

CHROMIUM METHOD 2

Using Diphenylcarbazide

PRINCIPLE OF THE METHOD

Chromium(VI), in acid solution, reacts with diphenylcarbazide to give a red violet colour the intensity of which is proportional to the concentration of chromium(VI) present in the solution. This colour is then compared with a series of Lovibond permanent colour glass standards. By analysing the sample for chromium before and after oxidation, the proportion of both chromate and of total chromium may be determined.

REAGENTS REQUIRED (All chemicals used should be of analytical reagent quality, but see Note 2).

1. **Diphenylcarbazide Solution.** (See Note 5). Dissolve 0.2g. diphenylcarbazide in 100ml. propan-2-ol. This solution must be kept as cool as possible and should be discarded immediately it becomes brown in colour.
2. **Sulphuric Acid (H₂ SO₄) 50%.** Cautiously add one volume of the concentrated acid to one volume of deionised water. Mix and cool.
3. **Silver Nitrate (AgNO₃) Solution 5%.** 5g. silver nitrate in 100ml. deionised water.
4. **Sodium Nitrite (NaNO₂) Solution 1%.** Dissolve 1g. Sodium nitrite in 100ml. deionised water.
5. **Ammonium Persulphate (NH₄)₂ S₂ O₈)**
6. **Phosphoric Acid (H₃ PO₄ sp.gr.1.75)**

THE STANDARD LOVIBOND DISCS, COMPARATOR DISC 3/59 AND NESSLERISER DISC NOK

Disc 3/59 covers the range 10 – 100µg/l. as chromium (Cr), with steps of 10, 20, 30, 40, 50, 60, 70, 80 and 100µg.. which corresponds to 0.4 to 4.0mg./l. when a 25ml. sample is taken.

Disc NOK covers the range 2 – 10µg. as chromium (Cr) with steps of 1, 2, 3, 4, 5, 6, 7, 8 and 10µg which corresponds to 0.08 – 0.4mg./l. as chromium (Cr), when a 25ml. sample is taken.

To convert Cr to chromate in terms of CrO₄, multiply reading by 2.23.

METHOD

a) Chromium present as Chromate

1. Take 25ml. of the sample solution in a Nessler tube or measuring cylinder. Filter if necessary through sintered glass and add 5ml. of sulphuric acid (reagent 2).
2. Dilute to the 50ml. mark with deionised water and add 1ml. of phosphoric acid (reagent 6). Mix well.
3. Add 2ml. of diphenyl carbazide solution (reagent 1) mix again and allow to stand for 5 minutes.
4. Prepare a blank using deionised water in place of the sample.
5. Compare the colour of the sample with the disc by taking a 50ml. volume in a Nessler tube in the case of the Nessleriser disc NOK or 10ml. in a 13.5mm./10ml. moulded cell in the case of the Comparator disc 3/59, placing the cell in the right-hand and the blank solution in the left hand compartment of the measuring instrument.

6. Place the instrument in the Lovibond Daylight 2000 Unit, or failing this, facing North Daylight (not fluorescent lighting) and rotate the disc until the nearest colour match is obtained.
7. The value displayed in the bottom right-hand corner is the amount of chromium present in the sample taken in μg . See Note 1.
8. The concentration of Chromium in $\text{mg./l.} = \frac{\text{Disc Reading}}{\text{vol. of sample}}$

e.g. With a sample size of 25ml., a reading of 10 μg . the concentration = 10/25 = 0.4 mg./l.

b) Total Chromium

1. Take 25ml. of the sample solution in a Pyrex beaker and add 5ml. of sulphuric acid (reagent 2).
2. Remove any chloride ions which may be present by evaporating until white fumes appear. Cool and dilute to about 30ml. with deionised water.
3. Bring the solution nearly to the boiling point and then add 1ml. of silver nitrate solution (reagent 3), followed by about 1g. of ammonium persulphate (reagent 5).
4. Boil for at least 10 minutes.
5. If the solution at this stage still has a pink tinge, due to the presence of manganese (See Note 3), add sodium nitrite solution (reagent 4) dropwise until the colour just disappears.

NOTE: - Care must be taken not to add too much nitrite as excess will reduce the chromate and therefore give a low reading.

6. Cool and transfer the solution to a Nessler tube or measuring cylinder, add 1ml. of phosphoric acid (reagent 6) and make up to 50ml. with deionised water. Mix well.
7. Add 2ml. of diphenyl carbazide solution (reagent 1), mix again and allow to stand for 5 minutes to ensure full colour development.
8. If considered necessary carry out a blank on the reagents by carrying out all the steps listed above using deionised water in place of the sample.
9. Compare the colour of the sample with the disc by taking a 50ml. volume in a Nessler tube in the case of Nessleriser disc NOK or 10ml. in a 13.5mm./10ml. moulded cell in the case of the Comparator disc 3/59.
10. Place the blank solution behind the disc in the left hand compartment of the instrument.
11. Place the instrument in the Lovibond Daylight 2000 Unit or failing this facing North Daylight (not fluorescent lighting) and rotate the disc until the nearest colour match is obtained.
12. The value displayed in the bottom right-hand corner is the amount of total chromium present in the original 25ml. of sample taken, in μg .
13. The concentration of Chromium in $\text{mg./l.} = \frac{\text{Disc Reading}}{\text{Vol. of sample}}$

NOTES

1. If the colour produced is darker than the top step on the Nessleriser disc repeat the colour measurement using 13.5mm./10ml. moulded cells and the Comparator disc. Alternatively repeat the test procedure using a smaller volume of sample.
2. Iron interferes with the determination of chromium by giving a yellow/brown coloration. It is suppressed by the addition of phosphoric acid, provided the ratio of iron to chromium does not exceed 100:1. If it is greater than this the iron must be removed from the sample by precipitation as ferric hydroxide before proceeding with the chromium test.
3. In the method for total chromium, manganese interferes if it is present in amounts greater than 0.2mg/l.. The presence of manganese is indicated by the appearance of a pink colour during the total chromium determination, and the interference can be removed by discharging the pink colour by the addition of sodium nitrite dropwise as described in the method.
4. The readings obtained by means of the Lovibond Nessleriser and disc are accurate only when the Nessleriser glasses used conform to the specification employed when the disc was calibrated; that is the 50 ml calibration mark is at a height of 113 ± 3 mm. measured internally.
5. Best results are obtained when using Diphenylcarbazide Laboratory Reagent Grade, but when using purified AnalaR grade reagent which produces a deeper colour, high results may be given. Such results obtained should be multiplied by the factor 0.8 to give the true concentration.

REVISION HISTORY

Date	Change Note	Issue
12/03/02	36/460	2
20/04/05	CA243	3
12/09'06	JC21	4
15/01/09	JC 139	5
06/05/10	JC 142	6