TECHNICAL REPORT

ISO TR 11422

First edition
1996-02-15

Iron ores — Recommended procedures for iron ore dissolution using either acid digestion or alkali fusion

Minerais de fer — Méthodes recommandées de dissolution des minerais de fer par digestion acide ou fusion alcaline

Reference number
ISO/TR 11422:1996(E)

Contents

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The main task of technical committees is to prepare International Standards, but in exceptional circumstances a technical committee may propose the publication of a Technical Report of one of the following types:

— type 1, when the required support cannot be obtained for the publication of an International Standard, despite repeated efforts;

— type 2, when the subject is still under technical development or where for any other reason there is the future but not immediate possibility of an agreement on an International Standard;

— type 3, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example).

Technical Reports of types 1 and 2 are subject to review within three years of publication, to decide whether they can be transformed into International Standards. Technical Reports of type 3 do not necessarily have to be reviewed until the data they provide are considered to be no longer valid or useful.

ISO/TR 11422, which is a Technical Report of type 3, was prepared by Technical Committee ISO/TC 102, *Iron ores*, Subcommittee SC 2, *Chemical analysis*.

This page intentionally left blank

Iron ores — Recommended procedures for iron ore dissolution using either acid digestion or alkali fusion

1 Background

From time to time in ISO/TC 102/SC 2, the view had been expressed that some degree of unification of procedures for the dissolution of iron ore test portions, based on selected established SC 2 procedures, would be of considerable benefit in the development of new analytical methods. This objective, coupled with the need to investigate possible procedure changes when increasing the mass of test portion in trace element methods, led to formation of the Dissolution Study Group in 1982.

The activities of this Study Group and the details and results of an interlaboratory dissolution test were reported in document ISO/TC 102/SC 2 N772 E (annexes A and B to this report). Based on these results and consideration of certain dissolution procedures already in use in SC 2, several proposed dissolution procedures for various test portion masses were presented in document ISO/TC 102/SC 2 N887 E, constituting a consolidated study group report for the period 1982 to 1986.

Before these procedures could be finalized as acceptable models for use in future analytical methods, certain discrepancies of detail in the conduct of acid digestions had to be resolved. Accordingly, SC 2 members' opinions were invited in the form of an explanatory note and questionnaire (documents ISO/TC 102/SC 2 N886 E and N888 E). A summary of the replies is appended (annex C), from which the conclusions to be drawn are as follows:

a) In acid digestions, the beaker should be totally covered; in evaporations it should be partially covered.

b) Temperatures (obtained in a test beaker) should be, for the initial digestion, 95°C and, for subsequent digestion and evaporation, 105°C.

c) The evaporation to dehydrate silica should continue to dryness with 15 min further heating.

d) The fused residue should be leached in the crucible, and not in the reserved main solution.

These conclusions have been incorporated in the procedures presented in this report. It is not possible to recommend only one method for acid digestion, because of the slightly different conditions required for varying test portion masses. Accordingly, methods are proposed for 2 g, 1 g and 0,5 g test portions, based on SC 2 methods applicable to or using such test portions.

An important conclusion from the interlaboratory test was that not all of the parameters temperature, time of heating and target volume can be specified simultaneously. The test results showed that, if target volume needs to be specified, temperature and target volume take precedence, and heating time should be given only as a guide.

2 Sources of the recommended procedures

Acid digestion	4.1.1 2 g test portion	:	ISO 9685: 1991,
"	4.1.2 1 g test portion	:	ISO 9685: 1991,
"	4.1.3 0.5 g test portion	:	ISO 9682: 1991,
Alkali fusion	4.2.1	:	ISO 9682: 1991,
"	4.2.1	:	ISO 4687: 1991,
"	4.2.2	:	ISO 9683: 1991,
Alkali sinter fusion	4.3.1	:	ISO 7834: 1987,
"	4.3.2	:	ISO 9683: 1991,

NOTE 1 To take into account the survey responses and other considerations, the recommended procedures differ in minor detail from those in the above sources.

3 Assessment of acid digestion vs alkali fusion or sinter fusion Alkali fusion and sinter fusion processes have the distinct advantage of providing one-step dissolution which does not require time-consuming residue treatment; hence they are the first choice wherever possible. They have the major disadvantage, however, of adding very materially to the salt concentration of the solution, imposing difficulties with atomic absorption and ICP measurement techniques. To address this problem, the "8-4-5" low flux ratio procedure (4.2.1) has been devised to provide the lowest flux-to-sample ratio so far available in iron ore dissolution (2,4 flux to 1 test portion). Where the method can permit a separation of the fusion salts from the analyte, or where spectrophotometric techniques are involved and the salt concentration is accordingly less relevant, the flux ratio adopted in 4.3.1 (3 flux to 1 test portion) and in 4.2.2 (4 flux to 1 test portion) can then become acceptable.

Alkali fusion or sinter fusion is, in general, limited to test portion masses not greater than 1 g. Where trace element determinations requiring 2 g test portions are involved, acid digestion tends to be preferred. However, it would not be impossible to devise an alkali sinter fusion method with a 2 g test portion and 6 g of sodium peroxide if separation of the analyte from the high concentration of salts could be contemplated.

4 Recommended procedures

4.1 Acid digestion procedure

4.1.1 2 g test portion

A Reagents

During the procedure, use only water of a grade that complies with ISO 3696:1987, *Water for analytical laboratory use—Specification and test methods.*

A.1 Sodium carbonate (Na_2CO_3), anhydrous.

A.2 Sodium tetraborate ($Na_2B_4O_7$), anhydrous.

A.3 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml.

A.4 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 1 + 1.

A.5 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 2 + 100.

A.6 Nitric acid, ρ 1,4 g/ml.

A.7 Sulfuric acid, ρ 1,84 g/ml.

A.8 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 1.

A.9 Hydrofluoric acid, ρ 1,13 g/ml, 40% (*m/m*), or ρ 1,19 g/ml, 48% (*m/m*).

B Apparatus

Ordinary laboratory equipment, and

B.1 Glass beakers, 250 ml capacity.

B.2 Platinum crucibles, minimum capacity 20 ml.

B.3 Hotplate, calibrated using a partial-immersion thermometer, to produce in a 10 mm depth of sulfuric acid (A.7) in a 250 ml test beaker, temperatures of 95°C and 105°C.

C Procedure

Transfer a 2,0 g test portion to a 250 ml beaker (B.1) and moisten with water. Add 50 ml of hydrochloric acid (A.3), cover with a watch glass and heat on a hotplate (B.3) for about 1 h at a temperature of 95°C.

NOTE 2 If after this digestion the amount of insoluble residue is high, raise the hotplate temperature to about 105°C and continue heating, avoiding boiling.

Add 5 ml of nitric acid (A.6) and 0,2 ml of sulfuric acid (A.8), and digest for 15 min at 105°C. Displace the cover to provide a 6 mm gap and evaporate the solution at the 105°C hotplate setting to dryness. Continue heating for a further 15 min.

NOTE 3 If the test sample contains significant amounts of barium, omit the addition of sulfuric acid.

Add 30 ml of hydrochloric acid (A.4) and heat to dissolve the salts. Add 20 ml of water and mix, then wash the watch glass and wall of the beaker and filter the solution through a close-texture filter paper containing filter pulp (0,3 g to 0,4 g dry mass) into a 200 ml beaker. Carefully remove all adhering particles with a rubber-tipped glass rod or piece of moistened filter paper and transfer to the filter. Wash the paper with hydrochloric acid (A.5) until visibly free from iron, then finally wash with three or four portions of warm water. Reserve the filtrate and washings as the main solution.

Transfer the filter paper and residue to a platinum crucible (B.2). Dry and char the paper at a low temperature, then ignite at 750°C to 800°C. Allow the crucible to cool. Add 0,3 ml of sulfuric acid (A.8) and 5 ml of hydrofluoric acid (A.9), evaporate slowly to remove silicon dioxide, then continue heating to remove the sulfuric acid. Ignite at 800°C for several

minutes and cool. Add 0,8 g of sodium carbonate (A.1) and 0,4 g of sodium tetraborate (A.2) and mix. Heat at 1000°C in a muffle furnace or over a pressurized air burner for a period sufficient to produce a clear melt, then allow the crucible to cool.

Add 10 ml of hydrochloric acid (A.4) and heat to dissolve the melt and expel carbon dioxide. Cool, combine the solution with the evaporated and cooled main solution, transfer to a 100 ml volumetric flask, dilute to volume and mix. (This is the test solution.)

4.1.2 1 g test portion

A Reagents

During the analysis use only water of a grade that complies with ISO 3696:1987.

A.1 Sodium carbonate (Na_2CO_3), anhydrous.

A.2 Sodium tetraborate ($Na_2B_4O_7$), anhydrous.

A.3 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml.

A.4 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 1 + 1.

A.5 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 2 + 100.

A.6 Nitric acid, ρ 1,4 g/ml.

A.7 Sulfuric acid, ρ 1,84 g/ml.

A.8 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 1.

A.9 Hydrofluoric acid, ρ 1,13 g/ml, 40% (*m*/*m*), or ρ 1,19 g/ml, 48% (*m*/*m*).

B Apparatus

Ordinary laboratory equipment, and

B.1 Glass beakers, 250 ml capacity.

B.2 Platinum crucibles, minimum capacity 20 ml.

B.3 Hotplate, calibrated using a partial-immersion thermometer, to produce in a 10 mm depth of sulfuric acid (A.7) in a 250 ml test beaker, temperatures of 95°C and 105°C.

C Procedure

Transfer a 1,0 g test portion to a 250 ml tall-form beaker (B.1) and moisten with water. Add 25 ml of hydrochloric acid (A.3), cover with a watch glass and heat on a hotplate (B.3) for about 1 h at a temperature of 95°C.

NOTE 4 If after this digestion the amount of insoluble residue is high, raise the hotplate temperature to about 105°C and continue heating, avoiding boiling.

Add 2 ml of nitric acid (A.6) and 0,2 ml of sulfuric acid (A.8), and digest for 15 min at 105°C. Displace the cover to provide a 6 mm gap and evaporate the solution at the 105°C hotplate setting to dryness. Continue heating for a further 15 min.

NOTE 5 If the test sample contains significant amounts of barium, omit the addition of sulfuric acid.

Add 20 ml of hydrochloric acid (A.4) and heat to dissolve the salts. Add 20 ml of water and mix, then wash the watch glass and wall of the beaker and filter the solution through a close-texture filter paper containing filter pulp (0,3 g to 0,4 g dry mass) into a 200 ml beaker. Carefully remove all adhering particles with a rubber-tipped glass rod or piece of moistened filter paper and transfer to the filter. Wash the paper with hydrochloric acid (A.5) until visibly free from iron, then finally wash with three or four portions of warm water. Reserve the filtrate and washings as the main solution.

Transfer the filter paper and residue to a platinum crucible (B.2). Dry and char the paper at a low temperature, then ignite at 750°C to 800°C. Allow the crucible to cool. Add 0,3 ml of sulfuric acid (A.8) and 5 ml of hydrofluoric acid (A.9), evaporate slowly to remove silicon dioxide, then continue heating to remove the sulfuric acid. Ignite at 800°C for several minutes and cool. Add 0,8 g of sodium carbonate (A.1) and 0,4 g of sodium tetraborate (A.2) and mix. Heat at 1000°C in a muffle furnace or over a pressurized air burner for a period sufficient to produce a clear melt, then allow the crucible to cool.

Add 10 ml of hydrochloric acid (A.4) and heat to dissolve the melt and expel carbon dioxide. Cool, combine the solution with the evaporated and cooled main solution, transfer to a 100 ml volumetric flask, dilute to volume and mix. (This is the test solution.)

4.1.3 0,5 g test portion

A Reagents

During the analysis, use only water of a grade that complies with ISO 3696:1987.

A.1 Sodium carbonate (Na_2CO_3), anhydrous.

A.2 Sodium tetraborate ($Na_2B_4O_7$), anhydrous.

A.3 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml.

A.4 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 1 + 1.

A.5 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 2 + 100.

A.6 Nitric acid, ρ 1,4 g/ml.

A.7 Sulfuric acid, ρ 1,84 g/ml.

A.8 Sulfuric acid, ρ 1,84 g/ml, diluted 1 + 1.

A.9 Hydrofluoric acid, ρ 1,13 g/ml, 40% (*m/m*), ρ 1,19 g/ml, 48% (*m/m*).

B Apparatus

Ordinary laboratory equipment, and

B.1 Glass beakers, 250 ml capacity.

B.2 Platinum crucibles, minimum capacity 20 ml.

B.3 Hotplate, calibrated using a partial-immersion thermometer, to produce in a 10 mm depth of sulfuric acid (A.7) in a 250 ml test beaker, temperatures of 95°C and 105°C.

C Procedure

Transfer a 0,5 g test portion to a 250 ml tall-form beaker (B.1) and moisten with water. Add 20 ml of hydrochloric acid (A.3), cover with a watch glass and heat on a hotplate (B.3) for about 1 h at a temperature of 95°C.

NOTE 6 If after this digestion the amount of insoluble residue is high, raise the hotplate temperature to about 105°C and continue heating, avoiding boiling.

Add 2 ml of nitric acid (A.6), 0,2 ml of sulfuric acid (A.8) and digest for 15 min at 105°C. Displace the cover to provide a 6 mm gap and evaporate the solution at the 105°C hotplate setting to dryness. Continue heating for a further 15 min.

NOTE 7 If the test sample contains significant amounts of barium, omit the addition of sulfuric acid.

Add 20 ml of hydrochloric acid (A.4) and heat to dissolve the salts. Add 20 ml of water and mix, then wash the watch glass and wall of the beaker and filter the solution through a close-texture filter paper containing filter pulp (0,3 g to 0,4 g dry mass) into a 200 ml beaker. Carefully remove all adhering particles with a rubber-tipped glass rod or piece of moistened filter paper and transfer to the filter. Wash the paper with hydrochloric acid (A.5) until visibly free from iron, then finally wash with three or four portions of warm water. Reserve the filtrate and washings as the main solution.

Transfer the filter paper and residue to a platinum crucible (B.2). Dry and char the paper at a low temperature, then ignite at 750°C to 800°C. Allow the crucible to cool. Add 0,3 ml of sulfuric acid (A.8) and 5 ml of hydrofluoric acid (A.9), evaporate slowly to remove silicon dioxide, then continue heating to remove the sulfuric acid. Ignite at 800°C for several minutes and cool. Add 0,8 g of sodium carbonate (A.1) and 0,4 g of sodium tetraborate (A.2) and mix. Heat at 1000°C in a muffle furnace or over a pressurized air burner for a period sufficient to produce a clear melt, then allow the crucible to cool.

Add 10 ml of hydrochloric acid (A.4) and heat to dissolve the melt and expel carbon dioxide. Cool, combine the solution with the evaporated and cooled main solution, transfer to a 100 ml volumetric flask, dilute to volume and mix. (This is the test solution.)

4.2 Alkali fusion procedure

4.2.1 Carbonate-borate flux (8-4-5 flux)–0,5 g test portion

Na_2CO_3 : 0,8 g
$Na_2B_4O_7$: 0,4 g
Test portion : 0,5 g

A Reagents

During the analysis, use only water of a grade that complies with ISO 3696:1987.

A.1 Sodium carbonate (Na_2CO_3), anhydrous.

A.2 Sodium tetraborate ($Na_2B_4O_7$), anhydrous.

A.3 Hydrochloric acid, ρ 1,16 g/ml to 1.19 g/ml, diluted 1 + 1.

B Apparatus

Ordinary laboratory equipment, and

B.1 Platinum or suitable platinum-alloy crucibles, minimum capacity 25 ml.

B.2 Muffle furnace, suitable for operation at a controlled temperature of 1020°C.

B.3 Combined magnetic stirrer-hotplate.

B.4 Stirring bars, polytetrafluoroethylene (PTFE)-coated, 10 mm long.

C Procedure

Add 0,80 g of sodium carbonate (A.1) to a platinum crucible (B.1), transfer the 0,5 g test portion to the crucible and mix well using a platinum or stainless steel rod. Add 0,4 g of sodium tetraborate (A.2) and repeat the mixing using the metal rod. Place the crucible in a muffle furnace (B.2) at 1020°C, for 30 min. Remove the crucible and quickly roll the melt as it solidifies. Allow to cool, then place a PTFE-coated stirring bar (B.4) in the crucible and place the crucible on its side in a 150 ml low-form beaker. Add 30 ml of hydrochloric acid (A.3) and 30 ml of water, cover and heat with stirring on a magnetic stirrer - hotplate (B.3) until dissolution of the melt is complete.

NOTE 8 The crucible may need to be rolled to ensure complete dissolution of the melt.

Remove and rinse the crucible and stirrer, cool the solution and transfer to a 100 ml volumetric flask. Dilute to volume with water and mix. (This is the test solution.)

4.2.2 Sodium peroxide—0,5 g test portion

Na_2O_2 : 2 g
Test portion : 0,5 g

NOTE 9 Direct fusions over a burner can produce mechanical losses with certain reactive ores. In this case, a preliminary sinter (4.3.2) may be indicated.

A Reagents

During the analysis, use only water of a grade that complies with ISO 3696:1987.

A.1 Sodium peroxide (Na_2O_2), dry, fine powder.

A.2 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml, diluted 1+ 1.

B Apparatus

Ordinary laboratory equipment, and

B.1 Vitreous carbon crucible, or zirconium metal crucible, 50 ml capacity.

C Procedure

Transfer 2,0 g of sodium peroxide (A.1) to a dry crucible (B.1). Add the 0,5 g of test portion and mix well with a dry spatula. Fuse over a Meker burner (low heat), swirling the crucible until the melt is cherry-red and clear. Remove from the heat, swirl until the melt solidifies on the inner wall of the crucible, place the crucible upright in a dry 300 ml beaker, and cover the beaker with a watch glass.

When cool, add about 5 ml of water into the crucible. After effervescence ceases, heat to complete decomposition, empty the contents of the crucible into the beaker and wash the crucible with about 10 ml of water. Add 20 ml of hydrochloric acid (A.2) via the crucible into the beaker. Rinse the crucible with water and acid as appropriate, and add the rinsings to the beaker. Boil to dissolve any residual material, cool, and dilute to specified volume as required. (This is the test solution.)

4.3 Alkali sinter fusion procedure

4.3.1 Sodium peroxide—1 g test portion

Na_2O_2 : 3 g
Test portion : 1 g

A Reagents

During the analysis, use only water of a grade that complies with ISO 3696:1987.

A.1 Sodium peroxide (Na_2O_2), dry, fine powder.

A.2 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml.

B Apparatus

Ordinary laboratory equipment, and

B.1 Zirconium or vitreous carbon crucibles, approximately 30 ml capacity.

B.2 Muffle furnace, to provide a controlled temperature at 520°C.

C Procedure

Weigh into a zirconium or vitreous carbon crucible (B.1) 3 g of sodium peroxide (A.1) and immediately add the weighed 1 g test portion. Mix with a thin non-magnetic metal spatula or glass rod and place in a muffle furnace (B.2) at 520°C ±10°C for 15 min. Remove from the furnace and heat on a Meker burner to the melting point with swirling, and continue the heating with swirling for 1 min to 2 min, to dissolve residual particles. Cool to room temperature (the crucible may be placed on a metal block if desired), add 20 ml of water, and cover. Heat on a hotplate just to boiling point, to complete the disintegration, and transfer the crucible contents to a 200 ml or 250 ml beaker with rinsing. Add 5 ml of water and 20 ml of hydrochloric acid (A.2) to the crucible, and warm to dissolve any residual material. Transfer the solution to the beaker with rinsing, cover and boil gently to expel chlorine. Cool and dilute to specified volume, as required. (This is the test solution.)

4.3.2 Sodium peroxide—0,5 g test portion

Na_2O_2 : 2 g
Test portion : 0,5 g

A Reagents

A.1 Sodium peroxide, (Na_2O_2), dry, fine powder.

A.2 Hydrochloric acid, ρ 1,16 g/ml to 1,19 g/ml.

B Apparatus

Ordinary laboratory equipment, and

B.1 Zirconium or vitreous carbon crucibles, approximately 30 ml capacity.

B.2 Muffle furnace, to provide a controlled temperature at 520°C.

C Procedure

Weigh into a zirconium or vitreous carbon crucible (B.1) 2 g of sodium peroxide (A.1) and immediately add the weighed 0,5 g test portion. Mix with a thin metal spatula or glass rod and place in a muffle furnace (B.2) at 520°C ±10°C for 15 min. Remove from the furnace and heat on a Meker burner to the melting point with swirling, and continue the heating with swirling for 1 min to 2 min to dissolve residual particles. Cool to room temperature (the crucible may be placed on a metal block if desired), add 20 ml of water and cover. Heat on a hotplate just to boiling point to complete the disintegration, and transfer the crucible contents to a 200 ml or 250 ml beaker with rinsing. Add 5 ml of water and 15 ml of hydrochloric acid (A.2) to the crucible, and warm to dissolve any residual material. Transfer the solution to the beaker with rinsing, cover and boil gently to expel chlorine. Cool and dilute to specified volume, as required. (This is the test solution.)

Annex A

Abridged report of international test of three methods of ore dissolution in document TC 102/SC 2 (DISLN SG-1)

A.1 Background of the test programme

Previous discussions at TC 102/SC 2 meetings (Pretoria 1980, Ottawa 1982), leading to Resolutions 43 and 4 respectively at those meetings, have centred essentially on the one major question of whether an increase in the mass of test portion to 2 g for trace element determinations should require any technical change in the acid-attack methods of iron ore dissolution used in the past. These established methods involve: digestion with hydrochloric acid; evaporation to dehydrate silica (either by evaporation to dryness or with perchloric acid); dissolution of salts; and filtration and ignition of the silica. After removal of silica with hydrofluoric acid, any residue is fused with either an acid or an alkaline flux, dissolved and combined with the main solution. The several variants based on this general principle are typified in such existing ISO/TC 102 Standards as:

Perchloric dehydration	Hydrochloric dehydration
ISO 2599 P	ISO 4692 Ca/Mg
ISO 3886 Mn	
ISO 4687 P	
ISO 4693 Cu	
ISO 5418 Cu	

The major problem that could arise with an increase of test portion to 2 g is that with high silica contents the filtration and washing of up to 600 mg of SiO_2 could be a difficult and inconvenient operation if the silica were present in a gelatinous form. In many cases, of course, the silica would be present as quartz, with filtration and washing problems being greatly diminished. An alternative technique to avoid problems from high amounts of gelatinous silica is to remove the silica during the ore-dissolution process with hydrofluoric acid, using a PTFE beaker. This technique has been used already in ISO 6831 Na/K, although for the different reason of avoiding contamination.

A.2 Aim of the test programme

The aim of the present test programme was to examine three methods of ore dissolution derived from the alternatives discussed above (but without using perchloric acid) as follows:

Method 1

The established procedure using hydrochloric acid dehydration of silica and silica filtration, improved to accommodate a 2 g test portion by using a larger beaker and specified temperatures for digestion and evaporation.

Method 2

Digestion in a PTFE beaker with hydrochloric and hydrofluoric acids to eliminate silica *before* filtration of any unattacked residue.

Method 3

Same as method 2, but with preliminary digestion with hydrochloric acid in glass before transfer to PTFE and addition of hydrofluoric acid.

Features of the test programme

The comparison of the three methods was made on the basis of:

1 Determining the *time taken* to prepare the stock solution (excluding drying and ignition of filter papers, because this could be either a slow or a fast operation depending on individual laboratory skills or preferences).

2 Determining the *mass* of any acid-insoluble residue (excluding silica, this having been volatilized with hydrofluoric acid either before filtration (Methods 2 and 3), or in the platinum crucible (Method 1). Mass of residue influences the amount of flux required. The amount of flux may be either important or not important, depending on subsequent operations in the method.

3 The volume of filtrate could be of interest in the overall aim of obtaining a 100 ml final volume of stock solution.

Test samples

The following samples were chosen for various reasons to highlight particular features that could cause problems in one or other of the three methods:

Test Sample		Reason for choice
79-4	Lorraine	High Ca
83-11	Hamersley	High Si
83-12	Mt Newman	Medium Si
83-13	Koolan HG	High grade
83-14	Solmer	High Ti

Analytical data on these samples are available in Document 2N 744E.

Details of the three methods tested, and the test results, are given in tables A.1 to A.5. Results for each sample indicate the average time taken and the average mass of residue. The averages for all samples are collated in a summary and given in table A.6. The grand means for all samples are given in table A.7.

Table A.1 - Sample 79-4 (Lorraine - High calcium)

	Time (h)			Residue (mg)		
	Method 1	Method 2	Method 3	Method 1	Method 2	Method 3
Australia						
Lab 1	8,1	5,7	5,5	9,5	28,4	5,1
Brazil						
Lab 1	2,7	3,3	3,9	12,6	5,8	4,6
2	2,7	3,3	3,9	13,3	5,7	4,5
France						
Lab 1	5,0	8,0	10,3	10,0	26,0	12,7
2	4,5	3,5	4,5	10,0	19,1	6,2
3	5,5	7,2	7,7	8,0	42,0	85,0
Germany						
Lab 1	5,5	4,2	5,1	8,7	1,8	8,3
2	6,3	4,5	3,5	9,9	1,2	59,5
Italy						
Lab 1	[1]	4,8	5,5	[1]	0,5	7,1
2	5,9	3,6	4,2	12,0	1,8	2,2
Japan						
Lab 1	4,2	4,8	5,1	11,8	22,1	4,1
2	3,2	4,6	5,1	12,4	97,0	11,0
3	8,5	5,0	5,6	5,6	3,0	1,2
4	4,3	7,3	8,7	10,0	0,6	1,6
Sweden						8,5[2]
Lab 1	9,2	9,5[2]	8,7[2]	13,0	6,5[2]	
2		4,5[3]			6,0[3]	
Mean	5,4	5,0	5,8	10,5	17,4	15,2

[1] equipment unavailable
[2] 100ml PTFE beakers
[3] 150ml PTFE beakers

Table A.2 - Sample 83-11 (Hamersley - High silicon)

	Time (h)			Residue (mg)		
	Method 1	Method 2	Method 3	Method 1	Method 2	Method 3
Australia						
Lab 1	6,3	4,8	5,8	35,1	5,3	1,5
Brazil						
Lab 1	2,9	3,7	3,8	56,6	6,6	6,3
2	2,9	3,8	3,8	56,2	6,5	6,6
France						
Lab 1	5,0	8,0	11,0	59,0	5,4	0,5
2	5,7	3,9	4,7	29,3	10,5	4,1
3	5,0	7,5	11,1	45,0	8,0	20,5
Germany						
Lab 1	5,5	4,2	4,7	38,0	4,5	4,6
2	6,5	4,5	3,9	53,4	7,9	12,0
Italy						
Lab 1	[1]	5,3	5,5	[1]	11,3	4,8
2	6,1	3,7	4,4	42,5	6,2	3,2
Japan						
Lab 1	4,2	4,8	5,1	61,5	18,0	4,7
2	3,0	4,5	5,3	51,3	5,9	1,2
3	8,5	5,3	5,9	19,4	1,3	0,8
4	4,1	7,1	8,7	50,5	5,3	0,7
Sweden						
Lab 1	9,0	9,6[2]	9,4[2]	45,5	18,0[2]	7,5[2]
2		4,3[3]			6,4[3]	
Mean	5,3	5,0	6,0	46,0	7,3	5,1

[1] = equipment unavailable
[2] = 100ml PTFE beakers
[3] = 150ml PTFE beakers

Table A.3—Sample 83-12 (Mt Newman - Medium silicon)

	Time (h)			Residue (mg)		
	Method 1	Method 2	Method 3	Method 1	Method 2	Method 3
Australia						
Lab 1	6,7	5,2	5,6	77,8	51,5	2,8
Brazil						
Lab 1	3,0	3,6	4,0	57,6	5,5	5,3
2	2,9	3,6	4,0	57,5	5,1	5,5
France						
Lab 1	5,0	8,3	11,1	56,7	23,4	1,4
2	5,8	3,7	4,9	46,1	41,7	21,0
3	4,8	7,5	8,1	58,0	17,0	45,5
Germany						
Lab 1	5,4	4,2	5,0	60,1	15,2	7,6
2	6,5	4,7	3,9	71,7	25,2	38,7
Italy						
Lab 1	[1]	5,6	5,6	[1]	32,2	18,2
2	6,0	3,6	3,6	53,3	8,0	4,0
Japan						
Lab 1	4,2	4,8	5,2	110,8	15,6	25,6
2	3,0	4,5	5,2	69,1	19,1	5,8
3	8,3	5,4	6,2	34,3	4,6	3,1
4	4,5	7,0	8,7	73,2	24,1	1,5
Sweden						
Lab 1	9,3	8,6[2]	9,9[2]	63,0	33,5[2]	18,5[2]
2		4,3[3]			12,3[3]	
Mean	5,4	5,1	5,8	63,5	20,0	13,3

[1] = equipment unavailable
[2] = 100ml PTFE beakers
[3] = 150ml PTFE beakers

Table A 4—Sample 83-13 (Koolun - High grade haematite)

	Time (h)			Residue (mg)		
	Method 1	Method 2	Method 3	Method 1	Method 2	Method 3
Australia						
Lab 1	6,4	5,1	5,4	1,6	32,7	17,3
Brazil						
Lab 1	3,0	3,6	3,9	1,8	24,4	25,1
2	2,8	3,6	3,9	1,8	25,0	24,2
France						
Lab 1	4,2	8,4	11,0	1,3	36,2	25,6
2	5,3	3,7	4,3	2,8	28,1	4,5
3	4,8	7,5	8,6	4,0	2,0	37,0
Germany						
Lab 1	5,3	4,0	4,6	2,0	35,1	69,9
2	6,4	4,6	3,8	6,9	16,0	0,7
Italy						
Lab 1	[1]	5,3	5,5	[1]	154,7	174,7
2	6,4	3,7	3,9	2,7	44,2	42,5
Japan						
Lab 1	4,2	4,6	4,9	2,0	29,7	1,6
2	2,9	4,7	5,4	5,8	13,3	11,2
3	7,8	5,3	6,0	1,3	0,7	0,8
4	4,3	7,1	8,8	5,8	163,1	21,6
Sweden						
Lab 1	8,5	9,4[2]	9,7[2]	3,5	127,0[2]	23,5[2]
2		4,3[3]			4,5[3]	
Mean	5,2	5,0	5,7	3,1	40,6	32,6

[1] = equipment unavailable
[2] = 100ml PTFE beakers
[3] = 150ml PTFE beakers

Table A.5—Sample 83-14 (Solmer - High titanium)

	Time (h)			Residue (mg)		
	Method 1	Method 2	Method 3	Method 1	Method 2	Method 3
Australia						
Lab 1	6,9	5,8	5,7	350,9	27,8	25,0
Brazil						
Lab 1	3,1	3,8	4,0	303,1	41,7	44,3
2	3,1	3,8	4,0	304,6	40,3	44,5
France						
Lab 1	4,7	8,7	11,3	325,3	39,6	60,0
2	5,1	4,4	4,6	306,3	36,3	56,3
3	8,6	10,3	8,4	302,0	25,0	103,0
Germany						
Lab 1	5,1	4,0	4,6	285,7	25,0	67,1
2	5,6	4,4	3,7	292,4	33,4	91,9
Italy						
Lab 1	[1]	5,4	5,5	[1]	31,9	66,6
2	5,9	3,7	3,9	29,2	33,2	28,6
Japan						
Lab 1	4,6	5,0	5,2	328,0	29,8	21,3
2	2,9	4,9	5,3	297,4	54,9	52,3
3	8,5	5,2	6,0	311,2	23,9	22,3
4	4,4	7,0	8,7	313,6	28,0	26,3
Sweden						
Lab 1	9,4	10,8[2]	9,4[2]	300,0	28,0[2]	26,5[2]
2		5,0[3]			34,5[3]	
Mean	5,6	5,4	5,8	289,3	33,7	50,7

[1] = equipment unavailable
[2] = 100ml PTFE beakers
[3] = 150ml PTFE beakers

Table A.6— Summary of results

Sample	Time (h)			Residue (mg)		
	Method 1	Method 2	Method 3	Method 1	Method 2	Method 3
89-4 (High Ca)	5,4	5,0	5,8	10,5	17,4	15,2
83-11 (High si)	5,3	5,0	6,0	46,0	7,3	5,1
83-12 (Medium Si)	5,4	5,1	5,8	63,5	20,0	13,3
83-13 (High grade)	5,2	5,0	5,7	3,1	40,6	32,6
83-14 (High Ti)	5,6	5,4	5,8	289,3	33,7	50,7

Table A.7—Grand means - All samples

	Time taken (h)	Residue mass* (mg)	Filtrate volume (ml)
Method 1	5,4	82,5	140
Method 2	5,1	23,8	100
Method 3	5,8	23,4	106
*Silica absent.			

A.3 Discussion

A remarkable outcome of the programme has been the wide variation between laboratories in time taken to carry out the same method, As the facilities for conducting quantitative evaporations will vary appreciably between laboratories, such time variations are not very important, but nonetheless some speeds reported for evaporations were nothing short of astonishing, One laboratory was able to evaporate 25 ml of solution to dryness from an almost completely covered beaker in 12 minutes! For the identical operation, numerous other laboratories reported times of 2 to 3 hours. Clearly, it is not desirable to attempt to specify a time to be taken for an evaporation, Probably only heating temperature and target volume to be achieved should be specified, High rates of evaporation are difficult to achieve when silica gel is being spattered onto the cover glass.

The following comparisons of the methods can be made:

Method 1

1 Operating time longer than Method 2.

2 Residues highest of the three methods.

3 The need for two hotplates set at different temperatures can be inconvenient, One laboratory was unable to carry out Method 1 because "suitable hotplates were not available".

4 The volume of filtrate is appreciably higher than 100 ml, requiring evaporation to meet the specification of 100 ml final volume.

Method 2

1 The 150 ml PTFE beaker is not a common size.

Method 3

1 Transfer of solution from glass to PTFE increases solution volume and working time.

A.4 Possible method improvements

Method 1

1 Decrease the volume of wash solution.

2 Reconsider hotplate temperature requirements.

Method 2

1 Increase the PTFE beaker size to 250 ml.

2 Increase the volume of acid for dissolving evaporated salts.

It should be noted that both Method 1 and Method 2 have been adopted in recent SC 2 methods. (Method 1, Cr/Ni, Method 2, Pb/Zn, V, AAS).

A.5 Conclusion

As method 3 shows no particular advantages in respect of time taken and mass of residue without silica compared with the other two methods, this method should probably be deleted from further consideration. At the Paris meeting, opinion will be sought on the modifications desirable in Methods 1 and 2 to optimize their capabilities. It will be proposed then that these improved methods be incorporated in a TC 102 Technical Report to enable future working group Conveners to choose either method, depending on particular requirements at the time. Such requirements may involve, for example, a need to restrict mass of flux salt, volume of test solution, etc.

The Paris discussions should also include attitudes to specifications (time, temperature, target volume) and whether beakers should be uncovered, partly covered or totally covered during evaporation. Comments have been made from this test programme that methods should be more rigidly specified.

Items for discussion at the Paris meeting:

1 Improvements to Method 1 (number of hotplates).

2 Improvements to Method 2.

3 Need to specify time, temperature, target volume, but not all three.

4 Method of setting hotplate temperatures (none, or contact thermometer or test beaker).

5 Extent of covering beakers during evaporations (none, part, or total).

E.S. Pilkington
Convener, Dissolution Study Group