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Abstract

The absorption properties of sulfuric acid at 295 K have been measured in the spectral range from 1.4 to > 2.7 μm at concentration levels relevant for modeling Venus's clouds and for understanding their optical properties.

Introduction

Venus's clouds, deep atmosphere, and surface can be probed using infrared spectral windows. However, near-infrared radiation is absorbed by sulfuric acid (SA), with the absorption varying with wavelength, H_2SO_4 concentration, and temperature. This absorption is particularly important for the broad 2.2- to 2.6- μm window, but there are few measurements of sulfuric acid absorption at concentrations appropriate for Venus, and there are no useful measurements in the 2.5 to 2.7- μm region. To remedy this, we measured the absorption by highly-concentrated solutions of SA over the full wavelength range of Venus's 1.7- and 2.3- μm spectral windows.

Experimental

Sulfuric acid is *extremely* hygroscopic, so we minimized H_2O contamination using a single transmission cell and rapid measurements, avoiding the lengthy time needed when using numerous cells with different path-lengths.

Our (demountable) absorption cell consists of two fused silica plates, teflon spacers, and a clamping sample holder. The thickness of the empty cell was accurately measured prior to each sulfuric acid measurement using interference fringes (Fig. 1); additional thickness measurements were obtained using H_2O -filled cells (see later).

The combined empty-cell and H_2O -filled measurements gave an average thickness of $51.9 \pm 1.4 \mu\text{m}$. (No observable interference fringes are formed with SA-filled cells because Fresnel reflection is low, due to the nearly equal refractive indices of SiO_2 and sulfuric acid.)

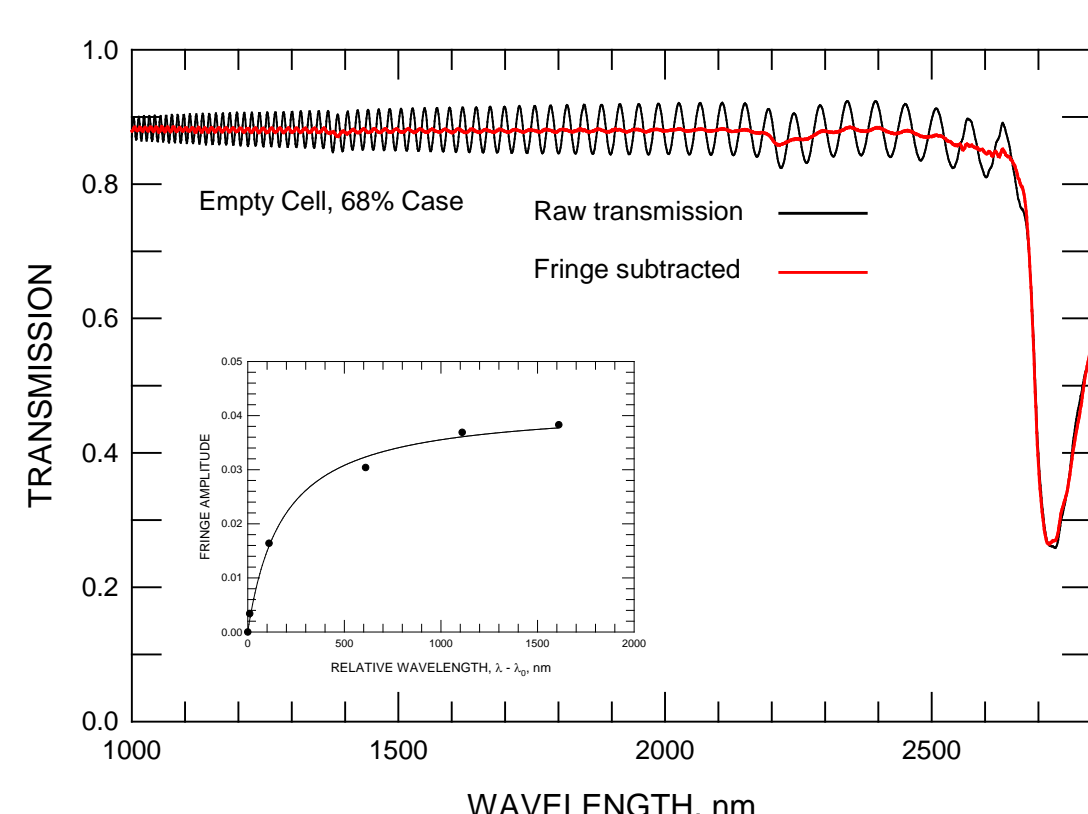


Fig. 1. An empty-cell measurement showing interference fringes (black curve) indicative of the absorption cell spacing. The fringes are removed (red curve) to the $\sim 0.5\%$ level using a cosine function weighted by the empirical amplitude function shown in the inset. The absorption features arise from Si-OH in the fused silica plates.

The wavelength-dependent Fresnel reflection losses (r_A , r_B) and interface transmissions (t_A , t_B) were determined from the refractive index (Wolfe, 1978) and we then used with the average empty-cell transmission T_{NET} to iteratively determine the internal SiO_2 transmission T_2 (Figs 2, 3 and Eq. 1, below).

$$T_{NET} = (T_2^2 T_3) (t_A t_B)^2 \left[1 + 2r_A r_B T_2^2 + T_3^2 (r_A^2 T_2^2 + r_B^2) \right]$$

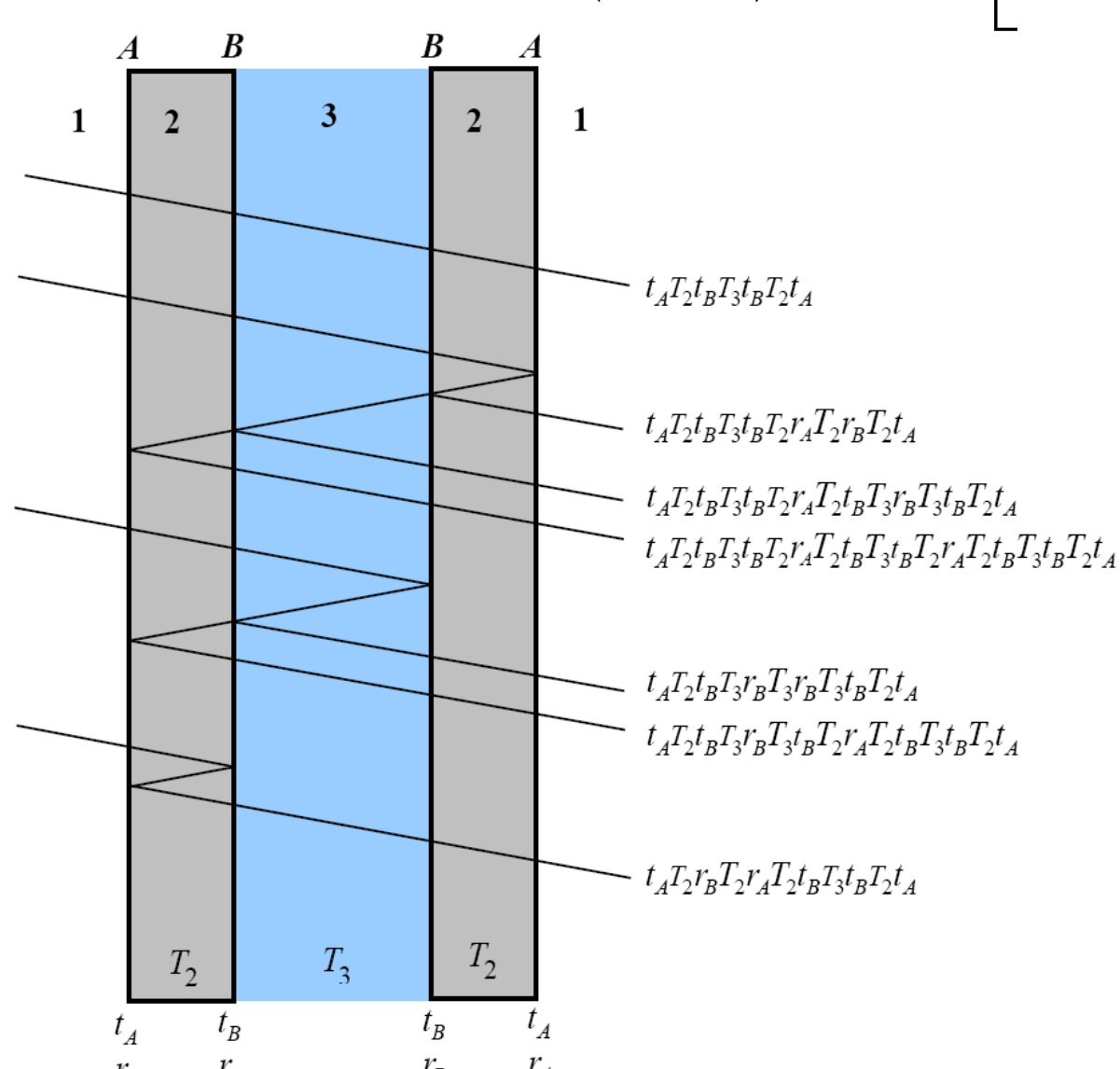


Fig. 2. First, second, and third order reflections that contribute to the net transmitted radiation, described in Eq. 1. The parameters r_A and t_A are reflection and the transmission at surface A, T_2 is the internal transmission of medium 2 (SiO_2), etc..

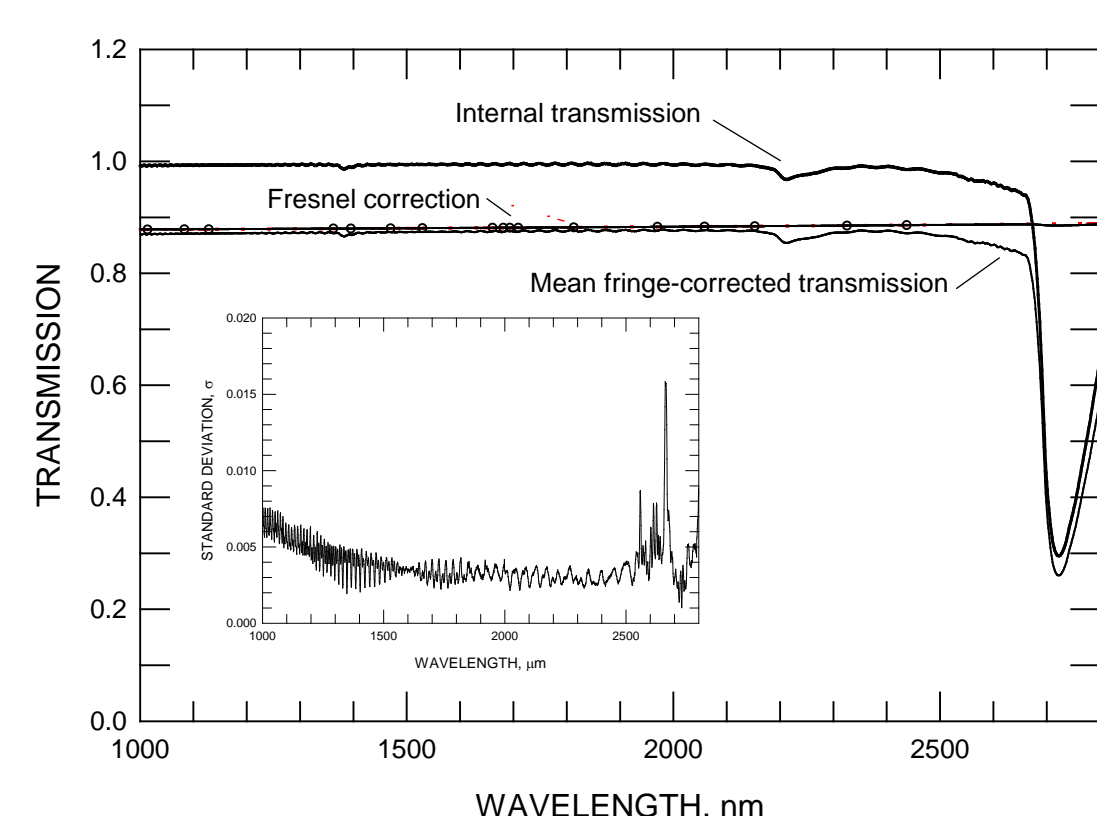


Fig. 3. Average empty cell transmission, Fresnel correction, and internal transmission of the two fused silica plates. The fringe-corrected average transmission is shown, along with the standard deviation of the transmission values (shown in inset). The Fresnel transmission factor ($T_{NET}/T_2^2 T_3$) is shown for the beginning and final (2nd) iteration. The internal of the cell (T_2^2) is then derived.

Prior to the SA measurements, we verified our technique by measuring T_{NET} for H_2O , determining its internal transmission (T_3 , Eq. 1), and from this, the imaginary component k of the refractive index (Fig. 4). The results are in excellent agreement with prior measurements where they exist.

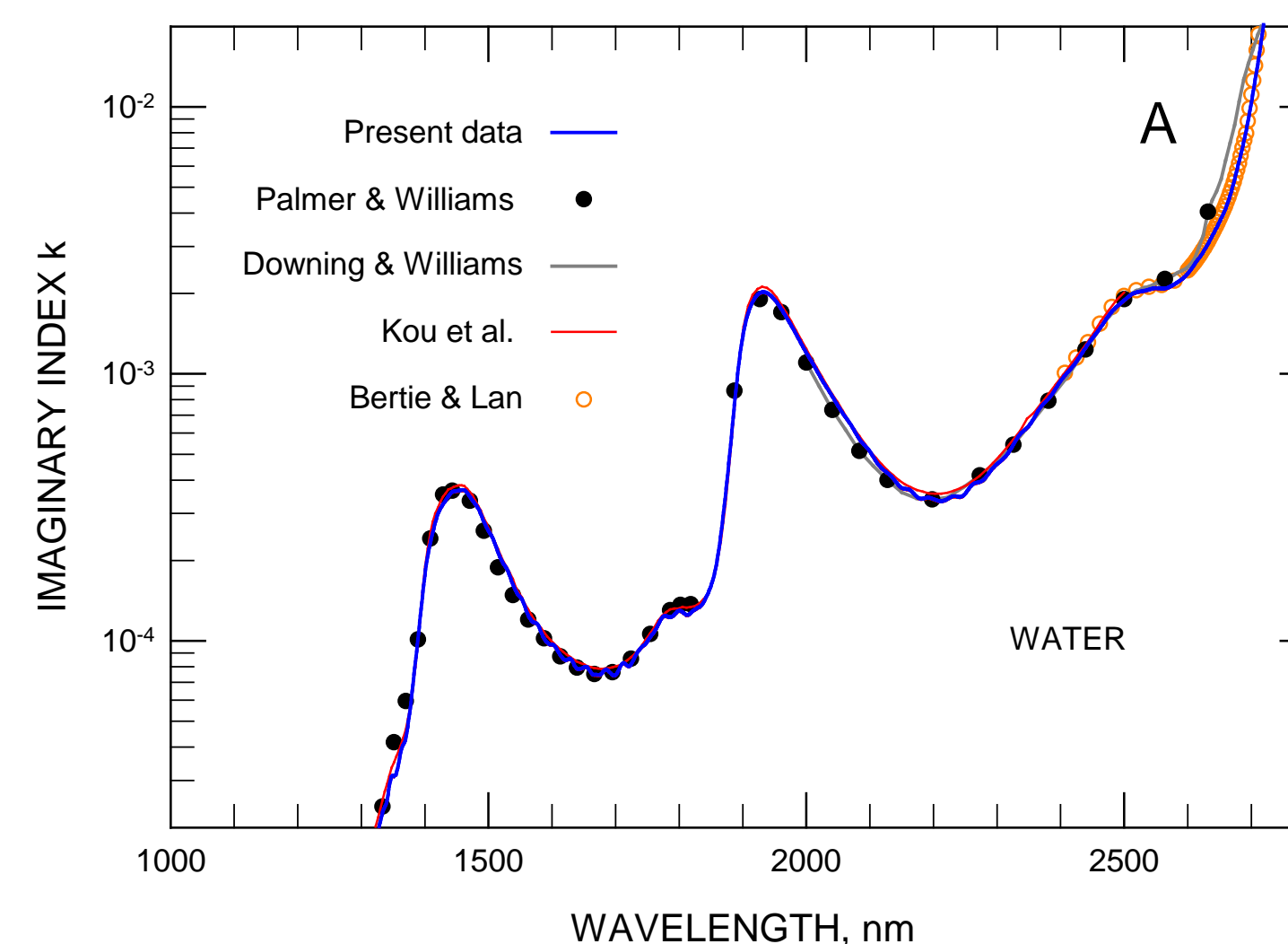


Fig. 4. Comparison of our absorption measurement for H_2O compared to Palmer and Williams (1974), Downing and Williams (1975), Kou et al. (1993), and Bertie and Lan (1996). The general agreement among the all of the various investigations is quite good. Our results are nearly identical to Kou et al.'s data which extend to 2.5 μm . Our values are close to Bertie & Lan's longer wavelength data.

The sulfuric acid solutions were made in a dry nitrogen atmosphere from 96% reagent grade sulfuric acid, whose concentration was determined by ion chromatography. Solutions were prepared gravimetrically and accurate to $\pm 1/2\%$. To avoid water uptake, a drop of sulfuric acid is placed on the silica plate and then rapidly (~ 30 s) sandwiched together and clamped, all under a blanket of dry nitrogen. Transmission spectra were then immediately acquired in a nitrogen-purged Cary 5000 spectrometer.

Experimental Results

The combined imaginary indices are shown in Fig. 5 while a subset (Fig. 6) is compared with the classic measurements of Palmer & Williams (1975) for 75% SA and the more recent data from Gosse et al. (1997) for 72% SA. Our indices are somewhat larger than those of P & W above 1.7 μm but are in excellent agreement with Gosse et al.'s values, except for a few-percent disagreement at the 2- μm H_2O band. A paper is in preparation and the data are now available by request to RWC.

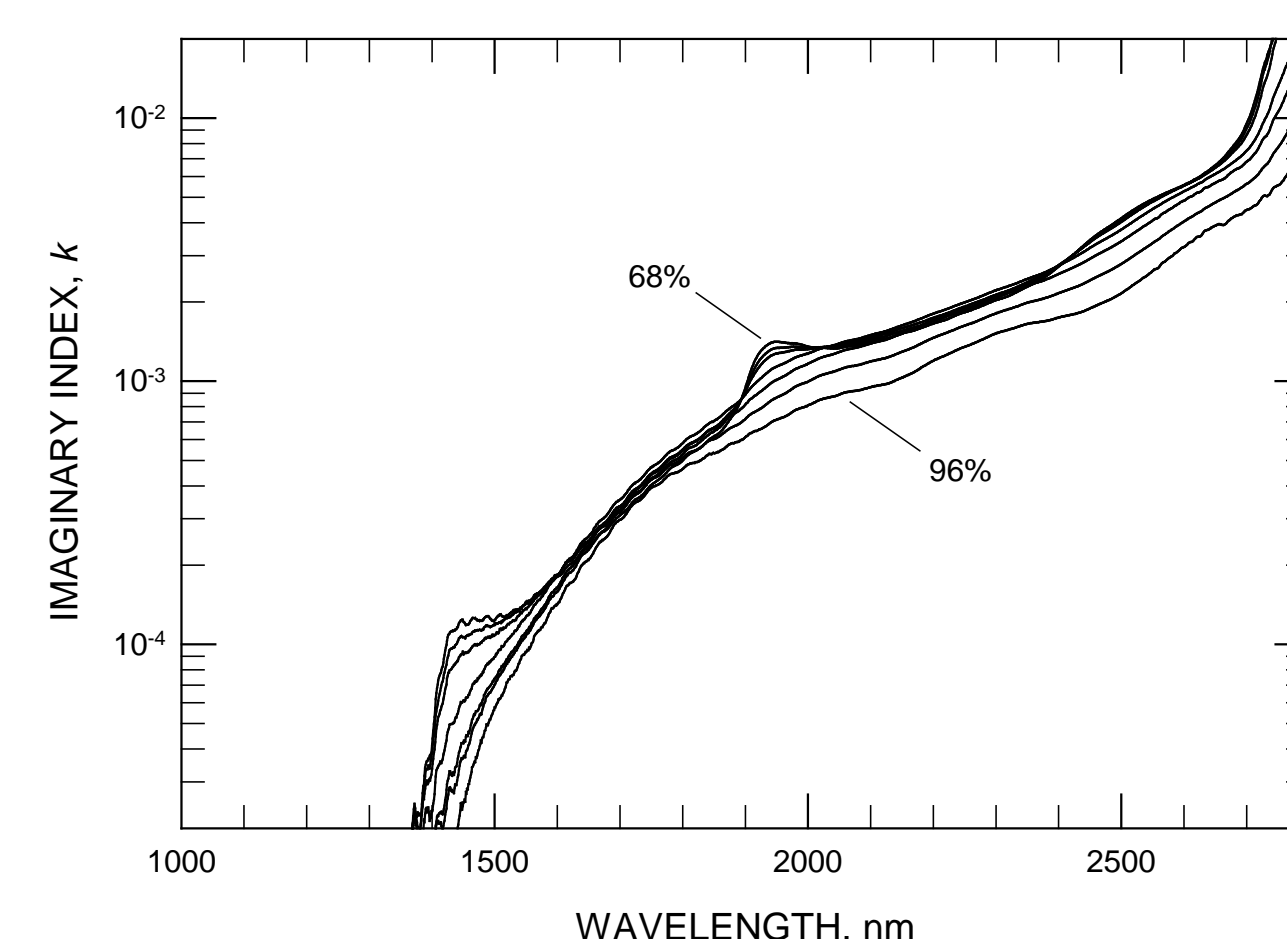


Fig. 5. Sulfuric acid imaginary indices for weight concentrations of 68, 72, 76, 84, 88, 92, and 96%.

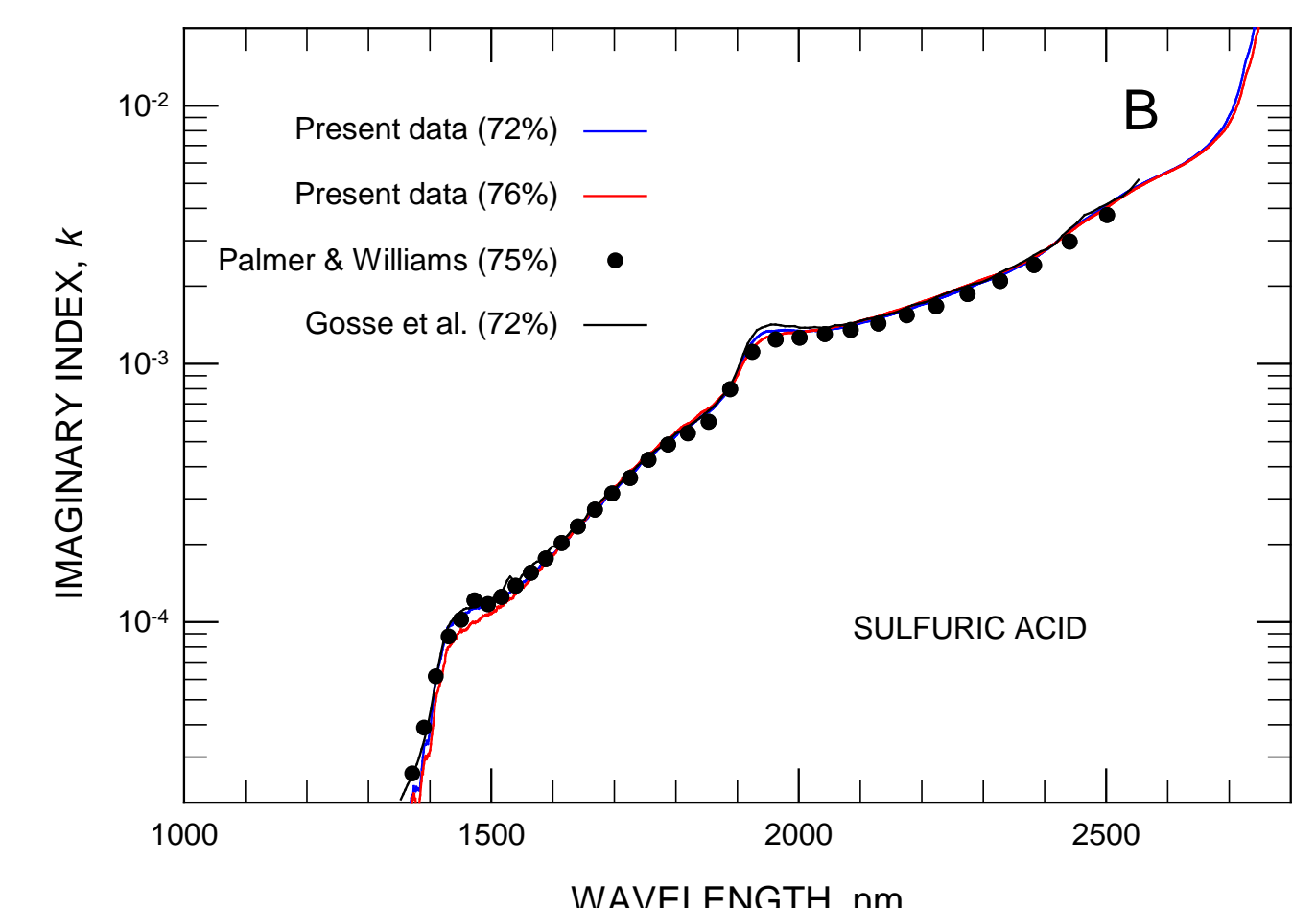


Fig. 6. Comparison of our 72% and 76% indices with those of Palmer and Williams (1975) for 75% concentration and Gosse et al.'s (1997) 72% data that extend to 2.55 μm and for which we find excellent agreement.

A comparison at 2.5 μm (Fig. 7) shows that our indices are generally higher than P&W's values by about 8% except for their highest concentration, where the agreement is within 3%. We estimate an accuracy in the k values of $\pm 4\%$ over the range 1.4 to 2.7 μm ; the main error source is the variance in the cell thickness.

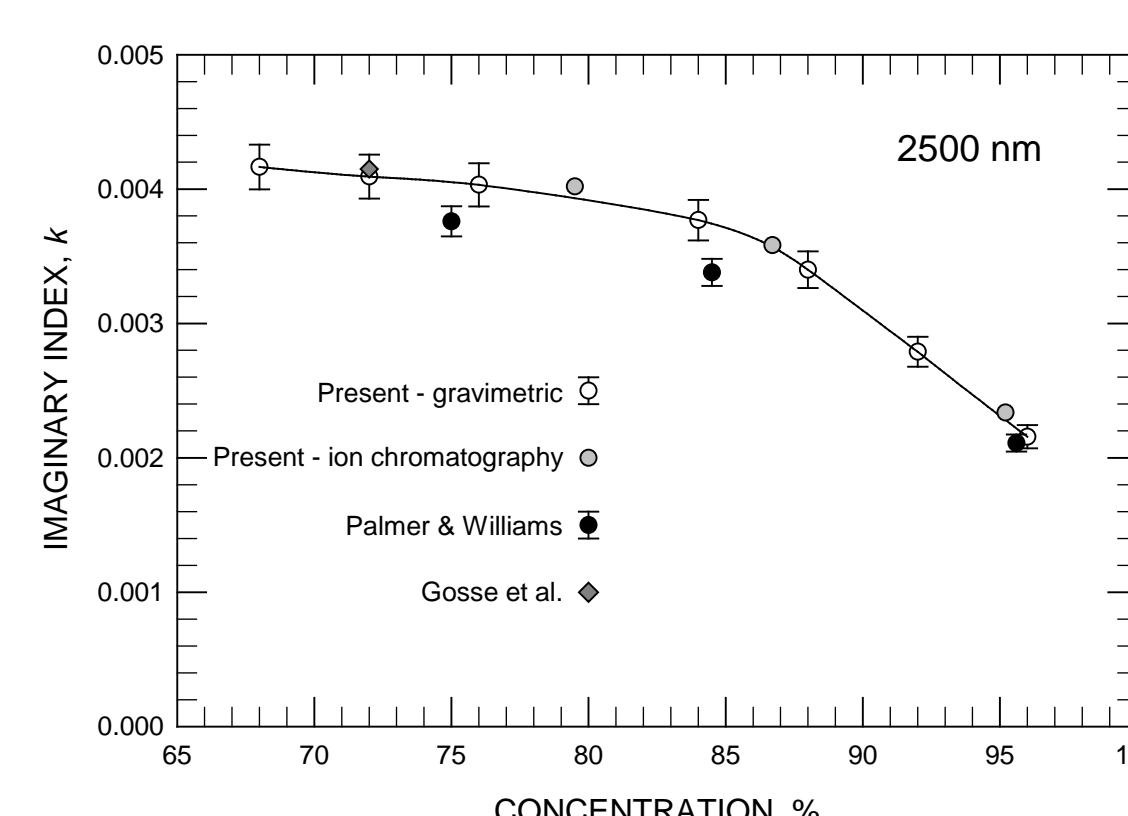


Fig. 7. Comparison at 2.5 μm of the current values (open and grey circles) with those of Palmer and Williams (black circles) and Gosse et al. (grey diamond). The P&W values at 75% and 84.5% are about 8% the lower than our values and that by Gosse et al., but the P&W value at 95.6% agrees with our measurements to within $\sim 3\%$.