

Determination of Aluminium

1 Scope

This method is applicable to all types of leather.

2 Definition

For the purposes of this method the following definition applies.

Aluminium content of leather. This is expressed in terms of the oxide, Al_2O_3 .

3 Principle

Leather is ashed to remove organic matter and the inorganic residue brought into solution by alkaline fusion or wet oxidation and the aluminium determined by complexometric titration with CDTA.

4 Reagents

The following reagents are required.

- (a) *hexamethylene tetramine* (solid).
- (b) *fusion mixture*, potassium carbonate and potassium chlorate in equimolar proportion (7:6).
- (c) *hydrochloric acid*, concentrated ($d = 1.18 \text{ g/ml}$).
- (d) *oxidizing mixture*, concentrated sulphuric acid ($d = 1.83 \text{ g/ml}$) 70 ml and 60% perchloric acid ($d = 1.54 \text{ g/ml}$) 230 ml.
- (e) *sodium hydroxide solution* 40% (m/v).
- (f) *ammonia* (equal volumes of ammonia solution ($d = 0.880 \text{ g/ml}$) and distilled water).
- (g) *0.05M disodium cyclohexane-1, 2-diamine tetraacetate (CDTA) solution* (prepared by suspending 18.2 g of the free acid monohydrate in 200 ml distilled water, adding 100 ml M sodium hydroxide and diluting to 1 litre pH approximately 6.3, The solution should be standardised before use by titration with 0.05M zinc chloride).
- (h) *zinc chloride 0.05M standard solution* prepared by dissolving 3.269 g chemically pure zinc powder in hydrochloric acid and heating on a water-bath, cooling and making up to 1 litre in a graduated flask.
- (i) *0.1% aqueous solution xylenol orange (indicator)*, stable for 2 to 3 weeks.
- (j) *chromium sulphate or chrome alum-solid*.

5 Apparatus

Usual laboratory apparatus is required and, in particular, the following.

- (a) *platinum crucible*.
- (b) *muffle furnace*.
- (c) *tall form beaker*.
- (d) *filter apparatus*.
- (e) *Erlenmeyer flask*, 300 ml, splash bulb.
- (f) *volumetric flask*, 100 ml.
- (g) *glass beaker*, 250 ml.
- (h) *magnetic stirrer*.
- (i) *pH measuring apparatus* fitted with glass and calomel electrodes.
- (j) *burette*, graduated in 0.1 ml divisions.
- (k) *pipettes*.
- (l) *analytical balance*, sensitivity 0.001 g.

6 Procedure

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

- 6.1 Weigh approximately a 2 g sample to an accuracy of 1 mg into a previously tared platinum crucible.

- 6.2 Ash the sample in a muffle furnace at a temperature not exceeding 750 °C and prepare the analytical solution by one of the methods described below.
- (a) Mix the ash with a 3 to 5 fold quantity of fusion mixture using platinum wire. Heat the crucible in a muffle furnace at 750 °C. When the melt has become homogeneous (approximately 30 minutes) cool and place in a tall form beaker containing sufficient hot distilled water to cover the basin; if necessary, heat to dissolve the melt. Filter to remove iron and zirconium, and wash the filter thoroughly with hot distilled water, collecting the filtrate and washing in a tall form beaker. Acidify the filtrate with hydrochloric acid to ensure the solution of the aluminium and to bring the pH within the range 1 to 3. Boil the acidified solution to remove carbon dioxide, cool and adjust the pH, if necessary, to bring it within the range 1 to 3. Transfer quantitatively to a 100 ml volumetric flask and make up to volume with distilled water. This is the analytical solution.
- (b) Transfer the ash to a 300 ml Erlenmeyer flask, rinsing out the crucible with oxidizing mixture, and add further oxidizing mixture to a total volume of 15 ml. If chromium is not present in the ash, add about 20 mg chromium sulphate to act as an indicator. Place a splash bulb in the neck of the flask. Transfer to a fume cupboard and heat gently until the mixture boils gently. Continue to heat until the colour changes from green to golden yellow, heat for a further minute, remove from the source of heat, cool for a further few minutes and add approximately 100 ml distilled water.
- NOTE. This operation requires great care, and has to be carried out in a fume cupboard with the mouth of the flask pointing away from the operator.
- The first 2 ml to 3 ml of water should be added drop-by-drop with shaking. Add a few earthenware chips or anti-bump granules and boil for 10 minutes to 15 minutes to expel chlorine. Cool, test the pH, and, if necessary, add sodium hydroxide to bring it within the range 1 to 3. Transfer quantitatively to a graduated flask (100 ml) and make up to volume. This is the analytical solution.

6.3 Place an aliquot of analytical solution containing 20 mg to 30 mg Al_2O_3 in a 250 ml beaker mounted on a magnetic stirrer and add 25.0 ml 0.05M CDTA. If a precipitate forms, the solution is insufficiently acid. Suspend the pH measuring electrodes in the beaker and adjust the pH to approximately 5.5 by adding sodium hydroxide. Buffer by adding 5 g hexamethylene tetramine. If the solution is still acid after adding the hexamethylene tetramine, neutralise further with dilute ammonia.

6.4 Dilute to approximately 100 ml, add several drops of xylenol orange and titrate the excess CDTA with 0.05M zinc chloride solution. Stirring should be continued during the titration and the pH maintained at 5.5. The colour change is lemon-yellow to red.

7 Notes on the procedure

7.1 Complexing of aluminium and CDTA takes place in the acid range pH 1 to 3. Although a 1:1 complex is formed, a 2- to 3-fold molar ratio of CDTA:Al is required to obtain quantitative recovery. This is obtained by using the quantities stipulated in this method. If the leather contains less than 1% Al_2O_3 , a larger sample should be ashed.

7.2 Whilst wet oxidation is a convenient procedure for leathers free from zirconium, it is one requiring care and skill on the part of the operator who shall observe appropriate safety precautions.

7.3 The analytical solution may be used for the determination of chromium in leather following the procedure given in SLC 8.

- 7.4 In order to assist in detection of the end point, it is useful to have comparator solutions present.
- 7.5 Chromium does not interfere with the determination, but concentrations above 0.1N make observations of the end point difficult. More dilution may overcome this effect.
- 7.6 Zirconium interferes with the determination and will be removed by procedure 6.2(a). If procedure 6.2(b) is followed, the digest, after boiling off the chlorine, must be made alkaline to precipitate zirconium and convert the aluminium to soluble aluminate. Zirconium and iron are removed as hydroxides by filtration, and the filtrate and washings acidified to pH 1 to 3 before making up to volume.

8 Expression of results

Calculate the following percentage.

Aluminium as Al_2O_3 in percentage by mass in the leather =

$$\frac{(25 - t)}{M_s} \times \frac{V_1}{V_2} \times 0.255$$

where M_s is the mass of leather taken (in g)
 t is the volume of 0.05M zinc solution consumed (in ml)
 V_1 is the volume of analytical solution (in ml)
 V_2 is the volume of aliquot taken for titration (in ml)
 0.255 is a factor that is obtained by taking into account the dilutions used in this method, and other constants, as follows:

$$0.255 = \frac{51 \times 0.05}{1000} \times 100$$

NOTE. 1 ml 0.05 CDTA = 1.349 mg Al or 2.55 mg Al_2O_3 .

9 Repeatability

The results of duplicate determinations by the same operator shall not differ by more than 0.1% calculated on the original mass of leather taken.

Differences between laboratories shall not be greater than 0.2% calculated on the original mass of leather taken.

10 Test report

The report shall include:

- the results obtained, to one decimal place;
- A reference to this method;
- details of any special circumstances which may have affected the results;
- identification details of the sample.