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Assessment of Chemical Oxygen Demand/Total Organic Carbon (COD/TOC) ratios in refinery effluents

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Assessment of Chemical Oxygen Demand/Total Organic Carbon (COD/TOC) ratios in refinery effluents

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ABSTRACT

Chemical Oxygen Demand (COD) analysis is one of the most commonly used analytical methods to indirectly measure organic pollutants in effluent waters. The standard COD methods use potassium dichromate which is restricted under the REACH regulation. The European Commission (EC) and EU member states are considering whether to replace COD analysis with Total Organic Carbon (TOC) analysis for effluent discharge monitoring. An empirical relationship has been applied between TOC and COD in regulatory contexts, where a global COD/TOC ratio of 3 is most commonly suggested. In the Commission Implementing Decision establishing Best Available Techniques (BAT) conclusion for the refining of mineral oil and gas (REF BATc), it states that where on-site correlation is available, COD may be replaced by TOC and the correlation between COD and TOC should be elaborated on a case-by-case basis. Further, the REF BATc states that TOC monitoring would be the preferred option because it does not require the use of very toxic compounds, i.e., potassium dichromate, in laboratory testing.

In this report we assess if, and which, value of COD/TOC ratio would be applicable for treated wastewater effluents arising from oil refineries. To achieve this, we first performed a scientific literature study on reported COD/TOC ratios in effluents. As a second step, we investigated the COD/TOC ratio for eight refinery effluents.

In conclusion COD/TOC ratios varied, and a single global COD/TOC ratio could not be established for refinery effluents due to the specific conditions of each refinery. COD/TOC ratios specific to each site is challenging to establish. Nevertheless, a site-specific assessment allows for a more meaningful discussion on values that could be considered for discharge permits. In the case that it is not possible to establish a reliable COD/TOC ratio for a specific site, and thus the COD analysis cannot be omitted, we would recommend the use of the Sealed Tube (ST) COD method to achieve significant reduction in the laboratory use of hazardous chemicals compared to the traditional open reflux method.

KEYWORDS

Chemical Oxygen Demand, Total Organic Carbon, Potassium dichromate, $K_2Cr_2O_7$, Analytical methods, Water analysis, Refinery effluents, Waste Water Treatment, BAT

INTERNET

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SUMMARY

Chemical Oxygen Demand (COD) is one of the most commonly applied chemical analyses conducted on wastewater effluents. The COD analysis measures abiotically-oxidizable substances in waters and expresses a result in terms of the mass of oxygen consumed to oxidize the substances. This is a useful indicator analysis for the maximum oxygen demand that an effluent might request in a surface waters environment, where dissolved oxygen is necessary for ecological health.

COD analysis methods typically use a strong oxidant agent, potassium dichromate ($K_2Cr_2O_7$), to chemically oxidise substances present in a sample. Potassium dichromate has been proven to be carcinogenic and mutagenic and the substance is restricted under Annex XIV of the REACH regulation. Thus, other analytical methods have been considered to replace COD for phasing out the use of potassium dichromate. Within that framework, the European Commission (EC) has suggested to replace COD analysis in effluent monitoring with Total Organic Carbon (TOC) analysis. TOC analysis measures the amount of carbon found in organic compounds and is often used as a non-specific indicator of water quality.

Both the Best Available Techniques (BAT) Reference Documents for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW BREF) [1] and Commission Implementing Decision establishing BAT conclusions for the refining of mineral oil and gas (REF BATc) [2] recognise that COD and TOC correlation needs to be well-established and elaborated on a case-by-case basis. However, despite the statement in the CWW BREF, the Commission Implementing Decision establishing BAT conclusion for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW BATc) [3] used a default COD/TOC ratio of 3 to establish the BAT-AEL for TOC. Other regulatory contexts such as the European-Pollutant Release and Transfer Registry (E-PRTR) [4] and German Ordinance on Requirements for the Discharge of Waste Water into Waters [5] also suggests default ratios of 3 and 4, respectively. It is currently unclear if a fixed COD/TOC ratio is representative of all refinery effluents or if a site-specific ratio would be more meaningful. Using an assumed (default) COD/TOC relationship in a possible revision of refinery permits may result in either reduced levels of environmental protection, or increased requirements for effluent treatment that provide no additional protection with regards to oxygen demand in the receiving water environment. In this report, we investigate if a global COD/TOC ratio would be applicable for treated wastewater effluents from oil refinery effluents.

This report firstly summarises the findings of the publicly available information regarding the possible substitution of COD by TOC to measure the quality of (refinery) treated effluents. The material and methods of this first part of the study are further explained in Section 1.2. From the results of the literature review, it became evident that papers/reports on the COD/TOC ratios for refinery effluents were scarce and the research was widened to wastewater effluents from other sectors.

In the second part of the study, treated effluent samples from seven volunteering Concawe member company sites were collected (corresponding to eight treated refinery effluents) with the aim to practically examine the applicability of COD/TOC ratio for refinery effluents. The statistical analysis resulted in an overall mean COD/TOC ratio of 3.4, but individual refinery COD/TOC ratio mean values varied between 2.3 and 4.3. The variation in COD/TOC ratio among refineries was

confirmed by average annual COD and TOC concentration data from Concawe Effluent Quality/Water Use Surveys of 2016 and 2019. Furthermore, for only two sites a site-specific relationship between COD and TOC could be established with confidence (R^2 = 0.73 - 0.80). These observations imply that even site-specific COD and TOC relationships may be challenging to establish for refinery effluents and deviate from those of other effluents types from UWWTP and chemical industry [9, 11, 1, 31]. In case a site-specific ratio is applied, some considerations were identified on how a single global COD/TOC ratio would affect refinery waste water treatment operations.

Based on the findings in literature and analysis of the eight refinery effluents from seven refineries, we recommend on-site studies to establish a site-specific COD/TOC ratio to support the use of TOC analysis instead of COD for refinery effluent monitoring. The conclusion of the study is in line with the REF BATc [2] recognitions to set correlations on a case-by-case basis. We also recommend to periodically check the correlation (ratio) as the ratio will likely vary with time, unless the effluent composition is extremely stable.

In case it is not possible to establish a site-specific COD/TOC ratio, this report also recommends applying the Sealed Tube (ST) COD method, as it generates less quantity of toxic waste compared to the conventional open reflux COD method and demonstrates an important step to achieve a significant reduction in generation of toxic waste [6]. This method has also started to be accepted in some countries, such as France [7]

1. INTRODUCTION

Chemical Oxygen Demand (COD) is one of the most widely measured wastewater treatment (WWT) parameters and is used to indirectly measure the presence of oxidizable contaminants. The COD analysis uses potassium dichromate ($K_2Cr_2O_7$), which is classified by the European Chemicals Agency (ECHA) [8] as health and environmentally hazardous, and thus, it is restricted under the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) regulation Annex XIV [9]. A ‘sunset date’ was set to 21 September 2017 after which the placing on the market and use of the substance is prohibited unless authorization is granted to the user.

Due to the presence of potassium dichromate, the European Commission (EC) and EU Member States (MS) have suggested replacing COD analysis in wastewater effluent monitoring with TOC analysis. The EC, in their Evolution of the Urban Waste Water Treatment Directive (UWWTD) [10], presents the possibility to monitor TOC, rather than COD. While neither in the REF BREF nor in the REF BATc a global COD/TOC ratio is suggested – it is noted that COD could be replaced by TOC and that any correlation should be established and elaborated on a case-by-case level – a global ratio has been suggested for other activities and in other regulatory contexts:

- Urban WWT plant (UWWTP) effluents have been reported to exhibit a strong correlation between COD and TOC, thus suggesting the potential replacement of COD by TOC. Regression analysis tends to suggest a value of around 3.0 (ranging between 2.5 and 4.1) [11].
- The Common Waste Water (CWW) BATc applies a global COD/TOC ratio of 3 (median value from the data collected) by setting BAT Associate Emission Levels (BAT-AELs) at 30-100 mg/l and 10-33 mg/l for COD and TOC, respectively. However, the CWW BREF Chapter 2 [1] notes that a COD/TOC ratio should be established and elaborated on a case-by-case level, which contradicts the fixed global ratio applied in the CWW BATc.
- E-PRTR [4] applies a ratio of 3.0 for all covered industrial activities to report TOC releases based on COD data (TOC = COD/3).
- German Ordinance on Requirements for the Discharge of Waste Water into Waters [5], TOC may be used as a surrogate measure for COD; provided that the TOC x 4 is less than the wastewater treatment site COD limit.

If a future discharge permit for refineries would be based on TOC instead of COD, a global conversion factor between COD and TOC values could result in a converted TOC limit value lower than the site’s current effluent TOC performance while before it was meeting the COD limit value. Thus, applying a single global COD/TOC ratio could have an influential impact. An investigation weather a global COD/TOC ratio would be applicable for treated wastewater effluents from oil refinery effluents is therefore important.

1.1. AIM AND OBJECTIVES

This study aims to assess whether a fixed COD/TOC ratio for refinery wastewater effluent would be scientifically credible.

The study was divided into two parts 1) a literature review; and 2) an analysis of available data on COD/TOC ratios for refinery effluents – to achieve the following objectives:

- Part 1 objectives: Undertake a literature review of COD/TOC ratios in refinery wastewaters and the factors that would influence such ratios and summarise the findings.
- Part 2 objectives:
  - Present COD/TOC ratios observed from refinery wastewater effluents;
  - Make statistical analysis on the ratios observed;
  - Identify influence of physical/chemical parameters (COD, TOC, Ammonium, Nitrous dioxide (NO_2), Sulfides, Total Kjeldahl Nitrogen (TKN), Total Suspended Solids (TSS), Cadmium (Cd), Chromium (Cr), Arsenic (As), Chloride (Cl) and choice of analytical method that have both previously been reported to cause variation in COD/TOC ratios;
  - Assess predictability of the ratio to determine if a global ratio could be used to replace COD analysis with TOC analysis for refinery effluents;

1.2. METHODOLOGY

The literature review included primarily peer-reviewed papers but also other sources such as conference poster presentations, published analytical methods, and publicly available ‘grey literature’ reports. Early in the literature search, it became evident that literature on COD/TOC ratios for refinery effluents was scarce, consequently, the search had to be widened to wastewater effluents from other sectors.

Effluent monitoring data of COD and TOC were gathered from eight effluent streams from seven different European refineries, located in France, Germany, the Netherlands and Norway. Following Concawe operating guidelines, sites were anonymized and referred to as sites A, B, C, D, E (two separate effluent streams), F and G. Site data was analysed both as a whole and on a site-by-site basis to establish mean, median, maximum and minimum values of the COD/TOC ratio. For site-by-site analysis, also a linear regression of the measurement data was established. All data analysis was done in Microsoft Excel, where correlation coefficient was calculated.

For all the site effluent data the following criteria were applied:

- COD and TOC analysis done on the same effluent sample;
- Any offline analysis to be based on 24h composite samples;
- Basic info on Waste Water Treatment (WWT) set-up, i.e. whether sampling was done after 3-stage treatment, after polishing stage or elsewhere in the WWT.

A short description of the WWT process of the studied sites and where samples for analysis were taken is described in **Table 1**.

Table 1: Description of WWT process and sampling points for each studied site

Site	Description of WWT process and sampling points
Site A	Sampling after 3-stage treatment: 1) Physical/Mechanical (e.g. API[1]/CPI [2]Separator) 2) Physical/Chemical (e.g. DAF[3]/IAF[4], Flocculation) 3) Biological (activated sludge, including nitrification and denitrification) Treated wastewater is then transferred to an urban WWT Plant.
Site B	Sampling after 3-stage treatment: 1) Physical/Mechanical (e.g. API/CPI Separator) 2) Physical/Chemical (e.g. DAF/IAF, Flocculation) 3) Biological (activated sludge)
Site C	Sampling after 3-stage treatment: 1) Physical/Mechanical (e.g. API/CPI Separator) 2) Physical/Chemical (e.g. DAF/IAF, Flocculation) 3) Biological (activated sludge, and nitrification and denitrification)
Site D	Sampling after 3-stage treatment: 1) Physical/Mechanical (e.g. API/CPI Separator) 2) Physical/Chemical (e.g. DAF/IAF, Flocculation) 3) Biological (activated sludge, and nitrification and denitrification)
Site E (effluent 1)[5]	Sampling after 3-stage treatment: 1) Physical/Mechanical (e.g. API/CPI Separator) 2) Physical/Chemical (e.g. DAF/IAF, Flocculation) 3) Biological (activated sludge, and nitrification and denitrification)
Site E (effluent 2)[6]	Sampling after 3-stage treatment: 1) Physical/Mechanical (e.g. API/CPI Separator) 2) Physical/Chemical (e.g. DAF/IAF, Flocculation) 3) Biological (activated sludge, and nitrification and denitrification)
Site F	Sampling after 4-stage treatment: 1) Physical/Mechanical (e.g. API/CPI Separator) 2) Physical/Chemical (e.g. DAF/IAF, Flocculation) 3) Biological (activated sludge) 4) Polishing step (sand filter)
Site G	Sampling after 3-stage treatment: 1) Physical/Mechanical (e.g. API/CPI Separator) 2) Physical/Chemical (e.g. DAF/IAF, Flocculation) 3) Biological (trickling filter)

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[1] An API oil-water separator is a device designed to separate gross amounts of oil and suspended solids from industrial wastewater produced at oil refineries and petrochemical plants. The name is derived from the fact that such separators are designed according to standards published by the American Petroleum Institute (API).

[2] CPI (Corrugated plate interceptor) separators are predominantly used in separation of free oil from effluent water or suspended solids for oily water treatment.

[3] DAF systems are designed to remove total suspended solids (TSS), biochemical oxygen demand (BOD), and oils and greases (O&G) from a wastewater stream. Contaminants are removed using a dissolved air-in-water solution produced by injecting air under pressure into a recycle stream of clarified DAF effluent

[4] Induced Gas Flotation (IGF) is a water treatment process that clarifies wastewaters (or other waters) by the removal of suspended matter such as oil or solids. The removal is achieved by injecting gas bubbles into the water or wastewater in a flotation tank.

[5] The effluent treated comes mainly from a desalter but also constituted by regeneration water from demineralised water plant, brine from reverse osmosis process, blow down from cooling water and water from crude oil tanks.

[6] The effluent comes from strippers, soda from merox unit, contaminated rain water and various refinery process steps. Merox is an acronym for mercaptan oxidation. It is proprietary catalytic chemical process developed by UOP used in oil by converting them to liquid hydrocarbon disulphides.

Additional monitoring data were also collected, to identify the influence of other parameters previously reported to cause variation in observed COD/TOC ratios. These parameters are suspected to influence the ratio because they are reported to influence COD and TOC measurements respectively [12, 13, 14]. The influence on either COD or TOC values implies potential influence on the COD/TOC ratio. This set of data was constituted by 89 samples provided for four different effluents from three different sites as stated in **Table 2**. A correlation matrix was constructed to statistically measure the strength of a relationship between COD/TOC ratio and the other parameters. Obtained correlation coefficients has a range from -1 to 1 with values close to -1 or 1 suggesting strong coefficient determination which means that almost all of the observed variations can be explained by the model's inputs. For this study correlation coefficients <0.6 were considered to exhibit a weak relationship.

Furthermore, with the additional monitoring data an attempt of multifactor analysis was made. However, main variables (combination of parameters) that could impact the COD/TOC ratio could not be determined and thus the data of this analysis is not included in this report.

Table 2: Summary of additional monitoring data collected to study potential influence the COD/TOC ratio.

Sites(effluent)	Additional parameter data collected
Site A, E(1,2) and F	• pH • Chloride • Total Petroleum Hydrocarbon • Sulfite • Total Nitrogen • Kjeldahl Nitrogen • Ammonium • Nitrite • Nitrate • Total Suspended Solids

2. LITERATURE REVIEW

2.1. CHEMICAL OXYGEN DEMAND (COD)

Definition

COD analysis is commonly used to indirectly measure the concentration of organic substances in waters, e.g. a WWT sample or surface water sample. The COD analysis is used to determine the oxygen equivalent of the organic matter that can be oxidized by a strong chemical oxidizing agent (commonly potassium dichromate) in an acid medium. COD is commonly expressed in the mass of oxygen consumed over a volume of solution in mg/l. COD analysis can be used to easily quantify the amount of oxidizable pollutants. COD is useful in terms of water quality by providing a metric to determine the effect an effluent will have on the oxygen status of the receiving body, much like biochemical oxygen demand (BOD) [15]. COD analysis results in the production of hazardous by-products, including potassium dichromate, mercury, and hexavalent chromium.

2.1.1. Analytical methods/ International Standards

There are two main variants of COD analytical methods, the Open Reflux method or Macro-digestion method and the Sealed Tube (ST) method or Micro-digestion method.

<u>Open Reflux method (Macro-digestion method)</u>

In the open reflux method, a water sample is oxidised by refluxing for a period of two hours with concentrated sulphuric acid and potassium dichromate. Boiling aids are added to the sample solution to lower the boiling point of the sample, and thus accelerate the boiling procedure. Subsequently, silver sulphite (Ag_2SO_4) is also included to catalyse the oxidation of some organic compounds and reduce chloride interference. A mercury salt is included when analysing saline samples to reduce interference by chloride oxidation.

There is a big variety of defined analytical methods and international standards for conducting COD analysis. In Europe the most common references are:

- 5220 B [16]
- ISO 6060 / ASTM D1252 [12]
- EPA (United States) 410.4 [17]

<u>The Sealed Tube (ST) method (Micro-digestion method)</u>

In short, COD is measured in prepared sealed vials. Vials are pre-prepared according to different ranges; low-range (3 - 150 mg/l) or high-range (20 - 1500 mg/l). This method uses the same principle and reagents as the open reflux method, but in smaller quantities [16]. The ST-COD method although making use of potassium dichromate, uses a fraction of the substance in comparison to the Open Reflux Method. For the open reflux method, the standard 5220B is making use of 12.259g of potassium dichromate whereas for the ST method, the standard 5220D, for low-range COD concentration, requires only about 10% of the potassium dichromate used in the open reflux method. Thus, ST-COD uses about 10 times less oxidant agent for the calculation using the same principle but a different technique [6].

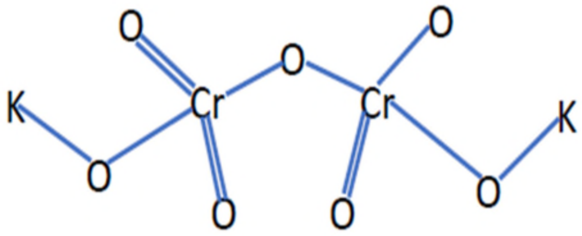
The most commonly used standards are:

- 5220 D [6]
- ISO 15705 [18]

2.1.2. Potassium dichromate

Potassium dichromate ($K_2Cr_2O_7$) (**Figure 1**) is an inorganic chemical reagent, used as an oxidizing agent in various laboratory and industrial applications.

Figure 1: Chemical structure of potassium dichromate



All hexavalent chromium compounds are acutely and chronically harmful to human health, and may adversely impact other ecological and environmental receptors. Potassium dichromate is labelled under the Classification, Labelling and Packaging of chemical substances and mixtures which are released on the EU market (CLP; Regulation (EC) No 1272/2008) [19] as:

- H272 May intensify fire; oxidizer.
- H301 Toxic if swallowed.
- H312 Harmful in contact with skin.
- H314 Causes severe skin burns and eye damage.
- H317 May cause an allergic skin reaction.
- H330 Fatal if inhaled.
- H334 May cause allergy or asthma symptoms or breathing difficulties if inhaled.
- H335 May cause respiratory irritation.
- H340 May cause genetic defects.
- H350 May cause cancer.
- H360FD May damage fertility. May damage the unborn child.
- H372 Causes damage to organs (Cardio-vascular system) through prolonged or repeated exposure if inhaled.
- H410 Very toxic to aquatic life with long lasting effects.

As a result, potassium chromate meets the criteria for classification as carcinogenic (category 1B) and mutagenic (category 1B) in accordance with REACH (regulation (EC) No 1272/2008) and therefore is included in Annex XIV to Regulation (EC) No 1907/2006 [20] set out in Article 57(a) and (b) of that Regulation.

Because of the toxicological properties of potassium dichromate the method of the determination of COD-Cr(VI), based on dichromate, are now sought to be substituted by other less hazardous analytical methods or parameters [11].

2.1.3. Interferences and method limitations

All COD analytical methods are subject to the following interferences and methods limitations as described in international standards [12, 16, 17] and the CWW BREF [1].

A) Interfering parameters: mode of interference

- Chlorides: reacts with silver ion to precipitate silver chloride, and thus inhibits the catalytic activity of silver. The interference from chlorides is reduced, but not totally eliminated, by the addition of mercury sulfate. Straight chain aliphatic compounds are effectively oxidized by the silver sulfate - sulfuric acid.
- Bromide and Iodide: react with dichromate to produce the elemental form of the halogen and the chromic ion. This reaction weakens the oxidant agent.
- Ammonia and its derivatives: are oxidized in the presence of chloride and high concentration of potassium dichromate (0.25-N) giving increased COD values. The interference is not observed when COD analysis is performed with low concentration of potassium dichromate (0.025-N) or when chloride is absent [21]. Furthermore, elemental chlorine reacts with these types of nitrogen compounds to form chloramines. Chloramines are then decomposed to give chloride, which is then re-oxidized to form chlorine. If not suppressed, chloride will cause increased COD values, the magnitude of which depends on the concentration of chloride and the COD value of the sample [16].
- Total Suspended Solids (TSS): High TSS values cause high concentrations of other parameters, namely BOD, COD/TOC, total phosphorus, total nitrogen, and metals. A portion of TSS, the volatile suspended solids, are degradable and exert an oxygen demand especially under high temperatures, consequently incising the COD value.
- Nitrite (NO_2^-): Nitrite is degradable and has a theoretical oxygen demand of 1.1mg O_2 per mg/. To eliminate a significant interference due to NO_2^-, 10 mg sulfamic acid is added for each mg NO_2^- present in the sample volume used.
- Inorganic reducing agents, such as nitrites, sulfides, and iron may be oxidized during COD analysis and therefore increase the result of the measurement.

B) Methods limitations

- Aromatic hydrocarbons and pyridine are not oxidized to any appreciable extent in the analytical methods. In that case, COD values are underestimated.
- Some very volatile organic substances may escape the oxidation of the analytical methods by evaporation. In that case, COD values are underestimated.

2.1.4. Comparison of open reflux method with ST-COD method

A.G.L.A.E.[7] has organised interlaboratory test campaigns where participants report results for ST-COD in addition to open reflux COD. A first study was published in 2013 [22] comparing these two methods using surface water and treated urban wastewater samples. The study was updated in 2019 [23] with data from the tests carried out in the meantime, adding a total of about 20 surface water tests and about 30 wastewater tests. The studies concluded that:

- ST-COD gives higher values of (2%) for concentration levels above 200 mg/l. It gives lower values of about 5.5 mg/l for concentrations below 200 mg/l.
- The precision of ST-COD analysis for concentrations above 100 mg/l is slightly lower than the open reflux method.
- On the other hand, the precision of ST-COD analyses is more accurate than the open reflux method for levels below 100 mg/l.

A.G.L.A.E studies [22, 23] concluded that the two methods may not be directly equivalent but their differences are minor. Both studies found that an increasing number of laboratories (predominantly in France) are implementing ST-COD measurement. This percentage increased from 34% in 2009 to 44% in 2013. The ST-COD became the most common COD analytical method in France since 2014 and by 2018 more than 60% of the laboratories were conducting ST-COD analysis [23]. Since 2020 ST-COD is integrated in new French regulations e.g. decree on applicable analytic methods [7].

2.1.5. Potassium dichromate-free COD analytical methods

As a result of the severe toxicological consequences of the use of potassium dichromate, EC has considered other COD analytical methods as alternatives to Open Reflux COD. The considered alternative analytical methods benefit from not using potassium dichromate and therefore do not bare its toxicological footprint. These COD analytical methods are summarized in **Table 3**.

Table 3: Potassium dichromate-free COD analytical methods, considered by EC [adopted from 4]

Alternative COD analytical methods to Open-Reflux COD	Description of the COD analytical methods
COD-Mn(III)	This method utilizes trivalent manganese, a strong, non-carcinogenic chemical oxidant that changes quantitatively from purple to colourless when it reacts with organic matter, instead of potassium dichromate. It typically oxidizes about 80% of the organic compounds. A standard operating procedure has been developed by Hach Company (Method 10067) [24].

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[7] A.G.L.A.E. stands for "Association Générale des Laboratoires d'Analyses et d'Essais" which means General Association of Analytical and Testing Laboratories. It is a non-profit-association, governed by the French law of 1 July 1901 which aims to improve analyses, especially chemical, microbiological and biological, in the fields of the environment and medical biology.

Alternative COD analytical methods to Open-Reflux COD	Description of the COD analytical methods
COD-Mn(VII)	This method was used prior to the Cr(VI) method for COD measurements under the name Kubel's method, where the sample is boiled with excess potassium permanganate in the presence of dilute sulphuric acid. An ISO standard is available for this method: ISO 8467:1993. Water quality determination - Determination of permanganate [25].
Electrochemical COD	The principle for the measurement is that a current is applied between two electrodes, creating hydroxyl radicals (OH·) that oxidise the compounds. Generally, an electrochemical process involves oxidation reaction at the anode and reduction reaction at the cathode. The measuring cycle is stated to take 4 minutes, making it significantly faster than the >2 h for the standard COD-Cr(VI) method.
Photoelectrochemical COD **(PeCOD)**	PeCOD (ASTM D8084-17) [26] is an analytical method that uses photo-electrocatalysis of organic and inorganic pollutants with titanium dioxide (TiO2) and UV light. This PeCOD test method is specific for measuring organics and inorganics in freshwater sources for drinking water treatment plants and treated drinking water matrices. This test method is not intended for domestic and industrial wastewaters to replace COD-Cr(VI) ISO 6060 / ASTM D1252 as it determines the oxygen demand for drinking water in only the range of 0.7 to 20 mg/l. Higher levels may be determined by sample dilution.

2.2. TOTAL ORGANIC CARBON (TOC)

Definition

TOC is the amount of carbon found in an organic compound and is often used as a non-specific indicator of water quality. TOC is a measure of the carbon content of dissolved and suspended organic matter present in the water. It is a more direct expression of total organic content than BOD or COD, which are indirect measurements. The organic carbon in water and wastewater is composed of a variety of organic compounds in various oxidation states. Some of these carbon compounds can be oxidized by biological or chemical processes, and COD and BOD analysis are typically used to characterize these fractions.

2.2.1. Analytical methods/International standard methods

There are two different methods to measure TOC, NPOC[8] or subtraction. In the NPOC method, TIC[9] and volatile carbon is purged before the analysis to measure the TOC. Contrary to NPOC, the subtraction method measures the Total Carbon (TC) and TIC.TOC concentration is calculated by subtraction of the total inorganic carbon from total carbon.

The main TOC international standards are the following:

- EN 1484:1997 [13]
- ISO 8245:1999 [14]
- Method 5310 [28]
- Method 415.3 [29]

TOC analysis only takes 5 - 10 minutes to complete and thus it is both faster and safer to run than COD. TOC analysers are also available for online monitoring, therefore providing real-time measurements of TOC in e.g. treated effluents. The TOC analysis procedures are relatively simple but are specific to the type of carbon-analysing instrument utilized in the laboratory. There are currently a lot of laboratory instruments that can measure TOC under specific circumstances such as carbon/water analyser, carbon/sulphur/hydrogen analyser, elemental analysers, portable TOC analysers, etc.

2.2.2. Method limitations

TOC analytical method is throughout its stages of the analysis subject to interferences that are described in the international EN 1484 (1997) [13] and ISO 8245 (1999) [14]. These interferences are the following:

A) <u>Interfering parameters: mode of interference</u>

- Volatile substances: can be lost during sample blending, particularly if the temperature is allowed to rise.
- Gases evolved from combustion, such as water, halide compounds, and nitrogen oxides, may interfere with the detection system

B) <u>Method limitations</u>

- Removal of carbonate and bicarbonate by acidification and purging with purified gas results in the loss of volatile organic substances.
- High-temperature combustion may be desirable for samples containing high levels of suspended organic carbon, which may not be efficiently oxidized by persulfate and/or UV methods.

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[8] <u>Non Purgeable Organic Carbon (NPOC)</u> is the organic fraction of the sample that is left in solution after acidification and removal of TIC from sample

[9] <u>Total Inorganic Carbon (TIC)</u> is the sum of Inorganic Carbon species in a solution and includes chemicals such as carbonic acid, carbon dioxide, and bicarbonate anions. Inorganic carbon is typically removed before introducing the sample into the TOC analyser with the use of strong acids. Inorganic Carbon can be measured directly or is removed from the sample before the determination of TOC and determined indirectly.

- The advantage of using lower temperatures (680°C) is that fusion of dissolved salts is minimized, resulting in lower blank values.
- Important loss can occur if large carbon-containing particles fail to enter the needle used for injection.
- Combustion temperatures above 950°C are required to decompose some carbonates. Systems that use lower temperatures must destroy carbonates by acidification.

2.3. COD/TOC RATIO DEPENDING ON WASTEWATER TYPE

Most of the COD/TOC ratio information found in the literature review were studies of domestic/municipal effluents, whereas peer review papers or reports on COD/TOC ratios specifically for refinery effluents were scarce. Despite the scarcity, some data is available that allow making some interpretations as to possible COD/TOC ratios. If not stated, no information was available on the analytical methods applied for COD and TOC analysis, respectively.

The standard method TOC 5310 A [28] discusses the possibility of TOC method to estimate the accompanying COD values, stating that a relationship must be established on a case-by-case basis for each studied matrix and only if a repeatable empirical relationship is established for a specific wastewater composition. The wastewater composition is important to any empirical COD/TOC relationship since TOC is independent of the oxidation state of the organic matter and COD includes as well organically bound elements (e.g. hydrogen and nitrogen) and inorganics [28]. Theoretically, COD/TOC ratios of organic substances range from 0.67 (oxalic acid) to 5.33 (methane). Values outside the theoretical range may be caused by the presence of oxidizable inorganic substances or measurement uncertainties [1].

2.3.1. Studies on domestic/municipal effluents

Dubber and Gray [30], collected BOD, COD and TOC data from 11 domestic wastewater treatment plants located in the Greater Dublin area (Ireland) during a period of almost 4 months[10]. The objective of the study was to evaluate if TOC could be used as an alternative measurement for the COD test. This was done by examining the relationship between TOC, COD and BOD of settled wastewaters (influents) and final effluents (after treatment) from the selected domestic plants. TOC was measured using high precision thermo-catalytic oxidation with a high-temperature TOC analyser (Shimadzu 5000A), while COD was measured using the Open Reflux COD method (ISO 6060:1989), employing Hach® COD digestion vials. The study found a highly significant correlation between COD and TOC for both influent and effluent wastewaters supporting the potential use of TOC as an alternative measurement to COD in wastewater analysis. The relevant regression equations derived from this study are shown below:

- For COD/TOC in the settled influent: COD= 3.00 x TOC + 49.2 (r^2=0.959)
- For COD/TOC in the effluent: COD = 2.99 x TOC + 7.25 (r^2=0.820)

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[10] (the actual number of individual samples and the frequency of the samples is not provided)

The strong linear relationship found in both the influent and effluent streams suggests COD could be reasonably predicted from TOC values for urban wastewaters. While the two slopes in the above equations are almost the same, the variation associated with the slope coefficient for the effluent data is larger than for the influent data [30].

In a study by Eckenfelder [31], the author recorded COD/TOC ratios[11] of 4.15 for raw sewage and 2.26 for treated effluent and suggested that the changes in the ratio are linked to the quality of wastewater and the degree of treatment. In this case, the variation found between influent and effluent was expected as COD is a specific measure of oxygen-consuming matter, and TOC directly assesses the carbon atoms present in the organic fraction. The study points out that this variation can be reduced by establishing predictive equations for specific wastewater streams and treatments. The study concluded by indicating that '*where the deficit of oxygen in surface waters is the primary concern, this should be measured directly with BOD and COD methods. However, for routine comparative performance analysis of wastewater influent and effluent, COD can be replaced with TOC'* [31].

Another study conducted by Umweltbundesamt GmbH Austria [11], includes the results of various evaluations of correlations between COD and TOC. Data from over 2,000 UWWTPs in Austria are presented in **Figure 2**, which however does not indicate the frequency[12] of the COD/TOC ratios data. The study also includes data provided by the Netherlands and Flanders (**Figure 3** and **Figure 4**, respectively). The Austrian study found a similar result to the outcome of the Irish study described earlier, while the Dutch and Flemish studies indicated that COD/TOC ratios ranged mostly between 2.5 and 3.5. The same report indicated that a Danish[13] study found that TOC did correlate well with COD but the correlation needed to be established for each UWWTP individually. The Umweltbundesamt GmbH Austria study concludes that ratios of COD/TOC vary between wastewater treatment plants, and between sample times, within a common range of 2.5 to 4.1.

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[11] The actual number of individual samples and the frequency of the samples is not provided

[12] The frequency (f) of a particular value is the number of times the value occurs in the data. The distribution of a variable is the pattern of frequencies, meaning the set of all possible values and the frequencies associated with these values.

[13] Krysell M. (2004) TOC(NVOC) as a replacement for COD-Cr for control of wastewater (in Danish). Danish Environment Agency (document not found)

Figure 2: Austrian data showing COD and TOC values for effluent of urban wastewater treatment plants (this figure is adopted with consent from Umweltbundesamt GmbH, Austria)[14]

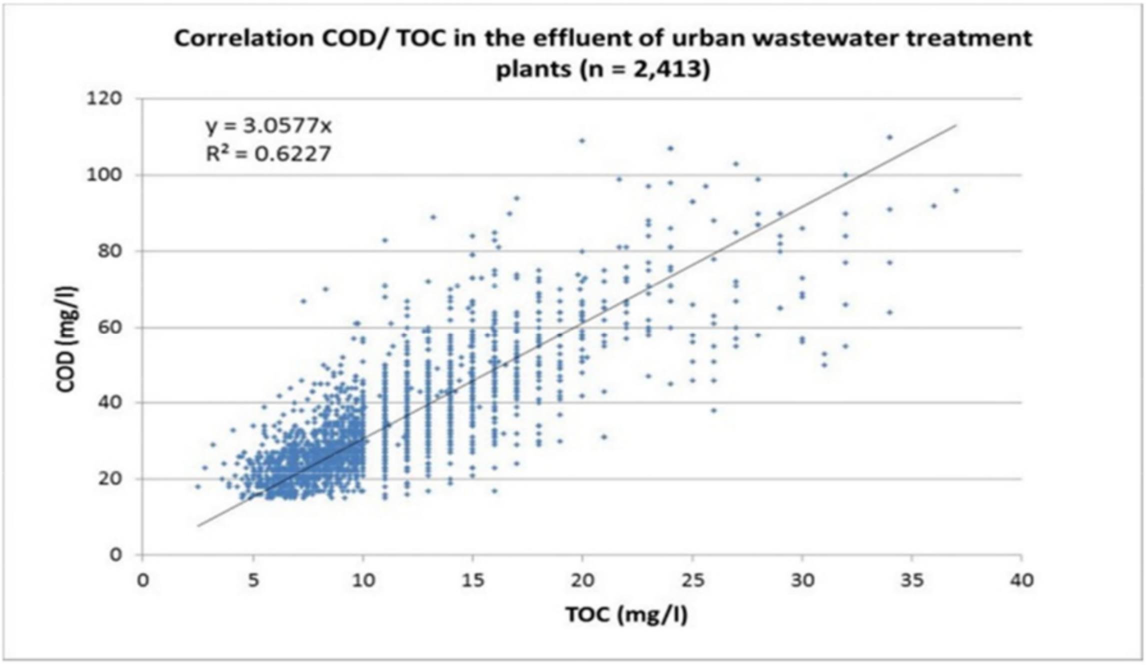
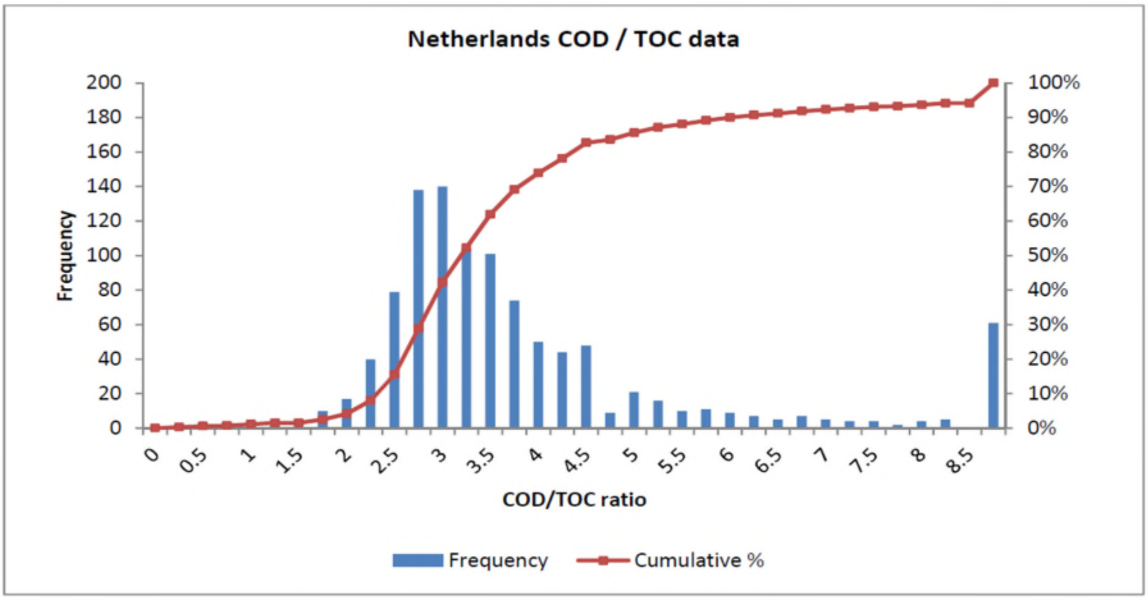


Figure 3: Dutch data showing COD to TOC ratios for wastewater samples (this figure is adopted with consent from Umweltbundesamt GmbH, Austria)



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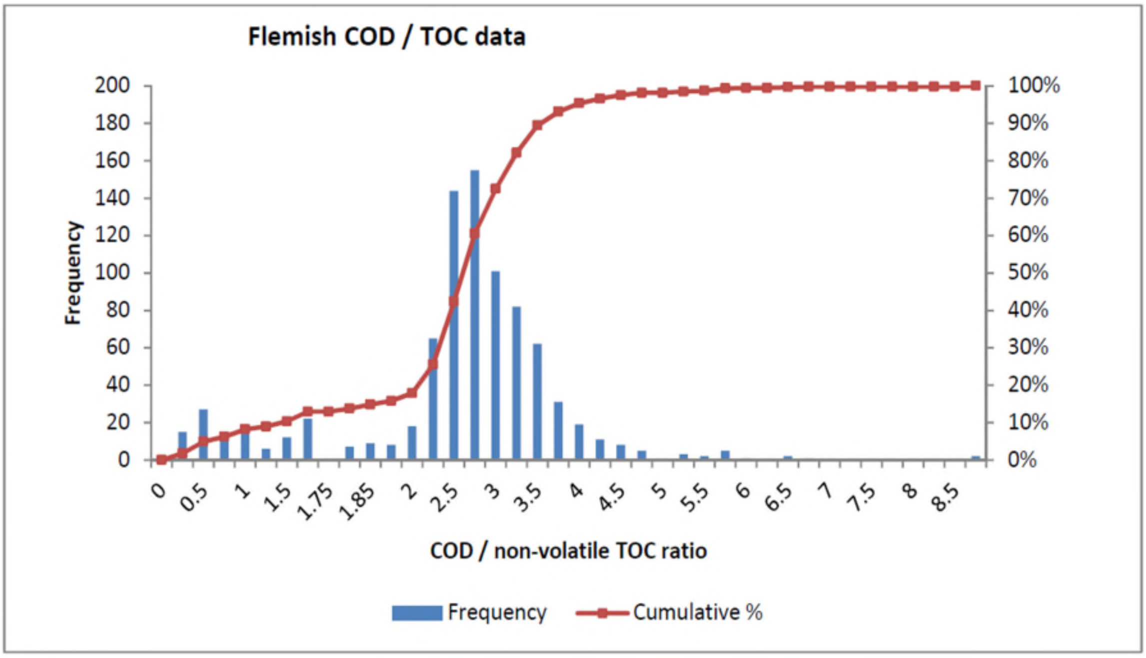
[14] The COD/TOC correlation in the effluent of urban wastewater treatment plants is forced through zero. This hypothesis implies that when TOC value is zero, COD value should also be zero. However, as described in the definition of these analytical techniques, TOC and COD are not equivalent analytical methods. COD incorporates inorganic elements and therefore is always higher than TOC. Consequently, a forced COD/TOC correlation to zero would suggest the total absence of inorganic elements which is unrealistic.

Figure 4: Flemish data showing COD to TOC ratios for wastewater samples (this Figure is adopted with consent from Umweltbundesamt GmbH, Austria)



2.3.2. Studies on industrial effluents (with similarity to refinery effluents)

The CWW BATc [3] specifies for direct emissions to a receiving water body BAT-AELs for COD 30-100 mg/l and TOC 10-33mg/l, thus suggesting the COD/TOC ratio to 3 for chemical sector. However, in the CWW BREF [1] chapter 2 it is noted that "*care has to be taken when converting COD to TOC or vice versa using ratios; these ratios need to be well-established for each case*". For WWTPs where both COD and TOC data for the effluent were reported (33 directly discharging WWTPs), the COD/TOC ratios ranged from 1.73 to 6.38 with a median value at 3.0 [1].

The EC JRC Reference Report on Monitoring of Emissions to Air and Water from Industrial Emission Directive (IED) Installations[15] [32], states that the COD/TOC ratio is usually plant- or site-specific, and are usually between 2.0 and 4.0. This indicates that in many cases, a ratio of 3.0 is considered a good approximation which is also reflected in in E-PRTR applying a ratio of 3.0 for all covered industrial activities to report TOC releases based on COD data (TOC = COD/3) [11]. A study conducted by the German Federal Environment Agency (UBA DE) [33] on different industrial sectors showed that, for the chemical industry, the COD/TOC ratio was mostly in the range of 2.5-3.5 (median 2.9; 1,053 samples from 38 effluents).

2.3.3. COD/TOC ratios from refinery effluents

Data collected from a heavy crude refinery in India as part of a BOD, COD and TOC correlation study [34], yielded a COD/TOC ratio of 3.85 based on the mean of 8 samples (no information is provided as to the analytical methods used). However, the ratio varied from as low as 1.5 to as high as 14.1 showing a big discrepancy in

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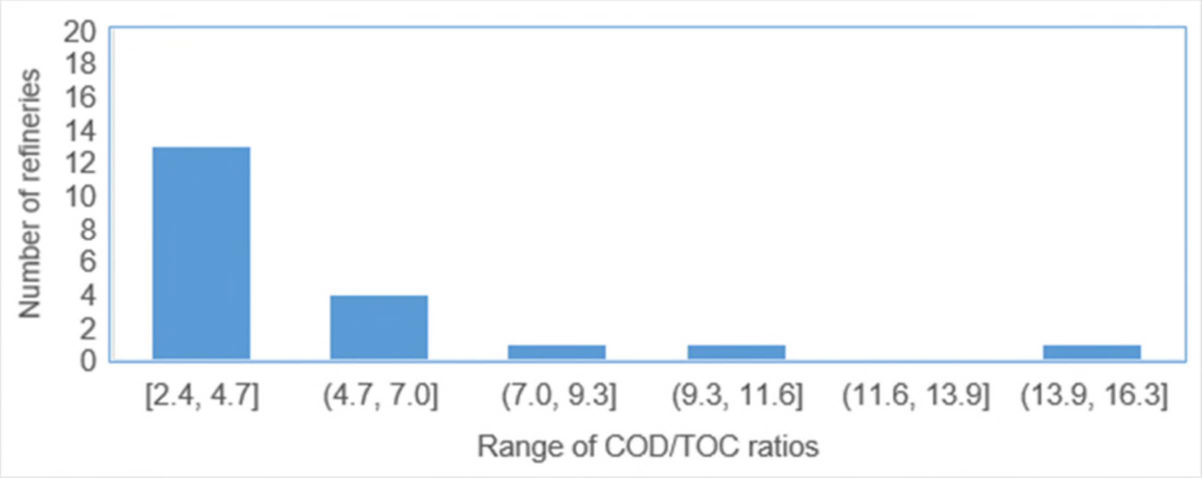
[15] No analytical methods are specified but the study does refer to catalytic combustion >600C for TOC.

the results. Values above 5.33 indicates presence of oxidizable inorganic substances or measurement uncertainties [1], see Section 2.3.

The REF BREF includes COD and TOC annual average concentration data for 2006-2008 for 20 refinery treated effluents (3 stage wastewater treatment) without specifying analytical methods used nor refinery processes [35]. This showed a mean COD/TOC ratio of 4.92. As shown in **Figure 5** below, most COD/TOC ratios were between 2.4 and 4.7, however, with great variation; a minimum of 2.37 and a maximum of 16.3. Annual average concentration data for COD and TOC collected by Concawe in 2016 (31 refineries) and 2019 (25 refineries) showed, similar to the data in **Figure 5**, a great variation between sites with COD/TOC ratio ranges of 2.54-20.1 and 1.06-13.1 for 2016 and 2019, respectively. The mean COD/TOC ratios for 2016 and 2019 were 5.06 and 4.24, respectively, for the treated effluents. As these values are derived from annual average concentrations rather than parallel analysis of the same sample a comparison with the COD/TOC ratio theoretical range (1 - 5.33) cannot be readily done, however high values may indicate presence of oxidizable inorganic substances or measurement uncertainties [1].

Figure 5: COD/TOC ranges [min, max] of 20 refineries, adapted from [35]



A combined refinery/chemical plant contacted as part of the literature review indicated a COD/TOC ratio of 3.5 when all processes are running. Furthermore, a refinery in Germany indicated a permitted yearly average value of 25 mg/l for TOC and 80 mg/l for COD, thus applying a ratio of 3.2.

For refining wastewaters, daily variability needs to be taken into consideration when attempting to establish meaningful COD/TOC relationships as this is dependent on local factors, such as crude changes, periodic activities upstream of the treatment (e.g. purges, cleaning, operational unit changes), or weather conditions, that may interfere with the WWTP performance. The REF BREF [35] indicates that the daily variability may be due to:

- Normal variations of WWTP efficiency;
- Normal variations of input streams to the WWTP;
- Presence of chemical process facilities discharging to the WWTP;
- Other than normal operating conditions (OTNOC) of the entire system (production units and WWTP).

3. REFINERY EFFLUENT DATA ANALYSIS

This section contains the results from effluent monitoring data of COD and TOC that were gathered from eight effluent streams from seven different European refineries (Sites A to G).

In order to remove outliers, potentially influenced by interfering substances affecting COD or TOC analytical methods, as described in chapter 2.1 and chapter 2.2, the data from all were verified to respect these following criteria:

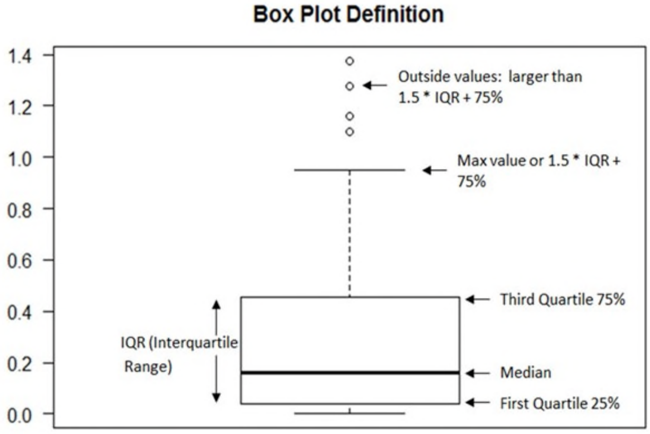
- COD/TOC ratio > 1
    - Theoretically, COD/TOC ratios of organic substances can range from 0.67 (oxalic acid) to 5.33 (methane). However, in practice ranges lower than 1 for wastewater treatments would suggest the absence of oxidizable inorganic compounds from the refinery effluents which is unrealistic.
- Chloride concentration ≤ 1000mg/l
    - Chloride is a known COD interfering parameter
- Sulphite concentration ≤ 1mg/l
    - Mercury or silver-sulphite is added in COD solutions to minimize chloride influence. However, additional sulphite presence may interfere to the COD analytical methods.
- Total nitrogen concentration ≤ 30mg/l
    - Gases evolved from combustion, such as water, halide compounds, and nitrogen oxides, may interfere with the TOC detection system.

By applying these criteria, 108 out of 1660 samples were omitted from the analysis.

3.1. ANALYSIS OF FULL DATASET

The numerical data from the seven refineries were studied firstly collectively to determine the general relationship and ratio between COD and TOC. For this analysis, a box plot type chart was used to illustrate visually the distribution of numerical data and skewness through displaying the data quartiles (or percentiles) and medians as explained in the **Figure 6**.

Figure 6: Box Plot chart description



All the data are referring to measurements from the year 2019. From the statistical analysis, **Figure 7** illustrates the variation of the COD/TOC ratio between the refineries. The red line represents the average ratio of 3.4 that was calculated for the eight datasets. The value of 3.4 is close to 3, the number most regulatory guidance have as a reference standard, but the distribution between the refineries varies significantly as indicated in the **Table 4**. A great majority of the values (98.6%) were within the theoretical COD/TOC range (1 – 5.33), however values above 5.33 indicates presence of oxidizable inorganic substances or measurement uncertainties [1].

The variation and the difference between the maximum value (7.93) and the minimum value (1.00) in **Figure 7** indicates that the ratio is different in each refinery, and thus every refinery effluent data was also analysed individually (Section 3.2).

Figure 7: COD/TOC ratio for all the refineries of the study (A to G). The red line represents the average ratio (3.4)

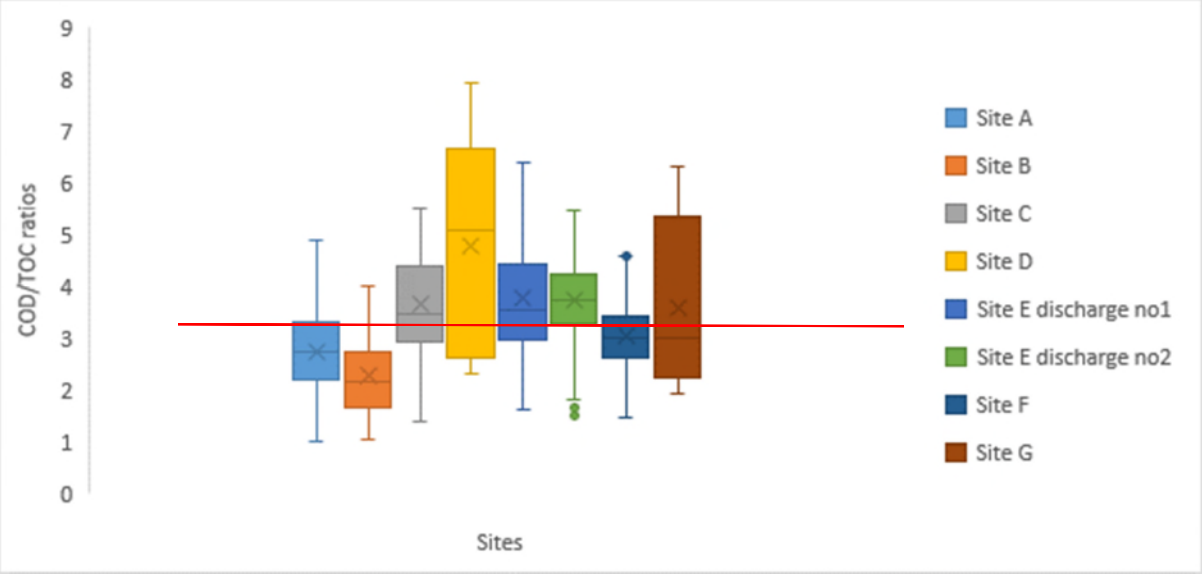


Table 4: Minimum, maximum, mean and median COD/TOC ratio values from the seven refineries including number of samples. For Site E 1 and Site G (highlighted in yellow) a majority of the samples had a chloride concentration of > 1000 mg/l, thus not fully respect the data selection criteria.

	SITE A	SITE B	SITE C	SITE D	SITE E 1	SITE E 2	SITE F	SITE G	All Sites
Number of samples	311	490	38	14	93	91	502	13	1552
Mean	2.75	2.26	3.65	4.79	3.77	3.74	3.03	3.59	3.45
Median	2.74	2.15	3.48	5.10	3.54	3.74	2.99	3.00	3.34
Minimum	1.00	1.05	1.40	2.31	1.61	1.50	1.48	1.92	
Maximum	4.87	4.00	5.51	7.93	6.38	4.45	4.74	6.31	

3.2. ANALYSIS OF INDIVIDUAL REFINERIES

Linear regressions of TOC vs. COD for each site were put together (**Figure 8** and **Table 5**). The criteria for removing outliers were not fully respected for Site G and Site E-1 as the majority of the samples had a chloride concentration higher than 1,000 mg/L. Despite that, the slope coefficient and R^2 calculated for Site E-1 gave results comparable with the other refineries, whereas Site G not, and therefore Site G was excluded from further analysis.

A site-specific relationship between COD and TOC could not be established with confidence for Sites A-F, because the coefficient of determination (R^2) ranged between 0.39 and 0.80, with a mean of 0.58 (**Figure 8** and **Table 5**). R^2 values were not higher for sites with many datapoints, e.g. site A and B, thus indicating that amount of datapoints of the datasets is not a reason for observing the weak correlations between COD and TOC. Sites C and E2 had highest R^2 values and a correlation between COD and TOC may be established for these sites with COD/TOC of 2.9 and 3.5, respectively.

Table 5: Linear regression details (y = a*x + m) for TOC (mg/l) vs. COD (mg/l) of the studied refineries without statistical outliers. For Site E effluent no1 and Site G (highlighted in yellow) a majority of the samples had a chloride concentration of > 1000 mg/L, thus not fully respect the outlier criteria.

	SITE A	SITE B	SITE C	SITE D	SITE E n*1	SITE E n*2	SITE F	SITE G	Sites A to F
Number of samples	311	490	38	14	93	91	502	(13)	1539
Slope coefficient (a)	1.4	2.2	2.9	1.8	3.0	3.5	2.6	(3.2)	Mean: 2.5
Intercept (m)	26.0	1.0	18.8	35.0	12.2	3.5	3.8	(2.4)	
R^2	0.56	0.39	0.73	0.44	0.46	0.80	0.65	(0.23)	Mean: 0.58

3.3. PARAMETERS AFFECTING COD/TOC RATIO

The impact on the COD/TOC ratio of each individual parameter was studied to obtain a correlation matrix. The results of this analysis are summarised in **Table 6**. The analysis did not conclude to any strong correlation between any parameter for the COD/TOC ratio (correlation factor above > 0.60).

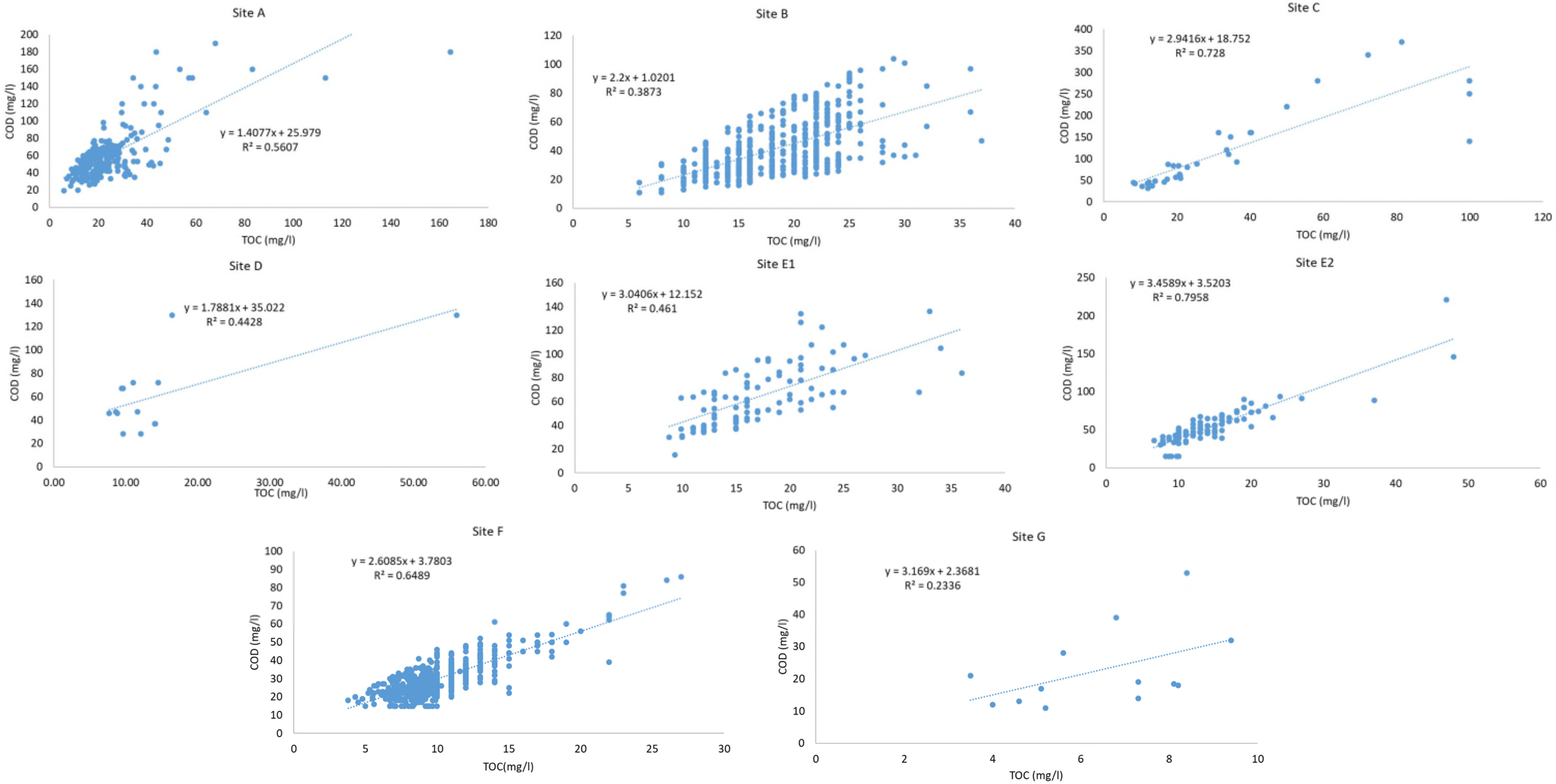
Table 6: Correlation coefficient between COD/TOC ratio and influential parameters

Correlation coefficient	pH	Chloride (mg/l)	TPH (mg/l)	Sulphite (mg/l)	Total Nitrogen (mg/l)	Kjeldahl Nitrogen (mg/l)	Ammonium (mg/l)	Nitrite (mg/l)	Nitrate (mg/l)	TSS (mg/l)
COD/TOC	0.2	0.09	0.06	0.11	0.29	-0.19	0.08	-0.02	-0.02	0.14

3.4. ANALYTICAL METHODS AFFECTING COD/TOC RATIO

The effect of analytical methods on COD/TOC ratio was investigated by comparing the average COD/TOC ratios when different COD and TOC methods were applied. The information submitted on the analytical methods applied was limited and indicated only that a variety of methods were applied, and no concrete correlation could be drawn between analytical methods and COD/TOC ratio.

Figure 8: Graphical analysis of individual refinery effluents without statistical outliers.



4. COD/TOC RATIO CONSIDERATIONS FOR REFINERY EFFLUENTS

As it could be observed that COD/TOC ratios varied between sites from the data in this study and overall only a weak correlation between COD and TOC could be established with any statistical relevance when looking at each site individually, we can conclude that global/generic COD/TOC ratio is inappropriate for refinery effluents.

If we take as basis that the maximum permitted COD is currently 125 mg/L, according to REF BAT AELs [2], with a ratio of 3, the TOC equivalent permit limit would be 42 mg/l. If this default ratio would be used, it may not represent a correct equivalence to COD as this may measure as well inorganic oxidizable content and thus affect the ratio. Subsequently, it may, in some cases, lead to additional treatment requirements to meet the new TOC limit while the COD emission is within the permit limit. In the case TOC is used in the permit in place of COD, site should develop a site-specific ratio and evaluate the variability of the ratio over time. If the level of COD from inorganic oxidizable content is significant, TOC measurement may not be the right parameter to monitor or additional inorganics monitoring may need to be considered.

5. REPLACING COD WITH TOC ANALYSIS FOR REFINERY EFFLUENT MONITORING?

The analysis done in this study for eight treated refinery effluents from seven refineries showed that a global COD/TOC ratio applicable to all sites' effluents cannot be set since there was a big variation in observed ratios between sites. The high variation in COD/TOC ratio between refineries was confirmed by average annual concentration COD and TOC data from Concawe Effluent Quality/Water Use Surveys of 2016 and 2019. The results confirmed that if a future discharge permit for refineries would be based on TOC instead of COD, a global conversion factor between COD and TOC values could result in a converted TOC limit value lower than the site's current effluent TOC performance, whereas before the effluent was meeting the COD limit value and not causing pollution. Thus, a global ratio could have an influential impact and not correspond to the realistic impact of the effluent to the receiving environment. The observations are in line with statements made in CWW BREF and REF BATc [1, 2], i.e. precautions have to be taken when applying COD/TOC ratios to replace COD analysis with TOC and ratios need to be well-established on a case-by-case basis. Although, the CWW BATc [3] used a COD/TOC ratio of 3 to establish the BAT-AEL for TOC, the range from data collected in this study was wide and the observations of this study highlights that site-specific evaluations are needed.

Even site-specific relationship between COD and TOC could be challenging to establish, as from the data of this study it could only be established with some certainty in two cases (R^2= 0.73 - 0.80) under the condition that the concentration of interfering parameters is low enough. These observations deviate from those of other effluents types from UWWTP and chemical industry [9, 11, 1, 31]. It is not surprising that COD/TOC relationships vary widely among refineries given the variability of measurements experienced on a monthly and even a daily basis. For refining wastewaters, daily data variability needs to be taken into consideration when attempting to establish meaningful COD/TOC relationships as this is dependent on local factors. COD/TOC ratio depends on the composition of samples; 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. If the level of COD from inorganic oxidizable content is significant, TOC measurement may not be the right parameter to monitor or additional inorganics monitoring may need to be considered.

If to replace COD with TOC analysis, a refinery would need to work with its competent authority to execute a long-term, correlation test to replace COD with TOC as a discharge parameter, similarly to what US EPA is stating in their National Pollutant Discharge Elimination System (NPDES) Permitting Program [36]. It is also likely that that the correlation of COD with TOC will vary with time, unless the effluent composition is extremely stable [11], thus there will likely be a need to confirm the correlation (ratio) from time to time.

5.1. REPLACE COD OPEN REFLUX ANALYSIS WITH OTHER CHROMATE -FREE ANALYTICAL METHODS?

For the replacement of COD methods using potassium dichromate (COD-Cr(IV), potassium dichromate-free methods have been considered by EC [11]. However, these methods have been disqualified and concluded to be inferior to the open reflux COD method for reasons summarized in **Table 7**.

Table 7: Analytical methods that have been disqualified to replace COD open reflux method.

Method	Reasons for disqualifying
COD-Mn(III), COD-Mn(VII)	The predecessors of COD-Cr(VI) are using other oxidants such as Mn(III) or COD-Mn(VII) for measuring or calculating COD exist but are inferior (far weaker oxidant) to the standard COD-Cr(VI) method [37]. Moreover, chloride ions (Cl^-) are known to interfere with the reaction, causing an overestimate of the COD. Ammonia has severe interferences on Mn(III) analytical method. COD-Mn(VII) analytical method is not recommended to determine COD for wastewaters.
Electrochemical COD	Similarly, as for PeCOD, there are no individual studies that support this transition, on the contrary, a recent Dutch study [37] has concluded that electrochemical COD is unlikely to be a suitable alternative based on the cost and quality of the measurements. The electrochemical COD analytical method is in addition not suitable for samples with solids.
PeCOD	The PeCOD method that makes use of titanium dioxide (TiO_2) also makes use of silver nitrates which is another environmental concern. Furthermore, PeCOD is proven to give lower values than COD-Cr(VI) methods. Unfortunately, no independent studies are proving any correlation with the COD-Cr(VI) methods and this method will likely provide lower COD values. The PeCOD method is in addition not suitable for samples containing solids.

5.2. REPLACE OPEN REFLUX COD ANALYTICAL METHOD WITH ST-COD?

The REACH regulation is currently being revised and the roadmap towards the revision sets out possible plans to ‘’*apply the concept of ‘essential use’ to chemicals*”, to “*make the process of phasing out these chemicals simpler, more effective, more predictable, and faster*” [38]. Currently, there is no definition of an ‘*essential use*’ under EU law. In this spotlight, if the use of potassium dichromate for COD analysis is to be considered an essential use exemption from REACH, that could spark a discussion on COD method alternatives that do make use of that substance but to a lesser extent and volume than the conventional open reflux method.

The ST-COD (micro-digestion) method could be considered to replace the open reflux (macro-digestion) method. As with the open reflux COD method, the ST-COD method could be affected by interferants, especially chlorides, but remains an important step to achieving a significant reduction in chemical use of hazardous dichromate. Compared to the open reflux method, the ST-COD method generates significantly lower quantities of potassium dichromate waste [11] and has shown good comparison results [22, 23]. Further, ST-COD is integrated into new regulations, e.g. French decree on applicable analytic methods [7] and, at least in France, the method is the most commonly used COD analysis method [23].

6. CONCLUSIONS

This work aimed to investigate whether a global COD/TOC ratio could be applied for refinery effluents and as such facilitate replacing COD with TOC measurements in discharge permits. Most of the literature references on COD/TOC ratios relate to effluents from UWWTPs while few were available for industries but not refineries. All studies suggest or applied a COD/TOC ratio of around 3, but due to variation between 2 and 4, it is often emphasised that ratios need to be well-established for each case.

Data collected as part of this study (eight refinery effluents from seven refineries) showed that a global COD/TOC ratio could not be established for refinery effluents. Median COD/TOC ratio values ranged between 2.3 - 4.3, with a mean value of 3.4, which showed that there are differences between sites and highlighted the risks of applying a global ratio. Using a default COD/TOC relationship in the modification of refinery permits may result in increased requirements for effluent treatment that provide no additional protection with regards to oxygen demand in the receiving water environment. The reason for the variation could not be determined but it is hypothesised to be due to specific characteristics compromised by the configuration, processes, wastewater treatment variations of each refinery.

Furthermore, a site-specific relationship between COD and TOC could be established with confidence (R^2 = 0.73 - 0.80) only for two sites. Nevertheless, a site-specific approach guarantees a more reliable COD/TOC ratio that would allow a more meaningful discussion on actual permitted values for the industry on site-specific basis. It is recommended that the site-specific ratio is reviewed on a periodic basis. This conclusion is in line with REF BATc [2] recommendations. Additionally, if the level of COD from inorganic oxidizable content is significant, TOC measurement may not be the right parameter to monitor or additional inorganics monitoring may need to be considered.

In case it is not possible to establish a reliable COD/TOC ratio at a refinery, this report also recommends applying the ST-COD method, as it generates less quantity of toxic waste compared to the conventional open reflux COD method.

7. GLOSSARY

As	Arsenic
BAT-AELs	Best Available Techniques – Associated Emission Level
BOD	Biochemical Oxygen Demand
BREF	European Union’s Best Available Techniques Reference Document
Cd	Cadmium
Cl	Chloride
CO2	Carbon Dioxide
COD	Chemical Oxygen Demand
Cr	Chromium
CWW	Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector
DAF	Dissolved Air Flotation
DO	Dissolved Oxygen
ECHA	European Chemicals Agency
EC	European Commission
E-PRTR	European Pollutant Release and Transfer Registry
IAWQ	International Association for Water Quality
IAF	Induced Gas Flotation
IED	Industrial Emissions Directive (2010/75/EU)
ITA	Instrument Testing Association
MS	Member State (of the EU)
NDIR	Non-Dispersive InfraRed (detection)
NO2	Nitrous dioxide
NPOC	Non Purgeable Organic Carbon
POC	Purgeable Organic Carbon,
Precision	Precision is defined as the extent to which results agree with one another. In other words, it is a measure of consistency, and is usually evaluated in terms of the range or spread of results. Practically, this means that precision is inherently related to the standard deviation of the repeated measurements.
REF	Refining of Mineral Oil and Gas
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals Regulations
S.I.	Système Internationale

SS	Suspended Solids, also called TSS
SPC	Static Pressurized Concentration
ST	Sealed-Tube
SVHC	Substance of Very High Concern
TC	Total Carbon
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TOD	Total Oxygen Demand
TOT-P	Total Phosphorus
TKN	Total Kjeldahl Nitrogen
TPH	Total Petroleum Hydrocarbons
TSS	Total Suspended Solids, also called SS
UV	Ultraviolet
UWWTP	Urban Waste Water Treatment Plan
UWWTD	Urban Wastewater Treatment Directive
WWT	Waste Water Treatment
WFD	Water Framework Directive

8. REFERENCES

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APPENDIX 1: STANDARD METHODS FOR COD ANALYISIS

This Annex includes the processes and definitions of international standards, describing COD analysis procedure.

- International standard 5220 [16a]

For this international standard 50 ml of the sample is diluted in the reaction flask with the addition of 1g of mercury sulphite. Slowly 5ml of sulfuric acid reagent is added to the solution with mixing to dissolve the mercury sulphite. The sample is cooled and mixed to avoid the possible loss of volatile material. After the mixing, 25 ml (of 0.04167 M) potassium dichromate solution is added to the solution alongside the remaining 70 ml of the sulphuric reagent. The sulphuric reagent consists of a mixture of silver sulfate with sulfuric acid in a ratio of 5.5 g silver sulfate/ sulfuric acid. The potassium dichromate solution consists of 12.259 g (0.04167 M) potassium dichromate previously dried at 150ºC for 2 h, in distilled water and diluted to 1000 ml. After the addition of the sulphuric reagent and the potassium dichromate solutions, the sample is heated to 150ºC and is kept in that state for another 2 hours. Finally, the sample is cooled and the condenser is washed with distilled water. Potassium dichromate is titrated with ammonium iron sulphate using ferroin as a visual indicator. The oxidizable matter is calculated in terms of oxygen equivalent.

- ISO 6060 / ASTM D1252 [12a]

10 ml of the sample are diluted in the reaction flask and 5 ml of potassium dichromate is added to the solution. The test portion always consists of 10 ml of the solution. After that 15 ml of sulphuric acid - silver sulphite is added to the solution. The flask is immediately attached to a condenser. Within 10 minutes the sample is heated to boiling (150ºC) and is kept in that state for another 110 minutes. Then the flask is cooled in cold water to 60˚C, the condenser removed and the flask further cooled to room temperature. Finally, potassium dichromate is titrated with ammonium iron sulphate using ferroin as a visual indicator.

- EPA (United states) 410.4 [17a]

In this method, 10 ml of the sample is put into a 25 x 100 mm tube. Then, 1.5 ml of a previously prepared digestion solution is added to the tube alongside 3.5mL of a catalyst solution. The digestion sample consists of 5.1g of potassium dichromate, 84mL sulphuric acid, and 16.7 g mercuric sulphite. The catalyst solution consists of 22 g of silver sulphite to a 4.09kg bottle of sulphuric acid. The test tube after the addition of the digestion sample and the catalyst is put into a block digester or oven to 150ºC for 2 hours. A residual non-reduced dichromate is measured either by using titration against iron (II), ammonium sulphate, or colourimetrically.

- ISO 15705 [18a]

In this international standard 2±0.02ml of the sample is added to the boiling tube alongside 0.20±0.02ml of mercury sulphite solution. The sulphite solution consists of mercury (II) sulphate in water at (20% w/w) ratio. In the solution, 1 mg of potassium dichromate is then added followed by 3.00±0.05ml of silver sulphate – sulphuric acid solution. The silver sulphite - sulphuric acid solution consists of silver sulphite in sulphuric acid at (10% w/w) ratio. The tube is then closed securely, swirled to mix the contents, and placed in a thermostatically controlled heating block, capable of accommodating digestion tubes to 150ºC for 120 minutes. After this process, the tubes are removed and cooled to 20ºC for approximately 5 minutes under running water and dried. The residual dichromate is measured colorimetrically or spectrophotometrically and the COD concentration of the sample is derived.

APPENDIX 2: STANDARD METHODS FOR TOC ANALYISIS

This Annex includes important definitions and the processes of TOC analysis. The international standards are referred under each relevant method.

All TOC analytical methods have the following basic stages:

- Acidification: Acidification of the sample for the removal of the TIC and POC[1] gases. Addition of acid and inert gas sparging allows all bicarbonate and carbonate ions to be converted to carbon dioxide, and this Inorganic Carbon product is vented along with any POC that was present.

- Oxidation: Oxidation of the carbon in the remaining sample in the form of carbon dioxide and other gases. Oxidation can be conducted with the following procedures:
    - Combustion technique (High-Temperature Catalytic Oxidation) [13a ,14a, 28a, 29a]: A small aliquot sample is injected onto a catalyst substrate in a combustion tube that it is held at 680 C. This temperature can be higher in some instruments that don't use catalysts. The advantage of using a low-temperature instrument is that fusion of dissolved salts is minimized. Replacement of the catalyst and in some cases full replacement of the combustion tube may be required which is particularly true for the analysis of salt-containing samples.
    - Heated Persulfate with Non-Dispersive InfraRed (NDIR) detection [13a ,14a, 28a, 29a]: Persulfate is added to the acidified sample, and heated to a determined temperature according to the instrument used (typically 98 ˚C) and reacted for a preset amount of time. It uses heat to magnify the oxidizing power of persulfate. Chemical oxidation of carbon with a strong oxidizer, such as persulfate, is highly efficient, and unlike UV, is not susceptible to lower recoveries caused by turbidity in the samples. Persulfate methods are used in the analysis of wastewater, drinking water, and pharmaceutical waters. When used in conjunction with sensitive NDIR detectors heated persulfate TOC instruments readily measure TOC ranges from one mg/L up to hundreds of mg/L depending on sample volumes.
    - UV Persulfate [28a]: In this method, persulfate is added to the acidified sample, and the mixture is then irradiated with UV light for some preset time. In this case, the UV light is the oxidizer, but the oxidation power of the reaction is magnified by the addition of a chemical oxidizer, which is usually a persulfate compound. The UV-chemical oxidation method offers a relatively low maintenance, high sensitivity method for a wide range of applications. However, there are oxidation limitations of this method related to samples with high amounts of particulates. It can also be affected by high chloride. This method is most suitable for ultrapure waters with relatively low TOC concentrations.

- Detection and quantification:
    - NDIR detection [28a, 29a]: NDIR offers the only practical interference-free method for detecting CO2 in TOC analysis. The principal advantage of using NDIR is that it directly and specifically measures the CO2 generated by oxidation of the organic carbon in the oxidation reactor rather than relying on a measurement of a secondary, indirect measurement such as used in conductivity measurements. Traditional NDIR detectors rely on flow-through-cell technology, where the oxidation product flows into and out of the detector continuously. As the gas continues to flow into and out of the detector cell the sum of the measurements results in a peak that is integrated and correlated to the total CO2 concentration in the sample aliquot. The Static

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[1] Purgeable organic carbon (POC) is the measure of the fraction of a sample that can be removed from the sample by sparging the dissolved phase with an inert gas followed by oxidation to carbon dioxide. It is usually negligible or of no concern in TOC determinations.

Pressurized Concentration (SPC) is a new type of NDIR technology where the exit valve of the NDIR is closed to allow the detector to become pressurized. Once the gases in the detector have reached equilibrium, the concentration of the CO_2 is analyzed increasing sensitivity and precision compared with the flow-through cell technology.

- Direct conductivity or membrane conductivity detection [29a]: Conductivity can be measured by mainly two methods known as direct and membrane. The direct conductivity method uses no carrier gas and is good at the parts per billion (ppb) ranges but has a very limited analytical range. Membrane conductivity relies upon the filtering of the CO2 before measuring it with a conductivity cell. Both methods measure TOC based on the conductivity difference before and after oxidization, attributing this differential measurement to the TOC of the sample.

There are two general approaches used to measure TOC:

1. <u>The NPOC approach</u>: In this mode, the TIC is first removed by acidification and the subsequent oxidation of the organic fraction of the sample provides the TOC concentration. This is true when the POC is negligible (true in most applications).

   In Europe, the most commonly referred standards are EN 1484 [13a] and ISO 8245 [14a]. Both standards are guidelines using the NPOC approach to measure TOC by oxidation via combustion, addition of an appropriate oxidant, UV radiation, or any other high-energy radiation. The carbon dioxide formed is determined either directly or after reduction while the final determination of carbon dioxide can be carried out by several different procedures, for example, infrared spectrophotometry, titration, thermal conductivity, conductometry, coulometry, use of carbon dioxide-sensitive sensors, and flame ionization detection. Inorganic carbon is removed by acidification and purging or is determined separately.

2. <u>TOC by difference (subtraction) [28a]:</u> In this mode, TC (total carbon) is measured first, then the TIC is measured by acidifying the sample and measuring the CO_2 generated. Subtraction of TIC from TC provides the TOC concentration. Two measurements are required in this mode.

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