HEAVY METALS

PRINCIPLE

Heavy metals are here defined as those metallic impurities that are colored by hydrogen sulfide under the conditions of this test. Concentration is determined by visual comparison with lead standards treated similarly. (Note 1). If there is color interference the organic matter in the sample is first destroyed by ignition in the presence of a small amount of sulfuric acid and the residue is dissolved in dilute acid.

SCOPE

The method applies to the determination of heavy metals in corn syrups, corn sugars, refined sugars and syrup solids, including USP dextrose (Note 2).

SAFETY NOTE

This procedure requires the use of several extremely hazardous chemicals. Thorough knowledge of the dangers and safety procedures is required. Proper protective equipment is also required.

SPECIAL APPARATUS

1. Muffle furnace: equipped with pyrometer and capable of operating at controlled temperatures up to 550 °C.

2. Platinum or silica dishes: 100 to 200 mL capacity.

3. Nessler Tubes: Matching 50 mL tall form tubes and viewing stand.

REAGENTS

1. Sulfuric Acid solution, (1:3): Cautiously pour 500 mL of concentrated sulfuric acid (96% H2SO4, sp g 1.84, lead free) into 1500 mL of purified water and mix.

2. Hydrochloric Acid Solution, (1:3): Add 500 mL of concentrated hydrochloric acid, (37% HCl, sp g 1.19) to 1500 mL of purified water and mix.

HEAVY METALS – continued

3. Acetic Acid, (CH_3COOH) 6%: Dilute 60 mL glacial acetic acid, sp g 1.06 to 1.0 L with purified water and mix.

4. Ammonium Hydroxide Solution, (NH_4OH) (1:1 v/v): Add 500 mL of concentrated NH_4OH, (28% NH_4OH, sp g 0.90; 14.8 *N),* to 500 mL of purified water and mix.

5. Hydrogen Sulfide Solution, Saturated: **Hydrogen sulfide gas is toxic . Use special precautions to contain in hood. Vent only through a scrubber (Notes 3, 4)**.

   Bubble hydrogen sulfide (H_2S) gas from a cylinder through cold water until saturated, (about 10 mins.). The saturated solution should produce, at once, a copious precipitate of sulfur when added to an equal volume of 10% ferric chloride solution. Prepare fresh solution just prior to use.

6. Standard Lead (Pb) Solution, 10 µg/mL:

   Stock Solution: Dry lead nitrate [$Pb(NO_3)_2$] overnight in a desiccator. Dissolve 0.1600 g of reagent grade lead nitrate in water, add 1.0 mL of concentrated nitric acid (HNO_3) and dilute with purified water to 1.0 L. Store in glass container which is free from soluble lead salts.

   Standard Solution: Pipet 10.0 mL of the stock lead solution and dilute with purified water to 100 mL and mix thoroughly. Prepare fresh standard solutions daily.

PROCEDURE

Weigh accurately about 5 g of sample and transfer with a minimum quantity of purified water to a 50 mL Nessler tube (Note 3). Pipet 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 mL of standard lead solution into 6 separate 50 mL Nessler tubes. From this point treat all tubes in the same manner.

Add 2 mL of 6% acetic acid, dilute to 25 mL with purified water and mix. Add 10 mL of saturated hydrogen sulfide solution, mix and allow to stand 10 minutes. Compare color in sample tube with that in standard tubes by viewing downward over a white surface.

Determine the volume of standard lead solution (to nearest 0.5 mL) required to obtain a color match.

If there is a color interference, follow the ash procedure below:

Weigh about 10.0 g of sample (dry basis) into a platinum or silica dish. Add 5 mL of 1:3 sulfuric acid, distributing the acid uniformly in the sample. Place the dish on a steam bath or low temperature hot plate to evaporate the water; increase heat to carbonize the sample and expel most of the sulfuric acid. Place the dish in a muffle furnace at 525-550 °C until the ash is free from carbon (refer to CRA ash procedure). Cool to room temperature. Carefully wash down sides of dish with 3-5 mL of purified water; add 5 mL of 1:3 hydrochloric acid and evaporate to dryness on a steam bath.

Pipet 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 mL of standard lead solution into separate beakers. From this point treat samples and standard in the same manner.

Add 5 mL of 1:3 hydrochloric acid and 10 mL of purified water. Bring to boil on a hot plate and boil gently for 10 mins. Cool and carefully add 1:1 ammonium hydroxide solution until the solution is neutral to litmus paper. Add 2 mL of 6% acetic acid solution. Filter quantitatively if solution is hazy.

Transfer solution to Nessler tube, dilute to 30 mL volume with purified water and mix. Add 10 mL of saturated hydrogen sulfide solution, mix and allow to stand for 10 mins.

Compare sample color with that of the standards. Determine volume of standard lead solution (to nearest 0.5 mL) required to obtain a color match.

CALCULATION

$$\text{Heavy Metals, ppm (as is, expressed as lead)} = \frac{(\text{mL Std. Pb Soln})(0.00001)(1{,}000{,}000)}{\text{Sample Wt., g}}$$

NOTES AND PRECAUTIONS

HEAVY METALS – continued

1. Lead, Bismuth, Copper, Silver and Tin are the principal contributors to the heavy metals value obtained by this colorimetric procedure.

2. Ashing as described in this method is required only when a color interference is obtained when following the procedure for the sample solution "as is". See reference 1, method I.

3. Hydrogen sulfide gas also may be generated from the reaction of ferric sulfide (FeS_2) and dilute hydrochloric acid (HCl).

4. Thioacetamide in a glycerine base may be used as a reagent instead of an aqueous saturated solution of Hydrogen Sulfide. See reference 3.

REFERENCES

1. Food Chemicals Codex. Fourth Edition. "General Tests and Assays," pp. 760-762, and "General Provisions and Requirements," p. 3, 1996

2. *The United States Pharmacopeia.* Twenty-Third Edition. 1995. "Chemical Tests: <23> Heavy Metals," pp. 1727-1728.

3. *The United States Pharmacopeia Supplement 3*, November 15, 1995. "Limit Tests: <23> Heavy Metals," pp. 3000-3001.

METHOD HISTORY

Combined the Heavy Metals methods for Corn Syrup (E-30) and Corn Sugar (F-26) on 11-09-2010.

Corn Syrup, Heavy Metals (E-30), Date of Acceptance 11-26-1956, Revised 4-28-1987.

Corn Sugars, Heavy Metals (F-26), Date of Acceptance 4-14-1978, Revised 4-09-1998.