Talanta 97 (2012) 468–472

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Evaluation of industrial cutting fluids using electrochemical impedance spectroscopy and multivariate data analysis

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ARTICLE INFO

Article history:
Received 21 December 2011
Received in revised form
27 April 2012
Accepted 3 May 2012
Available online 15 May 2012

Keywords:
Electrochemical impedance spectroscopy
Partial least squares
Sensor
Cutting fluid

ABSTRACT

In this paper we explore the combination of electrochemical impedance spectroscopy (EIS) and multivariate data analysis to evaluate the concentration and pH of an industrial cutting fluid. These parameters are vital for the performance of for instance tooling processes, and an on-line quality monitoring system would in such applications be very beneficial. It is shown that both the total impedance and the phase angle contain information that allows the simultaneous discrimination of the concentration and the pH. The final evaluation was conducted using the regression technique partial least squares (PLS), and this approach provided a way to quickly and easily find the correlation between EIS data and the sought parameters. The possibility to estimate both the concentration and pH level clearly indicates the potential of this method to be implemented for on-line evaluation.

1. Introduction

In many industrial processes it is desirable to measure and evaluate critical parameters on-line to provide the possibility for optimal process control. In addition, both time and money would be saved by minimizing the need for continuous sampling and laboratory analysis. Electrochemical impedance spectroscopy (EIS) is a technique well suited for investigating many physical and chemical parameters in liquids [1–3]. Based on the frequency dependence of the impedance, it is possible to determine for instance the conductivity, dielectric constant, and interfacial properties of a sample. By fitting the EIS data to equivalent circuits, valuable electrochemical information can be obtained. The data can also be evaluated to create physical and chemical models of the system, but yet another alternative is to combine EIS with statistical tools. This also allows for a quick classification of samples into categories, and a possibility to determine the most critical frequencies. This combination has, for example, previously been used to determine the state of charge in batteries [4], and to enhance the detection capabilities in bioanalytical experiments [5,6].

In industrial applications it is often necessary to perform measurements under harsh conditions. A common setup for electrochemical evaluations in these types of environments is a parallel plate cell using inert metal electrodes. Such a cell in conjunction with EIS provides an excellent method for on-line analysis of industrial process liquids. For instance, Smiechowski and Lvovich made several interesting EIS studies on industrial lubricants, including the detection of water leaks in engine oil [7] and the analysis of colloidal dispersions [8]. Also, they investigated the relationship between lubricant chemical composition and EIS data [9]. Moreover, Allahar et al. [10] studied the impedance of steels in new and degraded jet engine oil, while Wang and Lee [11] employed EIS to determine the amount of glycol contamination in regular engine oil. Finally, Zaengl [12,13] reviewed the application of dielectric spectroscopy for diagnosing electric insulation materials in power engineering.

Cutting fluid, which is a mineral oil based commercial product, is a vital part when operating tooling machines. The optimal cutting fluid concentration in water is usually between 6% and 12%. When used in the tooling machines at WIKA, the concentration is normally kept in a range between 8% and 10%. A lower concentration can give rise to decreasing stability, onset of corrosion processes, and a decreased cutting performance. A higher concentration will, on the other hand, lead to foaming and sedimentation. The optimal pH should be in the range between 8.5 and 9.2. Lower pH-values can give rise to ferro-

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0039-9140/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.talanta.2012.05.001

corrosion, low biological stability, bad smell, and separation of the emulsion. Higher pH-values can result in corrosion of aluminum, problems with gaskets, skin irritation, and foaming. In the cutting process nitrite is formed as a by-product and is considered to be a contaminant. The nitrite level should preferably be less than 20 mg/l, and optimally zero.

We have previously shown that the combination of EIS and multivariate data analysis can be used to simultaneously determine the amounts of soot and diesel in engine oil [14]. The data was evaluated with partial least squares (PLS), which provided a relatively quick and easy way to estimate the levels of soot and diesel. In this contribution, we report on the possibility to simultaneously estimate the concentration and pH level in an industrial cutting fluid. We employed a well-designed setup, and performed temperature-stabilized measurements over a wide frequency range. The temperature of the sample is a very important factor, which greatly affects the impedance behavior. Comparisons between samples mixed in the lab and those from a real application were also made, showing that the described method clearly is relevant as an on-line technique.

2. Experimental

2.1. Equipment and measurements

The impedance cell consisted of two circular stainless steel electrodes (Grade SUS 316 L) with a diameter of 3.0 cm, creating an effective electrode area of 7.1 cm^2 (Fig. 1). These electrodes were separated by 200 μm using PEEK housings, resulting in a cell volume of approximately 0.14 ml. Imbedded in the lower electrode, two 5 W resistors were used as heaters, and a Pt-100 element functioned as the temperature sensor. The cell was placed in a small shielding box and each electrode was contacted using short cables which were securely tightened. The box itself was connected to the shield of the instrument to further reduce the noise level. An excess of each sample was used to flush the cell in order to avoid air bubbles. Prior to each measurement the cell was cleaned by flushing it with more than 100 ml of Milli-Q (Millipore) water. This procedure was found to give reproducible results.

Impedance data was obtained with a Solartron SI 1260 Impedance/gain–phase analyzer, using a frequency range of 1 MHz–10 mHz. The voltage amplitude is an important parameter and should normally not exceed about 25 mV (at 25 °C) [1] to minimize non-linear electrochemical responses. On the other hand, a larger amplitude, and hence a larger current, generally improves the measurements by increasing the signal-to-noise ratio. Since the samples in this study had a relatively low conductivity and low concentration of electroactive species, the use of higher amplitudes (up to 60 $\mathrm{mV_{rmc}}$) were investigated. As this resulted in negligible differences in the general impedance behavior, 40 $\mathrm{mV_{rmc}}$ was chosen to ensure a high signal-to-noise ratio while still using a fairly low amplitude.

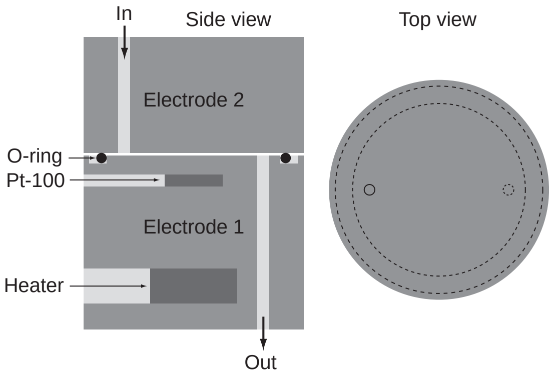

Fig. 1. Schematic representation of the impedance cell showing the two stainless steel electrodes pressed together to form the measurement chamber.

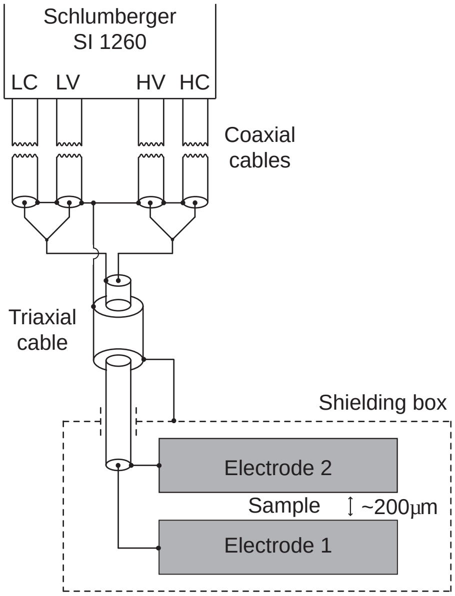

Fig. 2. Schematic representation of the measurement setup. LC: low current, LV: low voltage, HV: high voltage, HC: high current.

To be able to perform measurements over a large impedance range, a four-terminal pair configuration (Fig. 2) was used together with a coaxial/triaxial cable assembly for contacting the electrodes. Measurements were made at 80 logarithmically distributed frequencies, starting at 1 MHz. An in-house designed temperature controller (based on the Eurotherm 2408 PID controller) was employed to keep the sample at 25.00 ± 0.05 °C. A LabVIEW 5.1 (National Instruments) program controlled both the impedance analyzer and the temperature unit. The recorded parameters were the impedance magnitude ($|Z|$) and the phase angle (θ). These can be corrected for residual impedances, for instance using open and short compensations. This was, however, not performed here, as it was shown to have minor influence on the PLS modeling.

The pH was measured with a MA5736 pH meter (Metrel, Slovenia) with a pH electrode from BetaSensor, Sweden, while the conductivity was measured with an RS Components unit (model no. 180–7127).

2.2. Samples

Mineral oil based cutting fluid (Blasocut 4000 Strong, Blaser Swisslube Ltd., Switzerland) was provided by WIKA Alexander Wiegand SE & Co. KG, a German company mainly focusing on the manufacturing of pressure and temperature measurement equipment, as well as devices for calibration. It is a water-miscible metalworking fluid with a density of 0.99 $\mathrm{g/cm^3}$. The mixing of 10% cutting fluid either with tap water, deionized water, or Milli-Q water was first investigated. Impedance differences were found to be very small, showing that the influence of the cutting fluid was the dominating factor in the samples. Hence, to simulate real conditions, tap water was used to prepare samples with different concentrations (10 l of tap water were first stored in a refrigerator for 1 week, then 9 l were decanted and stored again for further use). A reduced experimental design was chosen, where the midpoint sample was evaluated three times, resulting in a total of 17 different samples prepared with various concentrations, pH,

Table 1
The mixed samples, showing the day of measurements, together with the concentration, pH, nitrite concentration, and conductivity.

Sample no.	Day	Concentration (%(w/w))	pH	Nitrite (mg/l)	Conductivity (mS/cm)
1	1	15	10.9	0	3.41
2	1	10	11.0	8	2.31
3	1	10	9.5	10	1.51
4	2	15	11.0	20	3.36
5	2	10	9.5	0	1.51
6	2	15	8.0	20	4.71
7	2	10	9.5	20	1.56
8	2	10	9.5	10	1.53
9	3	5	8.1	20	1.63
10	3	5	11.1	17	1.27
11	3	10	8.1	10	3.38
12	3	5	10.9	0	1.15
13	3	15	9.3	10	2.60
14	4	5	9.6	10	0.88
15	4	15	8.1	0	4.50
16	4	10	9.5	10	1.55
17	4	5	8.1	0	1.60

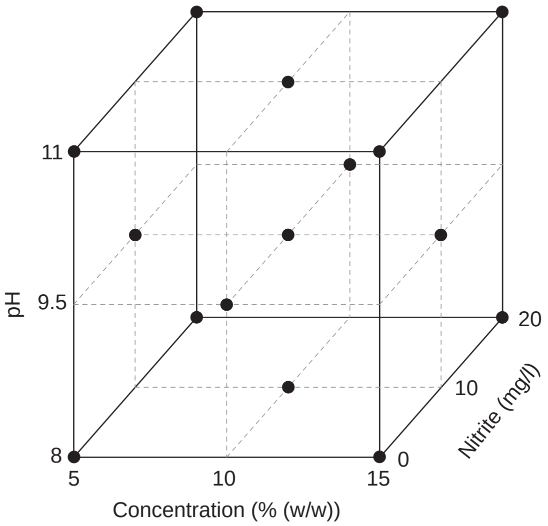

Fig. 3. Representation of the experimental design.

and nitrite levels, according to Table 1 and Fig. 3. These concentrations represent realistic values used in real applications. The measurement of each sample required more than two hours, and four days were consequently needed to perform the randomized measurement series. The pH was adjusted by adding a specific volume of stock solution of either NaOH or acetic acid. The nitrite concentration was adjusted by adding a specific volume of $NaNO_2$ (10 g/l). Each sample was prepared just prior to the measurement, to avoid any effects of storage.

2.3. Data evaluation

The data evaluation was performed using the software DXE (Proxedra, Sweden). Due to some outliers in the impedance magnitude ($|Z|$), 11 of the 80 frequencies were omitted for this parameter. The data analysis was based on partial least squares (PLS) [15], which is a well established regression technique for modeling a dataset of continuous parameters **Y** from another dataset of parameters **X**. In brief, PLS transforms the variables of **X** into a reduced set of variables, often called latent variables (LVs). These LVs are mutually linearly independent and have a high covariance with **Y**, and they constitute a good approximation of the full dataset **X** (in a least-squares sense).

The PLS model used for the concentration was based on four LVs, while for the pH only two were necessary. No modeling of the nitrite was made due to negligible correlation for this parameter. Since the dynamic range of the impedance was quite large, all data was standardized prior to evaluation, i.e. each variable was mean centered and divided by its standard deviation. The result was that each variable basically became equally important in the PLS analysis. Due to the limited amount of measurements, a validation of the model was not possible.

3. Results and discussion

Prior to any statistical analysis, the impedance spectra were evaluated and certain conclusions could be drawn concerning the influence of the different parameters. First the influence of cutting fluid concentration on the impedance magnitude and phase angle was investigated (Fig. 4A and B, respectively). The three midpoint samples are presented, together with samples 13 (15%) and 14 (5%), differing only in the concentration. As can be seen in Fig. 4A, the curves are separated over almost the entire frequency range. At high frequencies, this separation was more pronounced, indicating an obvious correlation between cutting fluid concentration and conductivity. This is also clearly seen in Table 1, demonstrating that higher concentrations result in an increase in conductivity. The frequency behavior of the phase angle (Fig. 4B) was more complex. In certain intervals the separation between the curves is distinct, but between these the curves cross and this behavior is repeated several times. Here, it seems that high- and low frequency regions provided the best basis for separation.

In Fig. 4C, the influence of pH on the impedance is shown. Again the three midpoint samples are presented, together with samples 2 (pH 11.0) and 11 (pH 8.1). There is a separation at high frequencies, but not as pronounced as for the concentration. In the middle region, however, the different pH values have a larger influence on the impedance. For the phase angle (Fig. 4D), both high and low frequencies show significant differences. It is especially the heights and the positions of the peaks that indicate the influence of pH. This is probably due to the effect of the pH on the micelle formation in the cutting fluid. Otherwise, different pH levels would most likely only affect the conductivity of the samples. Regarding the nitrite concentration, no variations could be found when evaluating the spectra. However, EIS is evidently suitable for determining both the cutting fluid concentration and pH, and PLS analysis was therefore employed to ascertain the correlation between these parameters and the EIS data.

As shown previously [14], the use of statistical tools can be very informative when interpreting impedance data. From the measured set of parameters, $|Z|$ and θ, the impedance function, $Z = Z' + jZ''$ can easily be calculated. Further, three more quantities are commonly used: the admittance, the modulus function, and the complex dielectric constant. All these functions are valuable in EIS due to their different dependence on, and weighting with, frequency. In this study, the analysis was based only on the quantities $|Z|$ and θ. The others were also evaluated, and provided very similar results in the PLS analysis. This method allows for the calculation of the correlation between the EIS data and different categories of samples. In Fig. 5, the correlations (based on the Pearson product-moment correlation coefficient) between the two measured parameters and the cutting fluid concentration, the pH, and the nitrite level are presented. From the figure, it was concluded that the frequency regions 10–35 mHz, 280 Hz–2.4 kHz, and 310 kHz–1 MHz were especially important. The correlation

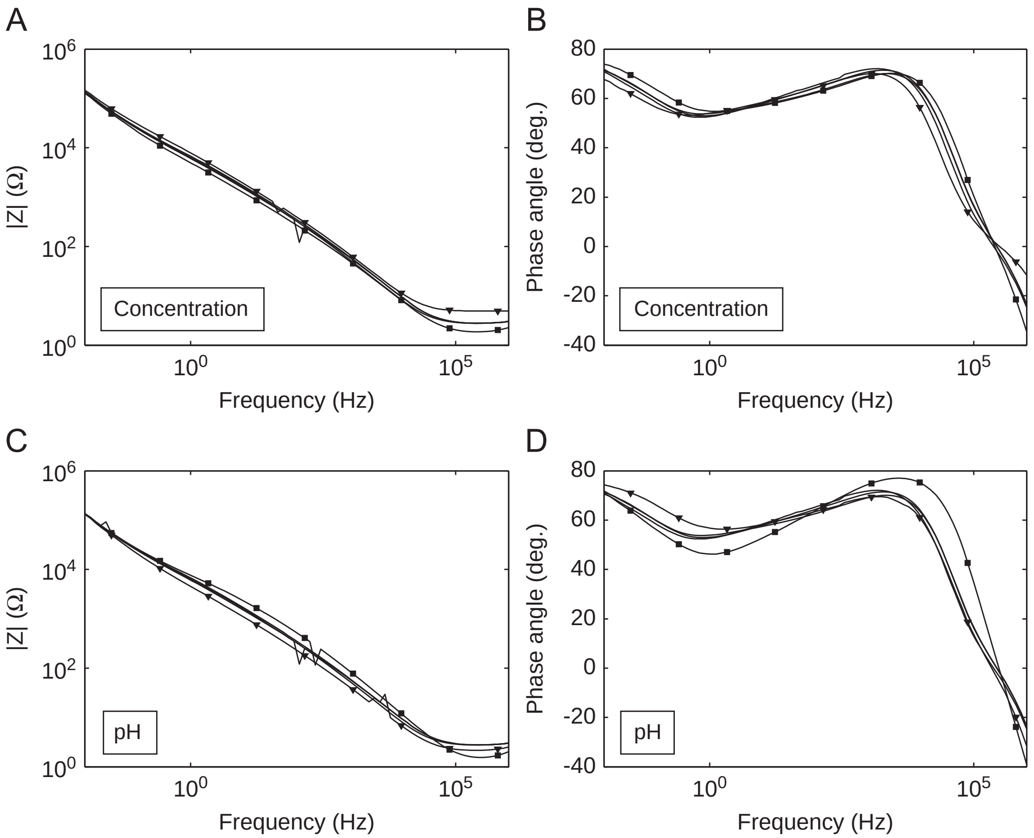

Fig. 4. Influence of different cutting fluid concentrations on the magnitude (A) and phase angle (B). The pH and nitrite levels were constant. Curves without markers represent the three midpoint samples, and triangles and squares represent 5% and 15%, respectively. (C) and (D) show the influence of different pH levels on the magnitude and phase angle, respectively. Here, the cutting fluid concentration and nitrite levels were constant. Again, curves with no markers represent the midpoint samples, but here triangles and squares represent pH 11.0 and pH 8.1, respectively.

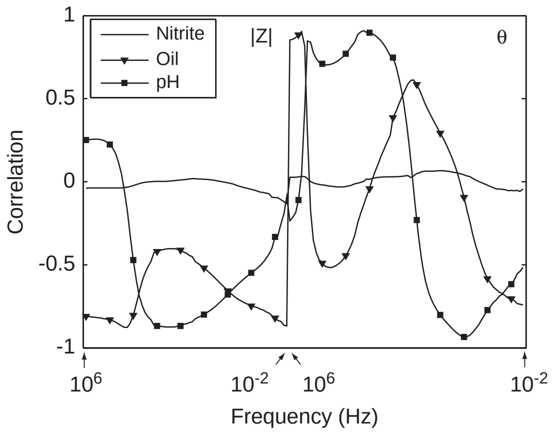

Fig. 5. Correlation of EIS data to cutting fluid (denoted oil in legend) concentration, pH, and nitrite level. The left part represents $|Z|$ and the right part θ.

between EIS data and the nitrite concentration was more or less zero, and it was therefore concluded that nitrite had no influence on the impedance. The correlations for the cutting fluid concentration and the pH level, however, clearly show different frequency dependence. Especially interesting is the fact that when the correlation for one parameter is zero, the correlation for the other is often relatively high (positive or negative). This should provide the means to separate their individual contributions to the impedance. Noteworthy is also that for frequencies where the curves in Fig. 4 cross, the corresponding correlations in Fig. 5 are consequently close to zero.

In Fig. 6, the PLS calibration data for the concentration and pH is presented. The results clearly indicate the possibility of estimating both parameters simultaneously. This is also evident when looking at the relative root mean squared error (RMSE) and the correlation for the different PLS models given in Table 2. If more samples were evaluated, model stability and accuracy would most likely improve, and this would also permit validations to be performed. The focus was, however, instead directed toward the analysis of real samples.

In an effort to test real life solutions, a few samples from tooling machines were collected at WIKA and shipped overnight to our laboratory. One of these samples was analyzed according to the procedure above, and the results were compared with those from the mixed midpoint sample. As is demonstrated in Fig. 7, the impedance data from the real and the mixed sample showed a very high correlation, being similar both in magnitude and frequency behavior. This validated the use of mixed samples to evaluate the possibility to determine the concentration and pH of cutting fluids. In addition to that, it was also found that the impedance results for the real samples displayed a drift over time. In Fig. 7, results from day seven and nine are also presented. These changes in the sample might be due to, for example, onset of bacterial growth. Given the time required to perform the experiments, an accurate off-line multivariate comparison of all the real samples was hence not valid. On the other hand, as indicated in the introduction, one advantage with the multivariate approach is to quickly be able to determine which frequencies are most important to determine the pH and concentration. In a final on-site analysis procedure, optimal frequencies could hence be selected to shorten the analysis time when evaluating either the chemical composition or the storage conditions.

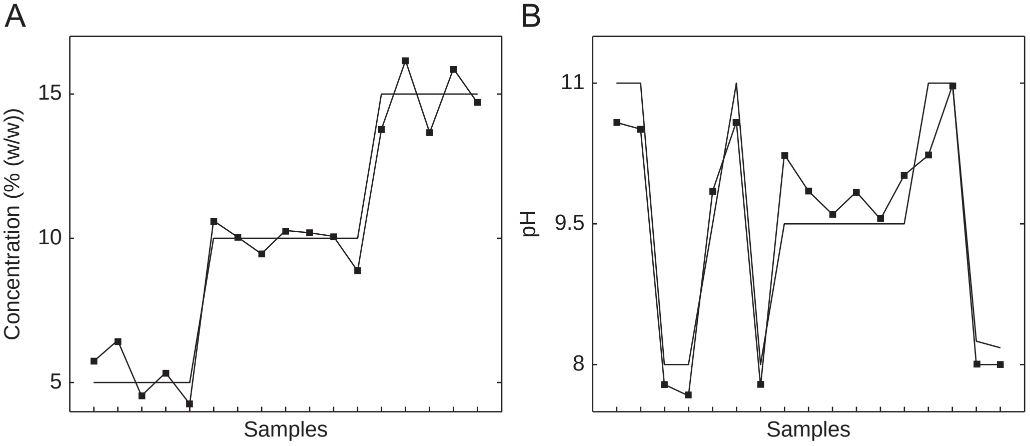

Fig. 6. PLS calibration data for the cutting fluid concentration (A) and the pH level (B). Real values (no markers) are also shown.

Table 2
Relative RMSE and correlation for the PLS models.

	RMSE (%)	Correlation
Concentration	10.5	0.98
pH	4.0	0.94

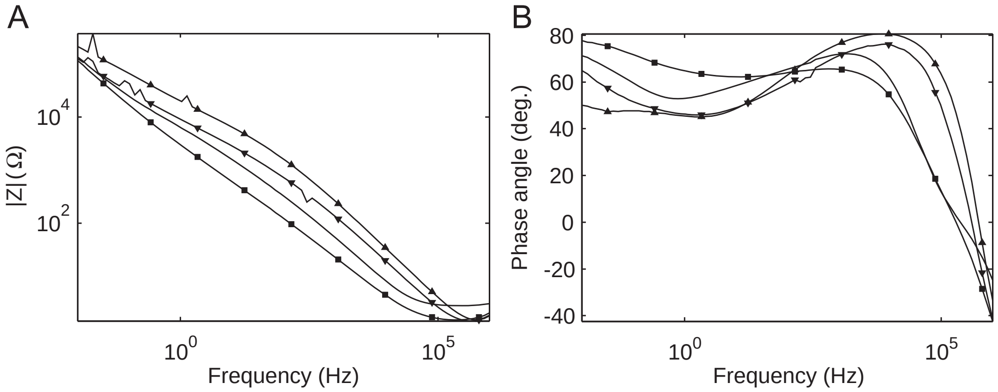

Fig. 7. $|Z|$ (A) and θ (B) for a real sample from day 1 (square), day 7 (down triangle), and day 9 (up triangle). The solid line with no markers is a measurement of the mixed midpoint sample.

4. Conclusions

We have demonstrated that it is possible to simultaneously estimate the concentration and pH level of an industrial cutting fluid based on impedance measurements and multivariate data analysis. A well defined and temperature-stabilized experimental setup was critical to obtain stable and reproducible results. The results clearly show the potential for this method to be implemented as an on-line technique in industrial processes. An important result of this study was also the identification of vital frequency regions, useful for the discrimination of the desired parameters. This can be very valuable, for instance when designing a low cost application specific impedance analyzer unit.

Acknowledgments

This work was supported by the Carl Trygger Foundation (CTS) and the Swedish Sensor Center (S-SENCE). We would like to thank Jaco Visser (Ford Motor Company) for lending us the impedance analyzer, and Hans Sundgren for valuable discussions.

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