OBSERVING THE SEDIMENTATION OF TiO$_2$ NANOPARTICLES IN AQUEOUS SOLUTION USING A QUARTZ CRYSTAL MICROBALANCE WITH DISSIPATION MONITORING

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by
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OBSERVING THE SEDIMENTATION OF TiO$_2$ NANOPARTICLES IN AQUEOUS SOLUTION USING A QUARTZ CRYSTAL MICROBALANCE WITH DISSIPATION MONITORING

Jacob Nolan Pursley, Candidate for the Master of Science Degree
University of Missouri-Kansas City, 2015

ABSTRACT
The development of a novel and less expensive approach to the quartz crystal microbalance with dissipation monitoring (QCM-D) is explored. Using a vector network analyzer (VNA) to measure harmonic ranges from the primary to the 89$^{th}$ harmonic of a 5 MHz crystal. The fast read and processing ability of the VNA let us monitor the change in frequency, full width at half max, and amplitude. This data allowed us to monitor the resonant changes on the desired harmonics producing a QCM-D. The use of a simple VNA and an in house made crystal resonant housing unit allowed us to achieve our goals.
The Faculty listed below, appointed by the dean of the College of Arts and Sciences, have examined a thesis titled, “Observing the Sedimentation of TiO$_2$ Nanoparticles in Aqueous Solution Using a Quartz Crystal Microbalance with Dissipation Monitoring”, presented by Jacob Nolan Pursley, candidate for the Master of Science degree, and certify that in their opinion, it is worthy of acceptance.

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Lastly, I would thank my team medical doctors, Dr. Mitchell Hamburg and Dr. Charles Weinstein, for without their care I would not have been able to participate in this experience, and definitely not as well.
CHAPTER 1
INTRODUCTION

Context

In the current paradigm of medical treatments for some life threatening diseases, such as cancer, either large doses of radioactive material are permeated through the large sections of the body or an invasive surgical procedure must be performed. A current area of research is to augment the atomic structure of radioactive treatments via dopant atoms such that the radiation will be directed to only the cancerous or infected cells. One such targeted treatment uses radioactive particles doped with ferromagnetic nanoparticles. Two questions exist with such a targeted approach: (1) By manipulating the dopant concentration, we can better control the destination of the radiation and amount. But how do we obtain precise levels of doping? (2) The organic material of the patient between the entrance of the treatment and the target site needs to be crossed by the medication in most cases, it needs to cross some blood barriers but not others. So, can the material simply traverse through the bloodstream and if so, how do we determine a material's adsorption ability and thus any possible unintended tissue interactions?

We can use a Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) to monitor the how the nanoscale world changes. QCM-D’s have several modes of operation. The first is the change of frequency mode, this measures the change in amount of material applied to the quartz surface. The first mode is well-suited for measuring the change in mass on the surface, primarily, making it an ultrasensitive mass sensor this is accomplished by measuring the subtle changes in frequency the quartz crystal experiences. The second mode, and the emphasis of this thesis, the dissipative
monitoring, the QCM-D measures the change in dissipated energy within the quartz-material system to allow researchers to monitor how the material is changing on the surface of the quartz. For example, if we were to apply a substrate, or base layer to the quartz surface, and measure the interaction between the test material and the substrate it is possible to see conditions like that of the nanoparticle doped radiation treatment that could be used in the human body².

Motivation

The main motivation for this project was not to develop a wholly new method for using the quartz crystal microbalance, rather it was to use existing technology to effectively create a QCM-D at a lower cost. Currently, companies like Biolin Scientific manufacture lines of QCM’s and QCM-D’s for research and medical development under the Q-Sense label. Our system followed in a similar fashion as theirs, both have the containment unit for the quartz and testing fluid connected to a signal driver. We are using a Vector Network Analyzer (VNA) as the signal driver, whose benefits come from the preprocessing done by the VNA on the signal before it is sent to the containment unit. We think this will allow for greater resolution in frequency change and thus probe to finer detail than units based on scalar analyzer or frequency generator based systems. Being able to see fine changes in viscoelastic properties and frequency changes allows for finer tuning of adsorption or depositing on the crystal surface. In the cases of doping and medical interactions plays key roles in reducing the error, and cost, while at the same time increasing efficiency.
Outline

The rest of this paper will be presented in the following sections: Methods, Procedure, Programs, Results for the harmonic peak graphs and full width at half max (FWHM) graphs, and then the Discussion. The Methods chapter will cover our hardware and its physical setup and maintenance. The Procedure section will go over quartz crystal care and handling as well as the care of our Apparatus. The section titled Programs will detail the Visual Basic for Applications (VBA) programs used to gather and process the data for the experiments. The third chapter will display the graphs generated from our QCM-D. The fourth and final chapter will discuss our results, and concluding thoughts. We will discuss how the tests were conducted, present the data, and try to make a statement about how well our QCM-D works.
CHAPTER 2

METHODS

The entirety of the experimental setup can be summarized by the use of the Rhode & Schwarz ZVB 4 – Vector Network Analyzer (ZVB4) connected to a standard desktop computer running Windows 7 and Microsoft Excel 2015 by an RJ-45 (Ethernet) cable. The ZVB4 is connected by zvz19 series test cable to an off the shelf coaxial cable which goes to our containment unit which we call the Apparatus. Please see Figure 1 below.

Figure 1 – The Apparatus housing the quartz crystal
The Apparatus houses a 5GHz Infineon Quartz Crystal with gold electrodes on the top and bottom that connect to a coaxial connection to the ZVB4. You can see the gold-plated electrode in Figure 2. On the bottom, there is a Teflon seat for the crystal and a silicon O-Ring is used to make it water tight once it is in place. Figure 4 shows the Teflon on the bottom of the Apparatus in detail. The Well is a bored-out area of the aluminum that can contain just over 1ml of fluid.

![Inside of the Apparatus showing the quartz crystal and the Well](image)

Figure 2– Inside of the Apparatus showing the quartz crystal and the Well

Upon initial inspection of the experiment, harmonics, or places of resonance inside the crystal, had to be found using manual methods due to the lack of automation. Manual finding of the harmonic values of the crystal, and any material in the Apparatus, was completed using the ZVB 4 and is conceptually very simple as we know that the harmonics are evenly spaced in frequency space following the primary harmonic. Thus, to locate the value of the primary harmonic peak (a Gaussian-shaped peak in amplitude-frequency space) we set the ZVB 4 to a frequency span of 1 MHz and center it such that it encompassed 5 MHz. Then we used the auto adjust feature of the ZVB4 to properly
display the line and delay. The max peak value which turned out to be our primary harmonic of 5.003854 MHz matched well with the specified properties of the INFICON 5 MHz quartz crystal. Being listed as a 5 MHz crystal indicates the primary harmonic is at 5 MHz. Since this was not a new crystal, as it had been handled and cleaned several times, the primary harmonic slightly changed due to tiny scratches and the build up of residue from handlings and cleanings. Any residue, scratch or slight tilt of the crystal in the well will change the primary harmonic of the crystal, and the following harmonics thereafter. Please, consult the crystal cleaning section of the Procedure section below for further details on proper cleaning and maintenance.

The search for the next harmonic continued by changing the centered frequency while keeping the same span of frequencies in view. The next peak value was found at 15.004504 MHz. This tells us that the first harmonic is 15.004504 MHz and that the gap between harmonics is roughly 10 MHz. Now, we can easily find however many harmonics we want to measure with our setup by simply adding 10 MHz to our last measurement to get a close approximation for the next harmonic. This makes sense as our crystal is akin to an open-air column oscillator as the crystal shears freely along its Y-axis producing a node at its fundamental harmonic at its center, and thus it will have half wavelengths \( \lambda = \frac{L}{2}; \) \((2n + 1)\) and \(n \in \mathbb{I}\) producing only odd harmonics. Where \(\lambda\) is the wavelength, \(L\) is the length of the crystals vibrational axis, and \(n\) is the harmonic or overtone number.

The crystal that we use in the Apparatus is an INFICON AT-cut quartz crystal. It is 25.4 mm in diameter and sits within said Apparatus by making contact with two gold leads connecting to a coaxial cable male input. AT-cut crystals shear along their Y-axis,
which in this case is parallel to the table the Apparatus sits on. Figure 3 shows an AT-cut crystal oscillating in a single axis.

Figure 3 - Graphic from Biolin showing an AT cut quartz crystal shearing in a QCM-D

AT-cut crystals come in two varieties, in regards to thermal stability, those that are frequency stable over long periods of time at 90 Celsius and those at 25 Celsius. We are using a crystal that is stable at 25 Celsius.

The Apparatus is 2.01 inches width, 2.02 inches on the side with the coaxial connector, and has a height of 1.499 inches from the table. The outer part of the Well is
1.151 inches in diameter and the inner part of the well is 0.972 inches in diameter. The well lip is 0.500 inches deep, and 0.100 inches from that lip to the crystal surface.

Figure 4 – Underside of the Apparatus showing the coaxial leads

The highest harmonic we found was done manually. Because, the fundamental frequency for our quartz crystal is measured at 5.003854 MHz every odd frequency will move us about 10 MHz farther higher. Therefore, the next would be about 15.004 MHz. And in fact, it was, 15.004505 MHz. We operated the system up to 446.26477 MHz with both air and 0.3 ml of De-Ionized H₂O this puts the system sensitivity at the 89th harmonic. Figures 5 and 6, respectively show the 89th harmonic unloaded and loaded. The higher harmonics we find the more distorted they will become due to the walls of the Apparatus clamping down on the crystal. This will cause the near 10 MHz difference between harmonics to lessen as we reach the higher harmonics. 
Figure 5 – 89th harmonic unloaded
It is our belief that the ability to clearly see a harmonic at such a high frequency is due to our use of a Vector Network Analyzer. VNA’s processes their signals by measuring both the magnitude and phase of the output and received signals. This allows for a fully reconstructed transform inside the VNA. We think that will help us to look for higher harmonics with more practice.
Procedure

Our procedure for handling the crystal goes as such, we must take extra care to not scratch the quartz crystal as this can introduce noise in our harmonics, and even shift the harmonics\(^3\). When handling the crystal use plastic tweezers and light pressure, at all times. If you must use your hands use nitrile gloves and a delicate touch.

First, disconnect all cabling to the Apparatus before starting the cleaning process. After removing the previous sample, by sucking it out with a pipette. Rinse the well of the Apparatus with de-ionized \(\text{H}_2\text{O}\) or doubly distilled \(\text{H}_2\text{O}\), the rinsing process should involve you swirling the \(\text{H}_2\text{O}\) around to catch as much particulate as possible, then repeat with Ethanol. And do this process over again until all residue is off the crystal. If you find there is some stubborn residue left on the quartz crystal place some Ethanol back in the well and fill a finger of a glove with air and use that to gently stir and unstick the residue. Again, suck out as much fluid as possible. Either let air dry (which takes us about 20 – 30 minutes at 21\(^\circ\)C) or gently dry with a non-reactive gas, compressed air is recommended. Be warned as compressed air in a can typically contains a reactive agent that corrodes the coating on the crystal\(^7\).
Collecting Data

Looking at Figure 7 above for reference we have our computer left, ZVB4 center and Apparatus right so, to start data collection we want the data on the desktop computer, so we developed a program using ZVx_TraceToExcel.xlsx from Rohde & Schwarz as a base to transfer data and to control the ZVB4. First, Excel initiates a single frequency sweep from the ZVB4 to the Apparatus. Then the Excel Program asks the ZVB4 to log the pre-chosen harmonic(s) and send the data back to Excel for viewing and saving.

Do this by starting the Excel program ZVB_Control_Wow.xlsx and setting the harmonics in the developers view in Excel, then placing our material into the Apparatus and start the program. Excel runs once through like we want and then starts a Macro that will run until canceled. Each collection receives 1000 points of trace data from the ZVB4. Currently, each collection cycle takes about 15 seconds.
Figure 8 shows our work flow, we start our program at our computer after the material is loaded into the Apparatus, using ZVB_Control_Wow.xls. Simultaneously, we start the Temp Sensor. Now ZVB_Control_Wow.xls communicates with the ZVB4 telling it which harmonic to look at and what span of frequencies to send data back. Once the data is back it is saved into a folder and name of your choosing along with a timestamp in yyyy_mm_dd hh_mm_ss format. This is repeated for each collection. After collection, has been stopped, use Book95.xls to open all .xls files in a directory to analyze the change in harmonic peaks with time, FWHM changes with time, or essentially a mix of the two. All three produce graphs.

![Diagram of work flow](image)

**Figure 8**– The work flow between hardware and software systems
While, Quartz Crystal Microbalance with Dissipation Monitoring is the focus of our work. QCM with no dissipative monitoring was first used in 1959 when Gunter Sauerbrey related deposited mass to the change in a resonate frequency, $\Delta m = -C \frac{1}{n} \Delta f^6$.

Where $m$ is mass, $C$ is a constant determined by the crystal properties, $n$ is the overtone number, and $\Delta f$ is the change frequency as mass deposition occurs. We are more interested in the later development of the Dissipative method. Which, uses the relation of dissipation value, $D$ (this is unit less), to one over the quality factor, $Q$, to the energy dissipated in the system over the energy stored in the system, $D = \frac{1}{Q} = \frac{E_d}{2\pi E_s}$.

QCM’s are typically used for ultrasensitive weighing instruments, and they rely on the rigidity of the mass on the piezoelectric to work. So, trying to use a QCM in an aqueous solution rather than in a vacuum or gaseous environment lead to the Kanazawa
and Gordon equation, \( \Delta f = -nf_o^3 \left( \frac{\eta \rho_l}{\pi \mu_q \rho_q} \right)^{1/2} \) which accounts for the added shearing and fluid mechanics in the quartz-liquid system in 1985. Where \( n \) is the overtone number, \( f_o \) is the fundamental frequency, \( \rho \) is the density of either the liquid or quartz, \( \mu \) is the shear modulus of an AT cut quartz crystal and \( \eta \) is the viscosity of the liquid. Trying to find more uses outside of mass sensing the Dissipative Method was developed for QCM’s giving, \( D = \frac{1}{Q} = \frac{E_d}{2\pi E_s} \) describing the energy dissipated \( (E_d) \) per one oscillation over the energy stored \( (E_s) \) in the Quartz-Liquid system, in 1995\(^6\).

QCM-D’s are mostly used to sense the rate materials are adsorbing on the surface of the crystal. This is a result of understanding the viscoelastic properties of the crystal-liquid interface. Mixing two elements together is also possible, they are done in stages with one already deposited onto the crystal and the second injected and monitored for its adsorption rate. Once we find the dissipation value, what good is it? In 1996, the infamous Rodahl and friends gave us this new equation that relates the change in dissipative value to the decrease in amplitude; \( \Delta D = 2 \left( \frac{f_o \eta \rho_l}{n \pi \mu_q \rho_q} \right)^{1/6} \).

The Programs

A Visual Basic for Applications (VBA) program controls the ZVB 4 through an Ethernet cable (RJ-45). It uses the networking capabilities of Windows XP Embedded to communicate through an Excel program to control the ZVB 4. Inside Excel’s Developer module the VBA language talks to the ZVB 4 via Standard Commands for Programmable Instruments (SCPI). The base program ZVx_TarceToExcel.xls found on the Rhode & Schwarz website\(^9\), and written by Martin Weiss of Rohde & Schwarz for the purpose of
interfacing a ZVB system with a computer over Ethernet or GPIB to collect the Trace data of what was currently on the ZVB’s viewer. This is perfect for our needs except we wanted to be able to collect multiple traces (one for each Harmonic), to automate the changes in each harmonic, and to loop through the harmonics until all the data had been collected.

The language used by the ZVB 4 is Standard Commands for Programmable Instruments (SCPI). It has a plain language for many of its commands and we will use them as they are formatted in Excel to describe their process and function. First, we automated the changing of the [CENTER] and [SPAN] [FREQUENCIES] inside of the program basically where the ZVB 4 is centered and what range of frequencies are spanned in a single sweep of collection. Next, we automated the system to a single mouse click rather than 17 button pushes on the ZVB4. This made long term data collection more efficient and accurate. We then added an auto save feature after each collection cycle, and made it save with a time stamped name for easier filing. Each collection cycle lasts about 15 seconds.

Another Excel program is run (Book95.xls) to take all the data and converge them into readable graphs. VBA was used to collect and cull the large amounts of files (~4,000) per concentration run to generate the graphs showing how the QCM-D worked. The graphs generated by Book95.xls can be chosen between harmonic peak data, full width half max (FWHM) data, or real vs stimulus data for all of the Excel files in the selected folder.

Measuring and tracking the temperature and humidity is important when trying to get precise and consistent measurements with crystals in air. Adding in the aqueous
solution complicates the problem as the viscoelastic properties of water are affected by temperature. A slight change in temperature can change the frequency and thus the measured mass or dissipative value. All measurements have put the lab at a stable 22 Celsius, and our crystal is stable over long periods of time at around 25 Celsius.

The program is very simple because it only needs to pole the sensor every 6 seconds and then displays the time/date/temp/humidity in the Arduino serial read out. We let this run until data collection is done and then copy and save it to a text file. We plot this data and look it over for any large temperature fluctuations and note them to see if they affect the data in any significant way.

To collect the data, we used a microcontroller based on the ATmega328P, Arduino UNO, paired with a Manylabs Grove Shield that interfaces the DHT22 Temperature and Humidity sensor to the UNO. In Figure 10 below you can see the temperature sensor setup.

Figure 10– DHT22 Temperature and Humidity sensor attached to an Arduino Uno
CHAPTER 3
RESULTS

Our procedure for making our samples is twofold. First, we used the Analytical Chemistry lab’s electronic scales to make three samples by mass, where we measured the mass TiO$_2$ and the De-ionized H$_2$O before mixing them. The ratios of TiO$_2$ to De-ionized H$_2$O we made are 1:250, 1:500, 1:1000. We first weighed out the De-Ionized H$_2$O in the scale, then we weighed out the TiO$_2$ into a weight bucket. Placing them together in a vial and hand mixing the two together.

Secondly, used a dilution method to make our samples. We weighed out 0.5 grams of TiO$_2$ and pipetted in 10 grams of De-ionized H$_2$O. The mixture was placed in the sonicator for 30 minutes, and each mixture thereafter was diluted by 1 ml into 10 ml of de-ionized of H$_2$O. Creating mixtures of $5 \times 10^{-2}$, $5 \times 10^{-4}$, $5 \times 10^{-6}$, $5 \times 10^{-8}$, $5 \times 10^{-10}$ g TiO$_2$/g H$_2$O. This created a more homogenous mixture by visual inspection.

We had planned to use a ZnO mixture as well, but the particle size that we had obtained was too large, and paired with the fact that it is insoluble in water or in Ethanol it proved difficult to use in the Apparatus as we did not have proper cleaning solution for the ZnO, as it needs acid based cleaners and our crystal cannot support such cleaners. So, we decided against using ZnO and instead will be comparing the various concentrations of TiO$_2$ to find the time constant for the settling of the material inside the Apparatus.
Harmonic Peak Graphs

We took all the harmonic peaks from each concentration and put them together over time to form these set of graphs using Book95.xls. Every point on the vertical axis represents the peak amplitude of the listed concentration at that measured time.

![Graph showing harmonic peaks](image)

**Figure 11** – TiO$_2$ 5e$^{-6}$ g/ml - GHz vs Time (s), $\tau = -1.43e^7$ sec$^{-2}$

The time constant, $\tau$, is the time the TiO$_2$ took to settle, is easily found to be $1/a$, where the equation for the line is $y = ax + b$. So, for the first graph we have $\tau = -1.43e^7$ sec$^{-2}$. This was accomplished by changing the vertical axis to a log base 10 scale, creating a semi-log plot. With visual inspection, it can be seen that they follow similar
flat slopes and stay in the same start and end range of [0.003, 0.002]. $\tau$ tells us the rate at which the peaks or amplitudes for each concentration changed with time.

Figure 12– TiO$_2$ $5e^{-10}$ g/ml - GHz vs Time (s), $\tau = -5e^6$ sec$^{-2}$
Figure 13—TiO$_2$ $5e^{-8}$ g/ml - GHz vs Time (s), $\tau = -(5/3)e^8$ sec$^{-2}$

Where the Amplitude range is still between [0.003, 0.002], but visually the graph does not have the same slope. An entire collection period can be seen in Figure 13, roughly 4051 time units (where a time unit is 15 seconds), which is 16 Hours 52 minutes and 48 seconds.
Figure 14—TiO$_2$ $5e^2$ g/ml - GHz vs Time (s), $\tau = -2.5e^6$ sec$^{-2}$
Figure 15— TiO$_2$ 5e$^{-4}$ g/ml - GHz vs Time (s), $\tau = -(10/3)e^5$ sec$^{-2}$
FWHM Graphs

Utilizing the same approach from the harmonic peak graphs on each Full Width at Half Max per concentration per measurement we will be able to see how the graph widens as the TiO₂ adsorbs on the quartz. The harmonics that we observe are displayed as Gaussian shaped graphs, this means as the graph widens the FWHM is increasing. This will also shed light into how the energy is dissipating in the quartz-liquid system, helping us demonstrate the change in dissipation.

Figure 16– TiO₂ 5 g/ml - GHz vs Time (s), \( \tau = (10/3) e^9 \) sec\(^{-2} \)
Figure 17– TiO$_2$ 5e$^{-2}$ g/ml - GHz vs Time (s), $\tau = (10/3) \, e^8 \, \text{sec}^{-2}$
Figure 18 – TiO₂ 5e⁻⁴ g/ml - GHz vs Time (s), τ = -5e¹⁰ sec⁻²
Figure 19 – TiO$_2$ $5\times 10^6$ g/ml - GHz vs Time (s), $\tau = 2 \times 10^{10}$ sec$^{-2}$
Figure 20—TiO\textsubscript{2} 5e\textsuperscript{-8} g/ml - GHz vs Time (s), $\tau = 2e^{10}$ sec\textsuperscript{-2}
Figure 21 – TiO$_2$ 5e$^{10}$ g/ml - GHz vs Time (s), $\tau = 5e^9$ sec$^{-2}$
CHAPTER 4
DISCUSSION

The development and use of a vector network analyzer in a quartz crystal microbalance with dissipation monitoring has been shown to be sensitive in the 0.5 ng/ml scale and has the potential to be more sensitive with its ability to detect clear harmonics up to the 89th harmonic. The Full Width Half Max graphs correspond with the harmonic peak graphs at the same concentration levels as the FWHM graphs broadened as the harmonic peak graphs lost amplitude. Giving the harmonic peak graphs decreasing slopes, and the corresponding FWHM graphs increasing slopes, save for the $5e^{-4}$ concentration. This is exactly what we were hoping to see. The FWHM graphs’ tau’s represents an increasing of the dissipative value ($\Delta D$). So, as the TiO$_2$ settles onto the quartz the harmonic graph it should widen giving us a larger FWHM, and thus an increased $\Delta D$. Coupling this with all but one harmonic peak graph showing a decreasing slope we can say that both methods showed a corresponding change in the dissipative value.

We could further compare the adsorption rate of the TiO$_2$ and see how change in frequency vs the change in dissipative value is related, and as you can see from Table -1 all but one concentration has the desired relation where they mirror each other in time. This is the strong suite of using a QCM-D. With 0.5 ng/ml detection scales, the ability to discern fine levels of adsorption for the sake of coating substances with new material$^1$. The system can even detect the changing of TiO$_2$ from a very well suspended liquid to a denser fluid similar to sun screen paste.

We were able to show that simple computer interfacing and programming can produce the desired readings from a vector network analyzer to form a QCM-D, but there
are several places where we can increase performance without putting forth huge amounts of money or effort. It would be best to use better shielded cables from the ZVB 4 to the Apparatus. This should provide better clarity of signal for higher harmonic readings. Coupling a power meter to the VBA to know the absolute amplitude might be a great step in the direction of better clarity for higher harmonic detections. We should also move away from VBA inside of Excel in order to decrease the latency between the computer and the ZVB 4. Possible solutions might be the use of R&S’s Forum software that runs Python, which is used routinely for scientific calculations.

While, we eventually got to a sufficient place using the dilution method for our TiO$_2$ + DDH$_2$O solutions it would be much better to automate this process as well. Currently on the market there is the OpenQCM$^{10}$ device and they use a small pump to move their fluids in and out of the crystal area. If we followed their open source resonator plans we could also run at vacuum and temperature controlled experiments, and possibly link multiple Apparatus and data together at the same time.
Table 1– List of Graphs by TiO$_2$ concentration, time constant, and page number

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<td>1</td>
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<td>$10/3e^9$</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>$5e^{-2}$</td>
<td>$10/3e^8$</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>FWHM</td>
<td>$-5e^{10}$</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>$5e^{-6}$</td>
<td>$2e^{10}$</td>
<td>29</td>
</tr>
<tr>
<td>5</td>
<td>$5e^{-8}$</td>
<td>$2e^{10}$</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>$5e^{-10}$</td>
<td>$5e^9$</td>
<td>31</td>
</tr>
</tbody>
</table>
APPENDIX

VBA Program for collections on many Harmonics

Tabelle3.Range("B2").Value = "---"

'clear previous data
Range("A4:C4").Select
Range(Selection, Selection.End(xlDown)).Select
Selection.ClearContents

command_s = Space(20)

With ZVX_IF
  If .OpenDevice(Tabelle3.Range("B1").Value) = True Then
    .ReadString "*IDN?", Buffer: Tabelle3.Range("B2").Value = Buffer 'read out instrument type
    .ReadString ":FORMat:DATA REAL" 'set transfer to real format (speed)
    .ReadString ":INSTrument:PORT:COUNt?", Buffer: Tabelle3.Range("C2").Value = Buffer 'detect no of ports
    If Buffer = "2" Then

    .WriteString command_y 'set measured quantity to Sxx
    .WriteString ":CALCulate1:FORMat REAL" 'set format to real
    .WriteString ":INITiate1:CONTinuous OFF" 'set single sweep

  'PRIMARY HARMONIC
  'Center the analyzer on the first harmonic
  .WriteString "FREQ:CENT 5.003248 MHz"
  'Set Span to 450 Hz
  .WriteString "FREQ:SPAN 30 KHz"
  'now memorize current timer value
  t = Timer()
  'display current time
  Tabelle3.Range("I16").Value = Now
  
  'start one sweep and wait for completion
  .WriteString ":INITiate1:IMMediate:*WAI" 'launch single sweep and wait to finish

  'get stimulus data
  .ReadFloatArray "TRAC:STIM? CH1DATA", Stim 'get stimulus data
  'write stimulus values to sheet
  For Index = LBound(Stim) To UBound(Stim)
    Tabelle3.Range("A4").Offset(Index, 0).Value = Stim(Index) / 1000000000#
  Next Index

Else
  Get_Spara16.Show '4-port instrument

33
End If
Else
  Tabelle3.Range("B2").Value = "INSTRUMENT NOT FOUND"
  'Save the workbook
  'wbNam = "DD_Test0pcnt_
  'dt = Format(CStr(Now), "yyyy_mm_dd.hh_mm")
  'ActiveWorkbook.SaveAs FileName:=wbNam & dt
  'Sheet1.SaveAs FileName:="C:\Users\schwarz\Documents\SuckIt" & dt & ".csv",
  FileFormat:=xlCSV, CreateBackup:=False

End If
End With

KeepRunning

End Sub

The KeepRunning Macro can keep the ZVB 4 collecting data for as many harmonics as
you would like. The problem is, of course, that the more you collect the longer the data
collection takes. Here is KeepRunning (It looks and works along the same lines as the main
program);

```
command_s = ":SEnSe1:FUNCtion:ON 'XFRequency:POWER:S11"

Dim Buffer As String
Dim Index As Integer
Dim Trace, Stim As Variant
Dim dt As String, wbNam As String

Set ZVX_IF = New VIF

Tabelle3.Range("B2").Value = "---"

'clear previous data
Range("A4:C4").Select
Range(Selection, Selection.End(xlDown)).Select
Selection.ClearContents

command_s = Space(20)

With ZVX_IF
  If .OpenDevice(Tabelle3.Range("B1").Value) = True Then
    .ReadString "*IDN?", Buffer: Tabelle3.Range("B2").Value = Buffer 'read out instrument type
    .WriteString ":FORM:DATA REAL" 'set transfer to real format
  End If
End With
```
.ReadString ",:INSTrument:PORT:COUNt?", Buffer: Tabelle3.Range("C2").Value =
Buffer ' detect no of ports
If Buffer = "2" Then

.WriteString command_y 'set measured quantity to Sxx
.WriteString ",:CALCulate1:FORMat REAL" 'set format to real
.WriteString ",:INITiate1:CONTinuous OFF" 'set single sweep

'PRIMARY HARMONIC
'Center the analyzer on the first harmonic
.WriteString ",:FREQ:CENT 5.003248 MHz" 'Set Span to 450 Hz
.WriteString ",:FREQ:SPAN 30 KHz"
'now memorize current timer value
t = Timer()
'display current time
Tabelle3.Range("I16").Value = Now

'start one sweep and wait for completion
.WriteString ",:INITiate1:IMMediate;*WAI" 'launch single sweep and
wait to finish
'get stimulus data
.ReadFloatArray ",:TRACe:STIM? CH1DATA", Stim ' get stimulus data
'write stimulus values to sheet
For Index = LBound(Stim) To UBound(Stim)
    Tabelle3.Range("A4").Offset(Index, 0).Value = Stim(Index) / 1000000000#
Next Index

'n now get trace data
.ReadFloatArray ",:TRACe? CH1Data", Trace 'get all of channel 1 data
'show elapsed timer value on sheet
Tabelle3.Range("I15").Value = (Timer() - t) * 1000
'write data to worksheet
For Index = LBound(Trace) To UBound(Trace) Step 2
    Tabelle3.Range("B4").Offset(Index / 2, 0).Value = Trace(Index)
    Tabelle3.Range("C4").Offset(Index / 2, 0).Value = Trace(Index + 1)
Next Index

'FIRST HARMONIC
'Center the analyzer on the first harmonic
.WriteString ",:FREQ:CENT 15.003377 MHz" 'Set Span to 450 Hz
.WriteString ",:FREQ:SPAN 30 KHz"
'now memorize current timer value
t = Timer()
'display current time
Tabelle3.Range("I1016").Value = Now

'start one sweep and wait for completion

.WriteString ":INITiate1:IMMediate;*WAI" 'launch single sweep and wait to finish

'get stimulus data
.ReadFloatArray "TRAC:STIM? CH1DATA", Stim ' get stimulus data
'write stimulus values to sheet
For Index = LBound(Stim) To UBound(Stim)
    Tabelle3.Range("A1004").Offset(Index, 0).Value = Stim(Index) / 1000000000#
Next Index

'n now get trace data
.ReadFloatArray ":TRACe? CH1Data", Trace ' get all of channel 1 data
'show elapsed timer value on sheet
Tabelle3.Range("I1015").Value = (Timer() - t) * 1000
'write data to worksheet
For Index = LBound(Trace) To UBound(Trace) Step 2
    Tabelle3.Range("B1004").Offset(Index / 2, 0).Value = Trace(Index)
    Tabelle3.Range("C1004").Offset(Index / 2, 0).Value = Trace(Index + 1)
Next Index

'SECOND HARMONIC
'Center the analyzer on the first harmonic
.WriteString "FREQ:CENT 25.003769 MHz"
'Set Span to 450 Hz
.WriteString "FREQ:SPAN 22 KHz"
'now memorize current timer value
  t = Timer()
'display current time
Tabelle3.Range("I2030").Value = Now

'start one sweep and wait for completion
.WriteString ":INITiate1:IMMediate;*WAI" 'launch single sweep and wait to finish

'get stimulus data
.ReadFloatArray "TRAC:STIM? CH1DATA", Stim ' get stimulus data
'write stimulus values to sheet
For Index = LBound(Stim) To UBound(Stim)
    Tabelle3.Range("A2004").Offset(Index, 0).Value = Stim(Index) / 1000000000#
Next Index

'n now get trace data
.ReadFloatArray ":TRACe? CH1Data", Trace ' get all of channel 1 data
'show elapsed timer value on sheet
Tabelle3.Range("I2029").Value = (Timer() - t) * 1000
'write data to worksheet
For Index = LBound(Trace) To UBound(Trace) Step 2
    Tabelle3.Range("B2004").Offset(Index / 2, 0).Value = Trace(Index)
    Tabelle3.Range("C2004").Offset(Index / 2, 0).Value = Trace(Index + 1)
Next Index
'THIRD HARMONIC
'Center the analyzer on the first harmonic
.WriteString "FREQ:CENT 35.00378 MHz"
'Set Span to 450 Hz
.WriteString "FREQ:SPAN 16 KHz"
'now memorize current timer value
t = Timer()
'display current time
Tabelle3.Range("I3045").Value = Now
'
'start one sweep and wait for completion
.WriteString ":INITiate1:IMMediate;*WAI"  
'launch single sweep and wait to finish
'get stimulus data
.ReadFloatArray "TRAC:STIM? CH1DATA", Stim  
'get stimulus values to sheet
For Index = LBound(Stim) To UBound(Stim)
    Tabelle3.Range("A3004").Offset(Index, 0).Value = Stim(Index) / 1000000000#
Next Index
'

'now get trace data
.ReadFloatArray ":TRACe? CH1Data", Trace  
'get all of channel 1 data
'show elapsed timer value on sheet
Tabelle3.Range("I3044").Value = (Timer() - t) * 1000
'write data to worksheet
For Index = LBound(Trace) To UBound(Trace) Step 2
    Tabelle3.Range("B3004").Offset(Index / 2, 0).Value = Trace(Index)
    Tabelle3.Range("C3004").Offset(Index / 2, 0).Value = Trace(Index + 1)
Next Index

'FOURTH HARMONIC
'Center the analyzer on the first harmonic
.WriteString "FREQ:CENT 45.004888 MHz"
'Set Span to 450 Hz
.WriteString "FREQ:SPAN 16 KHz"
'now memorize current timer value
t = Timer()
'display current time
Tabelle3.Range("I4060").Value = Now
'
'start one sweep and wait for completion
.WriteString ":INITiate1:IMMediate;*WAI"  
'launch single sweep and wait to finish
'get stimulus data
.ReadFloatArray "TRAC:STIM? CH1DATA", Stim  
'get stimulus values to sheet
For Index = LBound(Stim) To UBound(Stim)
    Tabelle3.Range("A4004").Offset(Index, 0).Value = Stim(Index) / 1000000000#
Next Index
'now get trace data
.ReadFloatArray ":TRACe? CH1Data", Trace            'get all of channel 1 data
'show elapsed timer value on sheet
Tabelle3.Range("I4059").Value = (Timer() - t) * 1000
'write data to worksheet
For Index = LBound(Trace) To UBound(Trace) Step 2
    Tabelle3.Range("B4004").Offset(Index / 2, 0).Value = Trace(Index)
    Tabelle3.Range("C4004").Offset(Index / 2, 0).Value = Trace(Index + 1)
Next Index

'FIFTH HARMONIC
'Center the analyzer on the first harmonic
.WriteString "FREQ:CENT 55.006663 MHz"
'Set Span to 450 Hz
.WriteString "FREQ:SPAN 16 kHz"
'now memorize current timer value
  t = Timer()
'display current time
Tabelle3.Range("I5075").Value = Now
',
'start one sweep and wait for completion
.WriteString ":INITiate1:IMMediate;*WAI"            'launch single sweep and wait to finish
'get stimulus data
.ReadFloatArray "TRAC:STIM? CH1DATA", Stim        'get stimulus data
'write stimulus values to sheet
For Index = LBound(Stim) To UBound(Stim)
    Tabelle3.Range("A5004").Offset(Index, 0).Value = Stim(Index) / 1000000000#
Next Index
',

'now get trace data
.ReadFloatArray ":TRACe? CH1Data", Trace            'get all of channel 1 data
'show elapsed timer value on sheet
Tabelle3.Range("I5074").Value = (Timer() - t) * 1000
'write data to worksheet
For Index = LBound(Trace) To UBound(Trace) Step 2
    Tabelle3.Range("B5004").Offset(Index / 2, 0).Value = Trace(Index)
    Tabelle3.Range("C5004").Offset(Index / 2, 0).Value = Trace(Index + 1)
Next Index

'SIXTH HARMONIC
'Center the analyzer on the first harmonic
.WriteString "FREQ:CENT 65.009767 MHz"
'Set Span to 450 Hz
.WriteString "FREQ:SPAN 22 kHz"
'now memorize current timer value
  t = Timer()
'display current time
Tabelle3.Range("I6090").Value = Now
Once the data comes back to Excel it gets placed into two 1,000 row columns for each harmonic, which gives a total of 8,000 rows. This contains the stimulus frequency for both the real and the imaginary reflected waves of the signal, and it is promptly time stamped, saved, and then the program waits until the specified time to run again.
'Save the workbook
'wbNam = "DD_Test0pcnt_"
dt = Format(CStr(Now), "yyyy_mm_dd_hh_mm_ss")
'ActiveWorkbook.SaveAs FileName:=wbNam & dt
'Sheet1.SaveAs FileName:="C:\Users\schwarz\Documents\BaseLine_DD2O" & dt & ".csv", FileFormat:=xlCSV, CreateBackup:=False
ActiveWorkbook.SaveAs FileName:="C:\Users\schwarz\Documents\Runs\BaseLine_DD2O" & dt & ".xls", FileFormat:=56
Else
    Get_Spara16.Show '4-port instrument
End If
Else
    Tabelle3.Range("B2").Value = "INSTRUMENT NOT FOUND DooooD!!"
End If
End With

Application.OnTime Now + TimeValue("00:01:15"), "KeepRunning"

End Sub
Private Sub CommandButton1_Click()
    Dim SummarySheet As Worksheet
    Dim FolderPath As String
    Dim SelectedFiles() As Variant
    Dim NRow As Long
    Dim FileName As String
    Dim NFile As Long
    Dim WorkBk As Workbook
    Dim SourceRange As Range
    Dim DestRange As Range

    Application.ScreenUpdating = False
    Application.DisplayAlerts = False
    Application.EnableEvents = False

    ' Create a new workbook and set a variable to the first sheet.
    Set SummarySheet = Workbooks.Add(xlWBATWorksheet).Worksheets(1)

    ' Modify this folder path to point to the files you want to use.
    FolderPath = "C:\Users\schwarz\Documents\Runs"

    ' Set the current directory to the the folder path.
    ChDrive FolderPath
    ChDir FolderPath

    ' Open the file dialog box and filter on Excel files, allowing multiple files
    ' to be selected.
    SelectedFiles = Application.GetOpenFilename(_
        filefilter:="Excel Files (*.xl*), *.xl*", MultiSelect:=True)

    ' NRow keeps track of where to insert new rows in the destination workbook.
    NRow = 1

    ' Loop through the list of returned file names
    For NFile = LBound(SelectedFiles) To UBound(SelectedFiles)
        ' Set FileName to be the current workbook file name to open.
        FileName = SelectedFiles(NFile)
        Set WorkBk = Workbooks.Open(FileName)

        ' Set the cell in column A to be the file name.
        SummarySheet.Range("A" & NRow).Value = FileName

        ' Set the source range to be A9 through C9.
        ' Modify this range for your workbooks. It can span multiple rows.
        "I19" = Peak, "I20" = FWHM, "A4:B1003" = Stimulus and Real
        Set SourceRange = WorkBk.Worksheets(1).Range("I19")
' Set SourceRange = WorkBk.Worksheets(1).Range("I20")
' Set SourceRange = WorkBk.Worksheets(1).Range("A4:B1003")

' Set the destination range to start at column B and be the same size as the source range.
Set DestRange = SummarySheet.Range("B" & NRow)
Set DestRange = DestRange.Resize(SourceRange.Rows.Count, _
              SourceRange.Columns.Count)

' Copy over the values from the source to the destination.
DestRange.Value = SourceRange.Value

' Increase NRow so that we know where to copy data next.
NRow = NRow + DestRange.Rows.Count

' Close the source workbook without saving changes.
WorkBk.Close savechanges:=False
Next NFile

Application.ScreenUpdating = True
Application.DisplayAlerts = True
Application.EnableEvents = True
'Save as xlsx format so it can have long enough columns
SummarySheet.SaveAs FileName:="C:\Users\schwarz\Documents\Runs\COLLECTIONS
SONICATED\TiO2_5e10(2)_Peak_Data.xlsx", FileFormat:=51
'SummarySheet.SaveAs
FileName:="C:\Users\schwarz\Documents\SomePeaksSameCon1.xlsx", FileFormat:=51

' Call AutoFit on the destination sheet so that all data is readable.
SummarySheet.Columns.AutoFit
End Sub
REFERENCES

Jacob Nolan Pursley was born on October 20th, 1981 in North Kansas City, Missouri. He graduated from North Kansas City High School in the year 2000. Thirteen years later he graduated from the University of Missouri – Kansas City with a Bachelor of Science in Physics. Mr. Pursley started the Masters of Physics program in the Fall of 2013 at the University of Missouri – Kansas City.