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Documentation operation procedures PSICAM

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Remark:

This document describes the operation procedure for a custom-made lab-based point-source integrating-cavity absorption-meter. It will be expended and updated when the first Protoool-PSICAM is available.

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Introduction

The measurements of particulate light absorption in natural waters, i.e. that of suspended phytoplankton algae, sediment, detritus etc., remains a difficult issue because with most measurement technique the light scattering of those particles deteriorates the results and the absorption is strongly overestimated. The normally observed light attenuation has to be corrected to receive the correct absorption by subtracting the scattering signal. Furthermore the generally low concentration of particles in natural water makes it necessary for most common techniques to concentrate the particles before their absorption can be measured. A typical technique is to concentrate particles on a glass fibre filter and measure the filter in a spectrophotometer (QFT, quantitative filter technique). However, this requires comprehensive sample handling, like filtration, preservation, storage etc. One possibility to overcome these problems is to measure the original sample inside an integrating sphere, that would reduce/avoid scattering problems and sample handling, and increase sensitivity by a rather long optical path length (up to several meters). To reduce scattering effects to an insignificant level the light distribution inside the sphere has to be homogeneous and isotropic, such that any additional scattering inside the sphere does not change the light field. A simple way to do this is to use a central isotropic light source, as proposed and theoretically described by Kirk (1995, 1997), a point-source integrating-cavity absorption meter (PSICAM). Another, more complex set-up was e.g. use to determine pure water absorption (Pope & Fry 1997, Pope et al. 2000). The PSICAM concept was further investigated by Leathers et al. (2002) and Lerebourg et al. (2002) and successfully tested by Röttgers et al. (2005). First results with natural sample are shown in Röttgers et al. (2007) and Röttgers & Doerffer (2007).

PSICAM setup

The integrating cavity of the PSICAM (Fig. 1a,b) has an inner diameter of 9.0 cm and is made out of a block (edge length: 12 cm) of a diffuse reflective plastic material (OP.DI.MA, Gigahertz Optik, Germany) which has similar properties as Spectralon (Labsphere Inc., USA). The reflectivity of this material is depending on the material thickness (97 and 98 % for a thickness of 10 mm). To simplify its manufacturing the raw material surface was used without any additional coating of the inner cavity surface. This surface is water-repellent and problems with contamination by natural soluble substances could not be observed when using river water with a high "Gelbstoff" concentration. Particulate matter can easily be washed out of the cavity. The central light source consists of a small scattering sphere made out of a diffuse quartz-glass with an outer diameter of 10.0 mm. The cavity has two openings which can be closed by Teflon stoppers. One for inserting and changing the central light source and one for filling and emptying the cavity. Light is provided by an electronically stabilized 150 W halogen bulb (IT 3500, Illumination Technology). The light beam from the lamp is guided to the central diffuse emission sphere by a custom-made quartz-glass fibre bundle. That part of the fibre bundle, which sticks into the cavity, is enclosed in a 10 cm long steel tube (\varnothing 3.0 mm) and carries at its end the emission sphere. A Ramses ACC UV/VIS spectroradiometer (TRIOS, Germany) is used as light detector. It includes a photodiode array which covers the spectral radiation from 300 to 725 nm with an usual interval of 2 nm (3.3 nm optical resolution). Another quartz-glass fibre bundle guides the light from the cavity to the detector entrance. The light collector at the end of this fibre bundle enters the integrating cavity through a small hole (\varnothing 3.1 mm) parallel to the steel tube holding the central emission sphere. The fibre has only a narrow field of view and, thus, does not collect any light coming from the central light source directly. It measures the light reflected at the cavity wall opposite to the collector as well as the path radiance, i.e. the light scattered into the receiving cone of the collector.

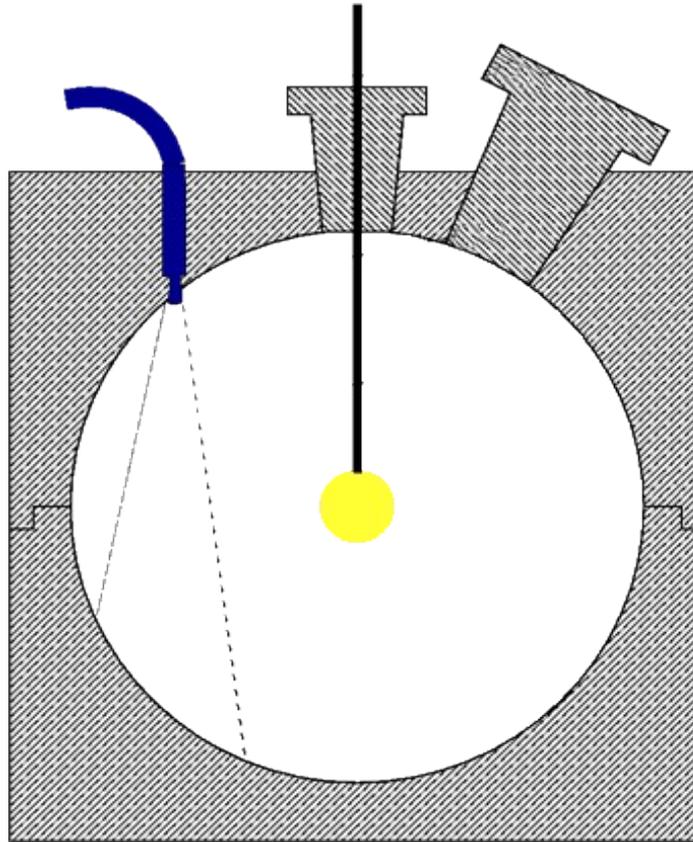


Fig. 1. Schematic cross section of the PSICAM showing the central light source (yellow), the light detector (blue) and the inner cavity (white). The light detector is a tip of a fiber optic which other end is connected to a spectroradiometer. The central light source is a sphere made from a diffuse quartz-glass sitting on the tip of a fiber optic connected to an external halogen light source.

Theoretical considerations

According to Kirk (1997) and Leathers et al. (2000), the “transmission”, T , measured in a PSICAM is the ratio of the diffuse reflected irradiance F_0 at the inner wall when the cavity is filled with either the sample A or B (Eq. 1). Each irradiance is proportional to the number of times a photon is reflected by the wall, N_C , before it is absorbed either by the wall or by the sample fluid. Hence,

$$T_{AB} = \frac{F_0^A}{F_0^B} = \frac{N_C^A}{N_C^B} \quad (1)$$

N_C is the fraction of photons reaching the wall directly and indirectly by reflection on the wall for one, or more times (Eq. 2). It depends (1) on the probability P_0 that a photon, coming from the central light source, reaches the wall directly, (2) on the reflectivity of the wall, ρ , and (3) on the probability P_s that a photon, which is reflected, will return to the wall. In the PSICAM set-up used here the detector does not collect light that comes directly from the light source, thus, for N_C this gives

$$N_C = P_0 \rho P_s + P_0 \rho^2 P_s^2 + \dots = P_0 \sum_{n=1}^{\infty} (\rho P_s)^n = \frac{\rho P_0 P_s}{1 - \rho P_s} \quad (2)$$

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Therefore,

$$T_{AB} = \frac{P_0^A P_S^A (1 - \rho P_S^B)}{P_0^B P_S^B (1 - \rho P_S^A)} \quad (3)$$

P_0 and P_S are related to the radii of the PSICAM $r_0 = r - r_s$ and r , respectively, where r is the inner radius of the cavity and r_s the radius of the central light source, and to the absorption coefficient a in the following way, (see Kirk 1997 for details):

$$P_0(a, r_0) = \exp(-ar_0), \quad (4)$$

$$P_S(a, r) = \frac{1}{2a^2 r^2} [1 - \exp(-2ar)(2ar + 1)]. \quad (5)$$

Finally the transmission in the PSICAM is related to the absorption coefficients a_A and a_B of the two solutions as

$$T_{AB} = \exp[-r_0(a_A - a_B)] \left[\frac{1 - \rho P_S(a_B, r)}{1 - \rho P_S(a_A, r)} \frac{P_S(a_A, r)}{P_S(a_B, r)} \right]. \quad (6)$$

When using Eq. (5) and (6) T_{AB} is a function of the light absorption of the samples a_A and a_B , the radii r and r_0 , and the reflectivity ρ .

Solving Eq. (6) for the reflectivity gives

$$\rho = \frac{T_{AB} \exp(-a_B r_0) P_S(a_B, r) - \exp(-a_A r_0) P_S(a_A, r)}{T_{AB} \exp(-a_B r_0) P_S(a_A, r) P_S(a_B, r) - \exp(-a_A r_0) P_S(a_B, r) P_S(a_A, r)}. \quad (7)$$

Hence, if ρ is not known, it can be determined by measuring the “transmission” by two solutions with known absorption coefficients using Eq. (7) and (5).

Calibration

The error for absorption determination in a PSICAM is related mainly to the error in determining the inner radius, r , the reflectivity of the PSICAM, ρ , and to the “transmission” determination in the PSICAM. The “transmission” measurement is further influenced by the stability of the light source and the spectroradiometer response. From these errors the error related to ρ has the strongest influence: a 1 % error in ρ leads to >10 % error in the absorption determination. Hence, ρ has to be known with a high accuracy. It is determined using Eq. (7), by measuring the “transmission” by two solutions with known absorption coefficients.

Determining ρ in this way has the advantage that it will eliminate errors associated with the true ρ of the wall material, and with r_0 , a_A , a_B , and the known water absorption. However, the error of the necessary determination of the absorption coefficient with a photometer, directly influences the error of the absorption determination with the PSICAM.

Practically ρ is determined following the suggestion and description of Leathers et al. (2000).

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Therefore the transmission T_{AB} is determined from a sample solution A with an absorption coefficient a_A measured against a reference solution B with an absorption coefficient a_B in the PSICAM. The reference solution B consists simply of purified water. The assumed absorption coefficient spectrum of this purified water, a_w , is taken from published pure water absorption coefficients, whose were adjusted and smoothed to have a complete spectrum for the considered wavelengths range (see attachment). As discussed above any error in this pure water absorption is compensated by the calibration procedure described here, the exact pure water absorption is of less significance.

The sample solution A is prepared from the coloured stain Nigrosine (Certistain, Merck, Germany), following suggestions of Kirk (1997). Compared to other dye solutions Nigrosine has the advantage of having a considerably high absorption coefficient at all required wavelengths.

A Nigrosine stock solution is prepared by dissolving a few crystals of Nigrosine in 100 ml purified water. The optical density of this solution is roughly determined photometrically in a 1 cm cuvette at 578 nm, to be able to calculate the necessary volume of this stock solution when later preparing the calibration solutions. Calibration solutions with an absorption (a_{578nm}) between 0.5 and 2 m^{-1} (on the \log_n scale) are prepared by diluting a few milliliters of the stock solution in ca. 2000 ml purified water. The exact spectral absorption coefficients of this Nigrosine in solution is determined photometrically in the range of ca. 350 to 800 nm using a 10 cm cuvette and purified water as the reference.

The transmission measurements in the PSICAM are conducted in triplicate by determining the light intensity inside the cavity when the cavity is first filled with purified water, F_w , and second with the calibration solution, F_{nig} . In each case the temperature of the fluid (t_w and t_{nig}) inside the cavity is recorded for a later temperature correction of the pure water absorption. After the calibration solution has been measured, the PSICAM has to be cleaned as the stain adsorbs considerably fast on the cavity wall of the PSICAM. Therefore the PSICAM is bleached for 15 min with a 0.1 % sodium hypochlorite solution (NaOCl, Riedel de Haen, Germany). Afterward the bleach is removed from the PSICAM by washing the cavity several times with purified water.

The reflectivity is calculated for each pair of pure water/calibration solution using the pure water absorption as a_B , and the sum of absorptions of pure water and Nigrosine as a_A . The pure water absorption is calculated beforehand for each fluid using the specific fluid temperature.

Calibration procedure in short!

- 1) preparation of ca. 100 ml Nigrosine stock solution (a_{580nm}^{1cm} ca. 3 OD)
- 2) preparation of 2000 ml Nigrosine calibration solution $a_{580nm} = 0.5 - 2 m^{-1}$
- 3) determination of Nigrosine absorption, a_{nig} , of the calibration solution (10 cm cuvette in spectrophotometer, or using a LWCC system, 3x)
- 4) determination of “transmission” (nigrosine solution vs. purified water) in the PSICAM, 3x, cleaning and bleaching of the cavity after each nigrosine solution
- 5) calculation of reflectivity (after temperature correction of pure water absorption), where

$$a_A = a_w(t_{nig}^{\circ C}) + a_{nig},$$

$$a_B = a_w(t_w^{\circ C}),$$

$$T_{AB} = F_{nig}/F_w,$$

$$r_0 = 0.040 \text{ m},$$

$$r = 0.045 \text{ m}.$$

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Measurement and calculation of the absorption coefficient

A regular measurement is done by measuring the light intensity inside the cavity when it is filled with either purified water or the sample. This can be done in an alternating way until the sample is measured three times. For each measurement the fluid temperature and the sample salinity need to be recorded for a later temperature and salinity correction of the pure water absorption. In addition the light intensity might be measured when an additional short-pass filter is placed in front of the external light source to measure the sample's chlorophyll fluorescence, which is used to correct the absorption for the influence of this fluorescence inside the cavity in the range of the fluorescence, i.e. 650 – 700 nm. For each sample measurement, T_{AB} can be calculated two times using the reference measurement taken before and after the sample measurement. The real T_{AB} is the mean of these two values, this corrects for possible constant drifts in the light intensity by either a drift in the lamp output or the detector response.

There is no analytical solution for the absorption coefficient $a(\lambda)$ in Eq. (6). When ρ is known, $a(\lambda)$ is determined by solving this equation numerically. This is done by minimizing the least square function $G(a(\lambda))$ for the measured transmission, $T_{exp}(\lambda)$ using a numerically calculated transmission $T_{num}(\lambda)$.

$$G(a(\lambda)) = \sqrt{(T_{num(\lambda)} - T_{exp(\lambda)})^2} \quad (8)$$

Measurement procedure in short!

- 1) fill the PSICAM with purified water, measure the fluid's temperature (t_w) and then the light intensity, F_w
- 2) fill the PSICAM with the sample, measure the fluid's temperature (t_{sample}) and then the light intensity, F_{sample} , record the sample's salinity (S_{sample}). Afterwards wash the cavity with purified water.
- 3) repeat step 1 and 2 three times for triplicate measurements, at the end measure purified water once more
- 4) calculate the transmissions as F_{sample}/F_w using the F_w measured before and after each sample
- 5) determine the absorption for each transmission using Eq (6) and (5) by minimizing Eq (8) after the pure water absorption has been corrected for the specific temperature and sample salinity, where

$$a_A = a_w(t_{sample} \text{ } ^\circ\text{C}, S_{sample} \text{ PSU}) + a_{sample},$$

$$a_B = a_w(t_w \text{ } ^\circ\text{C}),$$

$$T_{AB} = F_{sample}/F_w,$$

$$r_0 = 0.040 \text{ m},$$

$$r = 0.045 \text{ m},$$

and a_{sample} is the unknown absorption to be fitted.

Temperature and salinity correction of the pure water absorption

The absorption of pure water, a_w , is dependent on temperature and salinity. Any difference in temperature and salinity of the sample or the reference to that of the theoretical pure water absorption reference (i.e. 20°C and 0 PSU) has to be corrected using instrument-specific

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temperature and salinity correction coefficients, Ψ_T and Ψ_S as

$$a_w(T, \lambda) = a_w(T_0, \lambda) + (T - T_0) \Psi_T(\lambda) \quad (9)$$

and

$$a_w(S, \lambda) = a_w(S_0, \lambda) + (S - S_0) \Psi_S(\lambda), \quad (10)$$

where T is the specific temperature, S the specific salinity, and T_0 and S_0 the values at which the pure water absorption had been measured, i.e. 20 °C and 0 PSU. Values for Ψ_T and Ψ_S are given below.

Corrections for chlorophyll fluorescence inside the PSICAM

To be done!

Maintenance and service

The PSICAM cavity wall can be cleaned by using pure HPLC-grade Ethanol and a lint-free tissue. Touching the wall with unprotected finger should be avoided. Optical influences by organic material attached to the wall can further be removed by bleaching using a ca. 0.1% NaOCl solution (500 - 1000 μ l NaOCl in 500 ml purified water). The tip of the detector fibre optic can be cleaned with ethanol. The central light source can either be carefully cleaned with ethanol, or put shortly in concentrated HCl for a more rigorous cleaning.

The PSICAM should be filled with purified water 24 hours before the measurement/calibration are done, as water will enter the wall material and changes the reflectance.

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Attachment

row 1. wavelength [nm]

row 2. water absorption coefficient [m^{-1}] of Pope and co-workers (Pope & Fry 1997, Zheng & Pope 2005)

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row 3. temperature coefficient [$\text{m}^{-1} \text{ } ^\circ\text{C}^{-1}$], PSICAM measurements (04.05.2005 & Dec. 2007)

row 4. salinity coefficient [$\text{m}^{-1} \text{ PSU}^{-1}$], PSICAM measurements (04.05.2005 & Nov 2007)

350	0.01650	0.00003	0.00000
355	0.01517	0.00003	0.00000
360	0.01408	0.00003	0.00000
365	0.01208	0.00003	0.00000
370	0.01144	0.00003	0.00000
375	0.01161	0.00003	0.00000
380	0.00928	0.00003	0.00000
385	0.00836	0.00003	0.00000
390	0.00713	0.00003	0.00000
395	0.00659	0.00003	0.00000
400	0.00655	0.00003	0.00000
402	0.00640	0.00003	0.00000
404	0.00620	0.00003	0.00000
406	0.00600	0.00003	0.00000
408	0.00550	0.00003	0.00000
410	0.00520	0.00003	0.00000
412	0.00500	0.00003	0.00000
414	0.00480	0.00003	0.00000
416	0.00480	0.00003	0.00000
418	0.00470	0.00003	0.00000
420	0.00470	0.00003	0.00000
422	0.00500	0.00003	0.00000
424	0.00500	0.00003	0.00000
426	0.00510	0.00004	0.00000
428	0.00530	0.00005	0.00000
430	0.00540	0.00006	0.00000
432	0.00550	0.00007	0.00000
434	0.00580	0.00008	0.00000
436	0.00600	0.00008	0.00000
438	0.00610	0.00008	0.00000
440	0.00640	0.00008	0.00000
442	0.00680	0.00008	0.00000
444	0.00730	0.00008	0.00000
446	0.00770	0.00008	0.00000
448	0.00830	0.00008	0.00000
450	0.00880	0.00008	0.00000
452	0.00920	0.00008	0.00000
454	0.00950	0.00008	0.00000
456	0.00970	0.00008	0.00000
458	0.00990	0.00008	0.00000
460	0.01000	0.00007	0.00000
462	0.01000	0.00007	0.00000
464	0.01030	0.00006	0.00000
466	0.01050	0.00006	0.00000
468	0.01070	0.00006	0.00000
470	0.01100	0.00006	0.00000
472	0.01150	0.00006	0.00000
474	0.01170	0.00006	0.00000



476	0.01200	0.00006	0.00000
478	0.01240	0.00006	0.00000
480	0.01290	0.00006	0.00000
482	0.01300	0.00005	0.00000
484	0.01340	0.00005	0.00000
486	0.01380	0.00005	0.00000
488	0.01440	0.00005	0.00000
490	0.01500	0.00006	0.00000
492	0.01600	0.00006	0.00000
494	0.01720	0.00006	0.00000
496	0.01850	0.00007	0.00000
498	0.01990	0.00007	0.00000
500	0.02150	0.00008	0.00000
502	0.02330	0.00008	0.00000
504	0.02530	0.00009	0.00000
506	0.02770	0.00011	0.00000
508	0.03060	0.00013	0.00000
510	0.03380	0.00014	0.00000
512	0.03680	0.00016	0.00000
514	0.03930	0.00017	0.00001
516	0.04110	0.00017	0.00001
518	0.04220	0.00017	0.00001
520	0.04270	0.00016	0.00001
522	0.04349	0.00015	0.00002
524	0.04401	0.00014	0.00002
526	0.04456	0.00012	0.00002
528	0.04521	0.00011	0.00002
530	0.04598	0.00010	0.00002
532	0.04683	0.00009	0.00002
534	0.04775	0.00008	0.00002
536	0.04872	0.00007	0.00002
538	0.04976	0.00006	0.00002
540	0.05093	0.00006	0.00002
542	0.05231	0.00005	0.00002
544	0.05396	0.00005	0.00002
546	0.05588	0.00004	0.00002
548	0.05798	0.00005	0.00002
550	0.06340	0.00004	0.00002
552	0.06512	0.00004	0.00002
554	0.06694	0.00004	0.00002
556	0.06837	0.00003	0.00002
558	0.06948	0.00002	0.00002
560	0.07089	0.00001	0.00002
562	0.07244	0.00000	0.00002
564	0.07412	0.00000	0.00002
566	0.07602	-0.00001	0.00002
568	0.07825	-0.00001	0.00002
570	0.08093	-0.00001	0.00002
572	0.08401	0.00000	0.00002
574	0.08773	0.00001	0.00002

576	0.09246	0.00002	0.00002
578	0.09810	0.00005	0.00002
580	0.10482	0.00007	0.00001
582	0.11260	0.00011	0.00001
584	0.12177	0.00015	0.00002
586	0.13215	0.00021	0.00002
588	0.14375	0.00027	0.00002
590	0.15677	0.00033	0.00002
592	0.17107	0.00040	0.00002
594	0.18647	0.00048	0.00002
596	0.20381	0.00060	0.00003
598	0.22259	0.00072	0.00003
600	0.24017	0.00085	0.00004
602	0.25608	0.00096	0.00005
604	0.26905	0.00104	0.00007
606	0.27879	0.00106	0.00009
608	0.28494	0.00103	0.00011
610	0.28866	0.00096	0.00012
612	0.29155	0.00088	0.00013
614	0.29431	0.00078	0.00014
616	0.29795	0.00070	0.00014
618	0.30151	0.00061	0.00014
620	0.30424	0.00051	0.00014
622	0.30716	0.00042	0.00014
624	0.31087	0.00034	0.00014
626	0.31467	0.00026	0.00014
628	0.31823	0.00019	0.00014
630	0.32183	0.00012	0.00014
632	0.32503	0.00005	0.00013
634	0.32748	-0.00003	0.00013
636	0.32992	-0.00009	0.00013
638	0.33322	-0.00015	0.00013
640	0.33732	-0.00020	0.00013
642	0.34217	-0.00023	0.00013
644	0.34786	-0.00025	0.00013
646	0.35351	-0.00028	0.00013
648	0.35996	-0.00029	0.00012
650	0.36919	-0.00028	0.00012
652	0.37992	-0.00026	0.00012
654	0.39087	-0.00021	0.00011
656	0.40171	-0.00015	0.00011
658	0.41276	-0.00010	0.00011
660	0.42230	-0.00004	0.00012
662	0.42994	-0.00001	0.00012
664	0.43564	-0.00001	0.00013
666	0.44095	-0.00002	0.00013
668	0.44642	-0.00007	0.00013
670	0.45120	-0.00013	0.00013
672	0.45519	-0.00018	0.00013
674	0.45434	-0.00022	0.00013



676	0.45986	-0.00026	0.00012
678	0.46626	-0.00031	0.00011
680	0.47387	-0.00037	0.00011
682	0.48309	-0.00040	0.00010
684	0.49353	-0.00042	0.00009
686	0.50490	-0.00045	0.00008
688	0.51824	-0.00045	0.00007
690	0.53408	-0.00045	0.00006
692	0.55238	-0.00044	0.00005
694	0.57312	-0.00041	0.00004
696	0.59622	-0.00036	0.00003
698	0.62171	-0.00030	0.00002
700	0.65021	-0.00021	0.00001
702	0.68260	-0.00009	0.00000
704	0.71946	0.00006	0.00000
706	0.76103	0.00026	-0.00001
708	0.80821	0.00051	-0.00001
710	0.85804	0.00085	-0.00001
712	0.91936	0.00124	0.00000
714	0.98798	0.00172	0.00000
716	1.06366	0.00227	0.00002
718	1.14295	0.00289	0.00003
720	1.23831	0.00356	0.00005
722	1.33728	0.00431	0.00007
724	1.45097	0.00510	0.00008
726	1.57671	0.00596	0.00009
728	1.70964	0.00650	0.00010
730	1.86362	0.00740	0.00011
732	2.02968	0.00860	0.00014
734	2.19733	0.01020	0.00021
736	2.33979	0.01210	0.00032
738	2.44584	0.01400	0.00046
740	2.52924	0.01510	0.00063
742	2.59572	0.01560	0.00081
744	2.64083	0.01540	0.00096
746	2.67913	0.01490	0.00108
748	2.70889	0.01400	0.00117
750	2.72157	0.01310	0.00124
752	2.73133	0.01200	0.00128
754	2.75193	0.01100	0.00130
756	2.75361	0.01000	0.00130
758	2.73999	0.00900	0.00131
760	2.74468	0.00790	0.00129
762	2.74908	0.00690	0.00126
764	2.73042	0.00590	0.00122
766	2.72053	0.00490	0.00118
768	2.72345	0.00390	0.00115
770	2.70376	0.00300	0.00112
772	2.67648	0.00210	0.00109
774	2.65648	0.00130	0.00106



776	2.65926	0.00040	0.00101
778	2.65301	-0.00030	0.00097
780	2.61123	-0.00100	0.00091
782	2.55975	-0.00170	0.00085
784	2.50228	-0.00210	0.00079
786	2.46782	-0.00270	0.00073
788	2.44357	-0.00320	0.00067
790	2.40895	-0.00370	0.00060
792	2.38356	-0.00400	0.00053
794	2.36321	-0.00440	0.00044
796	2.31574	-0.00460	0.00036
798	2.26583	-0.00470	0.00030
800	2.24157	-0.00490	0.00025
802	2.22159	-0.00471	0.00020
804	2.20504	-0.00450	0.00014
806	2.19951	-0.00428	0.00008
808	2.20304	-0.00393	0.00001
810	2.21449	-0.00346	-0.00003
812	2.23497	-0.00296	-0.00006
814	2.26467	-0.00246	-0.00008
816	2.28299	-0.00192	-0.00009
818	2.29898	-0.00128	-0.00010
820	2.32809	-0.00054	-0.00014
822	2.36492	0.00030	-0.00020
824	2.44684	0.00122	-0.00025
826	2.59933	0.00210	-0.00028
828	2.83111	0.00292	-0.00027
830	3.06123	0.00369	-0.00022
832	3.21563	0.00446	-0.00013
834	3.36600	0.00515	0.00003
836	3.57482	0.00569	0.00027
838	3.70859	0.00615	0.00052
840	3.77637	0.00598	0.00071
842	3.86047	0.00508	0.00088
844	3.94197	0.00402	0.00099
846	4.00276	0.00337	0.00093
848	4.01406	0.00310	0.00089
850	3.99352	0.00290	0.00088