

Chemical Oxygen Demand - Waste water

BACKGROUND

The Chemical Oxygen Demand (COD) test is an empirical test that is a measure of the potential oxygen consumption of waste waters. The COD test has been used for a very long time as one of the components of the method that water utilities use to charge dischargers for their part of the effluent that enters a waste water treatment works via the Mogden Formula. This was also recognised in the Urban Waste Water Directive (91/276/EEC), in which COD is used as a limiting substance, with a limiting value of 125mg/l.

ANALYSIS

For the analysis of COD, samples are oxidised by heating the water in vials. Samples are oxidised by heating in vials with sulphuric acid and potassium dichromate. Mercuric sulphate is added to suppress chloride interference. The dichromate is reduced to chromate during the digestion and the chromate produced is measured colorimetrically.

Sample Oxidation/Dichromate Reduction

 $2Cr_{2}O_{2}^{2} + 16H^{+} \longrightarrow 4Cr^{3+} + 8H_{2}O + 3O_{2}$

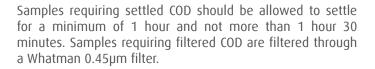
Chloride removal by Mercuric Sulphate

Hg²⁺ + 2Cl⁻ → HgCl,↓

Chloride Interference

 $Cr_2O_7^{2-} + 6Cl^2 + 14H^4 \longrightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O^2$

There is no sample preservative used. Samples should be analysed as soon after receipt as possible.



Samples requiring pH7 COD are adjusted to pH7 \pm 0.5, using 10% $\rm H_2SO_4$ and 1M NaOH and allowed to settle for a minimum of one hour. Samples are stable for 6 days (In-House Data) from sampling.

If not suppressed, chloride will cause positive interference. Inorganic reducing agents such as nitrites, sulphites and ferrous salts will contribute to the COD. Oxidising agents, e.g. Cr VI salts, can give false negative and low results. Bromide interference will not be controlled by mercuric sulphate.



Reference:

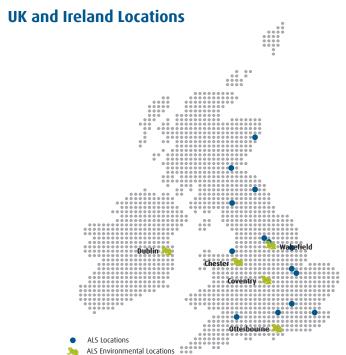
Chemical Oxygen Demand (Dichromate Value) of Polluted and Waste Waters 1986 (Second Edition). HMSO Methods for the Examination of Waters and Associated Materials. Method B. ISBN: 011 7519154.

ALS Environmental Limited

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