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Relative Vapor Pressure Measurements Using a Frequency-Modulated Tunable Diode Laser, a Tool for Water Activity Determination in Solutions

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Two-tone frequency modulation spectroscopy (TTFMS) is applied to the determination of water activity using an 820-nm GaAlAs diode laser. By measuring the relative light absorption of water vapor over a solution and over a pure water reference, the water activity in the solution is determined. Fast, nonintrusive, and selective measurements are demonstrated. The detection limit for measuring a relative water vapor pressure change was 0.3%. The application of laser modulation spectroscopy to the determination of water activity is discussed, and suggestions on increasing the sensitivity and accuracy are presented.

Introduction

The water vapor concentration in a gas in chemical equilibrium with a solution depends on the water activity in the solution. The aim of this work is to investigate the possibility of determining the water activity in a solution by measuring the water vapor pressure over the solution relative to the vapor pressure over a pure water reference, using a diode laser, wavelength-tuned to a water molecular transition. With laser techniques the water vapor concentration can be measured independently, of other components present in the gas. This opens new possibilities in chemical analysis.

The water activity depends on the composition and the concentrations of the dissolved molecules in the solution and is coupled to the interactions between the molecules.¹ For example, in colloid chemistry, dealing with solutions that contain aggregates in the range of 1–1000 nm, water activity measurements have given important information on the interaction between colloidal aggregates like proteins and liquid crystals.^{2,3} The chemical potential μ , an important quantity in describing thermodynamic properties of water solutions, can be determined from the activity a of the water by

$$\mu = \mu^\circ + RT \ln a \quad (1)$$

where μ° is the standard chemical potential of pure liquid water, R the universal gas constant, and T the solution temperature. Today, several techniques for water activity determination exist. In most of them a test solution of unknown water activity is compared with a reference solution, where the water activity can be altered so that the system reaches equilibrium. Among others, three different types of techniques can be distinguished:

1. *Osmometer with Semipermeable Membrane.*⁴ A test solution is set in contact with pure water through a semipermeable membrane that only permits water to pass. A small inflow of water establishes a pressure difference between the solutions and equalizes the water activity on both sides of the membrane. This pressure difference is the osmotic pressure of the test solution. Small activity differences can be measured, but the dissolved molecules must be large, e.g., macromolecules, so just water passes through the membrane.

2. *The Isopiestic Method.*⁵ A reference solution and the solution of unknown activity are placed in open vessels in an evacuated chamber, such as a vacuum desiccator. Water

evaporates from the solution of high water activity and condenses into the solution with lower activity. At the isopiestic point, the chemical potential of water and the water activity are the same in the two solutions. By measuring the composition of the two solutions, one can determine the activity in the test solution from the known activity of the reference solution at the measured composition. The method is simple to perform and is very accurate, but the vapor pressure of the dissolved components in the test solution must be low in order to keep the transport between the samples insignificant. Further, the concentration in the sample changes during the measurements, which makes it difficult to measure at a predetermined concentration.

3. *Vapor Pressure Measurements.* When a solution and the surrounding gas phase are in chemical equilibrium, the water activity in the solution can be determined from the water vapor pressure.⁶ Two main techniques to determine the water vapor pressure can be distinguished: (a) measurements of the total pressure, a technique which can be used if the total pressure only depends on the water vapor pressure; (b) composition determination of the gas with gas chromatography⁷ or other analysis equipment. However, the accuracy in the composition determination is often low.

As the examples above indicate, there is no appropriate method to determine the water activity in solutions that contains many compounds with high vapor pressure. We will show that laser spectroscopy provides a promising tool for measurements of water activities.

Background Theory

The water activity a is related to the vapor pressure $p_{\text{H}_2\text{O}}^0$ over the pure water solvent and the vapor pressure $p_{\text{H}_2\text{O}}$ when in a mixture through

$$a = p_{\text{H}_2\text{O}}/p_{\text{H}_2\text{O}}^0 \quad (2)$$

Accordingly, the activity of water present in a solution can be determined by measuring its vapor pressure in equilibrium relative to the vapor pressure of a pure water reference. The intensity of a laser beam transmitted through an absorption cell of path length L filled with an absorbing gas is described by Beer's law

$$I(\nu) = I_0(\nu)e^{-\sigma(\nu)NL} \quad (3)$$

where $I(\nu)$ is the transmitted intensity at frequency ν , $I_0(\nu)$ is the incident intensity, $\sigma(\nu)$ is the absorption cross section, and N is

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the concentration of the absorbing gas. In this experiment, where we will deal only with weak absorptions ($\sigma(\nu)NL < 10^{-2}$), the transmitted intensity can be approximated as

$$I(\nu) \approx I_0(\nu)(1 - \sigma(\nu)NL) \quad (4)$$

The concentration N of H_2O is determined by its vapor pressure through the perfect gas law. Thus, measuring the relative intensity attenuation, $\delta(\nu)$, by the vapor at pressure $p_{\text{H}_2\text{O}}$, of the laser beam

$$\delta(\nu) = \frac{I_0(\nu) - I(\nu)}{I_0(\nu)} = \sigma(\nu)p_{\text{H}_2\text{O}}L \quad (5)$$

relative to the intensity attenuation $\delta^0(\nu)$ of the vapor at pressure $p^0_{\text{H}_2\text{O}}$, brings us the water activity through

$$a = \frac{\int \delta(\nu) d\nu}{\int \delta^0(\nu) d\nu} \quad (6)$$

If $\sigma(\nu)$ is known, it is possible to determine the absolute vapor pressure, by measuring the integral absorption. Hence, development of a water vapor pressure monitoring device, using laser absorption spectroscopy, would be of great importance. The technique of two-tone frequency modulation spectroscopy (TTFMS) is a highly-sensitive absorption method, and we have decided to use this method as a starting point in our spectroscopic work.

Frequency Modulation Spectroscopy

A variety of frequency modulation (FM) methods implemented on diode lasers exists, with the purpose of increasing absorption sensitivity. Common to the different approaches is the shifting of the detection band to high frequencies to avoid laser excess ($1/f$) noise. By addition of an ac component to the laser injection (drive) current, a diode laser is easily frequency modulated. The various FM methods are discussed by Silver⁸ and by Wang et al.⁹ The FM methods using modulation frequencies that are much smaller than the absorption line widths are often referred to as wavelength modulation spectroscopy (WMS), derivative, or $2f$ spectroscopy. At frequencies comparable or greater than the absorption line width, the method is named frequency modulation spectroscopy (FMS). FMS has been described several times in the literature.^{10,11} Choosing a small modulation frequency involves a simpler and less expensive apparatus with somewhat easier operation. Nevertheless, the drawback is loss of sensitivity. Sensitivities possible to obtain with different FM methods are listed in ref 8.

The basic principle of FMS is as follows: When a diode laser is frequency-modulated, principally two optical frequency sidebands are generated on the laser beam. These sidebands, separated from the optical carrier by a frequency equal to the modulating frequency, are equal in magnitude but opposite in phase. The amplitude modulation (AM) arising from the beating of the upper sideband against the carrier perfectly cancels the AM arising from the lower sideband beating against the carrier. When the frequency-modulated laser beam is obstructed by a spectral feature, the sidebands will be differentially absorbed, giving rise to an amplitude modulation, beating at the modulation frequency. Using a photodiode, reacting fast enough for the modulation frequency, the beat notes can be detected and, through conventional radio-frequency (RF) techniques, be demodulated to a signal directly proportional to the differential absorption of the sidebands.

Since line widths of atmospheric gases often are several gigahertz, a comparable detection bandwidth can be difficult to implement. The technique of two-tone frequency modulation (TTFM) has been developed to avoid some of these difficulties.¹²⁻¹⁴ Using two closely-separated modulation frequencies, sideband

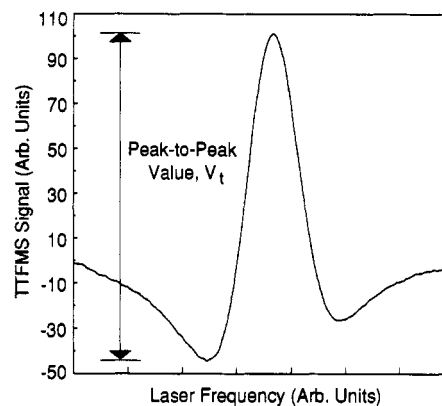


Figure 1. TTFMS signal from water vapor. The peak absorption is about 0.5%. The peak-to-peak value, used throughout these measurements to determine water activity is indicated.

pairs are generated on the laser beam. The TTFM method preserves a wide frequency separation between the sideband pairs but shifts the detection frequency to a low, easily manageable frequency regime. The detection frequency will be the frequency difference between the two modulation frequencies. Figure 1 shows a TTFMS signal from H_2O absorption. When the laser frequency is tuned first, the upper sideband pair is absorbed, giving rise to a negative signal. Further scanning of the laser brings the laser carrier onto the absorption line, resulting in a positive signal. Finally, the lower sideband pair is absorbed, resulting again in a negative signal.

Both single-tone and two-tone FMS offer the possibility of detector shot-noise limited detection of the absorption δ , with sensitivities of 10^{-7} – 10^{-8} . Such sensitivities have been achieved in several papers (see e.g. refs 14 and 15). The experimental setup we use normally has a detection sensitivity around 10^{-6} . The high sensitivity is suitable for work on small volumes of the absorbing gas, and it is possible to work in the near-infrared region, where molecular transitions are weak, but inexpensive diode lasers manufactured for communication purposes are commercially available.

One practically important advantage of two-tone over single-tone FMS is that in TTFMS the signal is recovered at a radio frequency (Ω) different from those of the two signal generators (ν_m and $1/2\Omega$). Thus, filtering techniques can be used to eliminate spurious signal pickup due to the signal generators.

Experimental Setup

Figure 2 shows the basic experimental arrangement used for TTFMS of water vapor. The diode laser, a double-heterostructure GaAlAs laser (Mitsubishi ML5415N-01) operating around 820 nm, is temperature and current controlled by a Melles-Griot 06DLD203 precision diode laser driver. During measurements the laser frequency drift is monitored to be less than 50 MHz over an hour. Wavelength tuning of the diode laser is performed by adding a current ramp (Tektronix FG504 function generator), with a frequency of about 350 Hz, to the diode laser injection current. Our TTFMS experiment uses laser modulation at $\nu_m - 1/2\Omega = 614.65$ MHz and $\nu_m + 1/2\Omega = 625.35$ MHz with signal demodulation at $\Omega = 10.7$ MHz. The two modulation frequencies ($\nu_m \pm 1/2\Omega$) are generated by the help of a double balanced mixer (Mini-Circuits ZFM-4H), which is fed by a Tektronix SG503 sine wave generator producing the frequency of $1/2\Omega$ and a Wavetek 2510A synthesized signal generator producing the frequency ν_m . The signals at the two frequencies are amplified (Mini-Circuits ZFL1000VH) and band-pass filtered prior to addition, in a HP33150A bias tee, to the diode laser injection current. By a variable attenuator, the radio-frequency power to the diode laser can be varied. The TTFMS absorption signal is monitored on an oscilloscope, and the signal amplitude is optimized

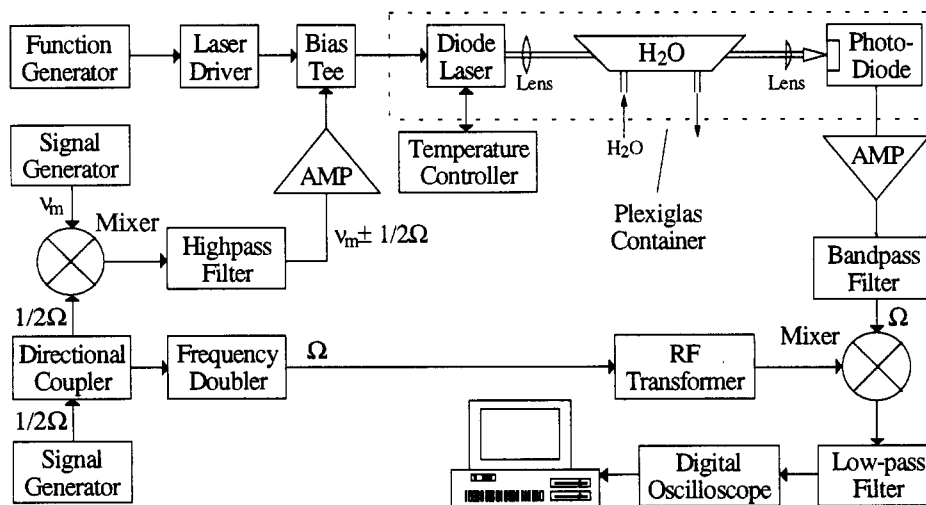


Figure 2. Schematic diagram of the experimental setup.

by increasing the modulation power until the demodulated signal reaches its maximum and just starts to broaden. The TTFM signal is detected by an EG & G FND100 photodiode, amplified (60dB) by two Miteq (AU-2A-0110) low-noise amplifiers, and band-pass filtered at 10.7 MHz. One band-pass filter is placed between the two amplifiers and prevents interaction between the amplifiers. The TTFM signal amplitude is recovered by a double balanced mixer (Mini-Circuits ZFM-3) driven by the RF port by the amplified detector signal and on the LO port by the suitably phase matched and frequency-doubled (Mini-Circuits FD-2 frequency doubler) output from the Tektronix SG 503 sine wave generator. The LO reference waveform is passed through an RF transformer (Mini-Circuits FTB-1-1) for ground isolation. The demodulated absorption signal from the mixer is amplified by a low-noise preamplifier (Stanford SR560) with a variable low-pass filter set to 10 kHz. This bandwidth matches the rate at which the laser is scanned across the absorption line. The spectrum is recorded on a Tektronix 2431L digital oscilloscope, connected to a 386 computer over a GPIB interface. The signal averaging is made in the computer, by adding 256 consecutive spectra consisting of 1024 channels of data.

All transmissive optics, such as lenses and neutral density filters, are placed with an angle to the optical path. Despite TTFMS being a technique offering shot-noise limited detection, the sensitivity is often limited by undesirable interference fringes, originating from parallel surfaces in the optical path. These interference or etalon fringes, appearing as a periodic oscillating base line sufficiently strong to obscure weak absorption signals, are highly reduced by angling all transmissive optics.

The absorption cell was constructed of a plastic tube with two inclined glass windows at the ends. In our initial measurements we used a sample compartment, in which a plastic jar with a solution could be placed, directly attached on the absorption cell. Although the absorption cell was well mounted on the optical table, the signal was seriously altered by etalon fringes, originating from the cell windows, when a solution was replaced. Therefore, we used a sample container connected to each end of the absorption cell by flexible hoses as shown in Figure 3. A fan was integrated in the system to circulate the system atmosphere through the sample container and the absorption cell. In parallel with the sample container a similar container with a jar containing a reference of distilled water was placed. By a set of valves any of the two compartments, and its atmosphere, could be connected to the fan and the absorption cell. Thus, a solution under investigation could be interchanges with the pure water solvent, without severe disturbance of the recording. The volumes of the sample compartment, the distilled water compartment, and the absorption cell were 180, 150, and 290 cm³, respectively. The optical path length in the absorption cell was 29 cm, and the open

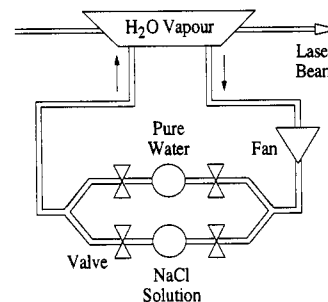


Figure 3. Schematic diagram of the absorption cell arrangement.

air path was 28 cm. The solution and distilled water volumes were about 30 cm³, which involves a negligible change of the concentration in the solution during a measurement.

Measurement Techniques

The strongest H₂O absorption line, which did not interfere with other lines, in the wavelength range of a given diode laser, was chosen, Figure 1 shows the H₂O line used throughout these measurements recorded with TTFMS around 819 nm. The peak absorption measured in direct transmission was about 0.5%. The TTFMS spectrum was averaged 256 times in a 10-kHz bandwidth, and the signal-to-noise ratio was estimated to 280. The signal-to-noise ratio was limited by optical feedback, i.e., laser light reflected back into the diode laser cavity. The feedback noise appears as a fluctuating intensity of the laser light. At the left in the spectrum, the influence of an etalon fringe from a neutral density filter is discernible. After an averaging cycle the spectrum is searched for the maximum and minimum value of the TTFMS signal (and their channel positions), and the peak-to-peak value is calculated. We will use this value as an approximation of the integral absorption in eq 6.

A pure water reference and a NaCl solution are placed in the reference and sample compartments, respectively. With the valves the pure water compartment is closed, and the sample compartment is connected to the absorption cell and the fan. The frequency-modulated laser beam is passed through the absorption cell, and the signal peak-to-peak value is monitored on the computer, with time intervals of about 20 s. When the NaCl solution has established equilibrium between the liquid and the gas phase, the solution under investigation is exchanged with the pure water reference by turning the valves. Throughout the measurement the fan is kept working in order to maintain a high speed of recording. The ambient temperature and humidity of the atmosphere and the temperature of the solutions and the solute are carefully monitored. The total pressure in the absorption cell is around 1 atm in all measurements.

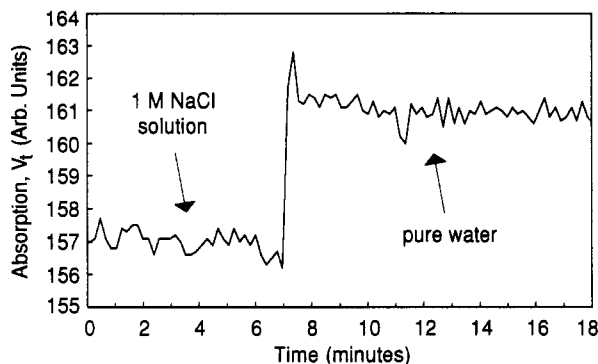


Figure 4. Recording of the peak-to-peak value of the TTFMS signal, when a 1.0 M NaCl solution, in connection with the absorption cell, is replaced by pure water.

The water vapor pressure is extremely sensitive to a fluctuating temperature. It is of great importance that the temperature of the solution and the pure water reference are equal and stable during a recording. We kept the solute and solutions, all the time, close to the two sample compartments to secure an equivalent temperature.

When the ambient temperature in the laboratory varies, the optical path length in the optical components change, causing etalon fringes to wander about the absorption signal. For this reason a large Plexiglas cover was placed over the optical setup. This eliminated the influence of temperature drifts and drifts due to air flow in the laboratory, in the time scale of a recording.

Results and Discussion

The recording in Figure 4 shows consecutive measurements of the peak-to-peak value of the TTFMS signal from H₂O absorption. The increase in the signal value is due to a change in the water vapor pressure, from $p_{\text{H}_2\text{O}}$ to $p_{\text{H}_2\text{O}}^0$, when a 1.0 M NaCl solution is replaced with the pure water reference. The signal increase is measured to be 2.58%. However, this value is affected by absorption from atmospheric H₂O in the optical path outside the absorption cell. The atmospheric contribution V_a to the total peak-to-peak value, V_t , is calculated by

$$V_a = \frac{1}{1 + \frac{l_c n_c}{l_a n_a}} V_t \quad (7)$$

where n_a is the humidity of the atmosphere outside the absorption cell, n_c is the humidity of the atmosphere inside the absorption cell, l_a is the air optical path length, and l_c is the optical path length in the absorption cell. Notice that the line shapes of the signal from the air path and the signal from the cell path have not been considered. The humidity in the atmosphere outside the absorption cell was 46%, and the solution temperature was 23 °C. Using eq 7, assuming 100% humidity in the absorption cell, the H₂O pressure change in the cell is calculated to be $3.68 \pm 0.30\%$. Calculation of the atmospheric contribution to the total absorption in eq 7 gave an absolute uncertainty of 0.04% in determining the relative pressure change. The signal-to-noise ratio in Figure 4 is estimated to be 14, which gives a minimum detectable pressure change of 0.3%, with a signal-to-noise ratio of one, with our current system. We conclude that the noise seen in Figure 4 is caused by optical feedback. Possible sources of error in the determination of the pressure change are an inhomogeneous vapor flow through the absorption cell, heating of the vapor and the solution and solute surfaces by the fan, and change of the H₂O line width during the recording. The water activity of the 1.0 M NaCl solution is determined to be 0.9632. The literature value, provided from ref 16, is 0.9663.

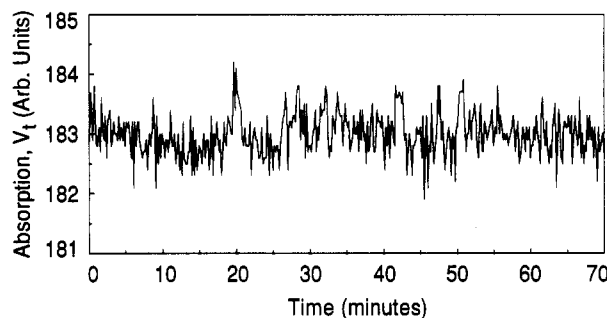


Figure 5. Recording of the peak-to-peak value of the TTFMS signal from H₂O absorption during 70 min.

For a 0.5 M NaCl solution we obtained the water activity to be 0.9821 ± 0.0018 compared with the literature value, from ref 16, of 0.9834. We noticed that the water vapor pressure change tended to increase after repeated measurements. Therefore, the absorption cell and the sample compartment were dried out carefully before a new NaCl solution was placed in the sample compartment.

The time taken for recording a relative vapor pressure change, long enough to determine the water activity, is a few minutes as seen in Figure 4. The speed limit of a recording is determined by the hydration, which for example is coupled to the solution heat transfer and surface area, and depends on the volumes of the solution and reference compartments and the absorption cell volume. The time taken to reach equilibrium can be decreased by stirring the solution and the reference solute and using a smaller absorption cell volume. The absorption cell volume should be kept small but the absorption path length maintained as much as possible.

We have assumed that the peak-to-peak value of a TTFMS signal is directly proportional to the integral absorption of $\delta(\nu)$, i.e., the water vapor concentration. This is true as long as the absorption line profile does not change, but if the line profile (only) is altered, the peak-to-peak value changes, since the sidebands will experience a different differential absorption. When the water vapor pressure increases, the absorption line width increases due to collisional self-broadening. Although the change of the line width due to the collisional self-broadening is linearly proportional to the vapor pressure, the TTFMS peak-to-peak value is not. The accuracy of TTFMS in quantitative measurements can be increased if the true absorption line profile, e.g., the direct transmission signal, is derived. Several papers on the derivation of line parameters from absorption measurements using low modulation frequencies (WMS) have been published.¹⁷⁻¹⁹ Wong and Hall have determined line parameters from weak absorptions using FMS,²⁰ and Kauranen and Avetisov have performed accurate determination of line parameters using TTFMS.²¹ Typical literature values of the O₂ and N₂ broadening of H₂O²² and the self-broadening^{18,23} are 1.5–2, 3–4, and 15–20 MHz/Torr (hwhm, half-width at half-maximum), respectively. At 23 °C, 1 atm total pressure, and 100% humidity the total H₂O line width is approximately 2.5 GHz (hwhm).

Since our purpose is to measure a very small signal change out of several consecutive TTFMS measurements of the absorption, the absorption signal should be as large as possible compared to the background fluctuations. The background fluctuation can be etalon drifts and laser amplitude noise. Figure 5 shows a typical recording of the peak-to-peak value of the TTFMS signal from H₂O absorption over an hour. The sensitivity can be increased by subtracting the background noise with a dual-beam subtraction scheme.²⁴ This will reduce laser amplitude noise and etalon fringes. Particularly, noise due to optical feedback can be reduced using an optical isolator. The TTFMS signal can be increased by increasing the H₂O absorption by using a longer absorption path length. If the path length is increased using a

multipass configuration,²⁵ it is possible to keep the cell volume small. The absorption can also be increased by selecting H₂O lines with stronger line intensity. In the 1.3- and 1.5- μ m regions, where considerably cheap diode lasers can be commercially obtained, H₂O lines of 1 or 2 orders of magnitude larger line intensity can be found.

Conclusions

We have shown that laser spectroscopy, e.g., TTFMS, provides fast, nonintrusive, and selective measurements of water activity. Especially the high wavelength resolution and tunability of diode lasers are ideal for selecting a noninterfering water molecular transition and determine the water activity without disturbances from other molecules. To our knowledge, this is the first time laser spectroscopy is applied for determining water activity by measuring relative water vapor pressure. We are confident that at least an order of magnitude improvement in sensitivity can be attained, for example, using stronger H₂O absorption lines and by reducing the noise by a dual beam subtraction scheme or using an optical isolator. The accuracy to which the water activities have been presented in this paper is far from the ultimate limit. The accuracy can be improved by a more suitable arrangement of the absorption cell and the test and reference solutions, by thermostating the absorption cell arrangement, by removing the influence from the ambient air, and by determining the line width change during a recording.

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