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Determination of water vapor pressure over corrosive chemicals versus temperature using Raman spectroscopy: Exemplified by application with a 85.5 % phosphoric acid

by

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Abstract

A method to determine the water vapor pressure over a corrosive substance was developed and tested with 85.5 ± 0.4 % phosphoric acid. The water vapor pressure was obtaineded at a range of temperatures from ~25 °C up to ~200 °C using Raman spectrometry. The acid was placed in an ampoule and sealed with a reference gas (either hydrogen or methane) at a known pressure (typically ~0.5 bar). By comparing the Raman signals from the water vapor and the references, the water pressure was determined as a function of temperature. A considerable amount of data on the vapor pressure of phosphoric acid is available in the literature, to which our results could successfully be compared. A record value of the vapour pressure, 3.40 bar, was determined at 210 °C. The method required a determination of the precise Raman scattering ratios between the substance: water and the used reference gas: hydrogen or methane. In our case the scattering ratios between water and reference ν_1 Q-branches were found to be 1.20 ± 0.03 and 0.40 ± 0.02 for H_2 and CH_4, respectively.

Keywords: Raman, Vapor pressure; Gas phase; Scattering cross section; Corrosive substance; Phosphoric Acid.

Introduction

The aim of this work was to develop a method to determine the water vapor partial pressure over a corrosive substance, here as an example 85.5 ± 0.4 % phosphoric acid (H_3PO_4 or PA) by weight in water. The method should be useful with other substances for which the water vapor partial pressure is sought. This experimental work was related to the art of making efficient fuel cells and water electrolysers.[1-4] As a fundamental substance phosphoric acid has been well studied and its vapor pressure is well known, making our results comparable with the literature. The method selected here was Raman spectroscopy that is ideal to study the vapor constitution over the acid versus temperature, since it allowed us to record quantitatively the presence of the water molecules in the gas, and relative to the amount of an internal calibration gas, methane or hydrogen, added to the ampoule before sealing. In spite of its rather weak scattering strength Raman spectroscopy is favourable because the signal is species-specific and the signal (intensity) should be linearly dependent on species concentration. The obvious choice of nitrogen as the calibration gas, externally or internally, was avoided here due to the risk of errors arising from the nitrogen content of the surrounding air. To get higher precision it was decided to accurately determine the Raman scattering cross section of water relative to methane or hydrogen under exactly the conditions in our experimental set-up. Previous results for PA and associated methods are reviewed and our experimental technique and the results are discussed. The known vapor pressure curves over PA are confirmed and the range of the 85.5 % PA was extended to a higher temperature.

Previous vapor pressure results

The vapor pressure of ~85 % phosphoric acid has been determined in several recent and perhaps other works.[5-8] *Fontana*[5] obtained the vapour pressure from the mass of PA and water vapor condensed in a porous substance, Drierite, and the mass of the Drierite alone. A measured amount of thermally equilibrated gas was passing from a bottle full of phosphoric acid through a pipe to another bottle full of Drierite. Sulphuric acid, soda and Drierite were used to make the gas (air) dry and free of CO_2. Constant temperatures were maintained at ± 0.1 °C and enough PA was used so that concentration changes resulting from water removal from the PA could be neglected. When the PA percentage exceeded 100%, apparent percentages of H_3PO_4 relative to the acid bonded with water were used (e.g. $H_4P_2O_7$ has 110.1 % of H_3PO_4). *Brown and Whitt*[6] determined the vapor pressure by means of measuring the boiling point at reduced pressures. Several concentrations of acids, expressed in % of P_4O_{10} in water, were made and heated. The acids were contained in an ampoule attached to an elaborate vacuum system connected to a mercury manometer that allowed the vapor pressure to be obtained. Essentially no PA was found in the vapor at temperatures (T) below 300 °C. *MacDonald and Boyack*[7] used a variation of the Stokes technique[9] in which connected flasks were filled up with several mixtures of PA (from 70 to 100 %) at T and cold water, and further connected to a manifold in order to obtain a vacuum. The composition of the solution changed until the vapor pressure was the same as that of water. Since the vapor pressure of pure water is accurately known, the vapor pressure over the solution could be calculated from the change in mass after the equilibration at the temperature. Most recently *Korte*[8] has made an extensive review of older[5,6,10] and newer vapor pressure determinations[7,11] and has given data for many PA concentrations. The data were modelled and plotted in ways useful to make interpolations for finding vapor pressures for concentrations and temperatures not previously given.

A comparison of the literature data for 85.5 % PA is plotted in Figure 1. As seen there is a quite good agreement between the data of the different researchers, except perhaps those of Fontana[5] that seem to be slightly too low.

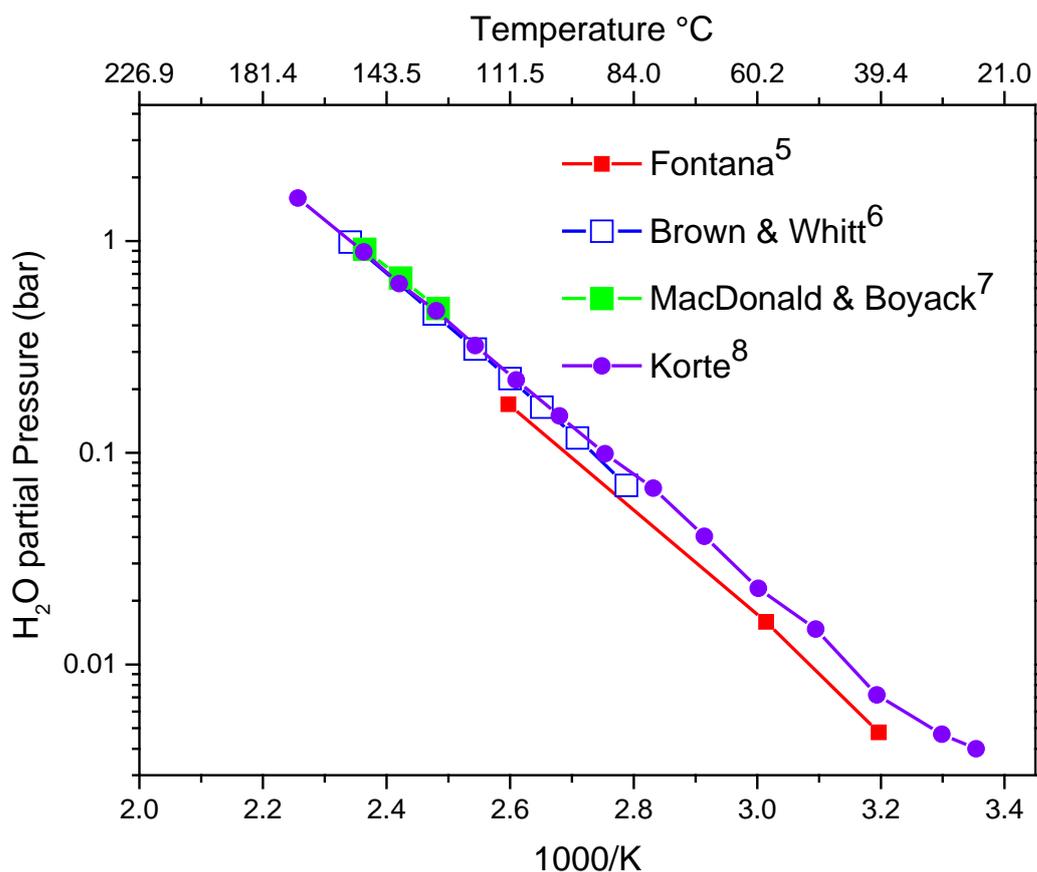**Figure 1.** Review of literature data for the vapor pressure over the ~85.5 % phosphoric acid.

Materials and methods

Chemicals

The used phosphoric acid was ~85 % by weight percentage of orthophosphoric acid (H_3PO_4, CAS: 7664-38-2) from Sigma-Aldrich. The *concentration* of the PA was accurately characterized: After dilution samples were titrated in an automatic device with combined pH glass and reference

electrodes, and controlled by Metrohm Tiamo[TM] 2.4 software. The titrant solution was ~0.2 M NaOH, standardized by dry potassium bitartrate ($KH_5C_4O_6$) dissolved in pure water in an accurate volumetric flask. The concentration was further checked by measuring the electrical conductivity. This was done by introducing the acid into a home-made Pyrex[TM] conductivity cell with a capillary tube connecting two separate electrode chambers.[12] The cell constant K (= $\sigma_{KCl} \times R_{KCl}$, where σ is a specific conductivity) was determined by measuring the resistance R_{KCl} (~4 kΩ) for a 0.1 Demal aqueous KCl solution of accurately known conductivity at room temperature.[13] The resistance was obtained from impedance versus frequency diagrams measured in an AC Wheatstone bridge setup (Princeton Applied Research VersaStat[TM] 4 potentiostat with VersaStudio[TM] software at an accuracy $\approx$ 0.1 %). The PA solution conductivity σ_{PA} (= K / R_{PA} in units of S cm^{-1}) was obtained similarly and the concentration of the acid was determined from the known conductivity data for PA solutions.[8]

Methane and hydrogen (>99.9% pure gasses) were obtained from AGA/Linde, Copenhagen S, DK and S. Frederiksen, Ølgod, DK. The Raman spectra showed no trace impurities, confirming that the gases were clean and dry.

Raman spectroscopy

Raman spectra were obtained by use of a DILOR-XY 800 mm focal-length Czerny-Turner type spectrometer[14] with 90° macro entrance and a 10x10 cm^2 1800 lines/mm plane holographic grating. Excitation was done using laser light from a continuous Spectra-Physics Millennia Laser (wavelength 532 nm, vertically polarized and with a power setting at up to ~1.5 W). The light was collected with a wide 10 cm focal length achromatic lens. Rayleigh scattering was removed with a Kaiser holographic SuperNotch-Plus filter. A quarter wave plate was mounted before the entrance slit to depolarize the light, making the grating efficiency independent of the polarization properties of the light. The slits were opened to 0.6 × 10 mm to obtain better signals at the expense of the

resolution.[15] The spectra were acquired with a multi-channel Horiba Jobin-Yvon Synapse[TM] CCD detector (1024 × 256 pixels) with thermoelectric cooling (-70 °C) running under Horiba Scientific Labspec[TM] 5.42 software. The Raman signal was not calibrated for the quantum efficiency of the CCD (response) versus wavelength. The spectrometer cm^{-1} scale was calibrated with cyclohexane.[16]

To obtain the H_2O partial pressures we measured quantitative Raman spectra of the gasses contained in home-made Pyrex[TM] ampoules (cells). In the beginning of this investigation we tried to use nitrogen as an inert reference gas, but this method was found to give unreliable results, the reason probably being that the N_2 signal from the laboratory air interfered. It could possibly be avoided by the use of square cuvette type cells, but we preferred round wide tubes that gave good gas spectra and much better stood up to high internal pressures. Quartz tube cells could not be used because of risk of decomposition of the reference gas (CH_4 or H_2) in the extreme heat needed for sealing of the silica material. Cells of Pyrex (~2mm wall thickness, ~16 mm internal diameter, see Figure 2) worked satisfactorily. Chemicals, e. g. phosphoric acid or water, were added and then the cell was connected via rubber tubing to a vacuum line, frozen, evacuated, filled repeatedly with the reference gas (hydrogen or methane) at a predetermined pressure (0.5 bar at 22 °C) and sealed with a butane-oxygen torch flame. Enough PA was used (cells were half full) so that the minute change in concentration by loss of water to the gas phase could be neglected.

Raman spectra were obtained from cells placed vertically in order to let light pass horizontally. Intensity data for the spectral lines were measured several times and for many minutes with an intensive excitation beam and automatic removal of cosmic spikes. The measurements were repeated and averaged in order to obtain reliability. The spectra were obtained and analysed with the Labspec 5.42 software. Some measurements were done at room temperature, others at higher temperatures in a range from ~50°C to ~200°C. The heating was achieved by use of a home-made (closed insulated aluminium-bronze-core vertical-tube electrical) furnace. The four silica windows

were protected with steel nets because of the **risk of ampoule explosion**. Temperatures were determined with several 4-wire-Pt-100-Ω resistors to a precision better than ~0.1 °C but the temperature inside the furnace was only precise to ~1 °C. Other experimental details (furnace, etc.) have been described elsewhere.[17]

Figure 2. Photograph of a sealed ampoule with a small amount of water/ice contained inside a capillary. This ampoule contained water and 0.5 bar of hydrogen. The carbon sooting (on the outside) helped avoiding crack formation in the glass after sealing.

Results and discussion

The concentration of the used phosphoric acid, determined by the titrations, gave a result of 85.4% ± 0.3% of H_3PO_4. The conductivity result gave a concentration of 86.0% ± 1.0% of H_3PO_4. The overall best estimate is that we had an acid of about 85.5 ± 0.4 %.

The aim was to determine the water vapor spectrum over the phosphoric acid as an example of getting the pressure. The water asymmetric top molecule of C_{2v} symmetry has a well-known Stokes Raman spectrum consisting of three active fundamental transitions: ν_1 (symmetrical O-H bond stretching), ν_2 (symmetrical H-O-H angle bending), and ν_3 (asymmetrical O-H bond stretching).[18-23] The ν_1 band is relatively strong; the other ones are very weak in Raman. Infrared absorption is much more intense but has the problem of the strong absorption of common window materials. The

relatively high pressures and temperatures broaden and populate higher rotation-vibration (ro-vib) levels so that most details of the Q-branch of ν_1 and details of other branches remain unresolved. The Q-branch corresponds to mode transitions with no change in the rotational state (**J** quantum number remains constant).

The Raman spectrum of water vapor above a typical sample in a sealed ampoule is shown in the middle of Figure 3. It can be seen that the band envelope at ~3655 cm^{-1} looks like what would be expected from a broadened band of a shape reminding of the H_2O spectra in the literature.[18-23] Calibration spectra of internal standard gasses for quantitative determination of the water are also shown in Figure 3, for the examples of methane to the left or hydrogen to the right. The methane gas phase spectrum contains the well-known[24-28] ro-vib Q-branch band structure of the $\nu_1(A_1)$ symmetrical C-H bond stretching at ~2917 cm^{-1}, and the hydrogen spectrum shows the ν_{H-H} stretching ro-vib Q-branch bands of hydrogen at ~4155 cm^{-1}.[29-30] For the diatomic hydrogen molecule the Q-branch contains separate Raman bands corresponding to the different values of the **J** quantum number corresponding to transitions with no change in the rotational state. We decided for our purpose to measure and integrate only the **J** $0 \rightarrow 0$ and $1 \rightarrow 1$ bands of the hydrogen Q-branch, as shown in Figure 3, right. The areas of the Q-branch peaks were integrated for each acquisition (two or more sets of spectra) with the Labspec software, for the water band envelope area (S_{H_2O}) at ~3655 cm^{-1}, from ~3590 to ~3693 cm^{-1}, and for the methane or hydrogen band envelopes from ~2890 to ~2943 cm^{-1} (S_{CH_4}) or ~4150 to ~4169 cm^{-1} (S_{H_2}), respectively, see Figure 3. Thanks to this, values for the ratio between the area of the water band envelope, S_{H_2O} to S_{CH_4} or S_{H_2O} to S_{H_2} were calculated.
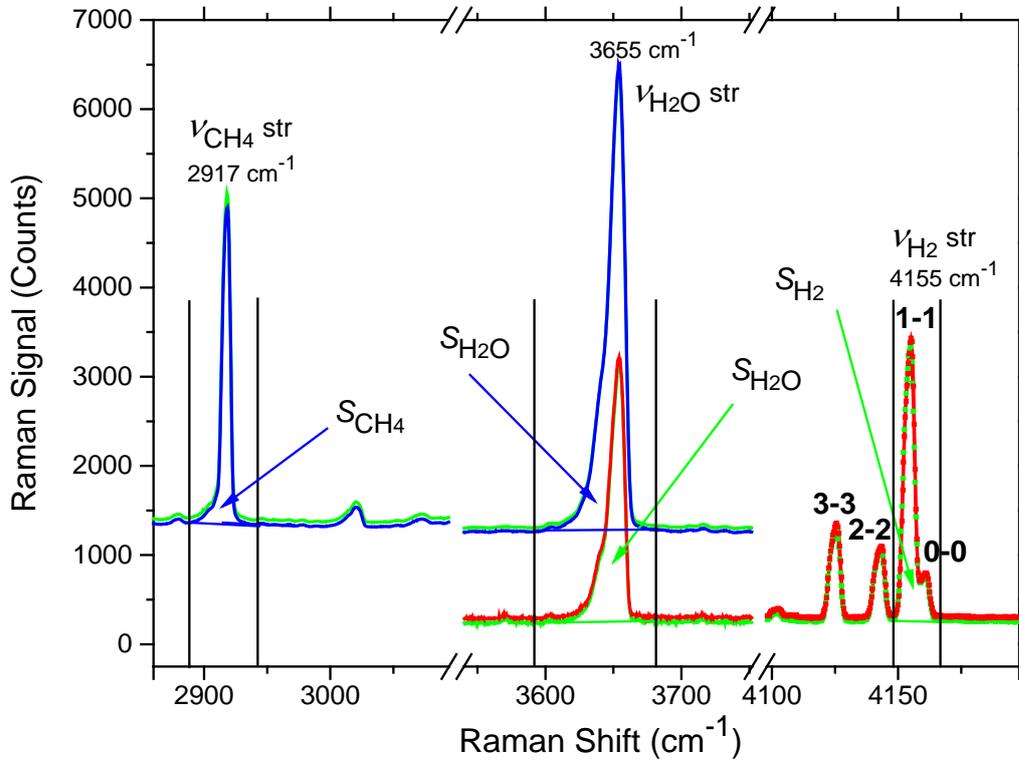
Figure 3. Raman spectroscopic quantitative determination of water in sealed ampoule with methane or hydrogen as references. Knowing e. g. the CH_4 pressure $p^o_{CH_4}$ at T_o, the water pressure p_{H_2O} at T is given by $p^o_{CH_4} \times (T \times S_{H_2O} \times \sigma_{CH_4})/(T_o \times S_{CH_4} \times \sigma_{H_2O})$. Here, S is the integrated Raman band signal above the background for the index molecule, water and methane. For hydrogen as a reference, the water pressure p_{H_2O} is similarly given by $p^o_{H_2} \times (T \times S_{H_2O} \times \sigma_{H_2})/(T_o \times S_{H_2} \times \sigma_{H_2O})$ with index H_2 signaling hydrogen. The scattering cross section ratio, $\sigma_{H_2O}/\sigma_{CH_4}$ or $\sigma_{H_2O}/\sigma_{H_2}$, between water and methane or hydrogen gas molecule Q-branch areas as defined here, is about ~0.40 or ~1.20, respectively, rather independent of the temperatures. A 532 nm green laser was used. Several acquisitions of each spectrum are shown to indicate the degree of reproducibility.

The water vapor pressure is given by taking this ratio times the *molecule to molecule* scattering ratio for water relative to methane or water relative to hydrogen. The pressure was calculated several times for each temperature. Thus the *water* pressure should be easily obtainable, provided that the scattering cross section ratios, $\sigma_{H_2O}/\sigma_{CH_4}$ or $\sigma_{H_2O}/\sigma_{H_2}$, respectively, between water and methane or hydrogen gas molecule Q-branch areas are accurately known. As an example for the H_2O/CH_4 case the scattering ratio is calculated as:

$$\frac{\text{area of water}}{\text{area of methane}} \times \frac{\text{concentration of methane}}{\text{concentration of water}}$$

The scattering cross section ratios between water and reference gas molecule areas ($\sigma_{H_2O}/\sigma_{ref}$) must be carefully defined and determined accurately using the Raman spectrometer. Several values were averaged in order to get good data as a function of the temperature.

Raman scattering cross section ratios

A normalized scattering cross section ratio between two molecules is determined by the absolute ratio of the scattered light relative to the incident light intensity. Alternatively one can compare (normalize) to a measured signal for a reference whose absolute intensity either is known under standardised conditions or can be calculated precisely.[21] According to the Placzek theory,[31] when a molecule is excited, the so-called 'scattering activity' of a chosen strong Raman line can be expressed as *g(45α'² +7γ'²)* where *g, α'* and *γ'* are the degeneracy of the particular Raman line, the average and the anisotropy of the derivatives of the polarizability tensor. This theory has been carefully examined and explained.[32-34] It is important to say that the Raman signal strength and thus the scattering ratio depends on the specific way the experiments were done, i.e. influenced by

conditions such as wavelength, direction of excitation and polarization of the incoming and scattered light,[35] the cone angle of observation, as well as of the grating efficiency, reflectivity versus polarization and wavelength, the quantum efficiency curve of the detector versus wavelength, etc.

Initially we considered to use scattering ratios that could be deduced from the literature thanks to several values available for water, methane and hydrogen, as reported in Table 1.

Table 1: Summary of literature ν_1 Q-branch scattering cross section ratios for molecules H_2, CH_4, H_2O, N_2[a].

Reference	Scattering Ratio Values given			Ratio Values Deduced		
	$\sigma_{H_2}/\sigma_{N_2}$	$\sigma_{CH_4}/\sigma_{N_2}$	$\sigma_{H_2O}/\sigma_{N_2}$	$\sigma_{H_2}/\sigma_{CH_4}$	$\sigma_{H_2O}/\sigma_{H_2}$	$\sigma_{H_2O}/\sigma_{CH_4}$
Yoshino et al.[32]		1/0.15 = 6.7				2.5/6.7 = **0.37**
Murphy et al.[36]	1/0.4 = 2.6	1/0.14 = 7.14		0.4/1 = 0.4	3.46/2.6 = **1.33**	3.46/7.1 = **0.48**
					3.51/2.6 = **1.35**	3.51/7.1 = **0.49**
Fouche & Chang[37]	2.2	8.0	-		3.46/2.2 = **1.57**	3.46/8.0 = **0.43**
					3.51/2.2 = **1.59**	3.51/8.0 = **0.44**
Penney et al.[38]		7.7 ±0.4	2.5 ±0.3			2.5/7.7 = **0.33 ±0.05**
Fenner et al.[39] [b]	1.6 (Q(1))	6.0	-	1.6/6.0=	3.46/1.6 = **2.16**	3.46/6.0 = **0.57**
				0.4	3.51/1.6 = **1.46**	3.51/6.0 = **0.585**
Penney & Lapp[19]	-		2.5 ±10%			
Schrötter[21]	3.4	9.1	3.46		3.46/3.4 = **1.02**	3.46/9.1 = **0.38**
		8.7	3.46			3.46/8.7 = **0.40**
		9.3	3.46			3.46/9.3 = **0.37**
Schrötter[22]	3.86	8.55	3.51		3.51/3.86= **0.91**	3.51/8.55 = **0.41**

	Differential Scattering cross section, x10^{-31} cm^2/sr		Scattering Ratio Values Deduced
	$d\sigma_{N_2}/d\Omega$	$d\sigma_{H_2O}/d\Omega$	$\sigma_{H_2O}/\sigma_{N_2}$
Murphy et al.[36]	4.4 ±0.4		
Fouche & Chang[37]	4.4 ±1.7		
Penney et al.[38]	4.3 ±0.2		
Hyatt et al.[40]	4.2 ±0.2		
Fenner et al.[39] [b]	3.3 ±1.1		
Abe & Ito[41]		2.16 ±0.06	2.16/~4.2 = 0.51[c]

	Scattering cross section, 10^{-30} cm^{-1}sr^{-1}				Scattering Ratio Values Deduced		
	$d\sigma_{H_2}/d\Omega$	$d\sigma_{N_2}/d\Omega$	$d\sigma_{CH_2}/d\Omega$	$d\sigma_{H_2O}/d\Omega$	$\sigma_{H_2O}/\sigma_{H_2}$	$\sigma_{H_2O}/\sigma_{CH_4}$	$\sigma_{H_2O}/\sigma_{N_2}$
Eichmann et al.[42]	3.9	0.46	1.78	1.68	1.68/3.9 = 0.43[c]	1.68/1.78= 0.94[c]	1.68/0.46 = 3.65

[a]Scattering cross section of a molecule is denoted $\sigma_{molecule}$. Ratio values are given for ν_1 Q-branch vibrational bands of the gases measured for 514.5 nm laser excitation if not otherwise specified. Solid angle differentials are denoted $d\Omega$ in units of steradians (sr).

[b]Measured for 488.0 nm laser excitation. Bold face values to be compared with our values.

[c]Not in accordance with column above.

In Table 1 important differences between the given data are obvious. As an example, for the water to hydrogen scattering ratio, $\sigma_{H_2O}/\sigma_{H_2}$, values at around 1.0 or higher are seen but the values given by different authors differ considerably (more than 10%). For the water to methane scattering ratio, $\sigma_{H_2O}/\sigma_{CH_4}$, values at around 0.4 are seen but again they deviate considerably, perhaps up to 20%. The known absolute differential scattering cross section values for nitrogen also vary, and if the ratio $(d\sigma_{H_2O}/d\Omega)/(d\sigma_{N_2}/d\Omega) = \sigma_{H_2O}/\sigma_{N_2}$ is taken, the deduced value, i.e. $2.16/{\sim}4.2 = 0.51$, is not even near the ratio 2.5 given by e. g. Penney et al.[19,39] Also the values given by Eichmann et al.[42] at the bottom of Table 1 differ considerably from the other values, and even the *ratios* do not agree with the literature.[1]

When plotting our results for phosphoric acid, we of course obtained differences corresponding to the used $\sigma_{H_2O}/\sigma_{reference}$ values. *The conclusion is therefore that some literature scattering values in Table 1 are not accurate.* Better values of $\sigma_{H_2O}/\sigma_{reference}$ are needed, determined for our experimental situation. Such scattering ratios will have the advantage that they reflect exactly the experimental situation for our spectrometer with the chosen wavelength, slit width and band integration range.

Determination of new Raman scattering cross section ratios

Accordingly it was decided to perform new experiments to determine good values for the scattering ratios between water and hydrogen or methane. Ampoules were made containing water in addition

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[1] We think that Eichmann et al.[42] cited Schrötter[22] wrongly, or at least they did not explain how they obtained their values.

to hydrogen or methane. It is not trivial to know the precise amount of water and reference gas in a sealed ampoule. Evacuation is needed to let the reference gas in, but during the evacuation some of the added water easily might evaporate. To minimize evaporation the water was solidified to ice by use of liquid nitrogen, but the presence of cold ice and the nitrogen freezing may condense additional water vapor. The determination of the mass of ice by weighing was influenced by the cold temperatures forming drifts around the weight. In some ampoules a large amount of water was chosen to let the water concentration in the gas phase be determind by the saturation density at the temperature. The water saturation concentration at a temperature is well-known and accurate values are available, see e.g.[43] The water concentration and partial pressure increase dramatically during heating. One should take precautions due to the **risk of explosion**.

A typical ampoule was made in this way: The open ampoule was dipped in liquid nitrogen until the added water had frozen, and the ampoule was quickly connected to the vacuum line via rubber tubing. Then evacuation and filling with a reference gas was done (repeated two times) while the ice was kept cold. Reading of the final reference gas pressure was done with a calibrated Bourdon manometer at ~23 °C, where after the sealing was done with a butane-oxygen torch flame. The approximate concentration n/V (in mol L^{-1}) of the reference gas can be calculated using the ideal gas law, $n/V = p/RT$. Here n is the number of moles, V is the estimated ampoule volume (~6 mL), p is the partial pressure, R is the *gas constant* (0.083145 bar×L×mol^{-1}×K^{-1}) and T is the *absolute Kelvin* room temperature. After sealing, the reference gas *concentration* stays constant whereas the *pressure* of course increases with T.

Raman spectra of the water gas phase and the references were determined after equilibration at several temperatures from ~80 °C to ~200 °C for each cell, and the areas S(H$_2$O) and S(ref) of the peaks determined as described in Figure 3. The scattering cross section ratio can then be calculated as $\sigma_{H_2O} / \sigma_{ref} = S_{H_2O} \times [ref] / (S_{ref} \times [H_2O])$. Here S is the Raman band integrated signal. [H$_2$O] and

[ref] are the concentrations of the water and the reference gas. Several experimental gas phase data sets were obtained (see Table 2). The mean scattering ratios were calculated by making an average of all values.

Table 2: Raman Scattering cross section ratios $\sigma_{H_2O}/\sigma_{ref}$ for water/methane or water/hydrogen. Water concentrations determined based on saturation. The average of the value for all the temperatures was taken.			
Temperature, ^{o}C	Water to methane, cell #12	Water to hydrogen, cell #20	Water to hydrogen, cell #21
53		1.38	1.28
80	0.36		
84		1.42	1.31
100	0.38		
105		1.45	1.33
126		1.48	1.43
150	0.43		
152			1.83
157		1.78	
194		1.65	1.50
215			1.59
Mean values	0.39	1.53	1.47

In Table 2 some disagreements between the values are seen. The scattering ratios appear as well to be slightly dependent on the temperature in a systematic increasing way. This may be allowable because the distribution of the bands among the integration range is expected to change slightly with temperature.

In order to be as accurate as possible, we tried to imagine a better way to determine the scattering ratios. In some cells we limited the amount of water to not more than what could all go into the gas phase at a temperature of ~100 °C: The empty ampoule was weighed, water added in a small amount (in a capillary) and the ampoule reweighed to get an approximate water mass of ~0.010 g to ~0.022 g in ~6 mL cells. The water was quickly frozen, the ampoule was connected to the vacuum line, the reference gas added and the ampoule sealed. The limited amount of water made it possible to determine quite accurately the water concentration. This is so because several standard Raman spectra could be recorded after equilibration at still higher temperatures. The recorded area ratio values when plotted versus temperature allowed us to make a curve that has a "breaking point" situated just at the particular temperature where all the water has evaporated (see Figure 4). The breaking point arrives on the curve because there is no more water to evaporate at that temperature so the concentration of water in the gas phase cannot increase from then on. Thus the "breaking point temperature" depends on the amount of water in the ampoule and its volume. The breaking point temperature determines the water concentration in the ampoule gas phase; at the breaking point temperature the gas is saturated and the concentration is specified in the literature.[43] The ratio $\sigma_{H_2O}/\sigma_{ref}$ between the scattering area per water molecule and the scattering area per reference gas molecule should always be the same for the given choise of instrument setup and conditions. However if too much water was in an ampoule no breaking point could be reached before the

ampoule exploded. This is of course so because more water in a volume needs a higher temperature for total evaporation and even then the pressure goes up with temperature ($p = nRT/V$).

Typical breaking point curves are shown in Figure 4. The estimation of the breaking point is however not so precise; we estimate the breaking point to be inside the colored rectangles shown in Figure 4, and the corresponding temperatures and estimated precisions are given in Table 3.
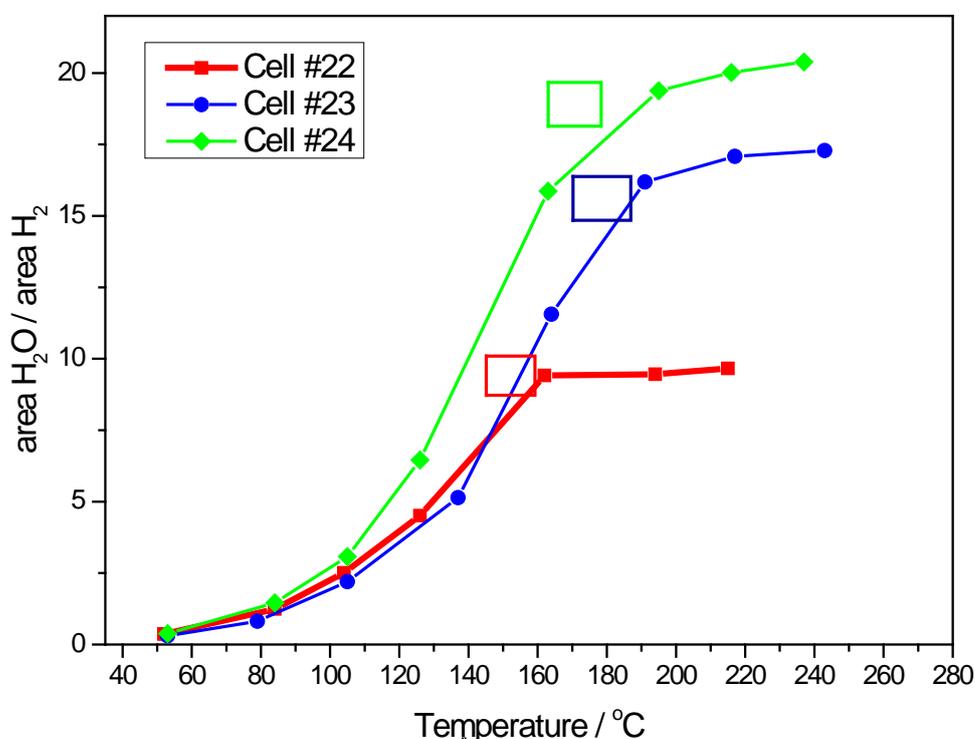

Figure 4. Determination of "breaking point temperatures" for cells #22, #23 and #24 containing water and 0.5 bar of hydrogen. For these cells the temperatures were found to be about 153 °C, 180°C and 163 °C (indicated by the colored rectangles). At these temperatures the vapor pressure and density of saturated steam are universally known, e.g. 6.67 bar and 3.50 kg/m^3 at 163 °C (values obtained by calculation).[43]

Table 3 shows scattering ratio values of water relative to *hydrogen* being about 1.2 to 1.8. These value are in rather good accordance with the values deduced from the literature, see Table 1 and our values in Table 2.

Table 3. Summary of the scattering ratio of water and hydrogen calculated at breaking points.			
Cell number	Breaking point temperature, °C	Area ratio at temperature	Scattering Ratio H_2O / H_2
Cell #22	153 ± 5	9.2 ± 0.8	1.18 ± 0.03
Cell #23	180 ± 5	16.0 ± 0.8	1.27 ± 0.05
Cell #24	163 ± 5	17.8 ± 1.2	1.80 ± 0.03
Estd. average			1.41 ± 0.05

The scattering ratio for water to *methane* was found to be about 0.39 ± 0.02 as reported in Table 2. Two more ampoules were made to check this: One with just ~0.85 bar of methane and one with enough water and no reference gas. *External* reference ratios from these cells gave scattering ratio values of water to methane of about 0.4 at different temperatures. The values fitted well with the results in Table 1 and Table 2. Similarly, from a single water/methane cell we determined a break point value close to 0.4 for the $\sigma_{H_2O}/\sigma_{CH_4}$ scattering ratio.

Calculation of the water vapor pressure over phosphoric acid.

As soon as the Raman scattering cross section ratios are known the water vapor pressures can be calculated from the Raman data of the phosphoric acid cells at each temperature as explained in the text to Figure 3. The water vapor pressures, calculated for a $\sigma_{H_2O}/\sigma_{H_2}$ scattering ratio of 1.2 and a $\sigma_{H_2O}/\sigma_{CH_4}$ scattering ratio of 0.4, are plotted in Figure 5 and the data given in Table 4. When checked with the literature results the fit is quite good. For the methane referenced data the values were close enough to each other to be judged as reproducible but small differences to the literature H_3PO_4 data are observed. Hydrogen referenced results for the vapor pressure of the phosphoric acid are also in quite good accordance with the literature, see Figure 5.
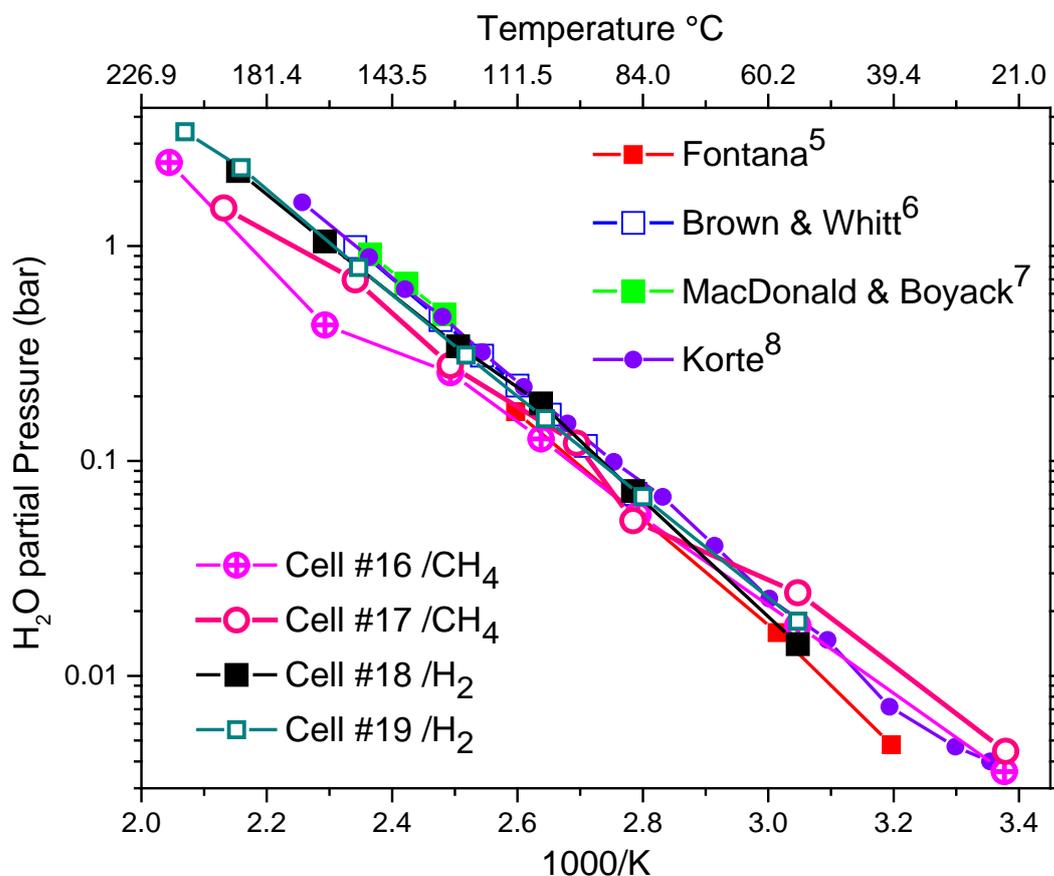
Figure 5. Vapor pressure (bar) of 85.5 % phosphoric acid compared to values in literature[5-8] for a temperature range of 23°C - 210°C. Cells #16 and #17 contained phosphoric acid and 0.50 bar of methane and the scattering ratio used to plot the curve was 0.40. Cells #18 and #19 contained phosphoric acid and 0.50 bar of hydrogen and the scattering ratio used to plot the curve was 1.20. For the data see Table 4.

Table 4. Observed vapor pressure data for 85.5 % phosphoric acid. SR = Scattering ratio. To obtain Figure 5, we ploted the data as log (pressure) versus 1000/T.

Temperature, ^{o}C	Pressure, bar			
	Using SR(CH_4) = 0.40		Using SR(H_2) = 1.2	
	Cell #16	Cell #17	Cell #18	Cell #19
23	0.004	0.004		
55	0.017	0.024	0.014	0.018
84				0.068
85	0.056			
86		0.053	0.072	
98		0.121		
105				0.157
106	0.127		0.185	
124				0.311
126			0.342	
128	0.257	0.278		
153				0.795
154		0.697		
163	0.429		1.050	
190				2.317
191			2.234	
196		1.503		
210				3.405
216	2.448			

From these results several observations can be made. First we saw that our points for both reference gases fit rather well with the data of the literature. We note that there is a slight difference between the phosphoric acid vapour pressure referenced to methane and the values relative to the hydrogen standard. Indeed the points for the hydrogen calibration fit best to the literature results, especially at high temperatures. This behavior may be due to several causes: It could come from the scattering ratio being more accurate with the hydrogen; it could also come from the spectral behavior of the methane at high temperature.

Conclusions

Raman spectroscopy can be used to determine the vapor pressure of 85.5 ± 0.4 % concentrated phosphoric acid. This is an example of an experimental way to obtain the water vapor pressure over a corrosive substance. For this to work, an internal reference intensity standard is needed. The Raman scattering molecular cross section *ratio* between vapor and a reference needs to be known. The present method is based on the determination of the areas of the peaks giving the vapor pressure or concentration of each chemical. We determined the scattering ratio of the water band area at ~3655 cm^{-1} relative to the hydrogen ro-vib Q-branch band area at ~4155 cm^{-1} or the methane ro-vib Q-branch band area of the $\nu_1(A_1)$ symmetrical C-H bond stretching at ~2917 cm^{-1}. The Raman scattering cross section *ratio* determined here between the water and hydrogen areas was equal to about 1.20. For the area ratios between water and methane the value was found to be about 0.40. These values must be fairly correct because they give results that compare well to the literature data on phosphoric acid. Also we conclude that the Raman spectroscopy method is working when used to obtain the vapor pressure of the phosphoric acid. The accuracy is perhaps better for the data based on the hydrogen internal reference. Indeed the results seem quite accurate and we have good confidence in our new record water vapor pressure data point (3.40 bar at 210 °C) obtained over ~85.5 % H_3PO_4 based on the hydrogen reference. The Raman spectrum of the gas

phase shows no bands from the phosphoric acid, so the vapour pressure must come alone from water molecules, in accordance with prior results.[6] The method is likely to work with other kinds of corrosive chemicals. Further experiments are being done to prove this, e.g. for a corrosive molten salt electrolyte, KH_2PO_4, that develops a water vapor pressure during heating.

Acknowledgements

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