Immersion experiments were used for monitoring using ENM with samples exposed to 0.5% Ammonium sulphate solution. The test area was 11cm^2 with the samples exposed for various time periods. Measurements were made in triplicate using three cells on each panel.

Experimental set-up – ENM

Results in this work were obtained using all three ENM techniques. The standard or Bridge Method illustrated in Figure 1, the Single Substrate method Figure 2 and the most recent development; the NOCS technique illustrated in Figure 3.
The NOCS technique is an extension of the Single Substrate in that it uses standard laboratory electrodes in isolated cells as the working electrodes. However, in the NOCS technique the reference connection from the ZRA is also made to a laboratory electrode which is contained in a 3rd isolated cell of electrolyte attached to the coating. Hence, no

electrical connection is required to the substrate material. Apart from the experimental configuration, all other parameters and hardware remained constant throughout the work. Different electrode types were tried with the new configurations to address questions over the influence of electrode type on the noise data. The data was gathered typically at 2 Hz for 300 seconds. The dedicated software calculated the noise values automatically. Further analysis of the data was done in Excel.

Data analysis

To address the question about the nature of the noise due to using different electrodes two approaches were adopted. First the absolute R_n values for each of the different configurations (Bridge, SS and NOCS) were compared and second the nature of the noise distributions and also the relative contributions of the potential noise and current noise values to the R_n value were checked. Note that as statistical analysis is used to calculate the R_n value, it is important that the noise data approximates a normal (Gaussian) distribution to be a valid measurement.

RESULTS AND DISCUSSION

Results from previous work

The data in figures 4 and 5, show an overview of results from previous work [10, 11] obtained using the standard (fig 1) configuration. Figure 4, shows the R_n values of a range of compliant short oil alkyd paints versus time. This figure demonstrates how R_n can be used to rank a series of coatings performance in a relatively short time and it can be seen clearly that paints H and J which were low solvent developments out perform the other three from early on in the test These tests were done in immersion, using 0.5% ammonium sulphate solution. Figure 5, is a good comparison of the single substrate technique and traditional bridge method for an acrylic paint. In addition the D.C. resistance values are included of the two separate cells which made up the electrochemical noise cell of two working electrodes and reference. If the D.C resistance values are taken to indicate that the coating is of a reasonable anti-corrosion performance, the R_n values from both the bridge and the single substrate method correlate nicely.

Results from the NOCS technique

Samples from the paints used in previous work [10] were separated at the end of the main tests into groups which had high ($>5.10^7$ $\Omega m.cm^2$), medium ($10^6 - 5.10^7$ $\Omega m.cm^2$) and low ($<10^6$ $\Omega m.cm^2$) resistances i.e. they would be expected to give high, medium and low level anti-corrosion performance. These groups were then used to investigate the NOCS method and particularly to see whether it worked over the full range of resistance.
The histogram in Figure 6, contains information from the three coating groups. Also included are readings from un-coated electrodes to demonstrate very low resistances which could be seen in the case of delaminated coating or studies of inhibitor performance on bare metal. For each of the systems all three ENM configurations

(Bridge, SS and NOCS) have been used to obtain an R_n value and for comparison the D.C. resistance value is included. D.C. measurements were done after ENM measurements were made so as not to disrupt the system. Although there is scatter on some of the results, the trend in the values for each measurement method is generally very good. Within each resistance range there is general grouping of the values which improve towards the lower resistance end of the scale. Variations in value at the high end of the scale can probably be attributed to instrument limitations.
There are obviously more sources of noise with three laboratory electrodes and although this was considered when the single substrate technique was first used it was never investigated fully. To investigate the question of electrode noise on the overall noise of the system, the NOCS technique was employed using different types of electrode. The sets of electrodes chosen for this investigation were saturated calomel (SCE) , silver / silver chloride (Ag/AgCl) and three pieces of platinum foil (Pt). This work was done again using samples from coating systems which gave results within the Bacon, Smith and Rugg ranges. The data in Figure 7 shows the results of this investigation. There was no visible ranking between electrode type, and again although there is the usual scatter within the data, the trend through the coating resistance ranges is clear.

Results from data analysis

As stated previously, for the R_n values and statistical operations to be valid, the data sets must approximate a normal or Gaussian distribution. In previous work, analysis of both the potential and current data, from the bridge method and single substrate method have shown this to hold good with intact coatings. Hence data distribution type was checked for sets of data from the NOCS method. This showed Gaussian distribution for both current and potential plots and a typical example is given in Figure 8.
Additional analysis of the data from the NOCS system involved examining the relative contribution of the potential noise and the current noise to the final R_n value. Figures 9 and 10 show the contributions using the three different electrodes on a high resistance coating. This was repeated on medium and low resistance coating systems with the same result (not presented here). It can be seen that the relative contributions of the potential noise, Figure 9, and the current noise shown in Figure 10, are very similar despite the different electrode types used.
The final analysis of the data involved comparing the relative contributions of current and potential noise to R_n, with the same coating system, but this time using all three experimental three set-ups. Figures 11 and 12 show potential contribution and current contribution respectively, for the NOCS technique, the bridge method and the single substrate method. Again there is good correlation between the R_n values obtained and more importantly the relative contributions are very close regardless of the experimental configuration. This analysis was also carried out on medium and low resistance coating data. These also gave consistent results although they are not presented here.

CONCLUSIONS

This work has shown that the R_n value obtained is independent of the experimental configuration, e.g. Single Substrate, NOCS, or traditional Bridge method.
Further, when NOCS is being used the distribution and contribution of the noise data is independent of the type of electrode.
As such, it would appear that ENM might compete with AC Impedance as an effective monitoring method in the field?
This work has helped buttress the technique and has greatly increased confidence in the R_n value obtained by the less conventional experimental configurations. However, there is a need to look at other practical considerations of making the ENM measurements.

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REFERENCES

1. Salt spray standard ISO 7253.
2. Wet / dry cycle standard !SO 11997.
3. G. P. Bierwagen, D.E. Tallman, J. Li, S. Balbyshev, M..Zidoune, "Corrosion 2000", Paper 0427 pub. by NACE.
4. J. B. Harrison, Journal of Oil and Colour Chemists Ass., **18** (1979) 62.
5. S. Turgoose , R. A. Cottis, Electrochemical Impedance - Analysis and Interpretation, ASTM STP 1188, (1991) 173-191.
6. G. P. Bierwagen *et al*., Proc. Symposium on Advances in Corrosion Protection by Organic Coatings II, Pub. Electrochemical Society, **95** (1995) 13.
7. C-T. Chen , B. S. Skerry., Corrosion , **47** No 8 (1991) 598-611..
8. M. Nagai., T. T. Taki., H. Tanabe, H. Kano, Advances in Corrosion Protection by Organic Coatings III (Proc. conf. Noda, Japan Oct 1997) Eds.: J. D.Scantlebury, M Kendig, D. J Mills , Publ. The Electrochemical Society PV **97-41** (1998) 199-205.
9. J. R. Scully, Corrosion , . **56**, 2, (2000) 199 – 218.
10. C. P. Woodcock, D. J. Mills, H..T. Singh, Progress in Organic Coatings, **52** (2005) 257-262.
11. C. P. Woodcock, D. J. Mills, Paper presentation at Conf . Advances in Corrosion Protection by Organic Coatings, Christ's College, Cambridge Sept 2004 submitted to on-line Journal of Corrosion Science and Engineering.
12. R. L. Rudesueli, J. N. Murray, "Corrosion 2004" paper 04297 publ. by NACE.
13. J. Bordzilowski, K. Darowicki, S. Krakowiak, A. Królikowska, Progress in Organic Coatings, **46** (2003) 216-219
14. Corrosion monitoring of electric transmission line tower legs by electrochemical methods, E.Garcia, J.M.Malo and J. Uruchurtu. ://www.intercorr.com/intercorr/techsess/papers/session4/absracts/garcia.html.
15. Dawn Eden , J Kintz, "Corrosion 2004", Paper 04238, publ by NACE.
16. M. Moon .and B. Skerry,., J of Coatings Technology, **67**, (1995) 35 – 44.
17. R.. M. Bacon, B. Smith., F. Rugg, Ind. Eng. Chem, **40**, (1948) 161-167.

18. S. Mabbutt, and D. Mills, British Corrosion Journal, **33** 2 (1998) 158-160.

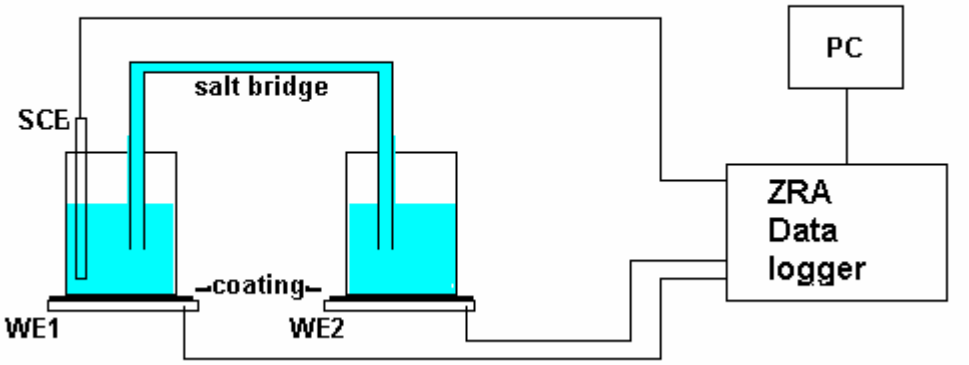

Figure 1. Bridge method for ENM measurements

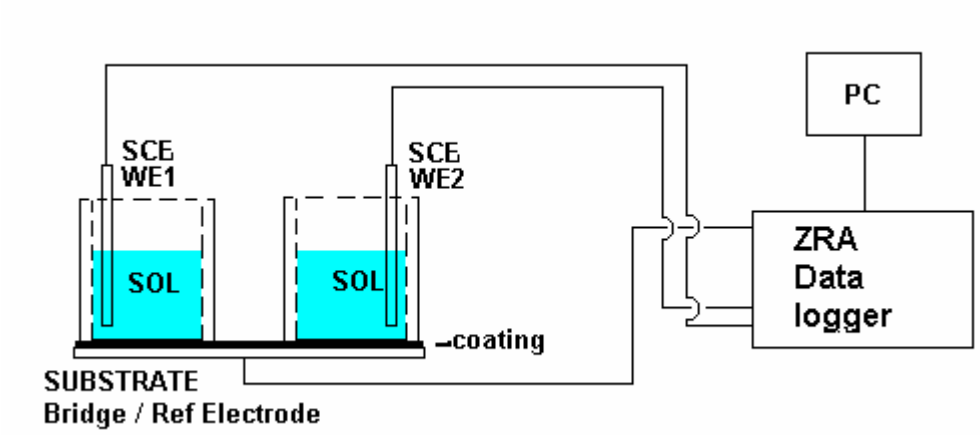

Figure 2. Single substrate method for ENM measurements

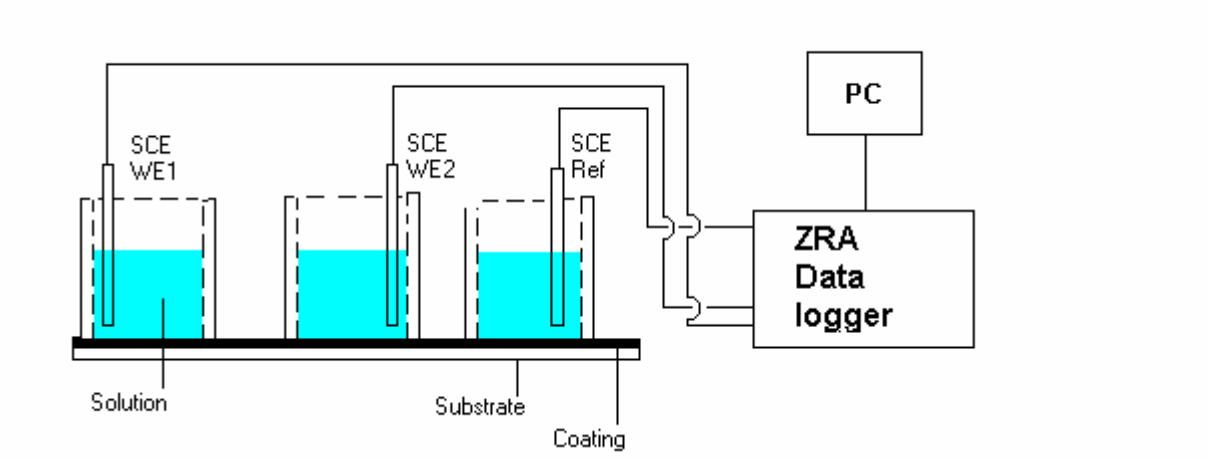

Figure3. NOCS set-up for ENM measurements

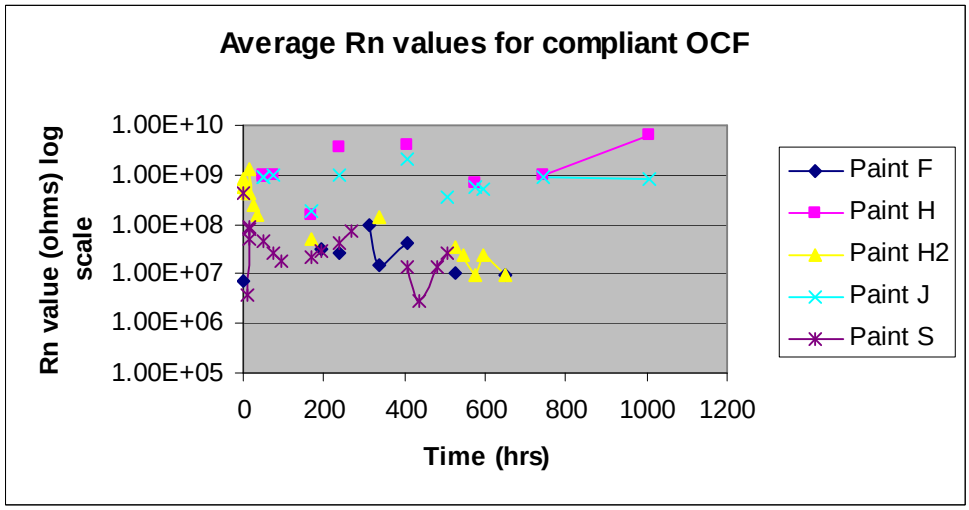

Figure 4. – Intact R_n values - Immersion in 0.5% Ammonium Sulphate

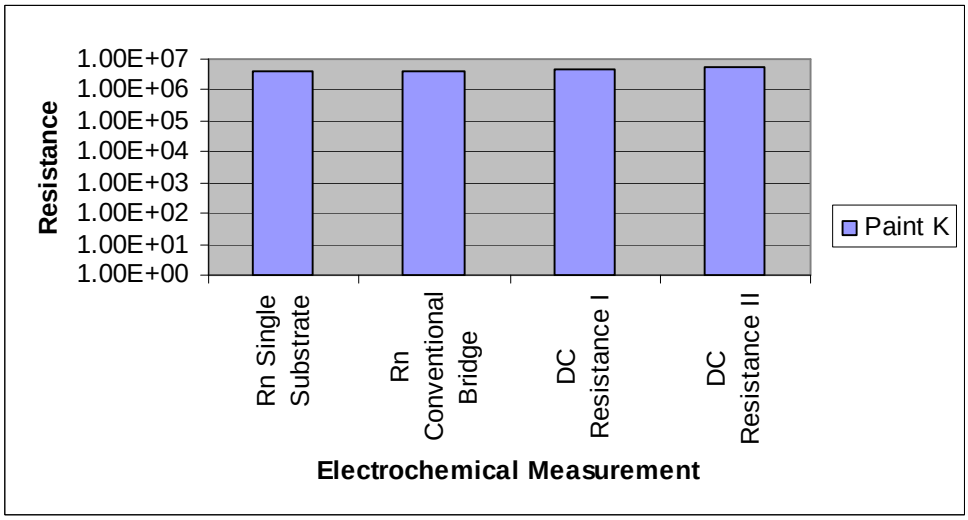

Figure 5. – Comparison of values obtained on the same sample by different methods

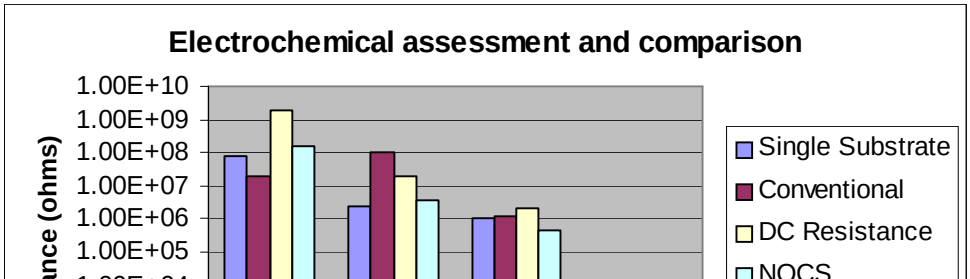

Figure 6. Comparison of NOCS with other methods for sets of samples with different resistances in 0.5% Ammonium sulphate

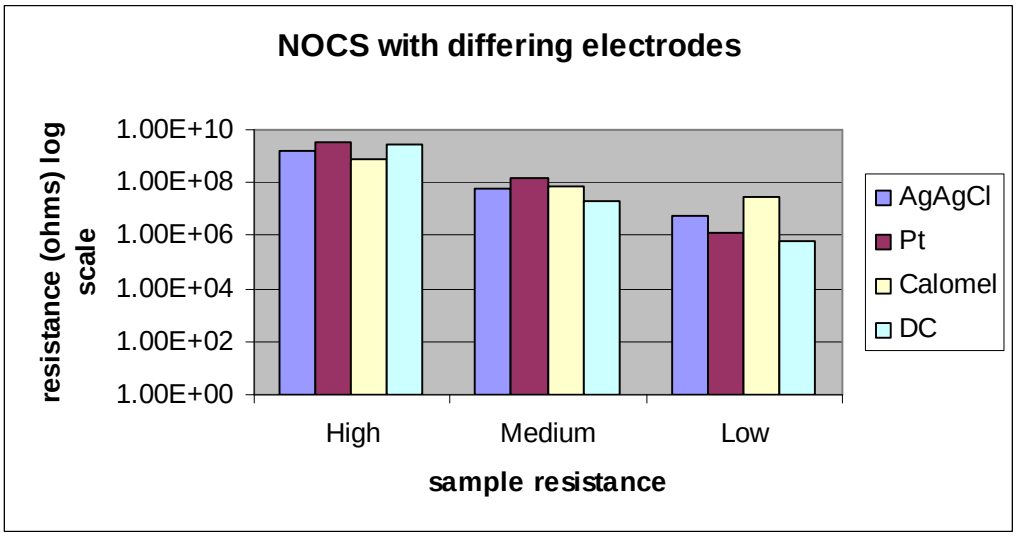

Figure 7. Comparison of NOCS using different electrodes with sets of samples of differing Resistance in 0.5% ammonium sulphate

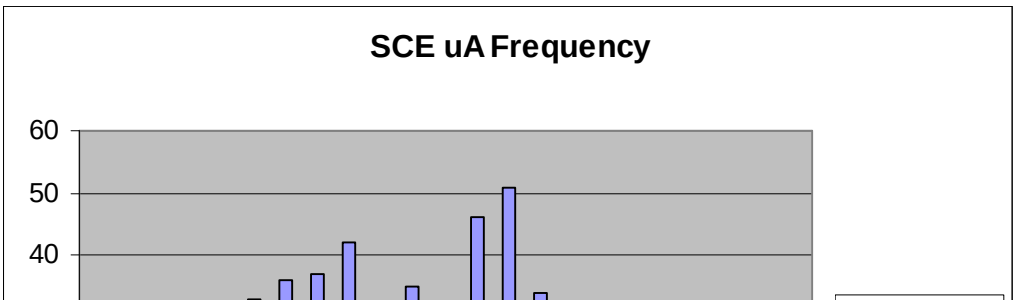

Figure 8. – Histogram of Current Distribution from NOCS Data set using calomel electrodes

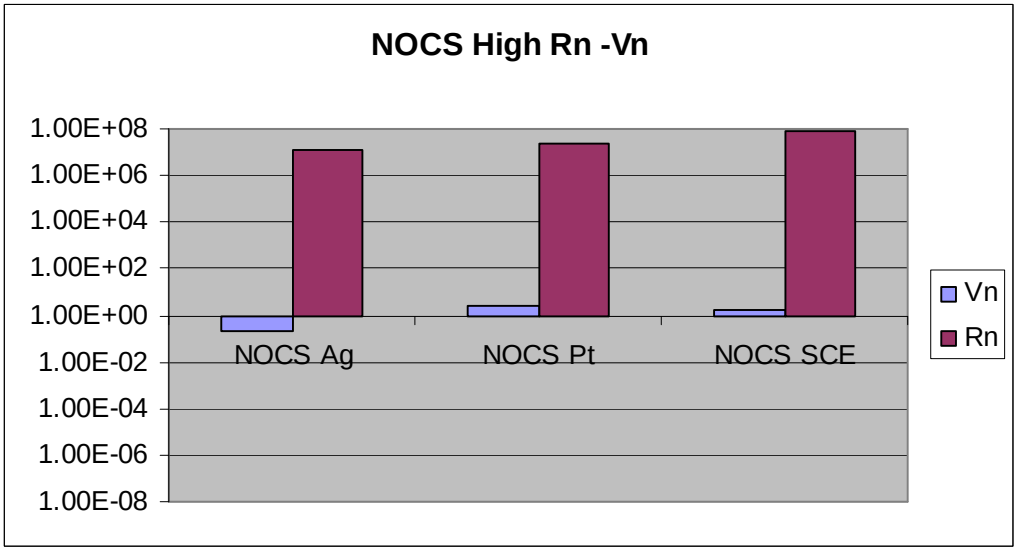

Figure 9. - Vn compared with Rn using NOCS for different electrodes (High R set)

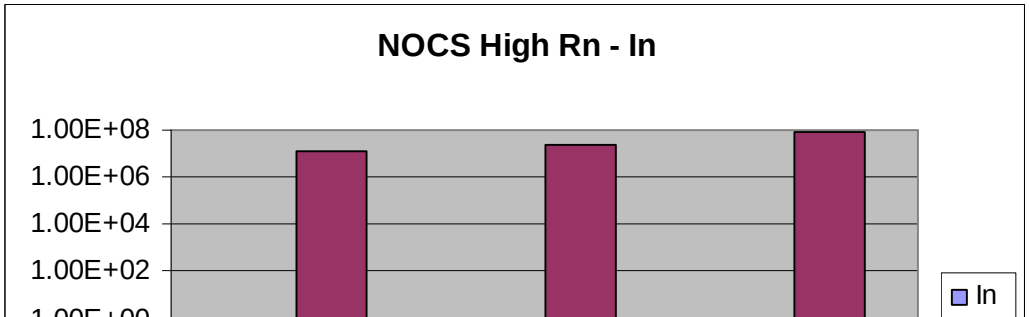

Figure 10. In compared with Rn using NOCS for different electrodes (High R set)

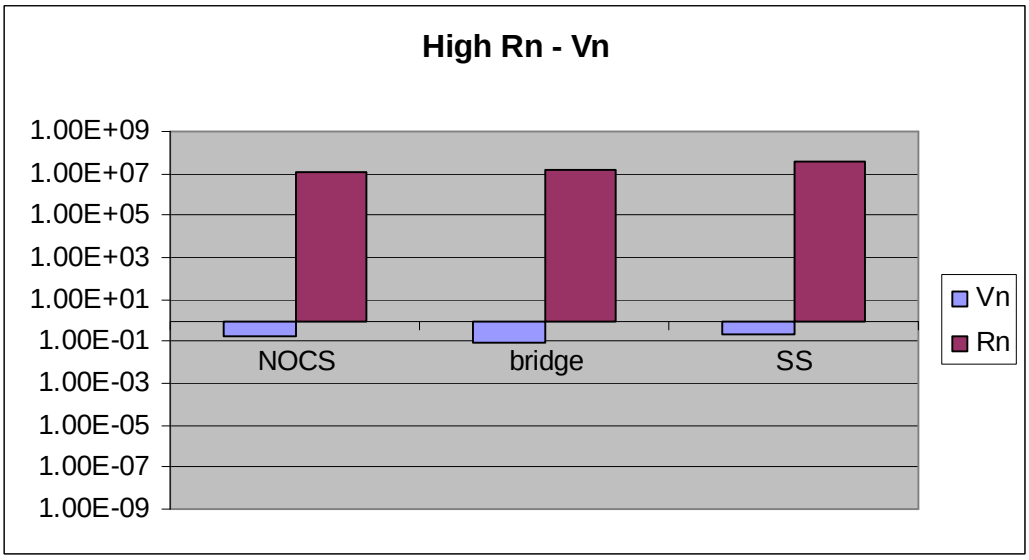

Figure 11. - Vn compared with Rn using calomel electrodes for different Noise gathering experimental arrangements (High R set)

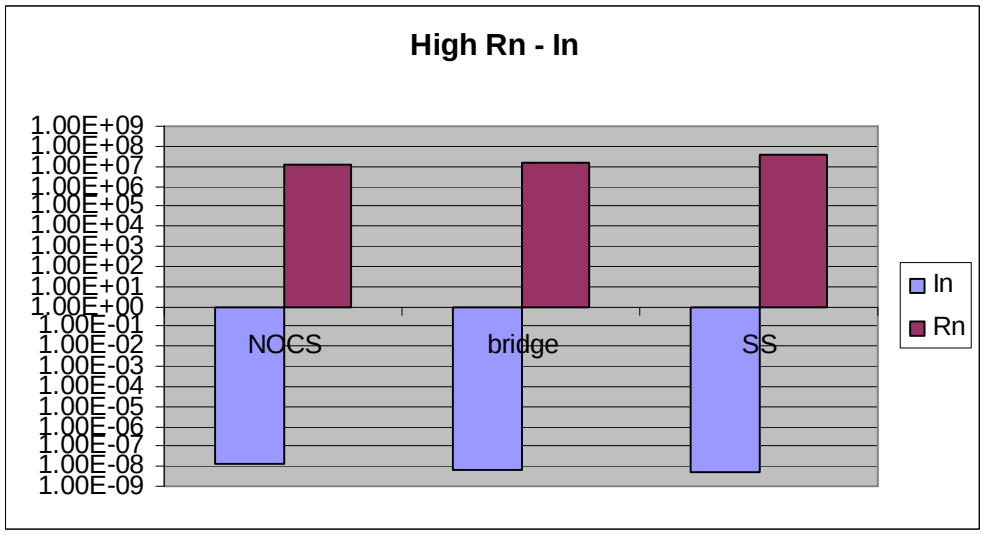

Figure 12. In compared with Rn using calomel electrodes for different Noise gathering experimental arrangements (High R set)

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Developments of the electrochemical noise method (ENM) for more practical assessment of anti-corrosion coatings

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