

Evaluation Of Automated Low-Field Nuclear Magnetic Resonance (NMR) Relaxometry For Analysis Of Silicone Polymers

Federal Manufacturing & Technologies

M. H. Wilson

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M.H. Wilson, Project Leader

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Abstract

Screening studies and Design of Experiments (DoE) were performed to evaluate measurement variation of a new, non-destructive Nuclear Magnetic Resonance (NMR) test system designed to assess age-induced degradation of Outer Pressure Pads (OPP). The test method and results from 54,275 measurements are described. A reduction in measurement error was obtained after metal support struts were replaced with plastic support struts adjacent to the front position of the test chamber. However, remaining interference and a lack of detecting any age-related degradation prevent the use of the NMR system as a non-destructive surveillance test for OPPs. A cursory evaluation of the system with cellular silicone samples obtained more uniform results with increased error as measurements approached the sample's edge.

Summary

New surveillance tests are being evaluated to improve diagnostics on aged polymer cushions and pads of Lawrence Livermore National Laboratory (LLNL) systems. A novel instrument has been designed using Nuclear Magnetic Resonance (NMR) coupled with automated data collection. A prototype has been installed at the Kansas City Plant (KCP) to evaluate its use for surveillance testing. The minispec ProFiler determines the ^1H NMR spin echo time constant, T_2 , which provides an indirect measure of average crosslink density as an indicator for extent of degradation with age.

Previous tests of the new system identified anomalous random noise in measurements, variance in curve fits, and possible error caused by a nearby metal component adjacent to measurement locations within the chamber [1]. The results indicated that a metal support strut adjacent to the front position in the chamber interferes with the measurements and there is a measurement property gradient from the front to the back of the chamber. Recommendations from a previous Design of Experiment (DoE) have been completed that replaced metal parts with plastic parts. The DoE was repeated to determine the effectiveness of the new plastic parts to reduce measurement variation. 41,472 measurements were taken during various screening tests and the repeated DoE. The results showed that replacing the metal parts with plastic parts had a strong effect and eliminated the major noise interference patterns observed in the previous DoE study. However, the level of variation is still relatively large and now indicates a property gradient in certain measurements from the left side to the right side of the chamber.

An additional 12,803 measurements were taken on surveillance Outer Pressure Pads (OPPs) and a cellular silicone sample. The ProFiler was not able to distinguish recently molded OPPs from surveillance-returned OPPs. This and other experimental variation limits the instrument's capability to primarily detecting combinations of large internal voids or grossly undercured areas that contain <50% of the recommended catalyst level. More importantly, whereas the ProFiler can detect large differences in crosslink density in flat slab samples, it appears the level of age-related changes in OPP crosslink density has not progressed enough, and are below the detection limit of the present configuration. Thus, the ProFiler, in its current configuration, is not recommended for use as a non-destructive surveillance test method for the OPPs.

The ProFiler may still be a suitable tool for other types of material, and results on a cellular silicone sample showed good repeatability considering the larger, more uniform sample thickness and after eliminating known adverse edge effects. Significant challenges would have to be overcome to measure samples with curved surfaces or unusual shapes in order to mitigate the kind of variation seen in these studies due to non-uniform amounts of material in the measurement field based on the sample area's relative proximity to the ProFiler's surface.

Discussion

Scope and Purpose

Evaluate new surveillance methods based on NMR testing to improve diagnostics on polymer cushions and pads of LLNL systems. Because OPP production plans were halted with the cancellation of the weapons project, the scope was modified to develop this test for surveillance OPP diagnostics and other applicable materials, accomplished through the installation and validation of the minispec ProFiler at KCP.

Prior Work

This report updates work previously reported and documents the results of replacing metal parts with plastic parts on the automated measurement system [1].

Activity

Background

In order to improve diagnostics on polymer cushions and pads of LLNL systems, new surveillance tests are being evaluated to detect crosslink density changes with age. A new test method has been developed and validated based on a unique system design using static, uniaxial NMR relaxometry coupled with automated data collection [2]. A prototype system has been installed at KCP to evaluate its use for surveillance testing.

The prototype installed at KCP comprises an automated system that was developed with Bruker Optics, Inc., (The Woodlands, TX) to allow multiple measurements without operator intervention. The magnet of the minispec ProFiler is mounted to a modified commercial Autosampler (Duratech, Waynesboro, VA) and controlled via an attached PC for automated measurements (Figure 1). Large numbers of manual sample measurements with the ProFiler are impractical and also are prone to measurement error because of variation in placement of the probe during repeated measurements. The precise control offered by the automated system greatly minimizes this variation.

An enclosure (metal honeycomb box) also was constructed to contain the entire system and block possible electromagnetic interference (EMI). Testing with and without the enclosure showed no effect within the local room environment. Nevertheless, the equipment is operated within the enclosure as a precautionary measure.

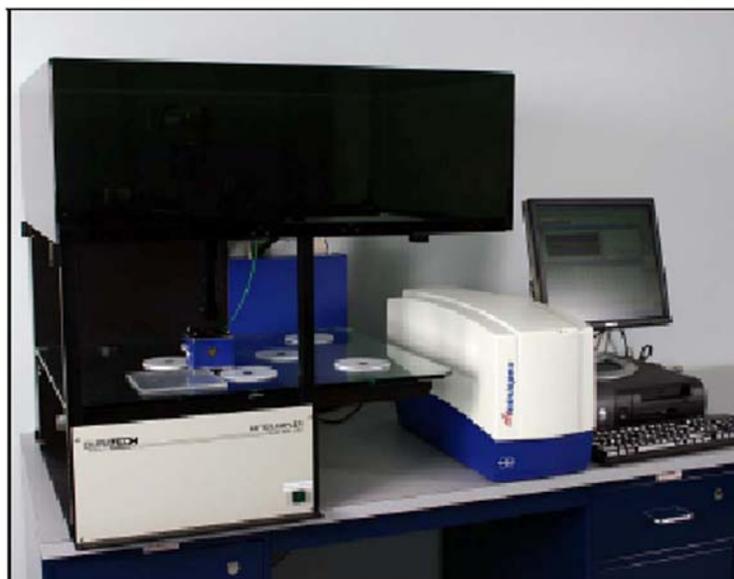


Figure 1. Minispec NMR and Automated System
(Note: EMI enclosure is not shown.)

The measurements are performed using spin-echo decay curves obtained via a Carre-Purcell-Meiboom-Gill (CPMG) pulse sequence [3] with the minispec ProFiler operating at 16 megahertz (MHz). The ProFiler determines the ^1H NMR spin echo time constant (T_2), which provides an indirect measure of average crosslink density [4]. The dimensions of the ceramic measurement window on the ProFiler are 53 by 20 millimeters (mm).

Previous DoE work determined the relationship between instrument parameter settings, material properties, and resulting T_2 values. The optimized parameter settings were: gain=115, echo time=0.5, number of echoes=500, recycle delay=1.0 sec. These settings were used for characterization studies on Dow Corning DC745 silicone test slabs (approximately 6 x 6 x 0.075 inch) molded with various peroxide curative levels (0% to 175% of recommended level). Typically, increasing T_2 values correlate with lower crosslink density because of the greater time scales involved for reduced crosslink regions to return to equilibrium. However, for the material samples in these studies, increasing T_2 values correlate with higher crosslink density (Figure 2). Physical properties dependent on crosslink density such as solvent swell (toluene) and tensile/elongation also were found to correlate with the T_2 results for these samples (Figure 3). This behavior is counterintuitive and possible explanations have been offered for the difference with high-field NMR observations; *e.g.*, influence and detection of unique sample effects only at the surface versus the bulk [5]. These samples reveal that significant quantities (<50%) of catalyst must be left out or a very inhomogeneous mix of the DC745/peroxide system must occur before noticeable changes are detected with T_2 .

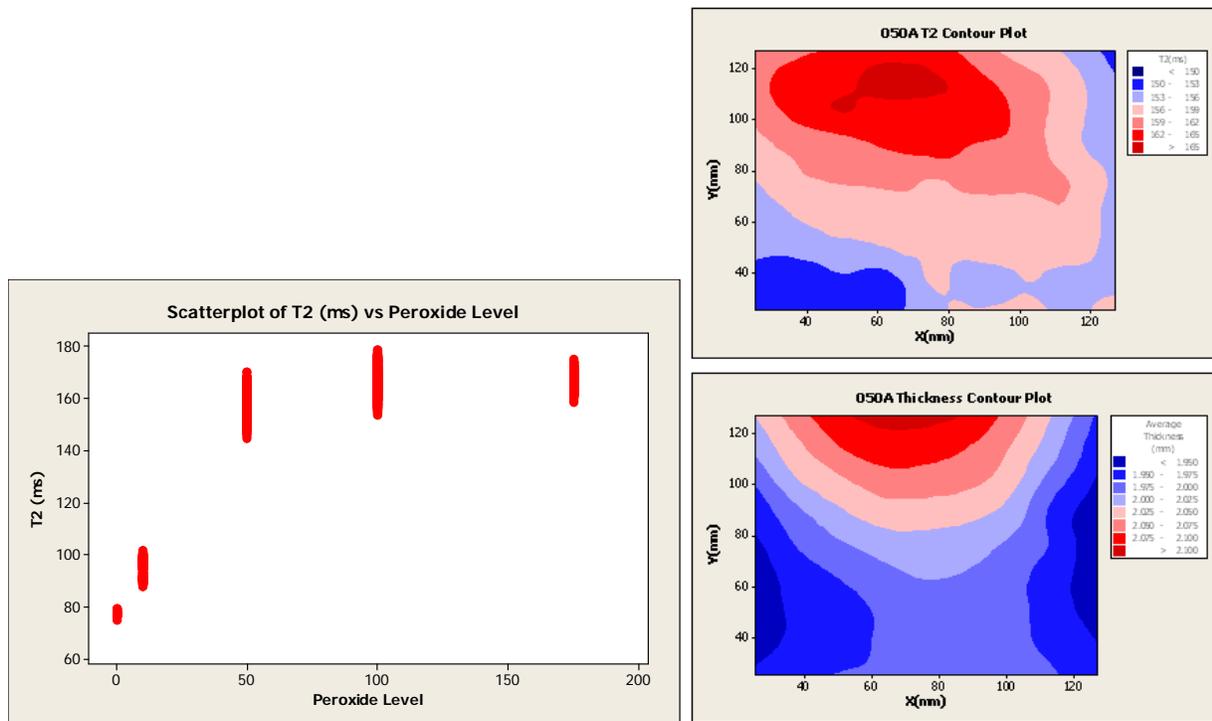


Figure 2. Minispec ProFiler Measurements Show a Correlation Between Increasing T_2 Values With Increasing Levels of Peroxide, *i.e.*, Average Crosslink Density That Reaches a Maximum Upon full Cure of the Available Reactive Sites (graph on left). Peroxide level is shown as a percent of recommended level. Also, a general increase in T_2 with thicker areas of the test slab is indicated showing a sensitivity to amount of material in the measurement field (contour plots on right).

T_2 measurements were found to be sensitive enough to distinguish which mold cavity was used and also to show a general correlation with thickness (Figure 2). Thus, it was discovered that the T_2 values obtained not only correlate with crosslink density, but also with the amount of material in the detection volume (*i.e.*, material bulk density reduced by thickness, voids, gaps, etc.). Consequently, lower T_2 values in damaged areas of OPPs may be confounded with the quantity and/or spatial morphology of the damaged areas. These damaged areas may contain less material or a redistribution of material that reduces T_2 relative to adjacent, undamaged areas. More study is needed to confirm this effect and to understand the relative contribution from lower crosslink density versus material distribution within the ribbed areas of the OPP.

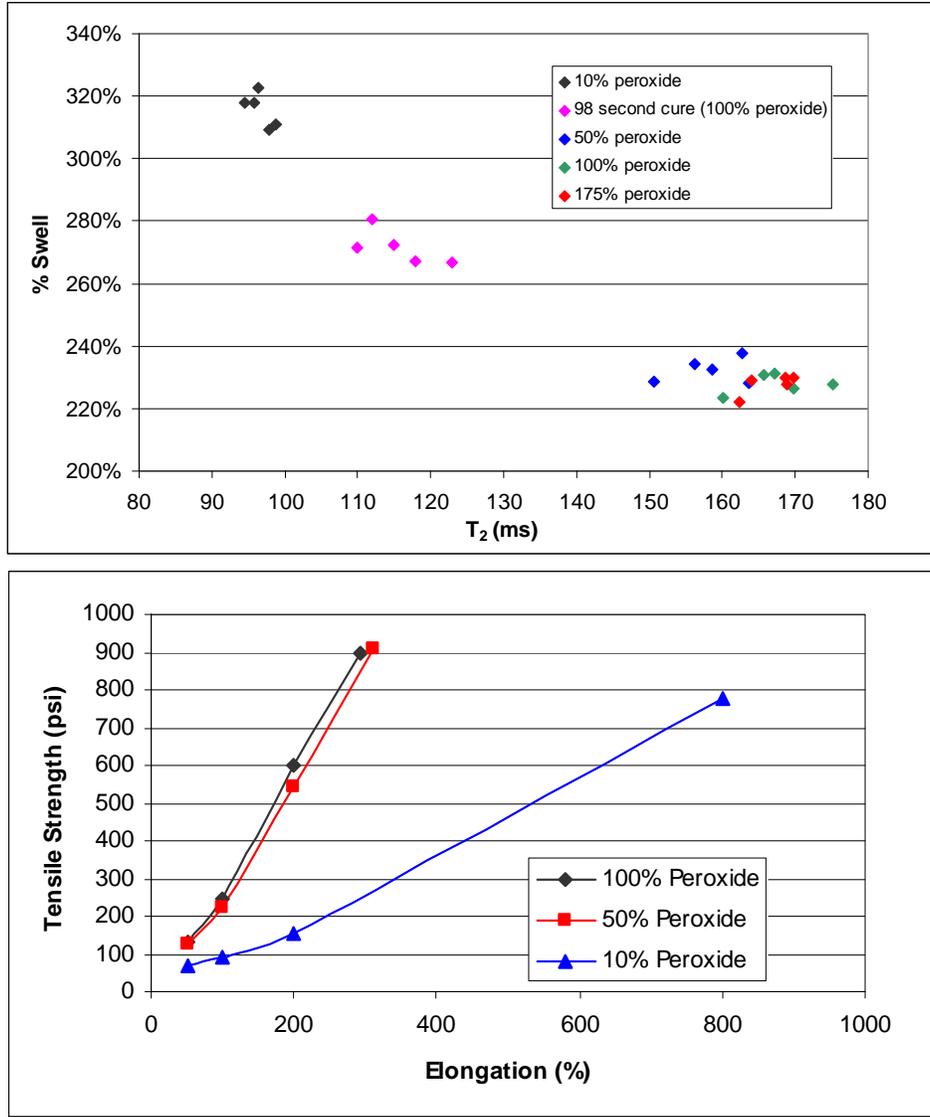


Figure 3. Solvent Swell and Physical Property Correlation With Peroxide Level and Measured T_2 Values. Peroxide level is shown as a percent of recommended level.

Other prior work focused on rotating OPPs beneath a stationary ProFiler and also on determining the proper orientation alignment of the magnet over the OPP during motion control by the Autosampler. Subsequent screening tests identified anomalous random noise in measurements, variance in curve fits to determine T_2 , and measurement error caused by nearby metal struts adjacent to arbitrarily assigned measurement locations within the chamber [1]. Results of a DoE lead to replacing three metal support struts that contributed to measurement interference with polyethylene parts (Figure 4). The DoE was repeated using the same OPPs to evaluate the effects of the plastic parts on T_2 measurements.

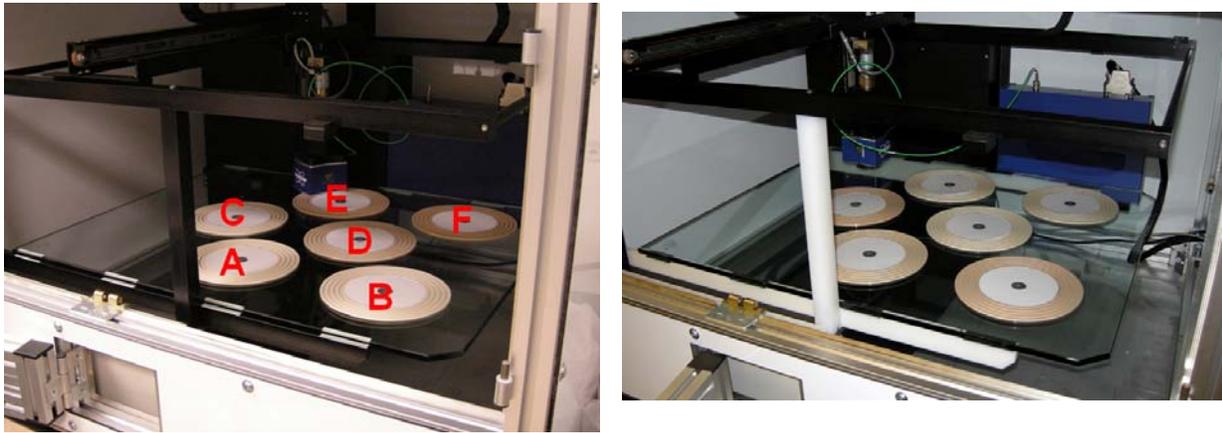


Figure 4. OPP Measurement Locations With Metal Support Struts on Left. Photograph on right shows plastic replacement parts (white) installed in front and back of measurement chamber. EMI enclosure is shown with front doors removed.

Simulated Data and Measurement Methodology

OPPs are marked at a single reference location by an ink pen with a + mark on the outer rib. T_2 is measured in 5° increments counterclockwise around the OPP at radiuses centered over the gaps at 62, 69, 77, and 84 mm. An idealized data set shows the difference in T_2 values after simulated measurements of an OPP for three conditions (Figure 5):

1. The black symbol (\) shows the baseline position with the + mark at 12:00 position on the OPP (*i.e.*, away from the front of the chamber).
2. The blue symbol (/) shows measurements after turning the OPP by 180° (*i.e.*, the + mark is at the 6:00 position on the OPP placing it closest to the front of the chamber).
3. The red circle (o) shows measurements with the + mark in the 12:00 position on the OPP away from the front of the chamber and then flipping the OPP upside down (*i.e.*, with the ribs contacting the glass).

An OPP (1) was measured in the baseline position and then these individual data measurements were assigned to be the same after rotating or flipping the part, thus assuming that there is no external interference on the measurements. With no interference (or experimental error), the three curves are identical in the top plot and represent the unrealistic goal of the measurement system to be exactly repeatable and thereby independent of OPP orientation.

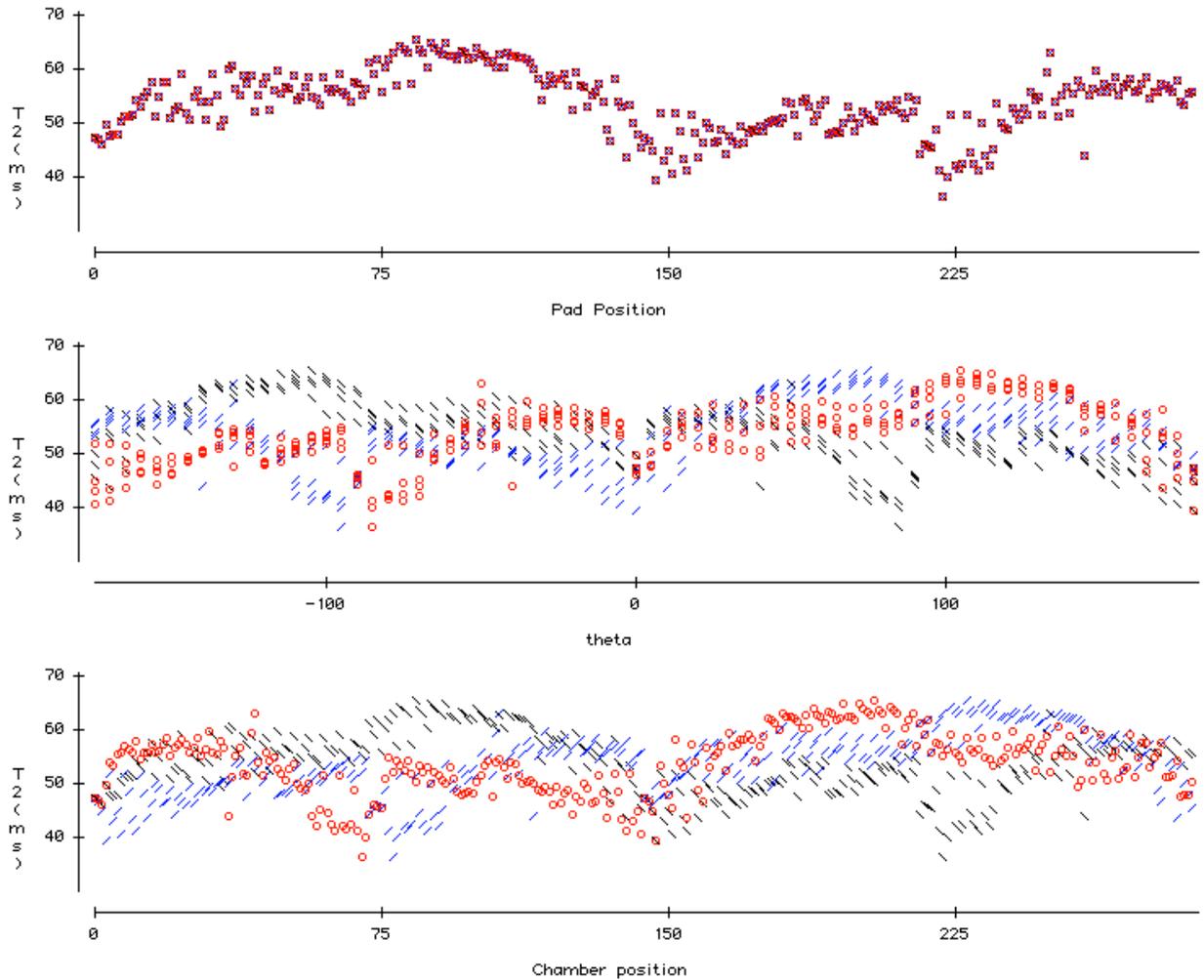


Figure 5. Simulated Data of Rotating or Flipping OPP. (Units for T_2 are ms)

Pad Position denotes the sequential measurement locations on the OPP starting with position 0 at 12:00 at a radius of 62 mm. The minispec moves radially out from the inner gap at 62 to 69, 77, and 84 mm and then moves counterclockwise 5° repeating this sequence while incrementing the number locations from 0 to 287. The middle plot shows the T_2 values versus theta angle position around the OPP. Theta is the ProFiler rotational angle relative to the chamber with theta = 0° at 12:00, (*i.e.* back of chamber), theta = -90° at 9:00, theta = 180° at 6:00, (*i.e.*, front of chamber) and theta = 90° at 3:00. At angle theta = 0, the Pad Position is location 0 and the + mark is farthest away from the front of the chamber. Chamber positions are the locations relative to the chamber at the theta measurement angle, as if the OPP were sitting in the chamber with locations marked on the glass.

If the data is independent of relative chamber position, then data measurements should have relatively low variability and have an appearance similar to the top plot where the data reasonably lies on top of each other after the described rotations. Furthermore, plotting data by chamber position or theta helps to identify areas that are more or less sensitive to variation due to relative location within the chamber.

DoE For Comparison of Metal Versus Plastic Chamber Struts

DoE evaluations of the robotics chamber were performed to determine the effects of the local environment on the NMR measurement repeatability before and after installation of plastic struts at the front and back of the chamber. A prior study [1] has been repeated after replacing the metal parts with plastic parts. The DoEs were designed to map all of the OPP locations in the chamber by measuring six individual OPPs in each of the six measurement locations to determine if there is a neutral measurement area unaffected by OPP position (Tables 1 and 2 and Figure 4). The Autosampler was programmed to record 288 measurements in 5° increments around the OPP centered over the gaps between the ribs at radial distances of 62, 69, 77, and 84 mm. Three replicates were measured per condition (288 x 3 = 864 measurements per OPP) comprising 31,104 measurements for the complete DoE. In addition, a repeatability study (Table 2 studies 22-24) was performed by measuring one of the DoE conditions two extra times for a total of 41,472 measurements for testing the effects of the plastic parts. The DoEs had the following factors:

Fixed Factors

- Echo Time: 0.500 ms
- Number of Echoes: 600
- Recycling Delay: 0.5 sec

Variable Factors

- Six OPPs
 - 3 surveillance: 2, 3, and 1
 - 3 newly molded: 4, 5, and 6
- Gain: 115 dB
- Six chamber measurement locations: A, B, C, D, E, and F

Study No.	OPP Chamber Position					
	A	B	C	D	E	F
11	2	3	4	5	6	1
12	3	4	5	6	1	2
13	4	5	6	1	2	3
14	5	6	1	2	3	4
15	6	1	2	3	4	5
16	1	2	3	4	5	6

Table 1. Location of OPP by Number Within Chamber for DoE With Metal Parts

Study No.	OPP Chamber Position					
	A	B	C	D	E	F
22	1	2	3	4	5	6
23	1	2	3	4	5	6
24	1	2	3	4	5	6
25	2	3	4	5	6	1
26	3	4	5	6	1	2
27	4	5	6	1	2	3
28	5	6	1	2	3	4
29	6	1	2	3	4	5
30	7	-	-	-	-	-
31	8	-	-	-	-	-
32	9	-	-	-	-	-
33	10	-	-	-	-	-
34	11	-	-	-	-	-
35	12	-	-	-	-	-
36	13	-	-	-	-	-
37	14	-	-	-	-	-
38	15	-	-	-	-	-
39	16	-	-	-	-	-
40	17	-	-	-	-	-
41	18	-	-	-	-	-
42	19	-	-	-	-	-
43	19	-	-	-	-	-
44	20	-	-	-	-	-

Table 2. Location of OPP by Number Within Chamber for DoE, Repeatability Study, and Comparison to Surveillance OPPs With Plastic Parts

Outliers and Anomalies

For reasons not completely understood, the level of noise and variation in distribution of signal/noise (S/N) ratios were much higher for studies 22-29, especially for study 22, than the previous DoE, studies 11-16 (Figure 6). The biexponential fit option within the software attempts to fit the CPMG data into a bi-exponential function and returns two time constants (T_21 and T_22), their amplitudes (A1 and A2), and an offset. If only a single exponential function is found, it will return a time constant (T_2), its amplitude (A) and raw data offset. If no fit is found or if the raw data is too weak, 0 or -1 will be returned as fitted results. Single exponential fitting will be applied if this option is de-selected.

T_2 Error is a measure of the bi-exponential goodness of fit algorithm with lower numbers indicating a better fit of the data. In studies 11-16 with metal struts, only 269 (0.86%) outliers out of 31,104 measurements were omitted from the analysis: 264 T_2 Error (≥ 1.3), four $T_2 = -1$, and one $T_2 = 0$. The level of high T_2 error values was much larger for the plastic part DoE and exhibited a bi-modal distribution (Figure 7). The only observable difference, besides the replacement of metal struts with plastic struts, was that the room temperature was as much as 10°F higher for most, if not all, of studies 22-29. Detailed temperature records were not kept for the room but the higher temperatures correlate with the HVAC system switching from summer

cooling to winter heating. During previous discussion with Bruker Inc., it was noted that temperature changes as small as a couple of degrees Fahrenheit could affect the data measurements and lead to variation in measurements.

Using the same criteria to discard outliers from studies 11-16 for studies 22-29, the following 8,155 (19.7%) outliers out of 41,472 measurements were omitted:

- 919 (2.2%) measurements (55 for OPP 4 at location D in study 22 and all 864 for OPP 1 at location B in study 29) were outliers and had poor S/N ratios ≤ 16 . These outliers had poor regression fits that produced much higher T_2 Error and spurious T_2 values. Poor S/N ratio behavior has been witnessed before when the minispec cable gets temporarily trapped between the probe and OPP. The 55 outliers at location D were limited to the lower right hand quarter of OPP 4 during the first rep which would be consistent with the cable getting briefly trapped. Although this may explain the low S/N values, it does not explain the higher overall noise values for study 22. The 864 outliers for OPP 1 indicate the cable may have been trapped during all three reps of the entire OPP. The cable being trapped for such a long measurement period spanning multiple reps has never been witnessed before.
- 12 (0.03%) measurements were outliers and also were omitted: nine $T_2 = -1$, and three $T_2 = 0$.
- Lastly, 7,224 (17.4%) measurements were omitted: 26 T_2 Error values ranging from 0 to 0.4, and 7,198 T_2 Error ≥ 1.3 . Graphs of the before condition and after omitting the outliers are shown in Figure 8.

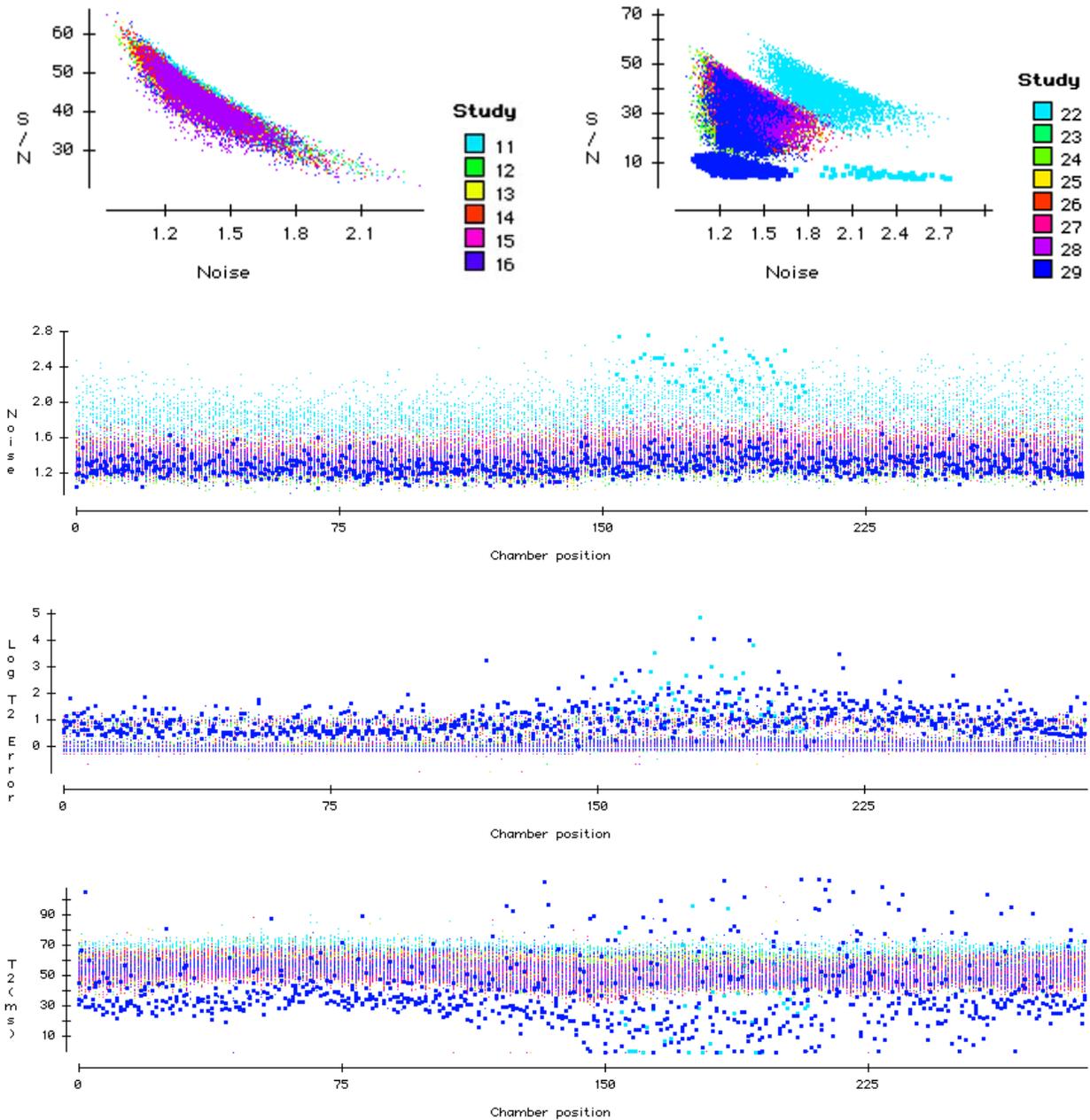


Figure 6. Plots Showing Bi-modal Distribution With Study 22 and Other Outliers Separated From the Other Studies. 881 (2.1%) out of 41,472 measurements (55 for OPP 4 at location D in study 22 and all 864 for OPP 1 at location B in study 29, 11 $T_2 = 0$ at random locations were outliers and had low signal-to-noise (S/N) ratios ≤ 16). Bold symbols show location of outliers and possible trapped cable.

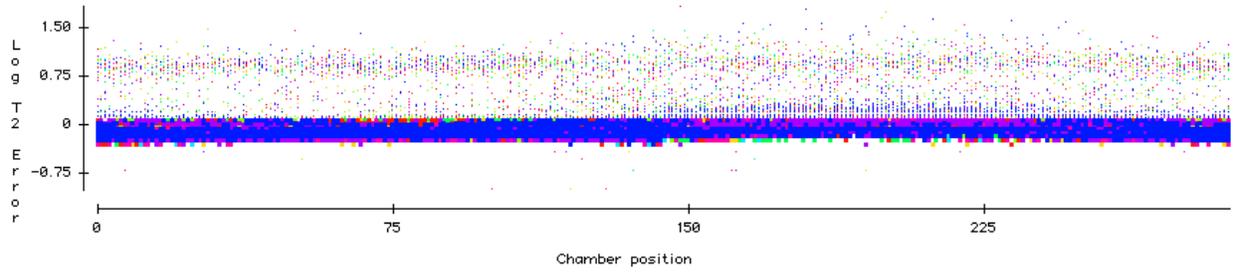


Figure 7. T_2 Error Bi-Modal Distribution Showing 7,224 Outliers as Unbolded Symbols

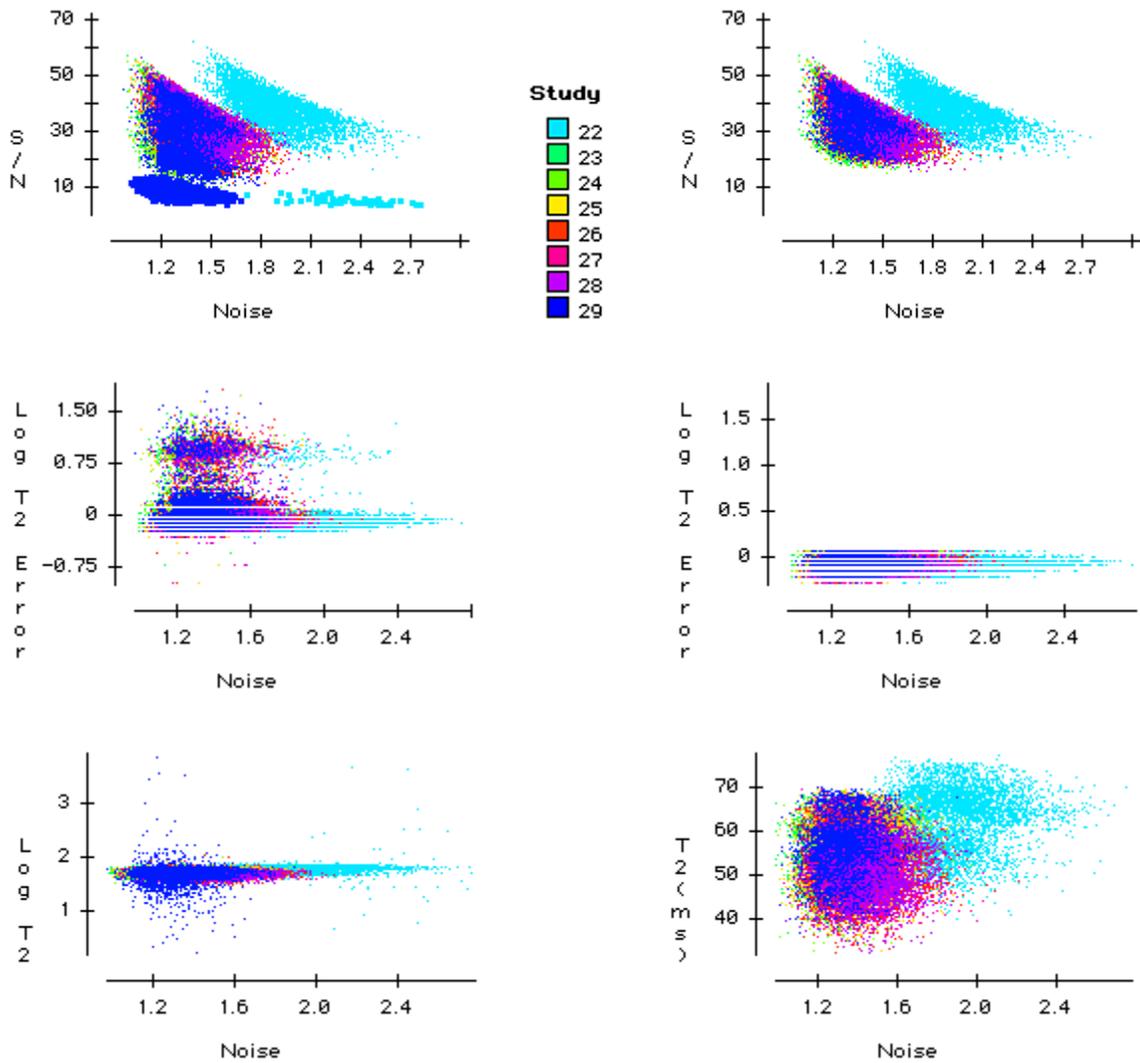


Figure 8. Graphs on the Right Show the Data set Remaining After Omitting 8,155 (19.7%) Outliers

Repeatability Study Results With Plastic Parts

Repeatability was evaluated by measuring OPPs in the same location 9 times over 3 separate study runs, studies 22-24 (Figures 9 thru 16). Between each study, the OPPs were removed from the chamber and replaced in the same location. The data show that study 22 was clearly very different than the subsequent two studies in terms of noise, therefore T_2 from study 22 and was omitted from the DoE statistical analysis. Study 22 was the first testing performed after installation of the plastic parts and study 23 began approximately a week after study 22 ended. The cause of this difference is unknown. Studies 23 and 24 had much more repeatable results but also are statistically distinguishable from each other.

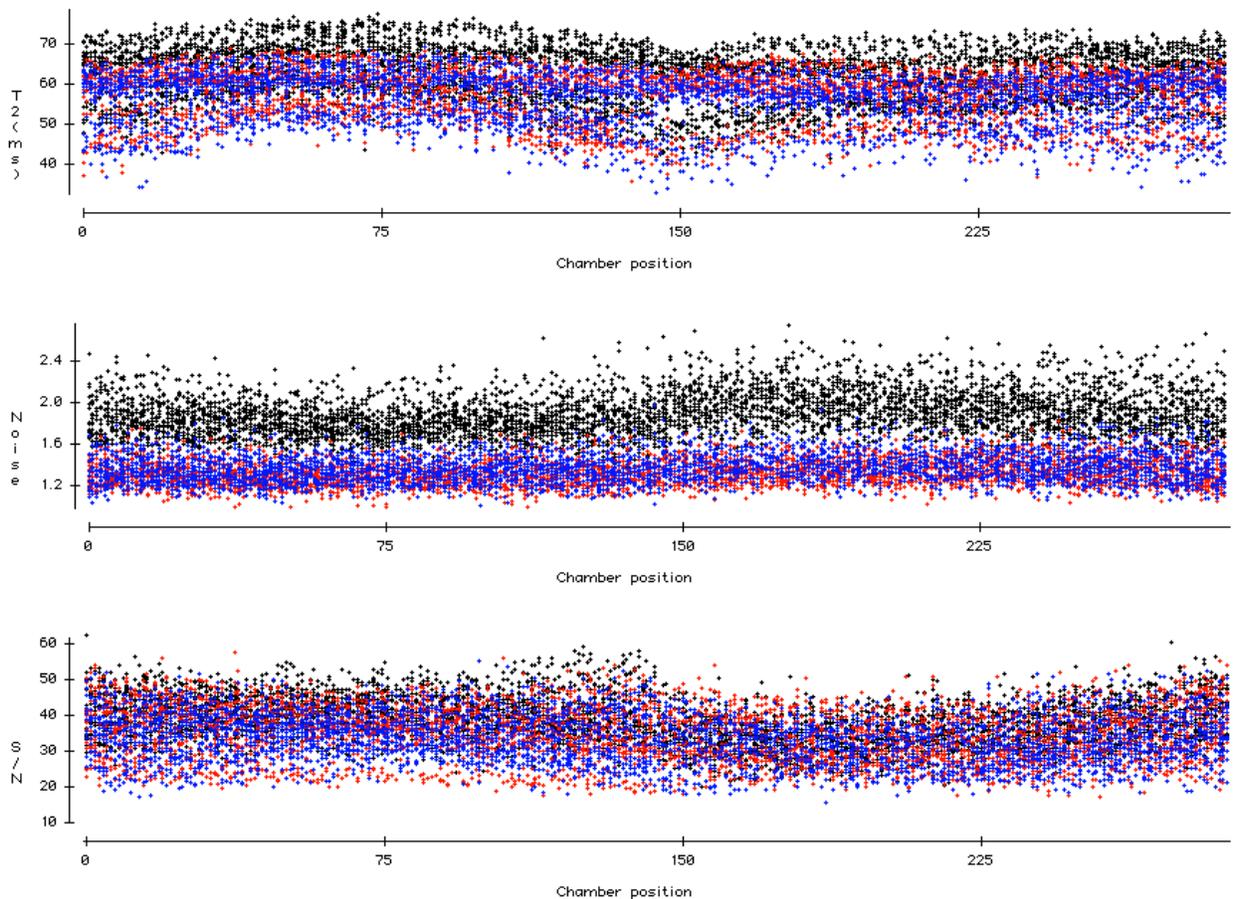


Figure 9. Repeatability Study Measurements With Outliers Omitted. These are black = study 22 (4,963 measurements), red = study 23 (4,238 measurements), and blue = study 24 (3,955 measurements).

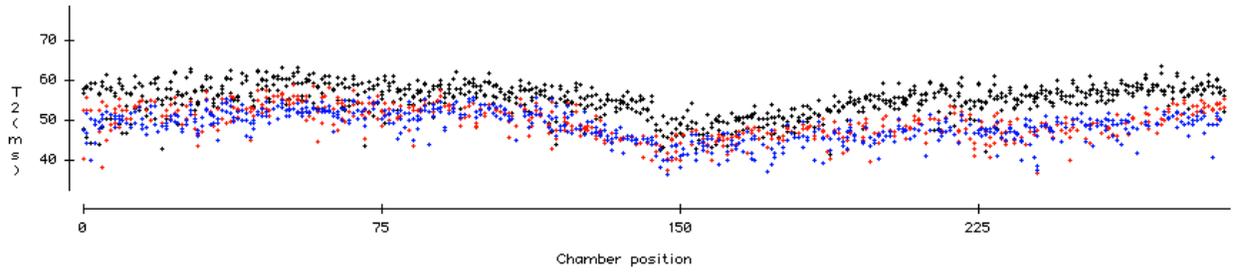


Figure 10. Repeatability Study Measurement of OPP 1 in Position A With Outliers Omitted. These are black = study 22, red = study 23, and blue = study 24.

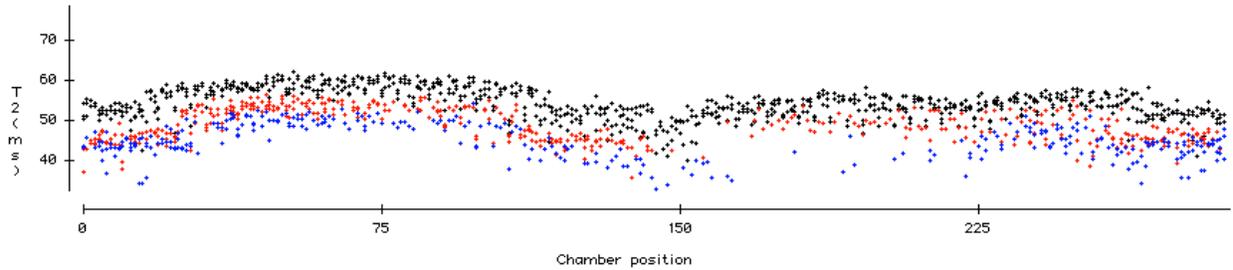


Figure 11. Repeatability Study Measurements of OPP 2 in Position B With Outliers Omitted. These are black = study 22, red = study 23, and blue = study 24.

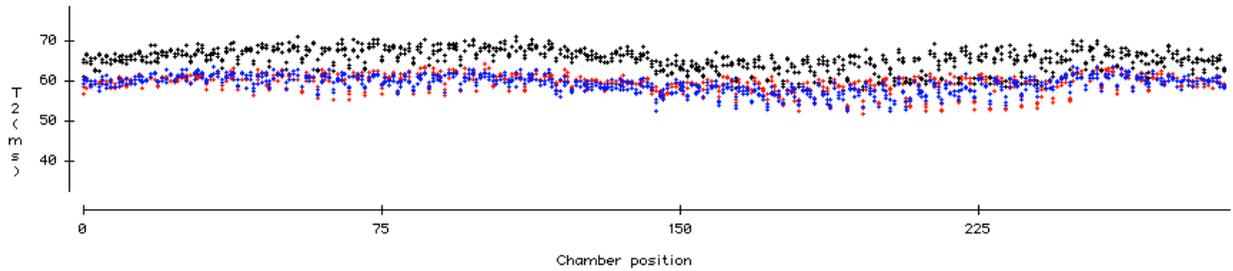


Figure 12. Repeatability Study Measurements of OPP 3 in Position C With Outliers Omitted. These are black = study 22, red = study 23, and blue = study 24.

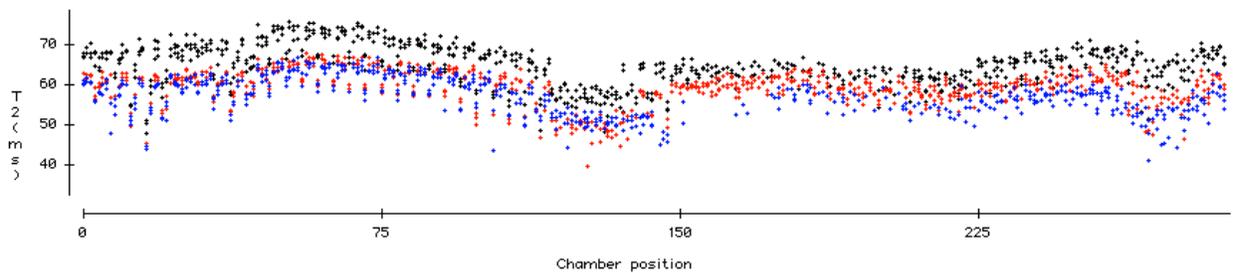


Figure 13. Repeatability Study Measurements of OPP 4 in Position D With Outliers Omitted. These are black = study 22, red = study 23, and blue = study 24.

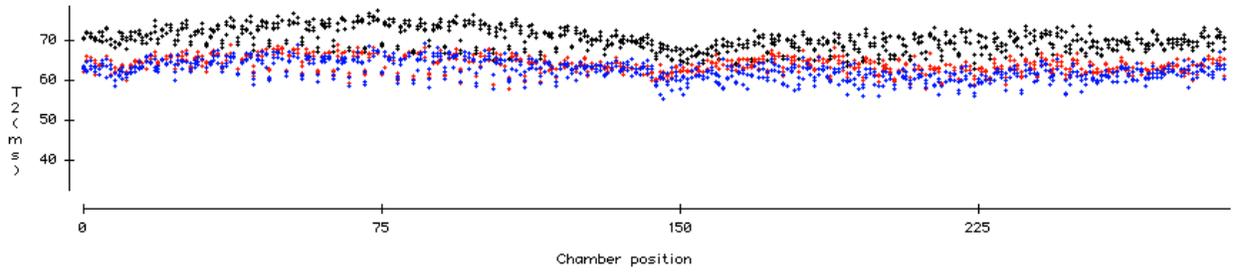


Figure 14. Repeatability Study Measurements of OPP 5 in Position E With Outliers Omitted. These are black = study 22, red = study 23, and blue = study 24.

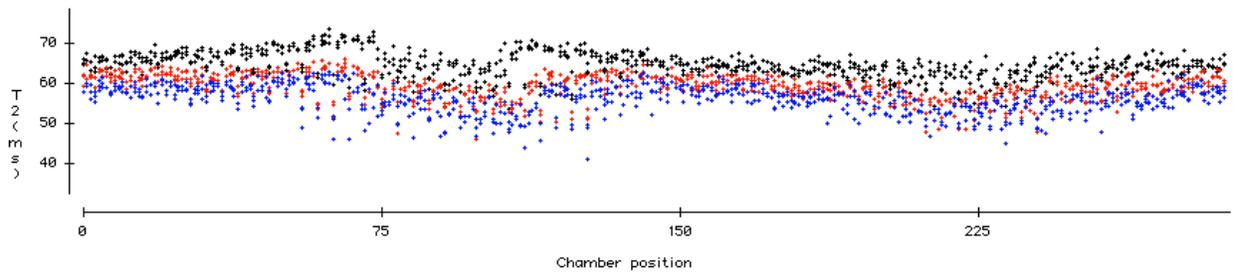


Figure 15. Repeatability Study Measurements of OPP 6 in Position F With Outliers Omitted. These are black = study 22, red = study 23, and blue = study 24.

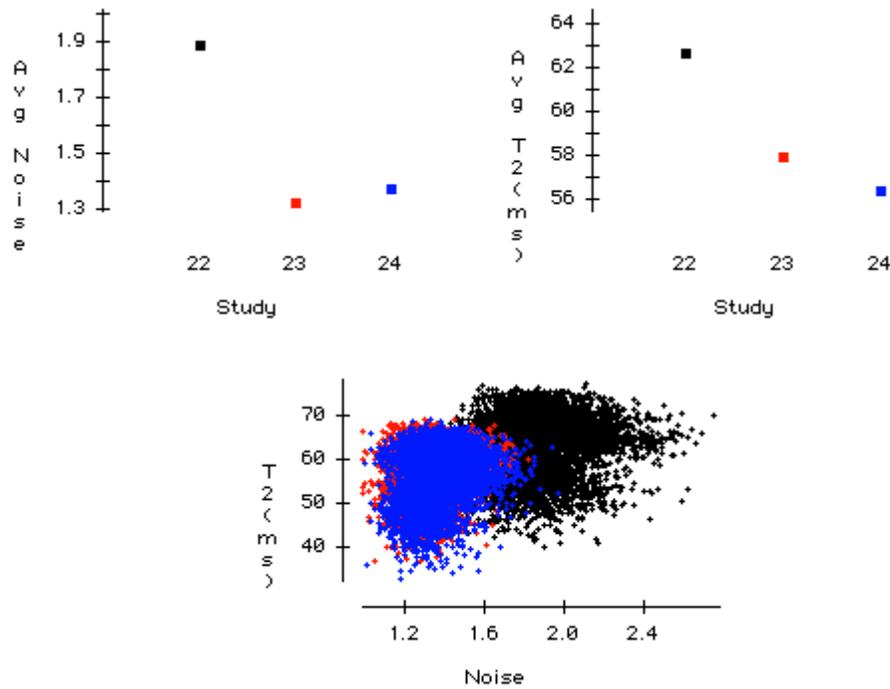


Figure 16. Repeatability Studies With Outliers Omitted Showing Average Values and Relationships

DoE Results Comparing Effect of Replacing Metal Parts with Plastic Parts

The statistical analysis of the DoE comprised 28,354 measurements from studies 23-29. Replacing the metal struts with plastic struts had a strong effect and eliminated the noise interference pattern observed at the front of the chamber in the previous DoE (Figure 17).

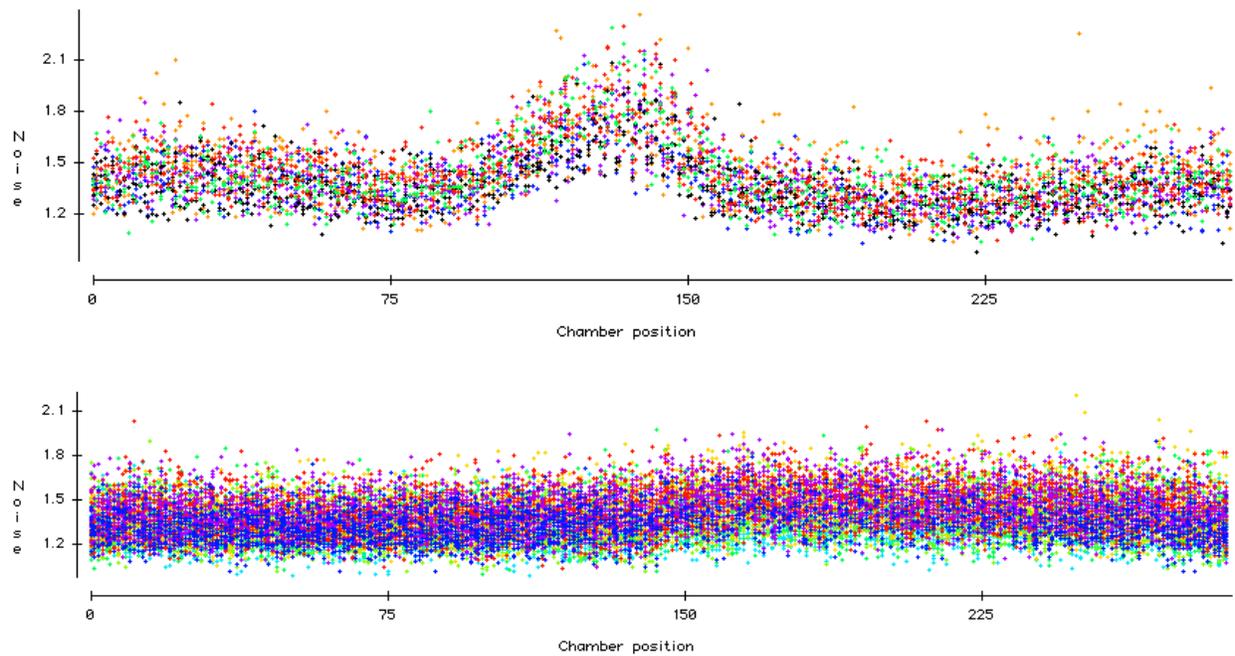


Figure 17. Noise Correlation With Chamber Location for all OPPs Showing Reduction in Noise at Position A After Replacing Metal Struts With Plastic Struts. *Top graph shows adverse effect of metal parts at Position A for studies 11-16. Bottom graph shows better noise uniformity for all positions A-F in studies 23-29.*

Figure 18 graphically depicts the effect on measurements by switching to plastic parts. The plastic parts affected all relationships for all of the measurements. One significant change is the trend in higher noise from front to back, which is the opposite of the noise trend with the metal parts previously observed. The S/N ratio is now significantly lower and chamber positions to the right have lower S/N relative to chamber positions on the left (Figure 19). T_2 values also were lower and the values in chamber positions to the right measure lower relative to chamber positions on the left (Figures 20-22).

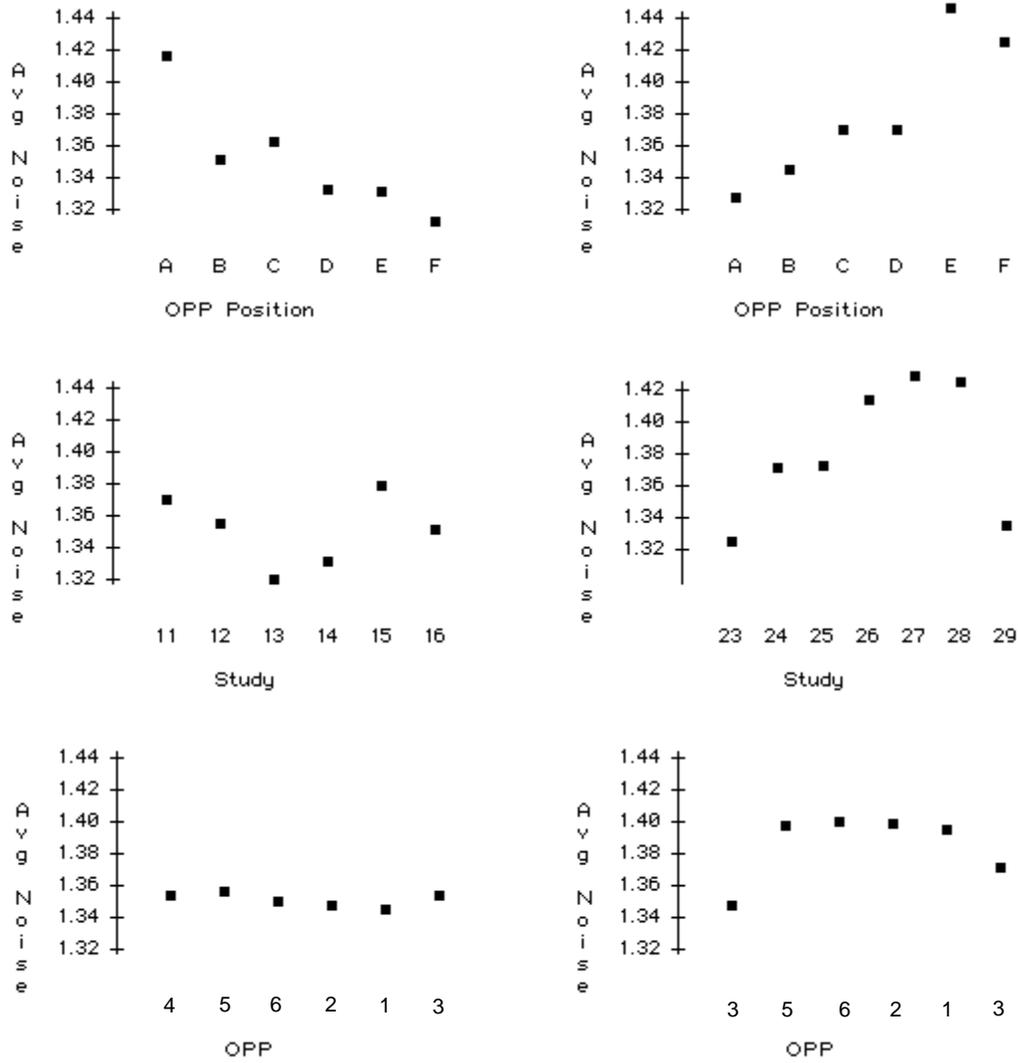


Figure 18. Noise Correlation for all OPPs in Chamber. *Graphs on left are from studies 11-16 and graphs on right are from studies 23-29.*

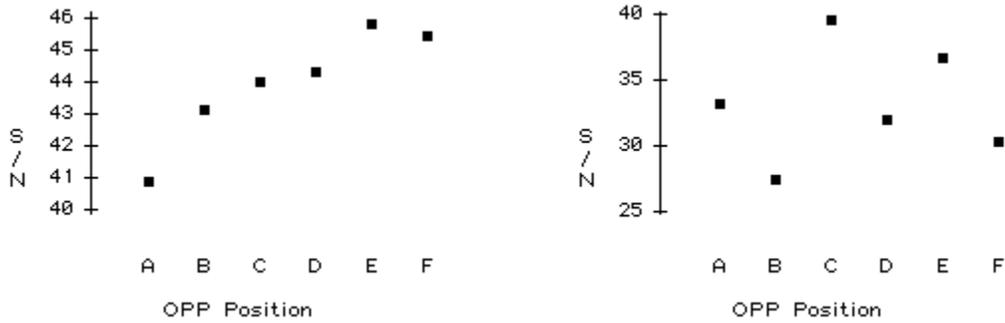


Figure 19. Results for all OPP Property Averages by OPP Location in Chamber. *Graphs on left are from studies 11-16 and graphs on right are from studies 23-29. All S/N values are shifted lower and chamber positions to the right now measure lower relative to chamber positions for plot on the left.*

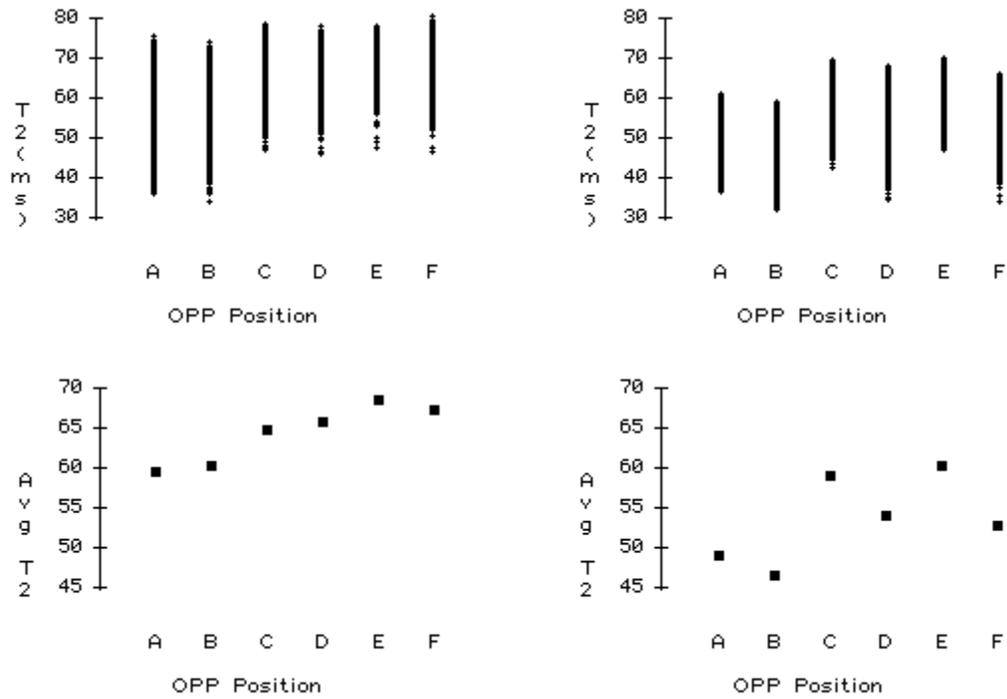


Figure 20. T₂ Correlation for all OPPs in all Locations in Chamber by Study. *Graphs on left are from studies 11-16 and graphs on right are from studies 23-29.*

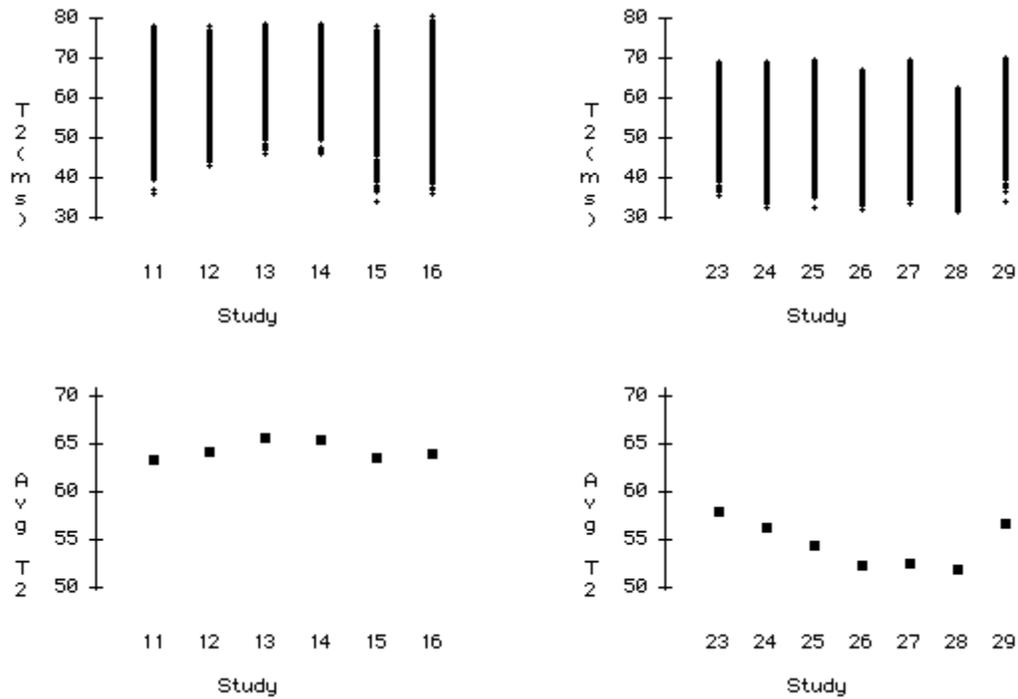


Figure 21. *T₂ Correlation for all OPPs in all Locations in Chamber by Study. Graphs on left are from studies 11-16 and graphs on right are from studies 23-29. Ideally, average data should approximate a horizontal line showing little to no instrument drift. Data on right from plastic part studies displays larger variation and all measurements have been shifted lower.*

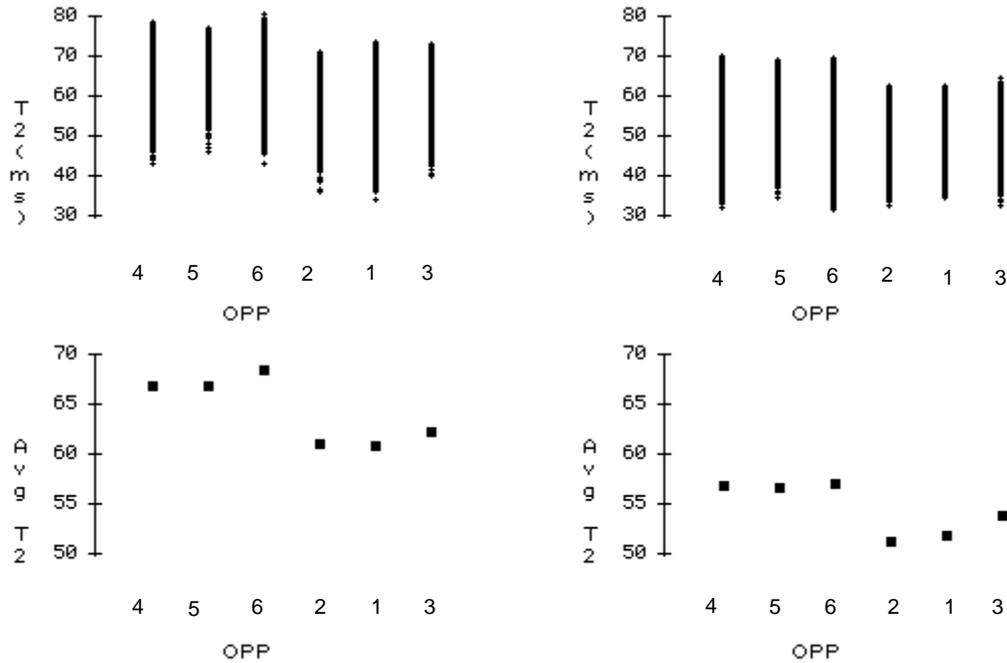


Figure 22. T₂ Correlation for all OPPs in all Locations in Chamber by OPP. *Graphs on left are from studies 11-16 and graphs on right are from studies 23-29. Data shows slightly lower T₂ values for aged OPPs.*

Surveillance Versus New OPPs

Thirty-one OPPs were molded in November 2005 as a part of process prove-in (PPI) activities. Ten of these parts were compared with 11 OPPs from surveillance (Table 2). Each OPP was measured in location A to minimize variation caused by chamber position in order to determine any T₂ correlation with OPP age.

A total of 19,008 measurements on 21 OPPS were taken by the previously described method with 3 replicates for each measurement location. 1,666 (8.8%) outliers were omitted leaving 17,344 measurements. Measurements with T₂ error values > 3.8 were arbitrarily chosen to be omitted based on the visual distribution appearance of the data (Figures 23 and 24). Although the plastic parts caused a reduction in variation, localized interference is still apparent (Figure 25).

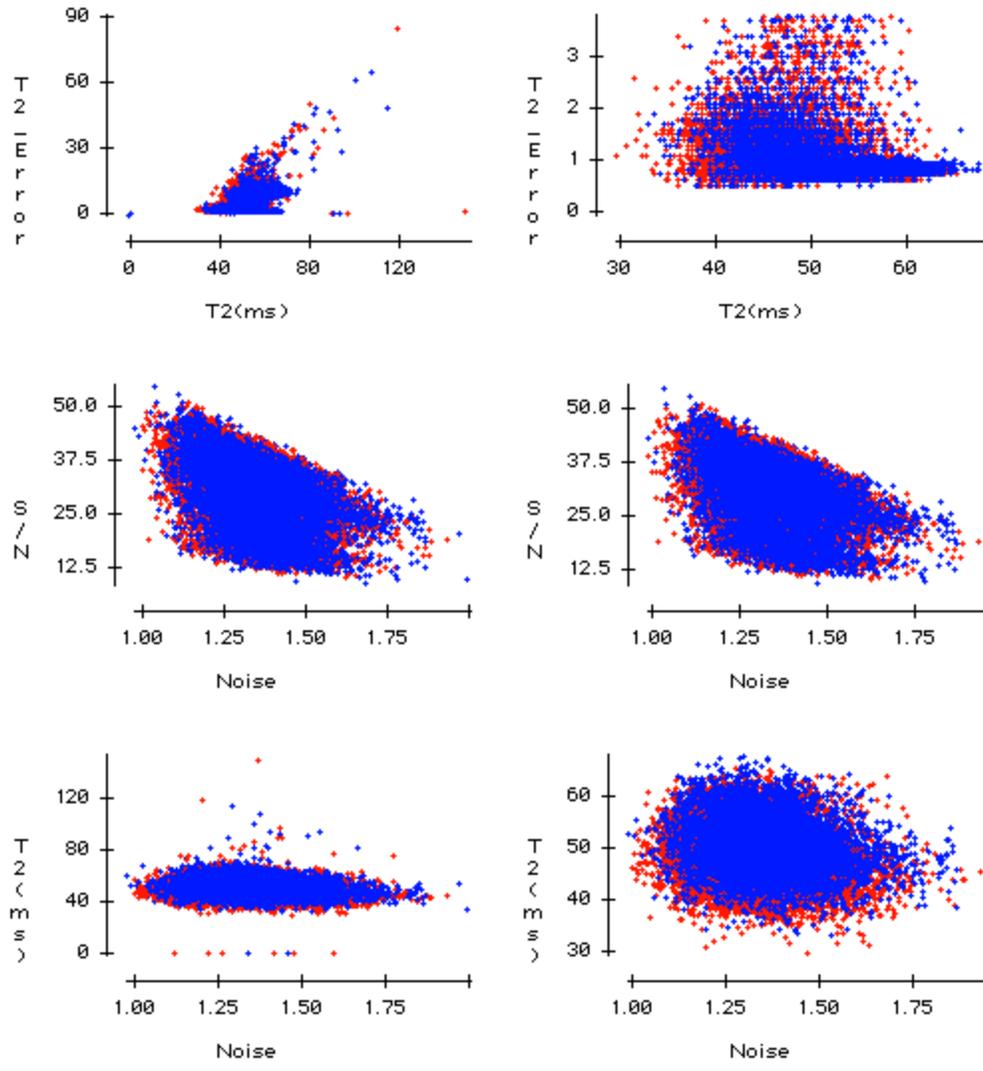


Figure 23. Correlation for all OPPs in Location A in Chamber. *Graphs on the right show the data set remaining after omitting 1,666 (8.8%) outliers. Blue symbols denote new OPPs and red symbols denote surveillance OPPs.*

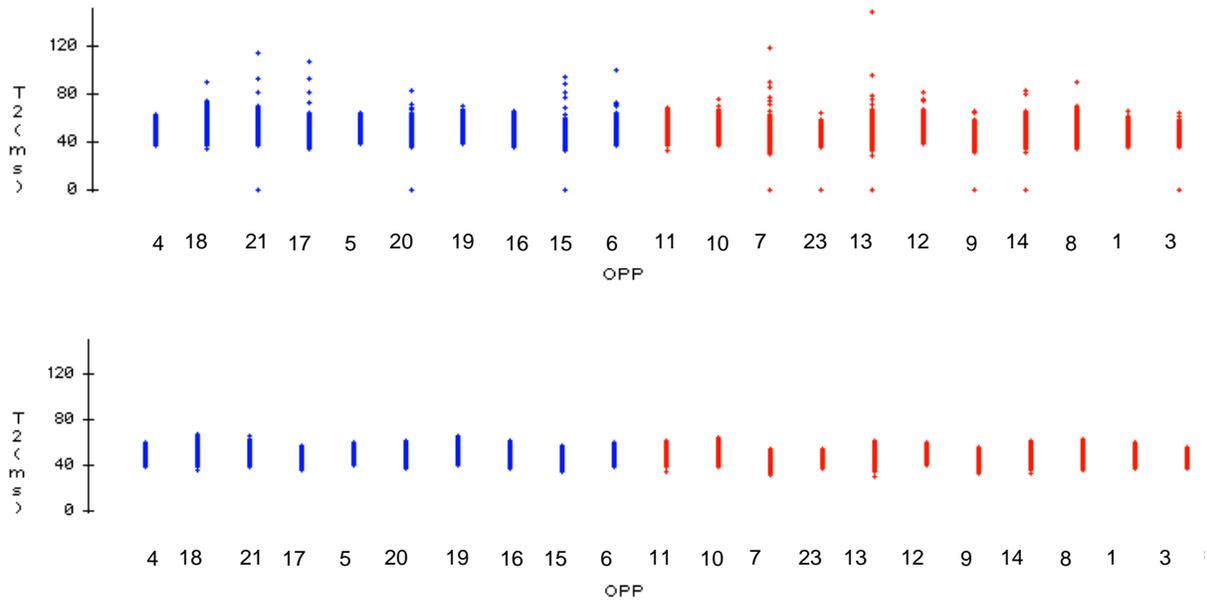


Figure 24. Correlation for all OPPs in Location A in Chamber. Graph on the bottom shows the data set remaining after omitting 1,666 (8.8%) outliers. Blue symbols denote new OPPs and red symbols denote surveillance OPPs.

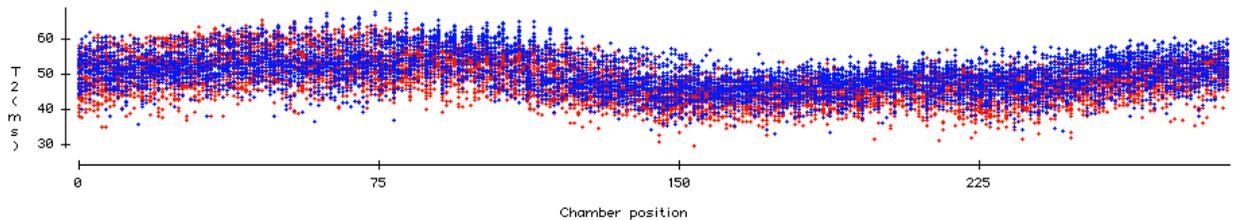


Figure 25. T₂ Values for all OPPs in Location A With Outliers Omitted. Blue symbols denote new OPPs and red symbols denote surveillance OPPs. Consistent broad wave pattern distribution across all OPPs indicates continuing effects of local chamber measurement environment on T₂ after the installation of plastic parts.

The age at disassembly for all but one of the surveillance OPPs was provided by LLNL. A comparison of the newly molded PPI parts with the OPPs returned from surveillance show no statistically significant difference in T₂ measurements averaged over the entire OPP surface. Consequently, no measurable degradation in average crosslink density with age is discernable using the Profiler (Figure 26).

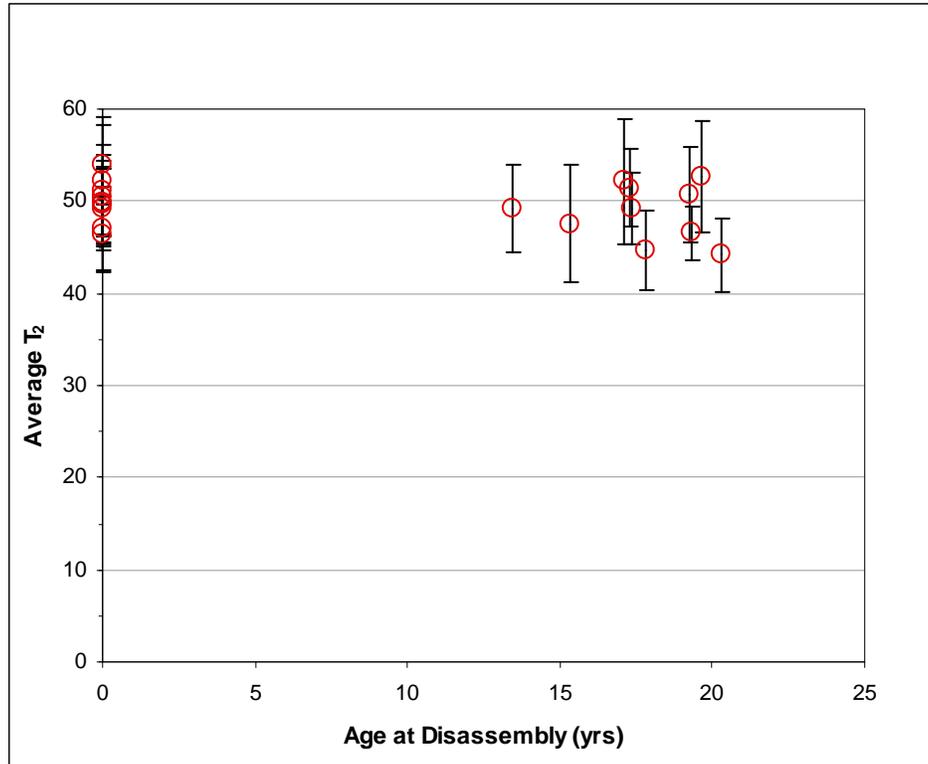


Figure 26. Correlation of Average $T_2 \pm \sigma$ With age for new and Surveillance OPPs. T_2 units are ms.

Cellular Silicone Parameter DoE

A cellular silicone sample, approximately 8 mm thick by 55 mm in diameter, was measured to determine preferred minispec ProFiler parameters based on a DoE evaluation (Table 3). Three replicates were measured per condition (Figure 27). Fifteen additional replicates were performed for certain of the higher scan rates at 115 Gain because of high T_2 error values. Of 123 measurements, 27 (22%) outliers were omitted. Many of the outliers can be traced to adverse measurement effects at the sample edge.

Factor	Number of Levels	Level 1	Level 2	Level 3
Gain	2	115	119	-
Number of scans	3	128	512	1024
Number of echoes	2	500	600	-
Echo time (ms)	3	0.44	0.50	0.60

Table 3. Details of DoE for Parameter Optimization

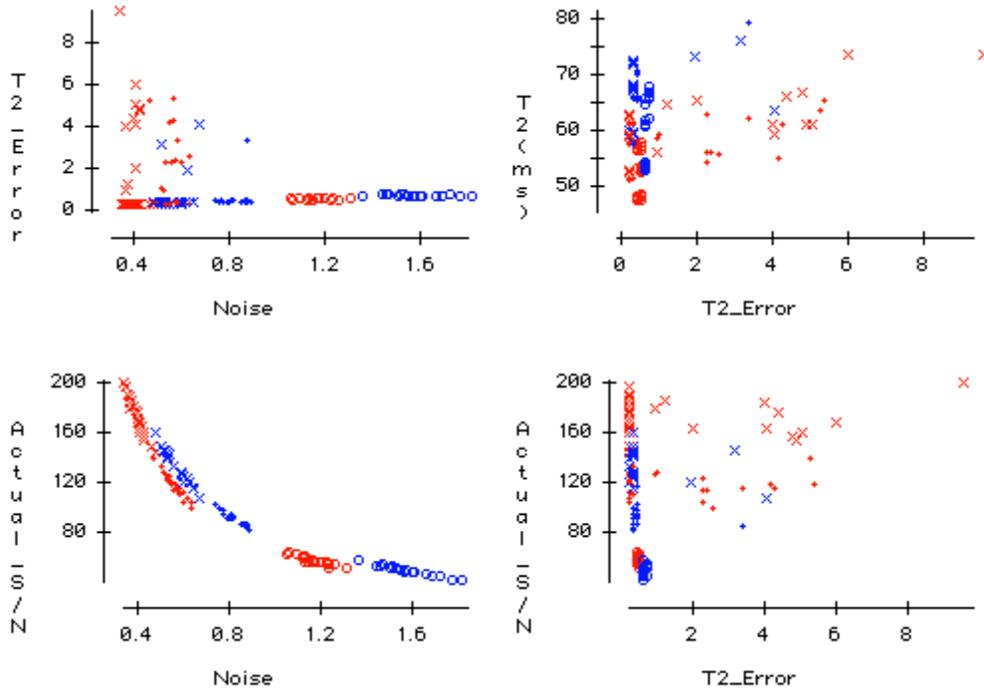


Figure 27. Response Results for Cellular Silicone Parameter DoE. Red symbols are 115 Gain and blue symbols are 119 Gain. Number of scans are symbolized as follows: o is 128, ■ is 512, and x is 1024.

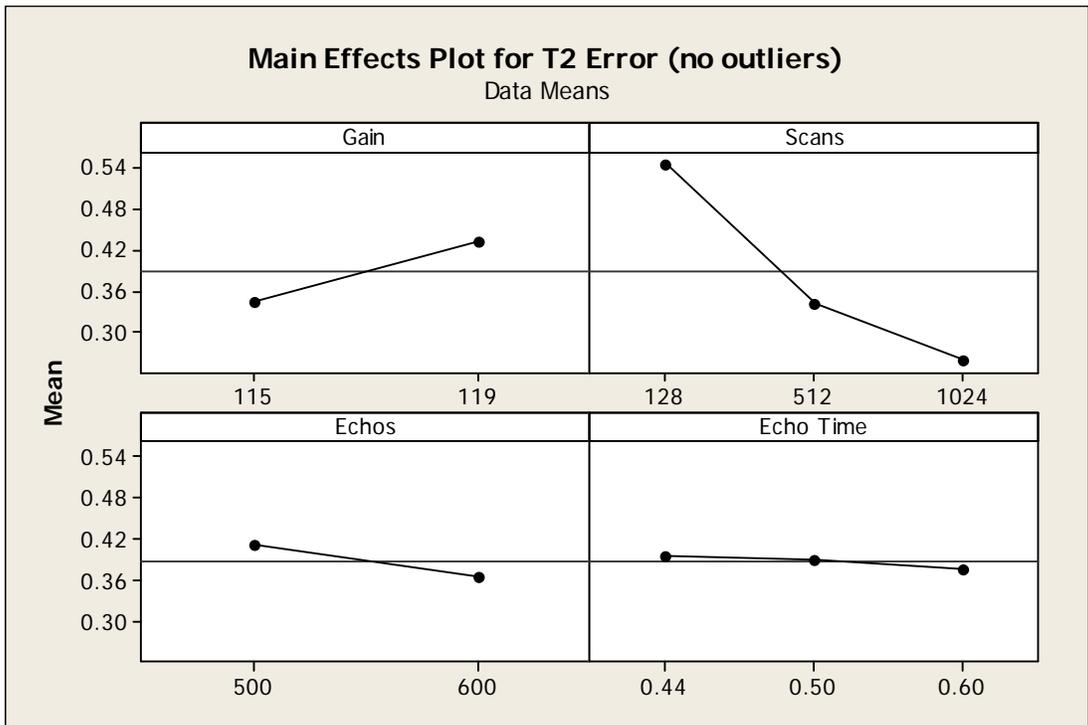
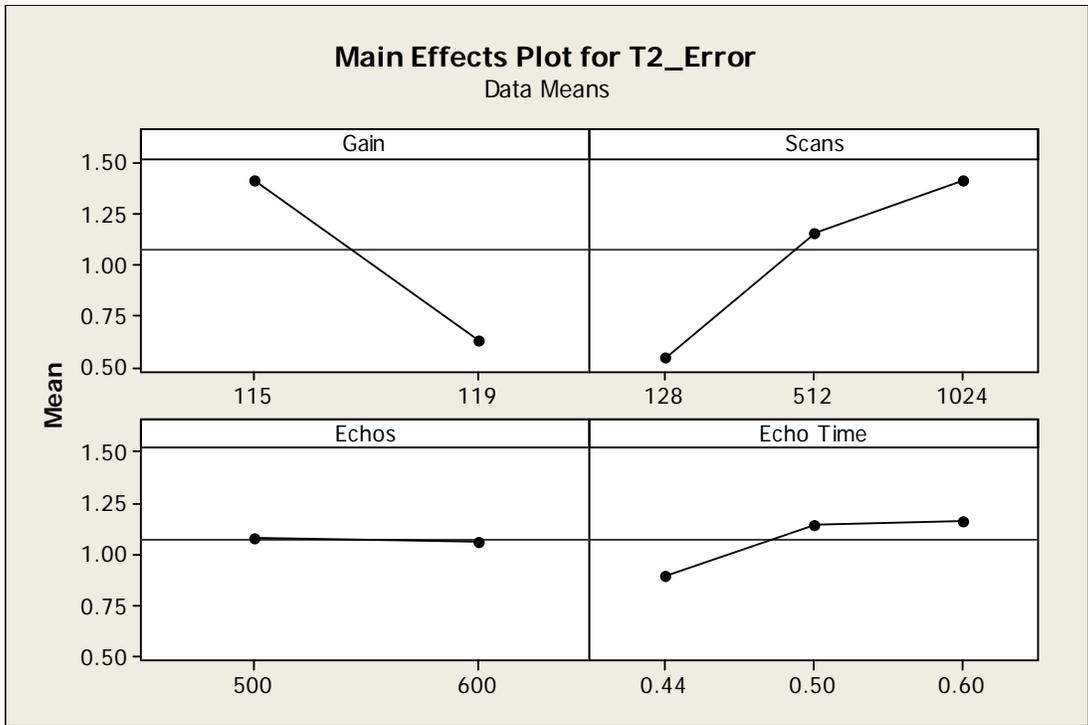


Figure 28. T₂ Error Response Results for Cellular Silicone Parameter DoE. *Top graph shows analysis of all data; only Gain had a statistically significant effect ($\alpha=0.05$ level). Bottom graph is a reanalysis after omitting the outliers; all of the effects are statistically significant.*

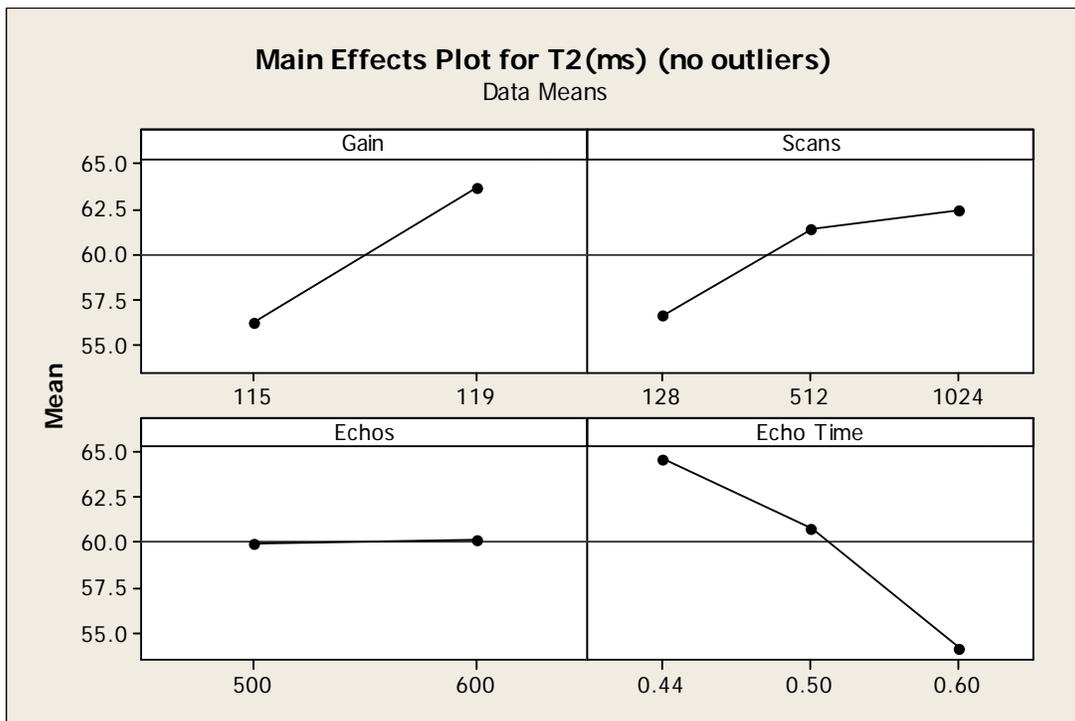
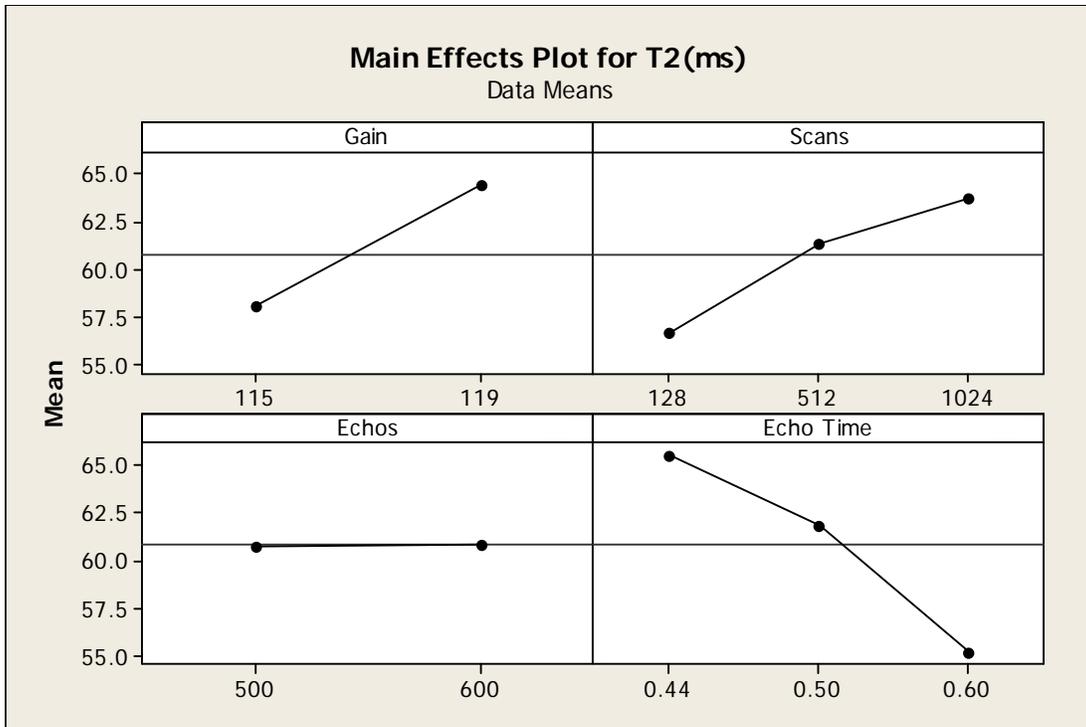


Figure 29. T₂ Response Results for Cellular Silicone Parameter DoE. *Top graph shows analysis of all data and bottom graph is a reanalysis after omitting the outliers; only number of echoes did not have a statistically significant effect ($\alpha=0.05$ level). Omitting the outliers had a negligible effect on the average T₂ value. All parameters except number of echoes were statistically significant.*

The following parameters were chosen for the cellular silicone sample to provide a balance between test speed, accuracy, and reduced potential for outliers:

Gain: 119
Number of scans: 128
Number of echoes: 500
Echo time: 0.5 ms
Recycle Delay: 0.5

Cellular Silicone Measurement Results

The cellular silicone sample was measured using the settings determined from the parameter DoE study. Four replicate measurements were performed at each of 169 locations separated from each other by 5 mm (Figure 30). The minispec probe measurement area is large relative to the cellular silicone sample area which resulted in higher variation and much lower T_2 values when the minispec probe was near the edge of the sample (Figure 31). As observed in previous studies, the measurement response is somewhat asymmetric and is off center slightly to the left of the minispec probe's center line which shifts the contour plot 5 mm to the right.

Measurement locations affected by the edge were omitted leaving 50 locations for analysis (Figures 32 and 33). The data is generally very uniform in the center of the sample but there are areas of statistically significant differences between high and low T_2 regions. Nevertheless, it is not possible to determine if the cause of these differences are variation in crosslink density or variations in material density since the minispec is sensitive to both. Because the range of average T_2 values was less than approximately 3 ms though, the magnitude of difference in either underlying property is considered negligible.

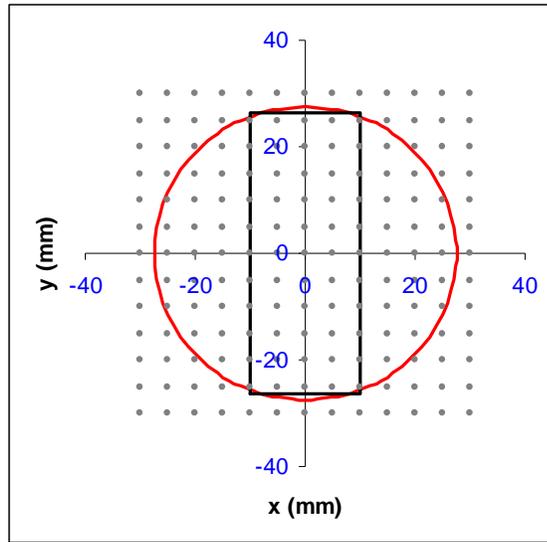
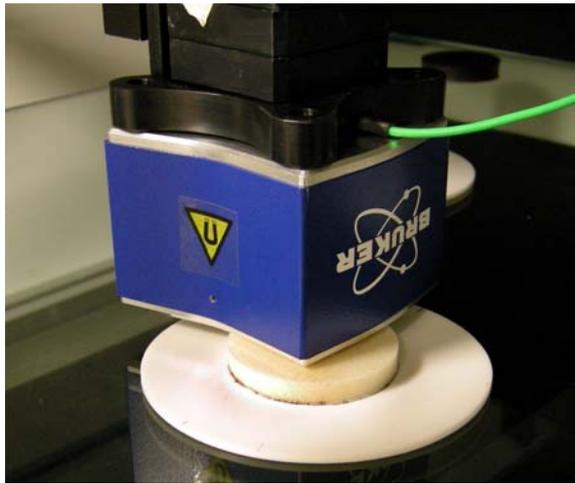


Figure 30. Cellular Silicone Sample Between ProFiler and the OPPs Polyethylene Centering Fixture. The circle shows the location of cellular silicone sample. Dot symbols represent the measurement locations centered within the minispec probe's measurement area. The rectangle shows the measurement boundaries of the probe's ceramic window centered at location number 84 (0,0).

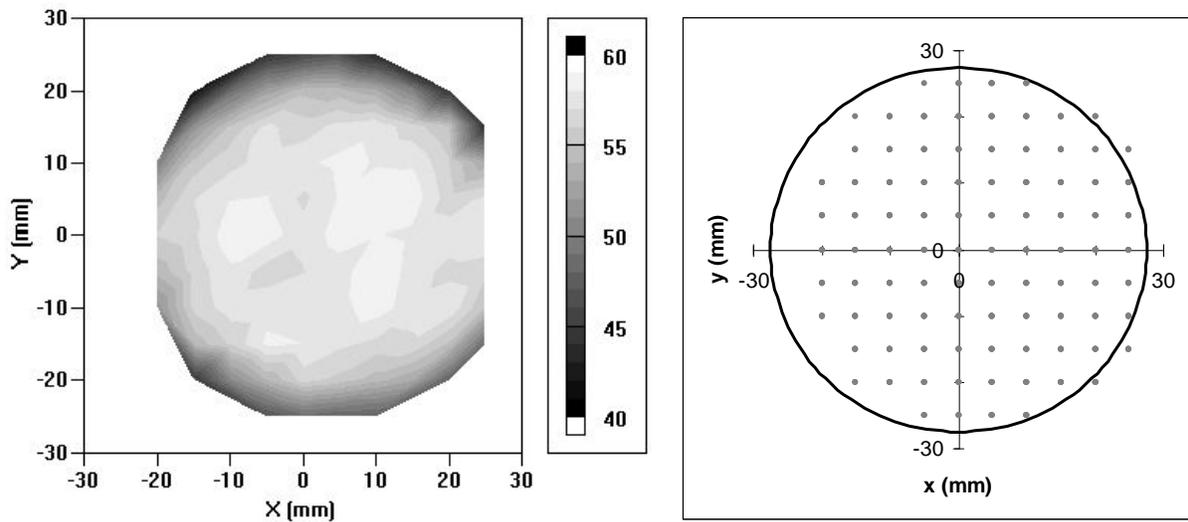


Figure 31. T_2 Value Contour Plot of Cellular Silicone Sample Showing Edge Effects for Scan Pattern in Graph on Right

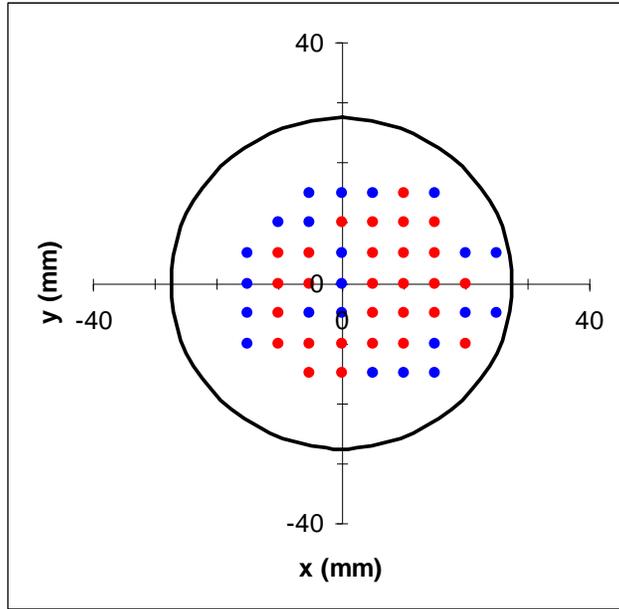


Figure 32. Circle Shows the Location of the Cellular Silicone Sample. The dot symbols show the minispec probe measurement pattern after removing outliers caused by edge effects. The average of the 50 locations was 57.5 ms. The red dot symbols have average T_2 values 57.5-58.9 and the blue dot symbols have average T_2 values 56.3-57.5.

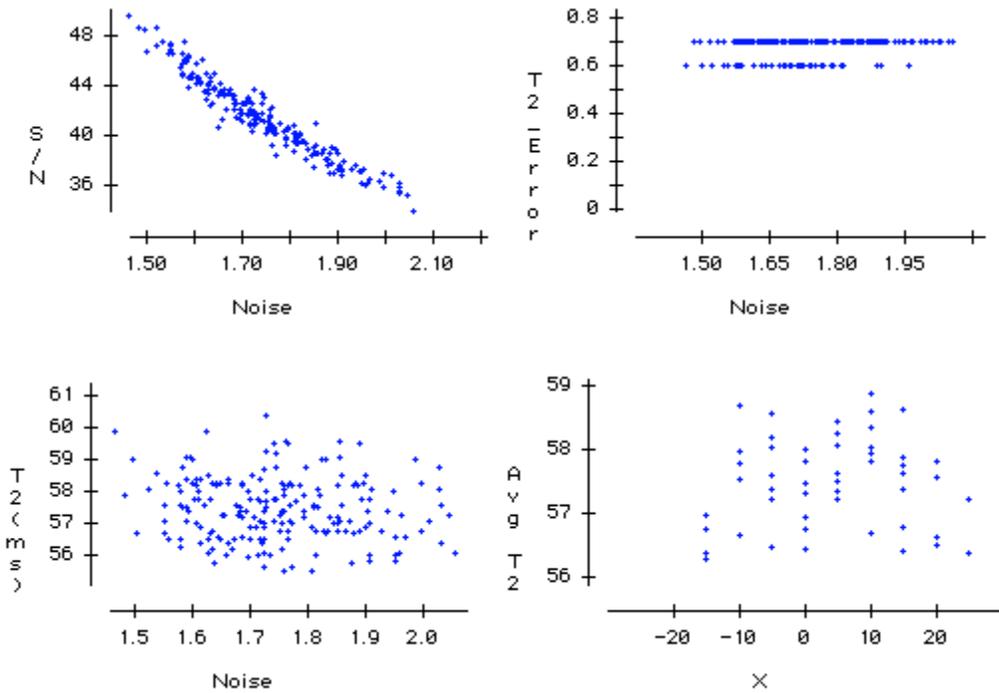


Figure 33. Plots of Various Minispec Response Variables for Locations in Figure 32

Conclusions

The repeated DoE discovered that replacing the metal parts with plastic parts had a strong effect and eliminated the major noise interference patterns observed in the previous DoE study. Nevertheless, the level of overall variation is still relatively large. The observed variation in measurement responses limits the instrument's capability to primarily detecting any combination of large internal voids or grossly undercured areas that contain <50% of the recommended catalyst level. More importantly, whereas the ProFiler can detect large differences in crosslink density in slab data, it appears the level of age-related changes in OPP crosslink density has not progressed enough and are below the detection limit of the present configuration. Thus, the current ProFiler system is not recommended for use as a non-destructive surveillance test method for the OPPs.

The ProFiler may still be a suitable tool for other types of material and the cellular silicone sample results showed good repeatability considering the larger sample thickness and after eliminating known adverse edge effects. Significant challenges would have to be overcome to measure samples with curved surfaces or unusual shapes in order to mitigate the kind of variation seen in these studies due to the amount of material in the measurement field and its relative proximity to the ProFiler's surface.

Accomplishments

54,275 measurements were performed during various screening tests and a DoE to determine the effect of OPP position on T_2 value within the measurement chamber of a new automated minispec ProFiler NMR system. In addition, a cellular silicone sample also was evaluated. This report documents the results.

Future Work

Other materials may show more potential for analysis than the current DC745 material and should be studied. Design modifications that include a stronger magnet have potential to increase S/N and depth of penetration. Also, a robotics system that can orient a sample as needed relative to a fixed ProFiler may produce significant improvements by decreasing measurement variation.

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