Designation: D5543 − 15

Standard Test Method for
Low-Level Dissolved Oxygen in Water[1]

This standard is issued under the fixed designation D5543; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the rapid determination of low-level (<100 µg/L) dissolved oxygen in thermal-cycle steam condensate, deaerated boiler feedwater, boiler water, and deaerated deionized water. Color comparators allow the estimation of concentrations ranging from 0 to 100 µg/L (ppb) oxygen.

1.2 This test method may be applicable to electronic-grade, pharmaceutical-grade, and other high-purity waters, although these were not addressed in the collaborative study.

1.3 It is the user's responsibility to ensure the validity of this test method for waters of untested matrices.

1.4 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1066 Practice for Sampling Steam
D1129 Terminology Relating to Water
D1193 Specification for Reagent Water
D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
D3370 Practices for Sampling Water from Closed Conduits
D5463 Guide for Use of Test Kits to Measure Inorganic Constituents in Water

3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D1129.

4. Summary of Test Method

4.1 The tip of a partially evacuated sealed ampoule is broken while submerged in a flowing water sample. The sample is drawn into the ampoule where it reacts instantaneously with the oxygen-sensitive indicator (leuco form of Rhodazine D) to produce a reddish violet color whose intensity is proportional to the concentration of dissolved oxygen.[3]

5. Significance and Use

5.1 Dissolved oxygen is detrimental in certain boiler and steam cycles because it may accelerate corrosion. Concentrations above 10 µg/L are unacceptable in many high-pressure boiler systems. The efficiency of dissolved oxygen removal from boiler feedwater by chemical or mechanical means, or both, is determined by measuring the concentration before and after the process. The measurement is also made to check for air leakage into the boiler system.

5.2 The oxygen treatment method for boiler corrosion reduction requires injection of oxygen into the boiler feedwater. The resulting oxygen level is monitored for control purposes.

6. Interferences

6.1 Color, turbidity, and oxidizing impurities interfere in this test method to yield high results. If the sample is colored or turbid or contains oxidizing impurities, the amount of interference that may be contributed by such effects must be determined independently prior to using this test method.

6.2 Easily reduced metal ions may interfere in this test method to cause high results. For example, 100 µg/L (ppb) Cu^{+2} may appear as 5 µg/L (ppb) dissolved oxygen, and 100 µg/L Fe^{+3} may appear as 7 µg/L dissolved oxygen. However, less than 50 µg/L Cu^{+2} or Fe^{+3} cause less than 1-µg/L interference.

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[1] These test methods are under the jurisdiction of ASTM Committee D19 on Water and are the direct responsibility of Subcommittee D19.03 on Sampling Water and Water-Formed Deposits, Analysis of Water for Power Generation and Process Use, On-Line Water Analysis, and Surveillance of Water.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Spokes, G. N., *Dissolved Oxygen in Water Measurement and Standardization*, EPRI PWR Plant Chemists' Meeting, San Diego, CA, Nov. 17–20, 1992. Copies obtainable from CHEMetrics Inc., 4295 Catlett Rd., Midland, VA 22728, https://www.chemetrics.com.

6.3 Hydrogen peroxide alone in concentrations up to 200 µg/L does not affect the measurement of 1.4 µg/L of dissolved oxygen. Above 200 µg/L hydrogen peroxide, there is a positive interference of 3.3 µg/L dissolved oxygen per 100 µg/L excess over 200 µg/L hydrogen peroxide.

6.4 The following interferences occur in the presence of 2200 mg/L boron present as boric acid: (*1*) at pH levels below pH 6, recovery can be as low as 80 %; (*2*) added hydrogen peroxide at a concentration of 0.1 mg/L yields a positive interference of 10 µg/L dissolved oxygen; and (*3*) added hydrogen peroxide in a concentration range from 0.5 to 650 mg/L yields a positive interference of 20 to 25 µg/L.

Note 1—Measurements of 0 to 100 µg/L of dissolved oxygen are unaffected by the presence of 2200 mg/L boron present as boric acid at pH 6 and above in the absence of hydrogen peroxide.

6.5 Benzoquinone, an oxidation product of hydroquinone, interferes with this test method. One hundred micrograms per litre of benzoquinone may appear as 33 µg/L dissolved oxygen.

6.6 Reducing agents such as hydrazine and sulfite do not interfere at 5-mg/L (ppm) levels in the sample.

6.7 Ampoules must be protected from light to prevent darkening. Follow the manufacturer's storage recommendations.

6.8 Color comparator tubes must be protected from light to prevent fading. Follow the manufacturer's storage recommendations.

7. Apparatus

7.1 *Color Comparator,* for 0, 2, 4, 6, 8, 12, 16, and 20 µg/L (ppb) of oxygen.

7.2 *Color Comparator,* for 0, 5, 10, 15, 20, 25, 30, and 40 µg/L (ppb) of oxygen.

7.3 *Color Comparator,* for 0, 10, 20, 30, 40, 60, 80, and 100 µg/L (ppb) of oxygen.

7.4 *Sampling Tube.* See Fig. 1.

8. Reagents and Materials

8.1 This test method does not require the preparation of any reagents. All the necessary analytical reagents are provided by the manufacturer in sealed ampoules.

8.2 *Purity of Water*—Reference to water shall mean water that meets or exceeds the quantitative specifications for Type II reagent water of Specification D1193, Section 1.1.

9. Precautions

9.1 Users should review the manufacturer's kit instructions before use.

10. Sampling

10.1 Sampling is the most critical part of any dissolved oxygen test. The sample stream must be completely leak-free, since even the smallest leak can elevate the oxygen level in the sample and cause large errors in the results. New or intermittently used sampling systems must be purged for a minimum of 4 h. Sample streams that are used routinely may require only a few minutes of purging.

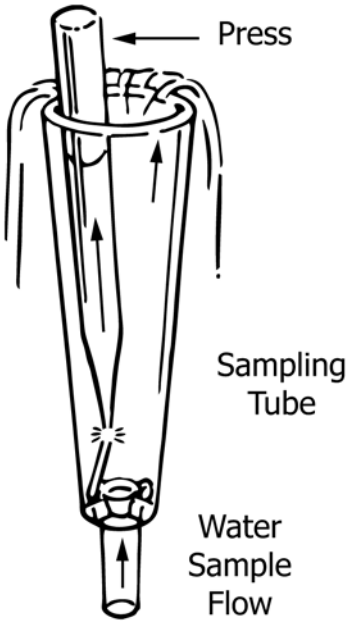

FIG. 1 Sampling Tube for Use with Ampoules to Measure Dissolved Oxygen in a Flowing Water Sample

10.2 Collect the samples in accordance with Practices D1066 and D3370.

10.3 With water under pressure, connect a tube of inert material to the inlet and extend the tube outlet to the bottom of the sample bottle or tube. Use stainless steel, Type 304 or 316, or glass tubing with short neoprene connections. Do not use copper tubing, long sections of neoprene tubing, or other types of elastomeric polymeric materials. If the water being sampled is above room temperature, the sample line shall contain a suitable cooling coil to cool it to approximate room temperature.

10.4 Attach the feedwater source to the plastic sampling tube as described in 10.3. Clamps may be attached to the tube to hold it vertical, or it can be attached to a vertical rod or pipe above a sink, drain, or bucket.

11. Calibration and Standardization

11.1 No calibration is required.

Note 2—The color comparator standards are precalibrated by the manufacturer for measurement of dissolved oxygen in water.

11.2 A dissolved-oxygen-in-water standard may be generated by following the procedures given in Appendix X1.

12. Procedure

12.1 Insert the ampoule into the sampling device, with the pointed end down. Allow the sample to flow at least 5 min. A 15-min wait time may be necessary to achieve the best accuracy for samples with below 20 µg/L of dissolved oxygen.

12.2 Gently press the ampoule toward the wall of the sampling tube to snap off the tip, and remove the ampoule, keeping the tip down, immediately after filling is complete.

12.3 Using a protective rubber finger cot, place a finger over the broken tip. (**Warning—**Glass may be sharp.) Invert the ampoule several times to mix the contents, allowing the bubble to travel from end to end each time. Wipe all liquid from the exterior of the ampoule.

NOTE 3—A small bubble of inert gas will remain in the ampoule to facilitate mixing.

NOTE 4—Due to the possibility of air leaking in during this step, it is advisable to run tests in duplicate. It should be noted, however, that some variation in observed concentrations may be due to changes in system conditions.

12.4 Use the color comparator as illustrated in Fig. 2 to determine the level of dissolved oxygen in the sample. Place the ampoule in the center (empty) tube of the comparator, with the flat end downward. Direct the top of the comparator toward a source of bright, white light while viewing from the bottom. Hold the comparator in a nearly horizontal position, and rotate it until the color standard below the ampoule shows the closest match. Complete this color matching procedure in less than 30 s after snapping the tip in the sample.

NOTE 5—The color intensity may continue to increase after the rapid initial color reaction. However, it is the initial color reaction that is complete within 30 s, and to which the system calibrations apply.

12.4.1 Find the analytical result from the concentration value of the closest matching color standard as designated on the comparator label. Estimate the concentration to within a half color standard interval.

13. Calculation

13.1 The dissolved oxygen content of the sample is the value obtained in 12.4.1. Use the average of the two resulting values if two ampoules are used.

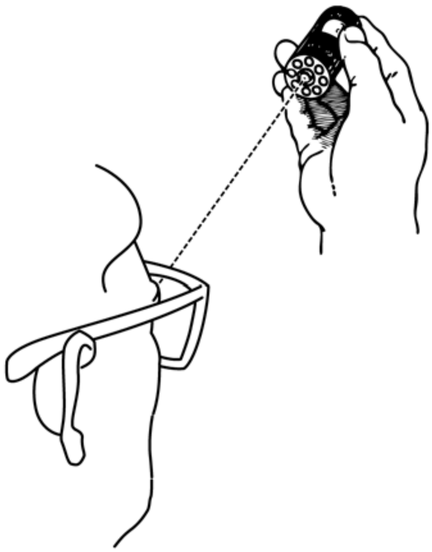

FIG. 2 Use of the Comparator

14. Precision and Bias[4]

14.1 The overall precision and bias of this test method cannot be determined by round-robin testing because of the instability of shipping solutions.

14.2 This test method was evaluated for single-operator precision by eight laboratories, with a total of 15 operators running a total of 200 samples in triplicate. The collaborative test data were obtained on the samples available at the laboratory site locations. These data may not apply for other matrices.

14.2.1 The single-operator precision, S_o, of this test method was found to be dependent on the ampoule type and to be partly dependent on the dissolved oxygen content of the sample. The data are summarized in the tables that follow.

14.2.1.1 The data in the following table were obtained using 0 to 20-µg/L (ppb) range ampoules and comparators.[5] A total of 66 samples was measured in triplicate by a total of 15 operators in 8 laboratories:

Range, µg/L (ppb)	0 to 0.9	1 to 4.9	5 to 9.9	10 to 14.9	15 to 20
S_o	0.20	1.6	2.5	1.4	3.2

14.2.1.2 The data in the following table were obtained using 0 to 40-µg/L (ppb) range ampoules and comparators.[6] A total of 78 samples was measured in triplicate by a total of 14 operators in 7 laboratories:

Range, µg/L (ppb)	0 to 1.9	2 to 9.9	10 to 19.9	20 to 29.9	30 to 40
S_o	0.15	1.4	2.8	2.7	2.2

14.2.1.3 The data in the following table were obtained using 0 to 100-ppb range ampoules and comparators.[7] A total of 56 samples was measured in triplicate by a total of 10 operators in 6 laboratories.

Range, µg/L (ppb)	0 to 4.9	5 to 19.9	20 to 39.9	40 to 59.9	60 to 100
S_o	0.95	1.1	1.4	5.3	2.9

14.3 Eight independent laboratories (and a total of fifteen operators) participated in this study. Precision testing for this test method conforms to Practice D2777.

15. Quality Control

15.1 Test kit quality control is the responsibility of the manufacturer. The manufacturer may be requested to furnish

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[4] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D19-1153. Contact ASTM Customer Service at service@astm.org.

[5] CHEMetrics Catalog No. K7511 kits or R7511 ampoule with a C7511 comparator The sole source of supply of the apparatus known to the committee at this time is CHEMetrics, Inc., 4295 Catlett Road, Midland, VA 20138, https://www.chemetrics.com. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee [1], which you may attend.

[6] CHEMetrics Catalog No. K7540 kits or R7540 ampoule with C7540 comparator. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters.

[7] CHEMetrics Catalog No. K7599 kits or R7540 or R7599 ampoule with a C7599 comparator. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters.

supporting quality control data. The user should verify that the final developed color in the snapped ampoule matches the hue of the color standards in the color comparator. If the color matching quality is poor, further investigation should be done to determine whether sample background color or sample matrix effects are a root cause and whether test results should be considered suspect. Refer to Guide D5463 for additional information about using test kits.

15.2 A procedure for generating dissolved oxygen in water standards is described in Appendix X1. However, it is likely that most analysts using the ppb dissolved oxygen test kit will not have gas standards available at their facility. Nonetheless some basic quality control steps that do not involve the use of gas standards are described below that serve to ensure dissolved oxygen test kit results are valid.

15.3 *Over-Range Calibration Verification:*

15.3.1 Snap an ampoule in a suitable snapping cup containing 25 mLs of water taken from a municipal drinking water supply or any other clean water supply that is not deaerated (that is, a sample that contains 2 – 14 ppm level of oxygen). Follow the steps given in 12.3 and 12.4.

15.3.2 The analytical result should exceed the highest color standard increment on the comparator.

15.4 *Under-Range Calibration Verification:*

15.4.1 Prepare 100 mL of a 0.4 M sodium sulfite solution: Dissolve 5 g of anhydrous sodium sulfite (Na_2SO_3) in 100 mL of reagent water.

15.4.2 Pour 25 mL of this solution in a suitable snapping cup. Allow the sample to sit undisturbed for 10 minutes.

NOTE 6—Failure to allow the Na_2SO_3 solution to sit undisturbed or agitating the sample prior to snapping the ampoule will cause false high bias.

15.4.3 Snap an ampoule in the Na2SO3 sample. Follow steps 12.3 and 12.4.

15.4.4 The analytical result should be nearly ≤ 5 ppb.

15.5 *Initial Demonstration of Laboratory Capability:*

15.5.1 If a laboratory has not performed the test before, or a new analyst is using the test kit, a precision and bias study should be conducted to demonstrate laboratory capability.

NOTE 7—A new analyst should practice snapping ampoules in the sampling device and reading them in the comparator in order to gain confidence with the procedure.

15.5.2 Snap three ampoules in quick succession in a flowing water sample. The three results should agree with one another to within two color standard increments.

15.6 *Laboratory Control Sample (LCS):*

15.6.1 Preparation of a LCS is possible only if gas standards are available. Refer to Appendix X1.

15.7 *Matrix Spike (MS):*

15.7.1 Dissolved oxygen is not an analyte that can be feasibly spiked into samples.

15.8 *Duplicate:*

15.8.1 To check the precision of sample analyses, follow the procedure given in 15.5.2.

15.9 *Independent Reference Material (IRM):*

15.9.1 Stable standards of dissolved oxygen in the ppb range are not commercially available.

16. Keywords

16.1 ampoules; boiler; boiler feedwater; colorimetric analysis; dissolved oxygen; oxygen; oxygen sensitive indicator; steam; steam condensate; petroleum refining; power generation

APPENDIX

(Nonmandatory Information)

X1. ESTABLISHMENT OF DISSOLVED OXYGEN IN WATER STANDARDS

X1.1 Dissolved oxygen-in-water standards may be made by bubbling oxygen-in-nitrogen gas mixtures through a water sample. The apparatus and procedures described in this appendix permit the inexpensive and easy establishment of dissolved oxygen-in-water standards of good quality. These standards may be used to check the accuracy of the self-filling ampoules and comparators.

X1.1.1 The dissolved oxygen concentration attained is determined by Henry's law: [8]

$$C(\mu g/L) = X(P - P_w)\exp \qquad (X1.1)$$

$$\{16.9775 - (5268.95 - 1004170/T)/T\}$$

The gas pressure is P(bar), the fraction of oxygen is X, and the absolute temperature is T kelvins. P_w(bar) is the water vapor pressure given by the following:

$$P_w = \exp\{11.857 - (3840.7 + 216961/T)/T\} \qquad (X1.2)$$

1-mm Hg pressure is equivalent to 0.001333 bar (0.1333 kPa).

X1.1.2 Ambient air pressure may be measured with an accurately calibrated barometer. It may also be determined from the barometric pressure recorded by a local weather station or airport, with a correction for the altitude difference between the laboratory and the weather station.

X1.2 Apparatus

X1.2.1 *Graduate,* cylindrical, 100 mL.

X1.2.2 *Aluminum Ampoule Snapper,* 254 mm.

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[8] Derived by J. M. Hale from B. B. Benson and D. Krause, Jr., *Limnol. Oceanogr.*, Vol 25, 1980, p. 662.

X1.2.3 *Square Plastic Tip Breaker.*

X1.2.4 *Gas Flow Meter,* equipped with needle valve, 0 to 2.5 L/min.

X1.2.5 *Compressed Gas Cylinder,* containing 5.66 m certified oxygen in nitrogen gas mixture(s) with pressure regulator adjustable to give 140 to 210 kPa.

X1.2.6 *Nylon Tubing,* 3-m length, 6.35-mm diameter.

X1.2.7 *Buret Stand and Clamps.*

X1.2.8 *Loose-Fitting Plastic Cap.*

X1.2.9 *Fritted Bubbler.*

X1.2.10 *Thermometer,* accurate to 0.2°C.

X1.2.11 *Barometer.*

X1.3 Cautions

X1.3.1 Use fresh water in a clean system. To obtain good results with this technique, use fresh water daily, and clean the graduate regularly with a dilute hypochlorite solution to prevent biological growth. Rinse thoroughly.

X1.3.2 Keep the system at atmospheric pressure. Do not permit pressure to build up in the graduate by, for example, putting tape or wax over openings in the cap. The system pressure and hence dissolved oxygen content will increase by approximately 1 % for each 102 mm of water pressure (1.00 kPa) that is applied. The high gas flow (20 mL/s) maintains a slight positive pressure in the graduate that is sufficient to prevent the ingress of atmospheric air.

X1.3.3 Avoid allowing bubbled gas to accumulate around the tip of the ampoule. Occasional agitation and tapping of the snapper on the bottom of the graduate can dislodge bubbles and prevent their occurrence near the ampoule tip. One millilitre of gas mixture typically contains more than 30 times as much oxygen as 1 mL of water in oxygen equilibrium. The reaction of oxygen with Rhodazine D is irreversible so that bubbles of gas aspirated accidentally into the ampoule can lead to an erroneous (high) determination.

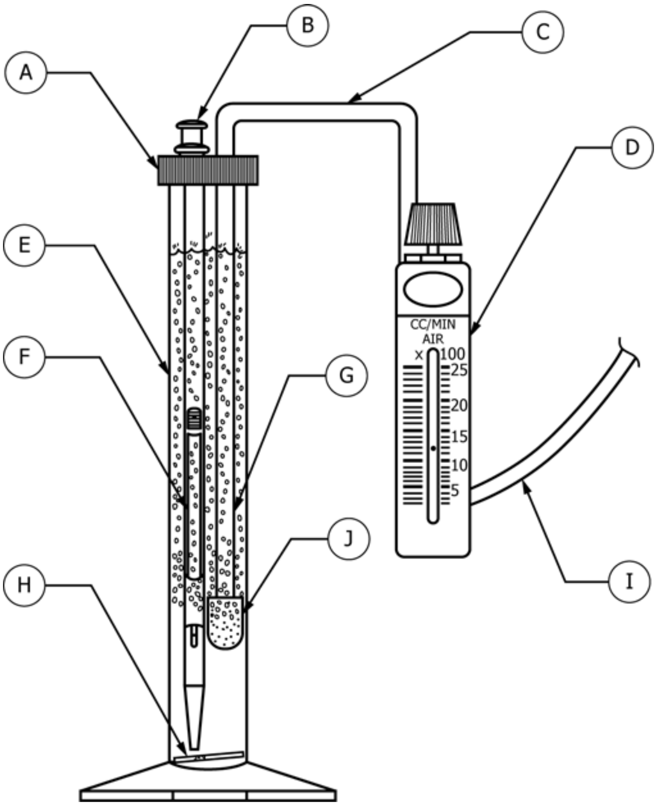
X1.3.4 Do not use oxygen scavenger chemicals. Oxygen scavenger chemicals prevent the achievement of equilibrium of oxygen and pure water, and the Henry's law (Eq X1.1) will not apply.

X1.4 Procedure

X1.4.1 Assemble the apparatus as shown in Fig. X1.1, with a thermometer in place of the 254-mm aluminum snapper. Clamp the graduate vertical and fill to 100-mL mark with deionized or distilled water. Ensure that the fritted bubbler is approximately 2 cm from the bottom of the graduate.

X1.4.2 Establish a gas flow of 15 to 25 mL/s. Sparge the water in the graduate for 20 to 30 min prior to making measurements. Measure the water temperature. Remove the thermometer.

X1.4.3 (When using ultra-low range 0 to 20-μg/L oxygen ampoules, skip to X1.4.4.) Place the self-filling ampoule tip down in the 254-mm aluminum snapper, and slowly lower the snapper assembly through the access hole in the cap to the bottom of the graduate. Ensure that the gas bubble stream does not pass immediately over the ampoule tip. Wait for 2 to 3 min and squeeze the syringe-like plunger of the snapper gently, thereby breaking the ampoule tip. Pause for a few seconds to allow the ampoule to fill with sample. Remove the snapper assembly from the graduate, and remove the ampoule from the assembly. Complete the quantification of dissolved oxygen within 30 s of snapping the tip.



Dissolved Oxygen Standard Parts List

Part	Description
A	Entry Cap
B	10 in. Aluminum Snapper
C	¼ in. Nylon Connection Tubing
D	Flow Meter
E	100 mL Measuring Cyclinder
F	Ampoule
G	Bubbler Connection Line
H	Tip Beaker Chip
I	Gas Mixture In
J	Bubbler

FIG. X1.1 Dissolved Oxygen Standard

X1.4.4 For 0 to 20-μg/L range ampoules, insert the ampoule tip down through the access hole in the cap and lower it to the bottom of the graduate. Wait 2 or 3 min, and use the edge of the square tip snapper at the bottom as a fulcrum against which to snap the tip. Pause until filling is complete. Then withdraw and quantitate according to step 12.4.

X1.4.5 Calculate the oxygen content of the water using the formulae of Eq X1.1 and Eq X1.2. The oxygen-in-nitrogen gas mixtures (ppm by volume) that will generate particular dissolved oxygen in water concentrations at 760-mm Hg (101.3 kPa) pressure are presented in Table X1.1.

TABLE X1.1 Oxygen-in-Nitrogen Mixtures ppm (by Volume) Required to Generate µg/L (ppb) Dissolved Oxygen Standards at 760-mm Hg (101.3 kPa) in Distilled Water

µg/L DO	15°C	20°C	25°C	30°C
10	208	230	253	277
20	415	461	507	554
30	623	691	760	831
40	831	921	1014	1108
60	1246	1382	1521	1662
80	1661	1843	2028	2216
100	2077	2303	2534	2770

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