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Development of a Sensitivity Multiplication Module for Improved Quartz Crystal Microbalance Measurements

PhD Thesis Summary

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Introduction

In our quest to better comprehend our environment, since the dawn of civilization, we have been compelled to create tools in order to improve our abilities or compensate for our lack of senses. Our tools have since become more complex and refined allowing us to gain further knowledge and thus create more tools to serve our purposes. Not much has changed in our tireless efforts to learn how to use every aspect of our environment to our advantage.

Sensing devices are a special category of tools. Advanced sensors have the ability to perceive things that elude us and by proper interfacing translate this information into data we can process. They thus allow us to gain knowledge into aspects of our environment we are not naturally equipped to be aware of. This has led to great advances mainly throughout the technological and medical field. However, when one stops to take a good look around, it is clear that few aspects of our lives have eluded improvements that include sensing devices. And if one does find one such aspect, it is highly probable that somewhere a group of scientists is working on changing that.

Quartz crystal oscillators have become one of the most commonly encountered devices in the technological field. They provide a series of advantages among which precision, cost efficiency and ease of use are the most appreciated. Any application that involves precision timing, from microcontroller applications to bank transfers are run using some form of crystal oscillator.

As sensing devices, they are most often found in laboratories, where they are employed as acoustic wave sensors. One of the most commonly employed devices is the Quartz Crystal Microbalance. This device has proven itself feasible as a sensing device over a large number of applications covering a diverse number of fields.

The subject of this thesis deals with the development, operation mode and results of a proposed sensitivity multiplication solution for the Quartz Crystal Microbalance. The chosen design solutions are justified in the context of existing options and the novelty of the approach is demonstrated as well as experimentally examined.

When working in the field of precise measurements, the design of the device and the experimental apparatus has to be chosen with great care. Only the best available devices and technologies have been applied for this device in order to minimize any unwanted interferences. A great number of parameters can negatively influence the outcome of measurements. Therefore, each possible interference has been carefully evaluated and minimized to yield a result of extremely precise measurements which improves the outcome of experimental results when applied.

The sensitivity multiplication module presented in this thesis is a patented device (RO patent no. 129483/30.05.2014) which increases the frequency shift of the Quartz Crystal Microbalance without changing the nominal frequency of the quartz crystal resonator or the frequency value delivered to the frequency counter. In other words, it allows a more precise reading of the frequency shift without affecting any other parameter of the system. The experimental setup including this sensitivity multiplication device was investigated under diverse load conditions. In order to most accurately predict the capabilities of the sensitivity multiplication module an Allan deviance analysis was performed, using the heterodyne method. Measurements were performed in air, water and 50% sugar-water mixture to investigate its behavior under different conditions encountered in QCM systems. This analysis confirms that the multiplication of the frequency shift is limited by the different quarts crystal load conditions which directly affect the quartz crystals quality factor (Q) and the oscillator’s stability. Despite the known problems concerning liquid measurements in QCM systems, the sensitivity multiplication device performs well, providing an increase of up to six times in the accuracy of frequency shift measurements [1].

1. The Sensitivity Multiplication Module – Schematic Description and Operation

The schematic of the sensitivity multiplication module, using a 10MHz quartz crystal resonator can be seen in Fig. 1. The sine wave obtained from the QCM oscillator is being run through an amplifier developed around the 2N2369A transistor in order to increase the amplitude of the signal. The multiplication circuit contains two ICS511 (Integrated Device Technology, Inc.) phase-locked loop (PLL) clock multipliers, a digital mixer based on the 74HC74 flip-flop and a PLP-10.7+ (Mini-Circuits Inc.) low pass amplifier as well as a few passive components. Figure 2 shows a completed module.

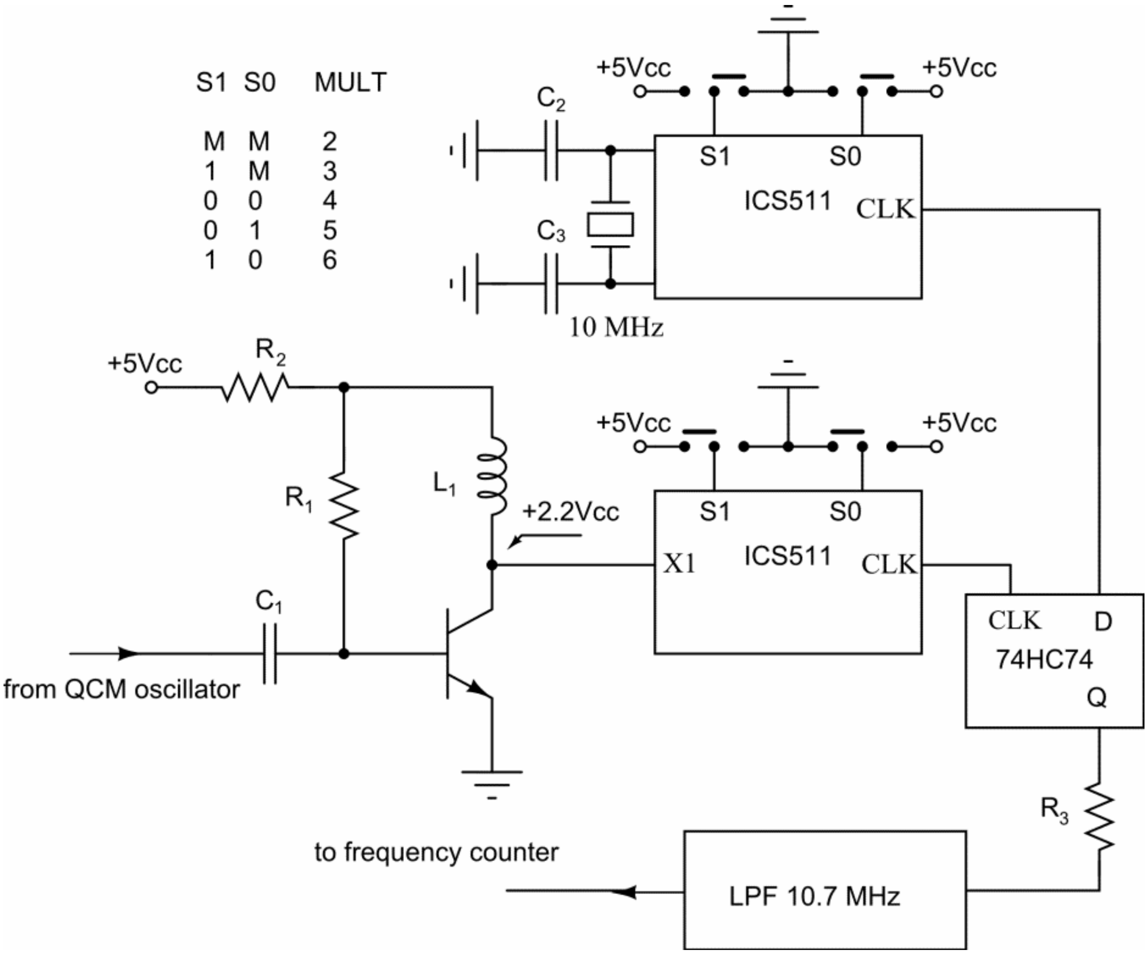

Figure 1 Schematic of the Sensitivity Multiplication Module

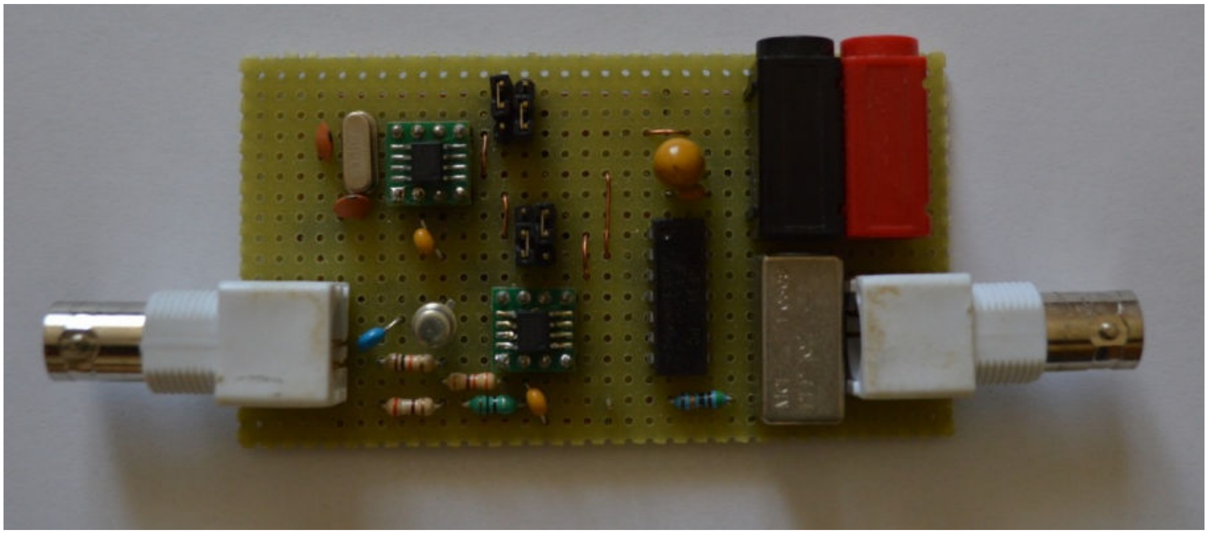

Figure 2: Completed Sensitivity Multiplication Module

The sensitivity multiplication module can be used for any n, n-1 multiplication setup in accord with the S1 and S0 inputs, as presented in the table from Figure 1 without having to adjust any other values of the circuit. Testing of the device for all multiplication combinations revealed a steady and precise output signal every time.

2. Measuring the Frequency Shift and Determining the Appropriate Method for Validating the Capabilities of the Sensitivity Multiplication Module

. In order to assess the validity of the presented device rigorous testing had to be carried out to establish its capabilities as a frequency multiplier. The best analysis method known to date for assessing frequency stability is the Allan Deviance method of calculus. However before being able to apply any statistical calculus the data acquisition process had to be considered and evaluated in order to assess the proper method for obtaining accurate results for the given case.

2.1 Choosing the Heterodyne Beat Frequency Method

When dealing with QCM systems, the parameter of most importance is the frequency shift measurement. This has to be achieved over long periods of time with no signal decay.

In order to assess the quality of the sensitivity multiplication module and assess the stability of the obtained QCM setup, the beat frequency method was considered to fulfill all requirements. It provides good frequency accuracy and frequency stability. It is also an affordable setup, which makes it more readily accessible.

2.2 Insertion of the Sensitivity Multiplication Module into the QCM Setup

The classical QCM setup is the one shown in Fig. 3 (a). It involves an oscillator whose frequency shifts are being monitored through a frequency counter. This setup is most frequently used in mass sensor application because of its simplicity and effectiveness.

The sensitivity multiplication module, whose operating principle is shown in Fig. 3 (b), adds a few advantages to the setup by multiplying the frequency, adding it to a mixer connected to a highly stable reference oscillator and running the signal through a low pass filter. The obtained signal has an improved resolution by a factor of n.

The device is designed as a post processing unit, inserted between the oscillator being studied and the frequency counter (Fig. 3 (c)). As such it is a practical addition to the classical setup of QCM systems, easily integrated in order to increase the frequency shift without modifying the fundamental resonant frequency of the quartz crystal resonator or the nominal frequency value delivered to the counter.

In accordance with the classical Sauerbrey Equation [2] which relates the frequency shift to the mass deposition:

$$\Delta f = \Delta f_m = -\frac{2 f_0^2}{\sqrt{\rho_q \mu_q}} \frac{\Delta m}{A}$$

the effect of the sensitivity multiplication module on increasing the fundamental frequency of the quartz crystal resonator in comparison to the classical approach is given by

$$f_{0_n} = f_0\sqrt{n}$$

where n is the multiplication factor.

One of the major benefits of the proposed system is preserving the Q-factor of the quartz crystals used in classical QCM investigations. This further ensures a better stability of the quartz oscillator by offering a higher resolution in data acquisition without the need to raise the oscillators' frequency, which has a range of disadvantages because decreasing the quartz sensors thickness affects its sensibility and yields less accurate data.

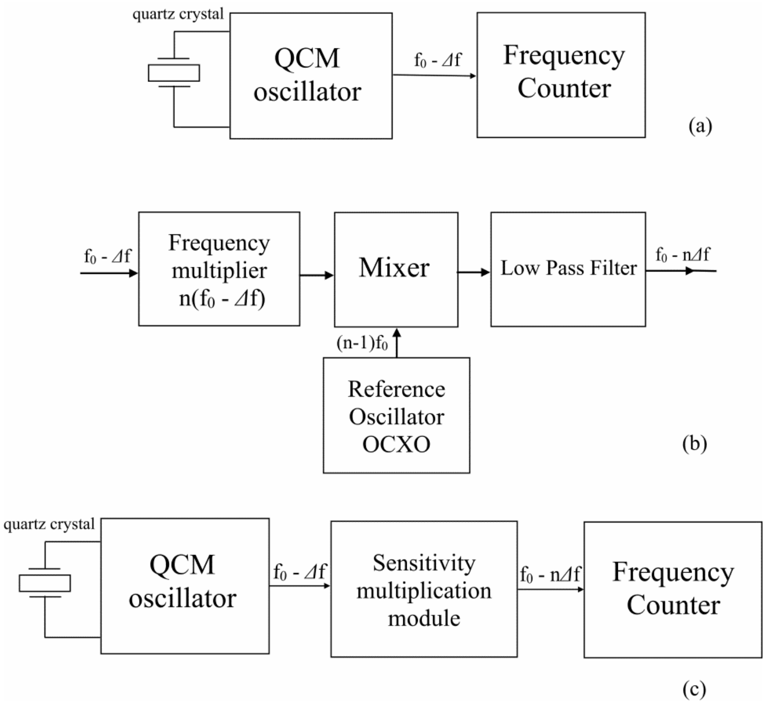

Fig. 3 (a) classical QCM setup; (b) the sensitivity multiplication modules operating principle; (c) insertion of the sensitivity multiplication module as a post processing unit

3. Validation Measurements and Experimental Integration of the Sensitivity Multiplication Module

After having chosen the appropriate measurement method for frequency stability determination, first, the experimental setup was constructed with each element involved carefully chosen. The Allan Deviation analysis was an obvious choice since it is widely regarded as the standard method for accurate frequency stability estimations. After the setup was constructed and before Allan computations were made, a Median Deviation Analysis was also performed in order to obtain information on statistical dispersion for assessing the acquired data’s accuracy.

3.1 Concepts Used for Implementation

An Allan Deviation study was carried out in order to determine the smallest frequency deviation that can be detected in the case of the sensitivity multiplication module presented here. For this purpose an m-sample Allan Variance was used. The m-sample Variance is, as its name suggests, a measure of frequency stability using a definite number of m samples. The Allan Deviation formula used for computation is expressed as follows:

$$\sigma_y(m,\tau) = \sqrt{\frac{1}{2f_0(m-1)}\sum_{k}^{m-1}(\overline{f}_{k+1}(\tau) - \overline{f}_k(\tau))^2}$$

where m is the number of samples used to estimate time average, τ is the observation time, f_0 is the reference frequency and $\overline{f}(\tau)$ represent the group of sample data acquired which allow the characterization of the oscillators stability in the time domain [3].

The oscillator detection limit (meaning: the smallest frequency deviation that can be detected in the presence of frequency fluctuations) is equal to

$$\Delta f(\sigma) = \sigma_y(\tau) f_0$$

By using the relationship between the detection limit and the sensitivity coefficient of a quartz resonator known as $k = -\frac{2.26 \cdot 10^{-6} f_0^{3/2}}{\sqrt{4\pi}} \frac{Hz}{\sqrt{\frac{g}{cm^3\,poise}}}$ the resolution limit of the QCM can be expressed as $\Delta f(\sigma)/k$

3.2. Experimental setup

As previously discussed, the time domain characterization was realized by means of a direct measurement of the QCM resonant frequency using the beat-frequency heterodyne method. Figure 4 shows the block diagram of the experimentally used setup. The signal generated by the QCM lever oscillator connected to our 10MHz quartz crystal is fed to the sensitivity multiplication module. From here the signal is run into a (HP-5316B) Universal Counter as is. The same signal is also fed into a (ZFM-2) Mixer together with the signal of a Rubidium Atomic Frequency standard (FE 5680A). The signal at the IF output of the mixer is run through a low pass filter and then fed to another (HP-5316B) Universal Counter. Both counters are identical and both use the Rubidium Atomic Frequency standard as a reference. These are also further connected to a PC for data acquisition through a GPIB-USB interface.

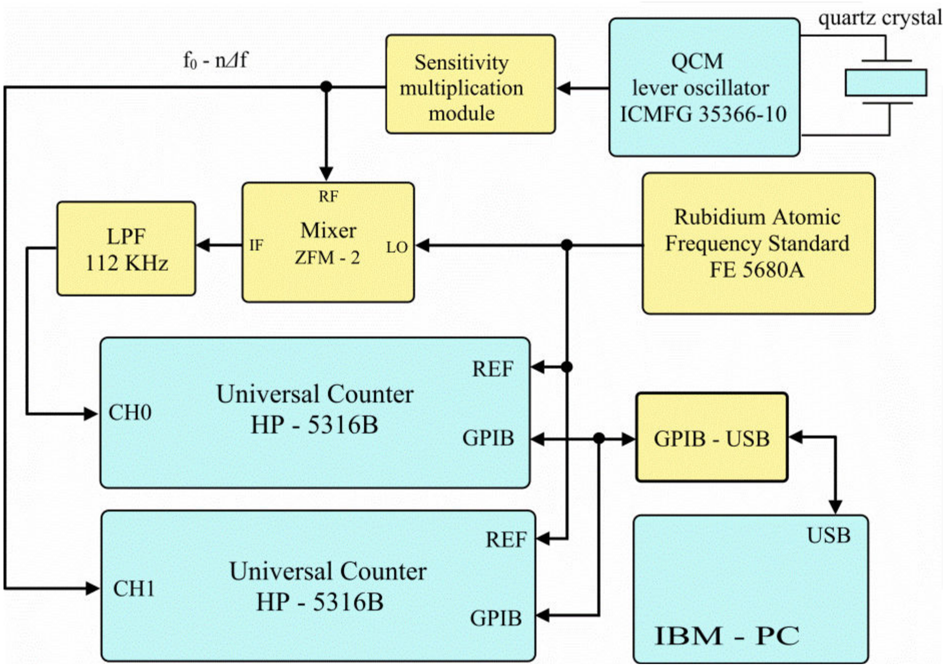

Figure 4: Diagram of the used Allan Deviation heterodyne method

3.2.1 Elements of the Experimental Setup

The key equipments of this setup are the high quality Rubidium Atomic Frequency Standard and the Universal Counters used in order to ensure the high precision of the acquired results. The measurement resolution is increased by the heterodyne factor (the ratio of the oscillator output frequency to the IF) and the well known high precision of this method is ensured by the stability of the reference oscillator.

Figure 5 depicts the Allan deviance experimental setup based on the heterodyne beat frequency method and all its components. The resolution of the setup presented is 100μHz for 1s gate time. This performance is ensured by the reciprocal counting technique implemented with the two HP-5316B universal counters and the stability of the rubidium frequency reference.

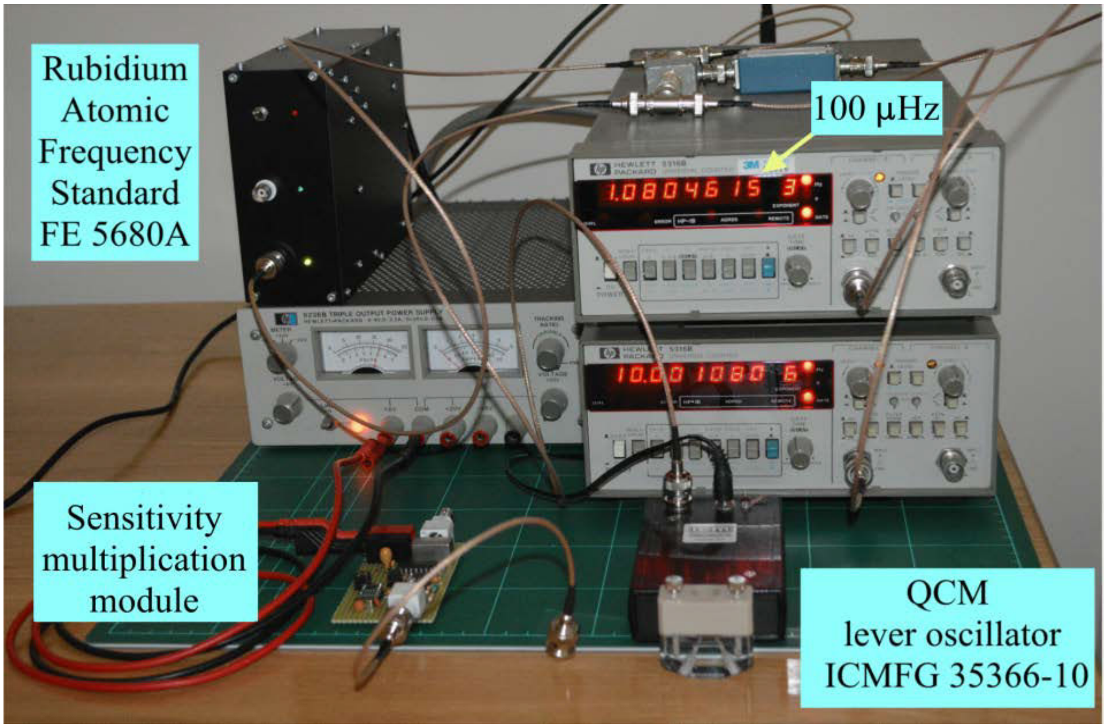

Figure 5: Allan deviation experimental setup based on the heterodyne beat frequency method

3.2.1.1 Quartz Crystal Resonator (151225-10) and QCM Lever Oscillator (ICMFG 35366-10)

For the purpose of this setup a quartz crystal resonator with 10Mhz fundamental resonant frequency (151225-10) produced by International Crystal Manufacturing Co., Inc. was selected. Its properties are an etched surface finish, gold electrodes (1000 Aº Au) with a blank diameter of 0.538” and an electrode diameter of 0.201” [4].

Used in conjunction with the quartz crystal was a QCM lever oscillator (ICMFG 35366-10), also produced by International Crystal Manufacturing Co., Inc. This is a simple and commonly used oscillator circuit especially designed to be used in liquid applications [5].

3.2.1.2 QCM Flow Cell

In order to perform liquid measurements a specially designed QCM flow cell is necessary. The device chosen for this setup was developed by ALS Co., Ltd. [6] as a stable and reliable cell suited for experiments both in a static configuration as well as in a dynamic flow mode. Figure 6 shows the used flow cell kit (model no. 011121)

Figure 6: The used flow cell kit (model no. 011121)

The quartz crystal resonator was fixed between silicon o-rings of the QCM flow cell kit (011121, ALS Co., Ltd.) in its static configuration. Measurements were carried out for demineralized water and a 50% sugar-water solution. In both cases 500µl of liquid was added to the static cell.

3.2.1.3 Mixer, Low Pass Filter and Impedance Matching

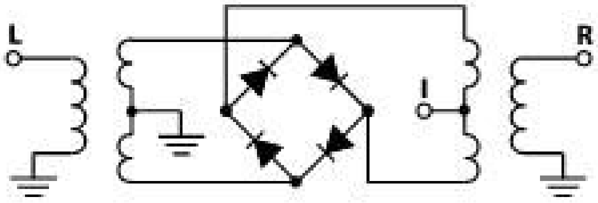

Figure 7: electrical schematic of the ZFM-2 passive mixer

The ZFM-2 (Mini-Circuits Inc.) +7dBm passive mixer ensures the accuracy of the intermediate low frequency. Figure 7 shows the electrical schematic of this particular device [7]. It is, as its name suggests constructed from passive components and based on a diode bridge and two transformers. This particular setup is called a ring modulator (also known as a diode ring double balanced mixer). It is a robust device used extensively in radio receivers, mobile phones and wireless networking systems. To further extract the desired frequency a low pass filter is needed after the output.

The particular device used in this setup is a high quality device with low conversion loss, good L-R isolation (a strict requirement for the beat frequency method since false results can occur if the signals interfere with each other) and a wideband from 1 to 1000 MHz [7].

At the output of the mixer, a low pass filter was inserted with 119 kHz cutoff frequency at - 3 dB and roll-off slope of 44,41 dB/decade. This particular device presents itself as a five pole low pass filter. It allows the passing of signals with a frequency lower than its cutoff frequency and attenuates signals with frequencies which are higher than the cutoff frequency. The implementation of such a device provides a smoother form of a signal by removing short term fluctuations.

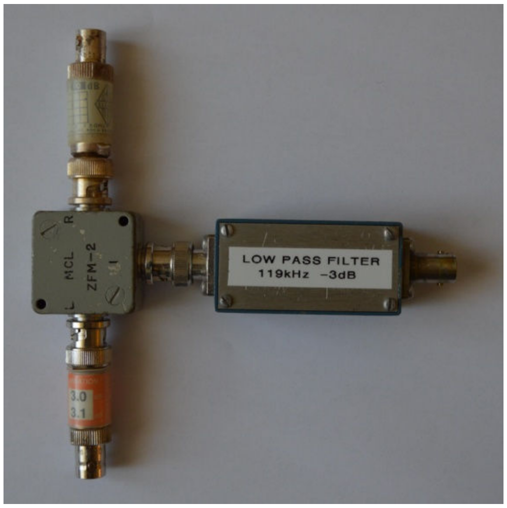

Figure 8: Low Pass Filter in its casing connected to the ZFM-2 passive mixer

The device used in this setup can be seen in Figure 8. The schematic of the implemented circuit is presented in figure 9. This low pass filter is a Butterworth filter which was designed to have as flat a frequency response as possible in the passband. Several topologies have been developed. The one chosen in this case was the so-called Cauer topology which uses only passive components.

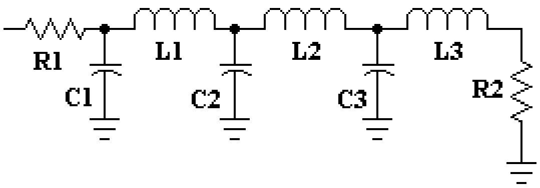

Figure 9: Schematic of Butterworth low pass filter using Cauer topology

Another important aspect when designing high performance experiments is impedance matching. This implies taking into consideration the opposition by a system to the flow of energy from a source. The design chosen in this case is that of a purely resistive network known as a π-attenuator. The impedance matching (50 ohms) in this experimental setup is ensured by a - 3 dB π-attenuator inserted between the output of the rubidium atomic frequency standard and the mixers LO (Local Oscillator) input and by a -10 dB attenuator inserted between the output of the sensitivity multiplication module (or QCM lever oscillator) and the RF input of the mixer.

3.2.1.4. Rubidium Atomic Frequency Standard FE 5680A

A stable reference is a key component to ensure the excellent precision of the heterodyne method. That is why, for this setup, a rubidium atomic frequency standard FE5680A from Frequency Electronics Inc. was used.

The rubidium atomic frequency standard (FE-5680A, Frequency Electronics Inc.) used in this setup has 1.4 x 10-11 σy(τ) (τ = 1 s) Allan deviation and a long term stability of 2 x 10-11 drift/day with an excellent temperature stability [8].

Figure 10 shows a simplified functional block diagram of the FE-5680A device. The used rubidium atomic frequency standard uses the property of atomic resonance in a Rubidium Physics Package to control the output frequency of a 50.255+ MHz Voltage Controlled Crystal Oscillator (VCXO) via a Frequency Lock Loop (FLL). Its functional blocks consist of an RF Generator, a Lock-in Amplifier and the Rubidium Physics Package.

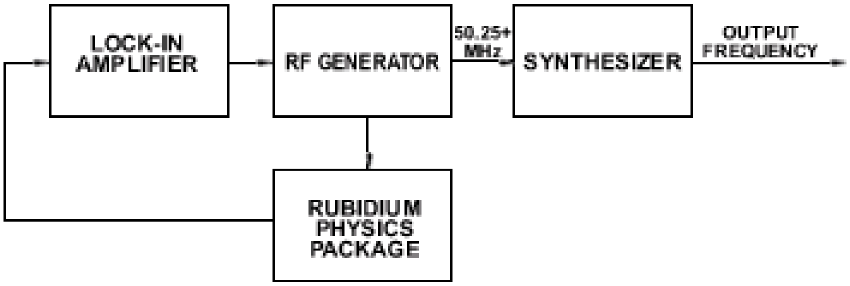

Figure 10 simplified functional block diagram of the FE-5680A rubidium atomic frequency standard

Various rubidium frequency standards are available providing output frequencies according to the users needs. For the experimental setup presented herein a device was chosen which provides a steady output of 10MHz. The device used in the experimental setup is shown in figure 11. It is housed in a metal encasing which further houses a good quality power source and an interface for operating in the desired setup.

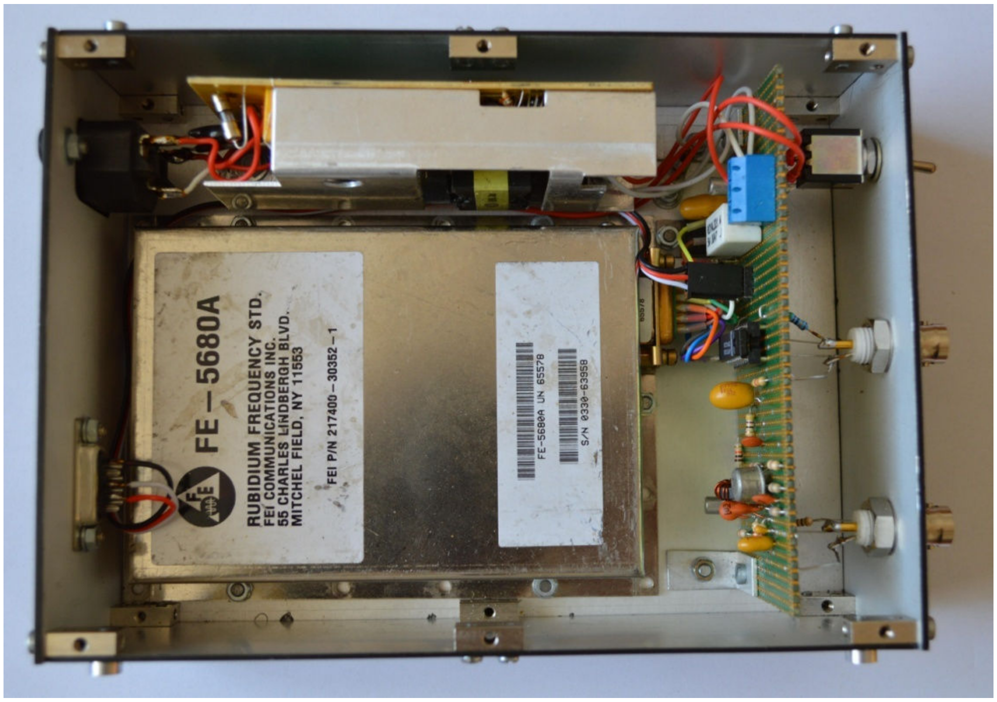

Figure 11: Rubidium Atomic Frequency Standard FE 5680A used in the experimental setup

3.2.1.5. Universal Counters HP-5316B

These counters provide an important link between experimental setup, experimenter and data recording device. The frequency is determined by comparing the signal to the counter's time base oscillator. The rubidium frequency standard used as reference has been previously discussed. The frequency counters used in this experiment were two HB-5316B devices. These are generally known for their high quality and precision and belong to a family of HP devices often used in high precision experimental setups. Both were rigorously calibrated and allowed to warm up and stabilize, thus eliminating any known error sources that could possibly be induced by improper experimental procedures.

3.2.1.6 GPIB – USB Interface

Both universal counters have a GPIB (General Purpose Interface Bus) port. This was developed by the manufacturer HP and has become a standard for automated test equipment. It is an 8-bit, electrically parallel bus, which employs sixteen signal lines — eight used for bi-directional data transfer, three for handshake, and five for bus management — plus eight ground return lines. Known as IEEE-488, it was not specifically planned to be a peripheral interface for general purpose computers - the focus was on instrumentation. However, GPIB can be connected to the USB port of a general purpose computer, using a physical converter and implementing fitting communication software.

3.2.1.6.1 Triggerable USB-based GPIB controller

For this experimental setup a special triggerable USB-based GPIB controller was used, that executes a sequence of GPIB commands each time a software trigger is received. Figure 12 shows the developed device. The connector implements an IEEE 488.1-compliant GPIB bus controller in the software by way of the PIC18F2550 microcontroller's external I/O lines. The PIC18F2550 microcontroller also incorporates an embedded USB 2.0, which helps in reducing both cost and complexity of build while enabling the integration of a number of critical functions into a single device.

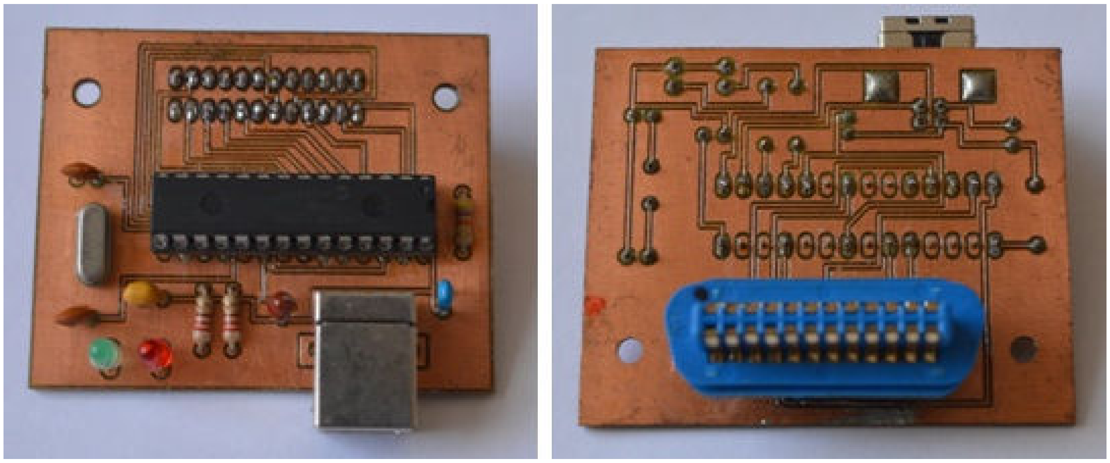

Figure 12: The USB-based GPIB controller used in the experimental setup. Top view (left) and bottom view with GPIB connector (right)

One of the primary concerns in the design of this device was the integration of as many functions as possible into a single device that would be cost efficient. In order to achieve this a PIC18F2550 microcontroller was chosen to lie at the heart of the system because of its high level of integration. It includes the primary flash memory storage for the software, an integrated USB 2.0 interface, and I/O pins. This microcontroller presented itself as the perfect solution for implementing the GPIB controller function in software. The I/O pins on the PIC18F2550 microcontroller allow it to be easily interfaced to the GPIB bus signals. Two LEDs are used to display the internal state of the triggerable USB-based GPIB controller. Figure 13 shows the schematic of the device with its components.

By purposefully omitting to use a dedicated GPIB controller, the device does not only reduce costs, but it also gives a measure of investment protection because any updates to the GPIB protocol can be made to the system via a software update to ensure a continuing compatibility. Also, the software implementation of the trigger version of the controller in this device improves the command and data transfer speed.

Since the GPIB bus signals require line drivers external to the PIC18F2550 microcontroller to ensure compatibility with IEEE 488 standard, two commonly used Texas Instruments transceivers (SN75160 and SN75161) can be integrated into the design to achieve best results. In the presently used version without transceivers (Figure 13) it is recommended to use short GPIB cables and no more than four devices on the bus. Since these requirements were not presented by the experimental setup this construction best fitted the necessities that had to be met.

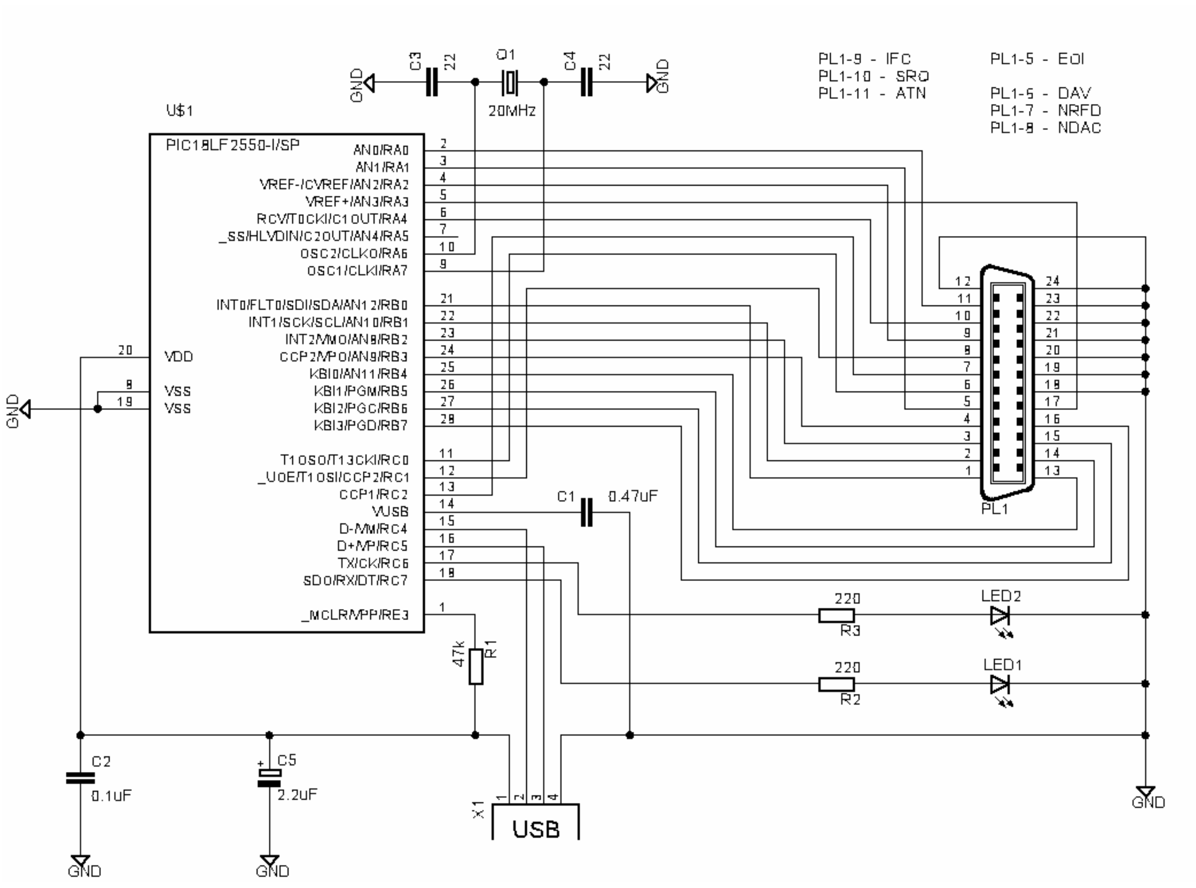

Figure 13: schematic of the USB-based GPIB controller

3.3 Median Absolute Deviation

Before the Allan deviance computation, recorded data was plotted together with outliers using 3 x MAD and 5 x MAD (Median Absolute Deviation) criteria for statistical dispersion validation. These graphs show how the system behaves in different mediums typical for QCM measurements. The studied mediums were air, water and a 50% sugar-water solution to test the devices operation in more viscous media typical for biological applications. Each time, 500µl of demineralized water or sugar-water solution was added to the static cell

Outliers are observed points that are distant from the other observations. In large samples of recorded data outliers are to be expected and therefore when assessing a devices quality such as in this case one has to ensure choosing a computation method that does not yield misleading results. The Median Absolute Deviation is one such computational method. For these measurements all possible precautions were taken to ensure accurate results. Measurements were carried out under constant temperature and humidity with no sources of vibrations of any kind in the proximity of the experimental setup.

3.3.1 Measurements in Air

Measurements were all taken under the same environmental temperature and humidity to ensure the results accuracy. The temperature was 19.8 ^{0}C and the humidity was 64%. The duration of measurements was 1 minute each.

Figure 14 shows the Allan Deviation (above) and the corresponding MAD (below) taken with a multiplication factor of 1. The deviation is well within the determined thresholds and spans from 0.2 to -0.2. Given that the quartz crystal used in QCM setup works best in air, no outliers are discernable and as stated the MAD is positioned between low values.

Figure 15 shows the Allan Deviation (above) and the corresponding MAD (below) taken with a multiplication factor of 6 (the maximal multiplication attainable with the sensitivity multiplication module). Since in this case the data is expanded by a factor of 6, it is to be expected that the MAD lies in a slightly larger interval. In this case: 4 to -4.5. In this case as well the deviation lies well within the thresholds and no outliers are present. While the data volume is increased, incorporating data that is more sensitive and susceptible to variation, the statistical dispersion still proves the reliability of the device and the accuracy of the delivered data.

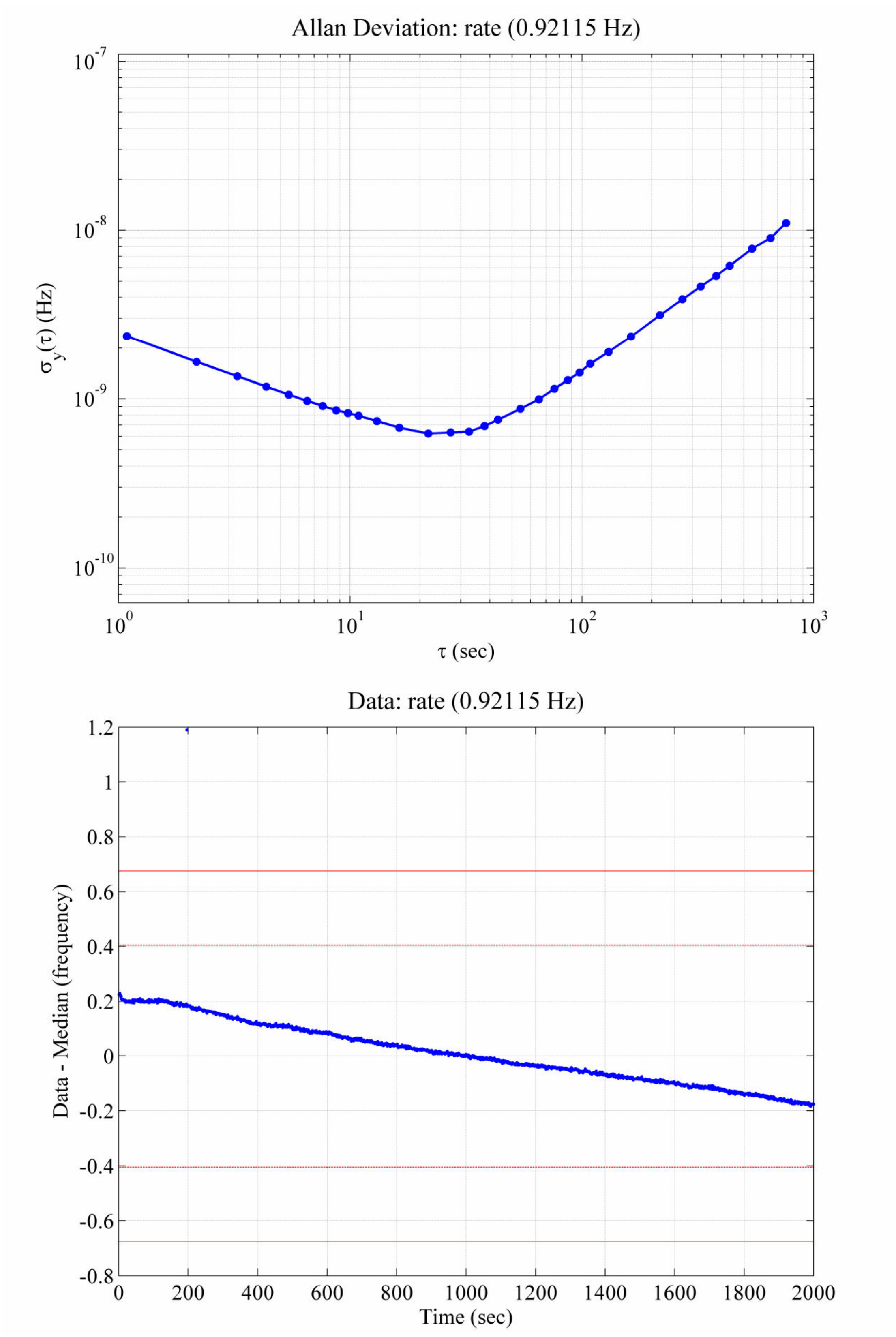

Figure 14: Allan deviation and MAD taken in air with a multiplication factor of x1

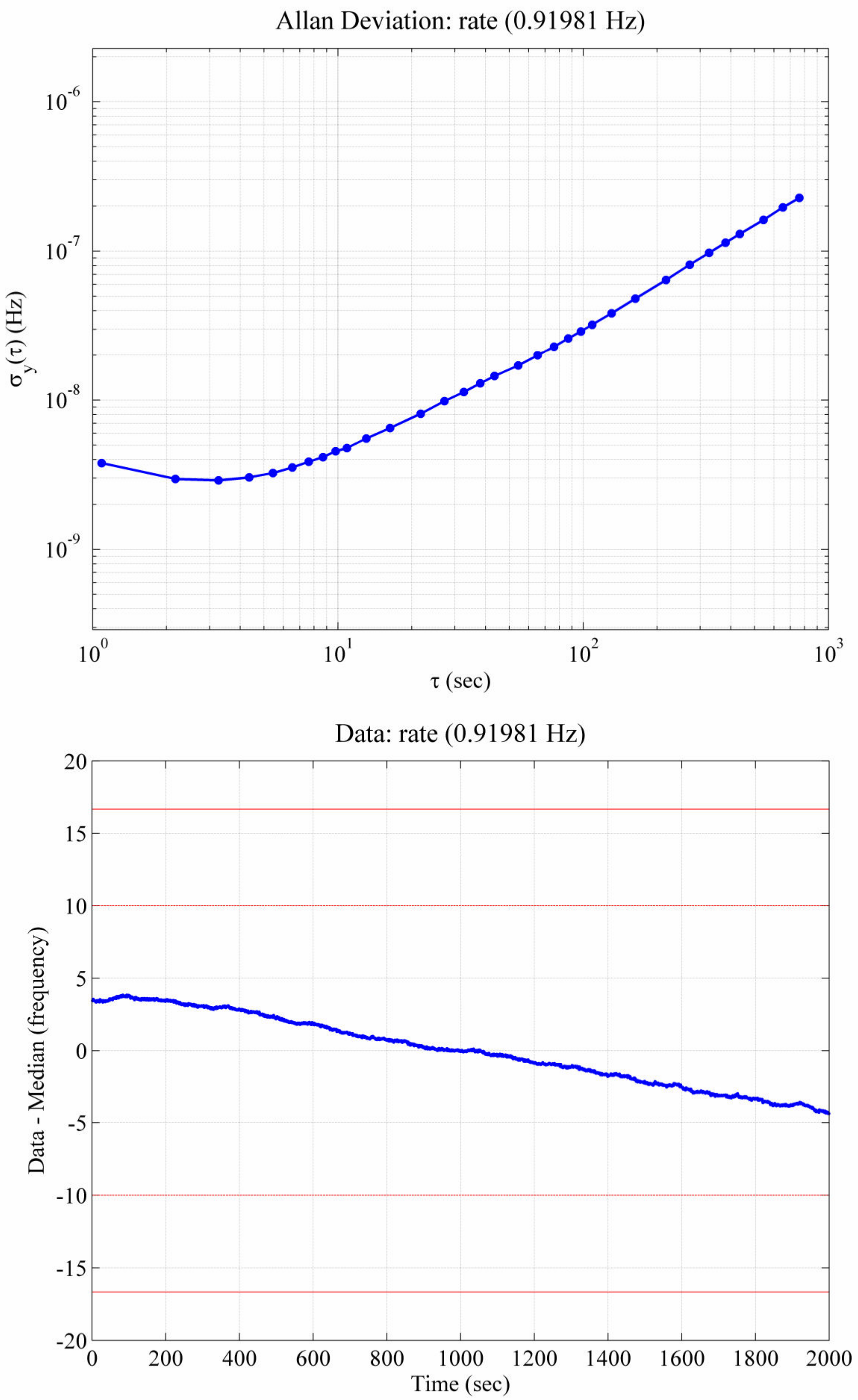

Figure 15: Allan deviation and MAD taken in air with a multiplication factor of x6

3.3.2. Measurements in Water

Since the 1980's when Kanasawa proved the possibility of extending QCM measurements to a water medium, provided one of the faces of the quartz crystal sensor remains exposed to air a large series of measurements are being performed under such conditions. Measurements in a water medium are however subjected to a higher damping factor than measurements taken in air.

Figure 16 shows the Allan Deviation (above) and the corresponding MAD (below) measured in pure water with a multiplication factor of 1. Again, the deviation is well within the determined thresholds and the deviation spans from 5 to -4. While outlying data points are discernable, these are present in a reduced quantity. Given the nature of the experiment they are to be expected but would only be cause for worry if they were present in large quantities, enough to influence the MAD computation and deviate its curb.

The Allan Deviation (above) and the corresponding MAD (below) taken with a multiplication factor of 6 (the maximal multiplication attainable with the sensitivity multiplication module) are shown in Figure 17. The MAD lies in an interval between 23 and -21. This is accountable due to the damping caused by the liquids viscosity. Still the MAD lies well within the thresholds and the few outlying data points are negligible. Again under the given conditions, with an increased data volume and incorporating data that is more sensitive and susceptible to variation, the statistical dispersion shows the device to be stable and reliable with accurately delivered data.

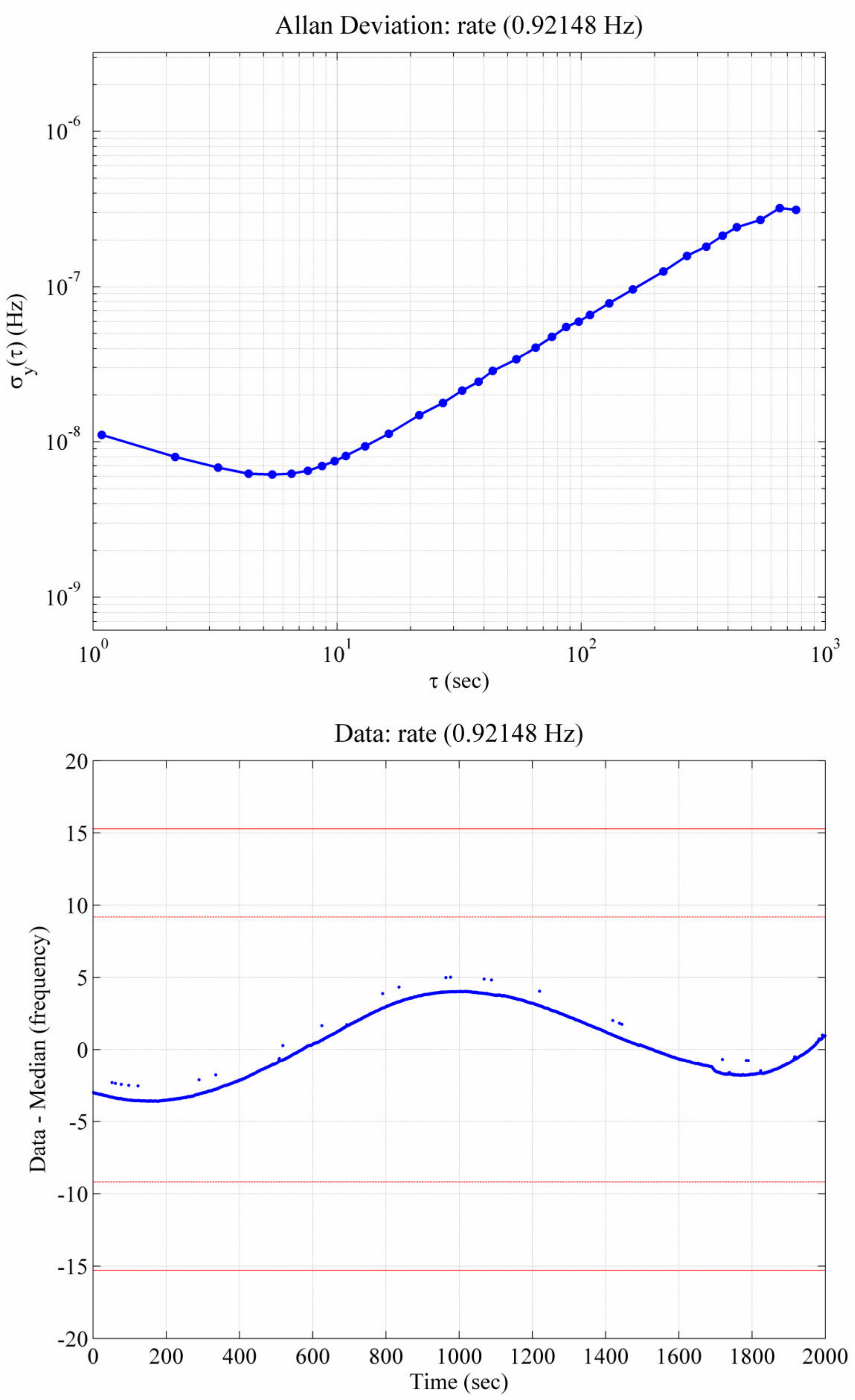

Figure 16: Allan deviation and MAD taken in pure water with a multiplication factor of x1

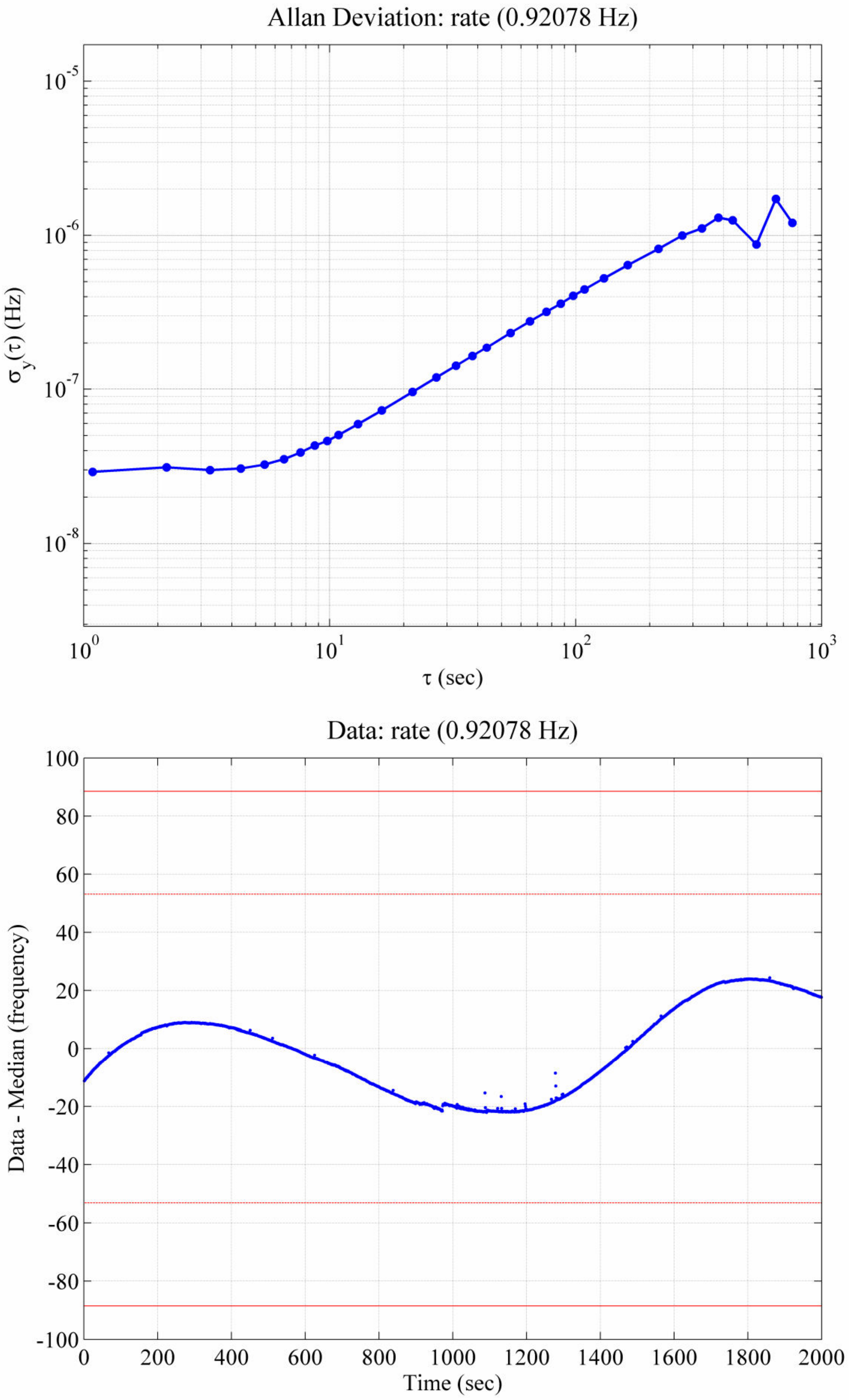

Figure 17: Allan deviation and MAD taken in pure water with a multiplication factor of x6

3.3.3. Measurements in Sugar-Water solution

Measurements performed on the QCM in biological medium prove to be a great strain on the quartz crystal sensor due to the increased viscosity of the liquid medium necessary for the experiments. To simulate these conditions a sugar water solution of 50% was prepared, based on pure sugar and demineralized water (0.22uS/cm).

In Figure 18 the Allan Deviation (above) and the corresponding MAD (below) taken in sugar-water solution with a multiplication factor of 1 are shown. The deviation lies in the interval between 30 and -30. The MAD lies again well within the determined thresholds and no outlying data points are present.

Measurements performed in sugar-water solution with a multiplication factor of 6 are shown in Figure 19. The Allan Deviation (above) and the corresponding MAD (below) show good stability. While again, increasing the data volume and incorporating data that is more sensitive and susceptible to variation the MAD occupies a larger interval (180 to -100), the determined thresholds are not overstepped and the statistical variation is shown to be relatively constant. The device is still operating stable and reliably even under the circumstances of dense liquid medium.

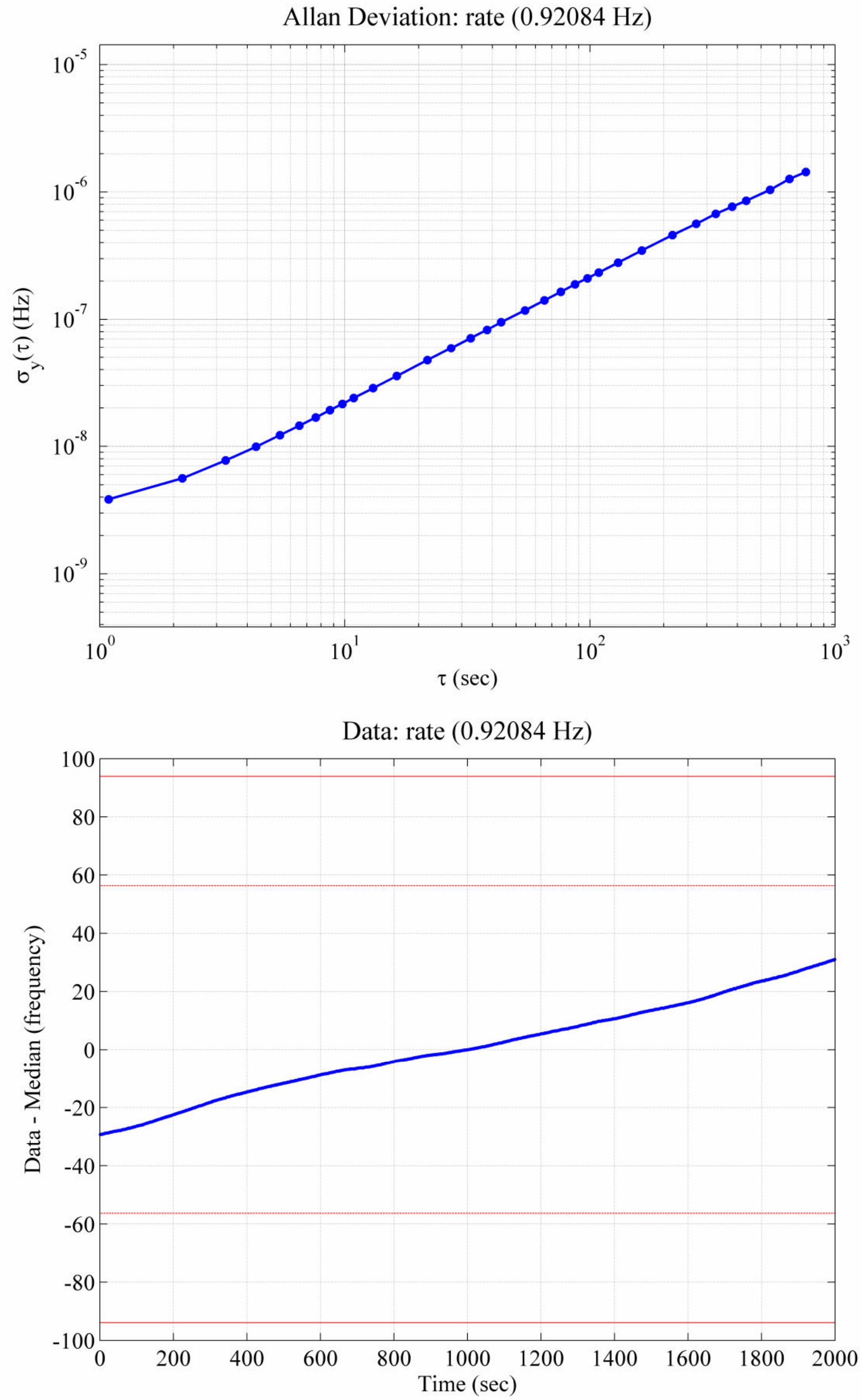

Figure 18: Allan deviation and MAD taken in sugar-water solution with a multiplication factor of x1

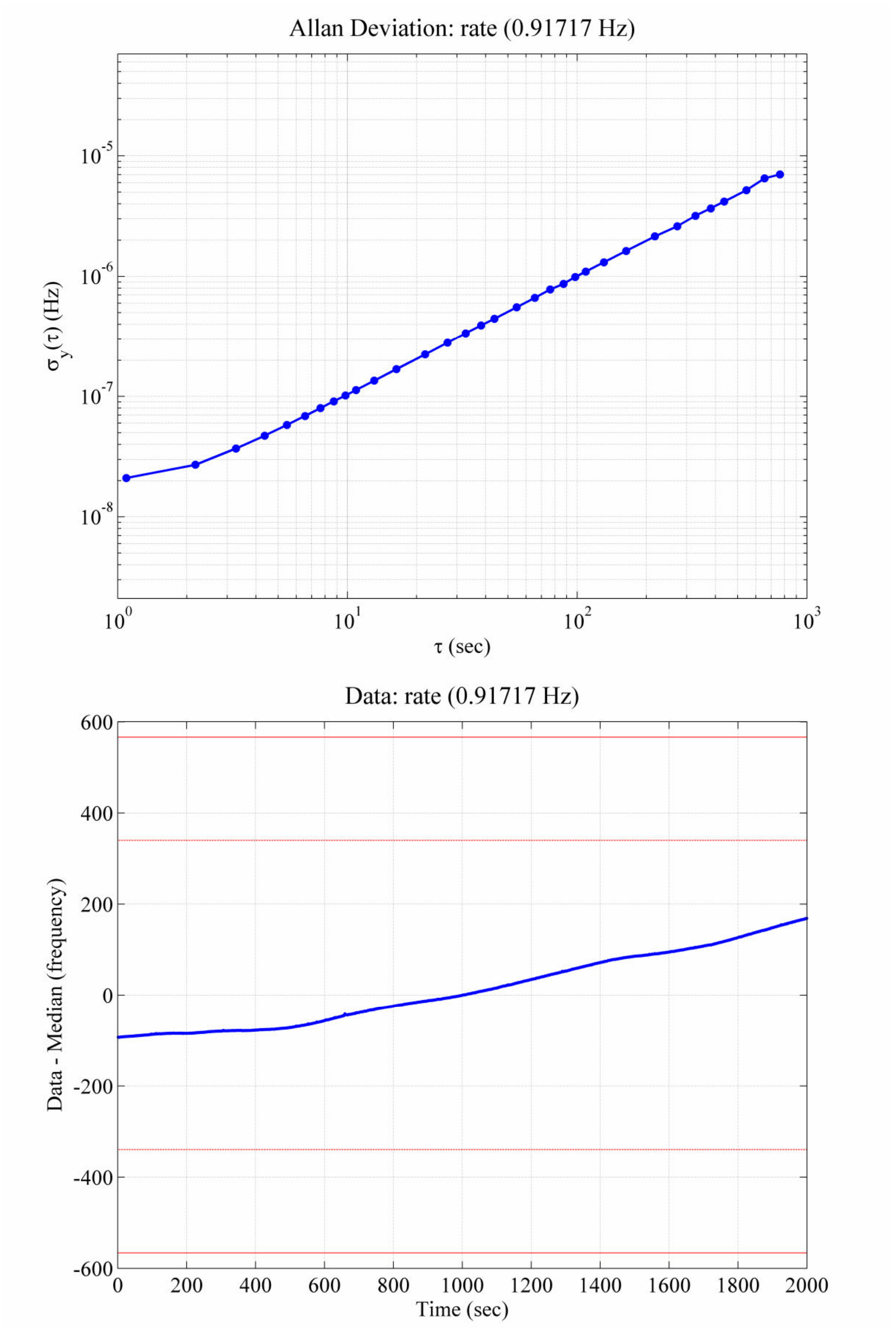

Figure 19: Allan deviation and MAD taken in sugar-water solution with a multiplication factor of x6

3.3.4. Conclusions on the Median Absolute Deviation Analysis

All common experimental mediums that are used in QCM experiments were studied in order to assess the statistical dispersion validation. Air, water and a 50% sugar-water concentration were used as experimental environments. The Median Absolute Deviation was chosen as a calculation method due to its suitability.

Outlying data points can be observed in negligible amounts and at no time were outliers present beyond the X3 or X5 threshold. While the most stable results were obtained as expected in air, the device maintains its reliability even under liquid flow conditions in water as well as in media with higher viscosity. Under liquid conditions the damping phenomenon behaves as expected hindering the quartz crystals resonance. Especially here the sensitivity multiplication module is of use in order to acquire data of greater precision, given that liquid medium is currently the most often encountered experimental medium for QCM studies.

Each time the Allan Deviation is shown to have stable values. This shows that the setup is operating steadily. The MAD occupies a greater interval as the viscosity of the medium rises but remains stable in its distribution.

These measurements prove that the statistical dispersion remains stable both in air and in liquid medium. Thus the acquired data maintains its precision even at the maximal multiplication factor attainable by the sensitivity multiplication module (6X). Data acquisition is stable and reliable. The setup altogether is therefore proven to be executed correctly. The sensitivity multiplication module itself proves to be a reliable device, serving its intended purpose without errors while providing enhanced data acquisition.

3.4. Allan Deviation Measurement Plot

The main goal of the Allan Deviation analysis was to evaluate the effect of the sensitivity multiplication module added to a classical QCM setup and determine what multiplication factor would be best suited in the studied environments. The goal of the device of course is to have no error effect in the setup by multiplying the signal without distorting it and achieve a high multiplication factor.

As with the MAD analysis, measurements were performed in order to validate the devices capability in three different settings usually encountered in QCM experiments. Measurements were performed in air, in water and in a 50% sugar-water solution (prepared from pure sugar and demineralized water (0.22µS/cm)). Each time, 500µl of demineralized water or sugar-water solution was added to the static cell.

Figure 20 presents two plots – one set of measurements in all studied mediums performed without the sensitivity multiplication module (above) and one set measured with the module inserted in the configuration (below). The multiplication achieved with the module and presented in the second plot was that of 6X. A certain random walk drift is present on the right side of the plots in each case. This was as expected due to the conditions in which quartz crystal resonators operate in QCM setups. Since the quartz crystal is exposed, its Q-factor decreases and random walk noise occurs in any QCM setup. However, what is of importance is that there is no significant difference in the drift between measurements taken with and those taken without the module inserted in the setup. This indicated that the configurations stability is maintained.

The most important aspect of the plots is, of course, the resolution enhancement and its effect on the systems stability. The minimum Allan Deviation in typical QCM setups is in the range of 10−6 to 10−8 σy(τ) (τ = 1 s). This limit is imposed in part by the limitations of the electronics setup. After applying the multiplication factor (n) of the sensitivity multiplication module, it is therefore of interest that the Allan deviation is kept below 10-7 σy(τ) (τ = 1 s). This can be seen in the second plot presented in Figure 20. This condition remains fulfilled even with a multiplication factor of 6X in all analyzed mediums (air, water and sugar-water solution)

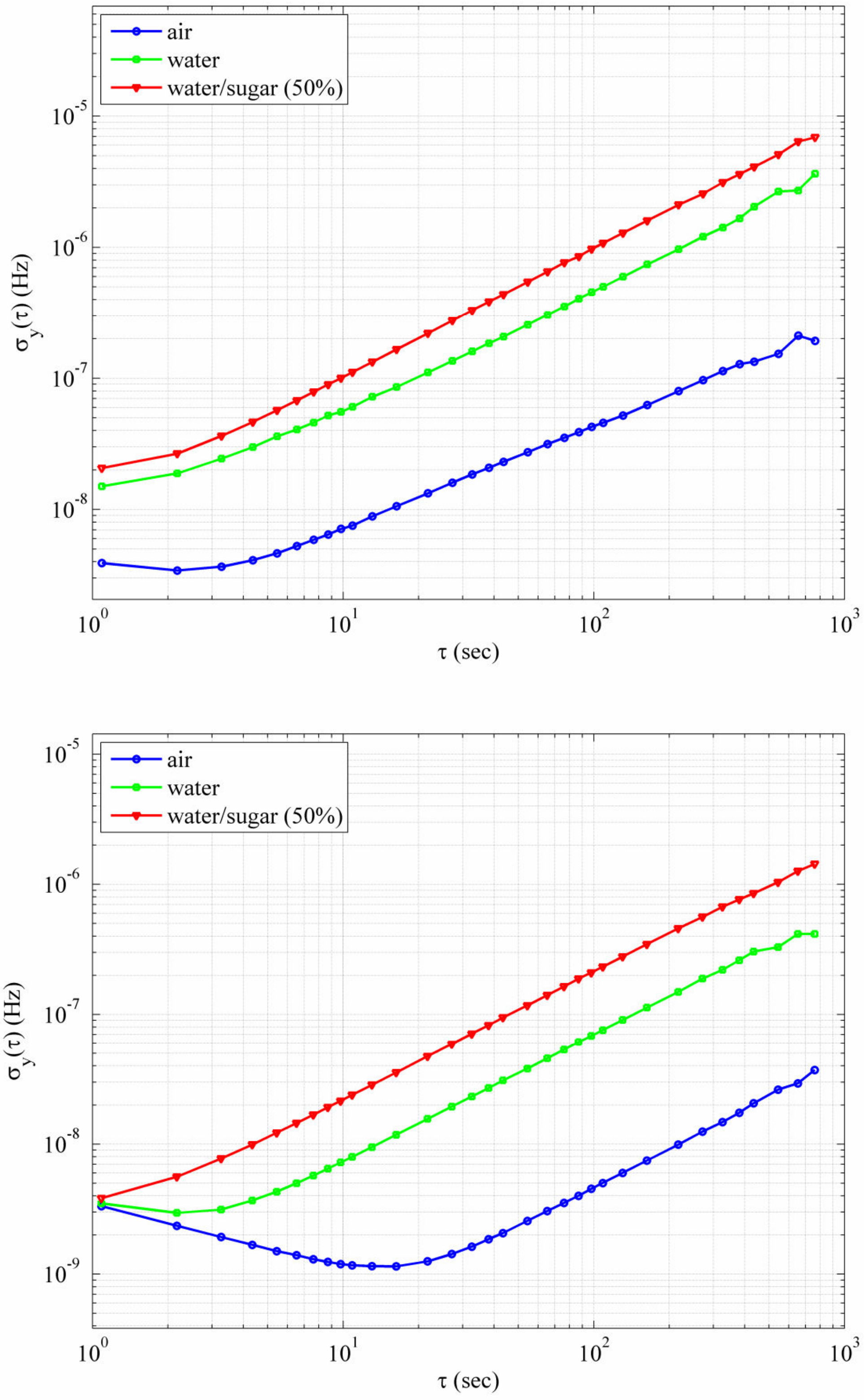

Figure 20: Allan deviation: (a) lever oscillator, (b) sensitivity multiplication module.

3.4.1. Conclusions on Allan Deviance Measurements

The behavior of the sensitivity multiplication module, integrated in a classical QCM experimental setup, while increasing the frequency shift (sensitivity) up to six times, has been proven to be stable and accurate. No additional noise factors are inserted to the system and while the data is acquired with greater precision it has been shown to be undistorted.

Even with a rise in sensitivity, the minimum Allan Deviation required in order to validate the device is not only met but done so without being anywhere near a limit that might raise suspicions on the devices performance in applications with high strain.

3.5. Conclusions on Validation Measurements

The sensitivity multiplication module was developed to be used in high speed QCM applications [9-12] based on frequency to voltage converters, with a typical resolution of 1Hz, limited by the conversion noise, or based on direct frequency counting with 1s gate time, which are typically developed around application specific integrated circuits (ASIC)[13], field programmable gate arrays (FPGA) [14] and/or microcontrollers [15,16] for portable applications.

An experimental setup was devised, resembling a classical QCM setup, in order to test the devices capabilities, evaluate its effect on the setup, determine its accuracy and prove the acquired data reliability. Experiments were performed in air, water and a 50% sugar-water concentration in order to assess the devices properties under regular QCM operation conditions. The sensitivity was multiplied up to a factor of 6X.

The MAD (Median Absolute Deviation) analysis performed for statistical dispersion validation, has shown that the devices data acquisition precision is reliable and stable.

The Allan Deviation analysis reveals that while the module performs its intended duty of multiplying the setups frequency shift, it does not induce any errors or noise. It does not have a negative effect on the systems stability, maintaining good deviation values in any medium. This validates first of all the devices conception and construction, but also shows that the right components were chosen to be used in its construction.

The device was shown to perform accurately, steadily and fast. This fulfills the requirements for its intended usage. Now, all that remains to be shown is that the device can indeed be inserted into a classical QCM setup, thus making it not just a nice concept but proving its usefulness beyond any doubt.

3.6 Inclusion of the Sensitivity Multiplication Module in a Classical Experimental Setup

For an experimental evaluation of the sensitivity multiplication module, the device was integrated in a dual channel QCM experimental setup as shown in the diagram from Figure 21. Note the similarity to the setup used for validation measurements. This is to show that in an experimental environment the device is expected to perform as well as in the validation analysis presented before.

The experimental setup consists of two HP-5316B universal counters both connected to a PC for data recording purposes through a GPIB to USB adapter, a rubidium frequency standard FE-5680A which is used as a reference for both counters, a QCM flow cell kit (011121, ALS Co., Ltd.) equipped with a QCM lever oscillator (ICMFG 35366-10, International Crystal Manufacturing Co., Inc.) and a quartz crystal resonator with 10MHz fundamental frequency (151225-10, International Crystal Manufacturing Co., Inc.) and of course the sensitivity multiplication module itself.

A Matlab script was again written to be able to collect data from the universal counters and generate a typical QCM plot based on the acquired information.

The main focus of the research presented herein was the sensitivity multiplication modules design and development. The focus was on the device and its capabilities. In the following section an experiment was designed to prove its functionality again, with the emphasis on the devices performance. To leave no room for speculations, the most straining environmental conditions usually found in QCM setups have been chosen for the experiment. That is why the experiment was performed in liquid. The quartz crystal oscillator was inserted between the silicon o-rings of the flow cell. The flow cell was used in static mode. 500 µl of demineralized water were added to the static cell. 4 µl of the 50% sugar water solution (based on pure sugar and demineralized water (0.22 uS/cm)) were added.

The results of the experiment performed are shown in Figure 22. This is a classical QCM output graph showing the measured frequency shift over time. The two plots present on the graph show the time-dependent frequency shift at the output of the lever oscillator (red line) with no sensitivity multiplication applied and the frequency shift at the output of the sensitivity multiplication module with an increase of resolution by a factor of 6X(blue line) after 4 µl drops of sugar-water were added. As can be seen from the image, two drops were added (one at t=100s and one at t=500s). The resonant frequency shift was monitored and recorded continuously throughout the frequency stabilization.

The experiment was conducted at a room temperature of 21° C and a relative humidity of 61%. Any slight fluctuations of room temperature or humidity have a minor influence on the frequency behavior. That is why in any QCM experiment, these have to be considered when making evaluations.

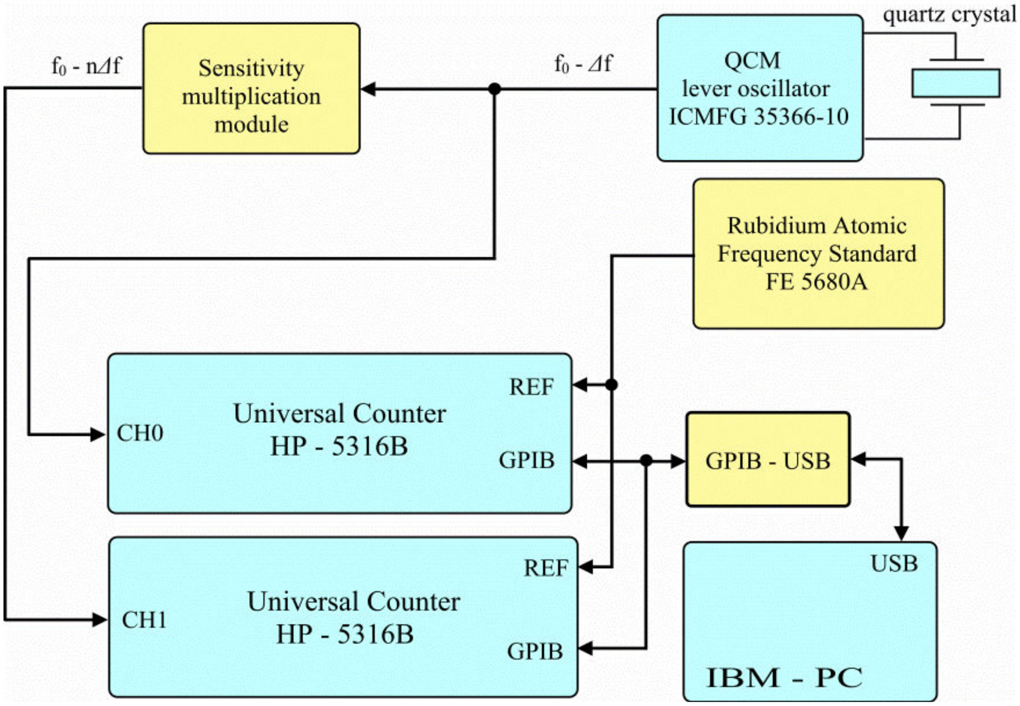

Figure 21: Diagram of the experimental setup

Figure 22 therefore presents the effect of the sugar-water drops in contact with the gold electrode, followed by a diffusion process that takes place in the static cell. What is of interest is the fact that while the measurements performed with the sensitivity multiplication module operating at a multiplication factor of 6X show a greater resolution, allowing better monitoring of the experiment, they only provide an enlarged version of the original signal with no difference and a rigorously maintained rapport between the two signals can be observed.

The measurements were repeated several times in order to confirm the stability of the sensitivity multiplication module. Each of the plotted graphs (not shown here) presents itself identically to the one depicted. Each time the graph of the sensitivity enhanced measurements maintains its rapport to the original signal while providing a more accurate depiction of it.

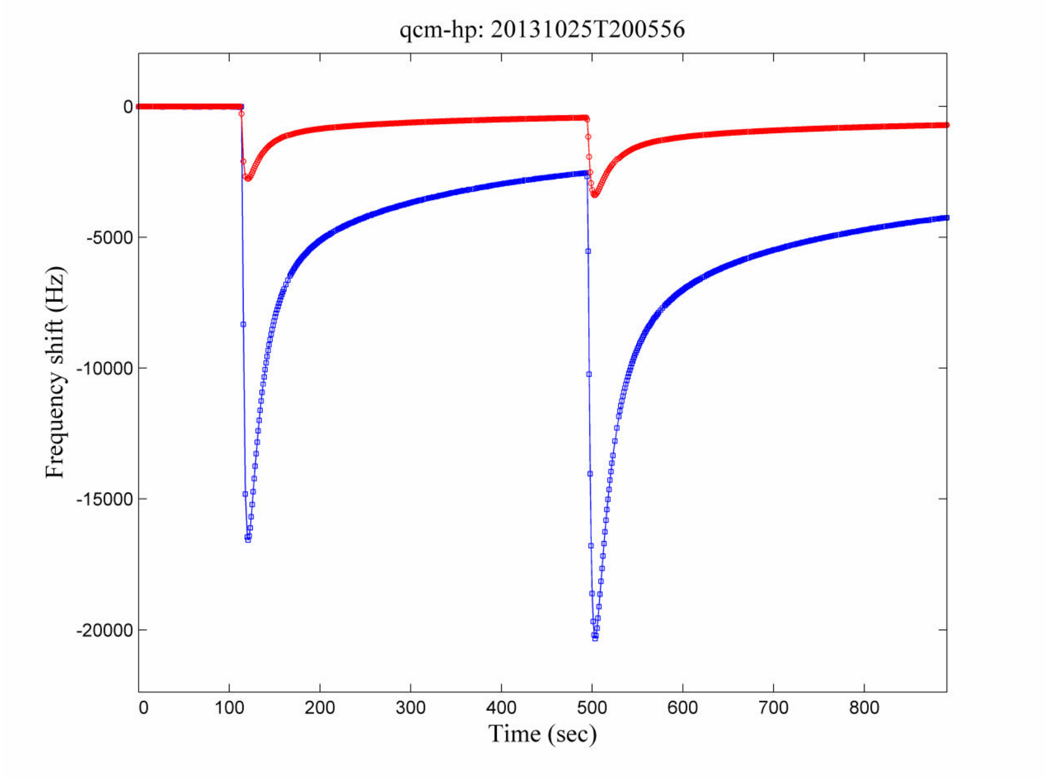

Figure 22: Time-dependent frequency shift at the output of the lever oscillator (red line) and with a multiplication factor of 6X added by the sensitivity multiplication module (blue line) obtained by adding two 4ul drops of 50% sugar-water concentration in demineralized water

This practical dual channel QCM experiment proves the functionality of the sensitivity multiplication volume and its capabilities in a practical setting. It shows how the module can be readily inserted in a classical QCM setup, making it easy to implement. Most importantly, its intended functionality was confirmed by the frequency shift at the output of the module in rapport with the frequency shift at the output of the lever oscillator. Thus the common compromise between resolution and sensitivity, which is a serious concern for any QCM experimenter, can be dealt with elegantly by using this module to improve data resolution while retaining the sensitivity of the quartz crystal sensor.

The continuous frequency shift can be easily measured with available instruments and show the high experimental potential of the sensitivity multiplication module, especially in high speed QCM applications based on frequency to voltage converters or in portable applications.

Conclusions on the Sensitivity Multiplication Module

The design, operation mode and results of the proposed sensitivity multiplication solution for the Quartz Crystal Microbalance have been discussed. The chosen design solutions have been justified in the context of existing options and the novelty of the approach was demonstrated as well as experimentally examined.

The objective of this device was to improve the existing QCM measurement technology in order to obtain data of higher quality. This device has hereby been proven to be a high performance device, able to improve the classical QCM method over a wide range of applications.

A serious compromise that has to be considered by QCM experimenters is the compromise between sensitivity and resolution. In applications where conventionally used quartz crystals are not sensitive enough for the desired experiment, sensors of higher frequencies have to be used. This however means that by increasing the physical sensitivity of the crystal, its Q factor drops and it becomes prone to higher levels of noise, making the resolution of the acquired data also drop significantly. This device eliminates this problem by allowing the use of stable oscillators while obtaining information up to six times more accurate without any loss in resolution. As the results have shown, inserting the proposed module between the QCM oscillator and the frequency counter as a post-processing unit presents itself as a simple and elegant method for overcoming the compromise between sensitivity and resolution, allowing the experimenter to have both by retaining the sensors resolution and improving the quality precision of the acquired data.

Validation measurements were carried out in order to assess the quality of the device, followed by an experimental setup in order to prove its practical functionality. Validation measurements were carried out in air, in water and in a sugar-water concentration of 50%, based on demineralized water and pure sugar (0.22uS/cm). The experimental setup used a liquid cell filled with water, where 4ul drops of sugar-water were added and recorded. Thus the module has proven its capabilities in all common environments common for QCM experiments.

Median Absolute Deviation Analysis was performed as a statistical dispersion validation method, proving the accuracy of measurements. Allan Deviance analysis of the QCM system with the sensitivity multiplication module was performed for each particular quartz crystal load in order to determine the real resolution of the QCM and to estimate an optimum multiplication setup for the ICS511 PLL clock multipliers. Experimental measurements confirm the theoretical predictions and validate the devices practical usability even in the harsh conditions found in liquid environments.

The design and choice of parts was carefully weighed in order to obtain a device which, as measurements show, transmits a high quality signal without injecting noise or producing errors into the recorded data. Its uncomplicated design makes this patented device cost feasible despite its high quality performance. An important aspect is also its modular form, making it easy to be inserted into classical QCM setups and therefore allowing a certain adaptability of the already existing method, thus making it easy to implement and compatible with a wide range of setups, including portable applications.

To sum things up, the proposed sensitivity multiplication module is not only fast and accurate but also easy to implement in a variety of setups while maintaining very good cost feasibility. It presents itself as a high quality instrument, as validation measurements have shown and tackles a very old problem of QCM devices (the compromise of sensitivity vs. resolution encountered in QCM systems) in a new and efficient way.

The results of the research into quartz crystal sensors conducted over the past three years have also yielded two patents:

I.Burda A.Tunyagi, A.Silaghi, S.Simon, O.Popescu; A Method for Measuring the Impendance Resistance of Resonance Immunosensors; RO patent no. 129482/30.05.2014

and

I.Burda, A.Tunyagi, A.Silaghi, S.Simon, O.Popescu; Sensitivity Multiplication Module for a Resonant Sensor; RO patent no. 129483/30.05.2014

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