CAN SOUND STOP SCALING: A NIR SPECTROSCOPY STUDY OF ULTRASOUND TREATED WATER

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ABSTRACT
We used Near Infrared (NIR) Spectroscopy on water to compare the characteristics of tap water subjected to various treatments: 1. Ultrasonication degassing, 2. Vacuum degassing and 3. Commercial de-scaling device based on sound (Amtech). Water treatment showed a significant change in the second-order harmonic stretch of the O to H bond. In IR this stretch is the vibration of the O-H bond within the single water molecule and is present from 3000 to 3400 cm^{-1}. Using the second-order vibration in the NIR region reveals harmonic oscillations between molecules and carries information of the interaction with its surrounding, such as secondary clustering around gas and ions such as Ca^{++} and Mg^{++}.

INTRODUCTION
Scaling is detrimental to many industries, and mitigation methods can be costly, both in lost production and inhibitor chemicals [1]. Therefore, noninvasive methods are favorable. Physical treatment of water, such as electromagnetic or acoustic interference, poses a viable option [2,3,4]. Some commercial de-scaling devices are based on pulsed sound and electro/magnetic emittance, and the mode of action of these devices is not fully understood. Other studies have shown that the mode of action of electro/magnetic water treatment occurs through a change in particle charge and on de-gassing of CO_2 gases and subsequently increasing the pH of the solution [5]. However, the potential direct effect of electromagnetic waves on the water molecules and their fundamental frequencies is unknown. [2,3,6]

For commercial relevance, such water treatment systems must have a long-term effect. Common proofs of the effects are often described as pictures of tubes and filters after months in contact with water. However, this is difficult to replicate in a lab environment and likewise are short term effects not easy to measure directly on water samples. This could explain some of the contradictory results of scientists and consumers/producers of electro/acoustic water devices [2]. In this work we investigate both short term and long-term effects, and its potential effects on water/ion solutions directly.

METHODS
To identify subtle effects that water treatment can have, we have performed a wide range of tests to the water samples. For duration, we have defined short-term exposure as 1 hour, while 1 month represents long-term exposure.

The samples are taken from DTU water (Lyngby, Denmark), a communal water source with a total lime scale hardness of 19 ^{O}dH , it is a collective of temporary hardness = 14 ^{OdH} (alkalinity hardness) and lasting hardness = 5 ^{O}dH. In the dry residue, there is $CaCO_3$ 47,5 % of the 527 mg/l. residue.

The experiments were carried out over 6 months in total.

The results of the tests performed are:

- Drop dry morphology (Coffee ring effect) on SiO2 (glass), and gold-coated nano grass substrate used for Raman spectroscopy.
- FT-IR and NIR of water samples, using a Shimadzu NIR/mid-IR spectrophotometer with an InGAs detector.
- ORP and pH of pure water
- Polarized light microscopy of almost dry water samples, possibly revealing a crystal structure change. Attention to the dry/wetness% as this could affect the outcome
- Dynamic light scattering DLS of reduced water samples to monitor the charge change of water particles.

MATERIALS
The electro-sound emitter was provided by a Danish company for free during the testing period. The audio signal is a weak audible signal with a pulse period of about 6 pr. second, there is potentially a ultrasonic component of the sound, the sound signature is proprietary to the company and is therefore not shown. In Figure 1, we can show the weak magnetic pulse from the emitter:

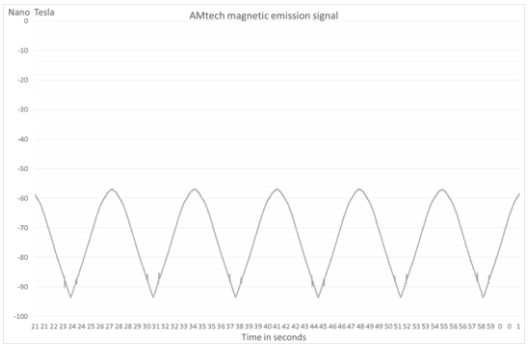

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Figure 1.: Electrical signal emitted from the transmitter of a commercial sound device; the pulse intensity is very weak 35 nano Tesla with a period of 6 seconds.

The Shimadzu IR tracer 100 was used with a tungsten lamp. Julabo Corio CD-200F (liquid cooling heat exchanger and pump); Falcon NIR Transmission -Peltier temperature control [Pike Technologies]

DLS zeta potential Anton Paar DLS zeta potential. CaCO3 calcite and aragonite were purchased at VWR. Milli-Q- water was provided by an in-house Direct-Q® Water Purification System.

Raman spectroscopy was done at DTU Nanotech using a Thermo Fisher surface scanning Raman spectrophotometer microscope and SILMECO silver coated nano grass SERS substrate with 120 nm pillars. (ref. www.silmeco.com)

Scanning electron microscopy was done at the DTU Nanolab, with assistance from personnel, samples were added to carbon tape and scanned. Some surface charging was seen since CaCO3 is not well conductive.

Ultrasound was performed for 15 min with a VWR ultrasonic cleaning bath with approximately 1 liter of water in the bath.

RESULTS

Several types of tests were performed according to the manufacturer's claim of effect on water; others were chosen based on previous findings and observations in the literature [1,2,3,5].

Surface tension, pH and ORP

Surface tension was tested with 3 different methods (Wilhelmy plate, contact angle, and pendant drop goniometer), but **no** difference was found. pH was also tested with **no** differential results. Oxidative reductive potential, a measurement that indicates ox/red changes of ions in the solution , also did not change significantly after 1 hour sound exposure.

XRD crystal analysis

The crystallinity of residual from dry water samples was tested twice with XRD, but with conflicting results, one sample had a higher calcite content after exposure, another higher content of aragonite CaCO3 content. These nonconclusive results are not shown, as the results do not exclude a potential differential effect but just show that in this case, we were not able to see a difference from the exposure to the pulsed electro/sound emitter.

NIR absorbance

Below in figure 2 is seen the absorbance spectrum from the Near infrared range, this shows a clear difference in absorbance between the Amtech treated water (green spectra) vs. untreated, ultrasound and degassed tap water (red, blue and black spectra). Approximately 15 samples of 40 measurements each were made, with at least 10 samples of 1 hour sound exposed water.

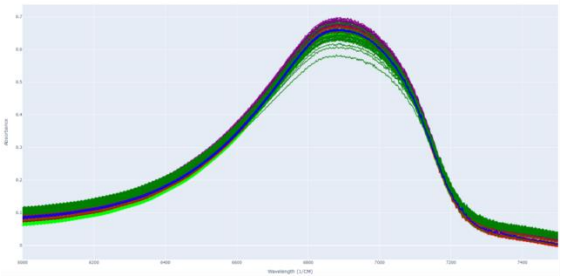

Figure 2.: Raw spectral data of NIR from 6000 (left) to 7400 (right) cm-1 containing the second-order harmonic stretch of O to H bond. Tap water (red) Tap water ultrasound bath (blue), Tap water AmTech (green), Ref tap water vacuum degassed (black)

Drop dry morphology and Raman spectroscopy

Observing the dynamics of drying drops can reveal information on seeding crystals, uniformity and particle charge changes in a solution. When performing raman on treated water drops, we unintentionally observed a clear change in the morphology of the drop. Below on fig. 3 is seen 2 picures of dry water drop residues on the nano substrate

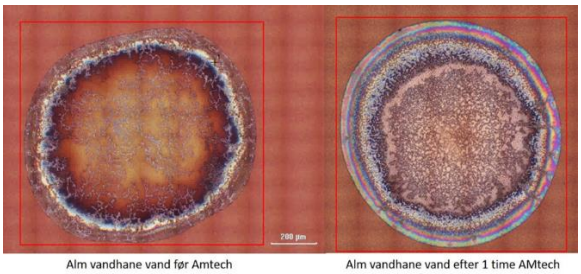

Figure 3.: Microscopy picture of a 1µl drop of tap water drying on a metal surface exposed to a sound device. Notice the more homogeneous pattern of the sound-exposure water sample.

Scanning Electron Microscopy (SEM)

It was hoped that Microscopy of dry residue from the water samples could reveal the types of CaCO3 crystal structures left behind. This was not so straight forward to determine. But other observations were useful. In figure 4 a difference is seen in seeding particles points, the treated sample was observed to be of a more uniform dendritic precipitation of dry residue,where the untreated had

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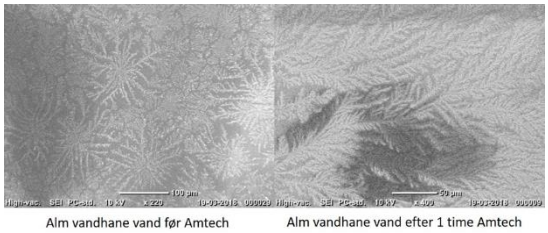
several different types of crystalline structures and more seeding points.



Alm vandhane vand før Amtech Alm vandhane vand efter 1 time Amtech

Figure 4.: Scanning electron microscope Raw spectral

Particle charge potential (ZETA)

Since a pulsed field is applied to a solution, it could be expected that particles could change their charge. Measuring the charge of suspended particels can be done using dynamic light scattering with a cuvette containing 2 electrodes with added charge. This moves the particles according to their internal charge in the solution. Below in figure 5 is seen the results of aragonite and calcite spiked samples.

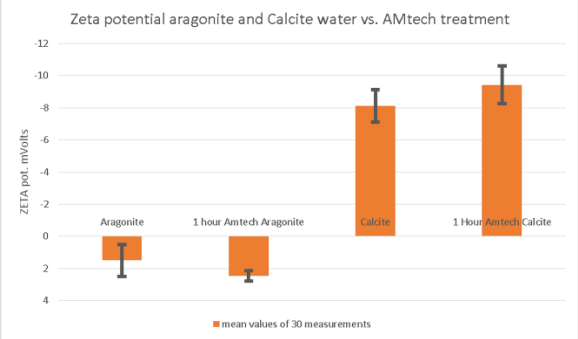


Figure 5.: Zeta potential of water samples spiked with calcite and aragonite affected by a commercial sound device. There is a slight tendency for an increase in particle charge after exposure to the sound device. Average of 30 measurements.

Below on figure 6 is seen the charge of un spiked water samples. The method is tricky as enough particles are needed to see a change, pure tap water is on the lower limit, leading to a large variation in the results. Pure Milli Q water has very high variation measurements as virtually no impurities were present to scatter the light. The variation on tap water was also quite high, and no significant conclusion could be made, although there was a tendency to a slightly more negative change.

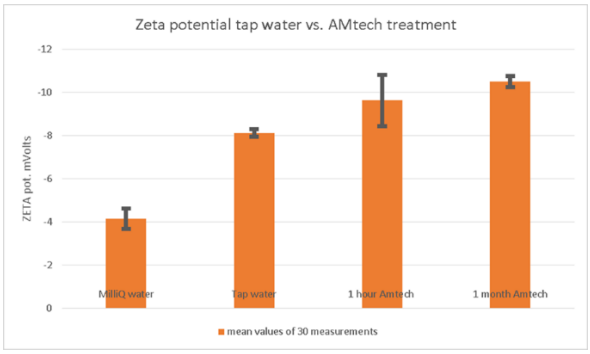


Figure 6.: Zeta potential of tap water samples affected by commercial sound devices. 1 hour exposure to sound increases the particle charge, a 1 month continuous exposure increases the charge slightly more. Average of 30 measurements.

DISCUSSION

Many of the claimed properties from the Amtech company were not measurable, such as surface tension, pH and ORP. This can not be expected as the producers of the device does not have a scientific background, the device was developed based on empirical observations on water over many years working on public drinking water installations in Denmark and East Germany.

However, a change was seen in other analysis methods. Such as a significant change in drop drying morphology using a Raman SERS substrate and standard SEM pictures, indicating a change in particle charge. The silver metallic SERS substrate probably contributes in differentiating the effect, as this was repeated on a simple glass slide but with less dramatic differences. None the less, the difference is also seen on SEM images of the dry residue from the water sample.

Using zeta potential measurements, we only observed a slight but not significant change in particle charge after both 1 hour and 1 month exposure. The Aragonite CaCO3 spiked sample saw less variation, perhaps the sound normalizes particle charge across the samples.

The change in Near infra-red does indicate a different change in the water compared to vacuum de-gassed and ultra sound treated water, we found this intriguing, but have no explanation as why this happens. The NIR region is governed by secondary harmonics of O-H stretch, revealing information about molecule to molecule interactions. Perhaps the sound affects certain molecular tendencies of water to form clusters or change hydrate formation around suspended particles and gas bubbles, but this is speculations.

CONCLUSION

The exposure to pulsed sound and electro/magnetic waves seems to have a small but noticeable effect on water samples dry residue morphology, NIR of water samples and particle

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charge in water samples, when performed in the laboratory.

The dry residue of exposed water samples is more homogeneous compared to nontreated drinking water samples. This indicates a uniform charge on the seeding crystals, leading to a more unified evaporation.

The results are linked to the equilibrium of solvation of dissolved ions in water combined with the charge of particles, as stated in ref [4] the precipitation of $CaCO_3$ is dominated by the seeding crystal population , a change in the particle charge is thus a plausible explanation for the effect of a pulsed electro/sound emitter. However, it is not concluded whether this will have a long-term effect on equipment in contact with water, as these effects can be reversed by changes in temperature, salinity, and pH. The next work will focus on understanding the fundamental mode of action and how long the effects last.

ACKNOWLEDGEMENTS

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