

Determination of Phosphorus

1 Scope

Small quantities of biologically derived phosphorus compounds arising from native hides and skins are present in leather. Inorganic polymeric phosphates are used as tanning auxiliaries and in the manufacture of other tanning materials. Organic phosphates are used as plasticizers in leather finishing. This method does not differentiate between phosphorus arising from different sources but gives a procedure for determining total phosphorus in leather.

2 Definition

For the purposes of this method the following definition applies.

Phosphorus content of leather. This is expressed in terms of the oxide, P_2O_5 .

3 Principle

Leather is ashed and fused, and the cooled melt is dissolved and filtered. The phosphorus present in the filtrate is in the form of ortho-phosphate and polyphosphate. An aliquot of the solution is depolymerized by boiling under acid conditions and the chromium present reduced to Cr(III) with sodium sulphite. Phosphorus is determined absorptiometrically as a phosphomolybdovanadate complex with an absorption maximum of 460 nm.

4 Reagents

The following reagents are required.

- (a) *sodium sulphite solid* (without water of crystallisation).
- (b) *nitric acid* dilute approximately 3M.
- (c) *5% ammonium molybdate solution* in distilled water (filter after ageing for 24 hours).
- (d) *0.25% ammonium vanadate* prepared by dissolving 2.5 g of the salt in 800 ml hot distilled water containing 20 ml concentrated nitric acid ($d = 1.43$ g/ml), made up to 1:1 after cooling.
- (e) *standard phosphate solution* containing 1 mg P_2O_5 /ml prepared by dissolving 0.9585 g potassium dihydrogen phosphate AR in distilled water and making up to 500 ml.
- (f) *sulphuric acid*, concentrated ($d = 1.83$ g/ml).

5 Apparatus

The usual laboratory apparatus is required and, in particular, the following.

- (a) *measuring cylinders.*
- (b) *pipettes.*
- (c) *volumetric flasks*, 50 ml and 100 ml.
- (d) *spectrophotometer* or *absorptiometer* with suitable filter.
- (e) *analytical balance*, sensitivity 0.001 g.
- (f) *Erlenmeyer flask.*
- (g) *pH measuring apparatus.*
- (h) *glass beads.*
- (i) *Bunsen burner.*

6 Procedure

Sample in accordance with SLC 1. Grind in accordance with SLC 2.

- 6.1 Obtain a filtrate as described in SLC 17, clauses 6.1 to 6.5. Make up the filtrate to 100 ml with distilled water in a volumetric flask.
- 6.2 Acidify a 50 ml aliquot to approximately pH 2 (glass electrode) in an Erlenmeyer flask with concentrated H_2SO_4 and boil gently for 30 minutes to depolymerize the polymeric phosphate to orthophosphate.

- 6.3 Reduce the chromium(VI) in the solution by adding about 1 g of sodium sulphite followed by boiling with a few glass beads. Boil gently for another 15 minutes after the appearance of the green colour to remove sulphur dioxide. Transfer the solution quantitatively to a 100 ml volumetric flask and make up to volume. This is the analytical solution for the determination of phosphorus.
- 6.4 Pipette an aliquot of the analytical solution containing not more than 5 mg of P_2O_5 into a 50 ml graduated flask, followed by sufficient distilled water to bring the volume up to 30 ml.
- 6.5 Add, in order, 5 ml dilute nitric acid (3M), 5 ml ammonium vanadate and 5 ml ammonium molybdate. Make up to volume with distilled water and mix well.
- 6.6 Prepare a blank solution in a similar manner but omitting the ammonium molybdate. Colour development is stable for at least 30 minutes.
- 6.7 Measure the absorption at 460 nm using the blank prepared from the sample under investigation. Convert to mg P_2O_5 by use of a standard calibration curve. For proper colour development the solution, after making up to volume, shall be between 0.2 and 1.6M HNO_3 (pH 1.0 to 1.3).
- 6.8 Prepare the standard calibration curve by taking aliquots of standard phosphate solution 0.5 ml to 5.0 ml in 0.5 ml intervals and develop the colour by the method described in 6.4 to 6.7.
- 6.9 Prepare the blank by using the standard phosphate solution and omitting the ammonium molybdate solution.

7 Notes on the procedure

- 7.1 Occasionally, if only a small sample is available, it may be necessary to estimate chromium on the same digest. In this case sodium sulphite is not added to the diluted digest prior to boiling off (6.3). Chromium(VI) will therefore be present in the analytical solution and will interfere. This interference can be eliminated by extracting the phosphomolybdovanadate with 25 ml *n*-butanol. The aqueous phase is run off and the *n*-butanol phase rinsed into a 100 ml volumetric flask with ethanol and made up to volume with ethanol.
- 7.2 Silicon may be present in the leather from silicon, China clay, kaolin, various retannage treatments or as a by-product of zirconium, and will interfere with the determination of phosphorus because the silicomolybdovanadate complex produced will absorb in the same ranges of the spectrum as the phosphomolybdovanadate complex. In all cases where silicon may be present in the leather, the ash should be treated with H_2SO_4 and hydrofluoric acid to remove the silicon by fuming (SLC 16).

8 Expression of results

Calculate the following percentage.

$$\text{Phosphorus as } P_2O_5, \text{ percentage by mass, in the leather} = \frac{M_1}{M_2} \times \frac{20.000}{V_1}$$

where M_2 is the mass of leather taken (in g)
 M_1 is the mass of P_2O_5 in the aliquot of analytical solution taken for colour development (in g)
 V_1 is the volume of analytical solution taken for colour development (in ml)
 20.000 is a factor taking into account the dilutions used in this method.

9 Repeatability

The results of duplicate determinations by the same operator should not differ by more than 0.1% calculated on the original mass of leather taken. Differences between laboratories should not exceed 0.2% calculated on the original mass of leather taken.

10 Test report

The report shall include:

- (a) the results obtained, to 1 decimal place;
- (b) a reference to this method;
- (c) details of any special circumstances which may have affected the results;
- (d) identification details of the sample.