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**Framework Service Contract ENV.D2/FRA/2012/0013**

Support to the implementation of the UWWTD:
COD substitution scoping study

# FINAL REPORT

**Final version**
**08 March 2017**

umweltbundesamt

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# 1 INTRODUCTION AND OBJECTIVES

**Background**

Under the Urban Waste Water Treatment Directive 91/271/EEC (UWWTD) specific requirements for the quality of treated wastewater from wastewater treatment plants are set out in Annex I Table 1. The parameter list contains 'Biochemical Oxygen Demand - BOD5', 'Total Suspended Solids - TSS', as well as the 'Chemical Oxygen Demand - COD'. The reference method of measurement of COD uses a homogenized, unfiltered, undecanted water sample and is based on the use of potassium dichromate, which is a chromium (VI) compound (Cr(VI)).

**REACH regulation**

REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Regulation (EU) No 348/2013 has identified potassium dichromate as a Substance of Very High Concern (SVHC) and this substance is included in the list of substances subject to the REACH authorisation requirement with a “sunset date” of 21 September 2017. For continued use, an authorisation request was required to be submitted by 21 March 2016. Each manufacturer or importer placing the substance on the EU-market for a use or a user must be covered by an authorisation (granted to them directly or to an actor further up in their supply chain).

The authorisation requirements, do not apply for potassium dichromate used in scientific R&D, carried out under controlled conditions and if usage of compound (calculated as pure substance) by a legal entity is <1 tonne/year. The allowance for continued use (without applying for authorisation) in scientific research and development also covers analytical activities such as monitoring, quality control and routine tests and life-cycle steps (such as formulation) preceding the end-use in scientific research & development. To be able to prove this, a user entity (company) is advised to keep records of use in terms of tonnage and it must also ensure adequate protection of staff handling the chemical. No sunset date exists for this type of scientific R&D use for quantities less than 1 tonne/year, such as COD-Cr(VI) analytical methods, but staff need adequate protection.

In line with Article 55, the aim of the REACH authorisation is: 1) to assure the proper control of risks from use of SVHCs and 2) progressive replacement of SVHCs by suitable alternatives where technically and economically viable. The aim is thus to eventually replace dichromate substances. The ECHA website FAQ Q&A 585 and 1030 clarify conditions for continued use of Cr(VI) compounds in R&D, including analysis.

Although dichromate can continue to be used for analytical purposes as described above, the use of Cr(VI) in general should preferably be phased out and substituted by safer alternatives. There is therefore a need to review the requirement to use COD-Cr(VI) analysis for wastewater effluents, as specified in the UWWTD and other Directives and identify if suitable alternatives are available.

**Purpose of measurements used in UWWTD**

The current UWWTD parameters of BOD5, COD and TSS, plus nitrogen and phosphate parameters, provide a direct measure of potential pollutants in terms of their impact on

the environment. BOD and COD are measures of the potential oxygen demand in an effluent and so are directly linked to short term and long term consequences of discharges.

- BOD is a biological test method that uses the analytical laboratory choice of a seed bio-culture mixed with the sample under test, to find the amount of oxygen used due to the bio-culture metabolism of substances in the sample, over a 5 day (or 7 or 10 day) period. Although it is standardised, it does not adapt to the particular liquor under test in the same way as a treatment plant, or a bio-flora in a catchment. BOD can, under the UWWTD, be replaced by TOC or TOD if a relationship can be established.
- COD is a chemical test, defined as a chemical oxidation of the sample material. The Cr(VI)-COD method measures close to the maximum possible oxygen demand of a sample, but generally at least 50% of the demand is from organic material that is not readily degradable in short-term biological processes such as the BOD test.
- TSS measurement provides an indication of the turbidity of an effluent as well as the possible organic load. The turbidity affects clarity of the water column in a catchment and therefore potential loss of transmission of light to oxygen producing organisms in a water column.
- TOC (total organic carbon), measures the amount of carbon in a sample after removal of inorganic carbon (carbonates and carbon dioxide). It does not provide any direct measure of potential or actual impact of the carbon containing material on oxygen demand in a catchment.
- TOD (total oxygen demand), measures the amount of oxygen required to oxidise material in a sample by means other than wet chemical methods. Instruments that carry out this determination have been offered by manufacturers since the 1970s, but have not been widely used. The use of TOD measurements has increased in the USA, but has not been validated in European conditions.

Standard numerical relationships between each of these parameters can be used either as general guidelines, or, for increased accuracy and certainty, be found for individual liquor streams. However, even for individual streams the relationships can vary significantly over a period of time. For example, a wastewater treatment works that includes industrial flows, or centralised sewage sludge treatment, can have significant periodic increases in COD without such significant increases in BOD, due to periodic operation of processes that release lower biodegradability substances.

**Relevance of measurements**

The UWWTD was implemented in 1991 to reduce the impact of sewage or wastewater discharges on the quality of receiving waters and the environment. The three primary measures of BOD, COD and TSS provide different types of measures of polluting potential and effectiveness of sewage treatment processes. Of the measures, only BOD is used to assess the quality of receiving waters under the Water Framework Directive requirements.

# 2 OVERVIEW OF PARAMETERS AND METHODS

## 2.1 COD-Cr(VI)

Potassium dichromate has been used for measurement of chemical oxygen demand in wastewaters for more than 60 years, during which time many evaluations on measurements of different substances in different conditions have been carried out.

Samples of wastewater (or other samples for COD analysis) are oxidised by refluxing for a period of two hours at 150°C with concentrated sulphuric acid and potassium dichromate. A mercury salt is included in some methods to reduce interference by chloride oxidation. A silver salt is included to catalyse oxidation of some organic compounds and reduce chloride interference. Residual non-reduced dichromate is measured either by using titration against iron (II) ammonium sulphate or colorimetrically. The amount of dichromate that has been reduced provides the COD measurement in terms of mass of oxygen required for oxidation per volume of sample, generally as mg/l.

There are two main variants, described as the Open Reflux method (sometimes called the Macro-digestion method) and the Sealed Tube method (sometimes called the Micro-digestion method) The standard methods ISO 6060:1989 and ASTM 5220B describe specific versions of the open reflux (Macro) method, and the standard method ISO 15705:2002 describes a specific version of the sealed tube (Micro) method. Other method descriptions and procedures are also used, including manufacturer specific variants used in commercially available sealed tube or cuvette digestion kits.

The oxidation reaction for an organic material with potassium dichromate can be summarised as:

$$C_nH_aO_bN_c + dCr_2O_7^{2-} + (8d+c)H^+ \rightarrow 2dCr^{3+} + nCO_2 + ((a+8d-3c)/2)H_2O + cNH_4^+$$

The digestion methods have been optimised to generally achieve in excess of 90% oxidation of most organic substances. There is only partial oxidation of some heterocyclic substances, and inorganic reducing compounds (nitrites, sulphites) can also reduce dichromate. The long period of use of the method has developed good understanding of measurements of a wide variety of wastewaters and wastes using dichromate digestion.

The COD measurement required in the UWWTD defines only that potassium dichromate is the reference method for measurement. There are specific further method requirements defined by individual member state legislation. In particular, use of the Macro method is specifically required in some states for some conditions. In others, there is no specific requirement, and allows use of the micro method in sealed tubes.

The difference in the amount of potassium dichromate used by the different methods is significant. The Macro methods, ASTM 5220B or ISO 6060 use 306.5mg/test or 58.8mg/test respectively. The Micro method, ISO 15705 (sealed tube), uses 14.8mg/test. For specific micro methods for lower COD concentrations, in cuvettes supplied by individual manufacturers, the amount can be 6mg/test or less.

## 2.2 COD-Mn(III)

The patent for COD measurement using Mn(III) was filed by Hach Company in June 1995. The patent describes the method in detail and it is summarised below.

Mn(III) is generally poorly soluble in water but is stabilised by concentrated (14-20 N or 7-10 M) sulphuric acid ($H_2SO_4$), forming a soluble Mn(III)-$SO_4$ complex. Mn(III) is also known to disproportionate to Mn(II) and Mn(IV) and Mn(II) is added to the test solution in a ratio of Mn(II):Mn(III) of approximately 3:1 to reduce the risk of this reaction happening.

The reaction between organic matter and Mn(III) was summarised by the Hach Company using potassium hydrogen phthalate (KHP) as:

$$KC_8H_5O_4 + 15\ Mn_2(SO_4)_3 + 12\ H_2O \rightarrow 8\ CO_2 + 30\ MnSO_4 + 14\ H_2SO_4 + KHSO_4$$

The reaction can be simplified in terms of oxygen as:

$$KC_8H_5O_4 + 7.5\ O_2 \rightarrow 8\ CO_2 + 2\ H_2O + KOH$$

The Mn(III) ion (free or in complex) is purple in colour. As Mn(III) is reduced it forms Mn(II), which is colourless. The intensity of the colour and colour change can be determined by a spectrophotometer and the concentration determined using suitable calibration solutions. The concentration can also be determined visually or through titration, although this is not recommended by Hach Company.

A standard operating procedure has been developed by Hach Company (Method 10067) using Test 'N Tube™ (TNT) vials, which is similar to the COD-Cr(VI) method by the same company. A 0.5 ml homogenised sample is added to a test vial, the vial is inverted several times to mix the sample and then digested for 1 h at 150°C. A blank (deionised water) is treated in the same way. When the sample and blank vials have cooled to room temperature, they are inverted several time to mix and then analysed at 510 nm using a Hach instrument.

Chloride ions ($Cl^-$) are known to interfere with the reaction, causing an overestimate of the COD. A method for chloride removal was developed, which was more complex than the COD-Cr(VI) method. For the analysis, 9 ml of homogenised sample is acidified with 1 ml concentrated $H_2SO_4$ and mixed. A blank (deionised water) is treated in the same way. A TNT vial per sample is placed in a Vacuum Pretreatment Device (VPD), a Chloride Removal Cartridge (CRC) is placed above the vial and 0.6 ml sample is filtered through the CRC using vacuum suction. Once filtering is complete, the glass fibre filter (which has no oxygen demand) from the top of the CRC is transferred to the vial (to ensure particulates are digested as well). The vial is capped and inverted, digested and analysed as above.

The VPD has now been withdrawn and the recommendation from Hach is to dilute the sample to assess the effect of chloride. The CRC is still available but information provided by Hach states that the concentration at which chloride interference affects the COD measurement is unknown.

Ammonia in the presence of chloride also interferes with the measurement and the interference is quoted as “severe” at high concentrations of the two ions but “high concentration” is not defined.

## 2.3 COD-Mn(VII)

The method used prior to the Cr(VI) method for COD measurements was the Kubel’s method, where the sample is boiled with excess potassium permanganate in the presence of dilute sulphuric acid. In permanganate the manganese ion is in oxidation state +VII and in Kubel’s method, permanganate is reduced to +II:

$MnO_4^- + 5\ e^- + 8\ H^+ \rightarrow Mn^{2+} + 4\ H_2O$

The excess of permanganate is determined by back titration with oxalate:

$2\ MnO_4^{2-} + 5\ C_2O_4^{2-} + 16\ H^+ \rightarrow 2\ Mn^{2+} + 10\ CO_2 + 8\ H_2O$

No manufacturer of test kits or instrumentation for this method was been found. There has been research[1] into the use of Mn(VII) for COD analysis using flame atomic absorption spectroscopy (FAAS) based on flow injection analysis (FIA) with ultrasound-assisted digestion and Mn speciation separation and similar complex systems that would require analytical laboratories.

An ISO standard is available for this method: ISO 8467:1993 Water quality -- Determination of permanganate index[2]. The method is not recommended for determining organic load in waste waters; for this purpose the chemical oxygen demand should be determined as described in ISO 6060:1989, Water quality- Determination of the chemical oxygen demand.

## 2.4 TOD

For the determination of Total Oxygen Demand (TOD), the sample is thermally oxidised at high temperature (approximately 1200°C) in a reactor and the oxygen consumption of this reaction is measured directly in the gas phase. The analysis time is about 5 minutes per sample, making it considerably faster than COD-Cr(VI) but the equipment required is more complex than COD-Cr(VI) equipment and is currently most suited to installation and use in an analytical laboratory.

Although site based on-line instrumentation is available, these tend to be considerably more expensive than laboratory based instruments as they need to handle sampling and be generally be more robust for conditions on site. These include variable sample composition, presence of particles, maintenance and exposure to environmental conditions. The method also oxidises reduced nitrogen compounds which could lead to variable measurements in some raw and final effluents. Future developments could improve sample preparation and handling, stability of oxygen measurements and increased robustness and accuracy at low concentrations.

A TOD instrument requires a high quality $N_2$ feed gas with a known amount of $O_2$. The intake to on-line instruments restricts large particles and may result in a difference in TOD measured on-line compared to a laboratory measurement. It is not possible to

[1] Zhang, Z-Q., Yan, H-T., Yue, L. (2004) Rapid determination of chemical oxygen demand by flame AAS based on flow injection on-line ultrasound-assisted digestion and manganese speciation. *Atomic Spectroscopy* 25(4) pp 191-196.

[2] http://www.iso.org/iso/iso_catalogue/catalogue_tc/catalogue_detail.htm?csnumber=15669

provide an estimate of differences in results between on-line and laboratory based methods as the result will be site dependent as a result of size and load of suspended solids and nature of organic material.

A standard test method has been developed by ASTM (ASTM D6238 - 98(2011))[3] where it is stated that "*This test method is particularly useful for measuring oxygen demand in certain industrial effluents and process streams. Its application for monitoring secondary sewage effluents is not established. Its use for the monitoring of natural waters is greatly limited by the interferences defined in Section 6.*" It provides for measurements of TOD in the range of 100mg/l to 100,000mg/l, so is less useful for WwTW final effluents. There is no current TOD standard method prepared at an EU level (ISO CEN EN standard).

TOD is a complete oxidation of substances present. Values should be similar to or slightly greater than the values obtained by COD measurement in some sample types.

## 2.5 PeCOD

PeCOD™ is a patented method that uses titanium dioxide ($TiO_2$) catalyst which is activated by UV light. The instrument measures photocurrent charge, originating from the oxidation of organic species. The reaction time quoted is 15 minutes. A silver nitrate ($AgNO_3$) doping agent in the sensor is included to remove interference from chloride.

The Ontario Ministry of the Environment has developed a method and the procedure and comments below are taken from this method. A minimum sample volume of 100 ml is required for analysis. Samples are to be stored at 5±3°C for a maximum of 7 days if not preserved. Samples may be preserved with sulphuric acid or nitric acid to pH<2 (0.2 ml of acid per 100 ml of sample). Preserved samples have a maximum storage time of 21 days from preservation.

The PeCOD measurement is not affected by the presence of chloride at concentrations lower than 400 mg/l. If the sample is suspected to have a higher concentration of chloride, the sample should be diluted. The central sensor element appears black in colour. If the sensor becomes white, it indicates that chloride tolerance has been lost.

The suitable pH range for samples is from pH 4-10. Samples having a pH>10 will result in measurements that are less than expected for the sample. PeCOD measures total soluble COD, which does not include proteins, macromolecules or cellulose. Cr(VI)-COD provides total COD, so differences will be observed. This has been confirmed in a recent Swedish study[4] where PeCOD underestimated the filtered COD (as measured by the reference Hach-Lange dichromate cuvette method) in the influent and effluent wastewater by 53% and 36%, respectively.

The PeCOD method, if valid, would have been expected to produce the same or very similar values to the COD Cr(VI) method.

[3] http://www.astm.org/Standards/D6238.htm

[4] Arnell *et al.* (2016) Pre-Commercial Procurement of a Mercury Free COD analysis method for Wastewater and Waste Products (in Swedish). SP Technical Research Institute of Sweden. SP Rapport 2016:39. http://vav.griffel.net/filer/C_SP2016-39.pdf

## 2.6 Electrochemical COD

Researchers have investigated the use of various electrode materials (e.g. copper-based or polystyrene based with catalytic material) for electrochemical measurement of COD. The principle for the measurement is that a current is applied between two electrodes, creating hydroxyl radicals (OH·) that oxidise the compounds. At least one instrument is commercially available (COD Analyser Elox100 from LAR Process Analyser AG). The instrument is an on-line type but it is envisaged it could readily be adapted using an auto-sampler for laboratory analysis. The measuring cycle is stated to take 4 minutes, making it significantly faster than the >2 h for the standard COD-Cr(VI) method. The manufacturer claims a good correlation with the standard COD-Cr(VI) method but no independent studies have been found to support this claim and it is likely that this method will provide lower COD values than COD-Cr(VI) method. This has also been confirmed for PeCOD (Section 2.5), which is a type of electrochemical COD. A recent Dutch study[5] also concluded that electrochemical COD is unlikely to be a suitable alternative based on cost and quality of the measurements.

An electrochemical COD method, if valid, would be expected to produce the same or very similar values to the COD Cr(VI) method.

## 2.7 BOD

Biochemical Oxygen Demand (BOD) is the amount of dissolved oxygen (DO) needed by aerobic biological organisms in a body of water to break down organic material present in a given water sample at a certain temperature over a specific time period.

The method consists of filling an airtight bottle of specified size with the diluted and seeded sample, and incubating it at the specified temperature for 5 days ($BOD_5$) (typically). The dissolved oxygen concentration is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occurring after this measurement is included in the BOD measurement. Measurement of BOD is therefore considerably slower and more time-consuming than carrying out and obtaining measurements from the Cr(VI)-COD method.

The BOD is always less than COD as some refractory material is not degraded, or not readily degraded by microorganisms, or may inhibit microbial oxidation, but can be oxidised in the Cr(VI)-COD determination. Although the COD/BOD ratio varies depending on the composition of the sample, a typical range for an urban wastewater final effluent is 3-5 but it can be both higher and lower than this range.

Instruments using tryptophan-like fluorescence with turbidity and temperature corrections have been developed as a rapid on-line surrogate of BOD.

## 2.8 Total suspended solids

Total suspended solids (TSS) is a laboratory gravimetric procedure where the solids from the water sample are filtered through a dried filter. The filter is dried again and weighed to determine the residue on the filter. The TSS is reported in mg/l.

[5] Pickup J. (2015) The upcoming prohibition of potassium dichromate. A review of alternative pollution indicators. *Rijkswaterstaat Internship Thesis.*

In addition to the laboratory method, on-line instruments are available that are based on either an optical method or the attenuation of ultrasound. Handheld optical instruments are also available. A correlation between instrument measurements and gravimetric TSS is used. It is, however, likely that there will be a variable difference between the gravimetric procedure and the methods based on optical or ultrasound principles as the composition and nature of samples changes.

The laboratory method is straightforward and readily implemented but the drying of the filter delays the results, with determinations in some laboratory methods taking 15 hours to completion.

A correlation between COD and TSS varies with the amount of inorganic solids present, the nature of inorganic solids present, the nature of the organic solids, and the amount of soluble organic material. Therefore a consistent low variance correlation between TSS and COD cannot be set.

For indicative checks and estimations, for influent urban wastewater COD/SS is 1.2 – 1.6:1, while for final effluent COD/SS may be 3 - 6:1.

## 2.9 Turbidity

Turbidity is a measure of the cloudiness of water. In natural waters this cloudiness comes from suspended and colloidal particles such as silt, clay, organic matter, algae and various other microorganisms. The turbidity is affected by factors such as:

- rainfall and catchment runoff;
- soil erosion;
- sediment disturbance, for example, by fish;
- waste discharge;
- algal growth;
- riparian vegetation;
- flow;
- soil types.

Particles scatter light from a light beam focused on them and the higher the turbidity, the more light is scattered. Turbidity measured in this way uses an instrument called a nephelometer with the detector usually at 90° to the incident light beam.

A range of turbidimeters are available, including handheld, bench top and on-line instruments. The majority of turbidimeters use some form of flowcell, the exception is the dip probe type. In some flowcells the sample is in direct contact with optical surfaces whereas others are partly or fully non-contact.

Good correlation can sometimes be seen between suspended solids and turbidity but the correlation should be seen as site specific. As with suspended solids measurements, it cannot generally be expected that there is a good correlation between COD and turbidity as turbidity includes inorganic solids (for example, clay particles), which are not measured using COD. Consequently there is a poorer correlation between COD and turbidity than between COD and suspended solids.

## 2.10 TOC

Total Organic Carbon (TOC) is the amount of carbon left in a sample after it has been acidified and purged with an inert gas to remove $CO_2$. The carbon in the organic

compound is oxidised to $CO_2$ using one of several methods, for example, high-temperature combustion, catalytic oxidation or photo(chemical) oxidation. The generated $CO_2$ is typically detected using an infrared (IR) detector.

TOC measurement uses well-established methods for which a standard method is described in ISO-CEN EN 1484. Automatic continuous sampling instruments are available for laboratories and as fixed on-site analysers for influent and effluent wastewater.

Test kits are available but have been found to underestimate the TOC measured using analysers. The correlation with COD depends on the composition of samples as a high portion of oxygen-containing organic compounds will have a lower COD than a sample with a low portion of oxygen-containing organic compounds, but the TOC could still be the same. In addition, some compounds consuming oxygen but not containing carbon will be included in COD but not in TOC.

A Danish investigation[6] found that TOC did correlate well with COD-Cr(VI) but the correlation needed to be established for each WwTW. In Germany TOC may be used as a surrogate measure for COD; provided that the TOC x 4 is less than the WwTW site COD limit then the discharge consent requirements are met.

Ratios of COD/TOC vary between works, and between sample times, within a common range of 2.5 – 4:1 (see section 2.12).

## 2.11 UV absorbance

UV absorbance of organic compounds relates to the aromatic groups present, that is, the greater the UV absorbance, the more aromatic groups in the organic molecules. The UV absorbance is typically measured at 254 nm on a 0.45 µm filtered sample and is then referred to as true $UV_{254}$ absorbance and reported in units of $m^{-1}$.

A range of UV absorbance instruments are available, including handheld, bench top and on-line instruments. As with TOC, the correlation with COD depends on the composition of samples.

## 2.12 Correlations between methods

Various evaluations of correlations between different determinand measurements have been carried out. These were reviewed by and for the working group, together with some additional comparisons carried out on data made available by members of the working group.

In particular, data from over 2,000 wastewater treatment works in Austria, comparing COD and TOC values was assembled by UBA for this project, together with data provided by working group members for the Netherlands and Flanders. Correlations for these data are shown in *Figure 1*, *Figure 2*, and *Figure 3*. Correlations between COD and BOD or SS were also reviewed. However TOC and COD correlations provided the largest body of data currently available to the working group.

[6] Krysell M. (2004) TOC(NVOC) as replacement for $COD_{Cr}$ for control of wastewater (in Danish). *Danish Environment Agency*. http://www.reference-lab.dk/media/2792874/cod-toc_rapport_2004.pdf

*Figure 1 Austrian data showing COD and TOC values for effluent of wastewater treatment plants*

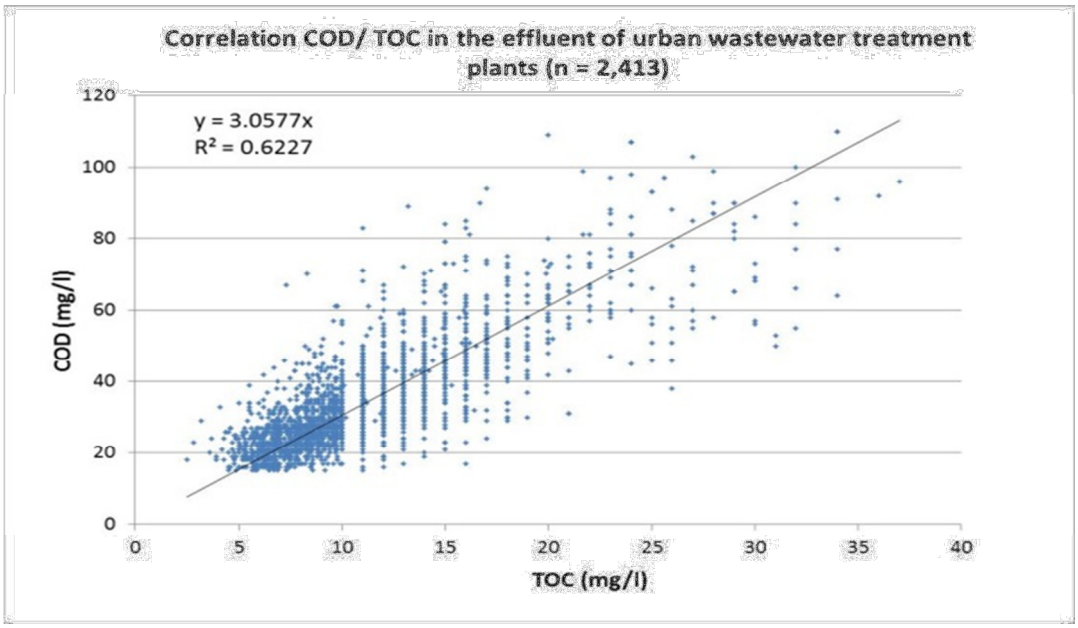



*Figure 2 Netherlands data showing COD to TOC ratios for wastewater samples*

*Figure 3 Flemish data showing COD to TOC ratios for wastewater samples*

The evaluations found that whilst there were general relationships, such as that:

- COD tends to be greater than 2 x BOD, and
- COD tends to be greater than 2.5 x TOC, and
- COD tends to be greater than 1.5 x SS,

the relationships are wide, and vary between treatment works and at different times for a single treatment works.

Analysis of the COD and TOC data showed that, dependant on the correlation value used, a simple conversion between COD and TOC values could result in a significant proportion of currently compliant effluents becoming non-compliant. This would also be the case if a simple conversion from the current COD limit value to a new non-COD value for a different determinand is used.

In conclusion, the evaluations found:

- Wide range of distributions of ratios;
- No clear difference in ratios of COD/TOC for different treatment plants;
- No single clearly identifiable direct or consistent relationship between COD and another determinand.

## 2.13 Summary

The eleven methods summarised in Section 2 all measure different polluting impacts. None have a direct correlation with COD-Cr(VI) measurements:

- COD-Mn(III), COD-Mn(VII), PeCOD and other electrochemical COD methods result in measurements that are less than the COD-Cr(VI) method. The difference varies depending on how readily the compounds in the sample degrade. The COD-Mn(VII) method is not suitable for wastewater and PeCOD and electrochemical methods are not suitable for samples with solids.
- TOD produces measurements that are greater values than the COD-Cr(VI) and measures compounds that are very hard to degrade under natural conditions. It therefore has a limited relevance to the waters receiving effluent from wastewater treatment works. Current instruments are subject to reduced sensitivity and accuracy at concentrations of less than 100mg TOD/l. TOD is also not suitable for natural waters. No standard is currently available at EU level, but this could be developed by CEN, particularly if instrument analytical sensitivities improve.
- Turbidity and suspended solids measurements typically can be correlated with each other for individual sites but generally have a highly variable correlation with COD-Cr(VI). These two parameters do not provide an estimate of the oxygen demand.
- TOC and UV absorbance can correlate with each other within a single site (WRc data not presented). TOC and COD-Cr(VI) can be correlated with each other, but the correlation is site dependent and likely to vary with time, unless the composition of the incoming wastewater is exceptionally stable. There is a current EU standard method described in ISO-CEN EN 1484.

There is thus no single analysis that can readily replace COD-Cr(VI) with a universal correlation and low variance. The supporting working group to this contract considered that it would be unlikely that any method could be identified that provides the same or directly equivalent measurements as the COD-Cr(VI) method without using Cr(VI).

Table 2.1 Standard analytical method descriptions available

| **TOC** | **COD** | **BOD** | **TOD** |
|---|---|---|---|
| Standard Method 5310B | DIN 38409 Teil41/43/44 | Standard Method 5210B | ASTM D6238 - 98(2011 |
| EPA 415.1 | ISO 6060:1989 | DIN EN 1899-1 | |
| EPA 9060A | EPA 410.4 | DIN EN 1899-2 | |
| ASTM D2579 | DIN ISO 15705 | ISO 5815 | |
| ISO 8245:1999 | ISO 8467:1993 (Mn(VII)) | EPA 405.1 | |
| ISO-CEN EN 1484 | UK SCA (2007)[7] | | |

[7] UK Standing Committee of Analysts (2007). The determination of chemical oxygen demand in waters and effluents. https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/316793/COD-215nov.pdf

# 3 MANAGEMENT OPTIONS

Six options were discussed within the working group and the advantages and disadvantages are summarised below. The first five of these options (Options A-E) were highlighted by the UWWTD Expert Group and the final option was suggested by the Working Group during this project.

## 3.1 Option A - To make no amendment and for individual EU Member States to choose whether to use an alternative (non COD-Cr(VI) analytical) method

The working group additional interpretations of this option were:

- Table 1 is not amended and the COD definition and limit values remain as currently in use. No adaptation is made despite the REACH requirement to cease using Cr(VI) unless used in controlled conditions for an authorised purpose.
- Individual MS can make individual state regulatory amendments to use an alternative COD measurement procedure. The alternative would need to make measurements and work to limit values that met the same pollution abatement objectives of the Cr(VI) measurement and limit values.

**Advantages**

- Subsidiarity, that is, the MS can decide which method to use; and
- Low cost implications as there would be no requirement to change specified requirements, for example, environmental permits.

**Disadvantages**

- Lack of consistency;
- No readily available alternative standardised COD method;
- Other COD methods give lower COD value;
- Output not relevant with respect to WFD (for example, if recommend COD-Mn, still not relevant to WFD); and
- Need to comply with REACH authorisation.

## 3.2 Option B - For EU Member States to use a different standard

The working group additional interpretations of this option were:

- The current Table 1 measurement method would be amended, replacing the current requirement to use the dichromate method with a different defined COD measurement method.
- Alternative COD methods include: Mn(III) & Mn(VII), Hg free methods under development; previously suggested methods include peroxodisulphate.
- Oxygen demand method could be retained using a suitable physico-chemical TOD method, as used to some extent in the USA. Major disadvantage for these is the lack of portable analytical capability.

**Advantages**

- Consistent across EU; measuring compliance; comparability.

**Disadvantages**

- No currently known standards; and
- The output not relevant with respect to WFD (for example: if recommend COD-Mn then the measurement remains irrelevant to WFD assessments).

## 3.3 Option C - To change the UWWTD and replace COD with TOC

The working group considered that this replacement option would require measurement method definition, and limits to be set. However, different methods, or no defined method, are currently used for COD-Cr(VI) (sealed tube and open reflux), within different member states.

**Advantages**

- A EN standard method exists (EN 1484:2001), providing consistency;
- No Hg or Cr(VI) used;
- Test kit available for on-site measurements;
- Consistency with modifications in other regulations; and
- Partly implemented in some industrial sectors already.

**Disadvantages**

- EN standard not completely fit for on-line measurement, and would need to use laboratory measurement for accurate values;
- Need to modify legal requirements in different member states;
- No consistent understanding of the behaviour of the discharge in the receiving medium for measured values based on TOC;
- TOC is highly variable between sites, which is also true for COD;
- Improved or modified treatment would be required, to securely meet any unsuitable TOC limit, without providing significant environmental benefit and could increase the $CO_2$ emissions;
- Use of TOC for trial correlation testing requires costly equipment; and
- Risk of setting inappropriate limits.

## 3.4 Option D - Set a ratio between different parameters and COD

The working group additional interpretation of this option was that the existing COD values would remain, but there would be allowance for a different measurement method to be used, with a conversion factor to be defined or derived from the different measurement method, as the function to use to test if compliance with the COD limit is achieved.

**Advantages**

- Simplicity – no change to requirements.

**Disadvantages**

- No parameter shows a fixed ratio to COD;
- Requires additional measurements and is therefore very costly; and
- The ratio may change with time due to local conditions.

## 3.5 Option E - Modify the UWWTD by complete replacement of COD-Cr(VI), BOD and SS parameters by a chosen single lumped measurement method

The working group additional interpretations of this option were:

- The COD measurement AND one or more of the BOD or SS measurements are removed entirely, either to choose to use only BOD, or SS, or to use an alternative single measurement method to demonstrate compliant treatment.
- Concerns with this include the risk of misuse, with treatment methods adjusted to fit the measurement parameter only. However, the WFD requirements mean that a local regulator would also have the power to impose compliance determinands and values that are appropriate for local conditions.

**Advantages**

- Ammonia, phosphorus and TOC can be used to demonstrate proper reduction of pollutants;
- BOD is not an operational parameter for WWTP management; and
- SS will be reflected in TOC.

**Disadvantages**

- No single measurement method identified;
- Each parameter provides unique information;
- BOD is a parameter for modelling; and
- SS is set by local-based discharge environmental permits.

## 3.6 Option F - Remove COD from UWWTD without a replacement parameter

The working group additional interpretations of this option were:

- The measurement of readily biodegradable oxygen demanding substances would continue to be measured for compliance purposes through the use of the BOD.
- The COD measurement is not used in any receiving water assessments. It does provide a chemical measurement of organic substances and is not subject to biological inhibitory substances that can affect the BOD measurement method.

**Advantages**

- Reduces the use of Cr(VI) and Hg in line with REACH regulation;
- Reduces costs;
- COD has no relevance to water catchment management; and
- Parameter still usable for operational purposes.

**Disadvantages**

- Relevance of COD to treatment processes is well established;
- Potentially miss poorly degradable substances;
- Less timely operational information;
- Less comparative compliance assessment.

## 3.7 Summary

The supporting working group found that all six alternatives had advantages and disadvantages that need to be considered. Options B and D are not possible as argued above. Option A is not suitable as no standardised method comparable to COD-Cr(VI) is available. No suitable "single lumped" parameter other than BOD exists for Option E.

The preferred option overall was Option F (removal of COD from the UWWTD without introducing a replacement parameter) but with TOC (Option C) as an optional parameter with a suggested value (possibly in the order of 35-40 mgTOC/l initially). The value needs to be underpinned with strong evidence. This option was chosen for a number of reasons:

- Reduces the use of Cr(VI) and Hg in line with REACH regulation;
- Reduces costs;
- COD parameter still usable for operational purposes;
- COD parameter can still be used by local authorities for permits and charging; and
- The WFD requirements should ensure that the removal of the COD determinand from the UWWTD does not have an adverse impact on the ecological and chemical status of receiving waters.

Timescales need to be clear, with conversion periods to be greater than 10 years if the changed condition is not optional. There is a need to consider economy and growth as well, as unnecessarily stringent regulations could see industries struggle to meet new compliance requirements. Supplementary permits should not include requirements for both COD and TOC, and should make the conditions clear for the permit holder.

Table 1 in the UWWTD could specify that COD-Cr(VI) can still be used under the REACH authorisation but that COD is no longer a required determinand for the UWWTD and not a reportable parameter under this Directive. A suggestion for an updated Table 1 in the UWWTD was considered and is presented below.

**Table 1: Possible revision to Table 1 of UWWTD proposed by working group**

Requirements for discharges from urban waste water treatment plants are subject to Articles 4 and 5 of the Directive. The values for concentration or for the percentage of reduction shall apply.

| Parameters | Concentration | Minimum percentage of reduction ([1]) | Reference method of measurement |
|---|---|---|---|
| Biochemical oxygen demand (BOD5 at 20°C) without nitrification ([2]) | 25 mg/l $O_2$ | 70-90<br><br>40 under Article 4 (2) | Homogenized, unfiltered, undecanted sample. Determination of dissolved oxygen before and after five-day incubation at 20°C ± 1°C, in complete darkness. Addition of a nitrification inhibitor |
| ~~Chemical oxygen demand (COD)~~ | ~~125 mg/l $O_2$~~ | ~~75~~ | ~~Homogenized, unfiltered, undecanted sample Potassium dichromate~~ |
| TOC ([3]) | 37mg/l ([3]) to be subject to further evidence collection | 75 ([3]) | EN 1484 |
| Total suspended solids | 35 mg/l ([3])<br><br>35 under Article 4 (2) (> 10 000 p.e.)<br><br>60 under Article 4 (2) (2 000-10 000 p.e.) | 90 ([3])<br><br>90 under Article 4 (2) (> 10 000 p.e.)<br><br>70 under Article 4 (2) (2 000-10 000 p.e.) | – Filtering of a representative sample through a 0,45 µm filter membrane. Drying at 105°C and weighing<br>– Centrifuging of a representative sample (for at least five minutes with mean acceleration of 2800 to 3200 g), drying at 105°C and weighing |

([1]) Reduction in relation to the load of the influent.

([2]) The parameter can be replaced by another parameter : ~~total organic carbon (TOC) or total oxygen demand (TOD)~~ if a relationship can be established between BOD5 and the substitute parameter.

([3]) This requirement is optional.

Analyses concerning discharges from lagooning shall be carried out on filtered samples; however, the concentration of total suspended solids in unfiltered water samples shall not exceed 150 mg/l.

COD CrVI (dichromate) method can continue to be used provided the requirements of REACH can be met, but is not a requirement or reportable under the UWWTD.

# 4 COSTS

Of the parameters reviewed in Section 2, TOC was seen by the working group as a well-established parameter with the least severe drawbacks and, as such, a potential **optional** parameter replacing the mandatory COD-Cr(VI) measurement. An important factor to consider when suggesting changes is the cost for implementing the changes. This section provides an estimate of the expected costs if COD-Cr(VI) is replaced by TOC, based on assumptions outlined below. One cost that has not been assessed, and would be significant, is the cost for updating treatment process models from being based on COD-Cr(VI) to being TOC based.

## 4.1 Comparison and correlation between COD-Cr(VI) and TOC

Typical analytical costs to measure TOC (ISO 1484 or similar), COD-Cr(VI) sealed tube method (ISO 15705 or similar) and COD-Cr(VI) open reflux method (ISO 6060 or similar) have been provided by eleven MS through the UWWTD expert group (member state data is reported in Appendix 1). The reported cost ranges are summarised in Table 4.1. The costs vary significantly between MS and some MS do not use the open reflux method for COD measurement.

Table 4.1 Analytical costs for TOC and COD-Cr(VI)

| TOC | | COD sealed tube | | COD open reflux | |
|---|---|---|---|---|---|
| Lab | Site | Lab | Site | Lab | Site |
| 4.4-40€ | 7-33€ | 5-30€ | 3-26€ | 2.5-33€ | 4.5-26€ |

To estimate the impact of analytical costs, two sets of costs for each of the TOC and the COD analysis in a laboratory have been used. A lower value of 7€ was used as a potential longer term cost for a regular sampling regime for both TOC or COD analysis using a laboratory. An approximated median value taken from the member state responses has also been used, with TOC at €17 and COD at €10 per sample analysis using a laboratory. Use of both sets of values provides a range of impact costs.

Reasons for the range of costs provided by MS from the questionnaire responses have not been established. Both COD and TOC measurements are well established, and in particular, the COD measurement has been routinely used for regulatory reporting. The extent of the cost distribution was therefore unexpected. Since there is a large range in costs for the COD measurement despite the COD measurement being well established, then for this estimation the full reported range of TOC costs has been used to find a median value for laboratory analyses, rather than attempting to forecast a value without reference to current reported values.

The sealed tube method for COD measurement was used for the comparisons below as it minimises use of Cr(VI) and can be directly compared to the TOC cuvette method.

For arrangements to collect, analyse and receive analysis reports we have assumed 1 hour per analytical parameter and the staff cost is 40€/h. To carry out a good comparison between COD-Cr(VI) and TOC, it is assumed that weekly samples of both

parameters will be collected over a year, that is, 52 samples will be collected per site and each sample is analysed for TOC and COD. It is further assumed that it will require 5 days to manage and analyse the collected data. The total cost per site for a comparative analysis of TOC and COD-Cr(VI) is therefore estimated to be 6,500€ to 7,200€ as summarised in Table 4.2.

Table 4.2 Assumptions and calculation for cost analysis

| Parameter | | Lower value | Value estimated from median |
|---|---|---|---|
| COD analysis (laboratory) | a | 7€ | 10€ |
| TOC analysis (laboratory) | b | 7€ | 17€ |
| Staff cost | c | 40€/h | 40€/h |
| Sampling collection time | d | 1 h/sample | 1 h/sample |
| Samples per year | e | 52 | 52 |
| Sampling cost per year ((a+b)*e)+(d*2*e*c) | f | 4888€ | 5564€ |
| Evaluating data | g | 5 days | 5 days |
| Total cost per site (g*8*c)+f | | 6488€ | 7164€ |

The estimation shown in the Table 4.2 shows that the largest cost involved validating a change is staff cost in sampling and in evaluating the data collected for each WwTW.

The European Environment Agency has reports for 18,700 wastewater treatment works (WwTW) across EU. If it is considered necessary to assess each over a one year period for equivalence of TOC measurements with COD Cr(VI) measurements, as outlined above, an indicative additional cost for evaluation could be in the region of 130 million Euros if COD-Cr(VI) is to be replaced by TOC.

A further cost, identified by the working group, would be expected to involve assessing changes to industrial discharges consents for discharges that enter WwTW and so impact on a WwTW treatment and effluent quality. For further estimates, on average, 20 industrial effluent discharge consents may be associated with each WwTW.

## 4.2 COD-Cr(VI) analysis

One of the attractive features with the COD-Cr(VI) method is that the sealed tube method can be readily used by staff without extensive laboratory experience, such as site operators or surveyors. Some test kits conform to EN standards and are routinely and extensively used by analytical laboratories for accredited COD analysis. The cost per sample has been estimated using the assumptions shown below (Table 4.3). If 40 samples are analysed per day, 250 days per year then the average cost per sample over 10 years is 5.1€.

**Table 4.3 Assumptions for cost of COD-Cr(VI) analysis, using sealed tube method**

| Parameter | Value |
|---|---|
| Reactor | 1280€ |
| Cooling rack | 96€ |
| Reader | 1664€ |
| Setting up 10 day | 3200€ |
| TOTAL - Equipment and procedures | €6240 |
| Yearly maintenance 1 day/year | 320€ |
| Test kit cost per sample | 3€ |
| Daily laboratory work at €40/h | 2 h x 40€ x 250 = 20000€ |
| TOTAL - annual costs, 10,000 samples / year | 30000€ (kits) + 20000€ (work) = 50000€ |

## 4.3 TOC analysis

TOC analysis requires staff with extensive laboratory experience and an analyser instrument. Test kits are available but are significantly more expensive than the corresponding COD test kit, and require more manipulations than the COD test kit method. In addition, the experience reported by the working group was that the TOC test kit underestimates the true TOC concentration.

In the following section, the cost per sample has been estimated using the assumptions shown below (Table 4.4). If 40 samples are analysed per day, 250 days per year then the average cost per sample over 10 years is 2.6€.

Table 4.4 Assumptions for cost of TOC analysis, using instrument analyser

| Parameter | Value |
|---|---|
| Analyser | 12800€ |
| Setting up 10 day | 3200€ |
| TOTAL – equipment and procedures | 16000€ |
| Chemicals cost per year | 100€ |
| Yearly maintenance 1 day/month, at €320/day | 3840€ |
| Daily laboratory work, 2h/day, 40€/h | 250 x 80€ = 20000€ |
| TOTAL – annual costs, 10000 samples / year | 20000 + 100 + 3840 = 23940€ |

## 4.4 Summary

As outlined in Section 4.1, a cost estimate for assessing a correlation between COD-Cr(VI) and TOC for EU WwTWs and changing permits from COD-Cr(VI) to TOC found a cost in the region of 130 million Euros excluding any costs associated with industrial effluent discharges. This excludes changing process models from COD to TOC. Most of the cost is associated with staff costs for sample collection and assessment of the information, rather than the analyses.

A larger cost may be involved in validating any changes in industrial discharge consents. However, as the COD-Cr(VI) method can still be used, changing industrial environmental permits may not be necessary although it would be preferable from a REACH perspective.

Although the initial cost to set up and prepare for TOC measurements is more than four times greater than to set up and carry out COD-Cr(VI) measurements, the cost for TOC analysis per sample may be expected to be less for each sample determination over a longer time period for a laboratory determination, particularly if many samples are analysed per day.

# 5 OVERALL CONCLUSIONS

## 5.1 Uses and function of the current COD measurement

In the initial consultation for this project participants described a number of the functions of the currently specified measurement of COD. These include:

- Regulatory measurements of wastewater effluents and influents;
- Process management within treatment works;
- Load determination of incoming organic materials including industrial wastewaters and outlying works sewage sludge;
- Design of new treatment works, assessing load, potential recoveries and costs;
- Optimisation of existing and new treatment works using modelling tools – the most important of which currently include the IAWQ COD models;
- Rapid and simple on-site tests to evaluate current operations;
- Rapid initial assessments of BOD in a sample before setting up the necessary dilutions.

It was clear that complete removal of the current COD-Cr(VI) method from any use would have significant implications. However, clarification of the meaning of the authorisation for continuing use of Cr(VI) compounds for research and development, that includes use for process monitoring, enables continued use, in particular for a transition and evaluation period.

The need to reduce and so far as possible eliminate exposure to Cr(VI) compounds was accepted by the working group, although the relative contribution of dichromate used for the COD measurement to total dichromate exposure was not assessed.

The current COD measurement method has been in use for more than 60 years, during which time a large body of data has been developed for wide variety of wastewater treatment plants. Establishing means of maintaining continuity of the data will be important, including assurance that works are neither under, or over-regulated as a result of any change. If the dichromate COD measurement is to be replaced then this should be over a long period of time to build up time series for individual sites.

Individual authorities, both member states and regulators, have defined discharges using the COD concentration, and have also developed charging regimes based on concentrations. In some authorities the COD measurement method has been precisely defined, and includes specific and required use of the open reflux method, which does use a great deal more dichromate than the closed tube method. These specific designations would also have to be changed in the event of a change to the requirements in the UWWTD.

## 5.2 Methods

There are a range of methods used to assess the polluting potential of a wastewater, in terms of biological, chemical and physical characteristics. Each method or determinand has a particular application. For example, BOD estimates the amount of oxygen that would be used biomass in a receiving water as a result of discharge of the wastewater, thereby reducing oxygen availability, whilst COD measures the total oxygen demand

from the wastewater without regard to the biological availability of the material for biomass growth.

Eleven determinands and methods were described in section 2. None of the determinands had a direct correlation with the currently used COD-Cr(VI) method.

- COD-Mn(III), COD-Mn(VII), PeCOD and other electrochemical COD methods result in measurements that are less than the COD-Cr(VI) method. The difference varies depending on how readily the compounds in the sample degrade. The COD-Mn(VII) method is not suitable for wastewater and PeCOD and electrochemical methods are not suitable for samples with solids.
- TOD produces measurements that are greater values than the COD-Cr(VI) and measures compounds that are very hard to degrade under natural conditions. It therefore has a limited relevance to the waters receiving effluent from wastewater treatment works. TOD is also not suitable for natural waters.
- Turbidity and suspended solids measurements typically can be correlated with each other for individual sites but generally have a highly variable correlation with COD-Cr(VI). These two parameters do not provide an estimate of the oxygen demand.
- TOC and UV absorbance can correlate with each other within a single site. TOC and COD-Cr(VI) can be correlated with each other, but the correlation is site dependent and likely to vary with time, unless the composition of the incoming wastewater is exceptionally stable.

There is thus no single analysis that can readily replace COD-Cr(VI) with a universal correlation and low variance. The working group considered that it would be unlikely that any method could be identified that provides the same or directly equivalent measurements as the COD-Cr(VI) method without using Cr(VI).

The consultations and discussions within the working group considered that a number of factors needed to be taken into account when assessing options for replacement of the current method. These included:

- Need to demonstrate reliability and accuracy
    - Limits of detection
    - Problems with particulates
    - Patented methods
- The economy or costs of a method
- Application to range of circumstances
- TOC is a well-established method that many commercial laboratories already use.

As part of the evaluation of options data from a variety of sources was obtained, both from existing evaluations, from a survey of TOC and COD wastewater concentrations in Austrian works with data analysis carried out for this project, and from additional data sources provided by the working group members.

The outcome from the evaluations agreed with previously carried out assessments, that there are no simple conversion factors between another determinand and COD-Cr(VI) analyses. There is also a wide scatter when correlation trials are carried out, even for a

single works over a period of time. Therefore a direct replacement of COD-Cr(VI) is not currently available.

## 5.3 Cost impact

Costs of transfer from use of COD-Cr(VI) to another determinand could be significant, involving evaluations for individual works, use of a new determinand and investment in new equipment. Costs also would include the cost of resetting environmental permits, ensuring that use of a new determinand does not result in a requirement for improved or new treatment processes, or that the new determinand could result in a control that does not meet the environmental targets.

Reviews of environmental permits, either for discharge into the environment (WwTW and some industrial dischargers) or for discharge into sewers for transport to treatment at a WwTW are carried out at intervals. Reviews take into account changes in the nature of a discharge, and in quality requirements for the catchment. A routine review uses currently available discharge quality information – there is not normally an assessment of alternative quality determinands. Consequently, although a change in a determinand to be measured may be brought in over a long conversion period, such a change may still require demonstration that the proposed value for the new determinand can be achieved, or to what extent new treatment process arrangements may be required. If costs are involved in making new arrangements for an individual discharge, a challenge may involve an assessment of the benefits against the costs.

The Urban Wastewater Treatment Directive does not directly deal with discharges from industrial wastewater. However, many industrial sites have consents that control the quality of wastewater discharged into sewers. Determinations of values to be used for discharge consents are linked to the operation of, and the consents applied to, the treatment works. Replacement of an existing determinand to a new determinand for an industrial discharge consent may also have a significant cost.

As the TOC determinand was considered the most likely to replace COD-Cr(VI) (if replacement is to be carried out), an outline estimate of potential costs was carried out.

A cost estimate for assessing a correlation between COD-Cr(VI) and TOC for EU WwTWs and changing permits from COD-Cr(VI) to TOC found a cost in the region of 130 million Euros excluding any costs associated with industrial effluent discharge re-evaluations. This excludes research to understand how TOC may relate to environmental objectives or to change process models from COD to TOC. Although additional costs may be in changing industrial permits as the COD-Cr(VI) method can still be used, changing industrial environmental permits may not be necessary although it would be preferable from a REACH perspective.

Although the initial cost for TOC is more than 4 times greater than for COD-Cr(VI), the cost for TOC analysis per sample is less over a longer time period, particularly if many samples are analysed per day.

## 5.4 Working group final conclusions

The working group found that all six alternatives had advantages and disadvantages that need to be considered. Different standards for different MS was not preferred, and there was no evidence that a simple ratio between another determinand and COD could be set.

The preferred option overall was Option F (removal of COD from the UWWTD without introducing a replacement parameter) but with TOC (Option C) as an optional parameter with a suggested value (possibly in the order of 35-40 mgTOC/l initially). The value needs to be underpinned with strong evidence. This option was chosen for a number of reasons:

- Reduces the use of Cr(VI) and Hg in line with REACH regulation;
- Reduces costs;
- COD parameter still usable for operational purposes;
- COD parameter can still be used by local authorities for permits and charging; and
- The WFD requirements should ensure that the removal of the COD determinand from the UWWTD does not have an adverse impact on the ecological and chemical status of receiving waters.

Timescales need to be clear, with conversion periods to be greater than 10 years if the changed condition is not optional. There is a need to consider economy and growth as well, as unnecessarily stringent regulations could see industries struggle to meet new compliance requirements. Supplementary permits should not include requirements for both COD and TOC, and should make the conditions clear for the permit holder.

Table 1 in the UWWTD could specify that COD-Cr(VI) can still be used under the REACH authorisation but that COD is no longer a required determinand for the UWWTD and not a reportable parameter under this Directive.

In summary:

- TOC is currently the best validated and tested alternative
- COD can be removed completely from Table 1, potentially without replacement
- COD or TOC are not used in Water Framework Directive assessments
- TOC could be used, or could be used as an optional parameter, under local regulatory direction
- No new determinand has any environmental monitoring benefit greater than COD
- There is no simple concentration ratio link between COD and other determinands
- In setting a concentration limit there is a risk that currently compliant treatment plants would become non-compliant

## 5.5 WRc conclusions - the contractor's view

This project has focused on the purpose of the UWWTD and how the UWWTD objectives can be made compatible with the REACH objectives. The UWWTD objectives are to minimise risk of harm to the environment, through setting requirements for discharges, and compliance assessment using indicator substance concentrations.

The reasons for the choice of the organic substance determinands and concentrations used in the UWWTD have not been established during the course of this project. The

COD value appears to have been set on the basis of five-times the BOD concentration limit, from experience of effluents subject to significant industrial effluent discharges into the WwTWs, and that this ratio was considered to demonstrate sufficient control of poorly degradable organic substances and any environmental risk posed by them.

Using two measures of organic content of effluents (and the optional measure of suspended solids), has provided an opportunity for wider understanding of the impact of effluents on the environment, and better assurance that WwTWs, and influents allowed into, and discharged from, them are not focused on control of only a single type of polluting substance. We did not investigate the extent to which having two measures of gross polluting potential material has been used to track improvements in performance, or in receiving water quality.

It is not at all clear that a WwTW could be readily designed or operated to only remove either COD or BOD, without having a significant effect on the other parameter. In terms of immediate polluting potential, the BOD measurement is more important as it replicates the potential oxygen demand of an effluent on a receiving water body, and consequent immediate, or short-term damage, as well as long term degradation. Hence measurement of the BOD of an effluent continues to be the primary measure of immediate polluting potential and therefore of control.

**Removing one of the two obligatory UWWTD parameters**

WRc was part of, and fully participated in, the working group discussions and conclusions. As such we support the working group conclusion, to remove the COD measurement requirement, and to replace it with an optional measurement of TOC.

We do have reservations:

- Removing one of the two measures of general organic substance pollution reduces the opportunity for cross-checking and validation of the other measure; and,
- Whilst BOD provides a measure of short term polluting potential, organic substances not measured as BOD may supply some longer term polluting potential that could build up unobserved in environmental sinks such as sediments.

The first reservation can be managed by a local regulator taking a wider view on all the control parameters, including individual substance measures, to which a WwTW is subject to protect receiving water bodies; but does not deal with the concern that at an EU level there could be some reduction in comparability between MS achieving the objective of pollution reduction.

The second can be managed locally by a regulator identifying additional substance controls as part of a discharge permit derived from the standards that apply in the appropriate receiving waters (i.e. in accordance with the combined approach required in the WFD Article 10(3)); and at an EU level, by the monitoring of water bodies into which treatment works discharge which is required as part of the monitoring requirements of the WFD.

There is a risk that by setting only BOD as the control determinand, that for some WwTWs, without additional controls, an excessive amount of poorly degradable organic material could be accepted into, and pass through the works into the effluent, with potential for long term build up in the downstream receiving water bodies.

**Options for replacement of COD**

This assessment has not identified an alternative that clearly provides a better measure, in terms of ease, cost or function as part of the suite of regulatory measures. Currently the closest to the targets is to measure TOC, which has advantages of currently being used in Industrial Emission Directive BREFS, has an EN standard (ISO CEN EN 1484), and has small-scale cuvette measurement methods as well as analytical instrument procedures.

Our working group considered, and WRc agree, that replacement of COD as currently measured, with any other determination (a different COD method, or another determinand), would not be a simple replication for the current position of COD in the regulation. Given the limitations of other procedures, and the existing knowledge about, and use of TOC, this determinand is the most appropriate immediate replacement for COD.

Regulators now have considerable experience of setting discharge permits according to the requirements of the receiving water bodies, and of taking into account the types of pollutant that are potentially present in the influent to a treatment works. Hence, rather than requiring use of a determinand, TOC, in all circumstances, the use of TOC as an option as part of the local regulatory regime we consider to be preferable.

Other measurement methods, such as Total Oxygen Demand, or a non-dichromate COD measurement method may become more useable, and would benefit from developing a standard method. As they develop, or new methods to assess polluting potential may appear, they should be encouraged by enabling their use as alternatives to BOD or the currently proposed optional TOC measurement.

**Dichromate COD use**

WRc supports the REACH objective to minimise risk of harm to health and to the environment by minimising use of CrVI substances. Consequently, the use of dichromate in the defined COD determination method should be appropriately minimised or replaced, so far as reasonably practicable.

The uses of the COD measurement method are highly varied: - for example, as part of a regulatory measure to check and record WwTW performances against a common compliance benchmark (the UWWTD); to monitor and improve treatment works performances; to provide data for process design and assessment, and to provide a measure that can also be interconverted with energy management values. It has proven to be a highly effective measurement method, readily, reliably and inexpensively carried out on-site and in laboratories. Other methods are not yet at the same stage of development; the nearest equivalent, the cuvette tube TOC method, requires more manipulations and is not as clearly linked to the more environmentally relevant measure of BOD.

There are current COD Cr(VI) procedures and suppliers that meet the criteria of minimising use, with analytical methods that substantially operate in sealed non-contact conditions, and supplier arrangements to collect and manage used reagents.

Some authorities have chosen to require use of larger scale analysis procedures, which does appear unnecessary for routine measurements. The continuing requirement for the larger scale ISO 6060 methods should be reviewed considering the balance of benefit, and risk and compliance with the REACH objective, and preferably be removed entirely.

# 1 APPENDIX 1

Member state analysis cost indications – response to questionnaire

| | COD | | | | TOC | |
|---|---|---|---|---|---|---|
| | ISO 15705 ST | | ISO 6060 OR | | EN 1484 | |
| Country | Lab | Site | Lab | Site | Lab | Site |
| Czech Republic | 4.5-5.5 | 2.5-3 | 2.5 | 4.5 | 15 | |
| Romania | 26.5 | 26.5 | 26.5 | 26.5 | 33 | 33 |
| Hungary | 7-10 | 3-7 | 7-10 | 7-10 | 13-22 | 13 |
| France | 5-15 | | 10-20 | | 10-40 | |
| Sweden | 27 | 3.3 | | | 22 | 7-26 |
| BE-Flanders | 6.5 | | | | 8.6 | |
| BE-Brussels | 5 | | 13 | | | |
| BE-Walloon | 22.5 | 5-24 | 16-28 | 13-18 | | |
| Germany | | | 33 | | 25 | |
| Austria | 13 | 4 | 25 | | | |
| Slovenia | | | 10 | | 16 | |
| Finland | 20-30 | | | | 10 | |
| UK | 6.5 | 3.1 | | | 4.4 | 7.6 |
| Range | 5-30 | 3-26 | 2.5-33 | 4.5-26 | 4.4-40 | 7-33 |
| Median (approximately) | 10 | 5 | 15 | 12.5 | 17 | 15 |

The wide variety of costs reported for either COD or TOC lead to considerable uncertainty in setting an analytical cost for COD or TOC for use in estimating the impact of a change in determinand. No reason for the large differences in reported costs, for established and routine measurements has been

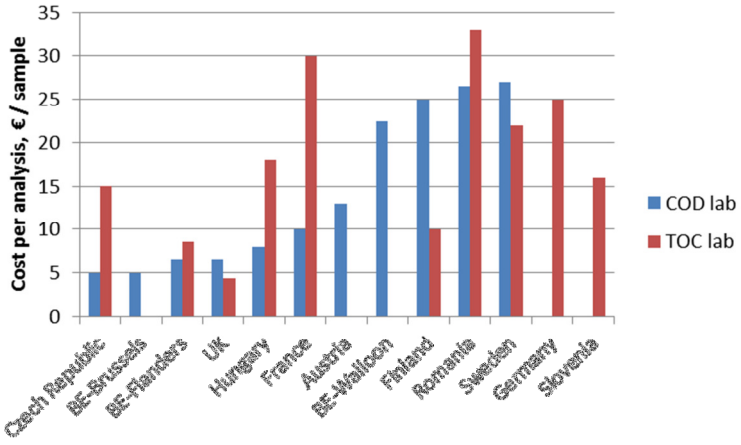
The COD ISO 15705 ST (sealed tube) test method is well established and well used with suppliers providing ready-made materials. Nevertheless, a wide range of analysis costs have been reported.

The reported TOC analysis costs also vary widely, both for laboratory or for site analysis costs. The questionnaire reported laboratory analysis costs, shown in the table above, are also shown in the chart below (Figure 4). The range for either laboratory or site analysis is greater than for the COD analysis costs. Since the COD costs remain wide, for a well-established and well-used measurement, despite standardisation and period of use, it may be that TOC costs would remain wide even if measurement becomes the standard test parameter.

For the estimation of costs provided in this report, two values are used; a lower value, and a median value, found from the reported costs. The lower value used for both TOC and COD is 7€, and the median, shown in the table above, is 10€ for COD and 17€ for TOC.

Analytical costs, in the estimation, are one part of the estimation. Other elements are staff costs associated with validating a change in parameters, and changing consent conditions.

*Figure 4 Comparison of laboratory analytical costs for COD or TOC*



# 2 APPENDIX 2

Working Group Members

| Name of Attendee | Affiliation |
|---|---|
| Onno Epema (OE) | Rijkswaterstaat, Ministry of Infrastructure and the Environment (The Netherlands) |
| Johan Annys (JA) | Flemish Environment Agency (Belgium) |
| Klaus Furtmann (KF) | Landesamt für Natur, Umwelt und Verbraucherschutz NRW (Germany) |
| Emma Lundin (EL) | SP Technical Research Institute of Sweden (Sweden) |
| Clive Harward (CH) | Anglian Water (UK) |
| Marie-Pierre Strub (MPS) | Environmental analysis Department- INERIS (France) |
| Christof Mainz (CM) | European Commission |
| Rod Palfrey (RP) | WRc |
| Jörgen Jönsson (JJ) | WRc |

# 3 APPENDIX 3

Glossary

| | |
|---|---|
| BOD | Biochemical oxygen demand |
| $CO_2$ | Carbon dioxide |
| COD | Chemical oxygen demand |
| DO | dissolved oxygen, dissolved oxygen concentration |
| ECHA | European chemicals agency |
| IAWQ | International Association for Water Quality |
| mg/l | milligrammes per litre, measure of concentration |
| MS | Member state of EU |
| R&D | Research and Development |
| REACH | Registration, evaluation, authorisation and restriction of chemicals regulations |
| SS | Suspended solids, also called TSS |
| SVHC | substance of very high concern |
| TOC | Total organic carbon |
| TOD | Total oxygen demand |
| TOT-P | Total phosphorous |
| TSS | Total suspended solids, also called SS |
| UWWTD | Urban Wastewater Treatment Directive |
| WFD | Water framework directive |