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Paper

SPECTRAL MEASUREMENT OF ELEMENT SOLUBILITY IN WATER UP TO 300 MPA

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ABSTRACT

High-pressure water jet technology is used progressively in industrial applications since 1971. The material behavior of pure water (H_2O without additions) has been studied for a wide temperature and pressure range. Usually, tap water is used as process medium for cutting applications. However, only little data is available for the behavior of tap water at elevated temperature and pressure changes. It is commonly known that the use of ion exchangers leads to a significant softening of the water, which has a negative effect on seal lifetime. Hard water has similar negative effects. It leads to calcification, which causes life reduction of high pressure pump components and also seals due to tribological effects.

In order to understand the relationship between water and its constituents at high pressure up to 300 MPa, a chamber for spectroscopic and photometric measurements was constructed and built. After loading the chamber with different water specimens, the pressure was increased in 25 MPa steps and the spectral light intensity was measured. In this study, deionized water was employed as a reference and compared to common tap water and pure water with added NaCl and $CaCl_2$. The results were evaluated statistically though a self-devised, “R”-based software. Significant alterations when applying given pressure could be observed both through photometric measurements and spectrometric investigations. By using deionized water as a reference, the pressure-dependent intrinsic behavior of the measurement setup was compensated.

With the described method, a variance in spectral intensities was shown when using different fluids and different pressure levels. Particularly, calcium chloride blended water solutions showed a behavior of the spectral intensities similar to tap water.

1. INTRODUCTION

Since its market launch in the 1970s, high-pressure water jet technology is used for industrial purposes. Due to high accuracy and quality of the cut, water jet technology offers many applications. The technique is used for example in the field of handicraft production, food industry and dismantling of nuclear facilities. These exemplary applications may be completely different, but have one thing in common: They need high pressure water. In classical mechanical engineering applications, various requirements exist for production, transport and supply of high-pressure water. The behavior of pure water (H_2O) is described in a wide temperature- and pressure range in several scientific papers [BAK75, HAR89, WAG08]. Pure water means water without any admixed components. For more complex systems such as tap water no extensive studies for the dependence of temperature or pressure exist.

Many studies have been carried out regarding the temperature behavior of water, because its temperature characteristics are very important for thermal power stations. In these studies, water is only considered as a pure substance and is thus idealized. In contrast to single observations of the temperature behavior, investigations at high pressure go along with an increased effort. For the investigation of its behavior at high pressure, only non-contact investigations with a defined examination volume are possible. State of art for non-contact investigations are spectrometric and photometric measurements.

Empirical data indicates that the water composition has a significant effect on the service life of high pressure components like pumps, valves or fittings. An excessive softening of water by ion exchangers results in a lifetime reduction, because this leads to increased corrosiveness. Likewise disadvantageous is hard water: In this case, deposits inside the machine can be detected. These are reported to lead to limited lifetime of seals and nozzles.

In this paper the implementation of spectrometric measurements at high pressure process-water up to 300 MPa is described. For the experiments, a suitable spectrometer and a high-pressure test chamber were constructed and built. Thereafter, specimens of tap water, pure H_2O and mixtures of H_2O with NaCl and $CaCl_2$ were investigated for their behavior under high pressure. The spectral intensity was measured, compared and analyzed. The change of spectral intensity is used to show a pressure depended compound solubility.

2. MATERIALS AND METHODS

2.1 MATERIALS

2.1.1 Used Fluids

For the experiments, it has to be exactly defined what is meant with the word “water”. It is necessary to differentiate between the pure substance “water” and the complex medium water, such as “tap water”. Tap water includes several dissolved, water-soluble elements (like salts), which differ in compilation and concentration dependent on where the sample was taken.. In Germany, the maximum concentration of certain constituents in tap water is regulated by law. The hereby available is however aimed at the hygienic harmlessness of drinking water, necessary specific values for industrial applications are still unknown. To achieve a certain water quality, water treatment can be carried out prior to the application to achieve a longer lifetime of valves or seals. To achieve this, there is also the possibility of applying additives to the water.

2.1.2 Spectrometry

In general, optical spectrometry can be differentiated between two functional modes of operation. These are “spectrometry by emission” on the one hand and “spectrometry by absorption” on the other.

“Spectrometry by emission” is based on the effect of a stimulated sample, which emits characteristic radiation. The radiation is directly diffracted and the hereby-generated energy levels are considered. This method only works with samples which emit radiation or can be stimulated to emit radiation, so the list of possible sample types is limited. Generally, spectrometry by emission only works with solids and gases [LOT06].

The main difference when regarding “spectrometry by absorption” is that the sample is loaded with radiation from an external beam source (see Figure 1). The output range can be determined as a reference value by measuring the emission spectrum of the radiation source without a sample in the beam path. Every sample absorbs the radiation energy level it was exercised with. The intensity of the corresponding energy levels decreases through irradiation through the sample, so a small specimen volume is advantageous [TIP04].

The radiation emanating from the specimen is spectrally diffracted by a prism or a diffraction grating. An optical sensor detects the hereby-generated diffraction pattern. This sensor detects the brightness values and the intensity of the individual spectral components. The detected emission spectrum quality is directly related to the intensity of the beam source. The resulting output spectrum is offset against the known input spectrum of the radiation source, hereby a difference spectrum can be deducted. The spectral energy levels of the difference spectrum reflect the alteration through the sample. Spectrometry by absorption is used for measurements of samples that cannot be stimulated to emit radiation itself. The only prerequisite is that the sample has to be transparent [LOT06, TIP04].

2.1.3 Spectrometer setup

The mechanical construction was designed in a 3D CAD system (Dassault Systems, SolidWorks). The spectrometer consists of two main optical components. Both are fixed in two different positions of the housing (compare Figure 2). On one side, the slit aperture is mounted through a carrier plate, while the other side houses the optical grating and the camera. The slit aperture and grating are adjustable in angle.

The slit aperture of the spectrometer is aligned to appear as a vertical line on the camera sensor. The alignment of the grid has a direct influence on the spectrum, which appears horizontally in the output image. For the calibration of the spectrometer, the housing can be closed, while the slot is illuminated and a picture is taken by the camera. The spectral image is analyzed by an image processing tool (GIMP). The imaging process and grid adjustment are iteratively repeated until the spectrum is mapped horizontally on the CCD sensor of the camera (see Figure 3). The used CCD sensor allows a resolution of 1280x720 pixels and can capture fixed images and videos.

2.1.4 Construction of the high-pressure cuvette

Cuvettes made for conventional spectrometric measurements are usually made of plastic or glass. This makes them solely usable for low pressure applications. Therefore, a high pressure cuvette was designed, which included two windows (see Figure 4). The windows (manufacturer SITEC) are intended for high pressure applications up to 400MPa and are sealed through a Bridgman seal. The cuvette is made of stainless steel (EN 1.4571, compare to AISI 316Ti). This is a common steal for high pressure components. The cuvette has a cylindrical shape with a diameter of 98 mm. Both windows have a leakage hole at the sealing position. The unit furthermore includes two high-pressure connectors (6 mm HP).

2.2 METHODS & EXPERIMENTAL SETUP

2.2.1 Implementation of experiments

For the experiments, the cuvette was integrated into the high-pressure piping system (compare Figure 5). Each experiment were started with a fluid-filled cuvette and closed valves V0, V1 and V2. After the opening of valve V0, the high-pressure pump applied the desired operating pressure. The pressure was iteratively increased in 25 MPa steps in order to apply static pressure to the test fluid. 2 minutes after the desired pressure was reached, the measurement was started. This waiting time allows the seals to settle and balancing processes to take place (due to changes in element solubility). Subsequently, the fluid-loaded cuvette is illuminated by the full-spectrum light source. The diffraction image is detected on the other side of the cuvette. Each experiment lasted 100 seconds with a picture recorded every 2 seconds.

2.2.2 Visualization

Results of the spectral measurements is a graph of the spectral intensity distributions for each pressure (compare Figure 6a). For a better evaluation of the occurring effects, a further processing of the measurement data was carried out (Figure 6c). In this graph, the blue colored curve was translated into a 3D bar chart. Every bar has an intensity interval range of 15 nm and represents the average intensity of this range. This way, 30 bars in the range of 400 and 850nm are generated. The bars are coded with color gradients from blue to yellow. Blue corresponds to a minimum light intensity (I = 0) and yellow to the maximum (I = 1). So the light intensity is characterized by bar height and color for one given pressure. To get information about pressure-dependent intensity variations, translation was done. In Figure 6b, the wavelength is now displayed on the y-axis while the wavelength is plotted on the x-axis. Now, a color-coded box represents the average light intensity of each measurement. This way, , the pressure-dependent changes of the wavelength range can easily be recognized as color change on the x-axis. This procedure is carried out for all the fluids. Finally, the results are normalized. For this purpose, the spectrum of pure water was subtracted from all graphs. An exemplary graph of the hereby-generated visualization of the normalized spectral measurement is displayed in Figure 6d.

3. RESULTS

H_2O The spectral intensity measurements of pure water show an influence of pressure on the spectral intensity distribution. The gradient alteration is displayed in Figure 7. In wavelength range between 475 nm and 520 nm, an increased spectral intensity can be recognized. Differences occur in the longer wavelengths range, for medium and short wavelengths no change can be detected.

Tap water Compared to H_2O, pressure increase shows a minor influence on the spectral intensity of tap water (see Figure 8a). In the low (< 460 nm) and high wavelength (> 800nm) ranges, no alteration of intensity detectable. In the middle wavelength range, intensity increases slightly. The normalized spectral intensity of tap water is displayed in Figure 8b. Differences to the reference H2O are displayed in green (higher intensity) and red (lower intensity). In the wavelength ranges between 520 nm and 610nm, color change from red to green can be recognized (Figure 8b). No differences in intensity compared to the reference H_2O are displayed in white.

NaCl-blended water The Sodium chloride blended water solution shows no alteration of spectral intensity changes on increased pressure (Figure 9a). However, four significant changes are visible regarding the complete wavelength range at the pressures 25MPa, 150MPa, and 280MPa. It can be assumed that these alterations occur through interference during measurement. A possible cause is a shift of the cuvette windows’ seals. This process is reversible, a pressure reduction reverts the seal to its initial state.

In Figure 9b, clear differences can be seen compared to the behavior of H_2O. The spectral intensity of the sodium chloride solution is lower in the lower wavelength range. In the middle wavelength range, the behavior of the NaCl-blend approximately corresponds to H_2O. In the higher range, the spectral intensity of the NaCl-blended water is much higher than of H_2O. A clear intensity increase can be detected between 775 nm and 790nm. An increase of pressure also increases the light intensity.

$CaCl_2$-blended water The Calcium chloride blended water solution shows a spectral intensity shift at the pressure of 25MPa (compare Figure 10a). This shift can be attributed to a measuring fault. Within these two blocks, a consideration is possible. At the high (715 nm - 850nm) and low (400 nm - 475nm) wavelength ranges, a low light intensity becomes apparent. Considering the spectral intensity distribution, it can clearly be shown that the spectral intensity of the calcium chloride solution is pressure-dependent.

The biggest differences compared to H_2O are located in the higher and lower wavelength range (Figure 10b). These ranges show an almost constant behavior. Higher wavelength result in a higher, lower wavelengths in a lower intensity compared to H_2O. For the medium wavelength range, a shift in intensity from 0.5 can be 1.3 detected.

4. CONCLUSIONS & DISCUSSION

The presented spectral analysis of high-pressure process water differs a lot compared to methods currently available in literature [FOU77, SAW07]. By using the described experimental procedure, no samples have to be removed from the high-pressure volume. For this reason, even temporary pressure effects can be shown, which only occur on high pressure. In the analyzed fluids H_2O, tap water, NaCl-blended water and $CaCl_2$-blended water, a correlation between spectral intensity and pressure could be shown.

The behavior of water at increased high-pressure has not been subject to extensive investigations, so far. In 1977, the solubility of amorphous silicates was researched by Fournier [Fou77]. In this study, a solubility of silicates in water could be shown with increasing pressure. Sawamura et al. [Saw07] examined the solubility of sodium chloride in water. This work differs from the actual paper, because that Sawamura et al. [SAW07] took water samples and investigated them under atmospheric pressure. Therefore, reversible effects could not be shown using his method.

Another possible effect is the occurrence of oppositional effects at the measurements, which can affect rising and falling spectrometric intensity values. A possible reason are two competing effects which effect the permeability of the liquid inside the high-pressure volume and change the measurable intensity. If the solubility is low and crystals are settling on the bottom of the cuvette, spectrally measurable intensity rises. For the case that the omitted components form floating crystals, light dispersion can rise and the measurable intensity decreases.

The chosen rest period of 100s before starting the measurement does not seem to be sufficient. To adjust the effect of crystal formation, sufficient time must be maintained after pressurization. Additionally, the addition of a resistance measurement method could give more information about the crystal formation.

Furthermore, the current measurement set-up needs to be improved. The accuracy the measurements can be improved by substitution of the slit aperture with a pinhole. This way, it would be possible to map the spectrum across the diagonal of the image sensor. Thus, the definition of the analysis could be improved.

Finally, in this paper only tap water, pure H_2O and water-blends with chloride were investigated. Prospectively, H_2O fluids with sulfates ($MgSO_4$, K_2SO_4, Na_2SO_4) or silicates like sodium silicate should also be investigated.

5. ACKNOWLEDGEMENTS

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7. TABLES

Table 1. Composition of the tested fluids

	H_2O in m.-%	NaCl in m.-%	$CaCl_2$ in m.-%	Rest m.-%
H_2O	100	0	0	0
Tap Water [NN15]	> 99.97	0.002	0.022	< 0.001
H_2O-NaCl	82.05	17,95	0	0
H_2O-$CaCl_2$	63	0	37.0	0

8. GRAPHICS

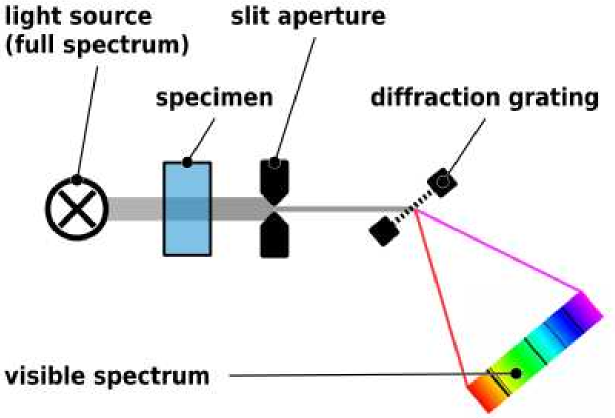

Figure 1. Functional principle of a grating spectrometer

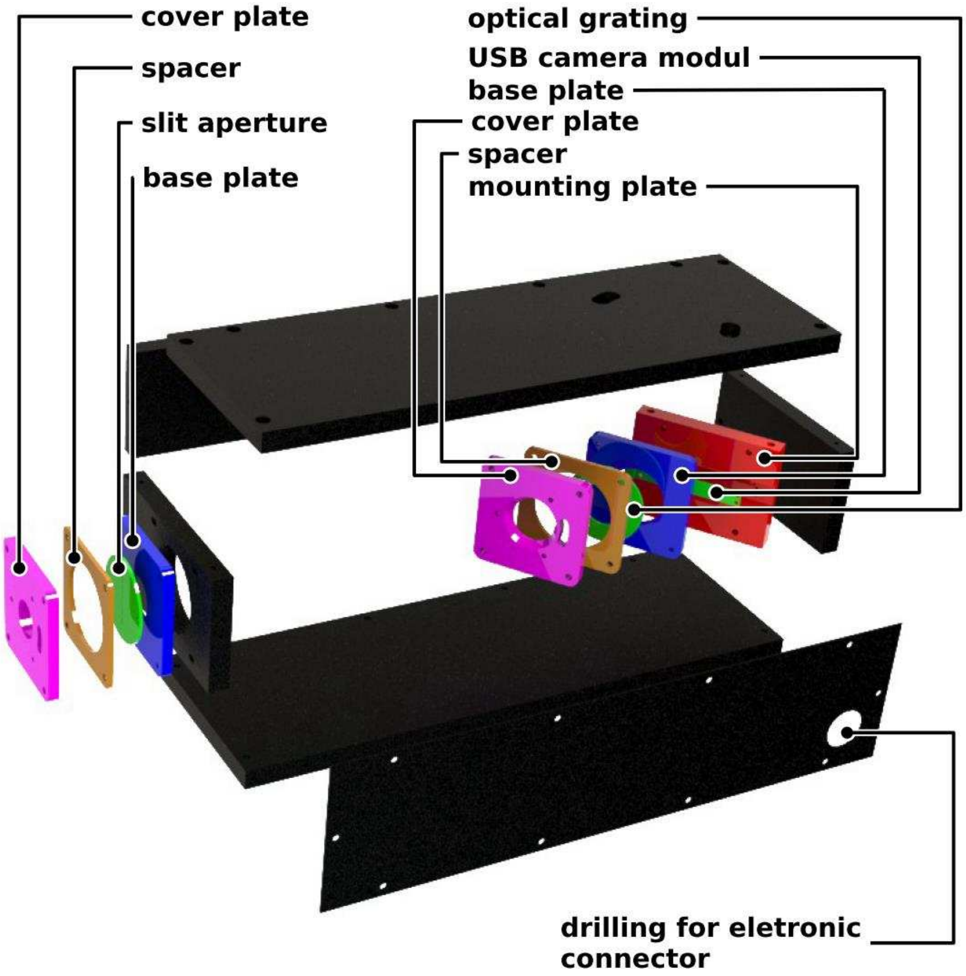

Figure 2. Exploded assembly drawing of the spectrometer setup

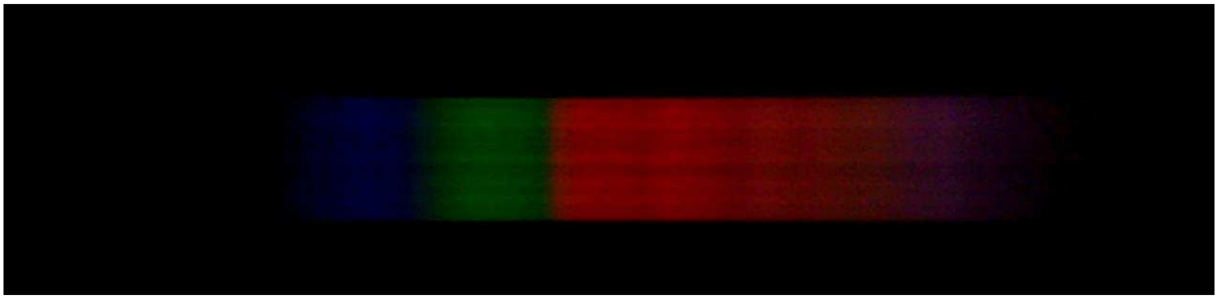

Figure 3. Calibration picture of the spectrometer

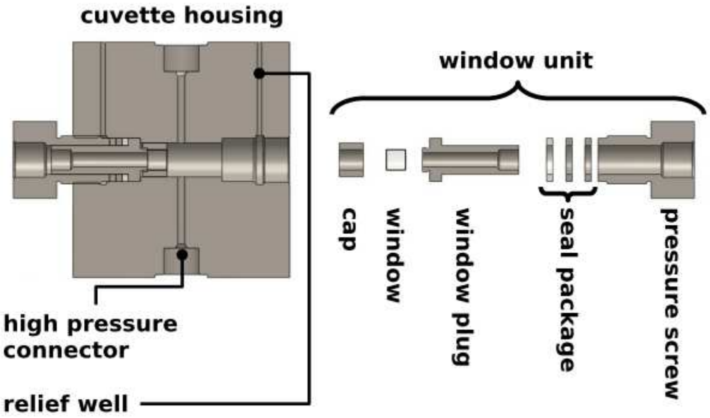

Figure 4. High-pressure cuvette

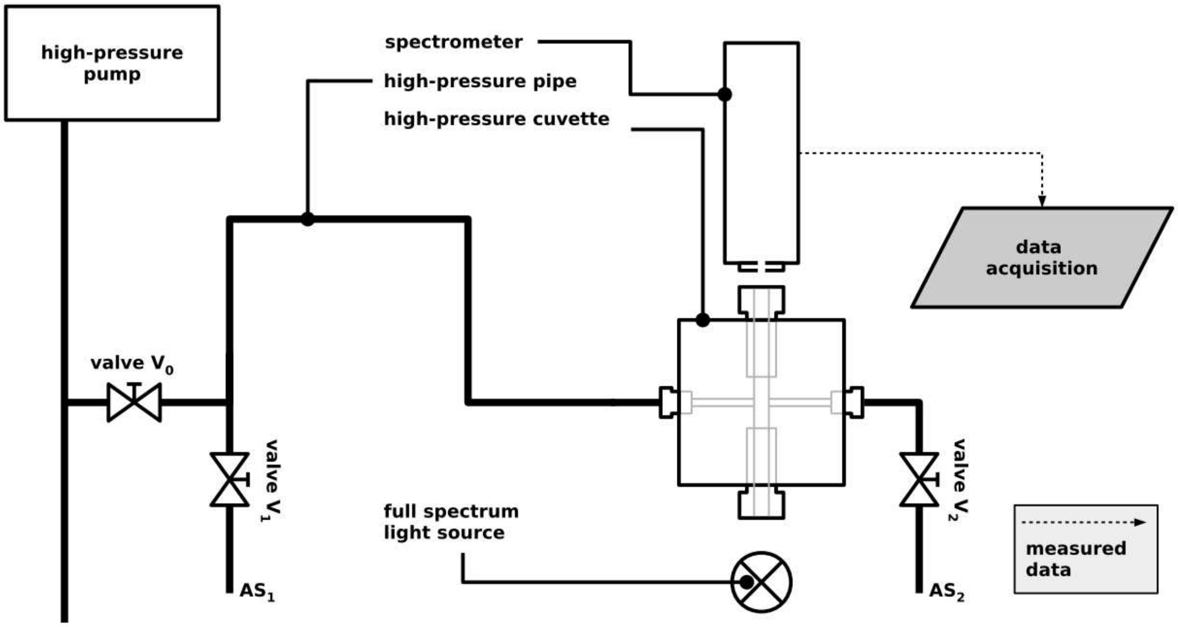

Figure 5. Experimental setup

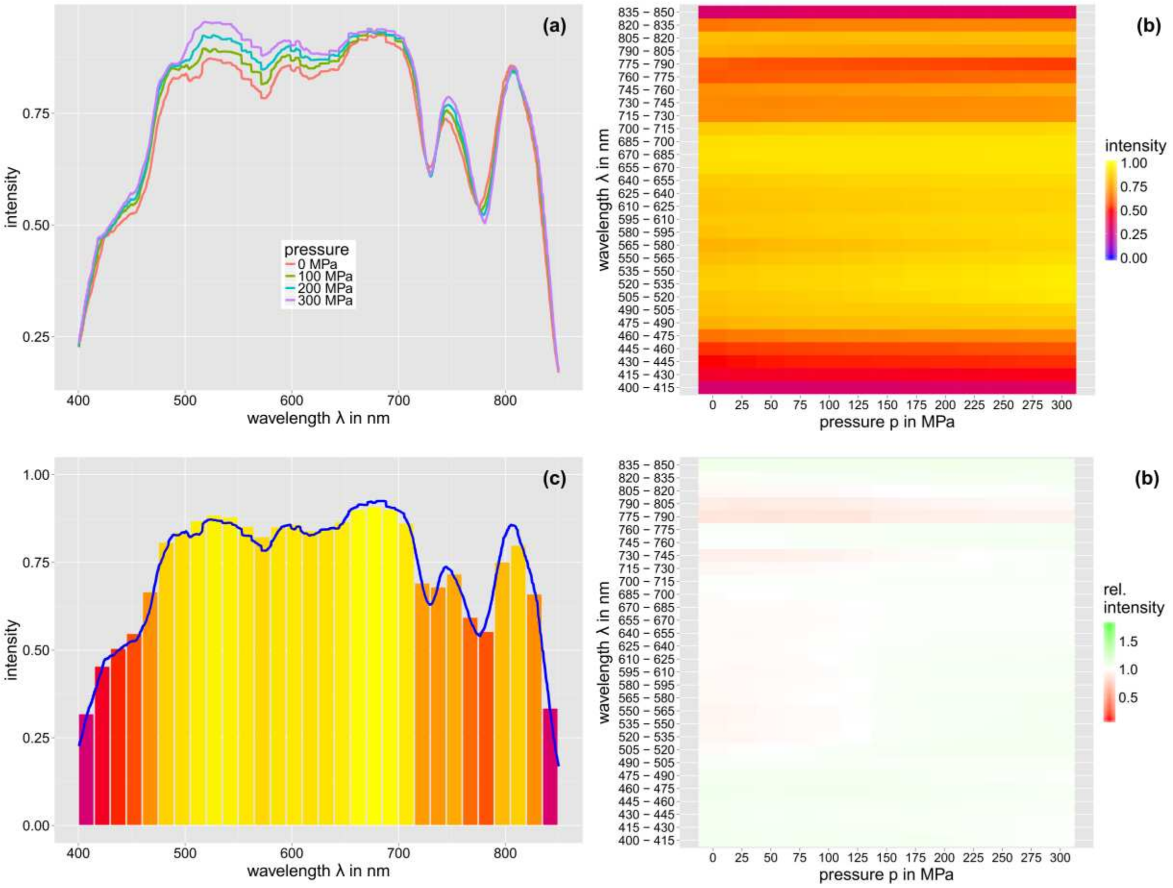

Figure 6. Graphical visualization methods: multiline plot (a), spectral intensity (b), combination of multiline plot and spectral intensity (c), relative intensity (d)

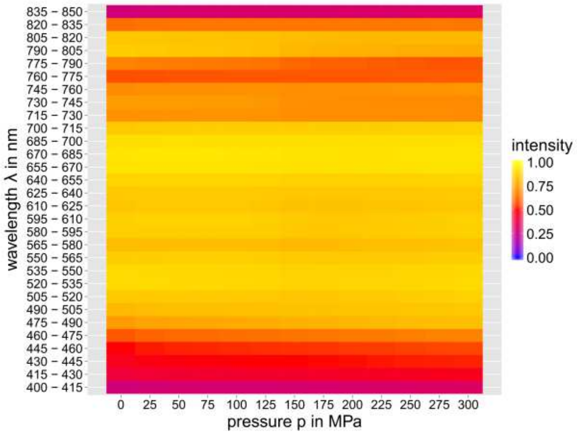

Figure 7. Spectral intensity of H_2O

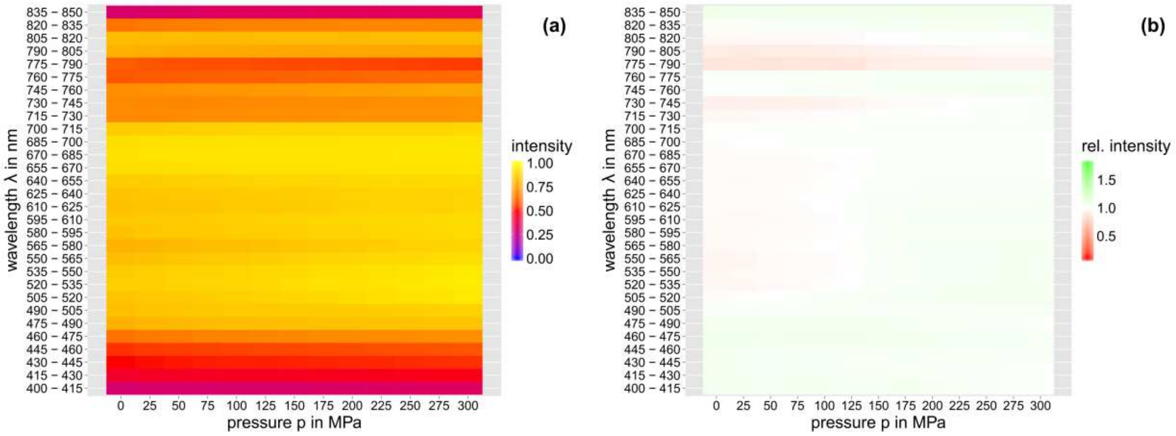

Figure 8. Spectral intensity (a) and normalized spectral intensity (b) of tap water

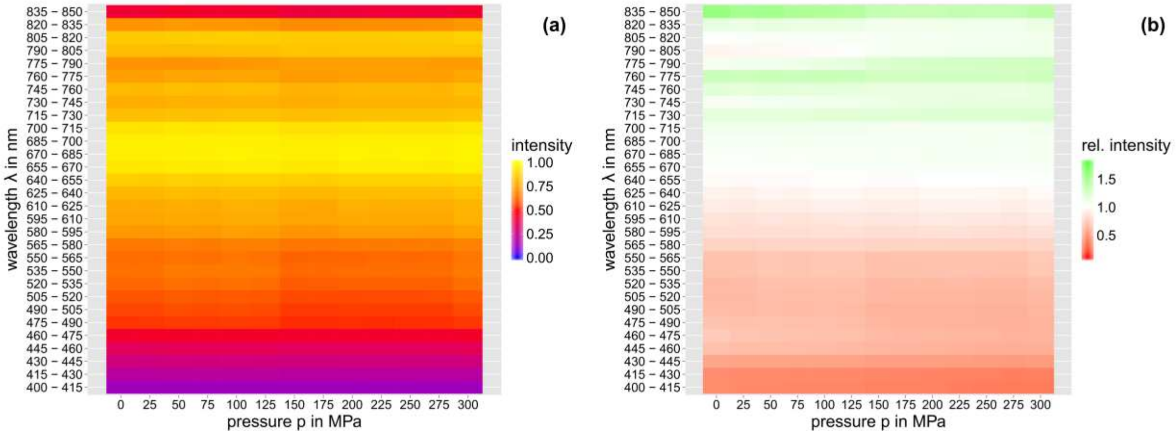

Figure 9. Spectral intensity (a) and normalized spectral intensity (b) of NaCl-blended water

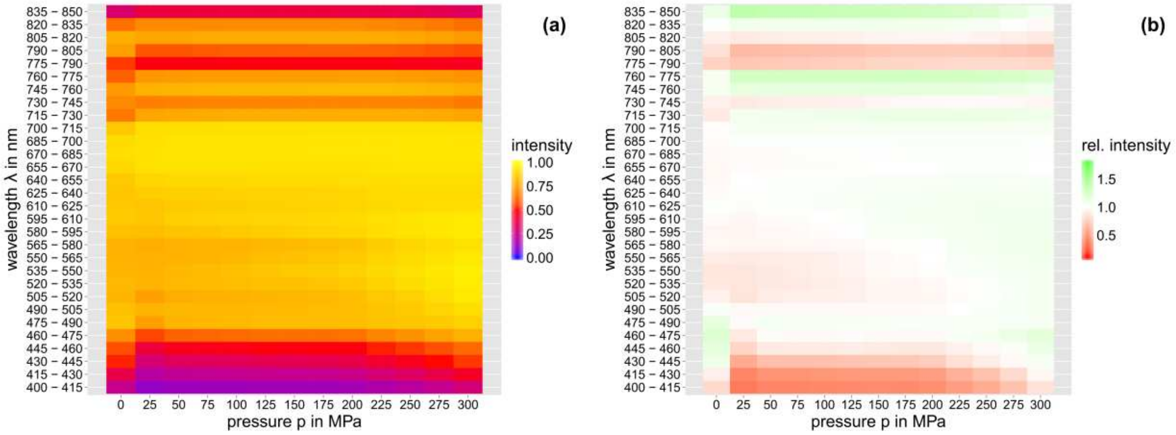

Figure 10. Spectral intensity (a) and normalized spectral intensity (b) of $CaCl_2$-blended water