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# Gravimetric Methods

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In many of the reagent monographs, it is directed that a precipitate or residue be collected and either dried or ignited so as to provide certain information concerning the purity of the reagent. Except where it is directed otherwise in the specific reagent tests, the following directions and precautions will be used in collecting, drying, and igniting precipitates and residues.

## General Considerations

It is imperative that the analyst use the best techniques in performing any of the operations included in this book. Exceptional cleanliness and protection against accidental contamination from dirt, fumes, and analytical containers are rigid requirements for acceptable results. Use of fume or clean-air hoods is recommended whenever possible. The choice of equipment is generally left to the discretion of the analyst, but it must provide satisfactory accuracy and precision. All weighings must be determined with an uncertainty of not more than  $\pm 0.0002$  g. [Moody (1982) and Zief and Mitchell (1976) wrote the classic works on this subject.]

When the use of a tared container is specified, the container will be carried through a series of operations identical to those used in the procedure, including drying, igniting, cooling in a suitable desiccator, and weighing. In general, desiccators should be charged with indicating-type silica gel. (Table 2-1 compares the different types of desiccators.) Stronger desiccants may be required for certain applications. The length of the drying or ignition and the temperature employed must be the same as specified in the procedure in which the tared equipment is to be used. Where it is directed to dry or ignite to constant weight, two successive weighings may not differ by more than  $\pm 0.0002$  g, the second weighing following a second drying or ignition period.

In those operations wherein a filtering crucible is specified, a fritted-glass crucible, a porous porcelain crucible, or a crucible having a sponge platinum mat may be used. Certain solutions may attack the filtering vessel; for example, both fritted glass and porcelain are affected by strongly alkaline solutions. Even platinum sponge mats are attacked by hydrochloric acid unless the crucible is first washed with boiling water to remove oxygen.

Table 2-1. Selection Chart for Desiccators

Desiccant	Suitable for Drying	Not Suitable for Drying	Residual Water <sup>a</sup>	Water Content <sup>b</sup>	Regeneration	Reaction Mechanism
Aluminum oxide	Hydrocarbons		0.003	0.2	175 °C	Chemisorption, absorption
Calcium chloride	Ethers, most esters, alkyl halides, aryl halides, saturated hydrocarbons, aromatic hydrocarbons	Alcohols, amines, phenols, aldehydes, amides, amino acids, some esters, ketones	0.4	0.2 (1H <sub>2</sub> O) 0.3 (2H <sub>2</sub> O)	None	Hydration
Calcium oxide	Low molecular weight alcohols, amines, ammonia gas	Acidic compounds, esters	0.007	0.3	1000 °C	Chemisorption
Magnesium oxide	Hydrocarbons, aldehydes, alcohols, basic gases, amines	Acidic compounds	0.008	0.5	800 °C	Hydration
Magnesium perchlorate, anhydrous	Inert gas, air	Most organics <sup>c</sup>	0.001	0.2	250 °C with vacuum	Hydration
Magnesium sulfate, anhydrous	Most compounds, including acids, ketones, aldehydes, esters, nitriles		1.0	0.2–0.8	None	Hydration
Molecular sieve, activated, 8–12 Mesh						
Type 3A	Molecules >3 Å in diameter	Molecules >3 Å in diameter		0.18	177–260 °C	Absorption
Indicating, Type 4A	Molecules >4 Å in diameter	Molecules >4 Å in diameter; ethanol, H <sub>2</sub> S, CO <sub>2</sub> , SO <sub>2</sub> , C <sub>3</sub> H <sub>4</sub> , C <sub>3</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>6</sub> , strong acids	0.001	0.18	250 °C	Absorption
Type 5A	Molecules >5 Å in diameter, e.g., branched chain compounds, those with 4 carbon or larger rings	Molecules >5 Å in diameter, e.g., butanol, <i>n</i> -C <sub>4</sub> H <sub>8</sub> to <i>n</i> -C <sub>22</sub> H <sub>46</sub>	0.003	0.18	250 °C	Absorption

Phosphorus pentoxide, granular	Saturated hydrocarbons, aromatic hydrocarbons, ethers, alkyl halides, aryl halides, nitriles, anhydrides	Alcohols, acids, amines, ketones	0.001	0.5	None	Chemisorption
Potassium carbonate, anhydrous	Alcohols, nitriles, ketones, esters, amines	Acids, phenols	0.2	0.2	200 °C	Hydrate formation
Potassium hydroxide pellets	Amines	Acids, phenols, esters, amides, acidic gases	0.3	—	None	Hydration and solution formation
Silica gel, indicating-type	Most organics	Acids, phenols, esters, amides	0.03	0.2	200–350 °C	Adsorption
Sodium hydroxide pellets	Amines	Acids, phenols, esters, amides	0.16	—	None	Adsorption and solution formation
Sodium sulfate, anhydrous, granular, or powder	Alkyl halides, aryl halides, aldehydes, ketones, acids		12.0	1.2	Usually not	Hydration
Sulfuric acid	Inert gases, air used in desiccators	Too reactive to contact organic materials	0.004	—	None	Hydration
Zinc chloride reagent, broken lump	Hydrocarbons	Ammonia, amines, alcohol	0.9	0.2	110 °C	Hydration

Notes: — indicates indefinite water content.

<sup>a</sup>Milligrams of water per L of dry air.

<sup>b</sup>Grams of water per g of desiccant.

<sup>c</sup>Magnesium perchlorate, anhydrous, may form an explosive compound when exposed to organic vapors.

Source: Reproduced courtesy of Mallinckrodt Baker, Inc.

### ***Collection of Precipitates and Residues***

In many of the tests, the amount of residue or precipitate may be so small as to escape easy detection. Therefore, the absence of a weighable residue or precipitate must never be assumed. However small, it must be properly collected, washed, and dried or ignited. The size and type of the filter paper to be used is selected according to the amount of precipitate to be collected, not the volume of solution to be filtered.

Often when barium chloride is added in slight excess to precipitate barium sulfate, the amount of precipitate produced is so small that it is hard to see and collect. If a small amount of a suspension of ashless filter paper pulp is added toward the end of the period of digestion on the steam bath or hot plate, the flocculation and collection of the sulfate are facilitated.

Some precipitates have a strong tendency to “creep”, while others, like magnesium ammonium phosphate, stick fast to the walls of the container. The use of the rubber-tip “policeman” is recommended, sometimes supplemented by a small piece of ashless filter paper. The analyst should guard against the possibility of any of the precipitate escaping beyond the upper rim of the filter paper.

Precipitates, especially if recently produced, may be partially dissolved unless proper precautions are taken with both their formation and subsequent washing. In general, precipitates should not be washed with water alone but with water containing a small amount of common ion to decrease the solubility of the precipitate. It is much better to wash with several small portions of washing solution than with fewer and larger portions. Calcium oxalate precipitates should be washed with dilute (about 0.1%) ammonium oxalate solution; therefore, mixed precipitates that may contain calcium oxalate and magnesium ammonium phosphate should be washed with a 1% ammonia solution containing also 0.1% ammonium oxalate.

### ***Weights of Precipitates and Residues***

With few exceptions, the weight of the sample used in the test will ensure that at least 0.001 g of the impurity to be determined will be present if the sample fails the test.

### ***Ignition of Precipitates***

The proper conditions for obtaining the precipitate are given in the individual test directions.

► **Procedure for Ignition of Precipitates.** Collect the precipitate on an ashless filter paper of suitable size and porosity (for example, a paper of 2.5- $\mu\text{m}$  retention for a precipitate made up of fine particles). Wash the residue and paper thoroughly with the proper solution, and fold the moist filter paper about the residue. Place the filter paper in a suitable tared crucible that has been preconditioned at the temperature required by the specific test, and dry the paper using a 105 °C oven, a hot plate, an infrared lamp, or (carefully) a gas microburner in a covered crucible. When the paper is dry, char it at the lowest possible temperature; gentle ignition destroys the charred paper. Finally, ignite the contents of the crucible in a vented muffle furnace at  $600 \pm 25$  °C for 15 min. Cool the ignited crucible in a suitable desiccator (using indicating-type silica gel or another desiccator as specified in the individual reagent monograph) and weigh it.

## Insoluble Matter

The intent of these tests is to determine the amount of insoluble foreign matter (for example, filter fibers and dust particles) present under test conditions designed to dissolve completely the substance being tested. After dissolution and before filtration, it is a good practice to check visually (using a white background) for insoluble foreign matter.

► **Procedure for Insoluble Matter.** Prepare a solution of the sample as specified in the individual test directions. Unless otherwise specified, heat to boiling in a covered beaker, and digest on a low-temperature ( $\approx 100$  °C) hot plate (or a steam bath) for 1 h. Filter the hot solution through a suitable tared, medium-porosity (10–15- $\mu\text{m}$ ) filtering crucible. Unless otherwise specified, wash the beaker and filter thoroughly with hot water, dry at 105 °C, cool in a desiccator, and weigh.

## Residue after Evaporation

This test is designed to determine the amount of any higher-boiling impurities or nonvolatile dissolved material that may be present in a reagent chemical. It is used chiefly in testing organic solvents and some acids.

The preferred container for the evaporation of almost all reagents is a platinum dish. However, in many cases, other containers (for example, dishes of porcelain, silica, or aluminum) may be found suitable. In a few cases, such as when strong oxidants are evaporated, platinum should not be used.

A low-temperature ( $\approx 100$  °C) hot plate is usually specified in the tests in this book for evaporations. A steam bath may be used, if the steam is generated from deionized or distilled water in a properly maintained apparatus.

The residue is not dried to constant weight in this test because continued heating may slowly volatilize some of the high-boiling impurities. The drying conditions specified will, however, yield reproducible and reliable results so that drying to constant weight is not necessary.

► **Procedure for Residue after Evaporation.** Place the quantity of reagent specified in the individual test description in a suitable tared container (see Containers, page 17). Evaporate the liquid gently so that boiling does not occur; do this in a well-ventilated muffle furnace or fume hood, protected from any possibility of contamination. Unless otherwise specified, dry the residue in an oven at 105 °C for 30 min. Cool the container in a suitable desiccator, and weigh. Calculate the percent residue from the weight of the residue and the weight of the sample.

## Loss on Ignition

This test is intended to determine the amount of volatile material due to occluded water or process contamination. The procedure follows directives in the Residue after Ignition test, except that the addition of sulfuric acid is eliminated. Specific variances are detailed in the individual monographs. Calculate the percentage of material lost on ignition.

## Residue after Ignition

These tests are designed and intended to determine the amount of nonvolatile inorganic material that may be present in a reagent. They are applied to those inorganic reagents that can be sublimed or volatilized without decomposition; among these are reagents such as ammonium salts and some inorganic acids. Various organic reagents are also tested against this specification.

The interpretation of the instruction to “ignite” has varied widely. After considerable study of the various residues involved, a temperature of  $600 \pm 25$  °C for 15 min in a well-ventilated muffle furnace or fume hood has been adopted. This method ensures constant conditions for conversion of the residues to the desired composition without causing appreciable loss of the impurities themselves. It should also be emphasized that certain organic reagents are difficult to volatilize, and slight variations in the test have been suggested where appropriate. Reagents with a high water content should be dried before ignition to prevent loss of sample. It is left to the discretion of the analyst as to the method of heating to be used, such as a hot plate, gas microburner, or infrared lamp. The final ignition at higher temperature should be done under oxidizing conditions, preferably in a muffle furnace.

► **Procedure for Residue after Ignition.** Ignite the quantity of reagent specified in the individual test description in a tared preconditioned crucible or dish in a well-ventilated hood, protected from air currents. Heating should be gentle and slow at first and should continue at a rate of 1 to 2 h to volatilize inorganic samples completely or to char organic samples thoroughly. If the sample is a liquid, evaporate completely by heating gently without boiling. Cool the crucible, and moisten the residue with 0.5 mL of sulfuric acid, unless specified otherwise. Ignite the crucible until white fumes of sulfur trioxide cease to evolve. Then, finally, ignite at  $600 \pm 25$  °C for 15 min. Cool in a suitable desiccator (using indicating-type silica gel), weigh, and calculate the percentage of residue.

## Loss on Drying

This test is designed to determine the amount of volatile material present in a sample due to process contamination, inherent affinity for volatile impurities, or designated moles of hydration. The volatile content must be removable at relatively low temperatures.

► **Procedure for Loss on Drying.** Accurately weigh the sample in a conditioned and tared vessel compatible with the material being tested (see Containers, page 17). Unless otherwise noted, dry the material to constant weight in an oven at 105 °C, typically for 4 h; care must be taken to avoid sample loss as a result of spattering or crystal fractionation. Cool sample in a desiccator and weigh. Calculate the percentage of material lost on drying.