Multivariate analysis of impedance data obtained for coating systems of varying thickness applied on steel

A. Miszczyk*, K. Darowicki

Gdansk University of Technology, Chemical Faculty, Department of Electrochemistry, Corrosion and Materials Engineering, 11/12 Narutowicza St., 80-233 Gdansk, Poland
IMPEDANCE SPECTROSCOPY is a well-established technique for evaluating the anti-corrosion protection of organic coatings.

However, ....
there are several limitations and constraints that can be overcome.

- interpretation of impedance data is difficult and requires highly skilled staff,
- selection of equivalent electrical circuit is complicated and often subjective,
- one spectrum can be excellently fitted with different equivalent circuits,
- impedance analysis needs special frequency-dependent elements (CPE, transmission lines, …) without clear physical meaning,
- impedance technique is sensitive to disruption and noise,
- in noisy situations there are many equivalent circuits that fit equally well,
- impedance data analysis is difficult for automation.
Case I: 

„a simple theory is preferred to a complicated one”

Sample figure from the paper:

Is it really appropriate electrical equivalent circuit for the presented spectrum?

How to check it?
Case II:

Some examples of electrical circuits used in the literature to analyse impedance spectra of coated metals:
Motivation

To mitigate these limitations we need a new approach!

Goal: extracting the relevant information from impedance data without use of a classical electrical equivalent circuit approach

Solution (?): chemometric approach based on principal component analysis
Principal component analysis is used in many spectroscopies

Number of papers and citations according to the Web of Knowledge for terms: principal component analysis + spectroscopy
Reviews on use chemometric methods in spectroscopies

Chemometrics in spectroscopy. Part 1. Classical chemometrics

Paul Geladi*

Unit of Biomass Technology and Chemistry, Swedish University of Agricultural Sciences, SLU Rödbäcksdalen, P.O. Box 4097, SE 90433 Umeå, Sweden

Chemometrics in spectroscopy
Part 2. Examples

Paul Geladia,*, Britta Sethsonb,*, Josefina Nyströmb,*, Tom Lillhonga, Torbjörn Lestander*, Jim Burger*

*Unit of Biomass Technology and Chemistry, Swedish University of Agricultural Sciences, SLU Rödbäcksdalen, Box 4097, SE 90433 Umeå, Sweden

bDepartment of Chemistry, Umeå University, SE 90187 Umeå, Sweden

*Centre for Biomedical Engineering and Physics, Umeå University, SE 90187 Umeå, Sweden

Swedish Polymeric, P/B6, FIN 85301 Vasa, Finland

Received 6 February 2004; accepted 23 June 2004
Multispectral impedance quality testing of coil coating system using principal component analysis
A. Miszczuk *, K. Darowicki
Gdansk University of Technology, Faculty of Chemistry, Department of Electrochemistry, Corrosion and Material Engineering, 80-952 Gdansk, 11/12 Nawotnicka St., Poland

A R T I C L E   I N F O
Article history:
Received 27 October 2009
Received in revised form 8 July 2010
Accepted 13 July 2010

Keywords:
Organic coating
Impedance spectroscopy

Corrosion Science 64 (2012) 234–242
Contents lists available at Sciverse ScienceDirect
Corrosion Science
journal homepage: www.elsevier.com/locate/corsci

Inspection of protective linings using microwave spectroscopy combined with chemometric methods
A. Miszczuk *, K. Darowicki
Gdansk University of Technology, Faculty of Chemistry, Department of Electrochemistry, Corrosion and Material Engineering, 80-952 Gdansk, 11/12 Nawotnicka St., Poland

A R T I C L E   I N F O
Article history:
Received 15 June 2011
Accepted 35 July 2012
Available online 4 August 2012

A B S T R A C T
A novel non-destructive method for quality control of new protective linings on a metal substrate and an assessment of their state during their service life using microwave spectroscopy within a wide frequency range from 6.5 to 13 GHz is described. The data obtained were processed by chemometric methods to reduce the dimensionality of the experimental data sets and to help visualise results. Theoretical fundamentals of the method are outlined. Results for the rubber linings with a thickness of 10 mm operating in
ANALYSIS OF IMPEDANCE DATA

tradicional approach

multivariate approach

Principal Component Analysis

traditional approach

PC1
PC2

PC1

PC2

PCA

time

time
Experimental details

Schematic cross-section of the test sample with named layers

Coating system for underwater part of the hull.

Measurement set:
Schlumberger 1255 + High Impedance Interface Atlas 8992
Two-electrode system, in the frequency range 1MHz-0.001Hz, 60 mV, exposed area: 5 cm²

measurement cell
Classical analysis of impedance data

[Graph showing Y/Fcm^2 s^-1 vs. t / days for different layers]

[R vs. t / days for different layers]

[Circuit diagram with R and CPE (Y, n)]

[Graph showing R/Ω cm^2 vs. t / days for different layers]
Transformation of impedance spectrum from n-dimensional in 2-dimensional space

mainly noise

new dimension

information

PC1

PC2

2-dimensional space

n-dimensional space

Transformation of impedance spectrum from n-dimensional in 2-dimensional space

Information

Dimension

Z''

Z'

n-dimensional space

2-dimensional space

PC1

PC2
The concept of dimensionality reduction of the measurement data presented for an example of two-dimensional data reduction on the xy plane into a one-dimensional axis of PC1. The data explained by the PC2 axis have been omitted.
Each spectrum corresponds to a specific point on the plane.
Mathematically, this procedure is implemented by determining the eigenvalues of the correlation matrix obtained on the basis of the measurement data matrix.

Each line contains data from one measurement (spectrum). Values obtained for the same frequency in different measurements are placed in a given column.

\[
\begin{pmatrix}
Z^1(f_1) & Z^1(f_2) & Z^1(f_3) & \ldots & Z^1(f_{n-1}) & Z^1(f_n) \\
& & & & &  \\
& & & & &  \\
& & & & &  \\
& & & & &  \\
& & & & &  \\
& & & & &  \\
& & & & &  \\
Z^m(f_1) & Z^m(f_2) & Z^m(f_3) & \ldots & Z^m(f_{n-1}) & Z^m(f_n)
\end{pmatrix}
\]

first spectrum

m-th spectrum
The principal component analysis determines the Xi(PCI) coordinates on the PCI axis *(in the new coordinate system)* as a linear combination of spectroscopic data:

\[
X_1(\text{PC1}) = a_{11} Z^1(f_1) + a_{12} Z^1(f_2) + \ldots + a_{1n} Z^1(f_n)
\]

\[
X_2(\text{PC2}) = a_{21} Z^2(f_1) + a_{22} Z^2(f_2) + \ldots + a_{2n} Z^2(f_n)
\]

\[
X_3(\text{PC3}) = a_{31} Z^3(f_1) + a_{32} Z^3(f_2) + \ldots + a_{3n} Z^3(f_n)
\]

................................................................. etc.
The matrix structure and the stages of data processing at PCA approach.
Score plot for the first and second components of the PCA model. The seven different systems with increasing number of layers (and thickness) and increasing time of immersion are presented. The total amount of information extracted from the data is $(89.14 + 7.25) 96.39 \%$. 

≈ barrier properties
The variance of each principal component as the result of principal component analysis

two independent processes with probability 0.9639 (89.14%+7.25%)
PC1 values plotted against measured thickness of the systems

![Graph showing the relationship between PC1 values and thickness over time for different numbers of layers (1 layer, 1 week, 2 weeks, 1 month, 4 months). The graph includes time markers for 1h, 1 week, 2 weeks, 1 month, and 4 months, and thickness markers for 200, 300, 400, 500, 600, 700, 800, 900, and 1000 µm.](image-url)
PC2 values plotted against measured thickness of the systems
Conclusions

- The combination of multivariate analysis and electrochemical impedance spectroscopy to study interactions with aggressive solution is very promising.
- The need for finding electrochemical model is reduced because scores plots for PCA models show most relevant information immediately.
- It was possible to discriminate between different systems with varying thickness (and barrier properties) using PCA.
- Role of the water on the coating systems with different thickness was studied. There are indications that the interaction with water can also be studied in this way.
- All data are used at once.
- Impedance spectroscopy can move out of laboratories - facilitated interpretation
- The next step is to extend the data set based on the results obtained for degraded systems.