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### C.6. DEGRADATION - CHEMICAL OXYGEN DEMAND

## 1. METHOD

#### 1.1. INTRODUCTION

The purpose of the method is the measurement of the chemical oxygen demand (COD) of solid or liquid organic substances in a standard, arbitrary manner, under fixed laboratory conditions.

Information on the formula of the substance will be useful to conduct this test and interpret the result obtained (e.g. halogen salts, ferrous salts of organic compounds, organochlorine compounds).

## 1.2. DEFINITIONS AND UNITS

The chemical oxygen demand is a measure of the oxidizability of a substance, expressed as the equivalent amount in oxygen of an oxidizing reagent consumed by the substance under fixed laboratory conditions.

The result is expressed in grams of COD per gram of tested substance.

### 1.3. REFERENCE SUBSTANCES

Reference substances do not need to be employed in all cases when investigating a new substance. They should serve primarily to calibrate the method from time to time and to allow comparison of results when another method is applied.

## 1.4. PRINCIPLE OF THE TEST METHOD

A predetermined amount of the substance, dissolved or dispersed in water, is oxidized by potassium dichromate in a strong sulphuric acid medium with silver sulphate as a catalyst, under reflux for two hours. The residual dichromate is determined by titration with standardized ferrous ammonium sulphate.

In case of chlorine-containing substances, mercuric sulphate (\*) is added to reduce chloride interference.

# 1.5. OUALITY CRITERIA

Because of the arbitrary manner of determination, COD is an 'oxidizability indicator' and as such is used as a practical method to measure organic matter.

Chloride can interfere in this test; inorganic reducing or oxidizing agents may also interfere with the COD determination.

Some cyclic compounds and many volatile substances (e.g. lower fatty acids) are not fully oxidized by this test.

## 1.6. DESCRIPTION OF THE TEST METHOD

A preliminary solution or dispersion of the substance is prepared to obtain a COD between 250 and 600 mg per litre.

## Remarks:

In the case of poorly soluble and non-dispersible substances, an amount of finely powdered substance or liquid substance corresponding to about 5 mg of COD can be weighed and put in the experimental apparatus with water.

The chemical oxygen demand (COD) is often and especially in case of poorly soluble substances determined advantageously in a variant of the method, i.e., in a closed system with a pressure equaliser

After use, solutions containing mercury salts should be treated to avoid dissemination of mercury in the environment.

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(H. Kelkenberg, 1975). In this modification compounds which are only with difficulty determined by the conventional method - e.g. acetic acid - may often be successfully quantified. The method also fails, however, in the case of pyridine. If the potassium dichromate concentration, as prescribed in ref.(1), is raised to 0,25 N (0,0416 M), the direct weighing-in of 5-10 mg of substance is facilitated which is essential for the COD determination of poorly water soluble substances (ref. (2)).

Otherwise, the COD is then determined following any suitable national or international standardized

### 2. DATA AND EVALUATION

The COD contained in the experimental flask is calculated following the selected normalized method, and converted to grams of COD per gram of tested substance.

### 3. REPORTING

The reference merhod used should be stated.

The chemical oxygen demand should be a mean of at least three measurements. All information and remarks relevant to the interpretation of the results have to be reported, especially with regard to impurities, physical state and inherent properties of the substance (if known) which would affect the results.

The use of mercuric sulphate to minimize the chloride interference must be reported.

### 4. REFERENCES

- (1) Kelkenberg, H., Z. von Wasser und Abwasserforschung, 1975, vol. 8, 146.
- (2) Gerike, P. The biodegradability testing of poorly water soluble compounds. Chemosphere, 1984, vol. 13,169.

List of standardized methods, for example:

NBN T 91-201 Determination of the chemical oxygen demand.

ISBN O 11 7512494 Chemical oxygen demand (dichromate value) of polluted and waste waters.

NF T 90-101 Determination of the chemical oxygen demand.

DS 217 = water analysis Determination of the chemical oxygen demand.

DIN 38409-H-41 Determination of the chemical oxygen demand (COD) within the range above 15 mg per litre.

NEN 3235 5.3 Bepaling van het chemisch zuurstofverbruik.

ISO 6060 Water quality: chemical oxygen demand dichromate methods.