Designation: D 2010/D 2010M – 98

Standard Test Methods for Evaluation of Total Sulfation Activity in the Atmosphere by the Lead Dioxide Technique[1]

This standard is issued under the fixed designation D 2010/D 2010M; 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 describe the evaluation of the total sulfation activity in the atmosphere. Because of its oxidizing power, lead dioxide (PbO_2) converts not only sulfur dioxide (SO_2), but other compounds, such as mercaptans and hydrogen sulfide, into sulfate. It fixes sulfur trioxide and sulfuric acid mist present in the atmosphere (see Note 1).

1.2 Test Method A describes the use of a PbO_2 candle, and Test Method B describes that of a PbO_2 sulfation plate.[2]

1.3 These test methods provide a weighted average effective SO_2 level for a 30-day interval.

1.4 The results of these test methods correlate approximately with volumetric SO_2 concentrations, although the presence of dew or condensed moisture tends to enhance the capture of SO_2 onto the candle or plate.

1.5 The values stated in SI units shall be regarded as the standard. The values given in parentheses are for information only and may be approximate.

NOTE 1—It has been shown that the rate constant of the chemical reaction between SO_2 and PbO_2 is independent of the concentration of SO_2 up to levels of 1000 ppm(v), if 15 % or less of the PbO_2 has been reduced **(1)**.[3] 15 % of the PbO_2 is equivalent to 11 to 12 mg of SO_2/cm^2 per day.

1.6 *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.* For specific precautionary statements, see Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 516 Test Method for Sulfate Ion in Water[4]
D 1193 Specification for Reagent Water[4]
D 1356 Terminology Relating to Sampling and Analysis of Atmospheres[5]
D 1357 Practice for Planning the Sampling of the Ambient Atmosphere[5]
G 91 Practice for Monitoring Atmospheric SO_2 Using the Sulfation Plate Technique[6]

3. Terminology

3.1 *Definitions*—For definitions of terms used in these test methods, refer to Terminology D 1356.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *sulfation*—the process by which sulfur-containing compounds are oxidized by the action of PbO_2.

3.2.2 *sulfation activity*—the capture rate of sulfur-containing compounds as they are oxidized by PbO_2 under the conditions of these test methods.

4. Summary of Test Methods

4.1 *Test Method A*—Inert cylinders are coated with PbO_2 paste and exposed to the atmosphere for an extended period of time, usually one month. Sulfur oxides react chemically with the paste, forming lead sulfate ($PbSO_4$) **(1-5)**.

4.2 *Test Method B*—Sulfation plates consisting of a PbO_2 paste in an inverted dish are likewise exposed to the atmosphere **(6)**.

4.3 *Test Methods A and B*—The cylinders or plates are returned to a laboratory after the sampling period; the paste is removed and suspended in hot sodium carbonate (Na_2CO_3) solution to dissolve the $PbSO_4$ and convert the sulfate to soluble sodium sulfate (Na_2SO_4). The Na_2SO_4 solution is separated from the PbO_2 slurry by filtration. The sulfate is determined by precipitation with barium chloride ($BaCl_2$) **(7)**.

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[1] These test methods are under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmosphere and are the direct responsibility of Subcommittee D22.03 on Ambient Atmospheres and Source Emissions.

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[2] Test Method B has been adapted from Test Method G 91, which is under the jurisdiction of ASTM Committee G-1 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.04 on Atmospheric Corrosion.

[3] The boldface numbers in parentheses refer to the list of references at the end of this standard.

[4] *Annual Book of ASTM Standards*, Vol 11.01.

[5] *Annual Book of ASTM Standards*, Vol 11.03.

[6] *Annual Book of ASTM Standards*, Vol 03.02.

4.4 The chemistry of the process is illustrated, for the case of SO_2, in the following reactions:

$$PbO_2 + SO_2 \rightarrow PbSO_4$$

$$PbSO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + PbCO_3$$

$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4\downarrow + 2\,NaCl$$

5. Significance and Use

5.1 Sulfur oxide gases are produced during the combustion of materials containing sulfur. These gases are precursors of atmospheric sulfuric acid, which has been shown to be injurious to living creatures and plants, as well as some inanimate materials such as metals, limestone and sandstone building materials.

5.2 Sulfur dioxide is moderately toxic and strongly phytotoxic to many species. Permissible ambient levels of SO_2 have been established by law.

5.3 When it is necessary to establish whether ambient air concentrations of sulfuric acid precursors, such as sulfur oxides, are present and to comply with legal criteria, manual and automatic monitoring systems specific for the individual sulfur species are used. Likely locations for monitoring sites for the estimation of concentrations and concentration trends over long periods of time can be screened conveniently using the PbO_2 candles or sulfation plates.

5.4 Atmospheric corrosion of metallic materials is a function of many weather and atmospheric variables. The effect of specific corrodants, such as SO_2, can accelerate the atmospheric corrosion of metals or structures significantly. The PbO_2 candle and sulfation plate test methods provide simple techniques to monitor SO_2 levels in the atmosphere independently to yield a weighted average result.

5.5 The results of these test methods are useful for characterizing atmospheric corrosion test sites regarding the effective average concentrations of SO_2 in the atmosphere at these locations.

5.6 These test methods are useful for determining microclimatic seasonal and long-term variations in effective average SO_2 concentrations.

5.7 The results of these test methods may be used in correlations of atmospheric corrosion rates with atmosphere data to determine the sensitivity of the corrosion rate to the SO_2 level.

5.8 These test methods may also be used with other test methods to characterize the atmosphere at sites at which buildings or other construction are planned in order to determine the extent of protective measures required for the materials of construction.

6. Apparatus

6.1 *Test Method A*:

6.1.1 *Lead Dioxide Candle*—An inert cylinder with a surface area of approximately 100 cm^2, covered with a fabric and coated with PbO_2 paste. See Appendix X1 for preparation of the candle.

6.1.2 *Sampling Apparatus*—This may be a louvered enclosure, such as a cylinder or a rectangular box. If cylindrical, it shall be not less than 20-cm (8-in.) high and 18-cm (7-in.) in diameter; if rectangular, it shall be not less than 20 by 20 by 20 cm (8 by 8 by 8 in.). Position the louvers at an angle of $\pi/4$ (45°) to provide maximum protection from the rain. Construct the enclosure of an inert material, such as plastic or wood. Do not coat the enclosure with a lead based paint. The sampling apparatus shall have provisions to hold the PbO_2 candle in a vertical position.

6.2 *Test Method B*:

6.2.1 *Sulfation Plate*—A polystyrene or polycarbonate culture (petri) dish, 50 or 60 mm in diameter, containing a filter paper disc, coated with PbO_2 paste. See X1.2 for preparation of the sulfation plate.

6.2.2 *Bracket*, to hold the plates securely in an inverted position so that the PbO_2 mixture faces downward. The bracket design shall include a retaining clip or other provision to hold the plate in the event of strong winds. The retainer clip may be made from stainless steel, spring bronze, hard aluminum alloy (3003H19), or other alloys with sufficient strength and atmospheric corrosion resistance. A typical bracket design is shown in Fig. 1.

7. Reagents and Materials

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, except where such reagents are not available.[7]

7.2 *Purity of Water*—References to water shall be understood to mean reagent water as defined by Type II of Specification D 1193.

7.3 *Acetone*—Reagent grade.

7.4 *Barium Chloride Solution* (50 g/L)—Dissolve 59 g of barium chloride dihydrate ($BaCl_2 \times 2H_2O$) in water and dilute to 1 L.

7.5 *Ethyl Alcohol* (95 %).

7.6 *Gum Tragacanth*, powdered.

7.7 *Hydrochloric Acid* (sp gr 1.19)—Concentrated hydrochloric acid (HCl).

7.8 *Hydrochloric Acid* (2 *N)*—Dilute 171 mL of concentrated HCl to 1 L.

7.9 *Hydrochloric Acid (0.05 N)*—Dilute 25 mL of 2 *N* HCl to 1 L.

7.10 *Lead Dioxide (Powdered)*—PbO_2 of the highest purity.

7.11 *Sodium Carbonate Solution* (83.3 g/L)—Dissolve 83.3 g of anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 L.

7.12 *Methyl Orange Indicator* (0.1 %)—Dissolve 100 mg in water and dilute to 100 mL.

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[7] *Reagent Chemicals, American Chemical Society Specifications,* American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

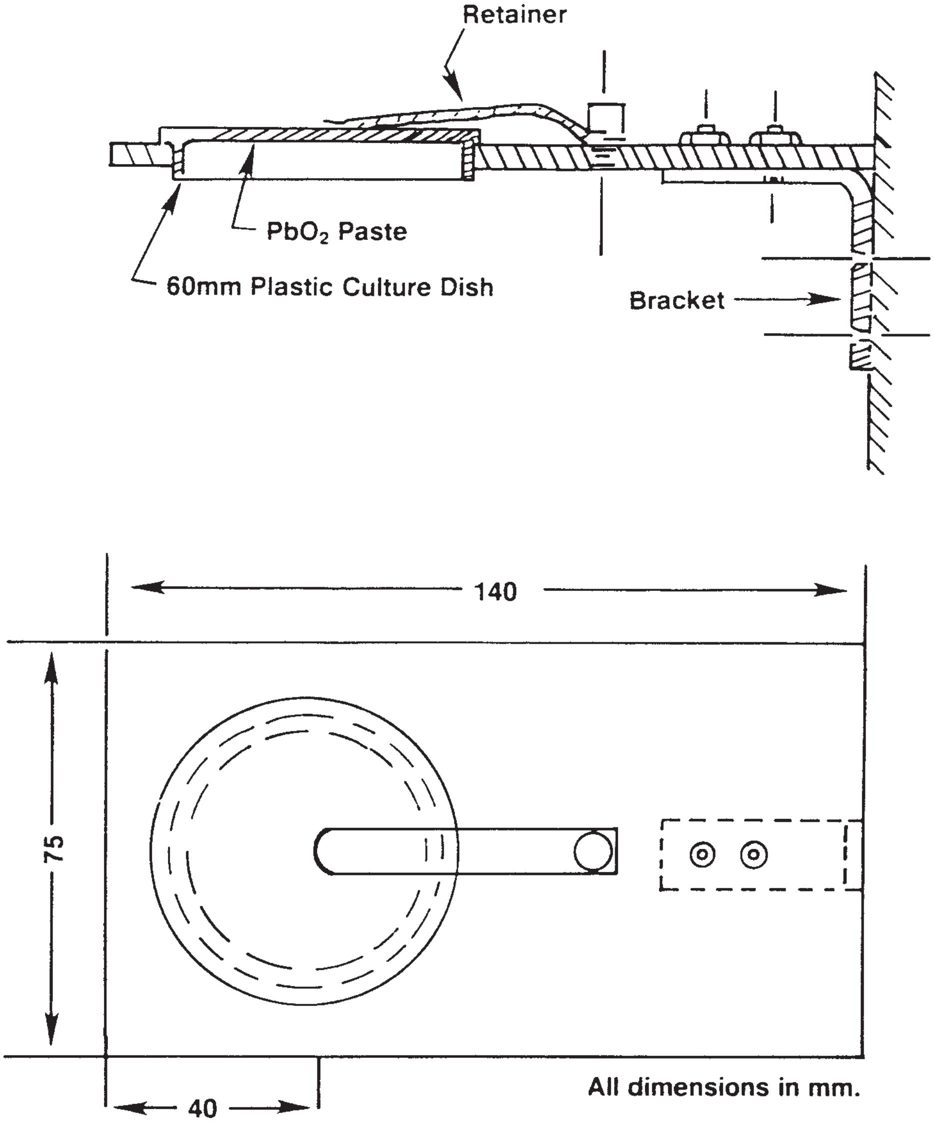


FIG. 1 Sulfation Plate Holder

8. Precautions

8.1 *Safety Precautions*—Since lead is a toxic material, prepare and analyze the PbO_2 candles and sulfation plates under a fume hood, or with a respirator approved for use with toxic dusts.

8.2 PbO_2, which is a strong oxidizing agent, can permeate and contaminate any laboratory area, making it impossible for use in conducting analysis of environmental samples for lead. Therefore, use a dedicated room that is well ventilated to the outside for the PbO_2 candle or sulfation plate work.

9. Sampling

9.1 Refer to Practice D 1357 for guidance in planning sampling programs.

9.2 When these test methods are used for estimating the SO_2 concentration over a designated area, select sampling stations at random on a uniform network grid over the area to be studied. The density of the sampling stations shall not be less than 1/km^2 (2/mile ^{2}).

9.3 *Location of Sampling Device*—Locate the box or bracket in a manner that will ensure protection from tampering and security from falling. The height from ground level shall be the same at all stations. The minimum height above the supporting surface shall be 1 m (3 ft). The sulfation plate shall be horizontal and placed so that it is not protected from normal winds and air currents.

9.4 The sampling period may be 1 month or long enough to provide a convenient minimum of total sulfate for analysis. The work of Keagy **(5)**, which is used as the criterion for the sampling procedure for candles, shows a range from 5 to 2000 mg of barium sulfate ($BaSO_4$) per candle. The sampling frequency shall be uniform and determined by the requirements of the survey. Monthly, bimonthly, and seasonal sampling periods have been shown to provide consistent and reliable data **(5)**.

10. Analytical Procedure

10.1 Return the candles or plates to containers that can be sealed from contamination at the end of the sampling period.

10.2 *Test Method A, Treatment of Candles*—Measure the surface area of the candle. Separate the impregnated cloth surface from the cylinder, using a spatula or knife point, if necessary. The fabric may be cut into smaller pieces. Transfer the PbO_2-covered fabric to a 250-mL beaker containing 60 mL of 83.3-g/L solution of Na_2CO_3 (7.11). Soak the immersed pieces for 3 h, with occasional stirring. Cover the beakers, and simmer the mixtures gently on a water bath plate for 30 min, taking care to minimize water evaporation in order to maintain an approximately constant volume. Filter the beaker contents through a fast filter paper, with appropriate washings, and adjust the filtrate with 2 *N* HCl (7.8) to a pH range of 3.0 to 4.0, using methyl orange as the indicator (7.12). Exercise care to prevent any loss of sample by foaming, particularly when the point of neutralization is approached.

10.3 *Test Method B*—Remove the contents of the sulfation plate to a 250-mL beaker, and add 12 mL of 83.3 g/L Na_2CO_3 solution (7.11). Cover the beaker, and proceed as described in 10.2.1.

10.4 *Determination of Sulfate as Barium Sulfate*—Determine the sulfate ion in accordance with the gravimetric test method (Test Method A) in Test Method D 516. The rapid addition of a boiling solution of $BaCl_2$ (7.4) to a gently boiling solution of the sulfate in 0.05 *N* HCl (7.9) will yield a granular and easily filterable $BaSO_4$ precipitate.

10.5 Determine the sulfate in the unexposed (blank) candle or plate, and subtract from the exposed sampler values.

11. Calculation

11.1 Calculate the total sulfation activity, expressed as SO_2 equivalent, as follows:

$$M = \frac{W \times 274.5}{A \times t} \tag{1}$$

where:

M = total sulfation activity, in mg $SO_2/cm^2 \times$ day,

W = mass of $BaSO_4$, in g, corrected for blank,

274.5 = ratio of the molecular weights of SO_2 and $BaSO_4$, × 1000 to convert g to mg,

A = area of candle or plate, in cm^2, and

t = time of exposure, in days.

12. Precision and Bias

12.1 *Test Method A* **(8)**:

12.1.1 The interlaboratory study of Project Threshold provided the following conclusions regarding the precision of Test Method A.

12.1.1.1 The standard deviation, S_b, for the reproducibility of total sulfation activity measurements by different laboratories ranging from 0.00178 to 0.01371 mg/$cm^2 \times$ day may be expressed by the following equation:

$$S_b = 0.0136\, M^{½} \tag{2}$$

where:

S_b *and* M = mg/$cm^2 \times$ day.

12.1.1.2 The standard deviation, S_w, for replicate measurements of total sulfation activity ranging from 0.00178 to 0.01371 mg/$cm^2 \times$ day by the same laboratory (repeatability) may be expressed by the following equation:

$$S_w = 0.00504\, M^{½} \tag{3}$$

where:

S_w *and* M = mg/$cm^2 \times$ day.

12.1.2 The average results of the analysis of spiked samples **(8)** indicates that the determination of sulfate by Test Method D 516 can be performed with a recovery of 98 %.

12.1.2.1 The standard deviation of the percent of sulfate spike recovery of the sulfate analysis step is 10 % for between-laboratory measurements and 21 % for within-laboratory measurements.

12.2 *Test Method B* **(9)**:

12.2.1 The standard deviation of replicate plates run under the same exposure conditions for a single laboratory has been found to be related to the mean sulfation level by the equation given below:

$$\sigma = 0.0790\, m_{avg} \tag{4}$$

where:

σ = standard deviation in mg $SO_2/m^2 \times$ day, and

m_{avg} = mean net SO_2 capture rate in mg $SO_2/m^2 \times$ day based on 10 runs with six or more plates per run.

12.2.1.1 The standard error of estimate for the regression equation was 0.69 based on eight degrees of freedom. This error is a lower limit value for σ regardless of m_{avg}.

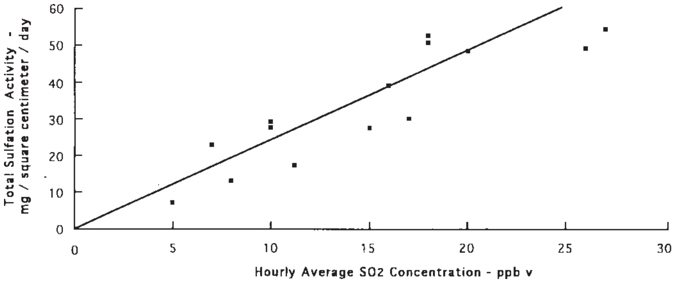
12.2.1.2 This estimate of the standard deviation for a plate may be used to test variation estimates within sites or between sites to determine whether the observed variations are significantly larger than the experimental error associated with measuring sulfation.

12.2.2 Correlations with volumetric SO_2 determination are somewhat variable because of the influence of temperature, humidity, wind, and exposure conditions. Correlation is shown in Fig. 2 for total sulfation activity versus volumetric SO_2 determination using 50-mm diameter plates **(9)**.

12.3 *Bias*—No statement on bias is being made since there is no accepted reference material suitable for determining the bias for the procedures in this test method.

13. Keywords

13.1 atmospheres; Huey plates; lead dioxide; lead dioxide candles; sampling; sulfation; sulfation plates; sulfur dioxide



NOTE 1—A regression analysis on these data yielded the following least squares results:

$$M = (2.216 \pm 0.016)\ C \tag{1}$$

where:

M = total sulfation activity in mg/cm ^{2}/day, and
C = mean hourly volumetric SO_2 concentration in ppb(v).

The correlation coefficient for this data set was 0.917, and the standard error of estimate was 7.5 with 13 degrees of freedom.

FIG. 2 Correlation Between Total Sulfation Activity and Mean Volumetric SO_2 Concentration

APPENDIX

(Nonmandatory Information)

X1. LEAD DIOXIDE CANDLE PREPARATION

X1.1 The following procedure may be used to prepare PbO_2 candles:

X1.1.1 Disperse 0.5 g of powdered gum tragacanth (7.6) in 5 mL of ethyl alcohol (95 %) (7.5) and add 30 mL of hot water (7.2) carefully, while stirring. Warm the mixture gently on a low-temperature hot plate until a clear, uniform gel has been obtained. Do not overheat the gum. Add 80 g of PbO_2 (7.10) to the mixture, in small portions, with continuous stirring to prepare the paste entirely free of lumps, and to ensure adequate dispersion of the PbO_2.

X1.1.2 This procedure will provide sufficient paste for 10 candles. Do not exceed 8 g of PbO_2 per candle. Do not vary the mass per candle by more than 10 %.

X1.1.3 Wash a fabric such as a tapestry cloth **(1)**, gauze, or stockinette **(5)** in boiling water (7.2). Dry the fabric in an SO_2-free atmosphere. Wrap the fabric around a glass or inert impervious plastic cylinder (6.1.1) with a surface area of approximately 100 cm^2. Secure the fabric to the cylinder with cotton or nylon thread.

X1.1.4 Apply the paste to the fabric to provide the reactive surface. Use a stiff-bristled brush 25-mm (1-in.) wide to spread the paste on the fabric.

X1.1.4.1 When large quantities of paste are made, exercise care to maintain an even dispersion of the PbO_2 reagent and to avoid excessive heating of the mixture. Control the viscosity of the paste by using a water bath **(8)**.

X1.1.4.2 When quantity batches of candles are prepared, a small, hand-operated centrifuge may be adapted to facilitate the task. This is done by removing the tube holders and fastening an appropriate device for securing the candle to the rotating shaft.

X1.1.5 Dry the coating in a SO_2-free atmosphere. Retain a blank, unexposed candle from every batch of candles prepared. Until used, store the candles in sealed containers and away from exposure to SO_2 and other sulfur-containing gases that would contaminate the reactive surface.

X2. SULFATION PLATE PREPARATION

X1.2 The following procedure may be used to prepare sulfation plates:

X1.2.1 Bond filter paper circles to the bottom of the culture dishes (6.2.1) by placing the filter paper circle, rough side up, in the bottom of the dish and adding reagent grade acetone (7.3) from a wash bottle until the filter just becomes saturated. Avoid splashing the acetone on the walls or outside the dish. Press the paper firmly with a glass rod so that all parts of the filter are pressed into the dish. Allow the acetone to evaporate. One 900-mL batch of PbO_2 will cover approximately 80 50-mm plates or 55 60-mm plates. The bonding may be conducted well in advance of the plate preparation procedure.

X1.2.2 Place a batch of bonded plates, 80 50-mm or 55 60-mm plates, in a rack and rinse them with water (7.2). Then fill the plates with water (7.2) again and allow them to stand for 1 h. Pour the water out and refill them one-quarter to one-half with water (7.2).

X1.2.3 Add 3.5 g of gum tragacanth (7.6) and 900 mL water (7.2) to a high-speed blender container. Set at low speed and blend for 2 h.

X1.2.4 Pour the contents of the blender into a 1-L beaker and return 350 mL of the solution to the blender container. Pulp 3.5 g of glass fiber filter paper in the 350 mL of gum solution with the blender set at a moderate speed until the mixture appears smooth and uniform.

X1.2.5 Return 400 mL of the gum solution previously removed from the blender and blend at moderate speed for 1 min.

X1.2.6 Turn the blender to high speed and add 112 g of PbO_2 (7.10). Blend for 2 min and turn the blender back to low speed.

X1.2.7 Carefully pipet 10 mL of the mixture into each 50-mm plate or 15 mL into each 60-mm plate. Ensure that the mixture spreads uniformly through the water layer in the plate to the edge of each plate.

X1.2.8 Place the rack of plates in an oven set at 40 to 50°C for 20 h.

X1.2.9 Remove the plates from the oven and allow them to cool. Seal the plates with tight-fitting covers to preserve them until the exposure begins. Store them in an SO_2-free environment.

X1.2.10 Number the plates and expose them within 120 days of preparation. Commercially obtained plates may be retained for up to one year before exposure if they are stored in an SO_2-free environment. Retain at least one plate from each as a blank.

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