Supporting Information

Complex Refractive Indices of Thin Films of Secondary Organic Materials by Spectroscopic Ellipsometry from 220 to 1200 nm

Pengfei Liu (1), Yue Zhang (1), and Scot T. Martin* (1, 2)

(1) School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, USA, 02138

(2) Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts, USA, 02138

E-mail: scot_martin@harvard.edu

http://www.seas.harvard.edu/environmental-chemistry

*To Whom Correspondence Should be Addressed

The following supporting information contains 12 pages and includes 2 figures and 1 table.

S1 Method validation

S1.1 Validation using squalane (non-absorbing standard)

Squalane (CAS#: 111-01-3, Sigma Aldrich, 99%) was used as a non-absorbing standard for method validation. Squalane is a low volatility liquid (vapor pressure of 10^{-7} Torr at room temperature[1]) that is stable in air at room temperature. A previous study reported zero values of imaginary part of refractive index *k* for squalane in the ultraviolet and visible regions for $\lambda > 200$ nm.[2] The real refractive index *n* has been measured using different techniques.[2-4] In a recent study, squalane was chosen as a calibration standard for cavity ring-down aerosol spectroscopy (CRD-AS).[5]

Similar to the synthesis of SOM thin films, the squalane thin film was produced by electrostatic precipitation of particles onto a silicon substrate using an electrostatic precipitator (TSI 3089). The method for squalane particle generation was similar to that described in Toole et al.[5] Pure squalane liquid was aerosolized by a disposable nebulizer (Hudson RCI, MICRO MIST nebulizer) with 1.50 sLpm (standard liters per minute) of pure air controlled by a mass flow controller. The aerosol flow was diluted with a 1.0 sLpm pure air flow in a mixing bottle and then drawn through a bipolar charger (TSI 3077) by the electrostatic precipitator at a flow rate of 1.50 sLpm. The synthesized squalane thin film was optically reflective.

The spectroscopic ellipsometry measurement for squalane thin film was similar to that described in section 2.3 for SOM samples. Based on literature[2], the *k* values were set to be zero in studied spectral region (310-700 nm) in the data analysis. The *n* values were obtained from two different fitting methods using *WVASE32* software: (1) point-by-point fitting, which fits *n* value at each measured wavelength and (2) Cauchy model fitting, which assumes that the wavelength dependence of *n* follows Cauchy dispersion relation (see Eq. 1 in main text). Data

analysis showed that the thickness of the squalane thin film was 40 nm, with non-uniformity of 15%. The *n* values from different fitting methods are in good agreement (Fig. S1). The absolute differences of *n* are smaller than 0.006. Literature data are also shown in Fig. S1 for comparison.

The *n* values of squalane obtained from this study agree well with literature data. For example, at λ = 355 nm, our results suggest values of n = 1.470 (±0.010) from point-by-point fitting and 1.472 (±0.008) from Cauchy fitting. In comparison, Toole[3] measured a value n = 1.471 at λ = 355 nm from bulk liquid measurement using a Snell's law cell. The ellipsometry measurement (J.A. Woollam, model M2000) conducted in J.A. Woollam laboratories suggested n = 1.471[3]. Painter et al.[2] reported n = 1.472 from reflectance measurement. The comparison validates the refractive index from ellipsometry measurement of thin films synthesized from electrostatic precipitation.

S1.2 Validation using nigrosin dye (light-absorbing standard)

Nigrosin (CAS#: 8005-03-6, acid black 2, Sigma Aldrich) is a water soluble dye that has been used in previous studies to generate absorbing particles for aerosol instrument validations.[6-8] Nigrosin has strong absorption in the UV and visible regions. Its water solution is dark blue. A complex refractive index value of nigrosin $m = 1.67 - 0.26i$ was measured in bulk form for 632.8 nm light.[9] Two CRD-AS measurements reported values of $m = 1.70 - 0.31i$[7] and $m = 1.649 - 0.238i$[8] respectively at 532 nm wavelength for nigrosin in particle form.

In the present study, two nigrosin thin film samples were synthesized from spin coating of a 1.0 wt% nigrosin water solution onto silicon substrates. The film thicknesses of the two samples determined from ellipsometry measurements were 14 nm and 11 nm, respectively. The complex refractive indices retrieved by spectroscopic ellipsometry from 220 to 700 nm are shown in Fig. S2. We also attempted to deposit atomized nigrosin particles onto a silicon

substrate using electrostatic precipitation. This method, however, formed micron-sized aggregated particles on the substrate instead of a reflective thin film and could not be used for ellipsometry measurement.

In addition to ellipsometry measurement of spin-coated nigrosin films, the UV-visible absorption spectrum of a water solution that contains 0.001 wt% nigrosin was measured by UV-visible spectrophotometry (Agilent, model 8453). The wavelength-dependent $k(\lambda)$ values can be calculated from the base-10 absorbance $A(\lambda)$ of a nigrosin solution with mass concentration c (g L^{-1}) measured over optical pathlength L (cm):[10]

$$k(\lambda) = 1000 \ln(10) \frac{A \cdot \rho \cdot \lambda}{4\pi \cdot c \cdot l} \quad \text{(S1)}$$

In this calculation, the material density ρ of nigrosin was taken as 1.5 g cm^{-3} (no literature data available). The calculated $k(\lambda)$ are shown in Fig. S2b for comparison.

Figure S2 shows that both $n(\lambda)$ and $k(\lambda)$ retrieved from ellipsometry measurements are in good agreement with literature data. The interpolation of ellipsometry data reported a value of m = 1.61 (±0.01) - 0.23 (±0.01)i at 532 nm, which supported the CRD-AS measurements of nigrosin particles from Lack et al.[7] (1.70 - 0.31i) and Dinar et al.[8] (1.649 - 0.238i). The interpolated value m = 1.73 (±0.02) - 0.27 (±0.02)i from ellipsometry data at 632.8 nm also agrees well with bulk form measurement from Pinnick et al.[9] The wavelength dependence of $k(\lambda)$ was confirmed by the absorption measurement of nigrosin water solution using a UV-visible spectrophotometer.

The validation experiments of S1.1 and S1.2 confirmed the applicability of the thin film ellipsometry measurements.

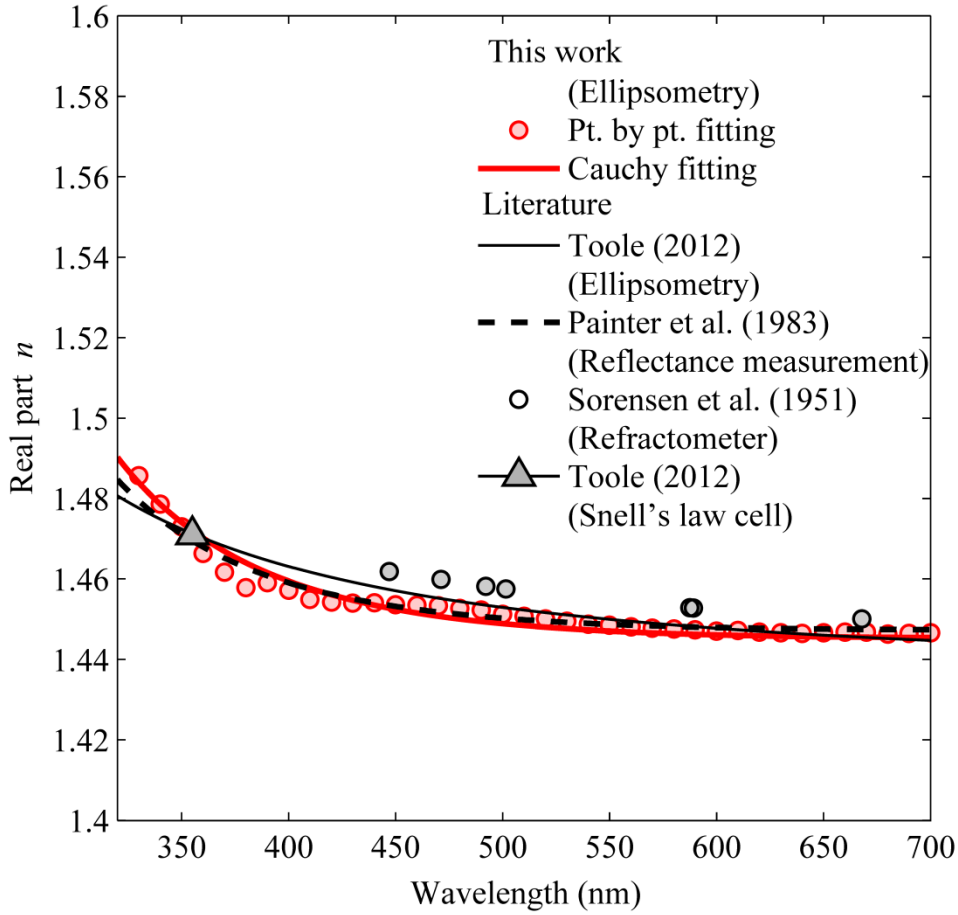

Figure S1. Wavelength-dependent real refractive indices $n(\lambda)$ for squalane. Results from literature are shown for comparison.

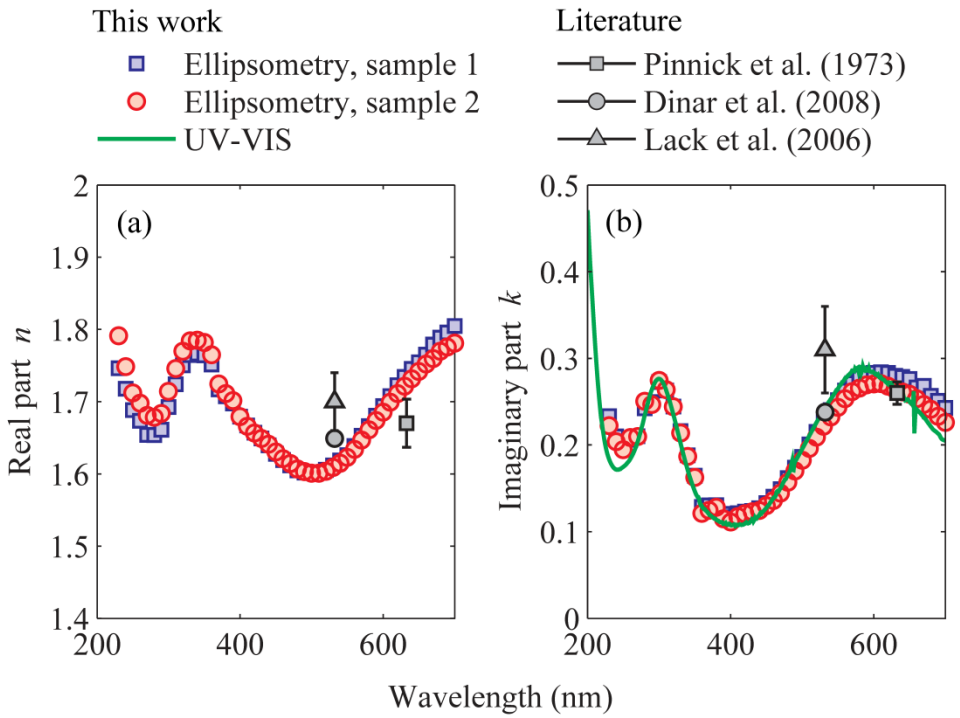

Figure S2. Wavelength-dependent complex refractive indices $m(\lambda)$ for nigrosin. Results for literature are shown for comparison.

Table S1. Wavelength-dependent complex refractive indices $m(\lambda) = n - i\,k$ for different types of secondary organic material.

SOM type:	α-pinene ozonolysis		limonene ozonolysis		catechol ozonolysis	
wavelength (nm)	*n*	*k*	*n*	*k*	*n*	*k*
220	1.6129	0.0088	1.6152	0.0050		
225	1.6050	0.0069	1.6079	0.0041		
230	1.5978	0.0065	1.6011	0.0039	1.6374	0.0678
235	1.5912	0.0055	1.5950	0.0036	1.6301	0.0558
240	1.5852	0.0037	1.5893	0.0031	1.6234	0.0477
245	1.5797	0.0032	1.5841	0.0029	1.6171	0.0422
250	1.5746	0.0029	1.5792	0.0026	1.6113	0.0402
255	1.5699	0.0026	1.5747	0.0024	1.6059	0.0391
260	1.5656	0.0024	1.5706	0.0027	1.6009	0.0378
265	1.5615	0.0022	1.5668	0.0027	1.5962	0.0365
270	1.5578	0.0026	1.5632	0.0024	1.5918	0.0335
275	1.5544	0.0028	1.5598	0.0024	1.5877	0.0303
280	1.5511	0.0030	1.5567	0.0024	1.5839	0.0270
285	1.5481	0.0026	1.5538	0.0018	1.5803	0.0239
290	1.5453	0.0020	1.5511	0.0013	1.5769	0.0205
295	1.5427	0.0019	1.5485	0.0012	1.5737	0.0180
300	1.5403	0.0018	1.5461	0.0009	1.5707	0.0157
305	1.5380	0.0015	1.5439	0.0008	1.5679	0.0139
310	1.5358	0.0012	1.5418	0.0009	1.5652	0.0129
315	1.5338	0.0011	1.5398	0.0007	1.5627	0.0118
320	1.5319	0.0009	1.5379	0.0002	1.5603	0.0108
325	1.5301	0.0008	1.5361	0.0004	1.5580	0.0101
330	1.5284	0.0007	1.5344	0.0005	1.5558	0.0093
335	1.5267	0.0006	1.5328	0.0003	1.5538	0.0088
340	1.5252	0.0006	1.5313	0.0003	1.5519	0.0073
345	1.5238	0.0007	1.5299	0.0004	1.5500	0.0059
350	1.5224	0.0005	1.5285	0.0003	1.5483	0.0051
355	1.5211	0.0002	1.5272	0.0001	1.5466	0.0042
360	1.5199	0.0001	1.5260	0.0000	1.5450	0.0034
365	1.5188	0.0001	1.5248	0.0000	1.5435	0.0028
370	1.5177	0.0002	1.5237	0.0001	1.5420	0.0026
375	1.5166	0.0003	1.5227	0.0000	1.5407	0.0027
380	1.5156	0.0002	1.5217	0.0002	1.5393	0.0024
385	1.5146	0.0002	1.5207	0.0002	1.5381	0.0021
390	1.5137	0.0001	1.5198	0.0004	1.5368	0.0020
395	1.5129	0.0001	1.5189	0.0003	1.5357	0.0020
400	1.5120	0.0001	1.5180	0.0000	1.5346	0.0020

405	1.5112	0.0001	1.5172	0.0001	1.5335	0.0019
410	1.5105	0.0002	1.5165	0.0002	1.5325	0.0016
415	1.5098	0.0003	1.5157	0.0002	1.5315	0.0014
420	1.5091	0.0004	1.5150	0.0001	1.5305	0.0012
425	1.5084	0.0003	1.5143	0.0001	1.5296	0.0012
430	1.5077	0.0004	1.5137	0.0000	1.5287	0.0012
435	1.5071	0.0005	1.5130	0.0000	1.5279	0.0013
440	1.5065	0.0004	1.5124	0.0001	1.5271	0.0012
445	1.5060	0.0002	1.5118	0.0001	1.5263	0.0015
450	1.5054	0.0001	1.5113	0.0001	1.5255	0.0015
455	1.5049	0.0000	1.5107	0.0001	1.5248	0.0012
460	1.5044	0.0000	1.5102	0.0001	1.5241	0.0010
465	1.5039	0.0000	1.5097	0.0000	1.5234	0.0008
470	1.5034	0.0001	1.5092	0.0000	1.5228	0.0007
475	1.5030	0.0000	1.5088	0.0000	1.5221	0.0006
480	1.5026	0.0000	1.5083	0.0000	1.5215	0.0006
485	1.5021	0.0000	1.5079	0.0000	1.5209	0.0006
490	1.5017	0.0000	1.5074	0.0000	1.5204	0.0004
495	1.5013	0.0000	1.5070	0.0000	1.5198	0.0002
500	1.5010	0.0000	1.5066	0.0000	1.5193	0.0001
505	1.5006	0.0000	1.5063	0.0000	1.5188	0.0001
510	1.5002	0.0001	1.5059	0.0001	1.5183	0.0001
515	1.4999	0.0001	1.5055	0.0000	1.5178	0.0002
520	1.4996	0.0001	1.5052	0.0001	1.5173	0.0003
525	1.4993	0.0001	1.5049	0.0000	1.5168	0.0003
530	1.4990	0.0001	1.5045	0.0001	1.5164	0.0004
535	1.4987	0.0001	1.5042	0.0005	1.5160	0.0004
540	1.4984	0.0001	1.5039	0.0004	1.5155	0.0004
545	1.4981	0.0001	1.5036	0.0003	1.5151	0.0004
550	1.4978	0.0001	1.5033	0.0000	1.5147	0.0004
555	1.4975	0.0001	1.5031	0.0001	1.5144	0.0004
560	1.4973	0.0001	1.5028	0.0001	1.5140	0.0003
565	1.4970	0.0001	1.5025	0.0001	1.5136	0.0003
570	1.4968	0.0002	1.5023	0.0001	1.5133	0.0003
575	1.4966	0.0002	1.5020	0.0001	1.5129	0.0002
580	1.4963	0.0002	1.5018	0.0000	1.5126	0.0002
585	1.4961	0.0002	1.5015	0.0000	1.5123	0.0002
590	1.4959	0.0002	1.5013	0.0001	1.5120	0.0001
595	1.4957	0.0003	1.5011	0.0001	1.5116	0.0001
600	1.4955	0.0004	1.5009	0.0002	1.5113	0.0001
605	1.4953	0.0004	1.5007	0.0002	1.5111	0.0000
610	1.4951	0.0004	1.5005	0.0002	1.5108	0.0000
615	1.4949	0.0003	1.5003	0.0003	1.5105	0.0000
620	1.4947	0.0003	1.5001	0.0003	1.5102	0.0000
625	1.4945	0.0003	1.4999	0.0003	1.5100	0.0001

630	1.4944	0.0003	1.4997	0.0003	1.5097	0.0001
635	1.4942	0.0003	1.4995	0.0003	1.5095	0.0001
640	1.4940	0.0003	1.4994	0.0004	1.5092	0.0001
645	1.4939	0.0003	1.4992	0.0004	1.5090	0.0001
650	1.4937	0.0004	1.4990	0.0005	1.5087	0.0001
655	1.4936	0.0004	1.4989	0.0005	1.5085	0.0001
660	1.4934	0.0004	1.4987	0.0006	1.5083	0.0001
665	1.4933	0.0004	1.4985	0.0006	1.5081	0.0001
670	1.4931	0.0004	1.4984	0.0006	1.5079	0.0001
675	1.4930	0.0004	1.4982	0.0006	1.5077	0.0001
680	1.4929	0.0004	1.4981	0.0006	1.5075	0.0001
685	1.4927	0.0004	1.4980	0.0006	1.5073	0.0001
690	1.4926	0.0004	1.4978	0.0006	1.5071	0.0003
695	1.4925	0.0004	1.4977	0.0006	1.5069	0.0004
700	1.4924	0.0004	1.4976	0.0006	1.5067	0.0005
705	1.4922	0.0004	1.4974	0.0006	1.5065	0.0004
710	1.4921	0.0004	1.4973	0.0006	1.5063	0.0003
715	1.4920	0.0004	1.4972	0.0006	1.5062	0.0004
720	1.4919	0.0003	1.4971	0.0005	1.5060	0.0006
725	1.4918	0.0003	1.4969	0.0005	1.5058	0.0007
730	1.4917	0.0003	1.4968	0.0005	1.5057	0.0008
735	1.4916	0.0003	1.4967	0.0005	1.5055	0.0007
740	1.4915	0.0003	1.4966	0.0005	1.5054	0.0006
745	1.4914	0.0003	1.4965	0.0004	1.5052	0.0006
750	1.4913	0.0002	1.4964	0.0004	1.5051	0.0005
755	1.4912	0.0002	1.4963	0.0004	1.5049	0.0005
760	1.4911	0.0002	1.4962	0.0003	1.5048	0.0005
765	1.4910	0.0002	1.4961	0.0003	1.5046	0.0007
770	1.4909	0.0002	1.4960	0.0002	1.5045	0.0005
775	1.4908	0.0001	1.4959	0.0002	1.5044	0.0004
780	1.4907	0.0001	1.4958	0.0002	1.5042	0.0003
785	1.4906	0.0001	1.4957	0.0002	1.5041	0.0002
790	1.4906	0.0001	1.4956	0.0001	1.5040	0.0003
795	1.4905	0.0001	1.4955	0.0001	1.5039	0.0003
800	1.4904	0.0001	1.4955	0.0001	1.5037	0.0003
805	1.4903	0.0001	1.4954	0.0001	1.5036	0.0002
810	1.4903	0.0001	1.4953	0.0001	1.5035	0.0002
815	1.4902	0.0001	1.4952	0.0001	1.5034	0.0002
820	1.4901	0.0001	1.4951	0.0001	1.5033	0.0002
825	1.4900	0.0001	1.4950	0.0001	1.5032	0.0001
830	1.4900	0.0001	1.4950	0.0000	1.5031	0.0001
835	1.4899	0.0001	1.4949	0.0001	1.5029	0.0002
840	1.4898	0.0000	1.4948	0.0003	1.5028	0.0001
845	1.4898	0.0000	1.4948	0.0001	1.5027	0.0002
850	1.4897	0.0001	1.4947	0.0001	1.5026	0.0002

855	1.4896	0.0000	1.4946	0.0001	1.5025	0.0002
860	1.4896	0.0000	1.4945	0.0000	1.5024	0.0002
865	1.4895	0.0000	1.4945	0.0000	1.5023	0.0002
870	1.4894	0.0000	1.4944	0.0000	1.5023	0.0002
875	1.4894	0.0000	1.4943	0.0002	1.5022	0.0002
880	1.4893	0.0000	1.4943	0.0006	1.5021	0.0002
885	1.4893	0.0000	1.4942	0.0004	1.5020	0.0001
890	1.4892	0.0000	1.4942	0.0001	1.5019	0.0001
895	1.4892	0.0000	1.4941	0.0001	1.5018	0.0001
900	1.4891	0.0000	1.4940	0.0000	1.5017	0.0000
905	1.4890	0.0000	1.4940	0.0000	1.5016	0.0001
910	1.4890	0.0000	1.4939	0.0000	1.5016	0.0000
915	1.4889	0.0000	1.4939	0.0000	1.5015	0.0003
920	1.4889	0.0000	1.4938	0.0000	1.5014	0.0001
925	1.4888	0.0000	1.4938	0.0000	1.5013	0.0002
930	1.4888	0.0000	1.4937	0.0000	1.5012	0.0003
935	1.4887	0.0000	1.4937	0.0000	1.5012	0.0003
940	1.4887	0.0000	1.4936	0.0000	1.5011	0.0004
945	1.4886	0.0000	1.4935	0.0000	1.5010	0.0004
950	1.4886	0.0000	1.4935	0.0000	1.5010	0.0004
955	1.4886	0.0000	1.4935	0.0000	1.5009	0.0004
960	1.4885	0.0000	1.4934	0.0000	1.5008	0.0005
965	1.4885	0.0000	1.4934	0.0000	1.5007	0.0005
970	1.4884	0.0000	1.4933	0.0000	1.5007	0.0006
975	1.4884	0.0000	1.4933	0.0000	1.5006	0.0006
980	1.4883	0.0000	1.4932	0.0000	1.5006	0.0006
985	1.4883	0.0000	1.4932	0.0000	1.5005	0.0005
990	1.4883	0.0001	1.4931	0.0000	1.5004	0.0007
995	1.4882	0.0001	1.4931	0.0000	1.5004	0.0006
1000	1.4882	0.0001	1.4930	0.0000	1.5003	0.0006
1005			1.4930	0.0000	1.5002	0.0006
1010			1.4930	0.0000	1.5002	0.0006
1015			1.4929	0.0000	1.5001	0.0006
1020			1.4929	0.0000	1.5001	0.0006
1025			1.4928	0.0000	1.5000	0.0007
1030			1.4928	0.0001	1.5000	0.0007
1035			1.4928	0.0001	1.4999	0.0007
1040			1.4927	0.0001	1.4998	0.0007
1045			1.4927	0.0001	1.4998	0.0007
1050			1.4926	0.0002	1.4997	0.0007
1055			1.4926	0.0001	1.4997	0.0006
1060			1.4926	0.0001	1.4996	0.0006
1065			1.4925	0.0001	1.4996	0.0006
1070			1.4925	0.0001	1.4995	0.0006
1075			1.4925	0.0001	1.4995	0.0006

1080	1.4924	0.0002	1.4994	0.0007
1085	1.4924	0.0001	1.4994	0.0006
1090	1.4924	0.0001	1.4993	0.0006
1095	1.4923	0.0001	1.4993	0.0006
1100	1.4923	0.0002	1.4993	0.0006
1105	1.4923	0.0002	1.4992	0.0006
1110	1.4922	0.0002	1.4992	0.0006
1115	1.4922	0.0002	1.4991	0.0006
1120	1.4922	0.0002	1.4991	0.0005
1125	1.4922	0.0002	1.4990	0.0005
1130	1.4921	0.0002	1.4990	0.0005
1135	1.4921	0.0002	1.4990	0.0006
1140	1.4921	0.0002	1.4989	0.0006
1145	1.4920	0.0003	1.4989	0.0006
1150	1.4920	0.0003	1.4988	0.0005
1155	1.4920	0.0003	1.4988	0.0005
1160	1.4920	0.0002	1.4988	0.0004
1165	1.4919	0.0003	1.4987	0.0004
1170	1.4919	0.0003	1.4987	0.0004
1175	1.4919	0.0003	1.4986	0.0004
1180	1.4919	0.0003	1.4986	0.0004
1185	1.4918	0.0003	1.4986	0.0004
1190	1.4918	0.0003	1.4985	0.0003
1195	1.4918	0.0003	1.4985	0.0003
1200	1.4918	0.0003	1.4985	0.0002

References

(1) Köhler, S. P. K.; Allan, M.; Kelso, H.; Henderson, D. A.; McKendrick, K. G. The effects of surface temperature on the gas-liquid interfacial reaction dynamics of O(3P)+squalane. *The Journal of Chemical Physics* **2005,** *122*, 024712.

(2) Painter, L. R.; Attrey, J. S.; Hubbell, H. H.; Birkhoff, R. D. Vacuum ultraviolet optical properties of squalane and squalene. *Journal of Applied Physics* **1984,** *55*, 756-759.

(3) Toole, J. R. Reducing uncertainties in aerosol optical properties with cavity ring-down spectroscopy. University of Georgia, Athens, Georgia, 2012.

(4) Sörensen, N. A.; Gillebo, T.; Holtermann, H.; Sörensen, J. S. Studies related to pristane VI. synthesis of digeranyl with some remarks on the physical constants of crocetane. *Acta Chemica Scandinavica* **1951,** *5*, 757-765.

(5) Toole, J. R.; Renbaum-Wolff, L.; Smith, G. D. A Calibration Technique for Improving Refractive Index Retrieval from Aerosol Cavity Ring-Down Spectroscopy. *Aerosol Sci. Technol.* **2013,** *47*, 955-965.

(6) Bond, T. C.; Anderson, T. L.; Campbell, D. Calibration and Intercomparison of Filter-Based Measurements of Visible Light Absorption by Aerosols. *Aerosol Sci. Technol.* **1999,** *30*, 582-600.

(7) Lack, D. A.; Lovejoy, E. R.; Baynard, T.; Pettersson, A.; Ravishankara, A. R. Aerosol Absorption Measurement using Photoacoustic Spectroscopy: Sensitivity, Calibration, and Uncertainty Developments. *Aerosol Sci. Technol.* **2006,** *40*, 697-708.

(8) Dinar, E.; Abo Riziq, A.; Spindler, C.; Erlick, C.; Kiss, G.; Rudich, Y. The complex refractive index of atmospheric and model humic-like substances (HULIS) retrieved by a cavity ring down aerosol spectrometer (CRD-AS). *Faraday Discussions* **2008,** *137*, 279-295.

(9) Pinnick, R. G.; Rosen, J. M.; Hofmann, D. J. Measured Light-Scattering Properties of Individual Aerosol Particles Compared to Mie Scattering Theory. *Appl. Optics* **1973,** *12*, 37-41.

(10) Sun, H.; Biedermann, L.; Bond, T. C. Color of brown carbon: A model for ultraviolet and visible light absorption by organic carbon aerosol. *Geophys. Res. Lett.* **2007,** *34*, L17813.