

# The assessment of natural atmosphere corrosivity by the use of electrochemical noise analysis

V. Torres-Mendoza, F. J. Rodríguez-Gómez, E. M. García-Ochoa and J. Genesca

Departamento Ingeniería Metalúrgica, Facultad de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, México

## Abstract

**Purpose** – The aim of this work is to evaluate the electrochemical noise (EN) method as a way of evaluating quickly the aggressiveness of natural atmospheres.

**Design/methodology/approach** – Wire-on-bolt tests were used, which implies an exposure of at least three months of bimetallic specimens such as aluminium wire/steel bolt and aluminium wire/copper bolt (CLIMAT units). Electrochemical noise measurements (ENM) also were used.

**Findings** – EN is a powerful tool in the assessing of aggressiveness of atmospheres in short time exposure. Statistical analyses of EN were carried out and provided clear differences between atmospheres depending on pollutants. Results of noise resistance ( $R_n$ ), root mean square of current ( $I_{rms}$ ) and localization index are discussed.

**Research limitations/implications** – The possible application of ENM to atmospheric corrosion is interesting from a practical point of view. However, more experiments are necessary in order to test a wide range of atmospheres.

**Practical implications** – EN has proved to be a useful tool when localised corrosion is detected and the presence of chlorides in atmospheres, due to sea fog, results in pitting on the metallic samples.

**Originality/value** – Illustrates that electrochemical noise can be a powerful tool for assessing the aggressiveness of natural atmospheres.

**Keywords** Atmospheric corrosion, Electrochemistry, Noise

**Paper type** Research paper

## Introduction

Electrochemical techniques have been used for a long time as a time-of-wetness register. Developments of these devices (González *et al.*, 1990) have been reported in literature, as well as the application of electrochemical techniques to study the prevailing atmospheric conditions in a particular atmospheres (Tsuru *et al.*, 1999; Tres *et al.*, 1998). From the existing electrochemical techniques, electrochemical noise measurements (ENM) seems to be a promising and powerful tool to determine corrosion rates and mechanisms (Tan, 1999; Cottis and Turgoose, 1999; Rothwell and Eden, 1992). Recently, electrochemical noise (EN) has been promoted as a tool for both corrosion science and corrosion engineering.

Historically, outdoor atmospheric corrosion sites have been performed at various test sites in many countries (Ailor, 1982). In México, a large number of test sites, designated as rural, urban, marine and industrial have been used to develop corrosion test data. There are no universally accepted quantitative demarcations between the constituents that typify atmospheric environments. Therefore, distinctions are often based on qualitative and semi-quantitative factors. For instance, marine environments are characterized by the

presence of airborne salt as the major corrosive constituent transported from the ocean. In comparison, sulphur dioxide ( $SO_2$ ), is the primary component in industrial and urban atmospheres. Environments containing relatively low levels of pollutants are considered rural. The effect of chloride in atmospheric corrosion has been underlined by several authors. Tests have been developed in order to assess the aggressiveness of an atmosphere on metals, but these evaluations imply a long-term exposure. Metal sheets exposed to an aggressive environment could yield a gravimetric estimation of corrosion rate. However, this test requires years to be carried out.

Inspiration for the technique used in the present work was taken from work by Compton *et al.* (1955) of Bell Laboratories. Included in their methods to obtain a quantitative assessment of the extent of galvanic corrosion between any two metals was a bolt and wire type galvanic couple, which permitted weight loss determination of the anodic member (wire) of the couple. Doyle and Wright (1982) at Alcan Laboratories developed the Bell method to determine not only quantitative data on galvanic couples but also to characterize the corrosivity of the atmosphere at the test locations. In order to avoid cumbersome descriptions of the test it has been termed the CLIMAT test (CLassify Industrial and Marine ATmospheres) and the test units CLIMAT units (Morcillo and Feliu, 1977; Genesca and Rodríguez, 1992; Flores and Palma, 1993; Calderon and

The current issue and full text archive of this journal is available at [www.emeraldinsight.com/0003-5599.htm](http://www.emeraldinsight.com/0003-5599.htm)



Anti-Corrosion Methods and Materials  
53/6 (2006) 348–356  
© Emerald Group Publishing Limited [ISSN 0003-5599]  
[DOI 10.1108/00035590610711688]

This work is part of a research program between IMP and FQ-UNAM, financially supported by IMP, project FIES 98-01-VI. Participants are acknowledged.

Arroyave, 1998; Mariaca *et al.*, 1999). The test period is only 90 days. Despite this short period, the fact that the exposures are carried out in the natural environments significantly improves the credibility of the results. A correlation of CLIMAT data with service experience has been published (Doyle and Godard, 1969). The samples consist of aluminium wire coiled on a metallic screw (bolt) usually copper or steel (copper is preferred if the atmosphere is of the marine type, but steel is used if the atmosphere is industrial). This test has proved to be highly effective in the classification of atmospheres in three-month exposures.

On the other hand, electrochemical techniques are a useful tool in determining the corrosion rate, but their use in atmospheric corrosion has been limited to some studies in order to record the time-of-wetness. González *et al.* (1990) proposed the use of a multi-layer cell made of metallic sheets forming a galvanic couple; this device develops a peak in galvanic current values when the surface of the probe is wet, even if this layer is invisible.

The aim of this work was to characterise natural atmospheres by using EN as a tool. A multi-layer cell analogous to the Gonzalez' cell was used.

## Experimental

The electrochemical monitor for atmospheric corrosion (EMAC) has been described in a previous paper (Garcia-Ochoa *et al.*, 2002) as being made of low carbon steel sheets (AISI 1018), alternated with plastic sheets, joined with a plastic screw and embedded in epoxy resin in order to show a multi-layer surface.

ENM, were carried out in three different atmospheres: City University, México City (urban type atmosphere), Villahermosa (urban tropical environment), and Coatzacoalcos (industrial tropical environment) (Table I). The location of these three testing sites is shown in Figure 1.

México is located between the latitudes 15° and 30° N and the longitudes 86° and 116°. Two-thirds of the country is located in the tropics, including 90 per cent of the coastal regions on the Gulf of México. The geographical characteristics of México are varied, from the large southwest coastline bordering the Pacific Ocean, the dry, hot regions in the north, the high central mountainous region, including México City, to the flat, heavily vegetated regions of the southern and eastern coast of the Gulf of México. The most easterly section of México includes the Yucatan Peninsula, a flat limestone tableland which is rich in Mayan culture and tradition. México's west coast, bordering the Gulf of México, is a region of agriculture and fishing, where the inhabitants have maintained their traditional living style, in contrast to the more popularly known tourist resorts on the

east coast along the Caribbean Sea from Cancun and Cozumel in the north to Chetumal 400 km to the south. The four main climatic zones in México are shown in Figure 1 (Mariaca *et al.*, 1999) along with the location of cities in which atmospheric exposure sites are located. The region along the Gulf of México is classified as Humid Tropical, having a mean annual relative humidity (rH) greater than 75 per cent and mean precipitation greater than about 1,500 mm/yr. The mean annual temperature is greater than 26°C which is about the same temperature as the Gulf waters in this region. One interesting exception to this classification is the north-west corner of the Yucatan Peninsula which is classified as Arid (Mariaca *et al.*, 1999).

City University in México City is a very well known site to test atmospheric corrosion, since it has been evaluated for years and reported recently (Mariaca *et al.*, 1999). The city of Villahermosa is not very far from the Gulf of México and has a very humid tropical weather. On the other side, Coatzacoalcos is a commercial port with oil industry. rH was given from meteorological stations in each site.

Noise measurements were carried out with a Gill ZRA equipment, sampling 2,048 points at a frequency of two points per second. Potential and current fluctuations were recorded every two hours throughout one week. In México City, measurements were carried out four times in a four-month period, while in Villahermosa, noise measurements were recorded in a three-month period; in both cases once a month. In Coatzacoalcos, measurements were taken during one week.

Analysis methods for EN data can be separated into three categories:

- 1 deterministic;
- 2 statistical; and
- 3 spectral (Kelly *et al.*, 2003).

Statistical methods were found to be particularly useful for the analysis of EN data, and are the most popular techniques. The potential difference and coupling current signals are monitored with time. The signals are then treated as statistical fluctuations about a mean level. Amplitudes are calculated as the standard deviations root-mean-square (rms) of the variance.

In this work, EN analysis was made with statistical tools. This statistical analysis involved the estimation of the EN resistance ( $R_n$ ) in terms of the standard deviations of the voltage and current data, as a measurement of corrosion aggressiveness, as well as the rms of current ( $I_{rms}$ ) as a measurement of corrosion products layer's stability. Finally, localization index (LI) parameter is used for identifying the type of corrosion, specifically localized corrosion.

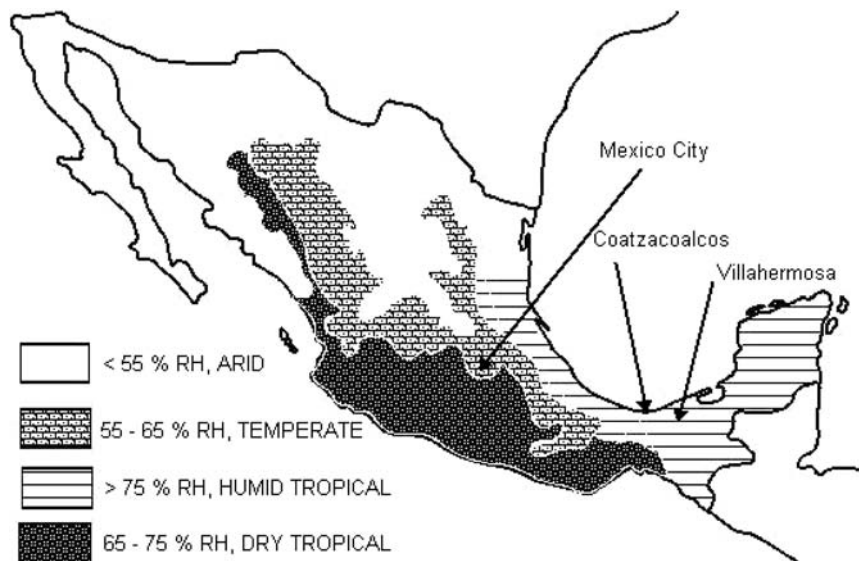
Evaluation of atmospheric galvanic corrosion was made according to ASTM G 116-93, "Standard practice for conducting wire-on-bolt test for atmospheric galvanic corrosion". The wire-on-bolt test has been used extensively under the name CLIMAT test to determine corrosivity of atmospheres.

Wire-on-bolt assemblies (CLIMAT units) were installed in City University, México City and Villahermosa, where the industrial corrosivity index (ICI), and marine corrosivity index (MCI), were calculated.

The Al/steel and Al/Cu, wire and bolt combinations have varied sensitivities depending upon the atmosphere. This is due to the variation in the galvanic corrosion between the materials.

Table I Predominant atmosphere at the Mexican testing sites

Location	Atmosphere type	Salient features
City University, México City	Highland, rural	2,300 m above sea level
Villahermosa, Tabasco	Urban	Tropical urban area
Coatzacoalcos, Veracruz	Marine/industrial	Large industrial center

**Figure 1** Climatic classification in México identifying the location of the three testing sites: México City, Villahermosa and Coatzacoalcos

It has been reported (Doyle and Wright, 1982) that the Al/Cu combination responds strongly to both marine and industrial sites, whereas the Al/steel combination responds strongly only to marine sites and is relatively indifferent to industrial sites. Because of this enhanced sensitivity, CLIMAT coupons can be conveniently exposed for a short time period of three months, thereby allowing seasonal variations in corrosivity to be determined. The enhanced sensitivity also facilitates differentiation of atmospheric corrosivity on the micro-environmental scale. CLIMAT corrosivity indices are derived from the percentage mass loss measured on the aluminium wires after the exposure period.

## Results

### Noise resistance ( $R_n$ )

EN resistance is defined (Cottis and Turgoose, 1999) as a resistance that is comparable to a linear polarization resistance, but estimated from EN parameters. The EN resistance,  $R_n$  is calculated as the standard deviation of potential divided by the standard deviation of the current, as follows:

$$R_n = \frac{\sigma_V}{\sigma_I}$$

where the value of  $R_n$  can be taken as  $R_p$  and then inversely proportional to corrosion rate according to the Stern-Geary equation, but with the necessary condition that a trend removal is applied over a baseline, as previously established (Tan, 1999).

### México City

During the first week of exposure, noise measurements were carried out. They are not shown in this report due to some mistakes in data collection. However, during the second week of measurements (i.e. second month of exposure) a correspondence between  $R_n$  and relative humidity (rH) was detected (Figure 2(a)).

### Villahermosa

rH showed oscillations similar to those obtained in México City during the sampling week, Figure 3(a) and (b), but oscillations were not as large in Villahermosa as they were in México City. In México City, rH can change from 20 to 90 per cent in hours, while in Villahermosa these changes are from 50 to 90 per cent (Figure 3(a) and (b)).

### Coatzacoalcos

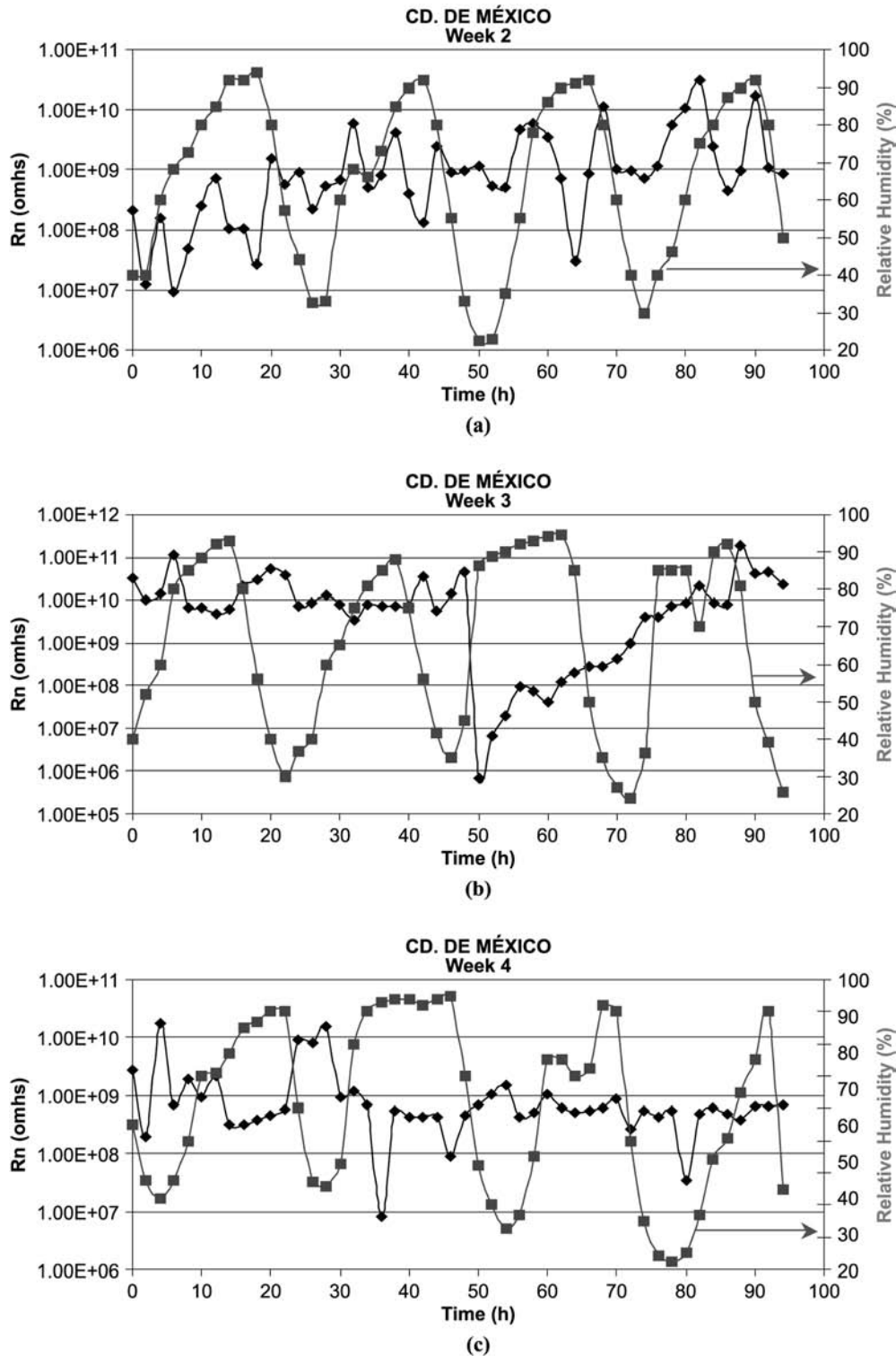
Unfortunately, in Coatzacoalcos, that has been reported as having a very aggressive atmosphere, the site of measuring was located in a place with predominant winds that blow against the industrial plants, so pollutants were not forced to act over the metallic samples. However, the EMAC was sensitive enough to show a low  $R_n$  value when compared with Villahermosa and México City. Therefore, this proves that this electrochemical device is not only a time-of-wetness detector, but also a pollutant detector and, as a consequence, an atmospheres' aggressiveness detector (Figure 4).

### Wire-on-bolt test

The wire-on-bolt test was traditionally used to monitor and evaluate the corrosivity of the environment. The interpretation of the results is based on per cent mass loss, normalized to 90 days exposure, of aluminium wire specimens wrapped around either steel and/or copper bolts. The aluminium-wire/steel-bolt and aluminium-wire/copper-bolt combinations were used for classifying the corrosivities of marine and industrial environments, respectively. After the exposure period, the per cent mass loss of the wires was determined and used for a qualitative classification of the corrosivity of the atmospheric environment, e.g. negligible, moderate, moderately severe, severe, or very severe.

The per cent mass loss from the Al/steel combination is generally regarded as the MCI and the per cent mass loss from the Al/Cu combination is generally regarded as the ICI. The CLIMAT indices (percent weight losses in 90 days) for aluminium wires wound onto mild steel and copper bolts at

**Figure 2** Noise resistance values in México City: (a) during a week during the second month of exposure; (b) during a week during the third month of exposure; (c) during a week in the fourth month of exposure



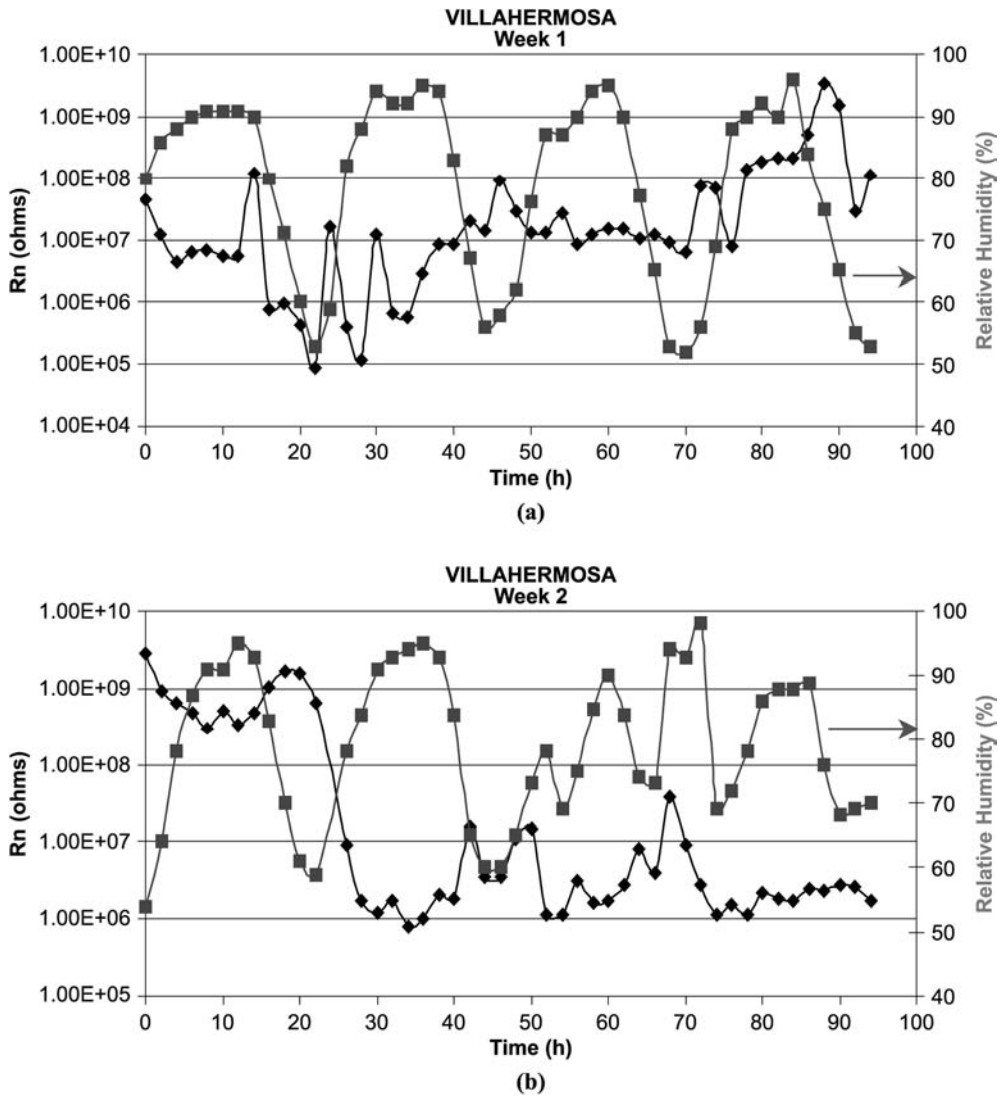
two locations are shown in Table II. The indices were adjusted by subtracting the small amount of corrosion that occurred on aluminium wires wound onto plastic rods at each site. Thus, the results reflect the increase in the amount of corrosion caused by galvanic influences.

**Discussion**

**México City**

It has been reported in literature (Ailor, 1982; Mariaca *et al.*, 1999) that atmospheric corrosion occurs only at a rH higher than 80 per cent, when the metallic surface is wet. According to this statement,

**Figure 3** Noise resistance values in Villahermosa: (a) during a week in the first month of exposure; (b) during a week in the second month of exposure



**Figure 4** Noise resistance values in Coatzacoalcos during a week of exposure

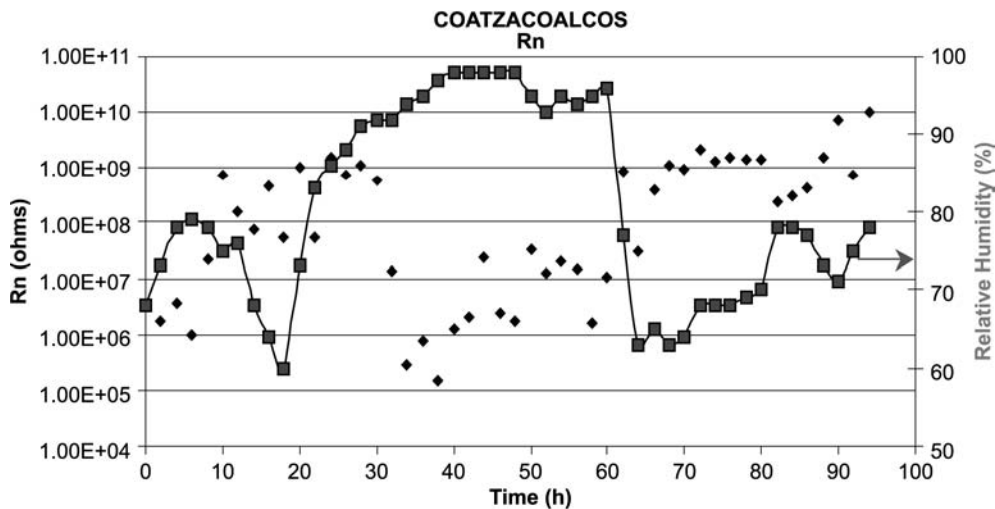


Table II Results of wire-on-bolt test

Site	Galvanic couple Al/Fe (aluminium wire/steel bolt)			Galvanic couple Al/Cu (aluminium wire/copper bolt)		
	Marine corrosivity index, MCI	Marine influence	Atmosphere type	Industrial corrosivity index, ICI	Classification	Significance
México City	0.0745	Negligible	1 (0 < MCI < 2)	0.2262	Negligible	Rural area
Villahermosa	0.0965	Negligible	1 (0 < MCI < 2)	0.0630	Negligible	Rural area

it can be established that just over the 80 per cent, the noise resistance measurement is meaningful. Actually, there was a very high oscillation in rH in a one day term, but when rH was over 80 per cent, there was a clear correspondence with a minimum in  $R_n$ .

During the third week of measurements in México City (Figure 2(b)), there was a storm that “cleaned” the metallic surface, resulting in a diminishing of  $R_n$  in almost four orders of magnitude (the rH corresponded to very high values during the storm). This cleaning was not very efficient, as it could be concluded from the value of  $1.00 \times 10^{06}$  Ohm as an  $R_n$  after the storm. However, the re-formation of corrosion products layer took about 35 h after removing the oxide film. During the first two days of this week, the relation between high rH and low  $R_n$  fitted quite well.

No great variation could be detected during last week of measurement corresponding to the fourth month (Figure 2(c)). Again,  $R_n$  values were between  $1.00 \times 10^{09}$  and  $1.00 \times 10^{10}$  Ohm as shown in Figure 2(a) and (b).

#### Villahermosa

Again, when the rH was higher than 80 per cent, a good correlation with low values of  $R_n$  was detected. It is important to say that Villahermosa is characterized for a tropical humid weather, but it is also an urban atmosphere with no great presence of pollutants, even though an oil industrial area is not very far from there. This fact results in an average  $R_n$  value around  $1 \times 10^{07}$  Ohm growing in relation to time.

During the second week of measurements in Villahermosa (Figure 3), three days of an almost continuous rH over 70 per cent resulted in low values of  $R_n$  in the range of  $1.00 \times 10^{06}$  Ohm. This correlation between rH and noise resistance as an atmosphere's aggressiveness measurement was also found during the third week of experiments.  $R_n$  values in Villahermosa were lower than those obtained in México City, maybe as a signal of the presence of chloride or sulphur which origin is in the Gulf of México. This location is not very far from Villahermosa, and the oil industry facilities. In previous studies, it has been demonstrated that a low concentration of chloride or sulphate is enough to promote corrosion in a very large rate, but changing pollutant's concentration is not very significant in promoting corrosion.

#### Root mean square of current, $I_{rms}$

The rms value is similar to the standard deviation, but calculated without removing the mean from the data (Cottis, 2001) and can be defined as the square root of the average value of the square of the current (without subtracting of the mean). In practical terms, it is a measure of the power available from the signal, including the effect of any dc or mean current (Cottis and Turgoose, 1999).

#### México City

In general, terms, the values of  $I_{rms}$  are related to the corrosion products layer's stability. The lower the value, the more stable the film.

In Figure 5(a) and (b), the results from  $I_{rms}$  for México City are shown. It is clear that the stability of the layer is growing with time, and in the second week of measurements (second month), after the storm, the value of  $I_{rms}$  grew suddenly, in good agreement with  $R_n$  value, re-forming the corrosion products as told before.

#### Villahermosa

During the first week of measurements,  $I_{rms}$  showed a tendency to low values, i.e. a stable layer of corrosion products could be formed, in the same way as in México City. In the second week of measurements, however, some days of high rH were detected and the stability of corrosion products layer diminished as a result of wetting of oxides, since the rH needed for total wetness is lower in the rust's capillary paths.

#### Coatzacoalcos

The higher values of the three sites regarding  $I_{rms}$  were found in Coatzacoalcos. It is important that even if predominant wind does not favour the corrosion on EMAC, nevertheless, the rust layer is unstable due to the presence of sulphur (mainly as sulphide) in atmosphere. Again, this is an evidence of the EMAC's sensitivity, because even low concentration of sulphur results in a very clear value in EN data.

#### Localization index (LI)

The localization parameter or LI is the standard deviation of the current noise divided by the rms current. In this case, the actual value will always be between 0 and 1, with a value approaching 1 implying a large standard deviation compared with the mean, and a value approaching 0 corresponding to a small standard deviation compared with the mean (Cottis and Turgoose, 1999).

#### México City

The values of LI in México City showed mixed corrosion as detected in a previous work (García-Ochoa *et al.*, 2002) due to the presence of crevice but also of small amounts of pollutants. When rH is over 80 per cent, LI clearly shows a mixed corrosion process. A clear example of this phenomenon is shown in Figure 6.

#### Villahermosa and Coatzacoalcos

The same behaviour of México City results was found in Villahermosa. In Coatzacoalcos, however, there was a difference, as it can be seen in Figure 7. In Figure 7, LI values are over 0.1 during almost all the data collection, resulting in a localized corrosion process. Once again, this is a clear evidence of the detection of chloride and sulphide in

Figure 5  $I_{rms}$  values in México City: (a) during a week in the first month of exposure; (b) during a week in the second month of exposure

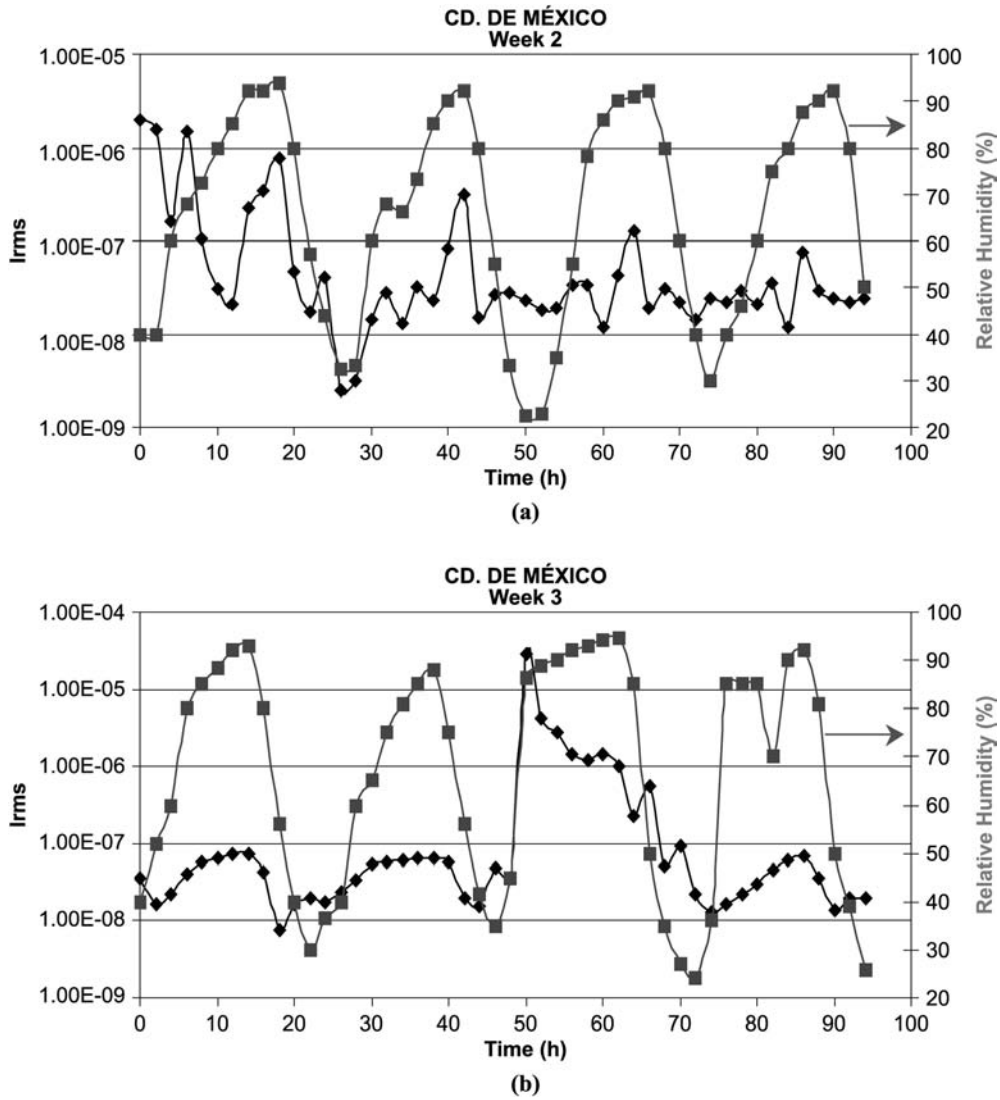
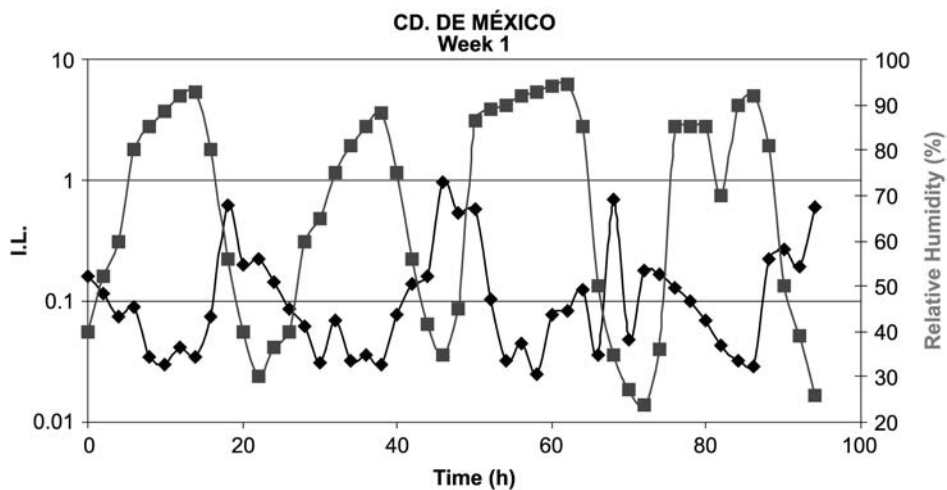
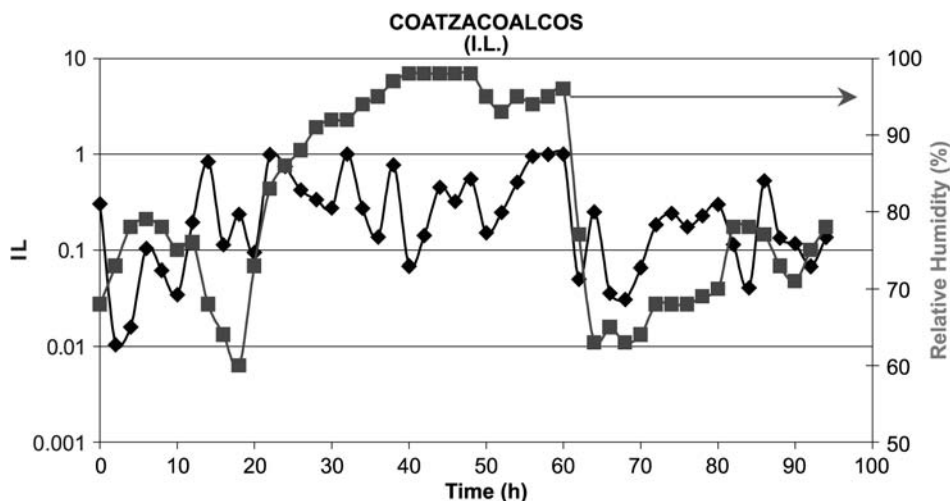


Figure 6 LI values in México City during a week in the second month of exposure



**Figure 7** LI values in Coatzacoalcos during a week of exposure

atmosphere, even when the exposure conditions were not as desirable in Coatzacoalcos site due to the winds.

#### Wire-on-bolt test

After examining all the results, Table II, it can be seen that there is negligible effect at the México City and Villahermosa sites. It is interesting to note that copper causes more galvanic corrosion than mild steel in México City. For Villahermosa site, it can be seen that mild steel causes more galvanic corrosion of aluminium. CLIMAT units consisting of aluminium wires on steel rods are a sensitive tool for measuring marine influences.

#### Conclusions

- EN is a powerful tool in the assessing of aggressiveness of atmospheres in short time exposure.
- EMAC seems to be not just a time-of-wetness sensor, but an atmospheres' aggressiveness sensor.
- Sensitivity of EMAC is quite superior to wire-on-bolt technique as expected, since made evident the presence of contaminants even at very low concentration.
- EN analysis can be carried out even in non-ideal conditions with reliable results.

#### References

- Ailor, W.H. (Ed.) (1982), *Atmospheric Corrosion*, Wiley, New York, NY, pp. 227-43.
- Calderon, J. and Arroyave, C. (1998), "Evaluación de la técnica de 'alambre sobre tornillo' en ensayos acelerados de laboratorio", Paper No. S04-06, paper presented at Latincorr'98, Cancun.
- Compton, K.G., Mendizza, A. and Bradley, W.W. (1955), "Atmospheric galvanic couple corrosion", *Corrosion*, Vol. 11 No. 9, pp. 35-44.
- Cottis, R. (2001), "Interpretation of electrochemical noise data", *Corrosion*, Vol. 57 No. 3, pp. 265-85.
- Cottis, R. and Turgoose, S. (1999), "Electrochemical impedance and noise", in Syrett, B.C. (Ed.), *Corrosion Testing Made Easy Series*, NACE International, Houston, TX.
- Doyle, D.P. and Godard, H.P. (1969), "Rapid determination of corrosivity of an atmosphere to aluminum", *Proceedings of the Third International Congress on Metallic Corrosion, MIR, Moscow*, Vol. 4, pp. 429-37.
- Doyle, D.P. and Wright, T.E. (1982), "Rapid methods for determining atmospheric corrosivity and corrosion resistance", in Ailor, W.H. (Ed.), *Atmospheric Corrosion*, Wiley, New York, NY, pp. 227-43.
- Flores, S. and Palma, E. (1993), "Estimación rápida de la corrosión atmosférica mediante la técnica 'alambre sobre tornillo'", in Morcillo, M. and Feliu, S. (Eds), *Mapas de España de corrosividad atmosférica*, CYTED, Madrid, pp. 381-93.
- García-Ochoa, E., Ramírez, R., Torres, V., Rodríguez, F.J. and Genesca, J. (2002), "Comparison of electrochemical noise and wire-on-screw technique in simulated marine atmospheres", *Corrosion*, Vol. 58 No. 9, pp. 756-60.
- Genesca, J. and Rodríguez, C. (1992), "Calibración de la agresividad de la atmósfera del suroeste de la ciudad de México", *Revista Internacional Contaminación Ambiental*, Vol. 8, pp. 81-90.
- González, J.A., Otero, E. and Cabanas, C. (1990), "Recording polarisation curves in thin electrolyte layers by electrochemical atmospheric corrosion monitors", *British Corrosion Journal*, Vol. 25 No. 2, pp. 125-30.
- Kelly, R.G., Scully, J.R., Shoemith, D.W. and Buchheit, R.G. (2003), *Electrochemical Techniques in Corrosion Science and Engineering*, Marcel Dekker, New York, NY.
- Mariaca, L., Genesca, J., Uruchurtu, J. and Hernández, L.S. (1999), *Corrosividad Atmosférica (MICAT-México)*, Plaza y Valdes, San Rafael.
- Morcillo, M. and Feliu, S. (1977), "Análisis de la corrosividad atmosférica en España mediante probetas 'alambre sobre tornillo'", *Revista Metalurgia Madrid*, Vol. 13, pp. 212-22.
- Rothwell, A.N. and Eden, D.A. (1992), "Electrochemical noise techniques for determining corrosion rates and mechanisms", Paper No. 223, paper presented at Corrosion'92, NACE, Houston, TX.

- Tan, Y-J. (1999), "Interpreting electrochemical noise resistance as a statistical linear polarization resistance", *The Journal of Corrosion Science and Engineering*, Vol. 1, Paper 11, available at: [www.jcse.org/](http://www.jcse.org/)
- Tres, G., Arriaga, R., Malo, J.M. and Uruchurtu, J. (1998), "Evaluación por Ruido Electroquímico de la Corrosión Atmosférica", Paper No. S04-11, paper presented at Latincorr'98, Cancún.

- Tsuru, T., Yamazaki, T. and Nishikata, A. (1999), "Organic coatings for cathodic protection in atmospheric condition", *The Journal of Corrosion Science and Engineering*, Vol. 2, Abstract 10, available at: [www.jcse.org/](http://www.jcse.org/)

**Corresponding author**

J. Genesca can be contacted at: [genesca@servidor.unam.mx](mailto:genesca@servidor.unam.mx)