SILICA, CRYSTALLINE, by XRD 7500

SiO_2 MW: 60.08 CAS: 14808-60-7 (quartz) RTECS: VV7330000
(quartz)
14464-46-1 (cristobalite) VV7325000
(cristobalite)
15468-32-3 (tridymite) VV7335000 (tridymite)

METHOD: 7500, Issue 3	**EVALUATION: FULL**	**Issue 1: 15 August 1990** **Issue 3: 15 January 1998**

OSHA : quartz (respirable) 10 mg/m^3/(%SiO_2+2); cristobalite and tridymite (respirable) ½ the above
NIOSH: 0.05 mg/m^3; carcinogen
ACGIH: quartz (respirable) 0.1 mg/m^3
cristobalite (respirable) 0.05 mg/m^3
tridymite (respirable) 0.05 mg/m^3

PROPERTIES: solid; d 2.65 g/cm^3 @ 0 °C; crystalline transformations: quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C; α-quartz to ß-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING

SAMPLER:	CYCLONE + FILTER (10-mm nylon cyclone, Higgins-Dewell (HD) cyclone, or aluminum cyclone + 5-µm PVC membrane
FLOW RATE:	nylon cyclone: 1.7 L/min; HD cyclone: 2.2 L/min; aluminum cyclone: 2.5 L/min
VOL-MIN:	400 L
-MAX:	1000 L
SHIPMENT:	routine
SAMPLE STABILITY:	stable
BLANKS:	2 to 10 per set (See step 12.g.)
BULK SAMPLE:	high-volume or settled dust; to identify interferences

ACCURACY

RANGE STUDIED:	25 to 2500 µg/m^3 [1] (800-L sample)
BIAS:	none known
OVERALL PRECISION ($\hat{S}_{rT}$):	0.09 (50 to 200 µg) [1]
ACCURACY:	± 18%

MEASUREMENT

TECHNIQUE:	X-RAY POWDER DIFFRACTION
ANALYTE:	crystalline SiO_2
ASH:	muffle furnace or RF plasma asher or dissolve in tetrahydrofuran
REDEPOSIT:	on 0.45-µm Ag membrane filter
XRD:	Cu target X-ray tube, graphite monochromator Optimize for intensity; 1° slit Slow step scan, 0.02°/10 sec Integrated intensity with background subtraction
CALIBRATION:	suspensions of silica in 2-propanol
RANGE:	0.02 to 2 mg SiO_2 per sample [2]
ESTIMATED LOD:	0.005 mg SiO_2 per sample [2]
PRECISION ($\bar{S}_r$):	0.08 @ 0.05 to 0.2 mg per sample [1]

APPLICABILITY: The working range is 0.025 to 2.5 mg/m^3 for an 800-L air sample.

INTERFERENCES: Micas, potash, feldspars, zircon, graphite, and aluminosilicates. See APPENDIX.

OTHER METHODS: This is similar to the method in the Criteria Document [3] and P&CAM 259 [4] which has been collaboratively tested [2]. This method is similar, except for sample collection, to S315 [5,6]. Method P&CAM 109 [7,8,9], which incorporates an internal standard, has been dropped. Colorimetry [10] is an alternate measurement procedure (used in Method 7601), as is IR spectrometry (Methods 7602 and 7603).

REAGENTS:

1. Silica Standards.
   - a. Quartz* (SRMs 1878 and 2679) and Cristobalite* (SRM 1879), available from Standard Reference Materials Program, Rm. 204, Bldg. 202, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899.
   - b. Tridymite*, available from NIOSH, DPSE, ARDB, 4676 Columbia Pkwy., Cincinnati, OH 45226.
2. 2-Propanol, reagent grade.
3. Desiccant.
4. Glue or tape for securing Ag filters to XRD holders.
5. Optional: tetrahydrofuran (THF)* (if LTA or muffle furnace are unavailable).
6. Optional (if calcite present): 25% v/v concentrated hydrochloric acid (ACS reagent grade) in distilled water and 25-mm filters of PVC or cellulose ester with pore size of 1 µm or less.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   - a. Filter: Polyvinyl chloride (PVC) filter, 37-mm, 5.0-µm pore size supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
     NOTE: Check each new lot of PVC filters by analyzing one or more by this method. For example, Gelman VM-1 filters (all lots) were found to be unacceptable because of high ash and background. If THF is used, check for complete dissolution by dissolving a blank PVC filter and following through steps 5c through 8.
   - b. Cyclone: 10-mm nylon, Higgins-Dewell (HD), Aluminum (Al), or equivalent.
2. Area air sampler: PVC membrane filter, 37-mm diameter, 5-µm pore size; three-piece filter cassette.
3. Sampling pumps with flexible connecting tubing, capable of the following flow rates: nylon cyclone, 1.7 L/min; HD cyclone, 2.2 L/min; Al cyclone, 2.5 L/min; and bulk sampler, 3 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-µm pore size.
5. X-ray powder diffractometer (XRD) equipped with copper target X-ray tube, graphite monochromator, and scintillation detector.
6. Reference specimen (mica, Arkansas stone, or other stable standard) for data normalization.
7. Low-temperature radio-frequency plasma asher (LTA) or muffle furnace, or ultrasonic bath (≥150 W), for filter preparation.
8. Vacuum filtration assembly and side-arm vacuum flask with a 25-mm filter holder.
9. Sieve, 10-µm. for wet sieving.
10. Analytical balance (0.001 mg); magnetic stirrer with thermally insulated top; ultrasonic bath or probe; volumetric pipettes and flasks; Pyrex crucibles with covers (muffle furnace); 40-mL wide-mouth or 50-mL centrifuge tubes (THF method); desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [3]. THF is extremely flammable and should be used in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at 1.7 ± 5% L/min with nylon cyclone, 2.2 ± 5% L/min with HD cyclone, ro 2.5 ± 5% Al cyclone for a total sample size of 400 to 1000 L. Do not exceed 2 mg dust loading on the filter.

   NOTE: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
3. Take an area air sample or collect a settled dust sample, if dust in the work environment has not been previously characterized.

SAMPLE PREPARATION:

4. Samples may be characterized by one of the following methods, as appropriate.
   a. **Interference check.** Prepare area dust sample or settled dust bulk sample for XRD analysis by mounting the collection sample directly on an XRD sample holder, or by depositing or redepositing the dust on another filter for mounting, or by packing an XRD powder holder. Proceed to step 11.

   b. **Qualitative Analysis.** Prepare the area air sample or settled dust sample for qualitative analysis by grinding and/or wet sieving to best match the airborne dust particle size. Wet sieve with a 10-µm sieve, 2-propanol, and an ultrasonic bath [11], followed by evaporation of excess alcohol, drying in an oven for 2 hours, and overnight storage in a desiccator. Deposit the end product on a filter (steps 7-8) or pack in a conventional XRD powder holder.

      NOTE 1: For quantitative determination of % SiO_2, weigh out, in triplicate, 2 mg sieved dust, transfer to a 50-mL beaker, add 10 mL 2-propanol, and continue with step 6.

      NOTE 2: In a bulk sample, if there is an interfering compound(s) that renders the identification and quantitation of quartz very difficult, the sample will need to be carefully treated in hot phosphoric acid [12] to dissolve the interfering compound(s) and avoid the loss of quartz. This treatment can be used to dissolve several 50-mg sample aliquots in order to concentrate the quartz content for the purpose of lowering the LOD.
5. Use one of the following methods to prepare filter samples and blanks:
   a. **Low Temperature Ashing:** Place the filters in 50-mL beakers within the low temperature asher so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, carefully add 15 mL 2-propanol to each beaker; or

   b. **Muffle Furnace Ashing:**
      1. If the samples contain a significant amount of calcite (>20% of total dust loading), silica may be lost due to formation of $CaSiO_3$. Remove the calcite by the following procedure: Place a 0.5-µm, 25-mm PVC filter in the filtration apparatus and clamp the filter funnel over it. Remove the sample filter from the cassette, fold, and drop it on the 25-mm filter. Add 10 mL 25% v/v HCl and 5 mL 2-propanol to the filter funnel and allow to sit for 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel, washing with three successive 10-mL portions of distilled water. Release the vacuum. Carry both filters through the ashing step together.
      2. Place the filter samples in porcelain crucibles, loosely cover and ash in muffle furnace for 2 h at 600 °C (800 °C if graphite is present). Add several mL 2-propanol to the ash, scrape the crucible with a glass rod to loosen all particles and transfer the residue to a 50-mL beaker. Wash the crucible several more times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to about 15 mL; or

   c. **Filter Dissolution:** Using forceps and a spatula, remove the filter from the cassette, fold the filter three times, and place in the bottom of a 40- or 50-mL centrifuge tube. Add 10 mL THF and allow to stand for at least 5 min. Cap the centrifuge tube with aluminum foil to prevent contamination. Gently agitate the centrifuge tube by hand or with a vortex mixer making sure the THF does not go near the top of the tube. Place the tube in an ultrasonic bath (water level 2.5 cm from top) for at least 10 min. (The filter should be totally dissolved.) Just prior to filtering, agitate the sample for 10 to 20 sec on a vortex mixer. Continue with step 6, substituting THF for 2-propanol and centrifuge tube for beaker.
6. Cover the beaker with a watchglass and agitate in an ultrasonic bath for at least 3 min. Observe the suspension to make sure that the agglomerated particles are broken up. Wash the underside of the

watchglass with 2-propanol, collecting the washings in the beaker.

7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel and apply vacuum. During filtration, rinse the beaker several times and add rinsings to the funnel.
8. Control the filtration rate to keep the liquid level in the funnel near the top during rinsing. Do not wash the walls or add 2-propanol to the funnel when the liquid level is lower than 4 cm above the filter. Leave the vacuum on after filtration to produce a dry filter. Remove the filter with forceps and mount it in the XRD sample holder.

CALIBRATION AND QUALITY CONTROL:

9. Prepare and analyze standard filters.
   a. Prepare two suspensions of each analyte in 2-propanol by weighing 10 and 50 mg of the standard material to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L of 2-propanol.
   b. Suspend the powder in 2-propanol with an ultrasonic probe or bath for 20 min. Immediately move the flask to a magnetic stirrer with thermally insulated top and add a stirring bar. Cool to room temperature before withdrawing aliquots.
   c. Mount a silver filter on the filtration apparatus. Place several mL of 2-propanol on the filter. Turn off the stirrer and shake vigorously by hand. Immediately remove the lid and withdraw an aliquot from the center at half-height of the 10 mg/L or 50 mg/L suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, discard the aliquot in a beaker, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the silver filter, keeping the tip of the pipet near the surface but not submerged in the delivered suspension.
   d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several times.
   e. Apply vacuum and rapidly filter the suspension. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the silver filter. Leave vacuum on until filter is dry. Transfer the silver filter to the diffractometer sample mount. Prepare working standard filters, in triplicate, at e.g., 20, 30, 50, 100, 200, and 500 µg.
   f. Analyze the working standards together with samples and blanks (step 12). The XRD intensities for the working standards (step 12.d) are designated I_x^o and are then normalized (step 12.e) to obtain $\hat{I}_x^o$. Correct the intensities of working standards >200 µg for matrix absorption (steps 12.f and 13).
   g. Prepare a calibration graph ($\hat{I}_x^o$, vs µg of each standard).

      NOTE: Poor repeatability (>10% above 0.04 mg silica) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/\sigma^2$ weighting) is preferable.
   h. Determine the slope, m, of the calibration graph in counts/µg. The intercept, b, on the abscissa should be within ± 5 µg of zero.

      NOTE: A large intercept indicates an error in determining the background, i.e., an incorrect baseline or interference by another phase.
10. NOTE: The following procedure for absorption correction is not necessary in situations that have been previously documented as requiring no corrections.

    Select six silver membrane filters as media blanks randomly from the same box of filters to be used for depositing the samples. These will be used to test for sample self-absorption. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL 2-propanol through the filter. Remove, let dry, and mount on XRD holders. Determine the net normalized count for the silver peak, $\hat{I}_{Ag}$, for each media blank (step 12). Obtain an average value for the six media blanks.

MEASUREMENT:

11. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80° 2θ) of the area air sample (or bulk settled dust) to determine the presence of free silica polymorphs and interferences (see APPENDIX). The expected diffraction peaks are:

	Peak (2-Theta Degrees)		
Mineral	Primary	Secondary	Tertiary
Quartz	26.66	20.85	50.16
Cristobalite	21.93	36.11	31.46
Tridymite	21.62	20.50	23.28
Silver	38.12	44.28	77.47

NOTE: There is an alternative to scanning an area air sample, settled dust sample, or ground bulk sample to prove lack of contamination. A slow scan of the three main peaks of quartz (also cristobalite and tridymite if their absence has not been previously confirmed) on a personal air sample, and verification that their intensity ratios are within 15% of pure quartz, is sufficient evidence that other materials are not interfering in the silica determination.

12. Perform the following for each sample, working standard, and blank filter:
    a. Mount the reference specimen. Determine the net intensity, I_r, of the reference specimen before and after each filter is scanned. Use a diffraction peak of high intensity that can be rapidly but reproducibly (S_r <0.01) measured.
    b. Mount the sample, working standard, or blank filter. Measure the diffraction peak area for each silica polymorph. Scan times must be long, e.g., 15 min (longer scan times will lower the limit of detection).
    c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
    d. Calculate the net intensity, I_x, (the difference between the peak integrated count and the total background count).
    e. Calculate and record the normalized intensity, $\hat{\imath}_x$, for each peak:

$$\hat{\imath}_x = \frac{I_x}{I_r} \cdot N.$$

NOTE: Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses. Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently-measured reference intensity.

    f. Determine the normalized count, $\hat{\imath}_{Ag}$, of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
    g. Field blanks may be analyzed by scanning the 2-theta range used for the analyte and silver peaks to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blank. Each laboratory should determine the specifics of field blank use for its application. When contamination does occur, the reason should be investigated and appropriate action taken. In practice, contamination of field blanks is extremely rare and usually is not consistent across filters. The analysis of blanks may be abbreviated if experience indicates that contamination is not likely with current field and laboratory operations; however, occasional confirmation of non-contamination is prudent.

CALCULATIONS:

13. Calculate the concentration of crystalline silica, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{\hat{\imath}_x \cdot f(t) - b}{m \cdot V}, \ \mathrm{mg/m^3}$$

$\hat{\imath}_x$ = normalized intensity for sample peak
b = intercept of calibration graph ($\hat{\imath}_x$ vs. W)

m = slope of calibration graph, counts/µg
f(t) = $-R \ln T/(1 - T^R)$ = absorption correction factor (Table 1)
R = $\sin(\Theta_{Ag})/\sin(\Theta_x)$
T = $\hat{I}_{Ag}$/(average $\hat{I}^{o}_{Ag}$) = transmittance of sample
$\hat{I}_{Ag}$ = normalized silver peak intensity from sample
average $\hat{I}^{o}_{Ag}$ = normalized silver peak intensity from media blanks (average of six values)

EVALUATION OF METHOD:

This method is based on P&CAM 259 which was collaboratively tested [1]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher (but not the use of THF), shipment of samples, ashing time, and ultrasonication time. None of these factors was found to have an effect. The method was shown to have no bias when referenced to the Talvitie spectrophotometric method [10] and when all standards and samples were Min-U-Sil 5. The relative standard deviations ($\hat{S}_r$) for intralaboratory, total measurement and overall (including sampling) variability are:

Measurement Precision, $\hat{S}_r$:	
Intralaboratory:	50 to 200 µg -- 0.08 [1]
	20 µg -- 0.20 [5]
	10 µg -- 0.28 [9]
Total (intra-and interlaboratory):	50 to 200 µg -- 0.17 [1]
Overall (Sampling & Measurement) Precision, $\hat{S}_{rT}$:	
Total (intra- and interlaboratory):	50 to 200 µg -- 0.29 [1]

REFERENCES:

[1] Anderson CC [9183]. Collaborative tests of two methods for determining free silica in airborne dust. U.S. Department of Health and Human Services, Publ. (NIOSH) 83-124.
[2] NIOSH [1983]. User check, UBTL, NIOSH Sequence #4121-M (unpublished)
[3] NIOSH [1974]. Criteria for a Recommended Standard: Occupational Exposure to Crystalline Silica. U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-120.
[4] NIOSH [1979]. Silica, crystalline: Method P&CAM 259. In: Taylor DG, ed., NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5., Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141.
[5] Ibid, Vol. 3, S315, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
[6] NIOSH [1977]. Documentation of the NIOSH Validation Tests. S315, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185.
[7] NIOSH [1977]. Silica (XRD): Method P&CAM 109. In: Taylor DG, ed., NIOSH Manual of Analytical Methods, 2nd ed., Vol. 1. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A.
[8] Bumsted HE [1973]. Determination of alpha-quartz in the respirable portion of airborne particles by X-ray diffraction. Am Ind Hyg Assoc. J *34*:150.
[9] Peters ET [1976]. Evaluation Of the NIOSH X-ray diffraction method for the determination of free silica in respirable dust. Final Report, NIOSH Contract CDC-99-74-51.
[10] Talvitie NA [1964]. Determination of free silica: gravimetric and spectrophotometric procedures applicable to airborne and settled dust. Am Ind Hyg Assoc J *25*:169-178.
[11] Kupel RE, Kinser RE, Mauer PA [1968]. Separation and analysis of the less than 10-micron fractions of industrial dusts. Am Ind Hyg Assoc J *29*:364.
[12] Talvitie NA [1951]. Determination of quartz in presence of silicates using phosphoric acid. Anal Chem *23* (4).
[13] Williams DD [1959]. Direct quantitative diffractometric analysis. Anal Chem *31*:1841.
[14] Abell MT, Dollberg DD, Crable JV [1981]. Quantitative analysis of dust samples from occupational environments using computer automated X-ray diffraction. Advances in X-Ray Analysis *24*:37.
[15] Abell MT, Dollberg DD, Lange BA, Hornung RW, Haartz JC [1981]. Absorption corrections in X-ray

diffraction dust analyses: procedures employing silver filters. Electron Microscopy and X-Ray Applications, V. 2, p. 115, Ann Arbor Science Publishers, Inc.
[16] Dollberg DD, Abell MT, Lange BA [1980]. Occupational health analytical chemistry: quantitation using x-ray powder diffraction. ACS Symposium Series, No. 120, 43.
[17] Altree-Williams S, Lee J, Mezin NV. Qualitative X-ray diffractometry on respirable dust collected on nuclepore filters. Ann Occup Health Hyg *20*:109.
[18] Leroux J, Powers C [1970]. Direct X-ray diffraction quantitative analysis of quartz in industrial dust films deposited on silver membrane filters. Occup Health Rev *21*:26.

METHOD REVISED BY:

Charles Lorberau, M. T. Abell, and D. D. Dollberg, Ph.D., NIOSH/DPSE.

APPENDIX: INTERFERENCES

Interferences include barite, micas (muscovite, biotite), potash, feldspars (microcline, plagioclase), montmorillonite, sillimanite, zircon, graphite, iron carbide, clinoferrosillite, wollastonite, sanidine, leucite, orthoclase, and lead sulfide.

The patterns for three forms of aluminum phosphate [JCPDS 10-423, 11-500, 20-44] are practically identical to those of quartz, cristobalite and tridymite, respectively. The quartz secondary and cristobalite primary peaks are close; cristobalite secondary peak is overlapped by a quartz peak; tridymite if present in sufficient quantity, will interfere with all of the main (primary, secondary and tertiary) quartz and cristobalite peaks. Silver chloride, if present on the silver filter, interferes slightly with the primary quartz peak. Many of these interferences occur in the presence of quartz; however, in a study of samples collected in 11 different industries, Altree-William [17] found no significant interferences.

The presence of elements such as iron can result in appreciable X-ray fluorescence which leads to high background intensity. A diffracted-beam monochromator will minimize this problem.

If calcite is present, loss of quartz will occur when samples are ashed in a muffle furnace. See SAMPLE PREPARATION (step 5.b) for procedure to remove calcite.

If interferences with the primary silica peak are present, use a less sensitive peak. When overlaps are not severe, a smaller receiving slit or chromium radiation may be used; however, a new calibration curve will be necessary.

Table 1. Absorption correction factor as a function of transmittance for some silica-silver peak combinations [13-18].

		f(T) (at indicated degrees 2-θ)							
Transmittance	Silica	26.66	26.66	20.83	20.83	21.93	21.93	21.62	21.62
T	Silver	38.12	44.28	38.12	44.28	38.12	44.28	38.12	44.28
1.00		1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.99		1.0071	1.0082	1.0091	1.0105	1.0087	1.0100	1.0088	1.0101
0.98		1.0144	1.0166	1.0184	1.0212	1.0174	1.0201	1.0177	1.0204
0.97		1.0217	1.0251	1.0278	1.0321	1.0264	1.0305	1.0268	1.0309
0.96		1.0292	1.0337	1.0373	1.0432	1.0355	1.0410	1.0360	1.0416
0.95		1.0368	1.0425	1.0470	1.0544	1.0447	1.0517	1.0453	1.0524
0.94		1.0445	1.0514	1.0569	1.0659	1.0541	1.0625	1.0548	1.0635
0.93		1.0523	1.0605	1.0670	1.0776	1.0636	1.0736	1.0645	1.0747
0.92		1.0602	1.0697	1.0772	1.0894	1.0733	1.0849	1.0743	1.0861
0.91		1.0683	1.0791	1.0876	1.1015	1.0831	1.0963	1.0844	1.0977
0.90		1.0765	1.0886	1.0982	1.1138	1.0932	1.1080	1.0945	1.1096
0.89		1.0848	1.0983	1.1089	1.1264	1.1034	1.1199	1.1049	1.1216
0.88		1.0933	1.1081	1.1199	1.1392	1.1137	1.1320	1.1154	1.1339
0.87		1.1019	1.1181	1.1311	1.1522	1.1243	1.1443	1.1261	1.1464
0.86		1.1106	1.1283	1.1424	1.1654	1.1350	1.1568	1.1370	1.1592
0.85		1.1195	1.1387	1.1540	1.1790	1.1460	1.1696	1.1481	1.1722
0.84		1.1286	1.1493	1.1657	1.1927	1.1571	1.1827	1.1595	1.1854
0.83		1.1378	1.1600	1.1777	1.2068	1.1685	1.1959	1.1710	1.1989
0.82		1.1471	1.1709	1.1899	1.2211	1.1800	1.2095	1.1827	1.2126
0.81		1.1566	1.1821	1.2024	1.2357	1.1918	1.2232	1.1946	1.2266
0.80		1.1663	1.1934	1.2150	1.2506	1.2038	1.2373	1.2068	1.2409
0.79		1.1762	1.2050	1.2280	1.2658	1.2160	1.2516	1.2192	1.2555
0.78		1.1863	1.2168	1.2411	1.2812	1.2284	1.2663	1.2319	1.2703
0.77		1.1965	1.2288	1.2546	1.2971	1.2411	1.2812	1.2447	1.2855
0.76		1.2069	1.2410	1.2683	1.3132	1.2540	1.2964	1.2579	1.3009
0.75		1.2175	1.2535	1.2822	1.3297	1.2672	1.3119	1.2713	1.3167
0.74		1.2283	1.2662	1.2965	1.3456	1.2806	1.3278	1.2849	1.3328
0.73		1.2394	1.2792	1.3110	1.3637	1.2944	1.3440	1.2989	1.3493
0.72		1.2506	1.2924	1.3259	1.3812	1.3084	1.3605	1.3131	1.3661
0.71		1.2621	1.3059	1.3410	1.3991	1.3226	1.3774	1.3276	1.3883
0.70		1.2738	1.3197	1.3565	1.4174	1.3372	1.3946	1.3424	1.4008
0.69		1.2857	1.3337	1.3723	1.4362	1.3521	1.4122	1.3576	1.4187
0.68		1.2979	1.3481	1.3885	1.4553	1.3673	1.4303	1.3730	1.4370
0.67		1.3103	1.3682	1.4050	1.4749	1.3829	1.4487	1.3888	1.4558
0.66		1.3230	1.3777	1.4218	1.4949	1.3987	1.4675	1.4050	1.4749
0.65		1.3359	1.3931	1.4390	1.5154	1.4150	1.4868	1.4215	1.4945
0.64		1.3491	1.4087	1.4567	1.5363	1.4316	1.5064	1.4383	1.5145
0.63		1.3626	1.4247	1.4747	1.5578	1.4485	1.5266	1.4556	1.5350
0.62		1.3765	1.4411	1.4931	1.5797	1.4659	1.5472	1.4732	1.5560
0.61		1.3906	1.4578	1.5120	1.6022	1.4836	1.5684	1.4913	1.5775
0.60		1.4050	1.4749	1.5314	1.6252	1.5018	1.5900	1.5098	1.5995
0.59		1.4198	1.4925	1.5511	1.6488	1.5204	1.6122	1.5287	1.6221
0.58		1.4349	1.5104	1.5714	1.6730	1.5394	1.6349	1.5481	1.6452
0.57		1.4504	1.5288	1.5922	1.6978	1.5590	1.6582	1.5679	1.6689
0.56		1.4662	1.5476	1.6135	1.7233	1.5790	1.6820	1.5883	1.6932
0.55		1.4824	1.5670	1.6353	1.7494	1.5995	1.7065	1.6092	1.7181
0.54		1.4991	1.6858	1.6577	1.7762	1.6205	1.7317	1.6306	1.7437
0.53		1.5161	1.6071	1.6807	1.8037	1.6421	1.7575	1.6525	1.7699
0.52		1.5336	1.6279	1.7043	1.8319	1.6642	1.7840	1.6751	1.7969
0.51		1.5515	1.6493	1.7285	1.8609	1.6870	1.8112	1.6982	1.8246
0.50		1.5699	1.6713	1.7534	1.8908	1.7103	1.8391	1.7220	1.8531