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Using Statistical Analysis Software to Advance Nitro Plasticizer Wettability

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Abstract

Statistical analysis in science is an extremely powerful tool that is often underutilized. Additionally, it is frequently the case that data is misinterpreted or not used to its fullest extent. Utilizing the advanced software JMP®, many aspects of experimental design and data analysis can be evaluated and improved. This overview will detail the features of JMP® and how they were used to advance a project, resulting in time and cost savings, as well as the collection of scientifically sound data. The project analyzed in this report addresses the inability of a nitro plasticizer to coat a gold coated quartz crystal sensor used in a quartz crystal microbalance. Through the use of the JMP® software, the wettability of the nitro plasticizer was increased by over 200% using an atmospheric plasma pen, ensuring good sample preparation and reliable results.

Introduction

JMP® is a statistical analysis software designed by SAS Institute Inc. to be used for design of experiments (DoE) and the complete statistical analysis of complex data sets[1]. This software was used to help solve an issue with a project that used a quartz crystal microbalance (QCM)[2] to detect mass changes from a nitro plasticizer (NP)[3] once exposed to the atmosphere. However, the gold coated quartz crystal sensor used in the QCM didn't allow for good wettability of NP over the surface, coating only ~10% of the surface. To increase wettability, the surface energy was to be increased using an atmospheric plasma pen treatment and analyzed by a drop shape analyzer (DSA). In order to accurately measure these miniscule mass changes, the NP needed to coat as much as the gold sensor as possible.

Though the software has many features, this review will focus on three of its highly functional tools: Design of Experiment, Statistical Analysis and Predictive Modeling[4] and their application.

Design of Experiments

When an experiment is being designed it is often the case that it is redesigned to fit constraints such as budget, time, and/or materials rather than running the best experiment to obtain the most reliable data. This can lead to results that are lacking critical data or possibly data that is completely wrong. Rather than changing the experimental design, JMP®'s DoE functionality allows an experiment to be conducted within these constraints without losing any data or modeling capabilities[4]. Additionally, the software allows the visualization of any confounding factors and attempts to optimize the experiment to reduce these effects.

Statistical Analysis

Once the data is collected, it is critical to make sure that it is valid, meaningful and statistically sound. These analysis can be time consuming if performed by hand and are prone to miscalculation. Within JMP®, nearly any statistic is available in seconds, ensuring accuracy and reliability of the data[1].

Predictive Modeling

Using this data for further predictive analysis can be difficult or impossible, often requiring hours or days of programming and scripting to set up. At its most simple, predictive analysis can help understand how each variable in an experiment effects the end result or how the interplay of variables work to achieve a result. At its most complex, the application of a neural network to the data can enable machine learning to intelligently model data and give powerful predictive power[5]. While these functionalities could take an unacceptable amount of time to produce from scratch, JMP® has them built in and ready for use at the click of a button.

Quartz Crystal Microbalance

The QCM is an instrument that uses the resonant vibrational frequencies of a quartz crystal to detect mass changes with sub-nanogram sensitivity. This is achieved by applying a potential across a quartz crystal that is sandwiched between two conductive layers (gold in this project). The resonance frequencies are measured and if mass is gained on the sensor surface, the frequency proportionally decreases and the converse is true. This allows the characterization of mass and structural changes to be analyzed in real time of the sensor surface.

Materials & Experimental Methods

Throughout this project, the JMP® 13.1.0 software from SAS Institute Inc. (Cary, NC) was used extensively. The primary uses were DOE, predictive modeling and statistical analysis.

The gold coated AT-cut quartz crystal sensors used in this experiment were purchased from Biolin Scientific (Västra Frölunda, Sweden). Treatment of the gold surface was performed with an atmospheric plasma pen, purchased from PVA TePla (Corona, CA), using N_2 gas at 80-85 psi. The sensors were treated for 0 to 600 seconds with distances from the gold surface ranging from 10 mm to 40 mm. The DSA used to analyze the contact angle and thereby the surface energy was a DSA25S, purchased from KRŰSS (Hamburg, Germany). For the calculation of surface energy, the solvents used were ultra-high pure water and diiodo-methane. The OWRK model was used for calculations of surface energy[6].

In an attempt to increase the wettability of the gold surface, an atmospheric plasma pen using N_2 gas was used to treat the surface. This has the effect of not only cleaning the surface by removing any residual organics but also increases the surface energy and thereby the wettability. However, it is known that prolonged surface treatment with plasma can have diminishing returns and so an optimal treatment time and distance was required to be found[7].

Results & Discussion

Design of Experiments

The experimental procedure that was decided upon included 2 factors (time of plasma exposure and distance from the gold surface) at 8 different levels as seen in Table 1.

Experimental Parameters for QCM Sensor Plasma Treatment								
Time (sec)	0	45	105	165	225	285	345	600
Distance (mm)	5	10	15	20	25	30	35	40

Table 1: Table representing the variables and levels for the QCM DOE.

In order to run every possible combination of experiments (full factorial), it would have required 64 runs. However, due to time and material constraints, this was not possible. To help reduce the number of required runs without losing any critical data, the DOE functionality in the JMP® software was used[8]. Using the custom design function (Figure 1), it was able to reduce the required runs from 64 with no replicates to just 12 including 4 replicate points, effectively reducing the experimental time and materials required by a factor of five.

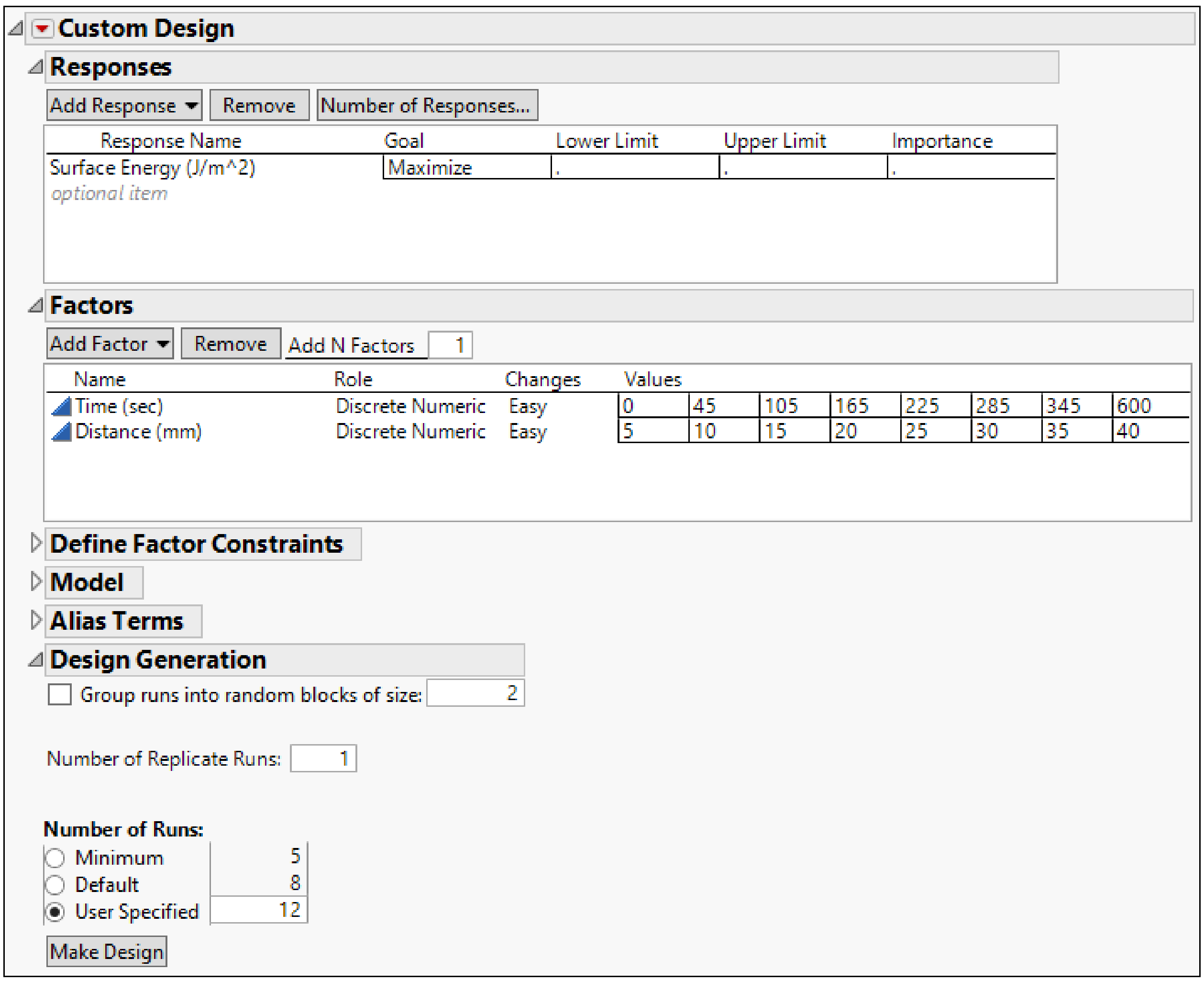

Figure 1: Design of Experiments user interface. In this example, surface energy is being maximized with the variables of time of exposure and distance from the sensor surface.

The DOE functionality takes into consideration that not every data point is required to generate reliable and statistically sound results. In this case, the surface energy wanted to be maximized while considering the effects of time and distance[8]. Once the experimental run table is generated, the experiments are performed as listed and their results entered (Figure 2). With this data, the statistical analysis and predictive modeling were performed.

	Pattern	Time	Distance	Surface Energy
1	1+	0	30	42.01
2	1−	0	10	42.61
3	2−	165	10	58.96
4	2+	45	30	58.14
5	2+	45	30	58.23
6	3+	300	30	70.23
7	3−	600	10	58.41
8	3−	600	10	59.11
9	2−	165	10	59.21
10	3+	300	30	65.39
11	1+	0	30	42.01
12	1−	0	10	42.61

Figure 2: Experimental matrix generated from the DOE. The required runs were reduced from 64 to 12.

<u>Statistical Analysis</u>

The next task was to determine whether the data collected was valid and statistically sound. By using the statistical analysis power of JMP®, this was done quickly and efficiently. To establish that the model being generated by JMP® fits the data well, the lack of fit data was analyzed (Figure 3)[1]. The F-ratio (the ratio of the Mean Square for Lack of Fit and Pure Error) in the lack of fit hypothesizes that the variances between the Lack of Fit and Pure Error mean squares are equal and there is no lack of fit. The null hypothesis is that there is no lack of fit between the model and data, which was confirmed by the p-value for the F-ratio of 0.2458.

Lack Of Fit

Source	DF	Sum of Squares	Mean Square	F Ratio
Lack Of Fit	2	11.969091	5.98455	1.7893
Pure Error	6	20.067950	3.34466	**Prob > F**
Total Error	8	32.037041		0.2458

Figure 3: Lack of Fit data to determine if the model represented the data well. The null hypothesis is that there is no lack of fit between the model and data.

It was then necessary to determine if any significant effects had been omitted from the model by analyzing the residuals. This data is the calculated residuals which are plotted against the predicted values (Figure 4)[1, 4]. If all significant factors are in the model, it would be expected to see the residuals normally distributed about zero.

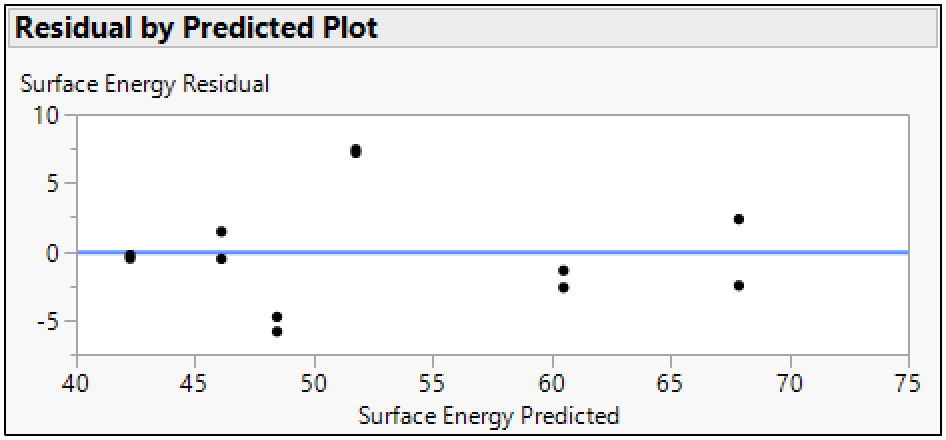

Figure 4: The residuals plot used to determine if any effects were missing from the model. Normally distributed about the zero line indicates that there are no missing effects.

To further confirm that these residuals do follow a normal distribution, a normal continuous fit was plotted against the residuals and the Shapiro-Wilk W-Test was ran against this fit[4]. With the Shapiro-Wilk test, the null hypothesis is that the data does follow a normal distribution and with a calculated p-value of 0.3138, we fail to reject the null hypothesis (Figure 5).

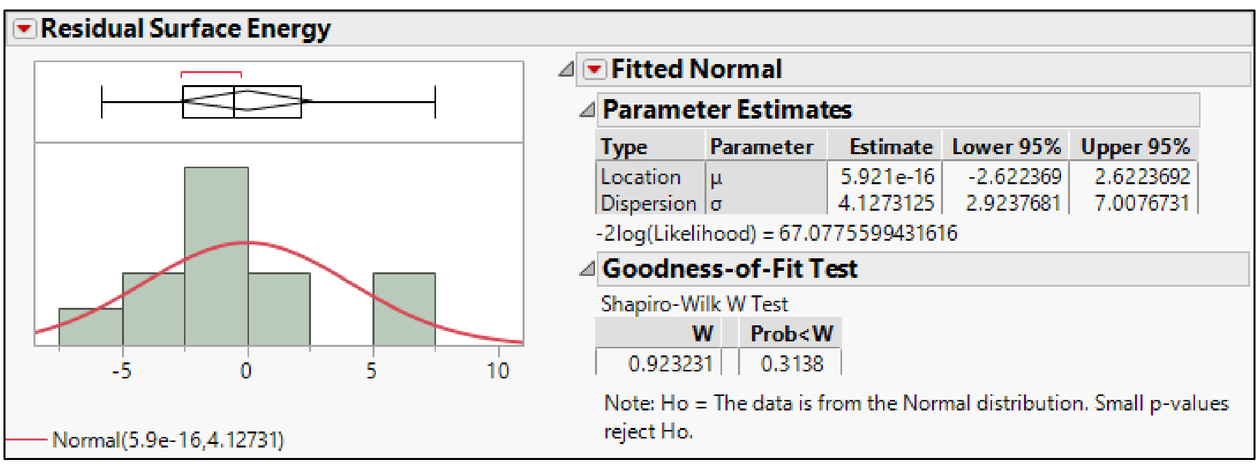

Figure 5: Further confirmation that the residuals follow a normal distribution, confirmed by running the Shapiro-Wilk W-Test. The null hypothesis is that the data comes from a normal distribution.

Now that the model had been confirmed to fit the data and that we aren't missing any major effects, the next step was to determine that we have at least one significant effect in the model and its impact on the results. This was done with the Analysis of Variance data from JMP®. This data showed a p-value of 0.0018 for the F-ratio which indicates that observing an F-ratio this large if all the parameters were zero is unlikely and that there is at least one significant parameter in the model (Figure 6).

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio
Model	3	924.5218	308.174	13.1570
Error	8	187.3818	23.423	Prob > F
C. Total	11	1111.9036		0.0018*

Figure 6: The analysis of variance data shows that there is at least one significant effect in the model. The null hypothesis is that there are no significant effects.

With at least one significant effect in the model, it was important to determine which effect it was. Looking at the Effect Tests in JMP® tells us this information. The F-ratio of this data represents whether or not the particular effect is zero; the larger the ratio, the more the impact of the effect[4]. The null hypothesis is that there is no effect and as can be seen in Figure 7, the parameters 'Time' and 'Time*Distance' have significant effects at the 95% confidence interval and 'Distance' at the 90% confidence interval.

Effect Tests

Source	Nparm	DF	Sum of Squares	F Ratio	Prob > F
Time	1	1	914.85649	39.0585	0.0002*
Time*Distance	1	1	350.57225	14.9672	0.0047*
Distance(10,30)	1	1	88.43373	3.7756	0.0879

Figure 7: The effects test shows which variables have the largest impact on the result. In this case, Time has the largest impact.

As can be seen, the statistical power of JMP® is not only very potent, but also extremely easy and fast. All the data discussed took less than 30 minutes to calculate and interpret, whereas if it had been done by hand, it might have been several hours or days. With these data, it was then possible to take the analysis a step further and look into predictive modeling.

<u>Predictive Modeling</u>

One of the true powerhouse functionalities of JMP® is its ability to take the data and predict what levels of the parameters presented will give optimal results[1]. Within the Prediction Profiler function, it was analyzed to maximize the surface energy and read out the optimal time and distance results. In this case, the prediction was a plasma treatment time of 300 seconds at a distance of 30 mm from the sensor surface would result in a maximal surface energy of 67.9 J/m^2 (Figure 8).

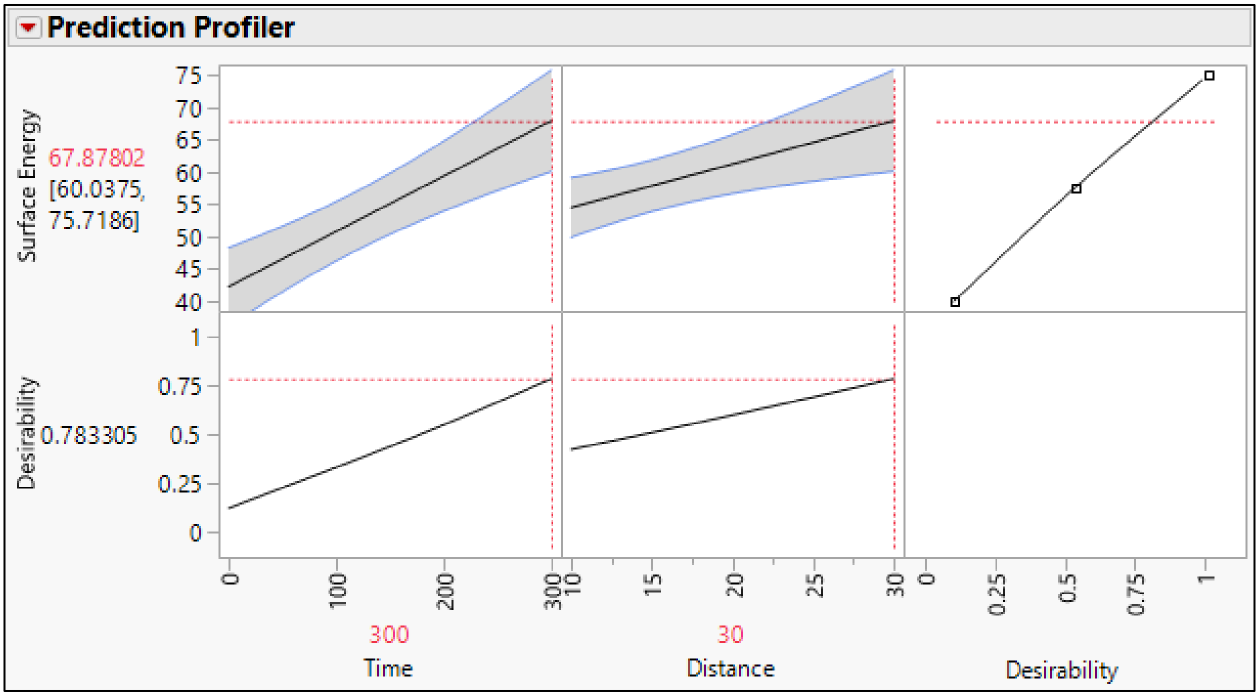

Figure 8: The prediction profiler shows that using a time of 300 seconds and a distance of 30 mm will achieve the best results for surface energy at 67.9 J/m^2.

In order to verify what the predictive modeling showed, three more experimental runs were done at these values. The results can be seen in Table 2, confirming that JMP® was able to predict the optimal levels for each parameter to maximize the surface energy.

Experimental Runs for Predictive Modeling Confirmation (300 seconds at 30 mm distance)	
Experimental Run	**Surface Energy (J/m^2)**
Run 1	67.23
Run 2	68.11
Run 3	67.59

Table 2: Experimental results after running prediction profiler parameters.

The goal of these analysis was to maximize the surface energy and thereby the wettability of NP. As can be seen in Figure 9 and Figure 10, there is a 200% decrease in contact angle. This correlates to a nearly 20 J/m^2 increase in surface energy which allowed this project to move forward with consistent results after being at a standstill for months.

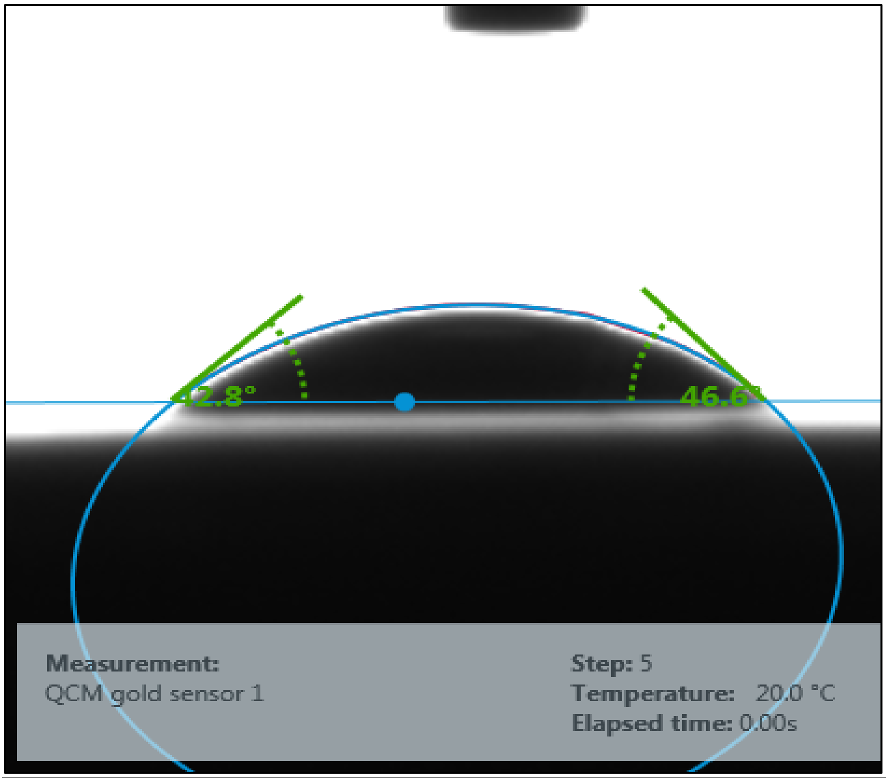

Figure 9: Analysis of contact angle of NP on an untreated gold coated quartz crystal sensor as measured by a drop shape analyzer.

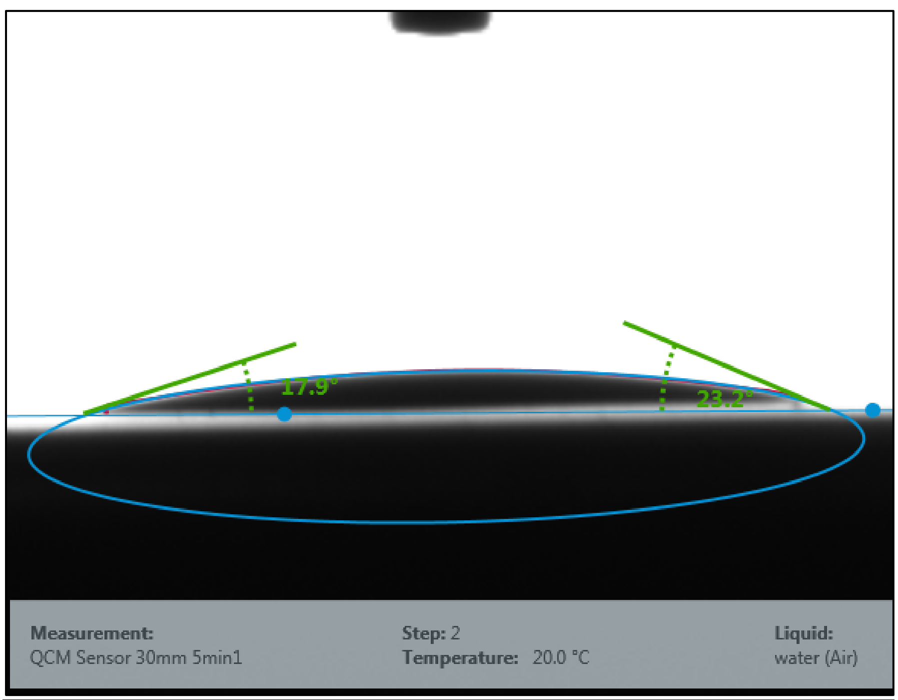

Figure 10: Analysis of contact angle of NP on a treated gold coated quartz crystal sensor as measured by a drop shape analyzer. There is a decrease of 200% in contact angle resulting in much higher wettability of the surface.

Conclusions

The JMP® software was used on this project to accelerate its progress with minimal use of time and resources. The DOE functionality allowed for the design of an efficient and optimal experimental designs, resulting in quick, reliable results. Using these results, the statistical analysis functionality was capable of creating a reliable model, indicate which effects had the largest impact and ensuring the data was statistically sound. Finally, predictive modelling allowed the use of these results to analyze the optimal levels of each parameter to maximize the surface energy of the gold coated sensor.

Using these methods, it was possible to increase the wettability of the gold coated quartz crystal sensor by over 200% with only two days of experimentation and minimal use of resources and time. This also allowed a project to continue that had been suffering sample preparation issues for months and has resulted in good, repeatable results.

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