

## Determination of Zirconium

### 1 Scope

This method is applicable to all types of leather.

A modified procedure is given in 11 for zirconium in the presence of iron. In the case of leathers which do not contain phosphate, a simpler procedure is described in 7.3.

### 2 Definition

For the purposes of this method the following definition applies.

*Zirconium content of leather.* This is expressed in terms of the oxide,  $ZrO_2$ .

### 3 Principle

Leather is ashed to remove organic matter and the inorganic residue is treated with hydrofluoric acid to remove silica. The residue is treated with a borax fusion mixture and it is hydrolysed to give insoluble zirconium oxyhydrates.

The precipitate is filtered, washed, redissolved in sulphuric acid and titrated with EDTA against xylenol orange. The filtrate and the coloured washings may contain chromium, phosphorus and aluminium and should be used to gain aliquots for determination of chromium (SLC 8) and phosphorus (SLC 19). Aluminium cannot be determined in this solution (see 7.2).

### 4 Reagents

The following reagents are required.

- (a) fusion mixture  $Na_2CO_3$  :  $K_2CO_3$  :  $Na_2B_4O_7$ , (in the ratio of 1:1:1 by mass).
- (b) sulphuric acid 5M AR.
- (c) EDTA solution 0.01M.
- (d) xylenol orange indicator solution, 0.1 % in water.
- (e) ammonia solution 7M.
- (f) potassium hydrogen sulphate.
- (g) hydrofluoric acid, 48 % solution in water.
- (h) sulphuric acid concentrated ( $d = 1.83$  g/ml).
- (i) sulphuric acid 1M.

CAUTION. Aqueous hydrofluoric acid is a highly corrosive liquid which attacks glass; the vapour is irritant and toxic. Its action on the skin and eyes is strongly corrosive, producing severe and painful burns which may not be immediately evident and which respond slowly to treatment. Samples should be handled only inside a well-ventilated fume cupboard. Rubber gloves, boots and a gown of a suitable size to give adequate protection to the individual, and full head and face protection must be worn when handling the material.

In the event of contact or suspected contact, flood the affected spot with water and seek immediate medical attention. The manufacturer's literature should be consulted for further information.

### 5 Apparatus

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

- (a) platinum crucible.
- (b) suitable pipettes and measuring cylinders.
- (c) glass beaker, 200 ml.
- (d) Erlenmeyer flask, 300 ml.
- (e) filter apparatus and AR filter paper or sintered glass filter\*.
- (f) muffle furnace, Bunsen burner.
- (g) analytical balance, sensitivity 0.001 g.
- (h) microburette, graduated in 0.02 ml.
- (i) electric hot plate.
- (j) glass beads.

## 6 Procedure

Sample and grind in accordance with SLC 1 and SLC 2.

- 6.1 Weigh, to the nearest 0.001 g, a 2 g sample (or sufficient to contain 0.02 mg  $\text{ZrO}_2$ ) into a platinum crucible previously heated to constant mass.
- 6.2 Ash the sample at a temperature not exceeding 800 °C in a muffle furnace. When the ashing appears to be complete, cool. Add 2 ml hydrofluoric acid and 0.5 ml 5M sulphuric acid and gently evaporate on an electric hot plate, using a low heat to avoid losses through spitting, and then carefully heat to red heat over a Bunsen burner. Repeat the hydrofluoric acid treatment once.
- 6.3 Cover the ash with 5 g of the fusion mixture (4(a)) and fuse the mixture over a Bunsen burner for as short a time as possible (approximately 20 minutes) for the melt to become homogeneous (see 7.1).
- 6.4 Cool and place the crucible in a 200 ml glass beaker containing 50 ml distilled water. Dissolve the melt by boiling and filter through a sintered glass filter. The insoluble matter should be white. (If it is yellow it may contain iron which interferes with the determination, and the procedure outlined in 11 should be followed.)
- 6.5 Wash the precipitate twice with 5 ml cold water. Transfer the filtrate and washings quantitatively to a 100 ml volumetric flask and make up to volume with distilled water. This solution may contain chromium, aluminium and phosphorus.
- 6.6 Dissolve the residue on the sintered glass filter by treating with two portions each of 10 ml hot 5M sulphuric acid. Allow each portion to stand for approximately 1 minute before applying suction. Wash the filter with 5 ml distilled water. Transfer the filtrate quantitatively with distilled water to a 300 ml Erlenmeyer flask, add a few glass beads and boil the solution to fuming. Allow fuming to continue for 1 minute before cooling the flask. Transfer the contents to a 100 ml volumetric flask and make up to volume with distilled water. Titration should be performed as soon as possible to avoid repolymerization of zirconium. (If filter paper is used instead of the sintered glass filter, ash the filter paper and fuse with 5 g  $\text{KHSO}_4$  to fuming. Continue fuming for 5 minutes, cool the melt and dissolve by heating in 1.0M sulphuric acid. Make up to volume with 1.0M sulphuric acid in a 100 ml volumetric flask.) Pipette a 50 ml aliquot into a 300 ml Erlenmeyer flask, dilute with 15 ml distilled water, add 8 drops of xylenol orange indicator and heat to boiling. Titrate the hot solution with 0.01M EDTA solution until a colour change from purple to pale orange occurs.
- 6.7 Add 10 ml ammonia 7M solution, re-boil the solution and continue to titrate until the colour change to lemon yellow is complete. Confirm the end point by adding a further 1 ml to 2 ml of ammonia solution, reheat, and no change in the lemon yellow colour should occur.

NOTE. Excessive addition of ammonia produces an alkaline purple colouration which cannot be discharged by addition of EDTA.

If the end point is missed, repeat the titration as described above after adding 10 ml sulphuric acid 10M and 5 ml to 10 ml nitric acid. Boil down to fuming and remove residual nitric acid by successive addition of two portions of distilled water (10 ml to 20 ml) and boiling down to fuming.

## 7 Notes on the procedure

- 7.1 The attack on the platinum crucible will be greater as the temperature and the time increase.

7.2 Aluminium may be present in the filtrate after the borax fusion (6.3) but it cannot be determined in such a solution. It is best determined on a separate sample by SLC 20 after wet oxidation or after fusion with an oxidative fusion mixture.

7.3 Phosphorous-containing materials are only rarely used in conjunction with zirconium in the manufacture of leather. Where they are absent, a simpler procedure, described in the *Journal of the Society of Leather Trades' Chemists* (1969) 59 389, may be used. In this the cooled ash should be broken down to a powder with a fine glass rod or platinum wire and mixed with 10 times its mass of potassium bisulphate; add 3 to 5 drops concentrated sulphuric acid. Heat to a dull red over a Bunsen burner, stirring continuously with a platinum wire. When the melt has become homogeneous, cool and place in a 500 ml tall form beaker containing sufficient distilled water to cover the basin. Carefully add 25 ml concentrated sulphuric acid with gentle shaking of the beaker. Bring to the boil and continue boiling until all the material has been removed from the basin and is in either solution or fine suspension. It may be necessary to break up the melt with a clean glass rod. Filter to remove any insoluble matter which may be retained for the estimation of silica, IUC 14. Wash the filter paper and funnel with successive portions of hot water (approximately 90 °C). Transfer the filtrate and washings to a 500 ml volumetric flask and make up to volume with distilled water. Pipette a 100 ml aliquot into a 500 ml Erlenmeyer flask, dilute with 100 ml distilled water and add 15 ml to 20 ml concentrated sulphuric acid. Add 15 ml hydrogen peroxide (3 %  $H_2O_2$  m/v aqueous solution) to complex any titanium which may be present. Heat the solution to 50 °C and add very slowly and with efficient stirring, 25 ml ammonium phosphate (10 % m/v aqueous solution). Allow the flask to stand for at least 2 hours then filter through ashless, acid resistant filter paper (a Buchner or other vacuum-assisted system is desirable), and wash the precipitate with ammonium nitrate (5 % m/v aqueous solution) at 40 °C until the filtrate is free from sulphate ions. Test with barium chloride (10 % m/v aqueous solution). Transfer the filter paper and precipitate to a platinum basin previously ignited at 1000 °C, cooled and weighed. Dry in an oven at 100 °C  $\pm$  2 °C for about 1 hour and ignite at 950 °C to 1000 °C in a muffle furnace for 1 hour. Cool in a desiccator and weigh as zirconium pyrophosphate  $ZrP_2O_7$ , and count to  $ZrO_2$  using the factor 0.47.

## 8 Expression of results

Calculate the following percentage.

$$\text{Zirconium as } ZrO_2 \text{ in percentage by mass} = \frac{MV \times 24.64}{M_s}$$

where  $M_s$  is the mass of leather taken (in g)

$M$  is the molarity of the EDTA

$V$  is the volume of the EDTA solution used (in ml)

24.64 is a factor that is obtained by taking into account the dilutions used in this method, and other constants, as follows:

$$24.64 = \frac{123.22 \times 2}{1000} \times 100$$

## 9 Repeatability

The results of duplicate determinations should not differ by more than 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.

## 11 Modification procedure for the determination of zirconium in the presence of iron

- 11.1 If iron is contained in the precipitate, dissolve the precipitate with hot nitric acid 20 ml ( $d = 1.2$  g/ml) and rinse with water into a 600 ml beaker.
- 11.2 Neutralise with a 10 % solution of ammonia diluted with distilled water to approximately 400 ml.
- 11.3 Add 30 ml to 40 ml  $H_2SO_4$  (concentrated diluted with water 1:1) and cool the solution to  $15^\circ C$ .
- 11.4 Add 10 ml of 6 % solution of cupferron whilst stirring and keep the mixture cool for 15 minutes in a bath of ice-cold water. The temperature should be not higher than  $2^\circ C$ .
- 11.5 Filter the zirconium cupferron precipitate and wash with ice-cold hydrochloric acid (1 volume of  $HCl$  ( $d = 1.19$  g/ml) per 9 volumes of water) until the filtrate is free from sulphate (test with 10 % solution of barium chloride).
- 11.6 Ash the precipitate in a muffle furnace and weigh as  $ZrO_2$ .

\* Jena G4 and Pyrex fine have been found to be suitable.