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Reproducibility of Sensitization with Polylaurilmetacrylate of Surface Acoustic Wave Gas Sensors Using the Spin Coating Process

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Abstract

The technology of surface acoustic wave-based (SAW) sensors greatly depends on the performance of the resulting sensing layer. To ensure real applications, the sensors must be produced with reproducibility, as well as the statistical consistency of analytical sensor response results must be assured. In this work, we investigated the reproducibility and the statistical performance of the coating procedure used in previous works for the development of new polymeric coating materials, and the statistics of the respective sensor responses were analyzed. The polylaurylmethacrilate (PLMA) is used as an example of polymeric coating material. Two series of sensors coated with distinct quantities of the polymer were produced and analyzed. The statistical analysis of the ultrasonic parameters of the sensor production presented very low variability for both series of sensors. The respective sensor responses, obtained with a set of analytes with distinct chemical functions, presented, in the same way, excellent reproducibility for both series of sensors. The very good reproducibility and statistical robustness of the sensor production data and of the respective sensor responses confirm the reliability of the methodology to produce sensors for the SAW technology.

Keywords: polymeric sensing layer; spin coating; statistical analysis; polymeric thin film

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1. Introduction

SAW sensors are among the most investigated chemical sensors for the detection of volatile compounds in the past years, due principally to the versatility, low cost, and simplicity of the technology [1–3]. The hardware for the SAW sensor systems has been satisfactorily developed in many versions and, together with the sample preparation techniques, allow the SAW sensor systems to reach limits of detection in the level of parts per billion [4,5]. Nevertheless, for real applications, the bottleneck of the SAW sensor technology is still the coating technology that includes both the choice of suitable sensing materials that can fulfill the necessary sensing and mechanical properties to form a suitable coating layer and the coating process itself [6,7]. The coating process shall work together with the sensing material to provide a stable and reproducible deposition of the sensing layer, that, in turn, shall provide reproducible sensor responses [8]. Therefore, along with the achievement of the sensibility and selectivity required for the analytical objectives, the quality of the coating layers is crucial to assure the applicability of the sensor technology in commercial applications. In this context, the coating materials and the coating process must be fine-tuned to provide coating deposition of high quality. Along with those requirements, the reproducibility of the sensor production is very important to ensure the production of sensors with the confidence necessary to enable their use in real applications [9].

This work aims to cover two important aspects of SAW technology. First, the validation of the data that can ensure future commercial application of our SAW sensor system, which will be tailored for the desired analytical applications using specific sensitization of the sensor elements. Second, in the development of new coatings materials, for the investigation of the selectivity mechanism of the sensing layers, the sensor responses must be statistically consistent and validated. In this context, this kind of evaluation represents a novelty itself because we did not find any reference in literature which deals specifically with the statistical behavior of the sensor responses. Therefore, it is very important to present and evaluate the uncertainty associated with the sensor responses in association with the coating process used to produce the SAW sensors investigated. With statistical validation, we can further investigate the selectivity and other properties of the coating materials with a consistent set of data that allows us to validate models and mechanisms for the interactions occurring between the coating materials and the analytes.

Once the reproducibility of the sensor production is achieved, it is also important to ensure that it will be reflected in the reproducibility of the sensor responses, which is ultimately the analytical responses of the SAW sensor technology. The sensor responses to the analytes shall be reproducible and statistically consistent. In this context, it is very important to know if the sensor response results depend only on the characteristics of the sensing materials or if there is any influence on the results due to variations on the quality of the coating layer, eventually caused by the variability of the coating methodology. Therefore, to compare the sensing results of different coating materials, it is very important to guarantee that the sensor responses reflect only the properties of the coating materials and of their interactions with the analytes and no influence of the coating process is affecting the results and the consequent assumptions and conclusions made, based on the sensor responses [10–13].

For all these reasons, it is important to determine the variability of the data and the domain of uncertainty obtained by the methodology used to produce the sensors. In the case of SAW sensors, the variation of the ultrasonic parameter frequency shift and attenuation (S12 parameter), due to the coating process, are used to characterize the coating deposition. The second important issue is to investigate the influence of the variability of the sensor coating in the respective variability of the analytical sensor responses.

It is well known that the spin coating methodology does not give the same results for all kinds of coating materials, because it depends on the properties of the material itself. In the case of SAW sensor technology, due to its high sensitivity, the coating method and the coating materials must work together to provide reliable sensors. For the sensitization of SAW sensors, a wide range of different types of materials have been used as coating materials for gas sensing applications [14–17]. Among them, polymers were one of the most investigated, due principally to the large spectrum of chemical environments provided by this class of chemicals and to their cost and availability in a high degree of purity [10,18–21]. Furthermore, the fact that most polymers can easily be dissolved in usual solvents makes possible their application by the processes used to coat SAW sensors [15,22]. In this work, the SAW sensors were produced using polylaurylmethacrylate (PLMA) as an example of polymeric coating material due to the good properties of interaction and detection of a large range of organic compounds of distinct chemical functions. The coating procedure used in this work was chosen due to the successful results obtained previously by the investigation of new polymeric sensing materials [23,24].

The variability of the coating procedure was evaluated with the statistical analysis of the ultrasonic parameters. Then, the reproducibility of the sensor analytical responses using the same series of sensors was determined for a series of analytes of different chemical functions. To investigate the influence of the amount of sensing material deposited in the reproducibility of the coating procedure, two series of sensors, coated with quite different amounts of PLMA, were analyzed. The variability of the coating process and the reproducibility of the corresponding sensor responses, as well as the correlation between them for both series of sensors, were evaluated.

2. Methodology

2.1. SAW Sensor Element

The SAW sensor element used is made of a highly polished piezoelectric quartz substrate with gold electrodes, lithographically deposited with dimensions of (5.9 × 3.9) mm^2, of which the design and geometry were optimized by our group [25] (Figure 1). The optimized sensor elements were produced by SCD Components Dresden, Germany, and we purchased the sensor elements from that company. The nominal fundamental resonance frequency of sensor element is 434 MHz.

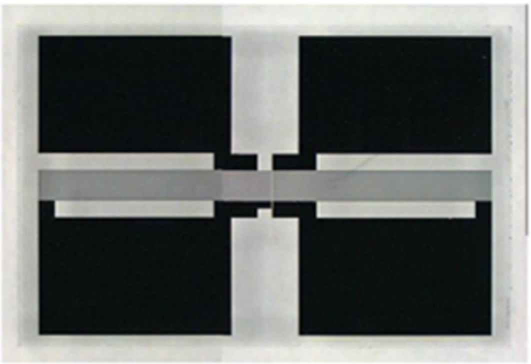


Figure 1. SAW sensor element used is made of a piezoelectric quartz substrate with lithographically deposited gold electrodes.

The SAW sensor elements were cleaned for the deposition by leaving them overnight in a bath of acetone, and, after this, they were washed several times with a stream of fresh acetone with the help of a 1 mL pipet. After the solvent cleaning, the sensor elements were dried for an hour with a flux of dry nitrogen.

2.2. SAW Gas Sensor System

The SAW sensor system was internally developed, and its construction is schematically represented in Figure 2. The sensor system consists of an uncoated piezoelectric sensor, used as a reference element, and positions for the insertion of eight sensor elements (numbered from 1 to 8 in Figure 2); each of them can be coated with different coating materials. The electronic works with nine integrated high-frequency oscillators with serial control using a special 8-fold multiplex technique. The system was designed to perform selective gas detection by recognition of the generated signal patterns, using a suitable data treatment, depending on the analytical application.

A picture of the real main board of the SAW sensor system with dimensions of 60 mm × 30 mm is presented in Figure 3, where three sensor elements are positioned over the two milled channels, through which flows the gas phase carrying the analytes. We have developed our own flip-chip technology, where we place the components upside down on electrodes.

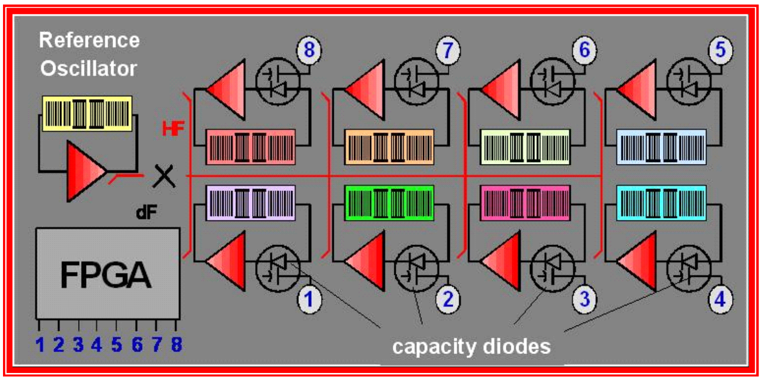


Figure 2. The 8-fold SAW sensor system internally developed to generate 8 independent sensor responses, schematically represented.

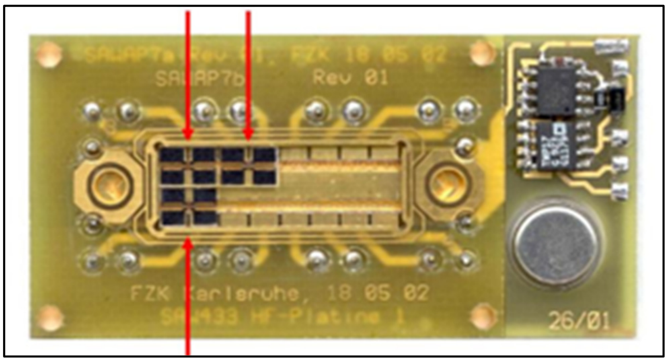


Figure 3. The main board of the sensor system (60 mm × 30 mm) with three SAW sensors elements (indicated by the red arrows) positioned over the two milled channels and the expansion showing the detail of the specially designed piezoelectric sensor element.

2.3. Experimental Section

2.3.1. Chemicals

All the chemicals, which included perchloroethylene (CAS 127-18-4), ethanol (CAS 64-17-5), isopropanol (CAS 108-88-3), p-xylene (CAS 106-42-3), tetrahydrofuran (CAS 109-99-9), ethylacetate (CAS 141-78-6) and acetone (CAS 67-64-1), polylaurylmetacrylate (CAS 25719-52-2), and toluene (CAS 108-88-3) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA); all had concentrations higher than 99%, and were used without further treatment.

2.3.2. Spin Coating Solutions

Two series of sensors were produced using coating solutions with two different concentrations of the sensing polymer, PLMA, in toluene, to investigate the influence of the quantity of the deposited layer on the reproducibility of the sensor properties. The first series of sensors were produced with a spin coating solution with a concentration of 7.7 mg.mL^{-1} of PLMA in toluene, and the second series of coated sensors was produced from a spin coating solution of 6.7 mg.mL^{-1}. Those concentrations were chosen to provide operational coated sensors with a significative difference in their deposited mass.

2.3.3. Spin Coating Procedure

The process of sensitization of the sensors is schematically represented in Figure 4. The deposition of the coating layer was carried out by dissolving the polymeric coating material (PLMA) in toluene at the desired concentration to produce the spin coating solution. Then, 200 microliters of the spin coating solution were dispensed using a micropipette over the cleaned SAW sensor element to be coated, already placed in the rotating plate of the spin coater. After the dispensing of the spin coating solution, the spin coater (Laurell MS-

400B-6NPP/LITE, Lansdale, PA, USA) was immediately turned on at a rotation speed of 8.000 rpm and maintained so for 120 s for all the experiments [22]. All the parameters were precisely controlled. The coated sensors were left in an oven for one hour at a controlled temperature of 45 °C to remove any of the residual solvent before the measurements. All the depositions were carried out with an ambient temperature of 24 °C and a relative humidity of 45%.

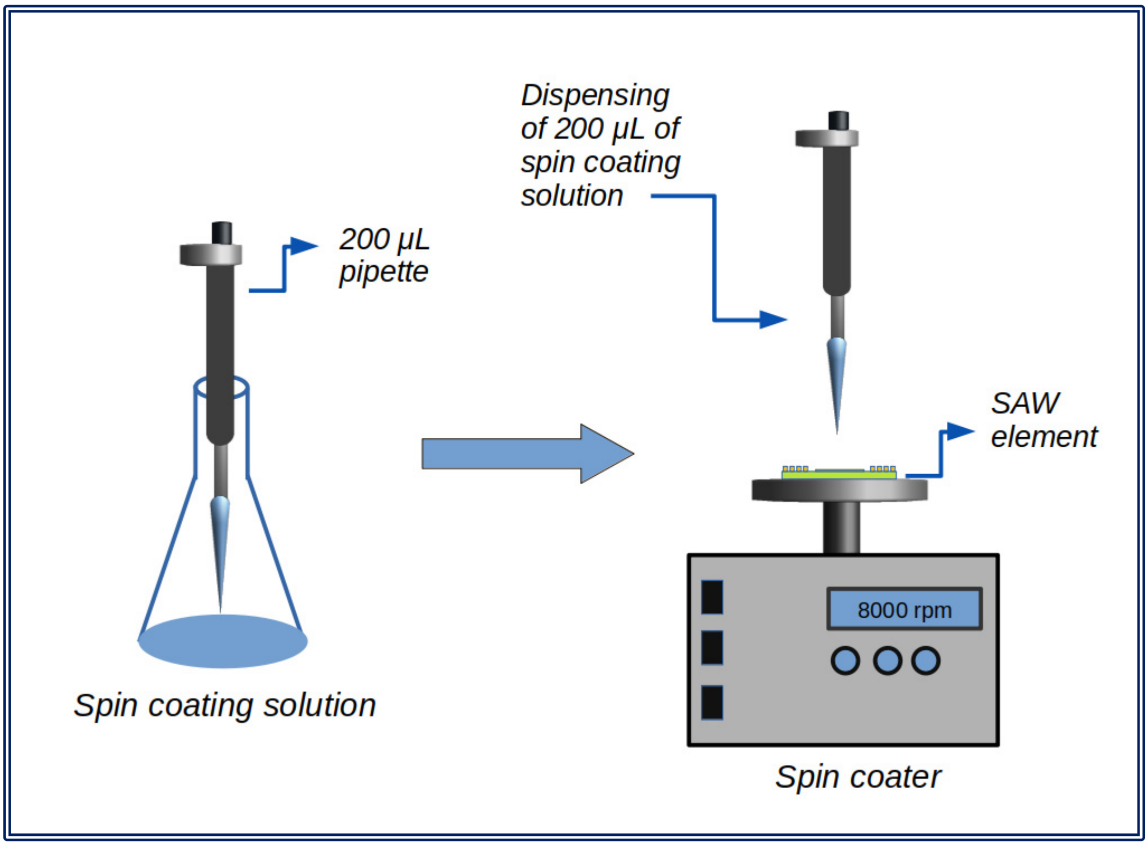


Figure 4. Representation of the spin coating method to the sensitization of the SAW sensors: 200 µL of the spin coating solution was dispensed by using a micropipette directly over the SAW sensor element, placed at the spin coater rotating plate, and afterward the spin coater was immediately turned on at the 8000 rpm, staying so for 120 s.

2.3.4. Ultrasonic Measurements

The ultrasonic parameters of each SAW sensor element were recorded by comparing the HF resonance frequency transmission parameters with a network analyzer (Hewlett Packard 8712ES, Waldbronn, Germany). The ultrasonic parameters, resulting in resonance frequency shift and attenuation change (S_{12} parameter) were measured before and after coating.

2.3.5. Sensor Responses with Analyte-Saturated Vapors

The analytical sensor responses are the measurements of the maximum frequency shift observed for each analyte. In this work, the analytes, perchloroethylene, isopropanol, ethanol, p-xylene, ethyl acetate, acetone, tetrahydrofuran (THF), and water were used. A stream of saturated vapor of each analyte at a constant temperature of 24 °C was supplied to the sensor system by a homemade multi-analyte array that accounted for a constant, reproducible, and high concentration of saturated vapor of each analyte. The schema of the multi-analyte array is shown in Figure 5. The multi-analyte array is controlled by the data acquisition program that allows the setup of cycles of analyte exposition with adjustable parameters. The cycles of exposition of each analyte ran automatically, as well as the simultaneous measurement of the respective frequency shift of each of the eight sensors in the array.

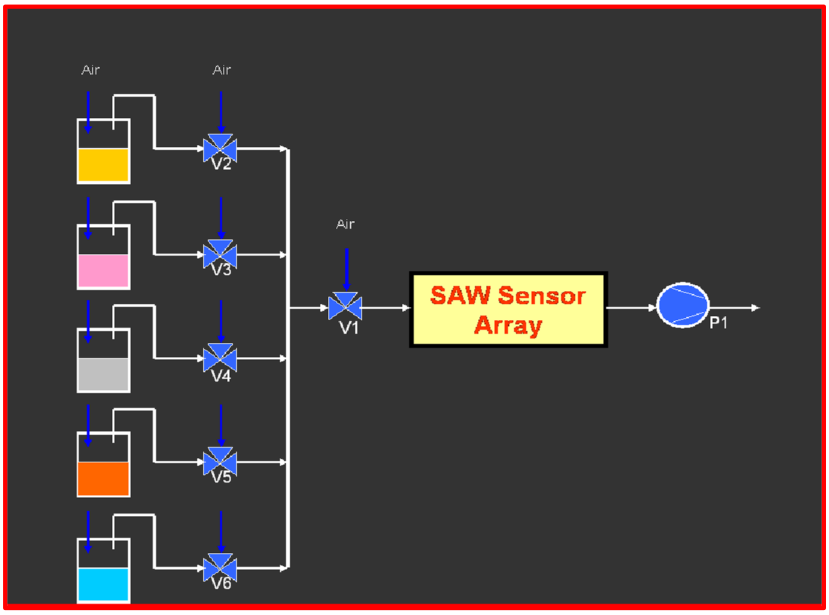


Figure 5. Schematic representation of the multi-analyte array. The setup provides a constant stream of saturated vapor of each analyte, which is automatically injected in the sensor system at a constant temperature.

The sensor responses are strongly affected by the coating itself. There are two main reasons for this: the uniformity of the coating, which results in scattering of the surface acoustic wave fronts (towards non-parallelism), and the viscoelastic properties (or intrinsic damping) introduced by the polymer layer material itself. In general, the attenuation of the SAW device is increased by both effects compared to the uncoated state. If the attenuation of a SAW device is increased, the Q-factor, of course, will be lowered as well.

2.4. Statistical Analysis

For the reproducibility analysis, the two series of six SAW sensor elements were sequentially coated with PLMA, according to the order given by their identification. Series 1 and 2 were coated with the spin coating solution of higher and lower concentration of PLMA, respectively. For the statistical analyses, the usual sample statistic parameters were used: the arithmetic mean value, the standard deviation, the amplitude (difference between the highest and lowest measured values), the semi-amplitude, and the coefficient of variation (quotient between the standard deviation and the arithmetic mean value, expressed in percentage). The coating of both sensor series was made by the same operator on different days, but both series were coated using the same coating solutions at the respective concentrations.

3. Results and Discussion

3.1. Analysis of the Ultrasonic Parameters

Table 1a,b presents the experimental results of the ultrasonic parameters for the two series of coated sensors.

Table 1. HF resonance peak results for the two series of six sensors, sequentially produced by the spin coating process.

(a) with the Spin Coating Solution of Concentration of 7.7 mg.mL^{-1} of PLMA		
Sensor	**Attenuation/dB**	**Frequency Shift/MHz**
Sensor#1	12.790	2.184
Sensor#2	12.585	2.137
Sensor#3	12.780	2.170
Sensor#4	12.701	2.260
Sensor#5	12.579	2.264
Sensor#6	12.790	2.279
(b) with the Spin Coating Solution of Concentration of 6.7 mg.mL^{-1} of PLMA		
Sensor	**Attenuation/dB**	**Frequency Shift/MHz**
Sensor#7	5.796	0.323
Sensor#8	5.841	0.329
Sensor#9	6.025	0.335
Sensor#10	5.943	0.329
Sensor#11	5.891	0.323
Sensor#12	5.632	0.329

Tables 2 and 3 show the statistical analysis for series 1 and 2 of sensors of the attenuation and frequency shift, respectively.

Table 2. Results of the statistical analysis of attenuation for each series of coated sensors.

Statistics	Series 1	Series 2
Mean value/dB	12.704	5.855
Standard deviation/dB	0.100	0.135
Amplitude/dB	0.211	0.393
Coefficient of Variation/%	0.79	2.31

Table 3. Results of the statistical analysis of frequency shift for each series of coated sensors.

Statistics	Series 1	Series 2
Mean value/MHz	2.216	0.328
Standard deviation/MHz	0.059	0.005
Amplitude/MHz	0.142	0.012
Coefficient of Variation/%	2.66	1.52

Due to the mass reduction of the coating layers of series 2, the measured values of both ultrasonic parameters of series 2 (Table 1b) were consequently lower than those obtained for series 1 (Table 1a). The standard deviation and the coefficient of variation for both series of sensors presented very small results. The very low variability of both ultrasonic parameters observed by both series of sensors indicates the good reproducibility obtained by the coating process (Tables 2 and 3).

The spread of the measured values for each sensor series was analyzed by the results of the absolute and relative deviation from the mean value for attenuation (Figure 6) and the frequency shift (Figure 7), where the values plotted are the difference between the mean value and the respective ultrasonic parameter (Tables 2 and 3) measured for each sensor (Table 1a,b).

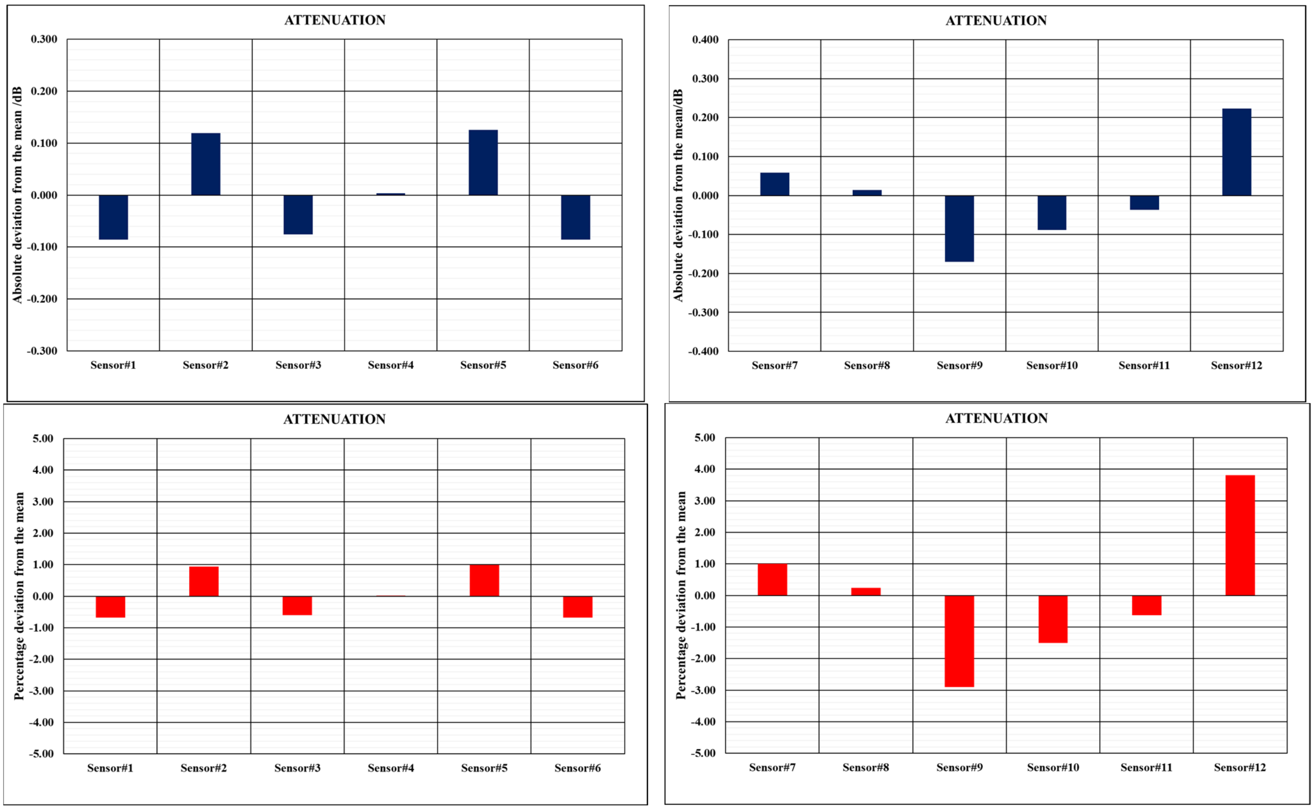


Figure 6. Absolute (**above**) and the percentage (**below**) deviation of the measured values of attenuation from the mean for each series of coated sensors. The scale of absolute deviation from the mean value was chosen to be equal to ±3 times the observed standard deviation (Table 2), while the percentage of deviation from the mean value was chosen to be ±5%.

The amplitude results are the interval which contains all the measured values, while the interval corresponding to ±3-times the standard deviation results shall contain 99% of all measurements results predicted by the sample statistics, assuming that the measured data can be described by a normal distribution.

The results show that the spread of the experimental data around the mean value was much less than predicted by the sample statistics for the attenuation of both series of coated sensors (Figure 6; above, left, and right). The deviation from the mean value of attenuation in terms of percentage for the series 1 of coated sensors was less than 1% of deviation from the mean value (Figure 6; left and below), while, for the series 2 of coated sensors, the deviation from the mean value was less the 4% (Figure 6, right and below).

Figure 7 presents the absolute and relative deviation from the mean value of frequency shift for each series of coated sensors (Table 1a,b).

The frequency shift data presented a small spread for both series of coated sensors (Figure 7), as observed by the attenuation data. All the measured data of frequency shift of both series of coated sensors presented a small deviation from the mean than predicted by the sample statistics (Figure 7 above, left and right).

The frequency shift data of the series 1 of coated sensors presented a percentage deviation from the mean less than 4% (Figure 7; below and left), while frequency shift data of the series 2 a maximum relative deviation from the mean of slightly above 2% (Figure 7; below and right).

The variability observed by each series of coated sensors for each ultrasonic parameter results can be interpreted considering the meaning of each ultrasonic parameter and how they can be influenced by the quantity of the coating material deposited by the spin coating process. Since attenuation is an integral parameter that represents, to some extent, the uniformity of the coating, in terms of both the mass distribution and the homogeneity of the coating layer itself, the presence of more material in the coating layer tends to contribute to an increase in the average of the uniformity of the deposition, reflected by the less spread of the data observed by the series 1, in comparison with that observed by series 2, which contains less quantity of deposited coating material.

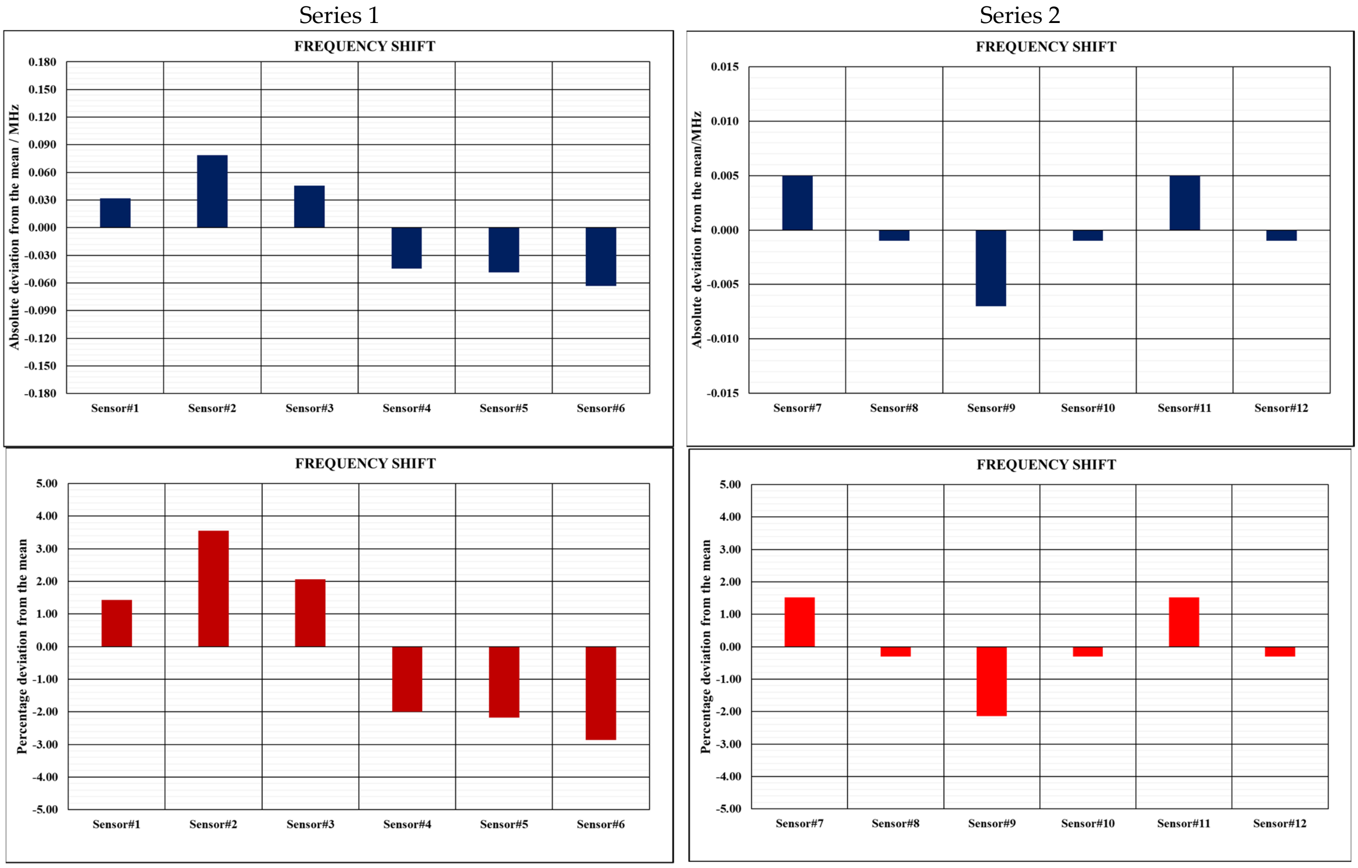


Figure 7. Absolute (**above**) and the percentage (**below**) deviation of the measured values of frequency shift from the mean for each series of coated sensors. The scale of absolute deviation from the mean value was chosen to be equal to ±3 times the observed standard deviation (Table 2), while the percentage of deviation from the mean value was chosen to be ±5%.

The higher variability observed in the frequency shift by series 1 in comparison with series 2 shall be related to the higher variation of the mass of the coating material deposited in each sensor series. The results indicate that a higher concentration of material in the coating solution leads to a higher variation in the quantity of material that remains over the surface of the sensors during the spin coating. In a simplified view, after the dispensing of the polymer solution over the sensor element surface and the subsequent start of the rotation step, part of the solution is ejected, and the remaining solution over the sensor surface loses the remaining solvent by evaporation. In this process, part of the deposited polymeric entities will be in direct contact with the sensor surface, being more strongly bound, while part of the molecules deposited above will be in contact just with themselves, being, in this way, less intensively bound than those in direct contact with the sensor surface. Therefore, as the concentration of coating material increases in the spin coating solution, more molecules will be stacked over themselves, increasing the upper layers of polymeric material with a higher probability of to be ejected during the rotation step, which shall lead to a higher variation of the quantity of remaining material deposited over the sensor, reflected by a higher spread of the frequency shift results.

3.2. Statistical Analysis of the Sensor Responses

After the coating procedure, both series of coated sensors were mounted in the sensor system and exposed to the saturated vapors of seven organic analytes of distinct chemical functions and structures and water. The respective sample statistics of the sensor responses for those analytes for series 1 of coated sensors (Table 1a) are shown in Tables 4 and 5, and the series 2 of coated sensors (Table 1b) are shown in Tables 6 and 7.

Table 4. Sample statistics of the sensor responses for the analytes isopropanol, ethanol, acetone, and ethyl acetate for series 1 of coated sensors.

Statistic	Isopropanol	Ethanol	Acetone	Ethyl Acetate
Mean value/kHz	45.99	78.86	100.21	126.62
Standard deviation/kHz	2.02	1.87	2.92	4.56
Amplitude/kHz	5.65	4.92	8.04	11.35
Coefficient of variation/%	4.39	2.37	2.91	3.60
Semi-amplitude	2.83	2.46	4.02	5.68

Table 5. Sample statistics of the sensor responses of the analytes THF, p-xylene, perchloroethylene, and water for series 1 of coated sensors.

Statistic	THF	p-Xylene	Perchlor.	Water
Mean value/kHz	236.21	301.36	554.09	4.79
Standard deviation/kHz	14.59	15.85	19.88	0.36
Amplitude/KHz	39.43	42.04	51.73	1.09
Coefficient of variation/%	6.18	5.26	3.59	7.47
Semi-amplitude	19.72	21.02	25.86	0.55

Table 6. Sample statistics of sensor responses of the analytes isopropanol, ethanol, acetone, and ethyl acetate for series 2 of coated.

Statistics	Isopropanol	Ethanol	Acetone	Ethyl Acetate
Mean value/kHz	13.20	27.45	30.49	31.62
Standard deviation/kHz	0.45	0.56	0.56	0.80
Amplitude/kHz	1.10	1.53	1.49	1.95
Coefficient of variation/%	3.45	2.03	1.85	2.53
Semi-amplitude	0.55	0.77	0.75	0.98

Table 7. Sample statistics of sensor responses of the analytes THF, p-xylene, perchloroethylene, and water for series 2 of coated sensors.

Statistics	THF	p-Xylene	Perchlor.	Water
Mean value/kHz	46.25	64.49	112.84	3.18
Standard deviation/kHz	0.94	0.78	1.43	0.30
Amplitude/KHz	2.45	1.89	3.57	0.81
Coefficient of variation/%	2.02	1.21	1.27	9.35
Semi-amplitude	1.22	0.95	1.79	0.41

The obtained standard deviations and coefficients of variation indicate a low variability of the sensor responses of all the analytes for both series of coated sensors. It is interesting to note that neither the standard deviation nor the coefficient of variation correlates with the magnitude of the sensor response of a given analyte. The different values of those statistical parameters observed shall be explained by the specific mechanism of interaction of each analyte with the coating layer. Nevertheless, the observed variability of the sensor responses by all the analytes was very small for both series of sensor responses.

The series 2 of coated sensors presented, in a general way, a lower variability of the sensor responses than that observed for series 1. This observation suggests a possible influence of the quantity of mass deposited on the sensor responses. By the assumption that a higher mass of the polymer deposited in the coating layer increases the coating thickness, the process of interaction with the analytes shall be influenced if the difference of thickness between the coating layers is very large, especially in saturation conditions. A thicker coating layer usually presents higher capacity of sorption of analyte molecules, which shall lead to an increase of diffusional effects that will affect the analyte–layer interaction, for instance by differences in the rate of sorption of the analytes, influencing, in this way, the variability on the sensor responses.

For all the analytes, the values of the coefficient variation of the sensor responses for both series of coated sensors were similar and very small, indicating a low variability of those results. The maximum value of the coefficient of variation was observed for water yet not trespassing 10%; however, it must be considered that water showed a negligible sensor response compared with the organic analytes. These results indicate that the good reproducibility obtained by the coating process, observed by the analysis of the ultrasonic parameters, was reflected in a good reproducibility of the sensor responses by all the analytes tested, independently of their chemical function or structure and of the magnitude of their specific sensor responses.

The spread of the sensor responses in terms of their semi-amplitudes and their percentual relative to their respective mean values are analyzed in Tables 8 and 9, for the series 1 and 2 of the coated sensors, respectively.

Table 8. Semi-amplitude and its percentual of the mean value of the sensor responses of each analyte for series 1 of coated sensors.

Analyte	Semi-Amplitude/kHz	Percentual from the Mean Value/%
Isopropanol	2.83	6.15
Ethanol	2.46	3.12
Acetone	4.02	4.01
Ethyl acetate	5.68	4.48
THF	19.72	8.35
p-Xylene	21.02	6.98
Perchloroethylene	25.86	4.67
Water	0.55	11.43

Table 9. Semi-amplitude and its percentual of the mean value of the sensor responses of each analyte for series 2 of coated sensors.

Analyte	Semi-Amplitude/kHz	Percentual from the Mean Value/%
Isopropanol	0.55	4.16
Ethanol	0.77	2.79
Acetone	0.75	2.45
Ethyl acetate	0.97	3.08
THF	1.22	2.64
p-Xylene	0.94	1.46
Perchloroethylene	1.78	1.58
Water	0.40	12.66

For both series of sensors, the semi-amplitude results were significatively lower than the interval expressed by three times the standard deviation, which defines the half of the interval that shall contain all the measurements, according to the sample statistics. The percentual of the semi-amplitude from the mean value for series 1 was below 9% for all the organic analytes (last column of Table 8), while, for series 2, those values were below 5% for all the organic analytes (last column of Table 9). As observed by the analysis of the ultrasonic parameters, the actual data presented a better reproducibility than that predicted by the sample statistics.

For visualization of the reproducibility of the sensor response results for both series of coated sensors, Figure 8 plots of the mean value as the height of the columns with error bars, whose ±lengths are the semi-amplitude observed for each analyte. The analytes were grouped according to the magnitude of their respective sensor responses.

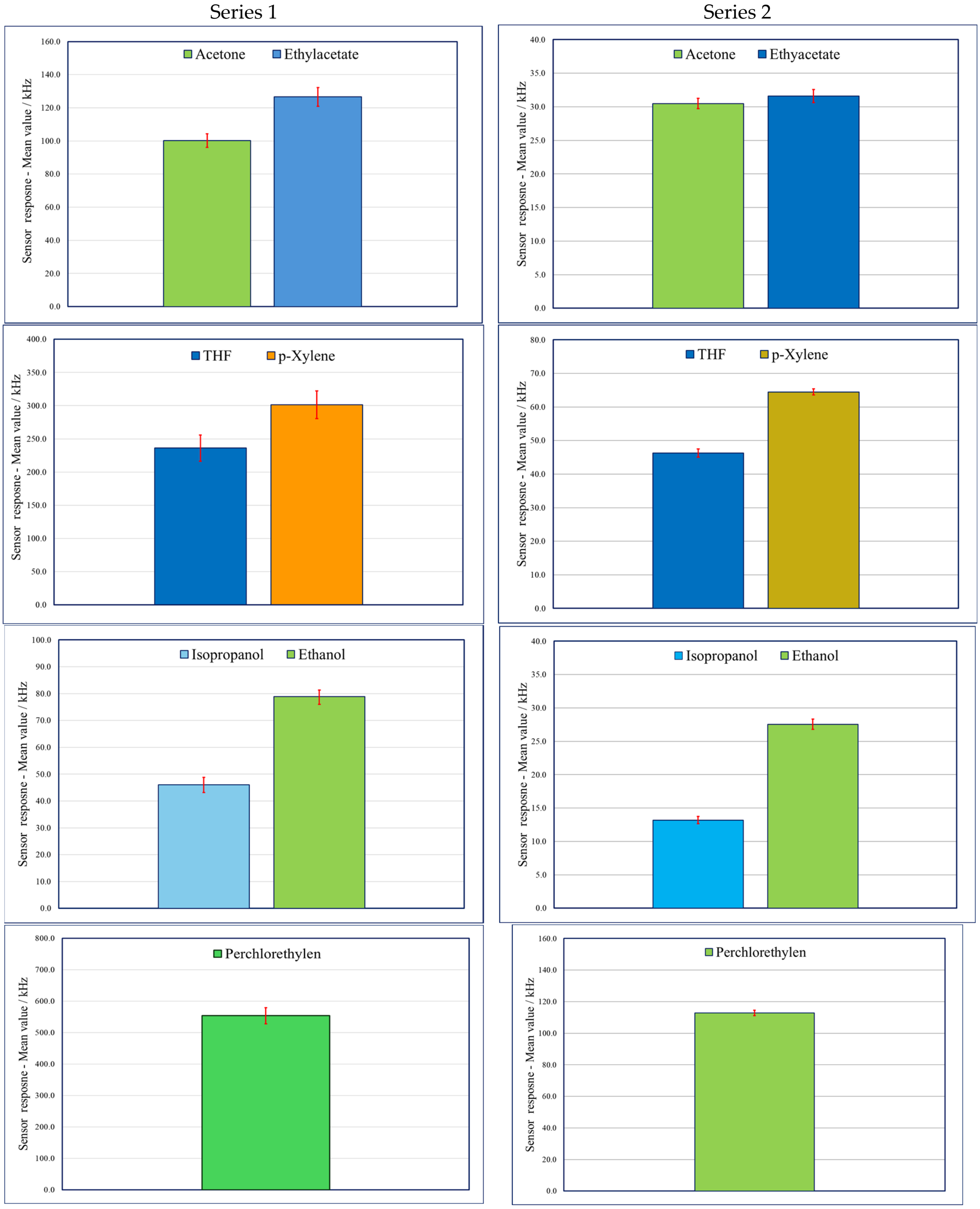


Figure 8. *Cont.*

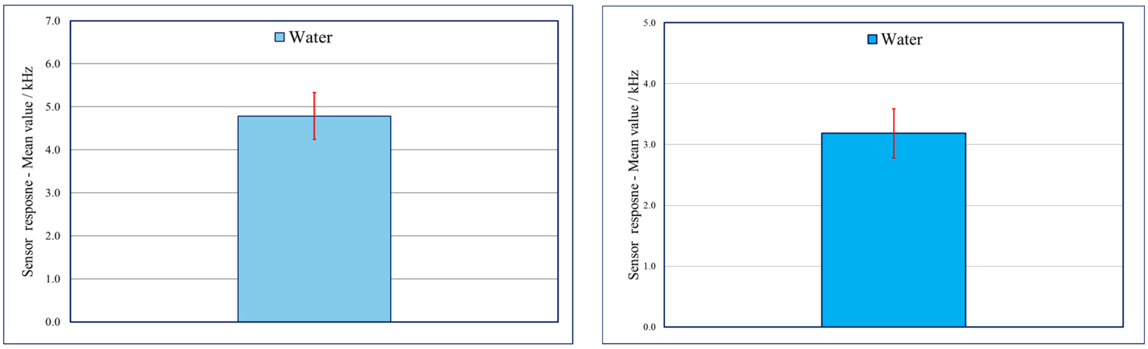
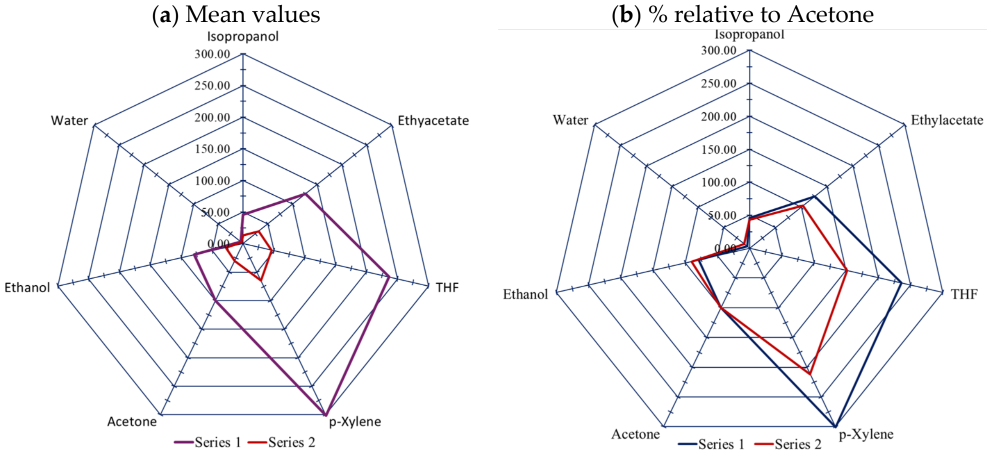


Figure 8. Plot of the mean value (height of the columns) with the error bars being ± the observed semi-amplitude for the sensor responses of each series of coated sensors.

The amplitudes observed by the sensor responses of both series of coated sensors indicate the small spread of the data around the mean value for the tested analytes (Figure 8). Both series of coated sensors presented internally very similar statistics and an overall very low variability according to the sample statistics, attesting the reproducibility of the sensor responses. The sensor responses of series 2 presented better result reproducibility than those observed for series 1 for all the analytes, which can be understood by the same arguments presented before.

In terms of the structure of the coating layer, the reproducibility of the coating process can be indirectly inferred by the inspection of the sensor responses of the analytes. As indicated by the ultrasonic parameters, the two series of coated sensors presented a very distinct quantity of mass deposited of the polymeric coating layer. If layers with a distinct deposited mass shall present, however, similar structures can be expected that the layers shall present the same chemical affinities, which can be recognized by the profile of the sensor responses obtained for the analytes of different chemical functions. Those layers shall just differ in the capacity of sorption of each analyte, given by the respective magnitudes of the sensor responses of the analytes.

In this sense, Figure 9 shows a comparison of the sensor responses of the analytes for the two series of coated sensors. Figure 9b presents the relative sensor responses of the analytes as a percentage of the sensor responses obtained to acetone for each series of coated sensors. The sensor response of acetone was chosen as the reference, because its values are approximately in the middle point of those observed by the other analytes.


(**a**) Mean values

(**b**) % relative to Acetone

Figure 9. Radar plot of the mean values of the sensor responses to the analytes for each series of coated sensors. (**a**) Mean values; (**b**) Percentage of the mean values relative to the mean value of acetone.

From Figure 9, it can be seen that both series of coated sensors presented very similar profiles for the sensor responses of the tested analytes. This is an indication that both coating layers show the same chemical affinity profile, which is expected for coating layers of the same chemical constitution and that they shall also present similar structures (distribution of the coating material and uniformity of the deposition).

Figure 10 shows the correlation between the mean values of the sensor responses for each analyte by each series of coated sensors.

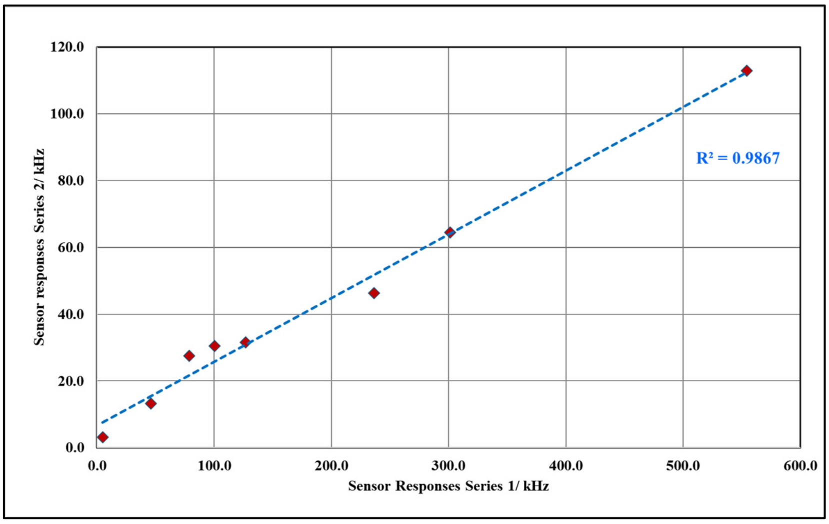


Figure 10. Correlation between the mean values of the sensor responses for each analyte by each series of coated sensors.

The good correlation observed between the mean values of the sensors responses indicates that the sorption of each analyte shall follow the same mechanism in both series of sensors. It is important to note that the individual sorption mechanisms as well as the individual chemical affinities shall be different for each analyte. However, under the same conditions, the same temperature, constant concentration (but not the same) of each analyte, and under saturation conditions, the results indicate that both coating layers respond equally to each analyte.

The main difference observed between the coating layers is in the capacity of sorption, which is also expected by layers having different quantities of deposited material. All these observations confirm the good reproducibility obtained by the coating process, as also indicated by the statistical analysis of the ultrasonic parameters and of the sensor responses of the analytes tested.

4. Conclusions

The statistical analysis of the ultrasonic parameters for the two sequentially coated series of SAW sensor elements obtained by the spin coating method used presented low variability, high reproducibility, and robustness. The ultrasonic data presented practically the same statistics for the two series of coated sensor elements, indicating no influence of the mass deposited in the reproducibility of the coating process in the range investigated.

The statistical analysis of the sensor responses for the two series of coated sensors also presented a low statistical variability for all the analytes investigated, in perfect agreement to that observed for the ultrasonic data. In general, all the results obtained for the sensor responses for the analytes investigated were far below a 10% deviation from the mean values, indicating a high reproducibility by both series of coated sensors. In general, the observed experimental variability was smaller than that predicted by the sample statistics. As observed by the ultrasonic parameters, the sensor response statistics were similar for both series of coated sensors. The variability of the sensor responses was independent of the chemical nature of the analytes for both series of coated sensors and presented high reproducibility for all the analytes investigated, independently of the chemical affinity of each analyte with the coating material.

The low variability observed by the sensor coating and its reproduction in the high reproducibility and precision of the sensor responses indicate that a consistent production of SAW sensors can be achieved with the coating method used. The high reproducibility, robustness, and precision of the results confirm the statistical validation of the sensor responses.

The results demonstrate that the methodology produced polymeric-coated SAW sensors with high precision, allowing production of sensors with constant quality potentially with any polymeric sensing material, which is crucial for future commercial applications. The reproducibility of the presented coating procedure shall be improved by the development of an automated setup to minimize operational variability of the manual steps.

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