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CHROMIUM using Diphenylcarbazide

PRINCIPLE OF THE METHOD

Hexavalent chromium, in acid solution, reacts with diphenylcarbazide to give a red violet colour the intensity of which is proportional to the concentration of hexavalent chromium present in the solution. This colour is 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

1. **Diphenylcarbazide Solution.** (See Note 5). Dissolve 0.2g diphenylcarbazide in 100ml isopropyl alcohol. This solution must be kept as cool as possible and should be discarded immediately it becomes brown in colour.

2. **Sulphuric Acid (H_2SO_4) 50%.** Cautiously add one volume of the concentrated acid to one volume of deionised water. Mix and cool.

3. **Silver Nitrate ($AgNO_3$) Solution 5%.** 5g silver nitrate in 100ml deionised water.

4. **Sodium Nitrite ($NaNO_2$) Solution 1%.** Dissolve 1g sodium nitrite in 100ml deionised water.

5. **Ammonium Persulphate $(NH_4)_2S_2O_8$)**

6. **Phosphoric Acid (H_3PO_4 sp.gr.1.75)**

All chemicals used should be of analytical reagent quality.

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

Disc 3/59 covers the range 10 to 100 μg of chromium (Cr) in steps of 10 μg,
i.e. 0.4 to 4.0mg/l on a 25ml sample.

Disc NOK covers the range 2 to 10 μg of chromium (Cr) in steps of 1 μg,
i.e. 0.08 to 0.4mg/l on a 25ml sample.

To convert Cr to chromate in terms of CrO_4, multiply answer 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 50 ml 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.

6. Place the blank solution behind the disc in the left hand compartment of the instrument.

7. 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. The figure shown in the bottom right-hand corner is the weight of chromium present in the sample in μg. To convert this to mg/l divide by 25 (the volume of sample taken for the test). See Note 1.

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 lead to low results.

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 10 ml 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. The figure shown in the bottom right-hand corner is the weight of chromium present in the sample in μg. To convert this to mg/l divide by 25 (the volume of sample taken for the test).

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 aliquot 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, if 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.

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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 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 that the 50 ml calibration mark shall fall at a height of 113 $\pm$ 3 mm measured internally.

5. Correct results are obtained when using Diphenylcarbazide Laboratory Reagent Grade, but when using purified AnalaR grade reagent which produces a deeper colour, high results are given. The results obtained should be multiplied by the factor 0.8 to give the true concentration.

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COPPER using Zinc Dibenzyldithiocarbamate

PRINCIPLE OF THE METHOD

Zinc dibenzyldithiocarbamate solution reacts with copper ions forming a mixture of zinc and copper dithiocarbamates. On making this mixture acid by means of dilute sulphuric acid, the zinc salt is transferred to the aqueous phase while the copper dithiocarbamate remains in the methyl chloroform. The following metals interfere; bismuth, nickel and cobalt, which form yellow complexes with the reagent; mercury (II), silver and antimony hinder the extraction of the copper complex.

REAGENTS REQUIRED

1. ***Zinc Dibenzyldithiocarbamate Solution*.** Dissolve 0.05g of zinc dibenzyldithiocarbamate $[(C_6H_5.CH_2)_2\ N.CS.S]_2Zn$ in 100 ml methyl chloroform (1,1,1-trichloroethane) analytical reagent grade.

2. ***Sulphuric Acid, Copper-Free***. 10% by volume in deionised water.

THE STANDARD LOVIBOND COMPARATOR DISC 3/39

The disc covers the range 2.5, 5, 10, 15, 20, 25, 30, 40 and 50 μg of copper (Cu). This corresponds to 1 to 20mg/l of copper if a 2.5ml sample is used.

TECHNIQUE

1. Measure a suitable volume of sample into a separating funnel (e.g. if the expected concentration is within the range 2 to 20mg/l take a 2.5ml sample; if between 1 and 10mg/l take a 5ml sample).

2. Adjust the sulphuric acid content to approximately 5% by addition of sulphuric acid (reagent 2) (see note 1) i.e. if a 5ml sample is taken add 0.25ml (5 drops) of sulphuric acid.

3. Add 10ml of zinc dibenzyldithiocarbamate solution (reagent 1), stopper the funnel and shake vigorously for 30 seconds.

4. Separate the lower yellow methyl chloroform layer into a 13.5mm/10ml moulded cell and place this in the right hand compartment of the Comparator.

5. Place the Comparator against a standard source of white light such as the Lovibond Daylight 2000 Unit or, failing this, North daylight (not fluorescent lighting) and rotate the disc until the nearest colour match is obtained.

6. The figure shown in the bottom right hand corner of the Comparator is the amount of copper in micrograms, present in the volume of sample taken. The concentration of copper in mg/l is equal to:

$$\frac{\text{DISC READING}}{\text{VOLUME OF SAMPLE TAKEN}}$$

NOTE

If the sulphuric acid used is not copper free, repeat the test using the same amount of the acid as is added in 2, dilute with an equal volume of water and carry out steps 3 to 6 above. Subtract this reading from the original reading obtained to give the copper content of the sample.

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CYANIDE Using Pyridine and *p*-Phenylenediamine

INTRODUCTION

The reaction of cyanogen bromide with pyridine and an aromatic amine (the Konig synthesis), which is a standard method for the determination of low concentrations of cyanide ion, has been examined[1] with a view to finding a better heterocyclic amine than pyridine and a less carcinogenic aromatic amine than benzidene.

No heterocyclic amine better than pyridine was found. The most favourable aromatic amine, when carcinogenic hazards were taken into consideration, proved to be *p*-phenylenediamine. The present test[2] was therefore developed for cyanide ion in concentrations of 0.05 - 1.0 mg/l in waters.

PRINCIPLE OF THE METHOD

In acid solutions cyanides react with pyridine and *p*-phenylenediamine to form a dark red coloured complex. The intensity of the colour of this complex, which is proportional to the concentration of cyanide ion, is measured by comparison with a series of Lovibond permanent colour glass standards.

REAGENTS REQUIRED

1. ***Hydrochloric Acid***. Concentrated.

2. ***Bromine Water, Saturated.*** Add 3ml of bromine to 100ml of deionised water

3. ***Pyridine.*** Add 3ml of reagent 1 to 18ml of pyridine dissolved in 12ml of deionised water.

4. ***p-Phenylenediamine Dihydrochloride.*** Dissolve 0.36g of *p*-phenylenediamine dihydrochloride in 100ml deionised water. Store the solution in a brown bottle.

5. ***Sodium Arsenite.*** Dissolve 1.5g of sodium arsenite ($NaAsO_2$) in 100ml of deionised water.

6. ***Pyridine-p-Phenylenediamine Reagent.*** Mix 3 volumes of reagent 3 with 1 volume of reagent 4.

All chemicals used for the preparation of reagents should be of analytical reagent quality.

THE STANDARD LOVIBOND COMPARATOR DISC 3/86

This disc contains standards corresponding to 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1.0 mg/l of cyanide (CN^-) ions.

TECHNIQUE

1. Place 5ml of sample solution in one 13.5mm/10ml moulded cell and 5ml of deionised water in a second, identical, cell.

2. Add 0.1ml (2 drops) of reagent 1, and 0.2ml (4 drops) of reagent 2 to each cell and mix thoroughly.

3. After 2 minutes add 0.2ml (4 drops) of reagent 5 to each cell to remove any excess bromine * (see note 1), add 4ml of reagent 6 and make up to the 10ml mark with deionised water.

4. Place the sample cell in the right-hand compartment of the Comparator and the second cell in the left-hand compartment.

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5. After 30 minutes place the Comparator before a uniform source of white light such as the Lovibond Daylight 2000 Unit or, failing this, North daylight, and rotate the disc until the nearest colour match is obtained.

6. The figure shown in the bottom right-hand corner of the Comparator is the concentration of cyanide in mg/l.

Acknowledgement is made to Lancy Laboratories Ltd for assistance in developing this disc.

NOTES

1. Excess bromine remaining causes the reaction to go blue.

2. All colorimetric methods for cyanide only react to "free" and simple complexes of cyanide, i.e., potassium, zinc, copper and cadmium cyanides.

   Heavy metals sodium e.g. nickel, iron, silver and gold, form tight complexes with cyanide which can only be broken down by distillation. If a sample containing a complex cyanide is distilled and the distillate collected in caustic soda, then the cyanide is present as sodium cyanide, and thus a figure for total cyanide may be obtained.

REFERENCES

1. L.S. Bark and H.G. Higson, *Talanta,* 1964, **11**, 471
2. L.S. Bark and H.G. Higson, *Talanta,* 1964, **11**, 621

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NICKEL Using Dimethyl-Glyoxime

PRINCIPLE OF THE METHOD

Nickel is often estimated gravimetrically by precipitation of the nickelous complex formed with dimethyl glyoxime. In the presence of oxidising agents however this divalent complex is converted into a soluble red tetravalent complex and this modified procedure serves as a very sensitive method for the estimation of traces of nickel.

Interference from small amounts of iron is prevented by the use of ammonium citrate. Appreciable quantities of other metals, including cobalt, copper and manganese, interfere and special procedures are necessary in their presence.

REAGENTS REQUIRED

1. ***Ammonium Citrate*** $((NH_4)_3C_6H_5O_7)$**.** Solution 10% w/v

2. ***Bromine Water Saturated***. Add 3ml of bromine to 100ml deionised water.

3. ***Ammonia Solution 10%*** **w/w.** Dilute 30 ml conc. Ammonia (0.880) to 100 ml with deionised water.

4. ***Dimethyl-Glyoxime***. 1% solution in Propan-2-ol.

THE STANDARD LOVIBOND COMPARATOR DISCS 3/36 and 3/36A

The colours in the 3/36 disc correspond to 1, 2, 3, 4, 5, 6, 7, 8 and 10 mg/l of nickel (Ni) using 10ml of the solution under test, and is used with 13.5 mm, 10 ml moulded cells.

The colours in the 3/36A disc correspond to 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 1.0 mg/l of nickel (Ni) using 100 ml of solution under test and is used with 40 mm moulded cells.

TECHNIQUE (DISC 3/36)

1. The sample solution should be rendered neutral with ammonia (reagent 3).

   Using a pipette or measuring cylinder transfer 10ml to a small beaker or flask. Add in the following order:

5 ml	Ammonium Citrate Solution	(reagent 1)
2 ml	Bromine Water	(reagent 2)
2 ml	Ammonia Solution	(reagent 3)
1 ml	Dimethyl Glyoxime Solution	(reagent 4)

   Mix thoroughly after each addition.

2. Transfer to a 13.5mm/10ml moulded cell and place in the right-hand compartment of the Comparator. In the left-hand compartment place a blank of the reagents which has been prepared in exactly the same manner.

3. Hold the Comparator facing a standard source of white light, such as the Lovibond Daylight 2000 Cabinet or, failing this, North daylight, and compare the colour of the solution with the colours in the disc, rotating the latter until the nearest match is obtained.

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4. The reading in the bottom right-hand aperture represents mg/l of nickel in 10ml of the neutral solution.

TECHNIQUE (DISC 3/36A)

1. The sample solution should be rendered neutral with ammonia (reagent 3).

2. Fill a 100ml stoppered measuring cylinder to the 100ml mark with this neutral solution and then add DOUBLE the volumes of reagents listed for disc 3/36. Mix well.

3. Pour the resultant coloured solution into a 40 mm moulded cell.

4. Carry out a blank test on the reagents using 100 ml of deionised water as the sample. Pour into another 40 mm cell.

5. Place the test cell in the right-hand compartment of the Comparator and the blank cell in the left-hand compartment.

6. Hold the Comparator facing a standard source of white light, such as the Lovibond Daylight 2000 Unit or, failing this, North Daylight, and compare the colour of the solution with the colours in the disc, rotating the latter until the nearest colour match is obtained.

7. The reading in the bottom right-hand aperture represents mg/l of nickel in 100ml of the neutral solution.

NOTES

1. Interference can be caused either by the precipitation of a metal as the hydroxide or by complex formation between the interfering ion and the reagent.

   In the former case separation can be effected by double precipitation or in certain cases by a special technique such as electrolysis.

   When complex formation takes place, advantage can be taken of the fact that nickelous dimethyl glyoxime is soluble in chloroform whilst complexes formed with the majority of other metals are insoluble. Copper dimethyl glyoxime is soluble in chloroform, but unlike the nickel complex this can be decomposed with dilute ammonia. The nickel can then be back-extracted from the chloroform by treatment with dilute hydrochloric acid. This procedure is suitable for the estimation of nickel in cobalt salts.

2. It should be noted that in the presence of oxidising agents (e.g. manganese) a trace of hydroxylamine sulphate may be necessary to prevent the formation of the tetravalent nickel complex which is **insoluble** in chloroform.

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ZINC Using Brilliant Green

PRINCIPLE OF THE METHOD

The method, using brilliant green, is based on Houghton's modification of the method of Hermanowicz and Sikorowska. It was developed specifically for the determination of zinc in water. Any ferric iron is inhibited with ammonium fluoride, and at pH 1.7 the interference from copper is slight and is almost entirely prevented by the addition of sodium diethyldithiocarbamate. The colour produced is measured by comparison with a series of Lovibond permanent colour glass standards.

REAGENTS REQUIRED

1. ***Sulphuric Acid 10%***. Add 100ml of analytical reagent quality H_2SO_4 slowly, with stirring, to 800ml of deionised water. When cool dilute with deionised water to 1 litre.

2. ***Fluoride-Thiocyanate Reagent***. Dissolve 30g of ammonium thiocyanate (NH_4SCN), of analytical reagent quality, and 5g of similar quality ammonium fluoride (NH_4F) in sufficient deionised water to make 100ml. Store in a polythene bottle.

3. ***Acacia Solution.*** Add 3g of finely crushed or powdered acacia to 100ml of hot deionised water and dissolve the powder by boiling. Cool, filter and add 0.1ml of toluene ($CH_3C_6H_5$) as a preservative.

4. ***Carbamate Solution***. Dissolve 0.1g of sodium diethyldithiocarbamate, analytical reagent quality, in 100ml of deionised water. **THIS REAGENT MUST BE PREPARED EACH DAY.**

5. ***Brilliant Green Solution***. Dissolve 0.1g of brilliant green C.I.42040 in 100ml of cold iso-propyl alcohol.

THE STANDARD LOVIBOND COMPARATOR DISC 3/69

This disc covers the range 0-50μg of Zinc (Zn) in steps of : 0, 2.5, 5, 10, 15, 20, 30, 40 and 50μg

This represents for example, a range 0 - 2 mg/l if a 25ml sample is used, or 0 - 10 mg/l with a 5ml sample.

TECHNIQUE

1. Measure a suitable volume, not exceeding 30ml, of the water under test, which should be between pH6 and 8, into a 50ml Nessler cylinder or measuring cylinder.

2. Make the volume up to 30ml with deionised water if necessary and add 2 ml of sulphuric acid (reagent 1). Mix well.

3. Add 2ml of fluoride-thiocyanate (reagent 2). Mix and allow to stand for 3 minutes.

4. Adjust the temperature to $20^oC \pm 1^oC$ and maintain the solution at this temperature for the remainder of the test.

5. Add 5ml of acacia solution (reagent 3). Mix and then add 2ml of carbamate solution (reagent 4). Mix and then **immediately** add 1.0ml of brilliant green solution (reagent 5).

6. Mix well and dilute to the 50 ml mark with deionised water. Mix again and allow to stand for 12 minutes.

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7. Fill a 13.5mm/10ml moulded cell with the solution and place this in the right hand compartment of the Lovibond Comparator. Place another cell filled with deionised water in the left hand compartment.

8. After **exactly** 15 minutes has elapsed from the addition of the brilliant green solution, place the Comparator in the Lovibond Daylight 2000 Unit or, failing this, North daylight (not fluorescent lighting) and match the colour against the disc. The figure shown in the bottom right hand corner of the Comparator represents the amount of Zinc in the sample in micrograms (μg). To obtain the concentration as mg/litre the disc reading must be divided by the original volume of sample taken for the test.

e.g. A reading of 10μg on a 25ml sample represents 0.4 mg/litre of Zinc.

NOTES

1. A blank should be determined on each batch of chemicals used in preparing the reagents by repeating the above procedure with 30ml of deionised water as the sample. Any blank reading should be recorded and subtracted from the readings obtained on samples under test.

2. It is essential to carry out the test at the temperature stated.

3. The colours produced fade on standing and so readings should be taken exactly at the time stated above.