

Report of WP1

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Summary

The determination of H_2SO_4 (0-10%) and H_2O_2 (0-4%) concentrations in DSP has been investigated by spectroscopic transmission and LED-based transmission measurements. Based on spectroscopic data two wavelength bands have been identified for optimum detection of either H_2SO_4 (around 2200nm) or H_2O_2 (around 280nm).

The LOD with spectroscopic determination is about 0.001% weight for H_2O_2 and 0.01% weight for H_2SO_4 , almost independent from whether air or water as reference medium is used (for water only slightly better). However, the LOD is not the relevant parameter for error of determination of the single components in the DSP but rather the error that is introduced by interference of the other component, respectively (at fixed concentration of component A the signal intensity spreads with different concentrations of component B and vice versa). The mean error of determination (taken over all concentrations measured), which is defined by the standard deviation of the mean value at a given concentration of the component, is about 2% for H_2O_2 and about 4% for H_2SO_4 , independent whether air or water was used as reference medium. From that it was concluded that air as reference medium should be chosen for LED-based measurements, since this later on reduces technical effort for making a device.

H_2O_2 concentration can be addressed by LED transmission measurement at a wavelength of around 280nm and air as reference medium very well. The LOD is about 0.01% weight and the mean error of determination is 1.6%, which is comparable to that of integral spectroscopic measurements (1.9%). H_2SO_4 concentration can be addressed by LED transmission measurements at wavelength of 2200nm with air as reference medium. The LOD in this case is clearly larger at the order of 1% weight but the error of determination of H_2SO_4 concentration is about 5%, being comparable to the corresponding value of 4% for integral spectroscopic measurements.

As the final conclusion it can be stated that in DSP the H_2O_2 concentration within the range of 0-4%, by using a 280nm LED, can be determined with a mean accuracy of $\pm 1.6\%$ and H_2SO_4 concentration within the range of 0-10%, by using a 2200nm LED, can be determined with a mean accuracy of $\pm 5\%$.

Report of WP1

Objectives

ATIK is interested in the development of a method for measuring the concentration of a DSP (Dilute Sulfuric Peroxide)) cleaning solution containing H_2SO_4 , H_2O_2 and HF online.

The solution is used for a chemical cleaning process and can be continuously sampled, e.g. by a bypass loop. The concentration of the three constituents shall be measured periodically on a timescale of 1s by optical and 10s by electrochemical methods. The goal of this project is to evaluate the feasibility of a simultaneous determination of the concentrations of the three constituents. The special goal of this work package (WP1) is to evaluate the feasibility of simultaneous determination of the concentrations of H_2SO_4 and H_2O_2 by optical absorption spectroscopy (OAS). The results of determination of HF concentration by an ion-selective membrane with electrochemical detection will be reported separately within the final report of work package 2 (WP2).

The specifications for a later device are the following:

1. Type: Online chemical concentration monitor
2. Sample: DSP
 - 0-10% of H_2SO_4
 - 0-4% of H_2O_2
 - 0-1000ppm of HF
3. Accuracy: $\pm 1\%$ for all three components
4. Flow rate: 20-60 ml/min in bypass ($< 5\text{ml/min}$ if accommodated)
5. Pressure: 0.1-0.2 MPa
6. Sample temperature: 20-30°C

The final goal is a demonstrator, combining the measurement methods for all three constituents into a dedicated physical device. The instrument shall contain a flow cell and be designed to be connected to the existing process in an industrial environment, to demonstrate the feasibility of such measurements. Of particular importance is a fast measurement time (1s for optical measurements, 10s for electrochemical measurements) and a compact design. The system should be suitable to work 7 days a week for 24 hours. The maintenance frequency of the system is aimed to be as long as possible (targeted are 12 months).

A quotation for the demonstrator will be formulated at a later stage of the project, after the feasibility studies have been conducted and the technical parameters and the effort necessary can be specified in more detail. If commercialization of the instrument is desired by ATIK, licensing of the IP has to be negotiated and will be subject of a separate quotation.

Measurements with Spectrometer

Preliminary studies with UV/VIS spectroscopy on samples containing H_2SO_4 and H_2O_2 as well as HF, showed that significant spectral features are present in the spectra correlating either with the H_2SO_4 or H_2O_2 concentration. However, HF could not be addressed by UV/VIS spectroscopy and is investigated separately within WP2 (Part B of the study).

Systematic measurements were carried out with the Perkin Elmer high performance UV-VIS-NIR spectrometer (Perkin Elmer Lambda 1050, quartz cuvettes QX 1mm, 350 μl , range 200-2500nm) on DSP with varying concentration of its components (see Annex A, all concentrations given in weight%). The spectral signatures at the band edge in the UV and around the water bands in the NIR were differentiated against deionized (DI) water (TKA GenPure Reinstwassersystem,

$\sigma=0.055\mu\text{S}/\text{cm}$) as well as air and were correlated to the concentrations of H_2SO_4 and H_2O_2 , respectively. The limit of detection (LOD), limit of quantitation (LOQ) and the accuracy of the method were determined, by considering different spectral regions, correlating with the corresponding acid concentrations. For that, spectral data in the regions 270-290nm, 1440-1460nm and 2100-2300nm was integrated, correlated with $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ concentrations and also compared to simple peak value analysis at corresponding center wavelengths.

Concentration dependence of spectra

For investigation of the concentration dependence of the spectra 64 different combinations of H_2SO_4 and H_2O_2 concentrations have been prepared (Annex B.). All combinations have been measured relative to air and to DI water as reference, leading to a total number of 128 spectra taken. Additionally some repeatability measurements were taken to determine the long term stability of the DSP solutions mixed up (see chapter Long term stability of DSP).

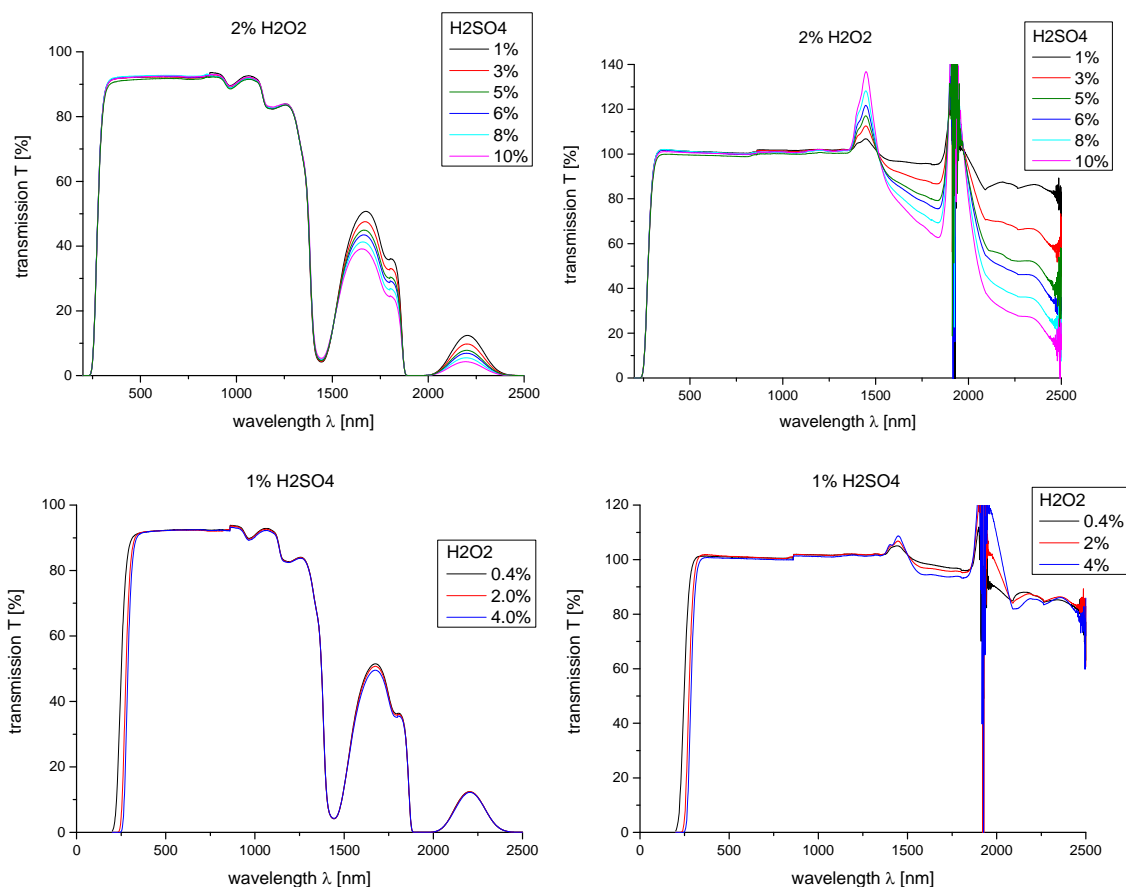


Figure 1: UV/VIS spectra of DSP relative to air (left graphs) and water (right graphs) background with varying concentration of H_2SO_4 (top graphs) H_2O_2 (bottom graphs).

Typical spectra of DSP show characteristic features varying with concentration of the different constituents (Figure 1). The characteristic features appear more or less significant in both types of spectra, either with air or water as reference.

For H_2O_2 the most prominent changes appear at the band edge at around 280nm, which shifts to higher wavelengths with increasing concentration of H_2O_2 . Minor changes are visible also at around 1450nm and even more at 1650nm, which is around the upper edge of the water absorption line located at 1450nm. Almost no influence of H_2O_2 can be detected at 2200nm.

For H_2SO_4 the most prominent changes appear at 1450nm, 1650nm (upper edge of the water absorption line at 1450nm) and 2200nm (upper edge of the water absorption line at 1900nm). Almost no influence of H_2SO_4 can be detected at 280nm.

Based on these findings, integral intensity around 280nm as a function of H_2O_2 concentration was used to determine H_2O_2 content of the DSP and integral intensity at around 1450nm and 2200nm as a function of H_2SO_4 concentration was used to determine H_2SO_4 content of the DSP. The corresponding results will be presented and discussed in chapter "Error of determination for single DSP components".

Temperature dependence of spectra

Since it is known that characteristic absorption band peak positions of water are temperature dependent, the temperature dependence of the DSP spectra was investigated within a limited temperature range of 21-28°C. To avoid any influence of the exothermal mixing reaction, the optical transmission spectroscopy was performed at least 90 min. after the mixing procedure of the DSP solution, since after that time solution has cooled down to room temperature (Figure 2).

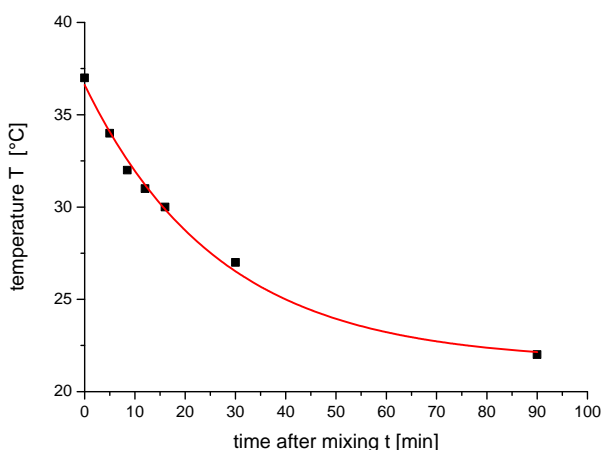


Figure 2: Temperature development in the DSP, as a function of time after mixing together the basic components ($\text{H}_2\text{O}+4\%\text{H}_2\text{O}_2+10\%\text{H}_2\text{SO}_4$).

During the feasibility study no heatable cuvettes were available for the Perkin Elmer Lambda 1050 spectrometer. Therefore, temperature was adjusted by natural heating of the spectrometers internal measuring room over the day (typically around 21°C in the morning and 28°C in the afternoon, after heating up due to the halogen lamps lost heat). The temperature in the measuring room was determined with a PT100 thermopile detector connected to a Voltcraft K204 Datalogger. Before measuring spectra, the samples typically have been thermalized within the closed measuring room for at least 10 minutes, to be sure that measuring and reference solution were at same temperatures.

A DSP sample with 10% H_2SO_4 and 4% H_2O_2 has been investigated as function of temperature, with water as reference medium (Figure 3). Obviously no significant changes are detectable between 200-1500nm within the temperature range of about 21-28°C. However, since the sample remained in the spectrometer overnight, part of the water from the sample cuvette (not gas tight) vaporized, giving an increased concentration of H_2SO_4 which becomes visible as a slight decrease of signal level around 2200nm, being sensitive against H_2SO_4 concentration.

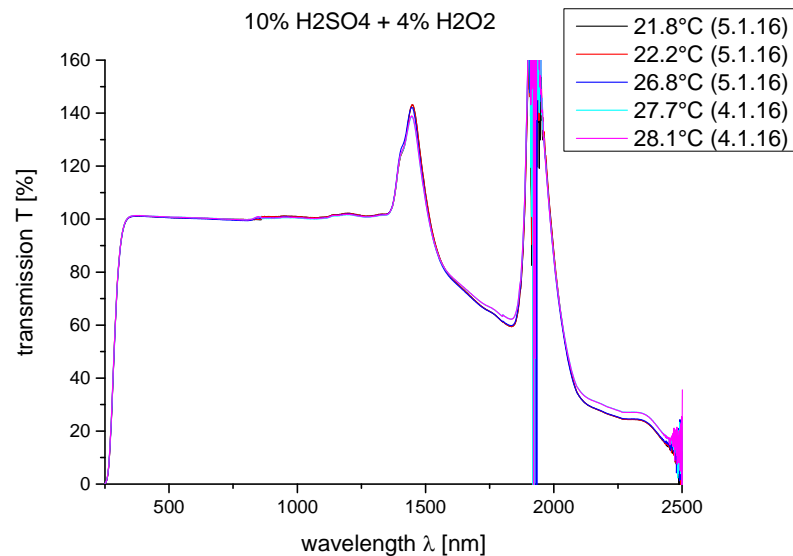


Figure 3: Temperature dependence of DSP spectra with reference water, in a temperature range of 21-28°C.

Long term stability of DSP spectra

To decide whether the DSP samples prepared (typically 100ml, a few samples 200ml) could be stored over a longer period and could be used either for spectroscopic as well as for LED-based measurements, a DSP sample containing 6% H_2SO_4 and 1.2% H_2O_2 , was investigated from time to time after about a week time interval (Figure 4).

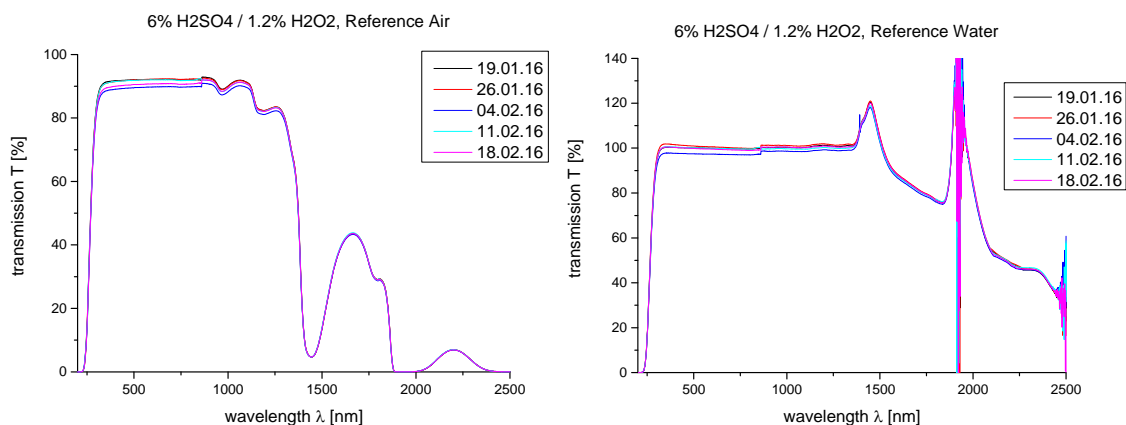


Figure 4: Weekly transmission spectra of DSP (6% H_2SO_4 and 1.2% H_2O_2) over a period of 1 month, with air and water as reference.

The transmission level remains constant over the whole wavelength range as function of time, except for the measurement from 04.02.16, where especially in the lower wavelength range a drop of transmission could be observed. The reason of this is not clear but might eventually be caused by a slightly polluted cuvette. However, since later measurements again recovered the data of the first spectra taken, it was concluded that the DSP solution remains chemically stable at least over a period of a month. Therefore, the same samples used for spectroscopic measurements, were also applied for the LED-based measurements.

Limit of detection (LOD) and limit of quantitation (LOQ)

The limit of detection (LOD_r) of the raw signal is defined as the sum of the blind value y_B (background at zero concentration) and three times the standard deviation (STD) of the blind value σ_B : $LOD_r = y_B + 3\sigma_B$.

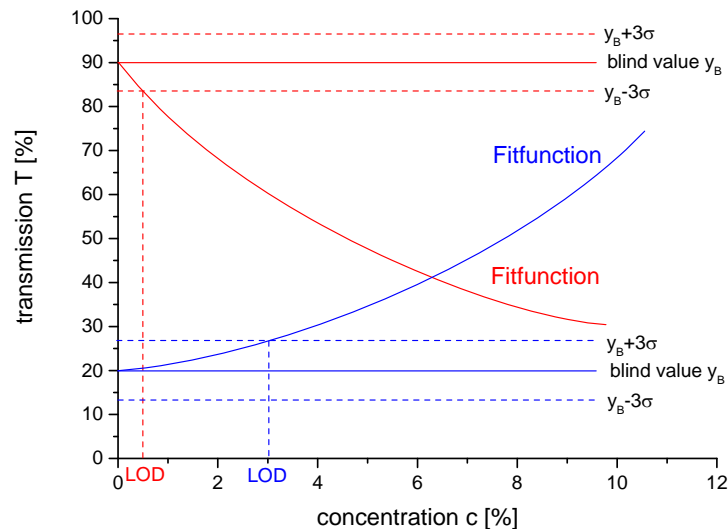


Figure 5: Schematic of concentration LOD determination from a blind signal and a fitfunction of experimental data.

The limit of quantitation (LOQ) is understood as the minimum value that can be determined quantitatively, is defined as 3.33 times the LOD: $LOQ = 3.33 \cdot LOD$.

The LOD and LOQ have been determined for both, air and water as reference medium, taking into account the wavelength interval from 270-290nm for H_2O_2 concentration determination and wavelength interval from 1440-1460nm as well as from 2100-2300nm for H_2SO_4 concentration determination. The LOD and LOQ was determined for pure dilute H_2O_2 (no H_2SO_4), pure dilute H_2SO_4 (no H_2O_2) and a mixture of dilute $H_2O_2 + H_2SO_4$ (data of second sample space plus main diagonal of Table 5).

Dilute H_2SO_4

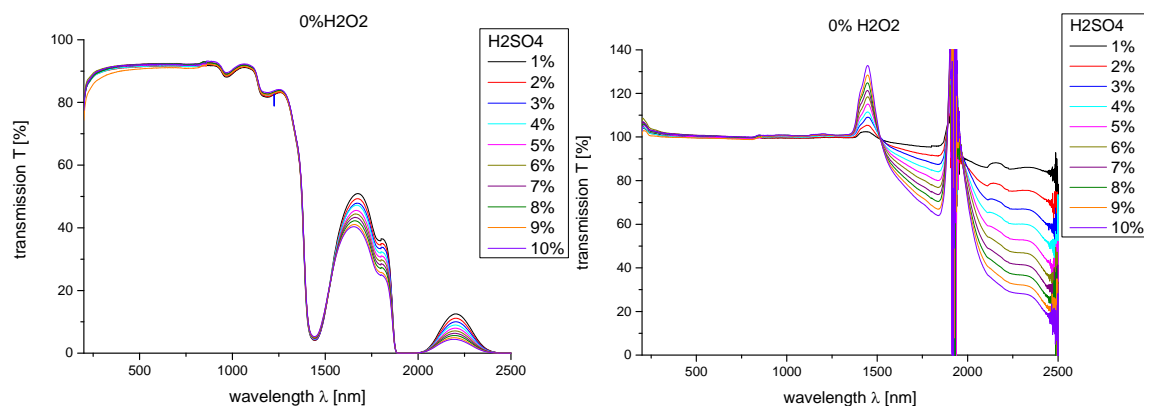


Figure 6: Spectra taken with 0% H_2O_2 concentration and varying concentration of H_2SO_4 , with reference air (left) and water (right), respectively.

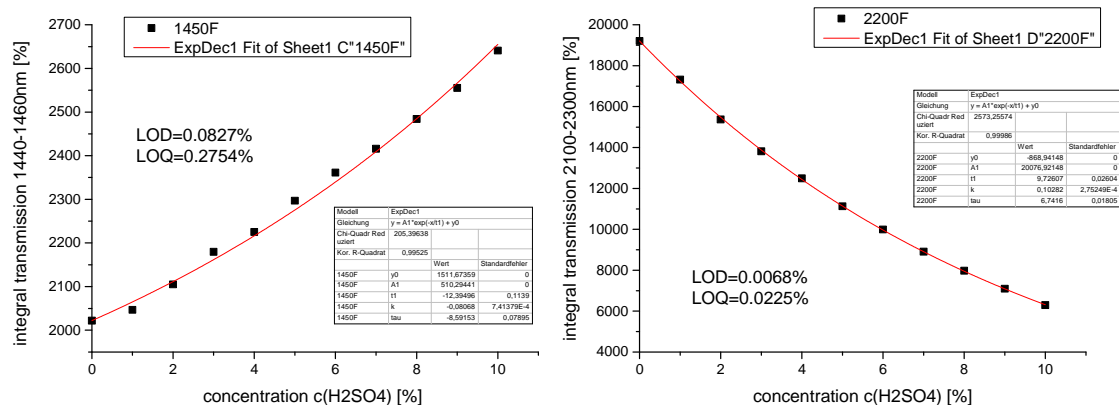


Figure 7: Integral transmission in the wavelength intervals 1440-1460nm and 2100-2300nm, as a function of H_2SO_4 concentration, with corresponding exponential fit functions (reference medium water).

Figure 6 shows the raw spectra for 0% H_2O_2 and varying H_2SO_4 concentration, with air and water as reference medium, respectively. The spectra were integrated between 1440-1460nm as well as between 2100-2300nm and integrated area under the curve was correlated with H_2SO_4 concentration (Figure 7 and Figure 8).

The LOD values were calculated from the corresponding fit functions, being the value where the fit function equals zero value plus 3 times STD (1450nm, increasing area as function of H_2SO_4 concentration) or zero value minus 3 times STD (1450nm, decreasing area as function of H_2SO_4 concentration), respectively. The corresponding results are summarized in Table 1.

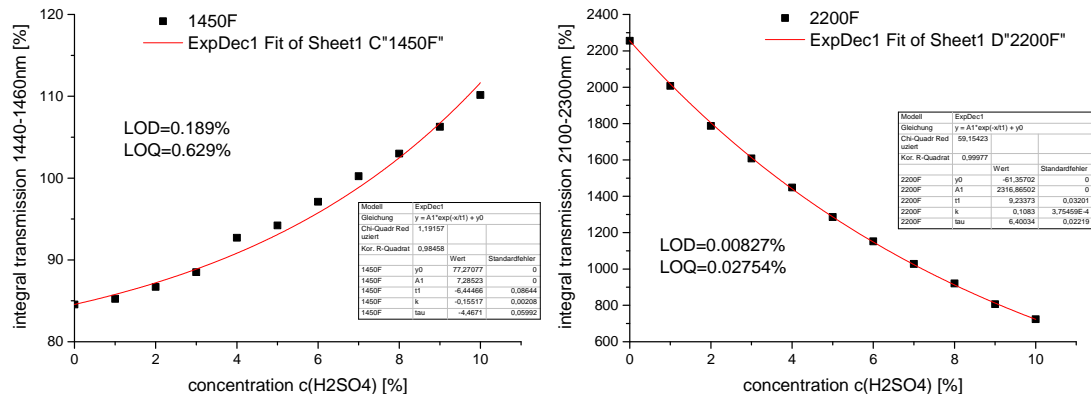


Figure 8: Integral transmission in the wavelength intervals 1440-1460nm and 2100-2300nm, as a function of H_2SO_4 concentration, with corresponding exponential fit functions (reference medium air).

Evidently, the LOD and LOQ values achieved with water as reference medium are slightly better the corresponding values achieved with air as reference medium. This especially holds, if the wavelengths range 1440-1460nm is used for H_2SO_4 concentration determination (about a factor of 2). However, if the wavelengths range 2100-2300nm is used for H_2SO_4 concentration determination, the difference is only 5 digits in the third decimal place. The LOD/LOQ values achieved by using the wavelength range 2100-2300nm is approximately 2 orders of magnitude better than those achieved by using the wavelength range 1440-1460nm.

	1440-1460nm [%]	2100-2300nm [%]
LOD, air	0.189	0.008
LOQ, air	0.629	0.028
LOD, water	0.083	0.007
LOQ, water	0.275	0.023

Table 1: LOD and LOQ values (rounded to three decimal places) for H_2SO_4 concentration, in pure dilute H_2SO_4 solutions with air and water as reference medium, respectively.

Dilute H_2O_2

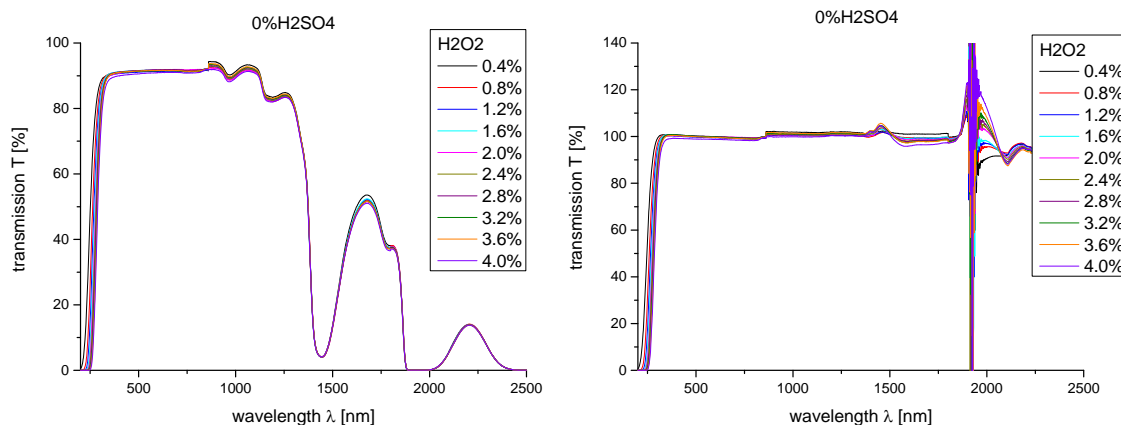


Figure 9: Spectra taken with 0% H_2SO_4 concentration and varying concentration of H_2O_2 , with reference air (left) and water (right), respectively.

Figure 9 shows the raw spectra for 0% H_2SO_4 and varying H_2O_2 concentration, with air and water as reference medium, respectively. The spectra were integrated between 270-290nm and integrated area under the curve was correlated with H_2O_2 concentration (Figure 10).

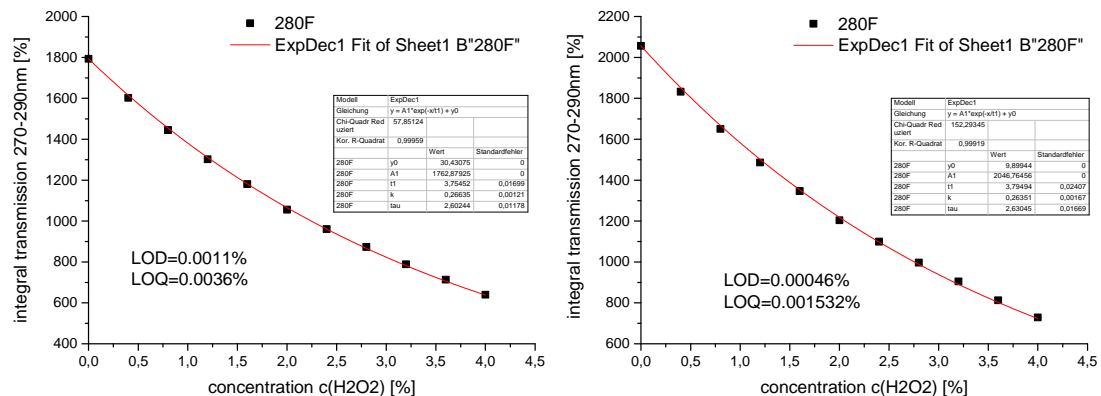


Figure 10: Integral transmission in the wavelength interval 270-290nm, as a function of H_2O_2 concentration, with corresponding exponential fit functions and reference medium air (left) and water (right).

The LOD values were again calculated from the corresponding fit functions, being the value where the fit function equals zero value minus 3 times STD (280nm, decreasing area as function of H_2O_2 concentration). The corresponding results are summarized in Table 2.

	270-290nm [%]
LOD, air	0.0011
LOQ, air	0.0036
LOD, water	0.0005
LOQ, water	0.0015

Table 2: LOD and LOQ values (rounded to four decimal places) for H_2O_2 concentration, in pure dilute H_2O_2 solutions with air and water as reference medium, respectively.

For H_2O_2 concentration determination using the integrated transmission in the wavelength range from 270-290nm the LOD/LOQ values are about an order of magnitude better than the corresponding values for H_2SO_4 concentration determination (compare Table 2 to Table 1). Also again, the LOD/LOQ values with water as reference medium are about a factor of 2 better than those achieved with air as reference medium.

Dilute $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$

For comparison, also the data lying on the main diagonal of Table 5 (H_2O_2 concentration increasing from 0-4% and simultaneously H_2SO_4 concentration increasing from 0-10%) was used for determination of LOD and LOQ values (Figure 11 and Figure 12).

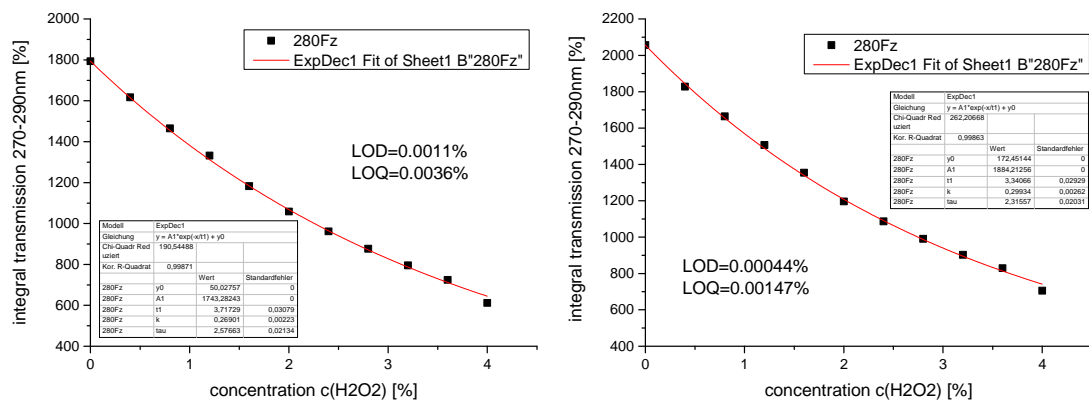


Figure 11: Integral transmission in the wavelength interval 270-290nm, as a function of H_2O_2 concentration, with corresponding exponential fit functions and reference medium air (left) and water (right).

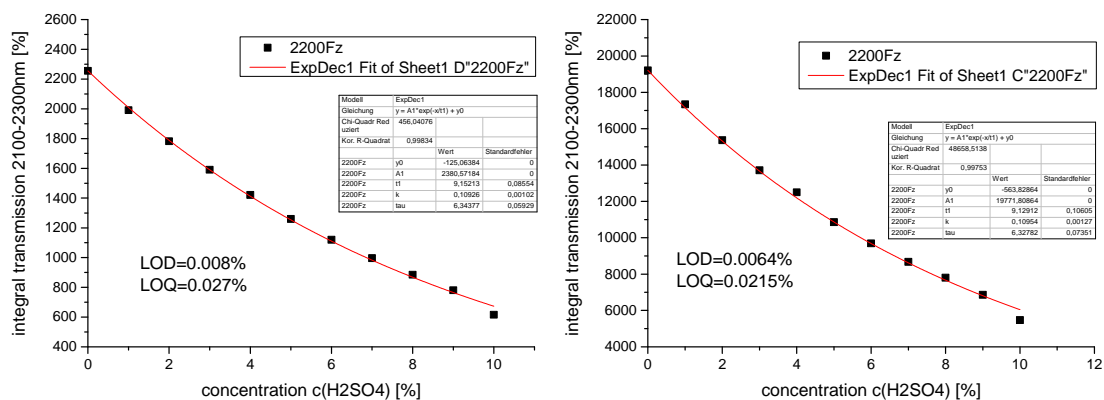


Figure 12: Integral transmission in the wavelength interval 2100-2300nm, as a function of H_2SO_4 concentration, with corresponding exponential fit functions and reference medium air (left) and water (right).

	H_2O_2	H_2SO_4	H_2SO_4
	270-290nm [%]	1440-1460nm [%]	2100-2300nm [%]
LOD, air	0.0011	n.a.	0.0080
LOQ, air	0.0036	n.a.	0.0270
LOD, water	0.0004	n.a.	0.0064
LOQ, water	0.0015	n.a.	0.0215

Table 3: LOD and LOQ values (rounded to four decimal places) for H_2O_2 and H_2SO_4 concentration, in dilute $H_2O_2+H_2SO_4$ solutions with air and water as reference medium, respectively.

The LOD values were again calculated from the corresponding fit functions, being the value where the fit function equals zero value minus 3 times STD (280nm, decreasing area as function of H_2O_2 concentration and 2200nm, decreasing area as function of H_2SO_4 concentration). The corresponding results are summarized in Table 3.

The integral data between 1440-1460nm could not be used to produce LOD and LOQ values for H_2SO_4 concentration, since no reasonable fits could be obtained from the corresponding data. This is attributed to the interference of H_2O_2 and H_2SO_4 in the spectral region of 1450nm (see also Figure 1). However, the LOD/LOQ values determined from the integral transmission between 270-290nm and 2100-2300nm are nearly the same, as obtained for the pure solutions.

Error of determination for single DSP components

More important than LOD/LOQ values for a later measuring device, is the error of determination of each component in the DSP, which is influenced by interferences of the other component in the spectral region used for concentration determination, respectively. To determine the influence of cross talk on the measurement accuracy, the samples from the first sample space (see Annex B) have been measured against air and water as reference and spectral data has been analyzed at wavelengths 280nm (H_2O_2) as well as 1450nm and 2200nm (H_2SO_4). For analysis on the one hand the peak intensity at the corresponding wavelengths were investigated and on the other hand the integral intensity in a defined wavelength range was analyzed (270-290nm, 1440-1460nm and 2100-2300nm) to reduce corresponding scatter of the data. The latter method is also better comparable to the measurements with a broad band emitting LED, used within the laboratory setup (see chapter Measurements with LED-based laboratory setup).

The measured data for peak intensities at defined wavelengths as well as integral intensity in the defined wavelengths ranges have been plotted against the relevant concentrations of H_2O_2 or H_2SO_4 , for air as the reference medium (Figure 13). The corresponding data for water as the reference medium looks quite similar and is not shown here for sake of overview (see Annex C for a complete overview on the analyzed spectroscopic data).

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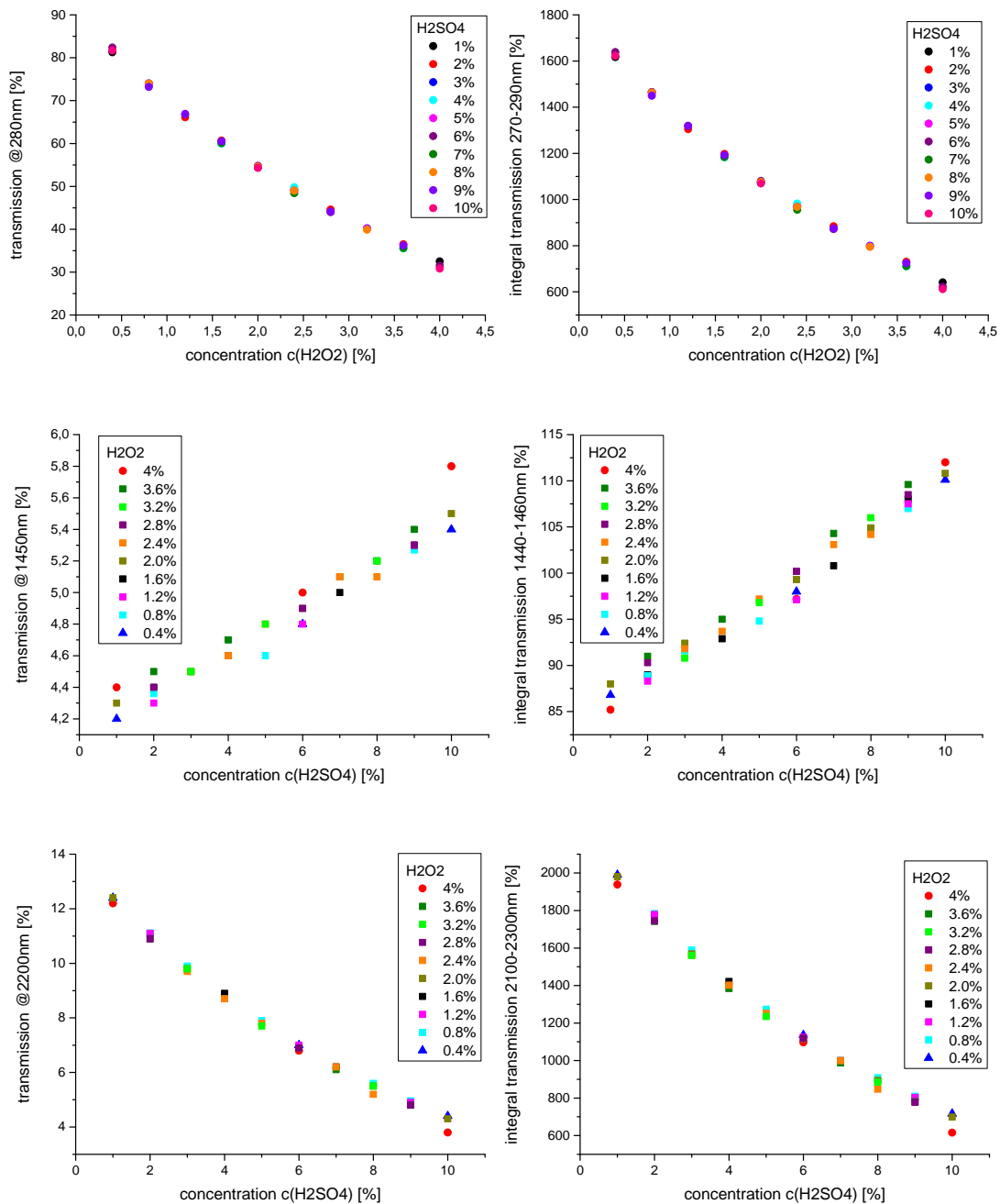


Figure 13: Peak intensities at wavelengths 280nm, 1450nm and 2200nm (left column) as well as integral intensities within intervals of 270-290nm, 1440-1460nm and 2100-2300nm (right column), as a function of H₂O₂ or H₂SO₄ concentration and air as reference medium.

The data at 280nm (first row of Figure 13) shows a strong dependence on the concentration of H₂O₂, the drop of intensity at 280nm is almost 50% in the range from 0-4% H₂O₂. When mean values (over all different H₂SO₄ concentrations) are plotted against H₂O₂ concentration, the intensity at 280nm decreases exponentially with increasing H₂O₂ concentration, as expected by Lambert-Beers-Law (Figure 14, top row). The error bars, defined by the standard deviation (STD) of the mean value for each H₂O₂ concentration, are very small. The mean percentage error for the integral

determination is 0.82% (0.86% for single wavelength determination, see Annex C), resulting in a mean error (averaged over the full concentration range) for the H_2O_2 concentration of 1.9% (also 1.9% for single wavelength determination, see Annex C), as can be calculated from the fit function.

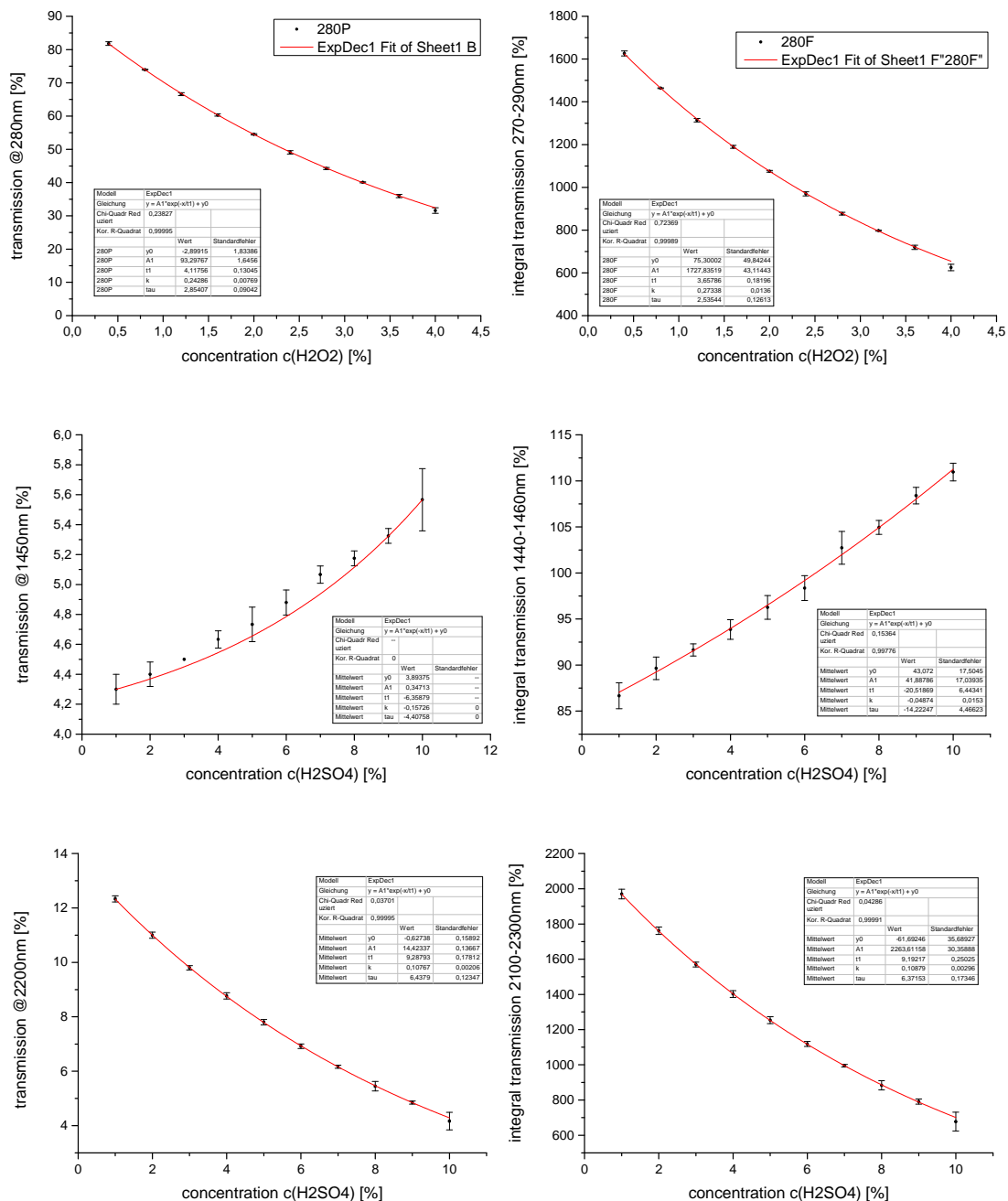


Figure 14: Mean peak intensities for air as reference medium, at wavelengths 280nm, 1450nm and 2200nm (left column) as well as mean integral intensities within intervals of 270-290nm, 1440-1460nm and 2100-2300nm (right column), as a function of H_2O_2 (280nm) and H_2SO_4 (1450nm and 2200nm) concentration (error bars STD).

The data at 1450nm (second row of Figure 13) shows an exponential increase with increasing H_2SO_4 concentration but also a strong scatter of the data, which is only slightly reduced for integral transmission between 1440-1460nm. The corresponding error bars, defined by the standard deviation (STD) of the mean value for each H_2SO_4 concentration, are comparatively large and an

accurate determination of the H_2SO_4 concentration seems not be possible. The reason for the strong scatter is the influence of the H_2O_2 in that wavelength region (see also chapter *Concentration dependence of spectra*). Much better is the situation at the wavelength band around 2200nm, almost no scatter is present, even if only data at the center wavelength is considered (third row of Figure 13). From the corresponding error bars, again defined by the standard deviation (STD) of the mean value for each H_2SO_4 concentration, a mean error for the integral determination of 2.10% (1.96% for single wavelength determination, see Annex C) can be deduced. From the exponential fit function, a mean error (averaged over the full concentration range) for the H_2SO_4 concentration of 4.0% (3.4% for single wavelength determination, see Annex C) can be calculated.

The corresponding values achieved for water as the reference medium are a mean error (averaged over the full concentration range) for the H_2O_2 concentration of 2.0% (also 2.0% for single wavelength determination, see Annex C) and a mean error (averaged over the full concentration range) for the H_2SO_4 concentration of 4.0% (2.9% for single wavelength determination, see Annex C).

Conclusions

H_2O_2 concentration can be addressed spectroscopically at a wavelength of around 280nm (absorption band edge) very well. The influence of H_2SO_4 concentration in that spectral region is almost negligible. The error of determination of H_2O_2 concentration is about 2%, not depending on the reference medium (either air or water) and also not depending whether an integral measuring (270-290nm, more realistic scenario for LED measurement) or a spot measurement at single wavelength (280nm) is made. H_2SO_4 concentration can be addressed best in the wavelength region of 2200nm, in that spectral region the influence of H_2O_2 concentration is smallest. The error of determination of H_2SO_4 concentration is about 4%, not depending on the reference medium (either air or water). For an integral measurement (2100-2300nm, more realistic scenario for LED measurement) the mean error of 4% is a little higher, compared to a spot measurement at single wavelength (2200nm), being about 3%. Since the difference between air and water as reference medium has no influence on the error of determination, it was decided to use air as background medium for the LED-based measurements, since this later on reduces technical effort for making a device.

Measurements with LED-based laboratory setup

Following the conclusions of the last chapter, an optical laboratory setup was realized allowing for difference absorption spectroscopy of DSP in the UV and the NIR, by using LEDs with 280nm as well as 2200nm center wavelength as light sources and suitable photo-detectors, making use of exactly the same cuvettes that has been used for the spectrometer measurements. The results were compared to those achieved with the laboratory spectrometer and accuracy of the technique was determined.

Experimental setup and procedure

The experimental setup used for the measurements with LED is shown in Figure 15. It consists of an LED-holder into which either a 280nm LED (Thorlabs, LED280J-OPTAN®) or a 2200nm LED (Roithner, LED22FC-PR) can be placed, a beam splitter (glass prism, coated with high reflecting aluminum layer) dividing the original beam of the LED into two separate beams, travelling opposite direction, a cuvette holder with cuvette, two photodiodes (280nm: FD10D-InGaAs, 2200nm: FGAP71-GaP) and electronics, connected to a PC, for controlling LED current and measuring photodiode currents.

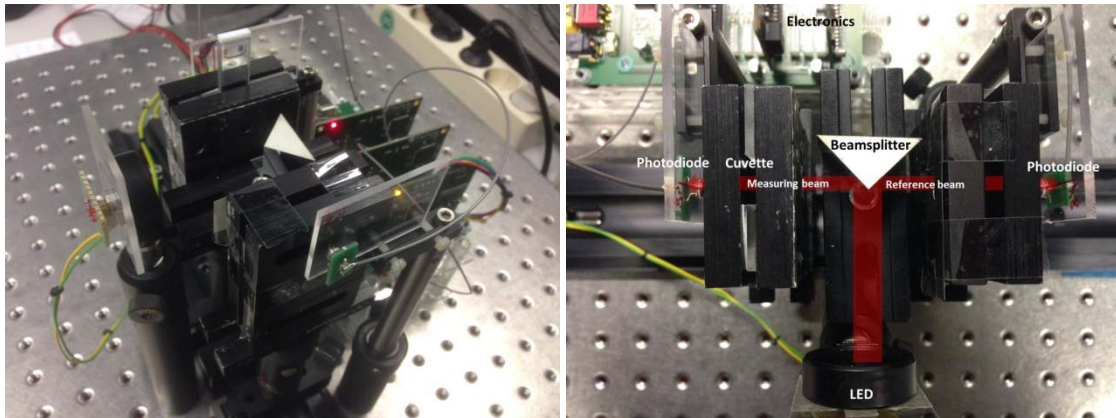


Figure 15: Images of the experimental setup used, for measuring with LED (either 280nm or 2200nm). Left: overview. Right: top view with indication of the light beam path and major components.

The measuring procedure is explained on the basis of Figure 16. The intensity at the reference photodiode is considered as zero intensity level (black curve in Figure 16). If the cuvette is removed from the setup, the signal level at the sample photodiode typically is about on the same level as the reference signal. However, due to slight asymmetries in the measuring setup, a slight offset may appear which will be corrected for when data is evaluated. When the sample cuvette is inserted into the beam path, a signal drop occurs at the sample photodiode, which is proportional to the H_2O_2 concentration. To achieve a stable saturation level of signal drop, the LED should be warmed up for about 5 minutes.

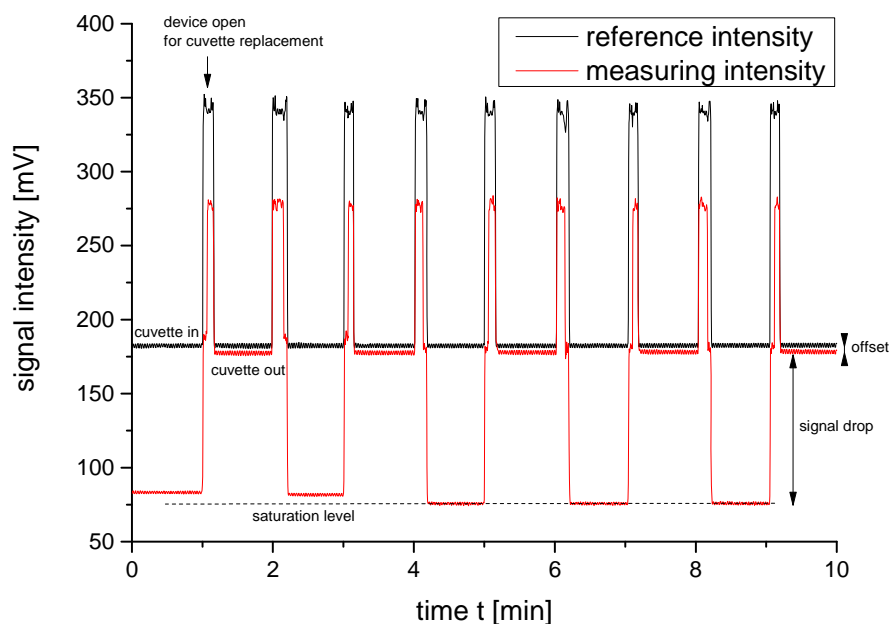


Figure 16: Signal intensity of the photodiodes (measuring and reference channel) as a function of time, with indication of all relevant parameters.

For measuring the individual samples (same samples, as used for the spectroscopic measurements, see Annex A+B), a time interval of about 1 minute was used, after appropriate LED warm up.

Limit of detection (LOD) and limit of quantitation (LOQ)

Dilute H₂O₂

The LOD values were measured by detecting the offset-corrected intensity ratio of signal levels with sample of defined H₂O₂ concentration in and out (air as reference), and calculation from the corresponding fit function, being the value where the fit function equals zero value minus 3 times STD (Figure 17). The limit of detection of H₂O₂ concentration with 280nm LED is LOD=0.015% weight and the limit of quantitation is LOQ=0.051% weight. Both values are about an order of magnitude higher than corresponding values achieved by spectroscopic measurements. This is attributed to the higher noise level of the standard photodiode detectors compared to the highly advanced cooled photodetectors used in the commercial Perkin Elmer spectrometer.

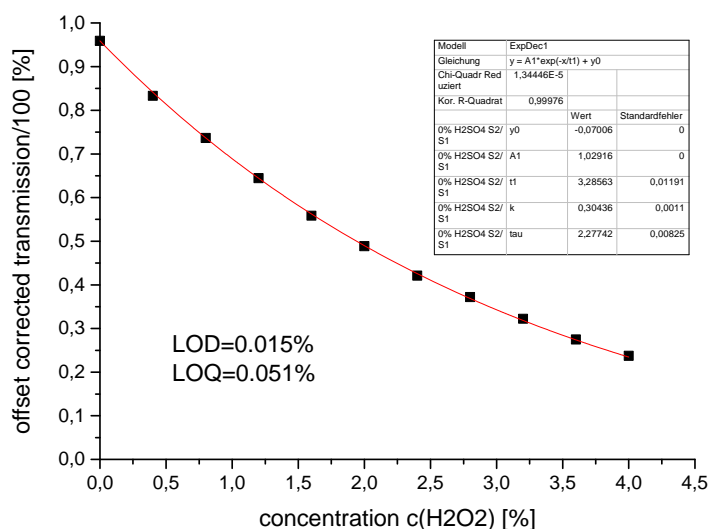


Figure 17: Integral transmission over the full 280nm LED emission, as a function of H₂O₂ concentration, with corresponding exponential fit function (reference medium air).

Dilute H₂SO₄

The LOD values were measured by detecting the offset-corrected intensity ratio of signal levels with sample of defined H₂SO₄ concentration in and out (air as reference), and calculation from the corresponding fit function, being the value where the fit function equals zero value plus 3 times STD (Figure 18). The limit of detection of H₂SO₄ concentration with 2200nm LED is LOD=0.7% weight and the limit of quantitation is LOQ=2.4% weight. Both values are much higher than corresponding values achieved by spectroscopic measurements. This is attributed to the higher noise level of the standard photodiode detectors (especially in the infrared) compared to the highly advanced cooled photodetectors used in the commercial Perkin Elmer spectrometer.

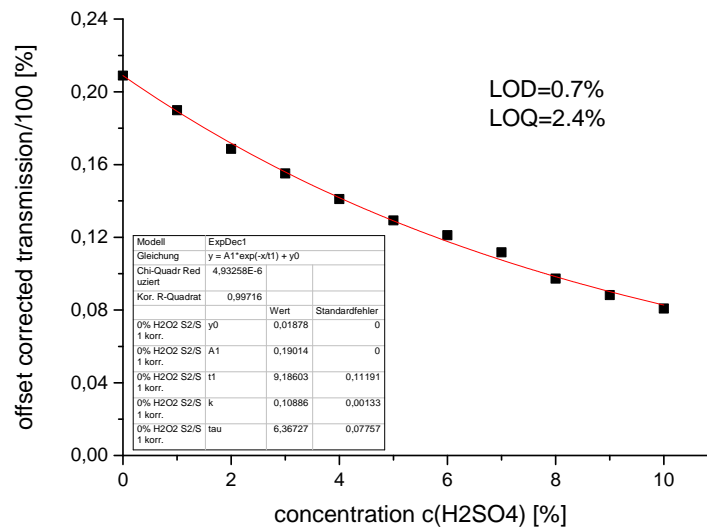


Figure 18: Integral transmission over the full 2200nm LED emission, as a function of H_2SO_4 concentration, with corresponding exponential fit function (reference medium air).

The larger LOD/LOQ also becomes evident for the error of determination (see next chapter), where errors at low concentrations becomes comparatively large. However, for concentrations above 2% H_2SO_4 , the method still gives good results, that are comparable to what was achieved with spectrometric data.

Error of determination for single DSP components

The error of determination of each component in the DSP, which is influenced by interferences of the other component in the spectral region used for concentration determination, for comparison was also determined with the LED setup. For that the samples from the first sample space (see Annex B) have been measured against air as reference and transmission data has been analyzed at wavelengths 280nm (H_2O_2) as well as 2200nm (H_2SO_4). For analysis on the intensity at the photodiodes over the full emission spectrum of the LED's was investigated which is more comparable to the integral intensity method, used with spectroscopic determination.

The measured data for relative photodiode intensities at wavelength 280nm has been plotted against the concentration of H_2O_2 , for air as the reference medium (Figure 19). Again, like the data collected with the spectrometer, an exponential decay of the transmission as function of the H_2O_2 concentration is observable. The scatter of the corresponding data points is mainly caused by the cross influence of H_2SO_4 . Like with the spectrometer data, the data from Figure 19 can be plotted as mean values with error bars, being the standard deviation (STD) of the corresponding mean value (Figure 20).

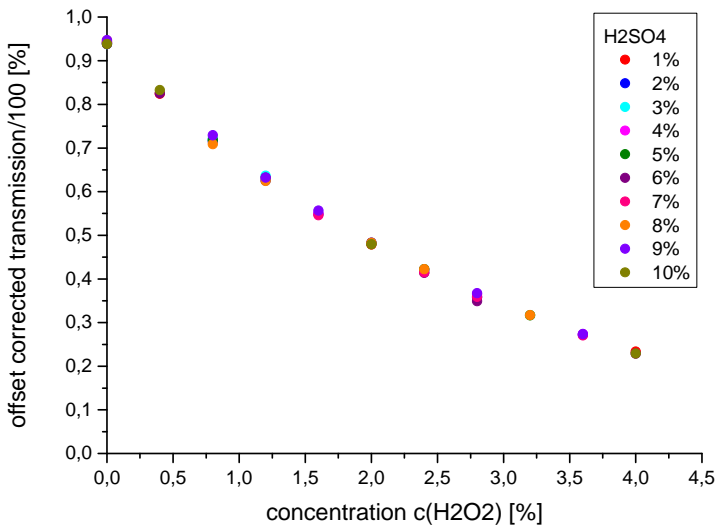


Figure 19: Relative intensity at wavelength 280nm, as a function of H_2O_2 concentration and air as reference medium.

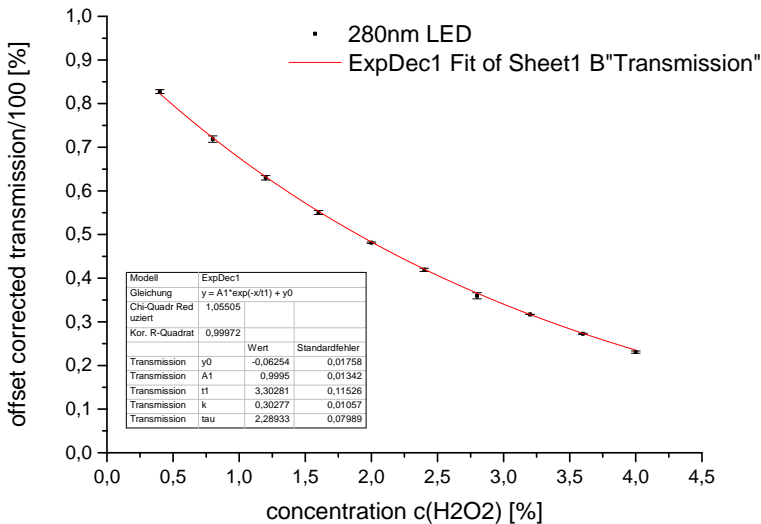


Figure 20: Mean peak intensities for air as reference medium, at wavelength 280nm, as a function of H_2O_2 concentration (error bars STD).

From the error bars in Figure 20 and the corresponding exponential fit function the error of the concentration can be calculated, as was made with the spectroscopic data. The detailed values are given in Annex D. A mean error in transmission of 0.81% in this case results in a mean error for H_2O_2 concentration of 1.6%. This value is even slightly smaller than the corresponding value of 1.9% achieved for spectroscopic measurements.

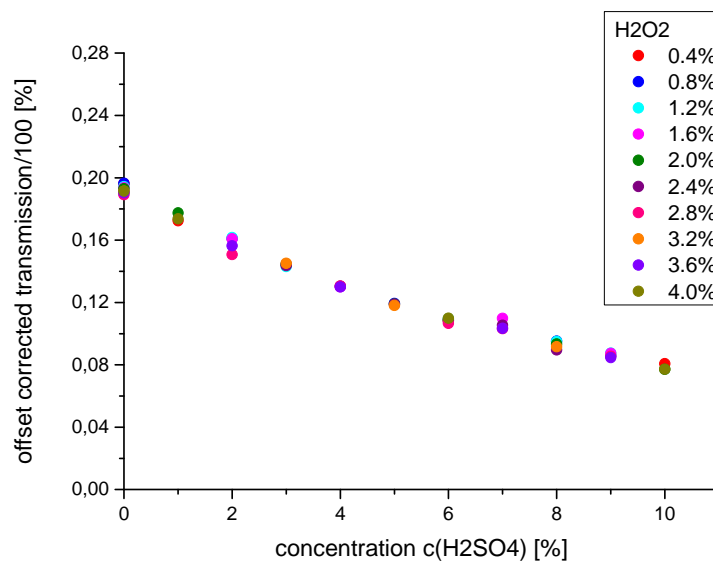


Figure 21: Relative intensity at wavelength 2200nm, as a function of H_2SO_4 concentration and air as reference medium.

The measured data for relative photodiode intensities at wavelength 2200nm has been plotted against the concentration of H_2SO_4 , for air as the reference medium (Figure 21). Again, like the data collected with the spectrometer, an exponential decay of the transmission as function of the H_2SO_4 concentration is observable. The scatter of the corresponding data points is mainly caused by the cross influence of H_2O_2 . Like with the spectrometer data, the data from Figure 21 can be plotted as mean values with error bars, being the standard deviation (STD) of the corresponding mean value (Figure 22).

From the error bars in Figure 22 and the corresponding exponential fit function the error of the concentration can be calculated, as was made with the spectroscopic data. The detailed values are given in Annex D. A mean error in transmission of 1.62% in this case results in a mean error for H_2SO_4 concentration of 5.0%. This value is slightly bigger than the corresponding value of 4.0% achieved for integral spectroscopic measurements (Annex C). The reason for this behavior is attributed to a worse signal-to-noise-ratio (SNR) of the LED setup compared to the SNR of the spectrometer with its cooled detectors, being especially relevant for the IR radiation, exhibiting a more thermal character.

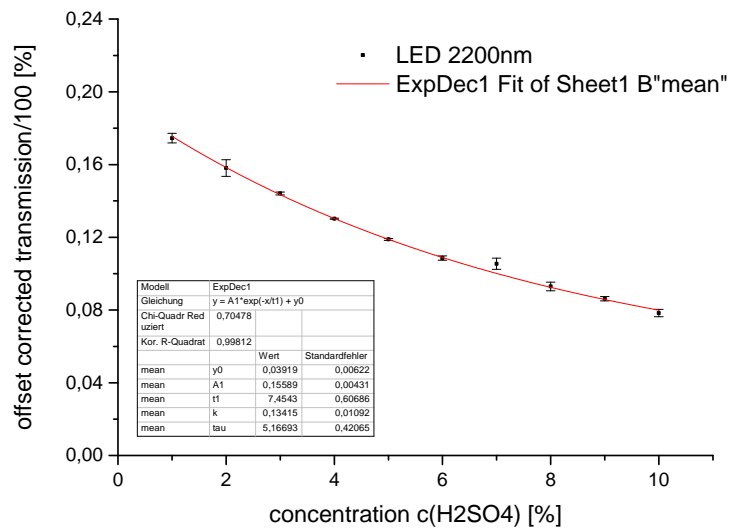


Figure 22: Mean peak intensities for air as reference medium, at wavelength 2200nm, as a function of H_2SO_4 concentration (error bars STD).

Conclusions

H_2O_2 concentration can be addressed by LED transmission measurement at a wavelength of around 280nm and air as reference medium very well. The corresponding mean error of determination of 1.6% is even slightly smaller than that of integral spectroscopic measurements (1.9%). The influence of H_2SO_4 concentration in that spectral region is almost negligible. H_2SO_4 concentration can be addressed by LED transmission measurements at wavelength of 2200nm with air as reference medium. The error of determination of H_2SO_4 concentration is about 5%, being a bit higher than the mean error of 4% for integral spectroscopic measurements. The higher error is attributed to a lower SNR with the LED setup compared to the spectrometer, which has cooled photodetectors.

Annexes

A. Table of DSP samples used for the study

Nr.	Date	Mass [g]	H2SO4 96%			H2O2 30%			H2O		
			[wt.% target]	[g target]	[g actual]	[wt.% target]	[g target]	[g actual]	[wt.% target]	[g target]	[g actual]
1	21.12.2015	200	10	20,83	20,85	4	26,67	26,72	86	152,50	152,54
2	12.01.2016	200	1	2,08	2,19	0,4	2,67	2,69	98,6	195,25	195,28
3	12.01.2016	200	1	2,08	2,11	4	26,67	26,69	95	171,25	171,29
4	12.01.2016	200	10	20,83	20,88	0,4	2,67	2,70	89,6	176,50	176,52
5	12.01.2016	200	1	2,08	2,08	2	13,33	13,37	97	184,58	184,57
6	13.01.2016	200	10	20,83	20,81	2	13,33	13,29	88	165,83	165,83
7	14.01.2016	200	6	12,50	12,69	0,4	2,67	2,63	93,6	184,83	184,84
8	14.01.2016	200	6	12,50	12,46	4	26,67	26,69	90	160,83	160,82
9	14.01.2016	100	5	5,21	5,18	2,4	8,00	7,99	92,6	86,79	86,77
10	14.01.2016	100	3	3,13	3,19	0,8	2,67	2,69	96,2	94,21	94,18
11	14.01.2016	100	8	8,33	8,32	0,8	2,67	2,67	91,2	89,00	89,01
12	14.01.2016	100	3	3,13	3,09	3,2	10,67	10,64	93,8	86,21	86,23
13	14.01.2016	100	8	8,33	8,30	3,2	10,67	10,66	88,8	81,00	80,99
14	14.01.2016	100	3	3,13	3,21	2,4	8,00	7,98	94,6	88,88	88,89
15	15.01.2016	100	8	8,33	8,64	2,4	8,00	7,95	89,6	83,67	83,67
16	15.01.2016	100	4	4,17	4,15	1,6	5,33	5,32	94,4	90,50	90,53
17	15.01.2016	100	7	7,29	7,30	1,6	5,33	5,30	91,4	87,38	87,44
18	15.01.2016	100	2	2,08	2,08	1,2	4,00	4,05	96,8	93,92	93,89
19	15.01.2016	100	2	2,08	2,08	3,6	12,00	11,98	94,4	85,92	85,90
20	15.01.2016	100	9	9,38	9,35	1,2	4,00	4,00	89,8	86,63	86,65
21	18.01.2016	100	9	9,38	9,39	3,6	12,00	12,02	87,4	78,63	78,66
22	18.01.2016	100	5	5,21	5,23	0,8	2,67	2,68	94,2	92,13	92,14
23	18.01.2016	100	6	6,25	6,23	1,2	4,00	3,97	92,8	89,75	89,73
24	19.01.2016	100	2	2,08	2,07	1,6	5,33	5,31	96,4	92,58	92,59
25	19.01.2016	100	9	9,38	9,35	1,6	5,33	5,33	89,4	85,29	85,32
26	19.01.2016	100	3	3,13	3,20	2	6,67	6,68	95	90,21	90,21
27	19.01.2016	100	6	6,25	6,27	2	6,67	6,66	92	87,08	87,05
28	19.01.2016	100	8	8,33	8,35	2	6,67	6,67	90	85,00	85,02
29	19.01.2016	100	4	4,17	4,16	2,4	8,00	7,95	93,6	87,83	87,85
30	20.01.2016	100	7	7,29	7,27	2,4	8,00	7,99	90,6	84,71	84,71
31	20.01.2016	100	2	2,08	2,11	2,8	9,33	9,31	95,2	88,58	88,59
32	20.01.2016	100	6	6,25	6,24	2,8	9,33	9,33	91,2	84,42	84,42
33	20.01.2016	100	9	9,38	9,40	2,8	9,33	9,33	88,2	81,29	81,26
34	20.01.2016	100	5	5,21	5,22	3,2	10,67	10,63	91,8	84,13	84,11
35	20.01.2016	100	4	4,17	4,17	3,6	12,00	11,98	92,4	83,83	83,87
36	20.01.2016	100	7	7,29	7,27	3,6	12,00	11,97	89,4	80,71	80,72
Nr.	Date	Mass [g]	H2SO4 96%			H2O2 30%			H2O		
			[wt.% target]	[g target]	[g actual]	[wt.% target]	[g target]	[g actual]	[wt.% target]	[g target]	[g actual]
37	01.02.2016	100	2	2,08	2,08	0,8	2,67	2,72	97,2	95,25	95,28
38	01.02.2016	100	9	9,38	9,39	0,8	2,67	2,66	90,2	87,96	87,98
39	01.02.2016	100	3	3,13	3,18	1,2	4,00	3,96	95,8	92,88	92,93
40	10.02.2016	100	8	8,33	8,36	1,2	4,00	4,03	90,8	87,67	87,65
41	10.02.2016	100	5	5,21	5,25	2	6,67	6,64	93	88,13	88,10
42	10.02.2016	100	6	6,25	6,28	2,4	8,00	7,98	91,6	85,75	85,75
43	10.02.2016	100	4	4,17	4,18	2,8	9,33	9,31	93,2	86,50	86,47
44	10.02.2016	100	7	7,29	7,27	2,8	9,33	9,31	90,2	83,38	83,38
45	11.02.2016	100	10	10,42	10,46	0	0,00	0,00	90	89,58	89,56
46	11.02.2016	100	4	4,17	4,15	0	0,00	0,00	96	95,83	95,83
47	11.02.2016	100	1	1,04	1,04	0	0,00	0,00	99	98,96	98,95
48	11.02.2016	100	9	9,38	9,41	0	0,00	0,00	91	90,63	90,65
49	11.02.2016	100	5	5,21	5,19	0	0,00	0,00	95	94,79	94,83
50	11.02.2016	100	2	2,08	2,10	0	0,00	0,00	98	97,92	97,90
51	12.02.2016	100	8	8,33	8,31	0	0,00	0,00	92	91,67	91,67
52	12.02.2016	100	6	6,25	6,25	0	0,00	0,00	94	93,75	93,76
53	12.02.2016	100	3	3,13	3,13	0	0,00	0,00	97	96,88	96,86
54	12.02.2016	100	7	7,29	7,33	0	0,00	0,00	93	92,71	92,72
55	15.02.2016	100	0	0,00	0,00	4	13,33	13,31	96	86,67	86,70
56	15.02.2016	100	0	0,00	0,00	3,6	12,00	12,02	96,4	88,00	87,96
57	15.02.2016	100	0	0,00	0,00	3,2	10,67	10,66	96,8	89,33	89,35
58	15.02.2016	100	0	0,00	0,00	2,8	9,33	9,34	97,2	90,67	90,66
59	15.02.2016	100	0	0,00	0,00	2,4	8,00	8,01	97,6	92,00	92,01
60	15.02.2016	100	0	0,00	0,00	2	6,67	6,65	98	93,33	93,32
61	16.02.2016	100	0	0,00	0,00	1,6	5,33	5,36	98,4	94,67	94,67
62	16.02.2016	100	0	0,00	0,00	1,2	4,00	3,98	98,8	96,00	95,98
63	16.02.2016	100	0	0,00	0,00	0,8	2,67	2,66	99,2	97,33	97,32
64	16.02.2016	100	0	0,00	0,00	0,4	1,33	1,35	99,6	98,67	98,67

Table 4: #1-36 → first sample space, #37-64 → second sample space

B. DSP sample concentration matrix

c(H ₂ SO ₄)	0	1	2	3	4	5	6	7	8	9	10
c(H ₂ O ₂)											
0	X	X	X	X	X	X	X	X	X	X	X
0.4	X	X					X				X
0.8	X		X	X		X			X	X	
1.2	X		X	X			X		X	X	
1.6	X		X		X			X		X	
2.0	X	X		X		X	X		X		X
2.4	X			X	X	X	X	X	X		
2.8	X		X		X		X	X		X	
3.2	X			X		X			X		
3.6	X		X		X			X		X	
4.0	X	X				X					X

Table 5: X → combinations of H₂SO₄ / H₂O₂ investigated (□ first sample space, ■ second sample space)

C. Analyzed spectroscopic data for air and water as reference

c(H ₂ SO ₄)	mean 2100-2300nm	STD 2100-2300nm	error [%]	error c(H ₂ SO ₄) [%]
1	1969.86667	27.61165	1.40	12.5
2	1761.675	20.8786	1.19	5.3
3	1569.375	13.62752	0.87	2.6
4	1402.23333	18.75802	1.34	2.9
5	1253.3	19.3202	1.54	2.7
6	1118.42	13.87271	1.24	1.8
7	995.2	6.85638	0.69	0.9
8	883.45	25.87747	2.93	3.1
9	791.05	14.46525	1.83	1.7
10	677.03333	53.83032	7.95	6.5
mean	-	-	2.10	4.0
c(H ₂ SO ₄)	mean 2200nm	STD 2200nm	error [%]	error c(H ₂ SO ₄) [%]
1	12.33333	0.11547	0.94	8.3
2	11	0.11547	1.05	4.6
3	9.8	0.08165	0.83	2.4
4	8.76667	0.11547	1.32	2.9
5	7.8	0.1	1.28	2.2
6	6.92	0.08367	1.21	1.7
7	6.16667	0.05774	0.94	1.1
8	5.45	0.17321	3.18	3.3
9	4.85	0.05774	1.19	1.1
10	4.16667	0.32146	7.71	6.1
mean	-	-	1,96	3.4
c(H ₂ O ₂)	mean 270-290nm	STD 270-290nm	error [%]	error c(H ₂ O ₂) [%]

0.4	1626.4	11.53776	0.71	6.8
0.8	1463.9	1.80278	0.12	0.6
1.2	1314.33333	8.21361	0.62	2.0
1.6	1189.3	7.12694	0.60	1.5
2.0	1075	4.0651	0.38	0.7
2.4	969.54	9.4775	0.98	1.6
2.8	876.86667	6.18088	0.70	1.0
3.2	797.4	2.40624	0.30	0.4
3.6	719.25	9.74149	1.35	1.5
4.0	625.13333	14.92526	2.39	2.4
mean	-	-	0.82	1.9
c(H₂O₂)	mean 280nm	STD 280nm	error [%]	error c(H₂O₂) [%]
0.4	81.8	0.55678	0.68	6.8
0.8	73.93333	0.11547	0.16	0.8
1.2	66.6	0.43589	0.65	2.1
1.6	60.325	0.3304	0.55	1.3
2.0	54.52	0.19235	0.35	0.7
2.4	49.08	0.502	1.02	1.7
2.8	44.23333	0.32146	0.73	1.0
3.2	40.06667	0.15275	0.38	0.5
3.6	35.95	0.47958	1.33	1.4
4.0	31.6	0.8544	2.70	2.5
mean	-	-	0.86	1.9

Table 6: Spectroscopic data and corresponding errors, for air as the reference medium.

c(H₂SO₄)	mean 2100-2300nm	STD 2100-2300nm	error [%]	error c(H₂SO₄) [%]
1	17142.66667	258.97132	1.51	13.7
2	15420.8	179.56382	1.16	5.3
3	13760.425	123.57293	0.90	2.7
4	12309.03333	191.65011	1.56	3.5
5	11022.5	189.02645	1.71	3.1
6	9808.34	184.87286	1.88	2.8
7	8778.53333	120.75356	1.38	1.7
8	7811.35	223.9824	2.87	3.1
9	6976.525	153.24491	2.20	2.1
10	6191.1	164.16565	2.65	2.2
mean	-	-	1.78	4.0
c(H₂SO₄)	mean 2200nm	STD 2200nm	error [%]	error c(H₂SO₄) [%]
1	86.6	0.95394	1.10	9.8
2	77.7	0.70238	0.90	4.0
3	69.125	0.4717	0.68	2.0
4	61.66667	0.80208	1.30	2.8
5	55.03333	0.73711	1.34	2.3
6	49	0.30822	0.63	0.9
7	43.6	0.45826	1.05	1.3
8	38.525	0.99457	2.58	2.7
9	34.4	0.65828	1.91	1.8
10	30.36667	0.66583	2.19	1.8
mean	-	-	1.37	2.9
c(H₂O₂)	mean 270-290nm	STD 270-290nm	error [%]	error c(H₂O₂) [%]
0.4	1840.86667	10.99879	0.60	5.9
0.8	1664.3	6.76683	0.41	2.0

1.2	1506.63333	9.40443	0.62	2.1
1.6	1361	9.44387	0.69	1.7
2.0	1225.16	8.82797	0.72	1.4
2.4	1104.68	10.00485	0.91	1.5
2.8	999.33333	6.70025	0.67	0.9
3.2	904.13333	1.55027	0.17	0.2
3.6	822.25	13.52787	1.65	1.8
4.0	720.46667	15.11103	2.10	2.0
mean	-	-	0.85	2.0
c(H₂O₂)	mean 280nm	STD 280nm	error [%]	error c(H₂O₂) [%]
0.4	92.6	0.60828	0.66	6.8
0.8	84.1	0.34641	0.41	2.1
1.2	76.33333	0.45092	0.59	2.0
1.6	69.075	0.47871	0.69	1.7
2.0	62.16	0.42778	0.69	1.3
2.4	55.96	0.54129	0.97	1.5
2.8	50.46667	0.37859	0.75	1.0
3.2	45.46667	0.05774	0.13	0.2
3.6	41.1	0.66833	1.63	1.6
4.0	35.7	0.8	2.24	1.9
mean	-	-	0.88	2.0

Table 7: Spectroscopic data and corresponding errors, for water as the reference medium.

D. Analyzed LED transmission data for air as reference

c(H₂SO₄)	mean 2200nm	STD 2100-2300nm	error [%]	error c(H₂SO₄) [%]
1	0.17454	0.00262	1.50	14.3
2	0.15812	0.00463	2.93	14.5
3	0.14416	8.10661E-4	0.56	1.9
4	0.13025	2.90105E-4	0.22	0.6
5	0.11885	5.33004E-4	0.45	1.0
6	0.10862	0.00118	1.08	2.1
7	0.10548	0.00307	2.91	5.4
8	0.093	0.00237	2.55	4.1
9	0.08622	0.00121	1.40	2.2
10	0.07834	0.00204	2.61	3.7
mean	-	-	1.62	5.0
c(H₂O₂)	mean 280nm	STD 280nm	error [%]	error c(H₂O₂) [%]
0.4	0.82769	0.00461	0.56	4.3
0.8	0.71875	0.00748	1.04	3.9
1.2	0.63013	0.00501	0.80	2.0
1.6	0.5505	0.00461	0.84	1.5
2.0	0.4813	0.00174	0.36	0.5
2.4	0.41909	0.00376	0.90	1.1
2.8	0.3598	0.0071	1.97	2.0
3.2	0.31683	1.56075E-4	0.05	0.04
3.6	0.27253	0.00134	0.49	0.4
4.0	0.23053	0.00261	1.13	0.7
mean	-	-	0.81	1.6

Table 8: LED transmission data and corresponding errors, for air as the reference medium.