Designation: D5517 – 14

Standard Test Method for Determining Extractability of Metals from Art Materials[1]

This standard is issued under the fixed designation D5517; 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 extraction of metals from art materials using an extractant that simulates the acid potential of gastric juice. This test method is similar to the extraction method in Specification F963, except that it requires conducting extraction steps at body temperature instead of at room temperature. The extraction procedure specified in this test method is more rigorous than that noted in Specification F963 because the procedure causes the extraction of a larger quantity of metal.

1.2 This test method is adapted from the European Toy Safety Standard, EN 71-3:1994 but differs from it in that a solvent extraction step is not required for processing waxes or oil-based products and no specific acceptable metal levels are specified.

1.3 The rational for this test method is discussed in Appendix X1.

1.4 This test method should be used on the art material as a whole and not an art material ingredient. Testing the art material as whole would be expected to give a more accurate estimate of soluble metal than from an extrapolation from testing ingredients.

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

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D4236 Practice for Labeling Art Materials for Chronic Health Hazards

E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals (Withdrawn 2009)[3]

E456 Terminology Relating to Quality and Statistics

F963 Consumer Safety Specification for Toy Safety

2.2 *International Standards:*[4]

EN 71-3:1994 Safety of Toys

ISO 3696 Water for Laboratory Use—Specifications

ISO 3856 Paints and Varnishes—Determination of "Soluble" Metal Content

Part 1: Determination of lead content—Flame atomic absorption spectrometric method and dithiazone spectrophotometric method

Part 2: Determination of antimony content—Flame atomic absorption spectrophotometric method and Rhodamine B spectrophotometric method

Part 3: Determination of barium content—Flame atomic emission spectrometric method

Part 4: Determination of cadmium content—Flame atomic absorption spectrometric method and polarographic method

Part 5: Determination of hexavalent chromium content of the pigment portion of the liquid paint or the paint in powder form—Diphenylcarbazide spectrophotometric method

Part 6: Determination of total chromium content of the liquid portion of paint—Flame atomic absorption spectrometric method

2.3 *USEPA Standards:*[5]

USEPA Test Method SW-846

[1] This test method is under the jurisdiction of ASTM Committee D01 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.57 on Artist Paints and Related Materials.

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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] The last approved version of this historical standard is referenced on www.astm.org.

[4] Available from European Committee for Standardization (CEN), 36 rue de Stassart, B-1050, Brussels, Belgium, http://www.cenorm.be.

[5] Available from United States Environmental Protection Association (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, http://www.epa.gov.

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6010 Test Method for antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, selenium, silver, thallium, vanadium, and zinc
6020 Test Method for aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, nickel, silver, thallium, and zinc
7040 Test Method for antimony
7041 Test Method for antimony
7060 Test Method for arsenic
7061 Test Method for arsenic
7080 Test Method for barium
7090 Test Method for beryllium
7091 Test Method for beryllium
7130 Test Method for cadmium
7131 Test Method for cadmium
7190 Test Method for chromium
7191 Test Method for chromium
7200 Test Method for cobalt
7201 Test Method for cobalt
7210 Test Method for copper
7421 Test Method for lead
7460 Test Method for manganese
7470 Test Method for mercury
7471 Test Method for mercury
7480 Test Method for molybdenum
7481 Test Method for molybdenum
7520 Test Method for nickel
7550 Test Method for osmium
7740 Test Method for selenium
7741 Test Method for selenium
7760 Test Method for silver
7840 Test Method for thallium
7841 Test Method for thallium
7870 Test Method for tin
7910 Test Method for vanadium
7911 Test Method for vanadium
7950 Test Method for zinc

3. Terminology

3.1 *Definitions:*

3.1.1 For formal definitions of statistical terms see Terminology E456.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *base material, n*—material upon which coatings are deposited or formed.

3.2.2 *bioavailability, n*—the extent that a substance can be absorbed in a biologically active form.

3.2.3 *coating, n*—all layers of material covering the base material.

3.2.4 *detection limit, n*—three times the standard deviation of the blank value.

3.2.5 *scraping, v*—removal of a coating down to the base material without removing any portion of the base material; the use of solvents is not permitted.

4. Summary of Test Method

4.1 A powdered, liquid, comminuted or ground art material is mixed with a 0.07 *N* hydrochloric acid solution and, after adjusting the pH to 1.5, is shaken for 1 h and then allowed to sit for an additional hour. These extraction steps are conducted at 37 ± 2°C. Solids are separated from the extractant by centrifugation and filtration through a 0.45-µm filter. The resultant eluate is then analyzed for the metal(s) of interest.

5. Significance and Use

5.1 This acid extraction method is intended to indicate the solubility of metals from art materials in a weak acid medium. This test method may be useful as one indicator of the amount of metal that is readily available for absorption. It is not meant as a replacement for *in vivo* tests of absorption of a metal.[6] Other relevant information, when available, should be included in the overall toxicological assessment of metal-containing art materials, such as physico-chemical properties, toxicokinetics (absorption, distribution, metabolism and excretion), and mechanisms of toxicity of the metal(s) of interest.

5.2 Maximum levels of metal extraction are seen with this test method when results are 250 ppm or less. If results are greater than 250 ppm, the extractant volume should be increased to 100 mL.[7]

6. Apparatus

6.1 *Metal Sieve* of aperture 0.5 mm.

6.2 *pH meter* with an accuracy of ±0.1 pH units.

6.3 *Membrane Filter* with a pore size of 0.45 µm.

6.4 *Centrifuge* able to centrifuge at a minimum of 13 600 g.

6.5 *Precision Reciprocal Shaker* 150 oscillations/min with 1 in. stroke length or *wrist-action shaker* capable of controlling the shaking amplitude to 4 ± 2 mm and the frequency to 9 ± 2 Hz.

6.6 *Constant Temperature Water Bath* at 37 ± 2°C.

7. Reagents

7.1 *Hydrochloric Acid* (0.07 *N*)—Add 2.55 g concentrated hydrochloric acid (HCl) to water and dilute to 1 L with water.

7.2 *Hydrochloric Acid* (0.14 *N*)—Add 5.10 g concentrated hydrochloric acid (HCl) to water and dilute to 1 L with water.

7.3 *Hydrochloric Acid* (2.0 *N*)—Add 72.9 g concentrated hydrochloric acid (HCl) to water and dilute to 1 L with water.

7.4 *Hydrochloric Acid* (6.0 *N*)—Add 218.8 g concentrated hydrochloric acid (HCl) to water and dilute to 1 L with water.

7.5 *Water,* of at least Grade 3 purity in accordance with ISO 3696.

[6] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1120. Contact ASTM Customer Service at service@astm.org.

[7] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1121. Contact ASTM Customer Service at service@astm.org.

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8. Preparation of Test Portions

8.1 A test portion is approximately 100 mg.

8.2 Art materials that are in the form of a liquid, dust or comminuted solid or are metals, are tested without further preparation.

8.3 Scraped coatings of art materials are prepared by comminuting the sample sufficient to pass through a 0.5-mm sieve.

8.4 Films, textiles, and paper are prepared by cutting into approximately 6 by 6 mm squares.

8.5 Solids are comminuted, ground or scraped to prepare a sample sufficient to pass through a 0.5 mm sieve.

8.6 100 to 200 mg of oil-based semi-solids should be spread on acid washed Whatman 40 filter paper circles (9 cm) prior to extraction.

9. Procedure

9.1 Mix the test portion with 50 times its mass of an aqueous solution of 0.07 *N* hydrochloric acid at 37 ± 2°C. In case there is less than a 100 mg test portion, mix the portion with 5.0 mL of this solution at the given temperature. Shake for min.

9.2 Check the acidity of the mixture. If the pH is greater than 1.5 add drop wise while shaking an aqueous solution of 2 *N* hydrochloric acid until the pH is between 1.0 and 1.5. If a pH meter is used, appropriate precautions to prevent cross-contamination should be taken. Protect the mixture from light. Shake the mixture efficiently for 1 h and then allow the mixture to stand for 1 h at 37 ± 2°C.

NOTE 1—It has been shown that the extraction of soluble cadmium can show a 2 to 5 fold increase when extraction is carried out in the light rather than in dark. Using brown flasks or aluminum foil-covered flasks will eliminate light effects.

9.3 If necessary, centrifuge the mixture and separate the solids from the mixture by filtration through a membrane filter with a pore size of 0.45 µm.

NOTE 2—Some fine pigments may break through a standard 0.45-µm filter. In these cases centrifugation of the eluate at 13 600 g for 15 min will remove remaining suspended pigment particles.

9.4 Paper products are prepared by first macerating the test portion with 25 times its mass of water at 37 ± 2°C so that the resulting mixture is uniform in color and texture. This mixture is than transferred quantitatively to a conical flask. Add 25 times the mass of the test portion of an aqueous solution of 0.14 *N* hydrochloric acid at 37 ± 2°C and shake for 1 min. Complete the extraction as in 8.2 and 8.3.

9.5 If a test portion contains large quantities of alkaline materials, generally in the form of calcium carbonate, adjust the pH to 1.0 to 1.5 with 6 *N* hydrochloric acid in order to avoid over dilution.

9.6 Determine metal(s) concentration in eluate with the appropriate analytical procedure (see ISO 3856 or USEPA Test Method SW-846).

TABLE 1 Comminuted Paint Sample

	Barium	Cadmium	Chromium
Mean value (mg/kg)	101	22.7	27.2
Degrees of freedom	12	14	13
Repeatability standard deviation	6.0	0.9	1.66
Repeatability 95 % limits	±17	±2.5	±4.6
Reproducibility standard deviation	21	4.9	3.74
Reproducibility 95 % limits	±48	±14	±10

TABLE 2 Acid Extract of Comminuted Paint Sample

	Barium	Cadmium	Chromium
Mean value (mg/l)	1.90	0.431	0.513
Degrees of freedom	12	14	13
Repeatability standard deviation	0.06	0.01	0.029
Repeatability 95 % limits	±0.17	±0.028	±0.081
Reproducibility standard deviation	0.36	0.051	0.062
Reproducibility 95 % limits	±1.0	±0.13	±0.17

10. Calculation

10.1 Determine the extractable metal level in a test sample in ppm (mg of metal per kg of test material) as follows:

$$\text{Metal concentration in sample (ppm)} = [\text{metal concentration in eluate (ppm)}] \times [\textit{eluate volume (mL)}]/[\textit{sample weight (gm)}] \quad (1)$$

11. Precision and Bias

11.1 *Precision*—The precision estimates are based on an interlaboratory study[8] in which one operator in 17 different laboratories analyzed identically prepared test materials in duplicate using the method specified in this test method. Precision of the extraction was estimated by analyses of a comminuted paint sample and the acid extract of this sample. Repeatability and reproducibility standard deviations and 95 % limits are determined as specified in Practice E180.

11.1.1 *Repeatability*—The within-laboratory standard deviations and 95 % repeatability limits for testing three metals are reported in Table 1 and Table 2.

11.1.2 *Reproducibility*—The between-laboratory standard deviations and 95 % reproducibility limits for testing three metals are reported in Table 1 and Table 2.

11.1.3 *Bias*—No systematic errors were detected between measured and true values on either intralaboratory or between laboratory testing.

12. Keywords

12.1 art materials; bioavailability; soluble metals

[8] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D01-1084. Contact ASTM Customer Service at service@astm.org.

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APPENDIX

(Nonmandatory Information)

X1. RATIONALE

X1.1 Practice D4236 requires that a toxicologist shall take into account the bioavailability of potentially toxic components of an art material in making a determination whether or not the art material would require labeling for a chronic health hazard. This test method may provide an estimate of the bioavailability after ingestion of selected metals in art materials.

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