Standard Test Methods for
Carbon Black—Surface Area By Nitrogen Adsorption[1]

This standard is issued under the fixed designation D 3037; 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.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope

1.1 These test methods cover the determination of the surface area of carbon blacks. The test methods appear in the following order:

	Sections
Test Method A—Surface Area by Ni-Count-1 Apparatus	9-14
Test Method B—Surface Area by Model 2200 Automatic Surface Area Analyzer	15-20
Test Method C—Surface Area by Continuous Flow Chromatography	21-27
Test Method D—Surface Area by Monosorb Surface Area Analyzer	28-35

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 Goal values for the standard reference blacks were determined by using Test Methods D 4820.

1.4 *This standard does not purport to address all of the safety problems, 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.* For specific precautionary statement, see Note 3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1799 Practice for Carbon Black—Sampling Packaged Shipments[2]

D 1900 Practice for Carbon Black—Sampling Bulk Shipments[2]

D 3324 Practice for Carbon Black—Improving Test Reproducibility Using ASTM Reference Blacks[2]

D 4483 Practice for Determining Precision for Test Method Standards in the Rubber and Carbon Black Industries[2]

D 4820 Test Methods for Carbon Black—Surface Area by Multipoint B.E.T. Nitrogen Adsorption[2]

3. Significance and Use

3.1 These test methods are used to measure the surface area of carbon black that is available to the nitrogen molecule.

4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[3] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean distilled water or water of equal purity.

5. ASTM D-24 Standard Reference Blacks

5.1 The apparatus shall be checked initially for correct calibration by testing the ASTM D-24 Standard Reference Blacks. These blacks shall be tested regularly, along with sample blacks, as described in Test Methods A through D. The standard value and range for each of the standard blacks, when tested by these test methods, is given in Practice D 3324.

5.1.1 In Test Methods A through D, all samples and standard blacks shall be dried for 1 h at 125°C before weighing. Cool and keep blacks in a well-maintained desiccator before taking

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[1] These test methods are under the jurisdiction of ASTM Committee D-24 on Carbon Black and are the direct responsibility of Subcommittee D24.21 on Adsorptive Properties of Carbon Black.

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[2] *Annual Book of ASTM Standards,* Vol 09.01.

[3] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

the weight. This precaution will minimize inaccuracies due to adsorbed water and other materials.

6. Sampling

6.1 Samples shall be taken in accordance with Practice D 1799 or D 1900.

7. Precision and Bias [4]

7.1 This precision and bias has been prepared in accordance with Practice D 4483. Refer to this practice for terminology and other statistical details.

7.2 The precision results in this precision and bias give an estimate of the precision as described below. The precision parameters should not be used for acceptance/rejection testing of any group of materials without documentation stating that they are applicable to those particular materials and the specific testing protocols that include this test method.

7.3 A Type 1 interlaboratory precision program was conducted. Both repeatability and reproducibility represent short term testing conditions. Six laboratories tested the six standard reference blacks (A4 to F4) twice on each of two different days. Therefore, $p = 6$, $q = 6$, and $n = 4$. A test result is the value obtained from a single determination. Acceptable difference values were not measured.

7.4 The results of the precision calculations are given in Table 1 with the materials arranged in ascending mean level order of the surface area by nitrogen adsorption.

7.5 The precision for the pooled values for surface area by nitrogen adsorption may be expressed as follows:

7.5.1 *Repeatability*—The repeatability, (r), of the nitrogen surface area adsorption has been established as 1.62 %. Two single test results (or determinations) that differ by more than 1.62 % must be considered suspect and dictates that some appropriate investigative action be taken.

7.5.2 *Reproducibility*—The reproducibility, (R), of the nitrogen surface area adsorption has been established as 4.59 %. Two single test results (or determinations) produced in separate laboratories that differ by more than 4.59 % must be considered as suspect and dictates that appropriate investigation or technical/commercial actions be taken.

7.6 *Bias*—In test method terminology, bias is the difference between an average test value and the reference (true) test property value. Reference values do not exist for these test methods since the value or level of the test property is exclusively defined by these test methods. Bias, therefore, cannot be determined.

8. Keywords

8.1 carbon black; continuous flow chromatography; surface area analyzer; surface area by nitrogen absorption

TEST METHOD A—SURFACE AREA BY NI-COUNT-1 APPARATUS

9. Apparatus

9.1 *Ni-Count-1 Specific Surface Area Apparatus*[5] (Fig. 1, Fig. 2, and Fig. 3), or an equivalent one-point adsorption apparatus. (See Fig. 4 for installation diagram.)

9.2 *Heater and Voltage Control Device*, to maintain a temperature of 300 ± 10°C for degassing the samples. The heater (Fig. 1) is furnished with the Ni-Count-1 apparatus.

9.3 *Vacuum Pump*, capable of ultimate pressure of 1.3 Pa (1×10^{-2} mm Hg abs).

9.4 *Dewar Flask*, 265-cm³ capacity, approximately 145 mm high (supplied with the Ni-Count-1 apparatus).

9.5 *Nitrogen Vapor Pressure Thermometer*, a part of the Ni-Count-1 apparatus (Fig. 2).

9.6 *Sample Tubes* (Fig. 5).

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[4] Supporting data are available from ASTM Headquarters. Request RR: D24–1021.

[5] The Ni-Count-1 is developed by Phillips Petroleum Co. and is available from Chandler Engineering Co., 7707 E. 38th St., Tulsa, OK.

TABLE 1 Precision Values—Type 1[A]

NOTE 1—Symbols are defined as follows:
Sr = within laboratory standard deviation,
r = repeatability, measurement units
(r) = repeatability, %
SR = between laboratory standard deviation,
R = reproducibility, measurement units
(R) = repeatability, %

Material	Mean Level, 10³m²/kg (m²/g)	Within Laboratories[B]			Between Laboratories[B]		
		Sr	r	(r)	SR	R	(R)
D-4 (N 762)	24.31	0.123	0.349	1.452	0.343	0.971	4.046
E-4 (N 660)	34.85	0.270	0.764	2.193	0.579	1.638	4.700
F-4 (N 683)	38.62	0.205	0.580	1.502	0.707	2.000	5.180
B-4 (N 330)	75.40	0.529	1.498	1.997	0.770	2.180	2.906
A-4 (N 326)	77.83	0.263	0.744	0.956	0.586	1.660	2.133
C-4 (N 121)	126.61	0.547	1.549	1.223	2.091	5.917	4.673
Pooled or Averaged Values	62.94	0.36	1.02	1.62	1.02	2.89	4.59

[A] This is short-term precision (days) where: $p = 6$, $q = 6$, and $n = 4$.
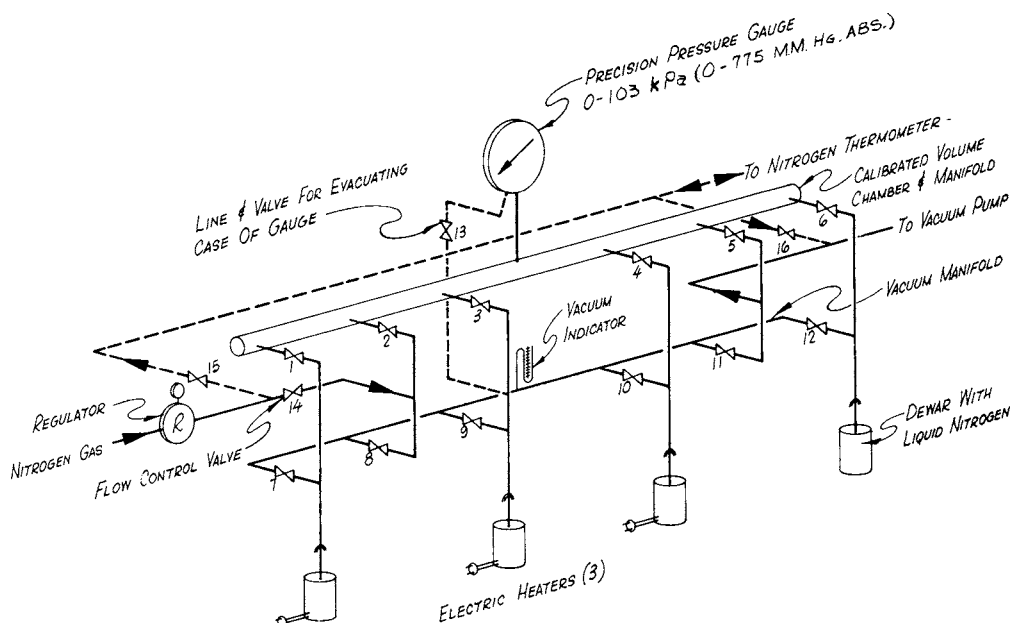[B] Report repeatability and reproducibility in percent.

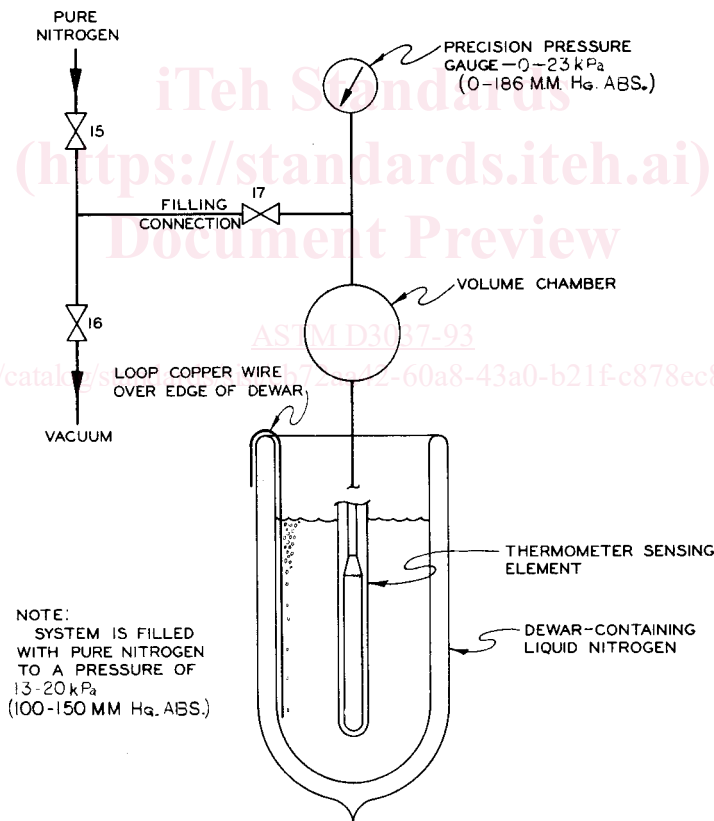**FIG. 1 Ni-Count-1 Apparatus with Provision for Four Samples**

FIG. 2 Nitrogen Thermometer

9.7 *Stopcock Grease,*[6] or polychlorotrifluoroethylene lubricant, supplied with Ni-Count-1 apparatus.

9.8 *Analytical Balance*, with 0.1-mg sensitivity.

9.9 *Fine Glass Wool.*

9.10 *Convection Oven*, capable of maintaining 125 ± 5°C.

9.11 *Desiccator.*

9.12 Supply of small flat-bottom vials for drying blacks.

10. Reagents

10.1 *Liquid Nitrogen*, approximately 300 cm^3/sample.

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[6] Spectro-Vac Stopcock Grease, Type 2, available from Robert R. Austin, Ph.D., P. O. Box 5374, Pasadena, CA 91107, has been found satisfactory.
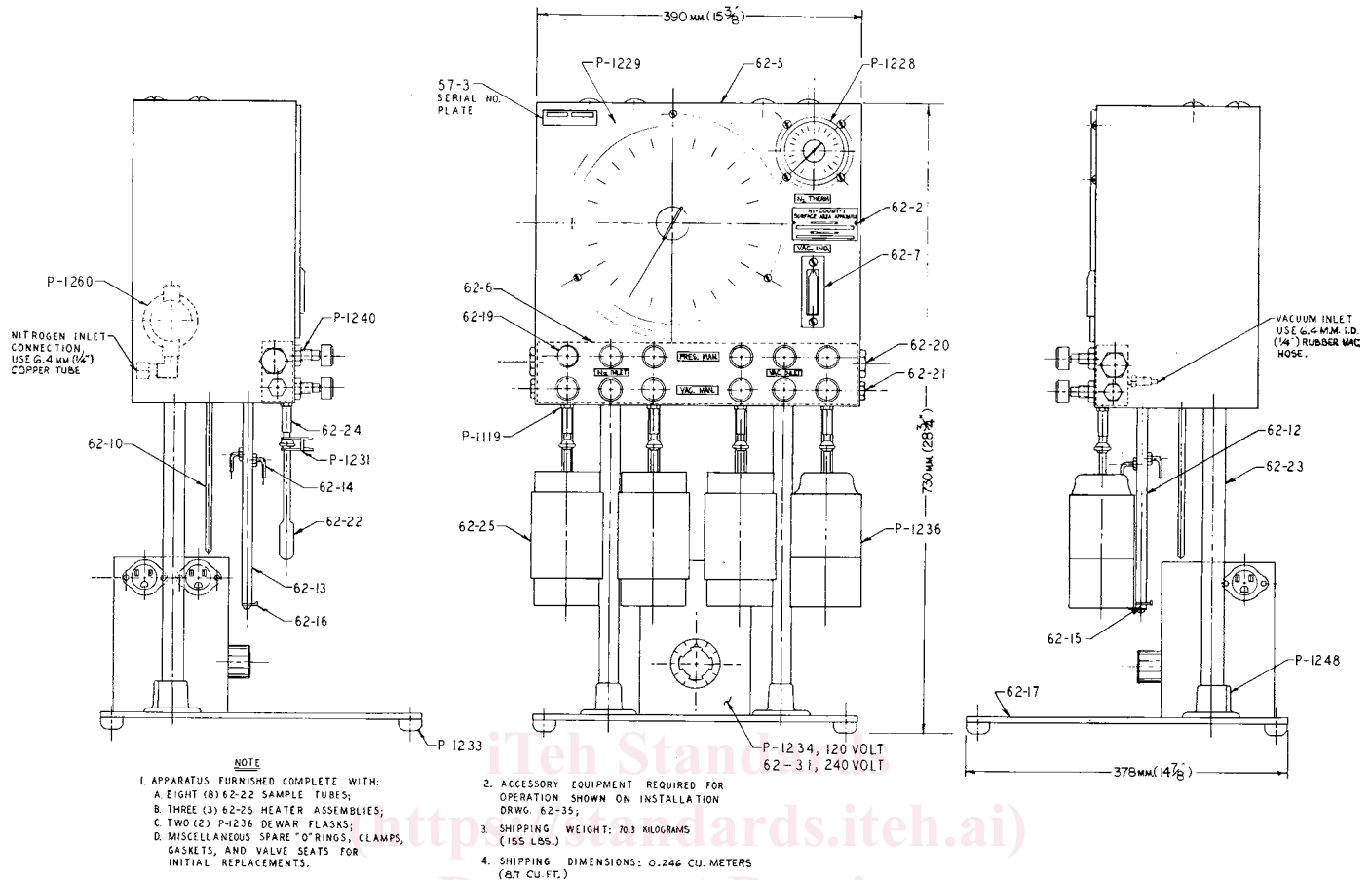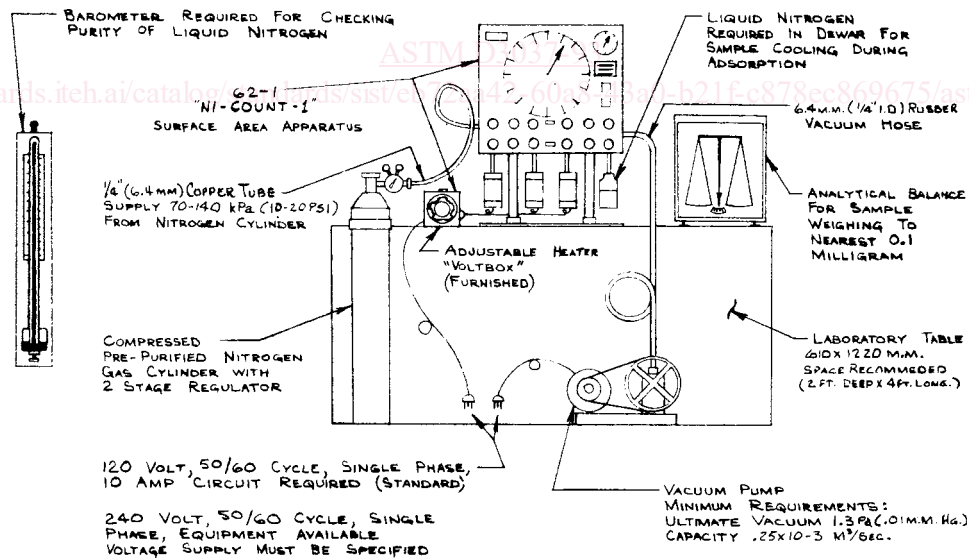
FIG. 3 Ni-Count-1 Apparatus

FIG. 4 Installation of the Surface Area Apparatus

10.2 *Nitrogen Gas*, cylinder or other source of prepurified nitrogen gas.

11. Preparation and Calibration of Apparatus

11.1 The all metal Ni-Count-1 apparatus has an adjusted internal volume of 139.5 cm^3. This internal volume includes all lines to the sample valve, and the volume in the bellows of the pressure gage so positioned that the gage indicates 66.7 kPa (500 mm Hg abs pressure). The tables of surface area versus pressure furnished with the Ni-Count-1 will yield accurate specific surface areas, if the internal volume of the instrument has been accurately adjusted at the factory to 139.5 cm^3.
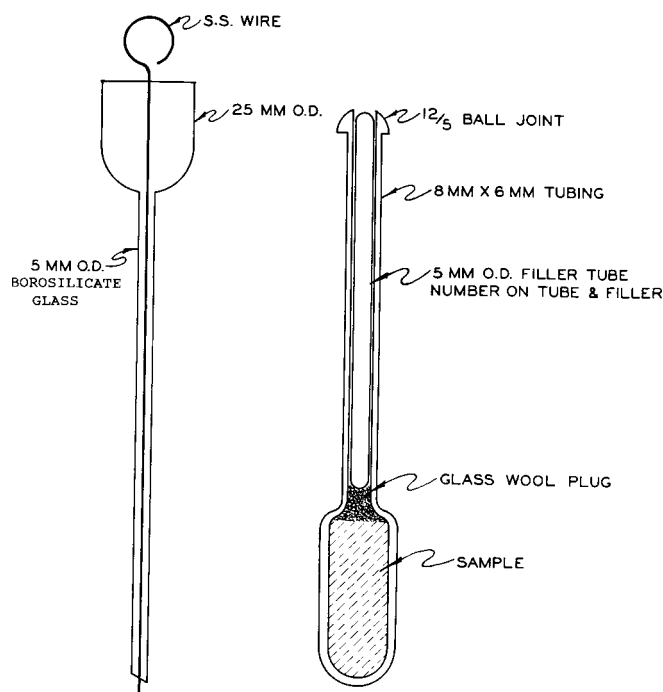
FIG. 5 Loading Funnel and Glass Sample Tube

Checking the ASTM D-24 Standard Reference Blacks, presented in Practice D 3324, is an essential step to confirm initial instrument calibration and is required each time a set of samples is to be run, as described in Section 12.

11.2 The Ni-Count-1 apparatus should be prepared as specified in the instructions furnished with the apparatus. This includes filling the vapor pressure thermometer with prepurified nitrogen gas, evacuating the case of the large pressure gage and closing the case valve, flushing the reservoir and vacuum manifolds with nitrogen several times until any air is eliminated, and setting the voltage on the heaters to maintain a temperature of 300 ± 10°C as measured with a thermometer in the heater well.

12. Procedure

12.1 In order to standardize results, use the data in Table 2 as a guide, select a sample tube, and place in it the suggested weight of the appropriate pre-dried (see 5.2) D-24 Standard

TABLE 2 Recommended Sample Tube Volumes and Sample Masses for Common Grades of Pressed and Pelleted Carbon Blacks

ASTM Series No.	Approximate Surface Area, m²/g	Tube Volume		Sample Mass, g
		Pressed, cm³	Pelleted, cm³	
N-900	20 to 6	15 to 30	10 to 25	10 to 15
N-600	30	22	11	5.3
N-500	44	18	9	3.6
N-300	80	10	5.5	2.0
N-200	110	7.5	4.5	1.5
N-100	140	5.0	3.5	1.1

Reference Black (one which is a reasonable surface area match for the sample blacks to be run). Proceed in accordance with instructions, skipping 12.1.1 and substituting the word "standard" for the word "sample" in 12.2-14.1.2.

12.1.1 Using the data in Table 2 as a guide, select a sample tube and fill it with the suggested mass of pre-dried black. If the identity of the black is not known, make a preliminary run to determine the mass of black to give an adsorption pressure between 20.0 and 33.3 kPa (150 and 250 mm Hg abs).

12.2 Prepare a tuft of glass wool of suitable size to support the filler tube in the sample tube stem. Record the mass to 0.1 mg.

12.3 Prepare a clean dry sample tube with its filler and glass wool tuft. Record the mass to 0.1 mg.

12.4 Roughly weigh the amount of sample to be placed in the sample tube. (This mass will not be used.)

12.5 Place the sample in the tube, introduce the tuft of glass wool, and shove in the filler rod to its proper position.

12.6 Lubricate the ball joint of the sample tube sparingly with high-vacuum grease, taking care not to place lubricant inside the stem. Wring the sample tube ball into the mating metal receptacle on the Ni-Count-1 apparatus and retain the sample tube in place with the metal spring clip.

12.7 Start the evacuation of the sample tube and raise the heater into place around the tube.

12.8 Several times during the evacuation, purge the sample momentarily with the nitrogen gas.

12.9 Close the vacuum valve and observe the leak detector to determine whether gases are still evolving from the sample. When the sample is properly degassed, the leak indicator should not show a change of pressure greater than 0.1 kPa (1 mm Hg) in 5 min.

12.10 Isolate the degassed sample from the vacuum manifold by closing the valve. Remove the heater.

12.11 Fill the purged reservoir, gage, and manifold with nitrogen gas to 66.6 kPa (500 mm Hg abs pressure), if the room temperature is 27°C. If the room temperature is not 27°C, add 0.222 kPa (1.67 mm Hg) pressure for each degree C above 27°C. Subtract the correction if the temperature is below 27°C.

12.12 Open the valve to the sample tube from the reservoir and gage.

12.13 Place the Dewar flask filled with liquid nitrogen around the sample tube.

12.14 Permit the adsorption to proceed until the pressure becomes constant. Observe and record the pressure to the nearest 1 mm Hg (see 12.9).

12.15 Lower the Dewar flask of liquid nitrogen away from the sample tube and place it around the sensing element of the nitrogen thermometer.

12.16 Observe the pressure gage on the nitrogen thermometer and record the pressure to the nearest 0.1 kPa (1 mm Hg).

12.17 Allow the sample tube to warm up above the temperature of water vapor condensation on the tube. A heat gun may be used to hasten the warming process.

12.18 Add nitrogen gas to the reservoir and sample tube until the pressure gage reads approximately 1.3 kPa (10 mm Hg) above the barometric pressure.

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12.19 Remove the sample tube from the apparatus, read the pressure gage for the barometric pressure, and record the pressure to nearest 0.1 kPa (1 mm Hg). Add the value obtained in 12.16 to the barometric pressure to obtain T_N for use in Table 3 to obtain the liquid nitrogen temperature correction factor, B.

12.20 Wipe away the vacuum grease from the ball of the sample tube as thoroughly as possible, weigh the tube, and record the mass. This step is very important because a small residue of grease could cause a significant error, especially when analyzing high-area blacks.

13. Calculation

13.1 Calculate the specific surface area, S_w, as follows:

$$S_w = [(S/W)(1 - F(V_T - V_{DT} - V_{GW} - W/d))B] \quad (1)$$

where:
S = value of surface area for the equilibrium pressure obtained from Table 4 for Ni-Count-1,
W = mass of dry black sample, g,
F = correlating factor from Table 4,
V_T = volume of sample tube with filler, cm^3,

TABLE 3 Liquid Nitrogen Temperature Correction Factor

Temperature factor $= 1 + 0.0573[(T_N - 98.7 (740) +)/(13.3 (100) +)] = B$

where:
T_N = vapor pressure of liquid nitrogen (N_2), kPa (mm Hg) by N_2 vapor pressure thermometer, and
98.7 kPa (740 mm Hg) = barometric pressure during calibration of apparatus to determine S versus equilibrium pressure.
    Parenthetical values are to be substituted for preceding numbers when using metric units.

T_N mm Hg	T_N kPa	B	T_N mm Hg	T_N kPa	B	T_N mm Hg	T_N kPa	B	T_N mm Hg	T_N kPa	B
660	88.0	0.95416	695	92.7	0.97422	730	97.3	0.99427	765	102.0	1.01432
661	88.1	0.95473	696	92.8	0.97479	731	97.5	0.99484	766	102.1	1.01490
662	88.3	0.95531	697	92.9	0.97536	732	97.6	0.99542	767	102.3	1.01547
663	88.4	0.95588	698	93.1	0.97593	733	97.7	0.99599	768	102.4	1.01604
664	88.5	0.95645	699	93.2	0.97651	734	97.9	0.99656	769	102.5	1.01662
665	88.7	0.95703	700	93.3	0.97708	735	98.0	0.99714	770	102.7	1.01719
666	88.8	0.95760	701	93.5	0.97765	736	98.1	0.99771	771	102.8	1.01776
667	88.9	0.95817	702	93.6	0.97823	737	98.3	0.99828	772	102.9	1.01834
668	89.1	0.95874	703	93.7	0.97880	738	98.4	0.99885	773	103.1	1.01891
669	89.2	0.95932	704	93.9	0.97937	739	98.5	0.99943	774	103.2	1.01948
670	89.3	0.95989	705	94.0	0.97995	740	98.7	1.00000	775	103.3	1.02005
671	89.5	0.96046	706	94.1	0.98052	741	98.8	1.00057	776	103.5	1.02063
672	89.6	0.96104	707	94.3	0.98109	742	98.9	1.00115	777	103.6	1.02120
673	89.7	0.96161	708	94.4	0.98166	743	99.1	1.00172	778	103.7	1.02177
674	89.9	0.96218	709	94.5	0.98224	744	99.2	1.00229	779	103.9	1.02235
675	90.0	0.06276	710	94.7	0.98281	745	99.3	1.00286	780	104.0	1.02292
676	90.1	0.96333	711	94.8	0.98338	746	99.5	1.00344	781	104.1	1.02349
677	90.3	0.96390	712	94.9	0.98396	747	99.6	1.00401	782	104.3	1.02407
678	90.4	0.96447	713	95.1	0.98453	748	99.7	1.00458	783	104.4	1.02464
679	90.5	0.96505	714	95.2	0.98510	749	99.9	1.00516	784	104.5	1.02521
680	90.7	0.96562	715	95.3	0.98568	750	100.0	1.00573	785	104.7	1.02578
681	90.8	0.96619	716	95.5	0.98625	751	100.1	1.00630	786	104.8	1.02636
682	90.9	0.96677	717	95.6	0.98682	752	100.3	1.00688	787	104.9	1.02693
683	91.1	0.96734	718	95.7	0.98739	753	100.4	1.00745	788	105.1	1.02750
684	91.2	0.96791	719	95.9	0.98797	754	100.5	1.00802	789	105.2	1.02808
685	91.3	0.96849	720	96.0	0.98854	755	100.7	1.00859	790	105.3	1.02865
686	91.5	0.96906	721	96.1	0.98911	756	100.8	1.00917	791	105.5	1.02922
687	91.6	0.96963	722	96.3	0.98969	757	100.9	1.00974	792	105.6	1.02980
688	91.7	0.97020	723	96.4	0.99026	758	101.1	1.01031	793	105.7	1.03037
689	91.9	0.97078	724	96.5	0.99083	759	101.2	1.01089	794	105.9	1.03094
690	92.0	0.97135	725	96.7	0.99141	760	101.3	1.01146	795	106.0	1.03151
691	92.1	0.97192	726	96.8	0.99198	761	101.5	1.01203	796	106.1	1.03209
692	92.3	0.97250	727	96.9	0.99255	762	101.6	1.01261	797	106.3	1.03266
693	92.4	0.97307	728	97.1	0.99312	763	101.7	1.01318	798	106.4	1.03323
694	92.5	0.97364	729	97.2	0.99370	764	101.9	1.01375	799	106.5	1.03381