Test for carbonate using hydrochloric acid and barium hydroxide

Purpose

To determine the presence of carbonate ions (CO_3^{2-}) such as calcium carbonate ($CaCO_3$) [some plasters, onyx marble, deposits in and on ceramics, soil], basic lead carbonate ($PbCO_3 \cdot Pb(OH)_2$) [a corrosion product found on lead], basic cupric carbonate ($CuCO_3 \cdot Cu(OH)_2$) [a corrosion product found on copper alloys] and other carbonate-containing materials.

Principle

When an acid is added to a material containing carbonate ions (CO_3^{2-}), carbon dioxide gas (CO_2) is evolved.

$$CO_3^{2-}\,(s) + 2HCl\,(aq) \rightarrow CO_2\,(g) + H_2O\,(l) + 2Cl^-\,(aq)$$

To confirm the presence of carbon dioxide gas (CO_2), a solution of barium hydroxide ($Ba(OH)_2$) is suspended over the effervescing sample. If carbon dioxide gas (CO_2) is present the solution will become cloudy.

$$CO_2\,(g) + Ba(OH)_2\,(aq) \rightarrow \underset{\text{(cloudy)}}{BaCO_3\,(s)} + H_2O\,(l)$$

Equipment

- balance (to weigh 0.1g)
- glass rod
- magnification
- graduated cylinder
- acid-resistant reagent container
- droppers
- microspatula
- test tube or dark spot-test plate

Reagents and safety

- Barium hydroxide ($Ba(OH)_2$): toxic and an irritant; severe health rating
- Hydrochloric acid (HCl): toxic and corrosive; severe health rating
- Water [boiled, distilled]

Protection

Wear goggles, gloves and protective clothing when using HCl and barium hydroxide.

Other tests to consider or confirm results

None.

Reference

Sorum C. H., 1960. *Introduction to Semimicro Quantitative Analysis*, 3rd edition. Englewood Cliffs, NJ: Prentice-Hall.

Reagent preparation

- 6M hydrochloric acid (HCl) solution (1:1): add equal parts concentrated HCl to distilled water. ALWAYS ADD ACID TO WATER!
- **3% barium hydroxide ($Ba(OH)_2$) aqueous solution:** add 1.5g $Ba(OH)_2$ to 50mL boiled water. Distilled water should be boiled for at least 5 minutes to remove all of the carbon dioxide (CO_2). This important step should not be ignored. The water should be allowed to cool in a tightly lidded container to prevent more CO_2 from dissolving in it while it is cooling. De-ionized water may be used if distilled water is not available but it also must be boiled before use.

Method of sampling

A small sample must be removed for testing. The wash from the surface of an object may be used if it is first evaporated in a watch glass.

Procedure

1. Place a small amount of the sample in a test tube or on a dark spot-test plate.
2. Add two to three drops of the HCl solution.
3. Observe for effervescence.

To confirm the presence of carbon dioxide gas (CO_2)

Suspend a drop of the barium hydroxide solution on the end of a glass rod or dropper. Insert the drop into the test tube while the contents are still bubbling. If the drop becomes cloudy, the gas is probably CO_2; interference can only occur because of the presence of sulfite, which is unlikely in an archaeological setting.

Observations and interpretation

If carbonate ions (CO_3^{2-}) are present, the solution will effervesce strongly. It is important to observe the reaction closely, as some materials will dissolve in the acid without effervescing. Just because a material dissolves in the acid does not mean that it contains carbonate ions (CO_3^{2-}). Carbon dioxide gas must be evolved for this test to be positive. Some metals such as zinc will also evolve gas when in contact with an acid. In this case, the gas evolved is hydrogen (H_2), not carbon dioxide. If the evolution of a gas which is not carbon dioxide is suspected, then the test to confirm the presence of carbon dioxide should be carried out. Note: The drop of $Ba(OH)_2$ may turn cloudy with prolonged contact with air.

Storage and reagent shelf life

Barium hydroxide is stable in ambient temperatures; it will react vigorously with acids. Hydrochloric acid (HCl) is stable when stored in a sealed, acid-resistant container in ambient conditions.

Test for copper using nitric acid and ammonia

Purpose

To determine if a metal alloy or pigment contains copper.

Principle

The dissolution of a trace amount of the metal with nitric acid (HNO_3), which is then exposed to ammonia vapor from a concentrated solution of ammonia (NH_4OH), which forms a copper-amine complex, which turns blue.

$$Cu^{2+}\ (aq) + 6NH_3\ (g) \rightarrow \underset{\text{(blue)}}{[Cu(NH_3)_6]^{2+}\ (aq)}$$

Equipment

- dropper
- graduated cylinder
- tweezers
- filter paper
- acid-resistant reagent container

Reagents and safety

- Concentrated ammonia solution (NH_4OH) [or household ammonia]: toxic, irritant and corrosive; severe health rating
- Nitric acid (HNO_3): corrosive, oxidizing and toxic; severe health rating
- Water [distilled]

Protection

Wear goggles, gloves and protective clothing when handling HNO_3 and NH_4OH. The reaction should be performed in a fume hood.

Other tests to consider or confirm results

- Test for copper using spot-test papers (p. 46).
- Test for copper using rubeanic acid (p. 52).
- Test for copper-based pigments using potassium ferrocyanide (p. 50).

Reference

Moss A. A.1956. *The Identification of Metals. Handbook for Museum Curators*, Part B, *Museum Technique*, Section 8, 2–8. London: Museums Association.

Test for copper-based pigments using potassium ferrocyanide

Purpose

To determine the presence of copper-based pigments and corrosion products [copper (Cu^{2+}) ions].

Principle

Copper ions in the sample are dissolved and converted to cupric ferrocyanide.

$$2Cu^{2+}\,(aq) + K_4Fe(CN)_6\,(aq) \rightarrow \underset{\text{(red-brown)}}{Cu_2Fe(CN)_6\,(s)}$$

Equipment

- balance (to weigh 0.1g)
- graduated cylinder
- scalpel
- droppers
- microspatula
- source of heat (lab oven or infrared lamp)
- filter paper
- acid-resistant reagent containers
- spot-test plate

Reagents and safety

- Concentrated hydrochloric acid (HCl): toxic and corrosive; severe health rating
- Potassium ferrocyanide [potassium hexacyanoferrate(II), $K_4Fe(CN)_6$)]: irritant; slight health rating
- Water [distilled]

Protection

Wear goggles, gloves and protective clothing when handling HCl.

Other tests to consider or confirm results

- Test for copper using nitric acid and ammonia (p. 48).
- Test for copper using rubeanic acid (p. 52).
- Test for copper using spot-test papers (p. 46).

Reference

Tabasso M. Laurenzi. 1993. *Mural Paintings Conservation Course – Identification of Pigments Lab Notes*, Part I: *Constituent Materials/Execution Techniques*. Rome, Italy: ICCROM.

Reagent preparation

- 3M hydrochloric acid (HCl) (1:3): add 5mL concentrated HCl to 15mL distilled water. ALWAYS ADD ACID TO WATER!
- Potassium ferrocyanide solution: dissolve 1g $K_4Fe(CN)_6 \cdot 3H_2O$ in 25mL distilled water.

Method of sampling

Use a few grains of pigment removed from a painting, mural or stains from soil, or a tiny amount of pigment may be brushed onto a piece of filter paper dampened with distilled water. The sample should be as pure as possible so that it contains no contaminants that might give rise to a false color.

Procedure

1. Dissolve some of the sample on a spot-test plate with concentrated HCl or place a drop of concentrated HCl on the pigment on the filter paper. Some of the sample must dissolve, but not necessarily all of it.
2. Dry completely under an infrared lamp or in a lab oven.
3. Add a drop of the potassium ferrocyanide solution.

Observations and interpretation

The formation of a red-brown color (cupric ferrocyanide) indicates the presence of copper. The reaction takes place almost immediately. The presence of iron(III) ions (Fe^{3+}) may interfere with the color interpretation of this test. Iron reacts with the potassium ferrocyanide solution and turns blue. This may mask the color formed by the copper.

Storage and reagent shelf life

Hydrochloric acid is stable when stored in a sealed, acid-resistant container in ambient conditions. The potassium ferrocyanide solution is stable when stored in a sealed container in ambient conditions.

Test for iron using potassium ferrocyanide

Purpose

To determine if corrosion products, stains, or pigments (such as iron pigments on white, non-iron slip pottery) contain iron(III) ions (also known as ferric ions or Fe^{3+}).

Principle

Iron(III) ions will dissolve in hydrochloric acid and react with potassium ferrocyanide ($K_4Fe(CN)_6$) to form ferric ferrocyanide ($Fe_4(Fe(CN)_6)_3$), a bright blue complex (Prussian blue).

$$4Fe^{3+}\,(aq) + 3K_4Fe(CN)_6\,(aq) \rightarrow \underset{\text{(blue)}}{Fe_4(Fe(CN)_6)_3\,(s)} + 12K^+\,(aq)$$

Equipment

- balance (to weigh 0.1g)
- graduated cylinder
- microspatula
- tweezers
- droppers
- heat source (lab oven or infrared lamp)
- acid-resistant reagent container
- filter paper
- magnification
- spot-test plate

Reagents and safety

- Hydrochloric acid (HCl): toxic and corrosive; severe health rating
- Potassium ferrocyanide ($K_4Fe(CN)_6 \cdot 3\,H_2O$) [also known as potassium hexacyanoferrate]: irritant; slight health rating
- Water [distilled]

Protection

Wear goggles, gloves and protective clothing when handling HCl.

Other tests to consider or confirm results

- Test for iron using hydrochloric acid (p. 64).

Reference

Tabasso, M. Laurenzi. 1993. *Mural Paintings Conservation Course "Identification of Pigments" Lab Notes, Part I: Constituent Materials/Execution Techniques*. Rome: ICCROM.

Reagent preparation

- 3M hydrochloric acid (HCl) solution (1:3): add 1mL concentrated HCl to 3mL distilled water. ALWAYS ADD ACID TO WATER!
- Potassium ferrocyanide solution: add 1g $K_4Fe(CN)_6 \cdot 3H_2O$ to 25mL water.

Method of sampling

A small amount of sample must be removed for testing.

Procedure

1. Dissolve some of the sample on a spot-test plate with concentrated HCl or place a drop of concentrated HCl on the pigments on filter paper. Some of the sample must dissolve, but not necessarily all of it.
2. Dry completely under an infrared lamp or in a lab oven.
3. *Optional*: the addition of a drop of the 3M HCl solution may assist the reaction with some metal surfaces.
4. Add a drop of the potassium ferrocyanide solution.

Alternative procedure for pigments

1. On a filter paper that has been dampened with distilled water, collect a tiny amount of pigment.
2. Place the filter paper on the spot-test plate.
3. Place a drop of concentrated HCl on the pigment on the filter paper.
4. Dry completely under an infrared lamp or in a lab oven.
5. Add a drop of the 3M HCl solution.
6. Add a drop of potassium ferrocyanide solution.
7. Observe under magnification.

Observations and interpretation

The formation of a blue color (Prussian blue) indicates the presence of iron. Copper ions (if present) may interfere with the interpretation of this test. Potassium ferrocyanide also reacts with copper ions to form a reddish brown color. Aluminum reacts to form a blue color. If both iron and copper are present in quantity, the final solution may appear to be slightly purple. If the test is carried out on filter paper, the color formation may only be visible near the pigment particles under magnification

Storage and reagent shelf life

Hydrochloric acid is stable when stored in a sealed, acid-resistant container in ambient conditions. Potassium ferrocyanide is stable in ambient conditions but the aqueous solution decomposes slowly on standing.

Test for iron using hydrochloric acid

Purpose

To confirm that a metal object, corrosion product or pigment contains iron.

Principle

The reaction of iron oxides with hydrochloric acid will form iron(III) chloride [ferric chloride ($FeCl_3$)] which is yellow.

$$Fe^{3+}\ (aq) + HCl\ (aq) \rightarrow \underset{\text{(yellow)}}{FeCl_3\ (aq)}$$

Equipment

- dropper
- spot-test plate
- filter paper
- heat source (lab oven, hot plate or infrared lamp)

Reagents and safety

- Hydrochloric acid (HCl): toxic and corrosive; severe health rating

Protection

Wear goggles, gloves and protective clothing when handling HCl.

Other tests to consider or confirm results

- Test for iron using potassium ferrocyanide (p. 62).

Reference

Moss, A. A.1956. *The Identification of Metals. Handbook for Museum Curators,* Part B, *Museum Technique,* Section 8, 2–8. London: Museums Association.

Test for lead using potassium iodide and electrolysis

Purpose

To determine the presence of lead in metal objects.

Principle

Small quantities of lead ions are dissolved by electrolysis onto filter paper soaked in nitric acid (HNO_3) and then tested with potassium iodide (KI). The filter paper turns bright yellow if lead ions are present. By using pointed paper test strips the area exposed to electrolysis may be greatly reduced. This test is probably the most sensitive of all the lead tests and it has been found to work well in almost all lead testing situations including those of lead-alloyed metals such as bronze or brass with lead content as low as 2%.

$$\mathrm{Pb}\,(s) + \mathrm{HNO_3}\,(aq) \rightarrow \mathrm{Pb^{2+}}\,(aq) \xrightarrow{\mathrm{KI}\,(aq)} \underset{\text{(yellow)}}{\mathrm{PbI_2}\,(s)}$$

Equipment

- electrolysis cables
- balance (to weigh 0.1g)
- filter paper
- acid-resistant reagent containers
- cotton swabs
- graduated cylinder
- spot-test plate
- 6V battery
- droppers
- microspatula
- stainless steel tweezers

Reagents and safety

- Acetone: flammable, and irritant; slight health warning
- Nitric acid (HNO_3): corrosive, oxidizing, and toxic; severe health rating
- Potassium iodide (KI): irritant; moderate health rating
- Water [distilled][tap]

Protection

Wear goggles, gloves and protective clothing while handling HNO_3.

Other tests to consider or confirm results

- Test for lead using spot-test papers (p. 66).
- Test for lead using potassium dichromate (p. 70).

Reference

Gedye, Ione, Henry Hodges and Andrew Oddy. 1973. *Notes for a Short Course in Conservation*. London: British Museum Research Laboratory.

Reagent preparation

- 0.5M nitric acid (HNO_3) solution (1:30): add 1mL concentrated HNO_3 to sufficient distilled water to bring the total volume to 32mL. ALWAYS ADD ACID TO WATER!
- 10% potassium iodide (KI) solution: dissolve 1g of KI in 9mL distilled water.

Method of sampling

Tests are performed directly on the surface of the object. The nitric acid will cause a black spot to form on some metals, therefore an inconspicuous area should be selected for testing. The alligator clips can scratch the soft metal.

Procedure

1. Degrease an area of the object with acetone and cotton swabs. This important step should not be overlooked. The reaction will not take place unless there is good contact with the metal.
2. Connect the electrolysis cables, attach one clip to the positive pole of the 6V battery and the other end to the object. If the metal is soft, the alligator clip may scratch the object. To avoid this, filter paper soaked in tap water can be used as a pad for the alligator clip. If this method is used, the filter paper must always be wet to conduct the current.
3. Place a drop of the HNO_3 solution on the spot-test plate.
4. Using stainless steel tweezers, dip a piece of filter paper into the HNO_3 solution.
5. Attach the tweezers to the negative pole of the 6V battery with the other length of wire using the remaining alligator clips. It is important that the tweezers hold the filter paper well within the wet part so that current will be conducted by the tweezers to the filter paper and on through the object. Hold the tip of the filter paper to the object for 5 seconds.
6. Remove the filter paper from the object and add one drop of the KI solution to the filter paper.
7. Rinse the test area with distilled water.

Alternative non-electrolysis procedures

1. Using stainless steel tweezers, dip the filter paper in a drop of the HNO_3 solution.
2. Hold the corner of the paper in contact with the object for 30 seconds or, if possible, lay a small HNO_3-soaked filter paper in contact with the object for 30 seconds. For corrosion products and pigments, sprinkle some of the pigments onto HNO_3-soaked filter paper.
3. Add one drop of the KI solution.
4. Swab the artefact with distilled water to remove the chemicals, then dry.

Observations and interpretation

The formation of a bright yellow color on the tip of the filter paper that was in contact with the object indicates the presence of lead ion (Pb^{2+}) in the object. A stronger acid or longer electrolysis will give a very dark colored reaction with lead. Most other metals will turn the test paper brownish red so an orange or brownish red color is not a positive result. The alternative procedure allows testing of materials that cannot be tested using electrolysis, such as powdered pigments, paint *in situ*, and glazes on ceramics. This is a very sensitive test but it requires longer time.

Storage and reagent shelf life

Nitric acid (HNO_3) is stable when stored in a sealed acid-resistant container in ambient conditions. Potassium iodide (KI) is stable in ambient conditions but on prolonged exposure to air it may become yellow. The KI solution is stable in ambient conditions but it should be stored in a dark bottle.

Test for calcium using nitric acid and sulfuric acid

Purpose

To determine the presence of calcium ions (Ca^{2+}) in a sample. This test can be used in conjunction with the *Test for carbonate using hydrochloric acid and barium hydroxide* (p. 102) to identify calcium carbonates such as those found in lime plaster or in accretions on artefacts.

Principle

Calcium ions (Ca^{2+}) in solution are treated with sulfuric acid and the formation of characteristic calcium sulfate ($CaSO_4 \cdot 2H_2O$)(gypsum) crystals is observed through a hand lens or microscope.

$$Ca^{2+}\ (aq) + SO_4^{2-}\ (aq) \rightarrow \underset{\text{(crystals)}}{CaSO_4 \cdot 2H_2O\ (s)}$$

Equipment

- glass slide and cover slip
- heat source (lab oven, infrared lamp or hot plate)
- acid-resistant reagent container
- droppers
- graduated cylinder
- magnification (≥20×)
- test tubes

Reagents and safety

- Nitric acid (HNO_3): toxic, oxidizing and corrosive; severe health rating
- Sulfuric acid (H_2SO_4): toxic, oxidizing and corrosive; severe health rating

Protection

Wear goggles, gloves and protective clothing when handling HNO_3 and H_2SO_4.

Other tests to consider or confirm results

None.

Reference

Schramm, Hans-Peter. 1995. *Historische malmaterialien und ihre identifizierung*. Stuttgart: Ferdinand Enke Verlag.

Reagent preparation

- 0.5M nitric acid (HNO_3) solution (1:30): add 1mL concentrated HNO_3 to 30mL distilled water. ALWAYS ADD ACID TO WATER!
- 2M sulfuric acid (H_2SO_4) solution (1:8): slowly add 5.5mL concentrated sulfuric acid to distilled water while stirring, making up to 50mL of solution. ALWAYS ADD ACID TO WATER!

Method of sampling

The sample must be in solution. If solid, place a small amount of the sample into a test tube and add 5–10 drops of the HNO_3 solution to dissolve the calcium-containing part of the sample.

Procedure

1. Place a drop of the sample solution on a glass slide
2. Evaporate to dryness in a lab oven (under the infrared lamp or carefully on a hot plate).
3. Cover the residue with a cover slip.
4. Place a drop of the H_2SO_4 solution next to the cover slip so that it is drawn under the cover slip.
5. Observe the edge of the residue with magnification (loupe or microscope).

Observations and interpretation

As the sulfuric acid dissolves some of the calcium-containing residue, calcium sulfate will precipitate and form characteristic gypsum needles. This occurs usually at the edge of the slide somewhere near the dried residue. It may take as long as 30 minutes for sufficient crystals to form so that they are visible. Not all of the residue will dissolve in the sulfuric acid. The crystals are long and needle-like and may group together in star-like clusters. The crystals are not visible to the naked eye. A microscope with at least 20× magnification works best, however, a magnifying glass/loupe at 15× or 20× may also work. As it is difficult to recognize these crystals the first time, it is advisable to perform this test on a known sample containing calcium.

Storage and reagent shelf life

Sulfuric acid (H_2SO_4) is stable when stored in a sealed, acid-resistant container in ambient conditions. Nitric acid (HNO_3) is stable when stored in a sealed, acid-resistant container in ambient conditions.