

## AMINES METHOD 1

### Using Bromocresol Green

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#### INTRODUCTION

This test<sup>1</sup> (Note 1) has been developed primarily for the determination of long-chain aliphatic amines in water. Film-forming amines of this type have been used in water treatment for the prevention of the growth of algae and also for the protection of steam lines. When used in this way, the determination of residual amines in cooling waters and condensates is essential for control purposes. Alternative methods<sup>2-11</sup> which have been proposed for this determination are unsuitable for field use, as they require exacting conditions for the production of accurate results. The present method, on the other hand, is capable of producing accurate results under field conditions, even in the hands of relatively unskilled operators.

Sulphonphthaleins react with primary, secondary, tertiary and quaternary amines (quaternary ammonium compounds-QAC) and this test, although primarily developed for long-chain amines can be applied to the determination of other amines provided that the disc is recalibrated in terms of the particular amine being estimated (see Note 5).

#### PRINCIPLE OF THE METHOD

Amines react with sulphonphthaleins, in acid solution, to form a yellow complex. This complex is extracted from the aqueous solution by shaking with trichloromethane (chloroform) in a special comparator extraction tube. The intensity of the yellow colour in the lower (chloroform) layer after extraction is proportional to the concentration of amine, and is estimated by comparison with Lovibond permanent colour glass standards.

#### REAGENTS REQUIRED

1. **Amine Test Indicator Tablets** (equivalent to 0.5ml of a 0.1% solution of tetra-bromo-*m*-cresol sulphonphthalein i.e. "Bromocresol Green", with an acid content equivalent to 15mg alkali, expressed as CaCO<sub>3</sub>).
2. **Trichloromethane (Chloroform (CHCl<sub>3</sub>))**, analytical reagent grade.

#### THE STANDARD LOVIBOND COMPARATOR DISC 3/58

This disc covers the range 1-10mg./l. of pure octadecylamine and is designed for use with special extraction tubes, which are available from The Tintometer Limited.

Other amines may be determined with this disc by using appropriate conversion factors for the disc readings (Note 5).

#### METHOD

1. Take two of the special calibrated extraction tubes and carefully add trichloromethane to each, up to the 5ml. mark. Place an indicator tablet in each tube.
2. Into one tube introduce 10ml. of sample, i.e. up to the 15ml. mark. To the other tube add 10ml. of deionised, or untreated, water to form the blank. Stopper both tubes and shake for 30 seconds.
3. Allow the layers to separate. If amine is present in the sample the lower (trichloromethane) layer will be coloured yellow. Place the sample tube in the right-hand compartment of the Comparator and the blank tube in the left-hand compartment.
4. The tubes have been designed so that the lower layers will cover the Comparator apertures avoiding the need to transfer the trichloromethane layers to separate comparator cells.

5. Compare the colour of the sample with the standards in the disc, using a standard source of white light, such as the Lovibond Daylight 2000 Unit or, failing this, North daylight.
6. The value displayed in the bottom right-hand corner of the comparator is the amine content of the sample as Octadecylamine.

## NOTES

1. This method has been developed by Houseman and Thompson Ltd. Permission to quote from the published literature is gratefully acknowledged.
2. This method is only applicable if the pH of the sample is below 8.5; amine treatment is not suitable for more alkaline waters. The hardness of the water is also critical and should not exceed 2,000mg./l. as calcium carbonate. Beyond this level, which increases with evaporation, amines are ineffective. The chloride concentration gives an indication of the hardness level as the chloride remains soluble while other salts precipitate from the water.
3. If the intensity of the colour in the sample tube is greater than that of the 10mg./l. standard, the test should be repeated using a smaller volume of sample and making the total volume of water added up to 10ml. by means of distilled water. The final reading should then be multiplied by the appropriate dilution factor, i.e. by 10 divided by the volume of sample used.
4. If the solution is insufficiently acidified, free ammonia tends to give a false reading. In the 10ml sample, there is sufficient acid in the tablet to allow up to 1,500mg./l. total alkalinity to be tolerated before the yellow colour is interfered with. Ammonium, iron and copper salts and hydrazine do not interfere.
5. Amines other than octadecylamine\* can be determined using this disc provided that a suitable correction factor is applied to the disc readings. The appropriate correction factor may be calculated in the following manner. The colour which is developed is proportional to the molecular concentration of the amino group, or groups, in the amine, irrespective of whether it is a primary, secondary, tertiary or quaternary amine. This molecular concentration is simply the molecular weight of the amine divided by the number of amino groups present in the molecule.

$$\text{Correction factor} = \frac{\text{Molecular Weight of new amine}}{\text{No. of amino groups} \times \text{Molecular Weight octadecylamine (269)}}$$

A few examples will make this clear:-

Amine 220  $C_{17}H_{33}N_2O$  Molecular Weight 350.6

No. of amine groups 2

$$\text{Correction factor} = \frac{350.6}{2 \times 269} = 0.6$$

Tetraethylammonium bromide  $(C_2H_5)_4NBr$  Molecular Weight 210.2

No. of amine groups 1

$$\text{Correction factor} = \frac{210.2}{1 \times 269} = 0.78$$

\* The following Amines have been found to be unreactive in this test:-

Diethanolamine, Triethanolamine, Cyclohexylamine, Morpholine.

## REFERENCES

1. A.S. Pearce, *Chem. & Ind.*, 1961, 825
2. A. Milun and F. Moyer, *Anal. Chem.*, 1956, **28**, 1204
3. E. Carkhuff and W. Boyd, *J. Am. Pharm. Ass. Sci., Ed.*, 1954 **43**, 240
4. P.J. Lloyd and A.D. Carr, *Analyst*, 1961, **86**, 335
5. K.B. Coates, *Corrosion Tech.*, 1960, **7**, 46
6. H.M. Hershenson and D.N. Hume, *Anal. Chem.*, 1957, **29**, 16
7. J. Johnston, *Anal. Chem.*, 1953, **25**, 1764
8. J. Johnston and F.E. Critchfield, *Anal. Chem.*, 1956, **28**, 436
9. *idem ibid*, 1957, **29**, 957
10. J. Johnston and G.L. Fink, *Anal. Chem.*, 1956, **28**, 436
11. A.J. Milun, *Anal. Chem.*, 1957, **29**, 1502

## REVISION HISTORY

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