Standard Test Methods for
Determination of Manganese in Iron Ores by Pyrophosphate
(Potentiometric) and Periodate (Spectrophotometric)
Techniques

This standard is issued under the fixed designation E314; the number immediately following the designation indicates the year of
original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A
superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

ε1 NOTE—Editorial changes made throughout E314 in November 2015.

1. Scope

1.1 These test methods cover the determination of manganese in iron ores, concentrates, and agglomerates. The following
two test methods are included:

<table>
<thead>
<tr>
<th>Test Method A (Pyrophosphate (Potentiometric))</th>
<th>Sections</th>
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<tbody>
<tr>
<td>Test Method B (Periodate (Photometric))</td>
<td>16 – 22</td>
</tr>
</tbody>
</table>

1.2 Test Method A covers the determination of manganese in the range from 2.5 % to 15.0 %. Test Method B covers the
determination of manganese in the range of 0.01 % to 5.00 %.

Note 1—The lower limit for this test method is set at 50 % relative error for the lowest grade material tested in the interlaboratory study in
accordance with Practice E1601.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this
standard.

1.4 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the
responsibility of the user of this standard to establish appropriate safety and health practices and determine the applica-

bility of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards:

| E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials |

3. Terminology

3.1 Definitions—For definitions of terms used in these test methods, refer to Terminology E135.

4. Significance and Use

4.1 This test method is intended to be used for compliance with compositional specifications for manganese content in
iron ores, concentrates, and agglomerates. It is assumed that all who use these procedures will be trained analysts capable of
performing common laboratory procedures skillfully and safely. It is expected that work will be performed in a properly
equipped laboratory and that proper waste disposal procedures will be followed. Appropriate quality control practices must be
followed such as those described in Guide E882.

5. Reagents and Materials

5.1 Purity of Reagents—The purity of the common chemical reagents used shall conform to Practices E50. Special appara-

bus and reagents required are located in separate sections preceding the procedure.

6. Hazards

6.1 For precautions to be observed in this method, refer to Practices E50.

3 The last approved version of this historical standard is referenced on www.astm.org.
7. Sampling and Sample Preparation

7.1 The gross sample shall be collected and prepared in accordance with Practice E877.

7.2 The analytical sample shall be pulverized to pass a No. 100 (150-µm) sieve.

Note 2—To facilitate decomposition some ores, such as specular hematites, may require grinding to pass a No. 200 (75-µm) sieve.

TEST METHOD A—PYROPHOSPHATE (POTENCIOMETRIC) METHOD

8. Summary of Test Method

8.1 The test sample is decomposed by treatment with HCl, HNO₃, HF, and HClO₄. After the addition of sodium pyrophosphate and the adjustment of the acidity, the manganese is determined by oxidation to trivalent manganese with a standard solution of potassium permanganate. The end point is determined potentiometrically.

9. Interferences

9.1 Provision has been made for the removal of chromium which under some conditions is an interfering element.

10. Apparatus

10.1 pH Meter—A number of pH meters are commercially available. Many of these instruments can accept a variety of electrodes and therefore can be used also for potential measurements. Although both line- and battery-operated pH meters are manufactured, the former is recommended for laboratory work because this type of pH meter contains an electronic or transistorized potentiometer which makes the emf balancing operation entirely automatic. Electrometer tube input is used on both the electronic and transistorized pH meters.

10.1.1 The pH meter must have electrode standardization (or asymmetry potential) and manual or automatic temperature compensation controls. The dial must read in pH directly, and permit readings that are accurate to at least ± 0.01 pH unit. For higher accuracies it is recommended that a pH meter with an expanded scale be used.

10.1.2 Because there is no accurate method for determining the absolute potential of an individual electrode, two electrodes are used for pH measurements. These are called the reference and indicator electrodes. By international agreement the hydrogen electrode is the standard indicator electrode for pH, but is inconvenient to use and subject to several limitations. The most widely used reference electrode is the saturated calomel electrode. It is most often used as a pencil-type unit that is immersed directly in the solution, but may also be utilized as an external cell (to prevent possible contamination) contacting the solution by means of a salt bridge. The silver-silver chloride reference electrode is also convenient to use, but it is more difficult to prepare than the saturated calomel electrode. The mercurous sulfate reference electrode may be used in solutions in which the chloride ions that diffuse out of the calomel cell might be harmful.

10.1.3 The most commonly employed indicator electrode is the glass electrode. The quinhydrone and antimony-antimonous oxide electrodes are used to a much lesser extent. Combination electrodes containing both the indicator and reference units are also available. The tips of the electrodes containing solutions must be covered with rubber caps when the electrodes are disconnected from the meter and stored. When pH measurements are not being made the electrodes connected to the pH meter should be kept in a beaker containing water. Prior to measuring the pH of a solution the electrodes must be thoroughly washed with water especially if they have been left standing for a long period of time.

10.2 Potentiometric Titration Apparatus—Instruments for detecting the end points in pH (acid-base), oxidation-reduction, precipitation, and complexation titrations consist of a pair of suitable electrodes, a potentiometer, a buret, and a motor-driven stirrer. Titrations are based on the fact that when two dissimilar electrodes are placed in a solution there is a potential difference between them. This potential difference depends on the composition of the solution and changes as the titrant is added. A high-impedance electronic voltmeter follows the changes accurately. The end point of the titration may be determined by adding the titrant until the potential difference attains a predetermined value or by plotting the potential difference versus the titrant volume, the titrant being added until the end point has been passed.

10.2.1 An elaborate or highly sensitive and accurate potentiometer is not necessary for potentiometric titrations because the absolute cell voltage needs to be known only approximately, and variations of less than 1 mV are not significant. Such instruments should have a range of about 1.5 V and a readability of about 1 mV. Many of the pH meters are also suitable for potentiometric titrations.

10.2.2 The electrode system must consist of a reference electrode and an indicator electrode. The reference electrode maintains a constant, but not necessarily a known or reproducible potential during the titration. The potential of the indicator electrode does change during the titration; further, the indicator electrode must be one that will quickly come to equilibrium. A platinum indicator electrode and reference electrode are required for this method.

10.2.3 Initially, a titration of the constituent in question is performed manually, and the volumes of titrant added and the corresponding potential differences are noted. By use of established techniques the end point potential is determined. For the analytical determinations, titration may be continued to a preset potential, the end point being signaled by a null meter, with or without automatic termination of the titration. This technique is applicable to reasonably rapid reactions involving strong oxidants and reductants, precipitates not more soluble than silver chloride, and ionization constants greater than that of boric acid.

10.2.4 Other techniques may be used for both slow and fast reactions. These include automatic recording of the titration curve on a strip chart, and the recording of the titrant end point volume on a tape. In the latter, an adjustable print-out delay prevents undertitrating when the reaction is slow.

10.3 Magnetic Stirrer—Use of a TFE-fluorocarbon-covered stirring bar is recommended.
11. Reagents

11.1 Hydrochloric Acid (sp gr 1.19)—Concentrated.

11.2 Hydrochloric Acid (1 + 1)—Mix one volume of concentrated HCl (sp gr 1.19) with one volume of water.

11.3 Hydrochloric Acid (1 + 10)—Mix one volume of concentrated HCl (sp gr 1.19) with ten volumes of water.

11.4 Hydrofluoric Acid (48 %)—Concentrated.

11.5 Hydrogen Peroxide (3 %)—Mix one volume of concentrated hydrogen peroxide (H₂O₂, 30 %) with nine volumes of water.

11.6 Nitric Acid (sp gr 1.42)—Concentrated HNO₃.

11.7 Perchloric Acid (70 %).

11.8 Potassium Permanganate, Standard Solution (0.1 N).

11.8.1 Preparation—Dissolve 3.2 g of potassium permanganate (KMnO₄) in 1 L of water. Let stand in the dark for two weeks. Filter, without washing, through a Gooch crucible or a fine porosity fritted-glass crucible. Avoid contact with rubber or other organic material. Store in a dark-colored glass-stoppered bottle.

11.8.2 Standardization—Dry a portion of a sample of sodium oxalate at 105 °C. Transfer 0.3000 g of the sodium oxalate to a 600-L beaker. Add 250 mL of H₂SO₄ (5 + 95) previously boiled for 10 min to 15 min and then cooled to 27 °C ± 3 °C, and stir until the oxalate has dissolved. Add 39 mL to 40 mL (Note 3) of the KMnO₄ solution, at a rate of 25 mL/min to 35 mL/min, while stirring slowly. Let stand until the pink color disappears (about 45 s) (Note 4). Heat to 55 °C to 60 °C and complete the titration by adding KMnO₄ solution until a faint pink color persists for 30 s. Add the last 0.5 mL to 1 mL dropwise, allowing each drop to become decolorized before adding the next drop. To determine the blank: Titrate 250 mL of H₂SO₄ (5 + 95), treated as above, with KMnO₄ solution to a faint pink color. The blank correction is usually equivalent to 0.03 mL to 0.05 mL.

Note 3—A 0.3000-g portion of sodium oxalate requires 44.77 mL of KMnO₄ solution (0.1 N).

Note 4—If the KMnO₄ solution is too strong, the pink color will not fade at this point; begin again, adding a few millilitres less of the KMnO₄ solution.

11.9 Potassium Permanganate, Standard Solution (0.05 N) (Note 5)—Dilute one volume of 0.1 N potassium permanganate solution with one volume of water. Standardize using 0.1500 g of sodium oxalate as described under 11.8.2. Confirm the standardization against an ore of known manganese content by carrying the known sample through all steps of the procedure. The difference between the two weights is the weight of the test sample.

Note 5—The 0.05 normality of the potassium permanganate (KMnO₄) solution used (1.5803 g/L) is based on the usual valence change of manganese in acid solution from 7 to 2. In the test method described, the manganese in the sample is oxidized from Mn (II) to Mn (III) while the KMnO₄ is reduced from Mn (III) to Mn (VII). The factor 0.04395 mentioned in Section 13, therefore, is based on the following calculation:

\[ \frac{5}{9} \times \frac{0.05494}{100} \text{ (Mn equivalent of KMnO₄ in the (7 to 2) valence change).} \]

11.10 Sodium Carbonate (Na₂CO₃).

11.11 Sodium Hydroxide Solution (200 g/L)—Dissolve 200 g of sodium hydroxide (NaOH) in 500 mL to 600 mL of water and dilute to 1 L.

11.12 Sodium Pyrophosphate (Na₄P₂O₇·10H₂O), Saturated Solution—This reagent shall be tested in the titration of a known amount of manganese. Only lots which rapidly provide steady potentials shall be used.

12. Procedure

12.1 Transfer approximately 0.5000 g of prepared sample to a small dry weighing bottle and place in a drying oven. After drying at 105 °C to 110 °C (Note 6) for 1 h, cap the bottle, and cool to room temperature in a desiccator. Momentarily release the cap to equalize pressure and weigh the capped bottle to the nearest 0.0001 g. Repeat the drying and weighing until there is no further weight loss. Transfer the test sample to a 600-mL beaker and reweigh the capped bottle to the nearest 0.0001 g. The difference between the two weights is the weight of the test sample.

Note 6—Most ores yield their hygroscopic moisture at the specified temperature. However, in the case of some ores, higher drying temperatures may be required.

12.2 Moisten the test sample with a few millilitres of water, add 20 mL of HCl, cover, and heat below boiling. When all soluble minerals are decomposed, add 10 mL of HNO₃, 4 mL to 5 mL of HF, and 15 mL of HClO₄, and evaporate without a cover to copious fumes of HClO₄. Cool, and rinse down the sides of the beaker and dissolve the salts in 10 mL of water (Note 7). Cover and again evaporate to fumes of HClO₄ and fume strongly for 1 min. Withdraw the cover slightly and volatilize any chromium present by the drop-wise addition of HCl. When chromyl chloride has been expelled, as indicated by the absence of orange vapor on the addition of HCl, replace the cover and evaporate to about 3 mL or until the salts form on the bottom of the beaker. Cool, add 10 mL of HCl (1 + 1) and 1 mL of H₂O₂, and boil for about 5 min.

Note 7—At this point manganese, which may have separated as manganese dioxide (MnO₂), should be dissolved by the dropwise addition of H₂O₂. If any residue remains, dilute with 50 mL of hot water and filter the solution through a medium-texture paper. Wash alternately with HCl (1 + 10) and hot water until the paper is free of iron stain, and then with hot water until perchlorates are removed. Reserve the filtrate. Place the paper and residue in a platinum crucible. Dry and ignite to destroy all carbonaceous matter. Add 1 g of Na₂CO₃ to the crucible and fuse until a clear melt is obtained. Cool and dissolve the melt in a small amount of water containing 5 mL of HCl and a few drops of H₂O₂. Rinse and remove the crucible and add the solution to the reserved filtrate. Proceed with evaporation to fumes of HClO₄.

12.3 To the solution add 250 mL to 300 mL of a cold, saturated solution of Na₃P₂O₇. Adjust the pH to 6.5 (using calomel and glass electrodes and a magnetic stirring device) with NaOH solution and HCl (1 + 1). The solution should be clear and colorless (Note 8). If a precipitate forms, dilute further with the Na₃P₂O₇ solution until a clear solution is obtained, maintaining a pH of 6.5. Cool to 10 °C to 20 °C and titrate the manganese potentiometrically with the 0.05 N KMnO₄ solution. Add the titrant rapidly until the first deflection of the galvanometer is noted and then dropwise to the...
equivalence point. The drop giving the largest potential change shall be taken as the end point.

Note 8—If at this point a pink coloration appears, the analysis must be repeated.

<table>
<thead>
<tr>
<th>TABLE 1 Precision Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average, %</td>
</tr>
<tr>
<td>2.80</td>
</tr>
<tr>
<td>4.12</td>
</tr>
<tr>
<td>5.53</td>
</tr>
<tr>
<td>7.81</td>
</tr>
<tr>
<td>10.09</td>
</tr>
</tbody>
</table>

Note: Each percentage represents a different kind of iron ore.

Relative Standard Deviation, RSD, in this test method is calculated as follows:

$$RSD = \left( \frac{100}{\bar{x}} \right) \sum \frac{d^2}{n(n-1)}$$

where:

- $\bar{x}$ = average, %,
- $d$ = difference of the determination from the mean, and
- $n$ = number of determinations, and in this case $n = 7$ as each value used is the average of two determinations from each laboratory.

13. Blank

13.1 Carry out a blank determination following the same procedure and using the same amount of all reagents.

14. Calculation

14.1 Calculate the percentage of manganese as follows (Note 5):

$$\text{Manganese} = \frac{[(A - B)C \times 0.04395 \times 100]}{D}$$ (1)

where:

- $A$ = millilitres of KMnO₄ solution required for the titration of the sample,
- $B$ = millilitres of KMnO₄ solution required for the titration of the blank,
- $C$ = normality of the KMnO₄ solution, and
- $D$ = grams of sample used.

15. Precision and Bias

15.1 Precision—Table 1 indicates the precision of the test method between laboratories using standard samples as the unknowns.

15.2 Bias—No information on the bias of this test method is known. Test results for the reference materials were not compared with reference values in the interlaboratory study. Users of the method are encouraged to employ accepted reference materials, if available, and to judge the bias of the method from the difference between the accepted value for the manganese and the mean value from interlaboratory testing of the reference material.

TEST METHOD B—PERIODATE (PHOTOMETRIC) METHOD

16. Summary of Test Method

16.1 The test sample is decomposed by digestion with HCl and HNO₃, followed by fuming with HClO₄. The insoluble residue is removed by filtration, ignited, and fused with sodium carbonate and the melt dissolved in the filtrate. The manganese is oxidized to permanganate by boiling with potassium periodate. The solution is cooled and photometric measurement is made at 545 nm (Note 9).

17. Interferences

17.1 None of the elements normally found in iron ores interferes with this test method.

Note 9—If a filter photometer is used, precautions are necessary. The HClO₄ oxidizes chromic to chromate ions which undergo no further change in spectral quality on treatment with periodate. Adjustment for absorbance by these ions must be made by selecting a filter with maximum transmittance between 545 nm and 565 nm. The filter must transmit not more than 5 % of its maximum at a wave length shorter than 530 nm. The band width of the filter should be less than 30 nm when measured at 50 % of its maximum transmittance. The spectral transmittance curve of permanganate ions exhibits two useful minima, one at approximately 526 nm and the other at 545 nm. The latter is recommended when a narrow band spectrophotometer is used. Determine the exact location of the minima for each spectrophotometer by obtaining spectra transmittancy data in this spectral region, thus, compensating for characteristics that are related to the instrument.

18. Reagents and Materials

18.1 Hydrochloric Acid (sp gr 1.19)—Concentrated.

18.2 Hydrofluoric Acid (48 %)—Concentrated.

18.3 Phosphoric Acid (85 %).

18.4 Nitric Acid (sp gr 1.42)—Concentrated.

18.5 Nitric Acid (1 + 9)—Mix one volume of concentrated HNO₃ (sp gr 1.42) with nien volumes of water.

18.6 Phosphoric Acid (85 %).

18.7 Perchloric Acid (70 %).

18.8 Potassium Periodate Solution (7.5 g/L).

18.8.1 Dissolve 7.5 g of potassium m-periodate (KIO₄) in 200 mL of hot HNO₃ (1 + 1), add 400 mL of H₂PO₄, cool and dilute to 1 L.

18.9 Sodium Carbonate (Na₂CO₃).

18.10 Sodium Nitrite Solution (20 g/L).

18.10.1 Dissolve 2 g of sodium nitrite (NaNO₂) in water and dilute to 100 mL. This solution shall be prepared daily.
19. Calibration and Standardization

19.1 The recommended percentage range is from 0.2 mg to 1.5 mg of manganese in 100 mL of solution using a cell depth of 1 cm.  

19.2 Calibration Solutions—Transfer exactly (0 (blank), 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, and 14.0)-mL aliquots of the standard manganese solution into separate 250-mL beakers.

19.3 Color Development—To each aliquot and a blank, add 50 mL of water, 15 mL of the KIO₄ solution, and cover. Heat to boiling and digest just below boiling until no further attack is apparent. It may be necessary to add more HCl, particularly if a 3-g sample is used. Add 5 mL of HNO₃ and 20 mL of HClO₄. Evaporate to heavy fumes, and fume for 10 min. Cool, add 30 mL of water and heat to dissolve the soluble salts. Filter through a fine-texture paper, receiving the filtrate in a 250-mL beaker. Wash the residue twice with warm HNO₃ (1 + 9) and eight times to ten times with hot water until free of perchlorates and reserve the filtrate.

19.4 Spectrophotometry—Using water as the reference solution, adjust the spectrophotometer to the initial setting. While maintaining this setting, take the spectrophotometric readings of the blank and the calibration solutions, using a light band centered at approximately 545 nm (Note 9).

19.5 Calibration Curve—Subtract the absorbance of the blank solution from absorbance of each calibration solution and plot the net absorbance of the calibration solution against milligrams of manganese in 100 mL.

19.6 Blank Determination—Perform a blank determination using the same amount of reagents and performing the same operations described in the test procedure.

20. Procedure

20.1 Weigh approximately (within ± 0.0025 g) an amount of prepared sample based on the estimated manganese as follows:

<table>
<thead>
<tr>
<th>Estimated Manganese, %</th>
<th>Weight of Sample, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 0.03</td>
<td>3.00</td>
</tr>
<tr>
<td>0.06 to 1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>1.01 to 2.00</td>
<td>0.50</td>
</tr>
<tr>
<td>2.01 to 4.00</td>
<td>0.30</td>
</tr>
<tr>
<td>4.01 to 5.00</td>
<td>0.25</td>
</tr>
</tbody>
</table>

20.2 Transfer the test sample to a small, dry weighing bottle and place in a drying oven. Dry at 110 °C for 1 h (Note 6). Cap the bottle and cool to room temperature in a desiccator. Momentarily release the cap to equalize pressure and weigh the capped bottle to the nearest 0.001 g. Repeat the drying and weighing until there is no further weight loss. Transfer the test sample to a 250-mL beaker and reweigh the capped bottle to the nearest 0.001 g. The difference between the two weights is the weight of the sample.

20.3 Moisten the test sample with a few millilitres of water. Add 10 mL of HCl for each gram of test sample or fraction thereof. Cover with a watch glass, and heat gently. Increase the heat and digest just below boiling until no further attack is apparent. It may be necessary to add more HCl, particularly if a 3-g sample is used. Add 5 mL of HNO₃ and 20 mL of HClO₄. Evaporate to heavy fumes, and fume for 10 min. Cool, add 30 mL of water and heat to dissolve the soluble salts. Filter through a fine-texture paper, receiving the filtrate in a 250-mL beaker. Wash the residue twice with warm HNO₃ (1 + 9) and eight times to ten times with hot water until free of perchlorates and reserve the filtrate.

20.4 Place the paper and residue in a platinum crucible. Char the paper at a low temperature in a muffle furnace, then ignite to 800 °C. Cool the crucible, moisten the residue with a few drops of water, add five drops of H₂SO₄, and HClO₄ mL of HF. Evaporate slowly to dryness to volatilize the silica and to remove the excess H₂SO₄. Cool, add 1 g of Na₂CO₃ and fuse until a clear melt is obtained. Cool the crucible, and place in a 250-mL beaker. Add 50 mL of HNO₃ (1 + 9) and warm to dissolve the melt. Remove and rinse the crucible and add this solution to the filtrate reserved in 20.3. Evaporate to fumes of HClO₄. Add 30 mL of water and warm to dissolve the salts. Cool, transfer to a 200-mL volumetric flask, dilute to the mark, and mix.

20.5 Select an aliquot measured exactly in accordance with the following:

<table>
<thead>
<tr>
<th>Manganese, %</th>
<th>Aliquot, mL</th>
<th>HClO₄ Additions to Aliquot, mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 0.01</td>
<td>100</td>
<td>7</td>
</tr>
<tr>
<td>0.06 to 0.25</td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>0.26 to 0.50</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>0.51 to 1.00</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>1.01 to 2.00</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>2.01 to 3.00</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>3.01 to 4.00</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>4.01 to 5.00</td>
<td>20</td>
<td>10</td>
</tr>
</tbody>
</table>

Transfer the aliquot to a 250-mL beaker. Add, if required, additional HClO₄ as indicated in the table. Evaporate or dilute to 50 mL and proceed with the development of the color according to 19.3.

20.6 Prepare a reference solution by adding a portion of the oxidized sample solution to a dry 50-mL beaker. Bleach the color of the permanganate by the dropwise addition of the NaNO₂ solution. Mix and add one drop of NaNO₂ solution in excess (Note 11).

Note 11—If more than one sample is analyzed, this reference solution must be prepared from a portion of each sample.

20.7 Fill a 1-cm cell with the reference solution and adjust the initial setting of the photometer with this solution. Discard the reference solution. Rinse and fill the cell with the solution from 20.5. Read the absorbance of the test solution using a light-band centered at 545 nm (Note 9).

21. Calculation

21.1 Convert the absorbance to milligrams of manganese by means of the calibration curve. Calculate the percentage of manganese in the sample as follows:

\[
\text{Manganese, %} = \frac{(A \times B)}{(C \times D \times 10)}
\]

where:

- \( A \) = milligrams of manganese,
22. Precision and Bias

22.1 Precision—Data on this test method were obtained by eight cooperators. Standard deviation of repeatability and reproducibility were numerically calculated as directed in Practice E173 (see Table 2).

22.2 Bias—No information on the bias of this test method is known. Test results for the reference materials were not compared with reference values in the interlaboratory study. Users of the method are encouraged to employ accepted reference materials, if available, and to judge the bias of the method from the difference between the accepted value for the manganese and the mean value from interlaboratory testing of the reference material.

23. Keywords

23.1 agglomerates; concentrates; iron ores; manganese content; related materials