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# INSTITUTET FÖR VATTEN- OCH LUFTVÅRDSFORSKNING

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DETERMINATION OF NTA IN WASTE WATERS  
(Preliminary adopted procedure)

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## DETERMINATION OF NTA IN WASTE WATERS

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### Principle

The sample is first treated with aluminum sulphate (alum) at pH 5.5 - 6.0 to flocculate organic matter. The excess of aluminum is removed, together with any heavy metals present, with oxine in chloroform. The pH is then adjusted to 7 and copper chloride added in excess to the amount of NTA present. The non-complexed copper is extracted with salicyl aldehyde in chloroform. The copper-NTA complex is then split by extraction of the copper with oxine in chloroform. The extracted copper is determined spectrophotometrically at 400 nm.

The procedure allows the determination of 0.5 - 1.0 ppm of NTA with fair accuracy.

The pretreatment with oxine is essential. The flocculation with alum might be omitted when no interference from organic matter (forming of emulsions, etc.) is expected. The sample volume may then be reduced.

Chelating agents, whose copper complexes are either split by salicyl aldehyde or not split by oxine, do not interfere. Tripolyphosphate, if not precipitated by alum, causes some interference.

### Equipment

Laboratory shaker (for instance Griffin and George Ltd. flask shaker).

Filter photometer for measurement at 400 nm or spectrophotometer.

### Chemicals

Aluminium sulphate (techn. grade or better), 5 % w/v in water.

Oxine (8-hydroxyquinoline p.a.) 0.5 % w/v in chloroform. The solution should be kept in the dark and frequently renewed.

Salicyl aldehyde (purum or better), 2 % w/v in chloroform.

Copper chloride, stock solution: Dissolve 2.2348 g of  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$  p.a. in distilled water and dilute to 1 000 ml.

Phosphate buffer, pH 7.0: To a 0.5 M solution of  $\text{Na}_2\text{HPO}_4$ , 12  $\text{H}_2\text{O}$  add 0.5 M  $\text{KH}_2\text{PO}_4$  until the pH is 7.0 (glass electrode).

### Standard curve

Take 10 ml of the copper stock solution and dilute to 100 ml.

Take 1, 2, 4, 8, 12 ml of the diluted copper solution and dilute further to 25 ml with distilled water. The flasks will contain copper equivalent to 1, 2, 4, 8, 12 mg NTA per litre, respectively.

To 10 ml from each flask in a separatory funnel, 1 ml of phosphate buffer is added, followed by ca. 7.5 ml of oxine solution. After shaking for about 2 minutes, the phases are allowed to separate and the chloroform layer transferred to a 10 ml measuring flask. The aqueous layer is washed with two 1 ml portions of chloroform. The volume of the combined extract and washings is adjusted to 10 ml and the extinction read in a 1 cm cuvette at 400 nm with chloroform as reference.

The standard curve is made by plotting the measured extinctions against the equivalent NTA concentrations.

### Procedure

To 200 ml of the waste water to be examined, 0.8 ml of alum solution is added and the pH quickly adjusted 5.5 - 6.0, with 0.5 M  $\text{KH}_2\text{PO}_4$  (glass electrode). The volume used is noted. At very soft waters 0.5 M  $\text{MNa}_2\text{HPO}_4$  may have to be used instead. After slow stirring (a 20 r/min paddle stirrer is recommended) for 20-30 min, the flocs formed are allowed to settle and about 100 ml of the supernatant run through a filter paper.

A suitable volume of the filtrate is transferred to a beaker for further analysis. The recommended volume is 10 ml when the expected NTA concentration is 5-12 mg/l and 20-50 ml at concentrations below 5 mg/l of NTA.

The pH of the solution is raised to 7.0 by adding 0.5 M  $\text{Na}_2\text{HPO}_4$ . After adding 1 ml of phosphate buffer the solution is transferred quantitatively to a 125 ml separatory funnel. The solution is extracted with 5 ml of oxine by vigorous shaking for 5 min using the laboratory shaker. The extraction is repeated (usually three times) until the chloroform phase shows no extinction at 400 nm against the oxine solution. The aqueous phase is washed three times with 5 ml portions of chloroform.

If the sample volume is 50 ml, one 25 ml and three 15 ml portions of oxine are preferably used.

Copper solution is then added and the solution is left standing for about 5 min to allow time for the copper-NTA complex to be formed. At concentrations up to 12 mg of NTA per litre, 1.2 ml of copper stock solution is taken.

10 ml samples are extracted, using the shaker, with four 5 ml portions of salicyl aldehyde for five minutes. For

50 ml samples one 25 ml and three 15 ml portions are used and the extraction times are increased to 10 or 15 minutes. Remaining salicyl aldehyde is removed by washing three times with small portions of chloroform.

The solution is extracted with 7.5 ml of oxine by shaking for two minutes and washed with two 1 ml portions of chloroform. The extract and washings are combined in a 10 ml measuring flask and the volume adjusted. The extinction is read against chloroform at 400 nm.

A blank using the same amount of copper solution diluted to 10 ml is run simultaneously through the extraction series.

#### Calculation

The concentration of NTA in mg/l will be

$$\frac{V_o}{V_o + 0.8 + V_A} (E - E_o) \frac{V}{\alpha}$$

where  $V_o$  = volume of sample originally taken

$V_A$  = volume used to adjust the pH at the alum treatment

$V$  = volume taken for the extractions

$E$  = extinction of the sample

$E_o$  = extinction of the blank

$\alpha$  = extinction coefficient

Note: It is recommended to check the efficiency of the extractions at intervals. This may be done by analysing a waste water to which a known amount of NTA has been added.

A report of the procedure will be published in the journal "Vatten".