SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

APPLIED SCIENCE & TECHNOLOGY DIVISION

LABORATORY SERVICES BRANCH

SCAQMD METHOD 318-95

**DETERMINATION OF WEIGHT PERCENT ELEMENTAL METAL IN COATINGS
BY X-RAY DIFFRACTION**

Approved July 1996

SCAQMD METHOD 318-95

DETERMINATION OF WEIGHT PERCENT ELEMENTAL METAL IN COATINGS
BY X-RAY DIFFRACTION

This method applies to the determination of weight percent elemental metal in coatings as regulated by various Rules in SCAQMD Regulation XI.

CONTENTS

Comment:

SCAQMD METHOD 318-95

DETERMINATION OF WEIGHT PERCENT ELEMENTAL METAL IN COATINGS BY X-RAY DIFFRACTION

1.0   Principle

1.1   Crystalline particles exhibit unique x-ray diffraction patterns characteristic of their crystalline structure. A dried sample is ground into a homogeneous powder and analyzed by X-ray diffraction. The weight percent of elemental metal is determined by comparing the integrated intensities of the sample with known amounts of standard. The addition of silicon as an internal standard is used to normalize the measured intensity of the analyte and to minimize effects of packing and partially compensate for density variations. The concentration of the metal particles in the sample is directly proportional to the integrated intensities.

2.0   Application

2.1   This method has been validated for the determination of percent weight elemental aluminum metal in coatings. This method may also be applicable for the determination of other elemental metals or crystalline materials for which appropriate standards are available and reasonable performance has been demonstrated.

3.0   Interferences

3.1.   Based on review of the *Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data (JCPDS), Powder Diffraction Files (PDF)* and the primary peak positions of metallic elements typically found in metallic coatings, no known common components of the metallic coatings interfere with all major peaks of interest. Some of the common components may include rutile, mica, quartz, gypsum, kaolinite, calcite, dolomite and metal oxides. Silver and gold are mutual interferences, but these metals are not typically found together as elemental metals in metallic coatings.

4.0   Apparatus

4.1   X-ray diffractometer equipped with:

4.1.1.   X-ray tube, Copper target, high intensity, fine focus

4.1.2.   Detector, X-ray, solid state peltier cooled, or scintillation with monochromator, focusing graphite crystal or nickel filter

4.1.3.   Stage, rotating

4.1.4.   Generator, constant potential with voltage and mA stabilizers

4.1.5.   Diffractometer, automated with step-scanning mode

4.1.6.   Data output accessories, digital printer or PC and software which has the capability to determine background response

      4.1.7.   Holders for powdered samples

4.2   Balance, analytical, capable of weighing to 0.1 mg

4.3   Oven, forced air drying capable of maintaining 110°C for 24 hours as specified in the most recent version of ASTM D2369.

4.4   Shaker, paint, high speed

4.5   Pans, aluminum, 58 mm X 18 mm as specified in the most recent version of ASTM D2369

4.6   Film, Teflon, virgin electrical grade, .002" thick, 12" wide

4.7.   Mixer/mill, Spex 8000 Mixer/Mill for brittle samples which are easily milled or Spex 6700 Freezer/Mill for pliable samples or samples which are difficult to mill with the Spex 8000 Mixer/Mill

4.8   Grinding vials, polystyrene with polyethylene caps and methacrylate balls suitable for the Spex 8000 Mixer/Mill

4.9   Polycarbonate center cylinders with stainless steel impactor and end plugs for the Spex 6700 Freezer/Mill

4.10   Containers, glass with Teflon-lined caps or silicone stoppers

4.11   Mortar and pestle (optional)

4.12   Spatulas, forceps

4.13   Hood, Class 1 or better

4.14   Razors or glass slides (optional)

4.15   Weighing paper (optional)

4.16   Microscope, Polarizing light with 100X magnification and a calibrated ocular micrometer

4.17   Sonicator, low level ultrasonic bath, 0.01 Watt per milliliter

4.18   Syringe, 5ml disposable

4.19   Wig-L-Bug or equivalent oscillating mixer

5.0   Reagents

5.1   Silicon, 99.5%, -325 mesh crystalline

5.2   Aluminum powder, 99.5%, -325 mesh

5.3   Surfactant, 1 percent Aerosol ® (registered trademark of American Cyanamid) OT aqueous solution or equivalent (optional)

5.4   Clear coats, unpigmented resin bases, with recommended diluents and thinners (may be obtained from local paint suppliers)

5.5.   NIST Reference Standard #1976, XRD flat plate intensity. The standard reference material consists of a sintered alumina plate, approximately 45mm on a side by 1.6 mm in thickness, intended for use in calibration of powder x-ray equipment for diffraction intensity as a function of the 2θ angle (instrument sensitivity).

6.0   Precautions and Safety

6.1.   This method does not purport to address the safety problems associated with its use. It is the responsibility of the user of this method to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

7.0   Analytical Procedure

7.1.   Preparation of Materials

7.1.1   Determination of Total Nonvolatile Content of Resin Base

7.1.1.1.   Analyze an appropriate aliquot of the wet resin base for total volatile content by following the procedure specified in the most recent version of ASTM D2369 *Standard Test Method for Volatile Content of Coatings*.

7.1.1.2   Calculate the total nonvolatile content of the wet resin base in weight percent. Record this as NV.

7.1.2   Microscopic examination of aluminum powder

7.1.2.1   Examine the standard aluminum powder (Section 5.2) under a microscope. The particles must be less than 40um in size. If the particles are not less than 40um, mill the powder or sieve the material through a 325 mesh screen.

7.1.3   Conditioning of standard aluminum powder (It has been shown that an opened stock aluminum standard is only good for one week. This may be attributed to oxidation of aluminum occuring on the surface of the particles. Therefore, the standard should be used within one week of opening. Only standards having an aluminum content greater than 95% by weight as determined by the method in Section 7.1.4.1 should be used.)

7.1.3.1.   Determine the amount of aluminum needed to prepare the standards. See Section 7.2.1.1.

7.1.3.2   Place an excess amount needed for the standards in a container which can be sealed and is appropriate for heating.

7.1.3.3   Heat in oven at 110°C for one hour.

7.1.3.4   Cool in a desiccator.

7.1.3.5   Cap and store up to 2 days for standard mixing.

7.1.4   Determination of Weight Percent Aluminum in Aluminum Powder

7.1.4.1   Analyze the conditioned aluminum powder for total weight percent aluminum by following the procedure as specified in *EPA Method 7000A, Atomic Absorption Methods (7020 Aluminum)* and *Method 3050A, Acid Digestion of Sediments, Sludges, and Soils* found in the most recent version of *EPA Test Methods for Evaluating Solid Wastes, Volume 1A: Laboratory Manual, Physical/Chemical Methods.*

7.1.4.2   Calculate the weight percent of aluminum in the aluminum powder. Record this as $AA_\%$.

7.1.5   Preparation of glass containers and caps for standard and sample mixing

Note: The size of the container will be determined by the final volume of standard to be prepared. Additional solvent may also be required to wet and suspend the aluminum for easy mixing and to thin out thick resins for recovery from the container. The container should not be more than one-half full with the final mixed standard to allow for thorough mixing.

7.1.5.1   Prepare the glass containers and caps by rinsing with acetone and heating in an oven at 110°C for one hour.

7.1.5.2   Label each glass container with a unique identification number. Allow the containers to cool in a desiccator. Weigh and record the glass containers to the nearest 0.1 milligram. Record as W_1.

7.1.6   Preparation of aluminum pans for standard and sample drying.

7.1.6.1   Mark each pan with a unique identification number. Cut out Teflon films large enough to cover the inside bottom and sides of the pans. Condition the pans with the Teflon lining at 110 °C for one hour, cool in a desiccator, and weigh to the nearest 0.1 mg. Record as W_2.

Note: Teflon sometimes will acquire a static charge when handled. The static charge must be allowed to dissipate before an accurate weight can be taken.

7.2   Preparation of Standards

7.2.1.   Prepare a resin base (Section 5.4) blank and five different concentration mixtures of the aluminum powder standard (Section 5.2) in the resin base. The range of aluminum concentrations after drying should span the analytical range of interest.

7.2.1.1   Determine the weights of aluminum powder and wet resin base needed to prepare each standard using the following calculations:

Calculate the weight of aluminum powder needed to prepare the standard:

$$D = (A \times B) / AA\%$$

Calculate the weight of wet resin base needed to prepare the standard:

$$E = (B - D) / (NV / 100)$$

Where: D = weight of stock aluminum powder needed to prepare the standard

E = weight of wet resin base needed to prepare the standard

A = weight percent aluminum in the dried calibration standard as determined by the desired analytical range

B = total weight of dried prepared standard (A two gram minimum is recommended for bulk XRD analysis.   More standard may be prepared for additional tests or procedures.)

$AA\%$ = weight percent aluminum in the aluminum powder as determined by Section 7.1.4.2

NV = non-volatile weight percent of the wet resin base as determined in Section 7.1.1.

Note: Sections 7.2.1.2 through 7.2.2.2 must be completed in a minimum length of time.

7.2.1.2   Add the weight of aluminum powder, D, determined in Section 7.2.1.1 to the weighed glass container, W_1, prepared in Section 7.1.5.2.   Record the weight of the glass container and aluminum powder to the nearest 0.1 mg as W_3.

7.2.1.3   Subtract W_1 from W_3 to determine the weight of the aluminum powder. Record to the nearest 0.1 mg as W_4.

7.2.1.4   Cap the container and immediately weigh to the nearest 0.1 mg, record the weight as W_5. (The cap weights are not stable over several hours.) Uncap the glass container.

7.2.1.5   Add solvent if needed to disperse the aluminum powder, to thin out high concentrations of aluminum powder and thick resins, or to aid in homogenizing or transferring the standard.

7.2.1.6   Quickly add the weight of wet resin base, E, determined in Section 7.2.1.1.

Note: A top loading balance may be useful to monitor the resin base weight being added.

7.2.1.7   Cap the container and weigh to the nearest 0.1 mg. Record the weight as W_6.

7.2.1.8   Subtract W_5 from W_6 to determine the weight of the resin base and solvent. Record the weight to the nearest 0.1 mg as W_7.

7.2.1.9   Calculate the weight fraction of aluminum powder in the wet mixture as follows:

$$W_{fx} = [W_4 / (W_4 + W_7)]$$

Where: W_{fx} = weight fraction of aluminum powder in the wet   mixture
              W_4 = weight of aluminum powder
              W_7 = weight of the resin base and solvent

7.2.1.10   Thoroughly mix the standards by hand shaking or brief sonication (less than 5 minutes at 0.01 Watt per milliliter or less.) If the standards show poor suspension (presence of dry metal or clumps of metal), a new standard should be prepared.

7.2.2   Drying of Prepared Standards

7.2.2.1   For each standard from Section 7.2.1.10, transfer an accurately weighed (W_8) aliquot to a pan to produce a minimum of two grams of dried standard.

7.2.2.2   Dry the standards in the oven at 110°C for 17 to 21 hours.

Note: Standards may require that they are flipped over on the Teflon film during the drying procedure for complete drying. Thick pliable films may require more time to dry. Exercise care while flipping the standards to avoid losses.

7.2.2.3   Cool the dried standards in the pans in a desiccator to room temperature.

7.2.2.4   Calculate the weight of aluminum powder in each pan as follows:

$$W_9 = W_8 \text{ x } W_{fx}$$

Where: W_9 = weight of aluminum powder in the pan
              W_8 = weight of aliquot transferred to the pan
              W_{fx} = weight fraction of aluminum powder in the wet mixture (Section 7.2.1.9)

7.2.2.5   Weigh the pan and standard to the nearest 0.1 mg and record as W_{10}.

7.2.2.6   Calculate the weight percent of aluminum in the dried standard as follows:

$$A_\% = [W_9 / (W_{10} - W_2)] \text{ x } (AA\%)$$

Where: $A_\%$ = weight percent of aluminum in the dried standard
              W_9 = weight of aluminum powder in pan (Section 7.2.2.4)

W_{10} = weight of the dried standard and pan
(Section 7.2.2.5)

W_2 = weight of pan (Section 7.1.6.1)

$AA_\%$ = weight percent aluminum in the aluminum
powder as determined by Section 7.1.4.2

7.2.3 Milling the Standards

7.2.3.1 Remove the dried standards from the Teflon film and break into smaller pieces by hand to fit in milling vials.

7.2.3.2 Mill the standards with a Spex 8000 Mixer/Mill or equivalent until the particles are homogeneous and less than 40um in particle size.

Note: The particle size can be determined by microscopic measurement.

7.2.3.3 Follow procedure 7.2.3.1 and 7.2.3.2 for all of the standards.

7.2.3.4 Mix all the milled powder standard of the same concentration together to form a homogeneous mixture.

7.2.4 Follow steps 7.2.2.1 through 7.2.3.4 for each set of standard.

7.3 Preparation of Samples

7.3.1 Sample mixing

7.3.1.1 Mix the sample with a high speed paint shaker to insure homogeneity and uniform suspension of the metal particles. If a residue of unsuspended particles is present in the container, a stir stick may be used to suspend the residue. Caution must be used to minimize the time that the container is opened to minimize loss of volatiles.

7.3.2 Determination of Total Nonvolatile Content of Sample

7.3.2.1 Analyze an appropriate aliquot of the sample for total nonvolatile content by following the procedure specified in the most recent version of ASTM D2369 *Standard Test Method for Volatile Content of Coatings*.

7.3.2.2 Calculate the total nonvolatile content of the sample in weight percent. Record this as NV.

7.3.3 Sample Drying

7.3.3.1 Transfer approximately 3 to 5 grams of sample into a Teflon lined pan prepared in Section 7.1.6.1 by weighing a 5 ml syringe filled with sample, delivering the appropriate amount of sample into the Teflon lined pans, weighing the loaded syringe after delivery and determining the aliquot delivered by weight difference.

7.3.3.2 Place the pans with the samples in the oven at 110°C and dry for 17 to 21 hours.

Note: Samples may need to be flipped over on the Teflon film during the drying procedure for complete drying. Thick pliable films may require more time to dry. Exercise care while flipping the samples to avoid losses.

7.3.3.3 Cool the dried samples in the pans in a desiccator to room temperature.

7.3.4 Milling the Samples

7.3.4.1 Mill the samples according to Section 7.2.3 using samples instead of standards.

7.4 Internal Standard

7.4.1 Properly label a set of vial and cap.

7.4.2 Weigh and record as W_{11}.

7.4.3 Transfer at least two grams of each milled sample or standard to the properly labeled and tared vial with cap. Reweigh and record as W_{12}.

7.4.4 Add -325 mesh silicon to result in approximately 10% by weight silicon in the final mixture. Reweigh and record as W_{13}. Thoroughly mix the final mixture using a Wig-L-Bug or equivalent to produce a homogeneous mixture.

7.4.5 Calculate the actual weight fraction silicon added to each sample or standard by the following calculation:

$$S_{fx} = [(W_{13} - W_{12}) / (W_{13} - W_{11})]$$

Where: S_{fx} = weight fraction silicon added
W_{13} = weight of the milled sample or standard, vial and silicon
W_{12} = weight of the milled sample or standard and vial
W_{11} = weight of the vial

7.4.6 Calculate the final weight percent aluminum in each standard after the addition of silicon by using the following calculation:

$$Al_\% = (1 - S_{fx}) \times A_\%$$

Where: $Al_\%$ = final weight percent of aluminum in the tared vial with silicon added
S_{fx} = weight fraction silicon added (Section 7.4.5)
$A_\%$ = weight percent of aluminum in the dried standard (Section 7.2.2.6)

7.4.7 Follow steps 7.4.1 through 7.4.6 for each standard and sample.

7.5   X-ray Diffraction Analysis

7.5.1 Load the appropriate sample holders with the milled samples and standards for X-ray diffraction analysis.

7.5.2 Mount the loaded sample holder on the sample spinner that is set at 60 RPM.

7.5.3 Obtain a qualitative X-ray diffraction scan of the samples to determine the presence of interferences. A full qualitative XRD scan (a 2θ range from 26° to 82°) should be done for all samples which exhibit diffraction peaks in the diagnostic regions of aluminum. Compare their diffraction patterns with standard reference powder diffraction patterns to verify that the aluminum peak assignments exactly match the aluminum reference pattern and to identify possible matrix interferences (e.g. peak overlapping or baseline shifts due to close proximity of peaks). The most intense diffraction peak which has been determined to be free from matrix interference should be used for quantitation. If all diffraction peaks exhibit problems with interference then an alternative technique such as standard addition may be utilized.

7.5.4 Based upon the review of the qualitative X-ray diffraction scan, step-scan the selected aluminum diffraction peak that is free from interference in increments of 0.05 2θ degrees for 15 seconds per step with a 2 mm divergence slit, a 2 mm anti-scatter slit and a 1 mm detector slit. Unknown samples should be scanned under the same conditions and 2θ range as the standards.

7.5.5 Step-scan the most intense peak of silicon under the same conditions.

7.5.6 Integrate the selected aluminum diffraction peak and record its integrated intensity as P_{al}. Integrate the selected silicon diffraction peak and record its integrated intensity as P_{si}. The procedure and units for determining the intensity must be consistent for standards and samples.

7.5.7 Measure the background on each side of the peak for equal the time used for peak scanning. Determine the average total background by adding the integrated intensity from each side of the peak and dividing by 2. Record as B_{al} for the aluminum peak and B_{si} for the silicon peak.

7.5.8 Calculate and record the net integrated intensity (the difference between the peak integrated count and total background integrated intensity) for the selected aluminum peak by:

$$I_{al} = P_{al} - B_{al}$$

7.5.9 Calculate and record the net integrated intensity (the difference between the peak integrated count and total background integrated intensity) for the selected silicon peak by:

$$I_{si} = P_{si} - B_{si}$$

8.0   Calculations

8.1   Normalize the net intensity of the aluminum peak to the silicon internal standard as follows:

$$D = (I_{al} \times 100) / (I_{si} / S_{fx})$$

Where: D = normalization factor
          I_{al} = net integrated intensity of the selected aluminum peak
               (Section 7.5.8)
          I_{si} = net integrated intensity of the selected silicon peak
               (Section 7.5.9)
          S_{fx} = weight fraction silicon added to samples and standards
               (Section 7.4.5)

8.2   Prepare a calibration curve by plotting the normalization factor, D, determined in Section 8.1 versus the percent by weight aluminum determined in Section 7.4.6 for each standard.

8.2.1   The data should fit a straight line equation. A value for "r" of at least 0.997
         is required to show that the data of six points (blank   and   5 standards) has a
         95% probability of a linear relationship and a positive slope.

8.2.2   Rejection of outliers can be determined by the following calculation:

$$Z = (A - B) / C$$

Where: Z = appropriate multiple
          A = the suspect data point
          B = the mean of all data points
          C = the standard deviation of the data points

Note: If Z is greater than 4, then the suspect data point may be considered an outlier.   Data point is the difference between the actual XRD response for a sample   and the   XRD   response   predicted   by   the regression line for that sample.

8.3   Determine the slope, M, of the calibration curve by using least squares linear regression.   The intercept, b, of the line should be approximately zero.   An intercept (calculated as D) that is not within ±0.3, indicates an error in determining the background due to an incorrect baseline setting or interference by another phase. If this problem occurs, review the baseline settings or prepare new standards then recalculate the net integrated intensity.

8.4   Calculate the weight percent aluminum in the dried sample from the calibration curve as follows:

$$X_1 = (D - b) / M$$

Where: X_1 = weight percent aluminum in the dried sample, uncorrected
          D   = normalization factor for the sample (Section 8.1)
          b   = intercept (Section 8.3)
          M = slope of the calibration curve (Section 8.3)

8.5   Calculate the weight percent aluminum corrected for the addition of silicon in the sample as follows:

$$X_2 = X_1 / (1 - S_{fx})$$

Where: X_2 = weight percent aluminum corrected for the addition of silicon in the dried sample
X_1 = weight percent aluminum uncorrected in the dried sample, (Section 8.4)
S_{fx} = weight fraction silicon added to sample (Section 7.4.4)

8.6   Calculate the weight percent aluminum in the original sample as follows:

$$X_3 = (X_2 \times NV) / 100$$

Where: X_3 = weight percent aluminum in original sample
X_2 = weight percent aluminum in the dried sample corrected for the addition of silicon (Section 8.5)
NV = weight percent nonvolatiles (Section 7.3.2)

8.7   Calibration and quantitation software which has been verified to provide equivalent results to the calculations specified may be used.

9.0   Quality Control Procedures

9.1   A known control sample or samples prepared at the time of analysis should be analyzed with every group of samples or after every tenth sample, whichever is more stringent. If the results vary by 10% relative from the known values, the calibration curve and/or standards should be re-evaluated. All calibration data must be documented.

9.2   A reference standard such as the NIST Reference Standard #1976 (XRD flat plate intensity) or an equivalent reference standard should be run at the beginning of each analysis day to determine and document instrument fluctuations. Significant fluctuations as specified by the instrument manufacturer should be reviewed and resolved.

10.0   Evaluation of the Method

10.1   Based on interlaboratory analysis of samples containing 0.80 to 3.08% by weight aluminum in the wet sample, the average percent relative standard deviation is 9.2 and the average accuracy is 94%. The limit of detection is 0.2 weight percent aluminum.

11.0   References

11.1   Standard Test Method for Volatile Content of Coatings, ASTM 2369

11.2   EPA Method 7000A, Atomic Absorption Methods (7020 Aluminum)

11.3   EPA Test Methods for Evaluating Solid Wastes, Volume 1A: Laboratory Manual, Physical/Chemical Methods - Method 3050A, Acid Digestion of Sediments, Sludges, and Soils

11.4   Standard Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial Chemicals, ASTM E 180-90