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The upcoming prohibition of Potassium Dichromate

A review of alternative pollution indicators

Rijkswaterstaat Internship Thesis

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Table 1: Abbreviations

Abbreviation	Definition
ANN	Artificial Neural Network
BOD	Biological / Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
EU	European Union
NKj	Nitrogen Kjeldahl
PeCOD	Photo-electro-chemical Chemical Oxygen Demand
RWS	Rijkswaterstaat
ThOD	Theoretical Oxygen Demand
TOC	Total Organic Carbon
TOD	Total Oxygen Demand
UVAS	Ultraviolet Absorption Spectroscopy

SUMMARY

ENGLISH

The main method utilised today for Licensing, Enforcement and Taxation of effluent waters within the Netherlands and most of the EU is the Potassium Dichromate Chemical Oxygen Demand (COD). This chemical analysis of COD incorporates some toxic substances such as Mercury and Potassium Dichromate, which are potentially harmful to the environment. Due to its toxicity the EU will enforce a ban in September 2017 on the application of potassium dichromate (Annex XIV of Regulation (EC) No 1907/2006 REACH regulation). This means that, from this date, the ban has the potential to have a major impact on the Licensing, Enforcement and Taxation of effluent waters. For this reason Rijkswaterstaat (RWS), as the governing body within the Netherlands, required more information on possible alternative pollution test methods. The aim of this paper is to review alternative organic pollution test methods for effluent waters, with the goal of finding a suitable alternative to the Potassium Dichromate-COD test.

This research commenced with a literature review into alternative methods and the development of a criteria list in which to compare the identified alternatives with that of the baseline (current method), allowing the identification of suitable alternatives. This was followed by consultations with relevant parties involved with the usage, manufacture or regulation of the current Potassium Dichromate COD test or the identified alternative methods. The aim was to gather sufficient information and data to enable a thorough comparison with the baseline and ultimately, to advise on the best method to employ for future effluent water testing.

There were four alternatives chosen to be compared to the baseline. BOD_5, PeCOD, TOC and UVAS. All of these alternatives exhibited good and bad points, however at this time the top candidate and recommended alternative is TOC. This is due to its accuracy, its present wide spread use and standardisation. At the time of writing this paper, RWS is conducting a trial regarding PeCOD. The results of the study will reveal more detailed information regarding this particular alternative and to ensure selection of the most suitable method, the results of this study should be taken into account.

DUTCH

De belangrijkste methode die op dit moment gebruikt wordt voor vergunningverlening, handhaving en belastingheffing op afvalwater in Nederland en de meeste EU landen, is de kaliumdichromaat chemisch zuurstofverbruik (CZV) index. Deze test maakt gebruik van een aantal stoffen waaronder kwik en kaliumdichromaat, die potentieel schadelijk zijn voor het milieu (Yao et al., 2014; Esteves et al., 2015 en Gutiérrez-Capitán et al., 2015). Als gevolg van de toxiciteit zal de EU in September 2017 een verbod afdwingen op het toepassen van kaliumdichromaat, zoals is opgenomen in bijlage XIV of Regulation (EC) No 1907/2006 REACH-verordening (Commissie verordening nr 348/2013 van 17 April 2013 tot wijziging van Bijlage XIV van REACH). Dit betekent dat vanaf die datum, het verbod op kaliumdichromaat mogelijk grote gevolgen heeft op de verlening en handhaving van vergunningen en de belastingheffing op afvalwater. Rijkswaterstaat heeft om deze reden, als belangrijk bestuursorgaan op het gebied van afvalwater binnen Nederland, meer informatie nodig over alternatieve methoden. Het doel van deze scriptie is het analyseren van alternatieve organische testmethoden voor afvalwaterstromen en het vinden van een geschikt alternatief voor de kaliumdichromaat CZV test.

Dit onderzoek is gestart met een literatuuronderzoek naar alternatieve methoden en het vastellen van een criteria lijst, waarmee de geïdentificeerde alternatieven vergeleken worden met de basislijn (huidige methode), om uiteindelijk betere alternatieven te identificeren. Vervolgens heeft er overleg plaatsgevonden met de betrokken partijen, die te maken hebben met het gebruik, de vervaardiging of de regulering van de huidige kaliumdichromaat CZV test of de geïdentificeerde alternatieve methoden. Het doel hiervan was om informatie en gegevens te verzamelen, waardoor de vergelijking met de basislijn mogelijk wordt.

In dit verslag worden vier alternatieven vergeleken met de referentiemethode: BZV5, PeCOD, TOC en UVAS. Deze alternatieven hebben goede en slechte punten, maar de beste kandidaat is TOC. Dit is te danken aan de hoge precisie van de methode, de huidige brede toepassing en de hoge mate van normalisatie. Echter, met meer onderzoek is PeCOD mogelijk een sterke concurrent en een onderzoek van Rijkswaterstaat naar deze methode zal binnenkort worden afgerond. Hierdoor zou het zinvol kunnen zijn om te wachten op deze resultaten, om te bepalen of de PeCOD een beter alternatief is dan TOC.

1 INTRODUCTION

1.1 WATER QUALITY MANAGEMENT IN THE NETHERLANDS

Water is the most important building block of life. It covers 71 percent of the Earth's surface and in the past it was seen as an infinite resource. However of all the water on the planet only 2.5 percent is freshwater, suitable for direct human use. In 2007 there were nearly 7 billion people on the planet. In the future, the global population is forecast to increase to an estimated 9 billion by 2050, thus creating an ever increasing demand for water (UN Press Release 2007). World water has seen a swiftly increasing usage over the last hundred years, with the total water use growing from approximately 600 to more than 3,000 cubic kilometres per year, between 1900 and 2000 (Chenoweth, 2008). When considering the future, with population rise and incorporating climate change scenarios this usage will only grow. This then has implications on the quantity of wastewater that is produced. Generally speaking wastewater is water that has been contaminated by anthropogenic influences and may be comprised of substances such as human waste, food scraps, oils, soaps and other chemicals. It originates from households, businesses and industries. Although people assume that rain is relatively clean, it is not once it flows over urban or agricultural land, as it picks up all the contaminants associated with those areas (Defra 2012). Thus water quality assessment and pollutant control are becoming global imperatives as water pollution becomes a serious issue, increasing the demand for wastewater treatment (Yao et al, 2014).

The Netherlands is no different in seeing these developments, as during the 20th century, the population of the Netherlands grew from 6 million to almost 16 million and now in 2015 is nearly 17 million (Population; key figures 2015). This increase has been linked to industrialisation, urbanisation and the modernisation and intensification of agriculture, all of which have amplified the pollution of surface waters. In the 1960s the deteriorating surface water quality within the Netherlands became obvious. The organic pollutants within the water bodies were causing acute oxygen deprivation problems. This was being caused by wastewater discharges from industry, agriculture, traffic and households. The discharge of large amounts of heavy metals, pesticides, hydrocarbons and organic chlorine compounds, led to the disappearance of indigenous species, deterioration of water quality and the pollution of sediments (Moel et al, 2006). This led in 1970 to the Netherlands' first real piece of environmental legislation, *the Pollution of Surface Waters Act*. This was as a consequence of the pollution being severe enough to threaten human health and consequently water usages such as agricultural, recreational as well as for drinking water and fisheries (Warmer & Dokkum 2002). The Act provided the legal means with which to improve water quality.

Since then, many developments and modifications of policy and legislation relating to water management have taken place, both within the Netherlands and in the European Union (EU) as a whole. The EU is the highest authority and it is each member state's responsibility for establishing the required regulating measures and to ensure that the legislation is implemented. The following directives along with numerous others have been developed by the EU:

- Dangerous Substances Directive (76/464/EEC) and its daughter directives.
- Urban Wastewater Treatment Directive (91/271/EEC).
- Nitrates Directive (Directive concerning the protection of waters against pollution caused by nitrates from agricultural sources, 91/676/EEC).
- Integrated Pollution Prevention and Control (IPPC) Directive (96/61/EC).
- The Drinking Water Directive (98/83/EC),
- Water Framework Directive of the European Union (2000/60/EC)
- Council Regulation (1907/2006/EC) of the European Parliament and the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH),

The Netherlands has a multi-layered system of water management. At the top is the National or central Government. The Ministry of Infrastructure and Environment (I&M) comes under the Central Government, and Rijkswaterstaat (RWS) is an executive body within I&M that plays a large role in the management of waterways and water quality. At the next level, 12 Provinces (Provincial Government) allocate water abstraction permits (Moel et al 2006). The Provincial Government also has the role to implement the policies devised by national government to comply with the EU directives, in their regions. Then there are Water Boards (24 across the 12 provinces www.uvw.nl), who are responsible for the quality and quantity of water in their regions. Figure 1 below outlines a brief overview of the principal parties involved with water quality management within the Netherlands.

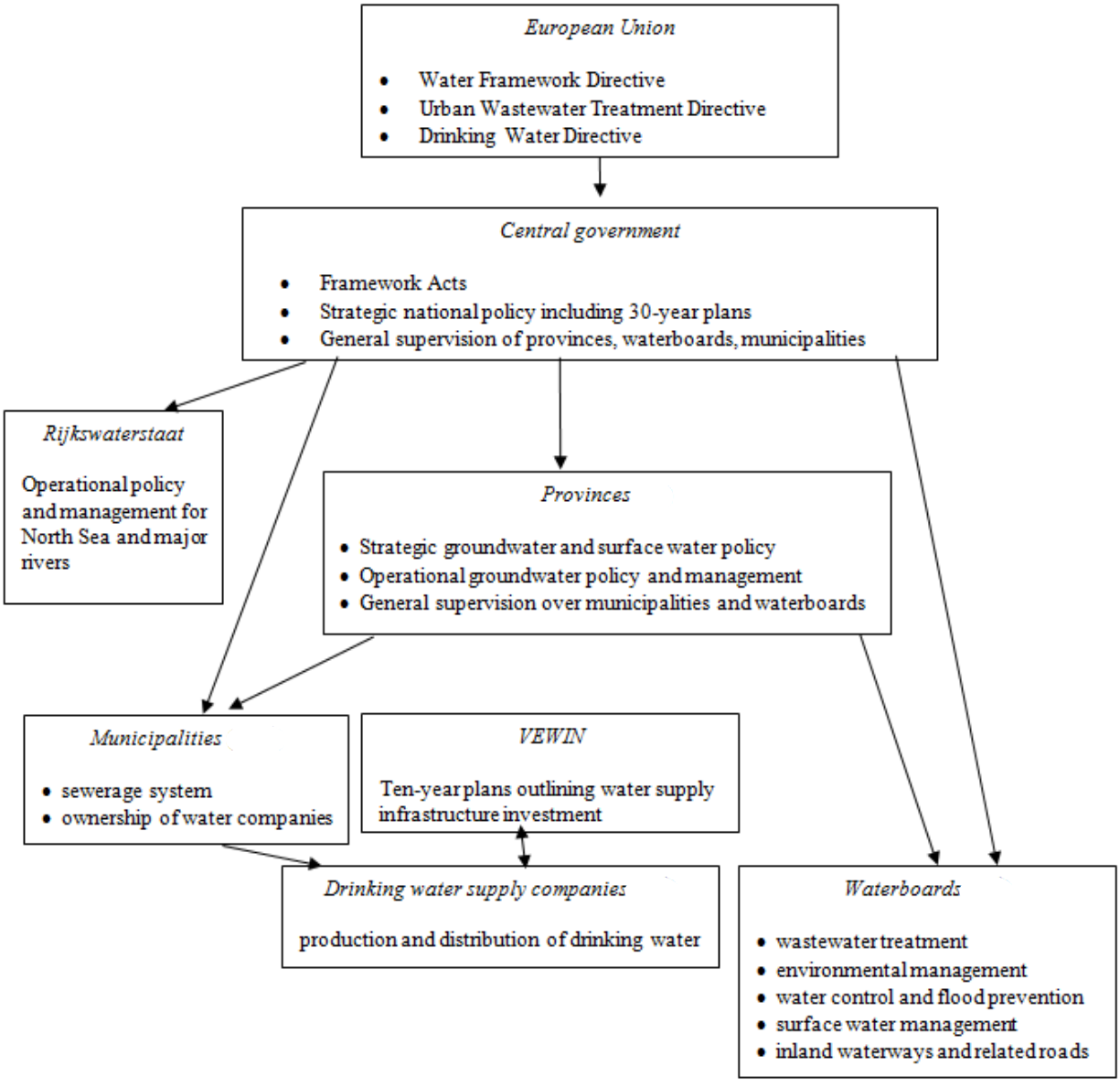

Figure 1: Brief overview of relationship between Main water quality parties and their responsibilities within the Netherlands (Source: de la Motte 2004).

The following Acts are some of the legal frameworks previously utilised within the Netherlands:

- The Seawater Pollution Act,
- The Groundwater Act,
- The Water Management Act,
- The Environmental Management Act,
- Land reclamation and Tidal Flats Act,
- Flood Structures Act,
- Parts of the Public Works Management Act and water Management and Public Works Act.

These were all replaced by the Water Act in 2009, which in combination with water permits derived from the General Administrative Law Act, is now the basis of water quality management in the Netherlands (Rijswick & Havekes 2012). There are more laws and regulations which are not included within the Water Act such as the Drinking Water Act but which do not specify the usage of COD. If they are found to be of consequence during the research they will be added into the main body of the report.

1.2 WATER QUALITY MANAGEMENT OF WATER DISCHARGE

Rijkswaterstaat is responsible for the main water ways, as the water boards are for the smaller provincial waters. This means that they are both responsible for upholding the water quality. The First National Policy Memorandum on Water Management (Rijkswaterstaat 1968) was one of the first discussions concerning water quality. It focused on salinity along with the concentrations of ammonium, nitrate, phenols, and radioactive compounds and most importantly the biological oxygen demand (BOD_5) of the Rhine. The BOD5 method determines the amount of oxygen consumed by microorganisms during a five day period (Reinhard & Folmer 2009). A major reason for the use of BOD_5, at that time was that it was the established method to show the oxygen demanded to break down substances in the wastewater. As stated earlier, in the 1960-70's the surface waters suffered from a lack of oxygen, due to the breakdown of the many organic substances present in the discharged wastewater. This environmental catastrophe led to the *Pollution of Surface Waters Act*, as mentioned previously in 1970.

Since the development of the BOD method in 1908, there has been the development of different organic content based tests such as Chemical Oxygen demand (COD), Total Organic Carbon (TOC) and Total Oxygen demand (TOD). Where BOD_5 is the oxygen demand required by microorganisms to degrade organic compounds (Boyles 1997 and Young et al, 2003), COD is the measure of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant (Stoddart & Gagnon, 2014). TOC measures the total organic carbon content of the water and TOD is the measure of the total amount of oxygen required when the combustible materials in a sample are burnt in the presence of an oxygen containing feed stream (Young et al, 2003).

A major aspect of maintaining good water quality is the management of wastewater discharge. The *Pollution of Surface Waters Act* prohibited the discharge of polluting or harmful substances into surface waters without a license, thus restricting the quantity of pollutants being discharged. In the Netherlands, companies are required to take samples and test their discharged wastewater to identify the quantity of organic pollution discharged in relation to oxygen binding substances. The companies are then charged according to their discharge amount. RWS also test to ensure that dischargers are maintaining the correct levels of water quality and are not exceeding permit limits.

The water Permit and levy system utilised today is still based on the discharge of the oxygen binding substances. The formula used to calculate this for industrial discharges is: $O_2 = V * (COD + 4.57Nkj)$, where O_2 is the Oxygen Demand, V is the volume or quantity of discharge, COD is the chemical oxygen demand and NKj is the amount of organically bound nitrogen (named after Kjeldahl). The municipal levy is based on a similar equation but is charged on a fixed rate per person per day, charged by the water boards (Rijkswaterstaat 2014). As shown in the equation above COD is used for taxation purposes, in

preference to the BOD_5 first discussed in the First National Policy Memorandum (Rijkswaterstaat 1968). A reason this test is used is because the method itself has very good performance characteristics, as the test "oxidizes" both organic and inorganic substances in a wastewater sample, thus resulting in a higher oxygen demand value than that of BOD or TOC (Del Valle et al, 1990., De Casseres et al, 1984 and Abyaneh 2014). COD has a real time application advantage as the testing time is two hours and is simple to perform making it cheaper than other standard Oxygen demand tests (Canelli et al 1976). COD is also easy to automate with self-sampling equipment which provides stakeholders with a great degree of confidence, due to regular testing (Cuesta et al, 1998 and Geerdink & Epema (Rijkswaterstaat) undated). COD is also recognised in the Urban Waste Water Directive (91/276/EEC), in which the potassium dichromate method is the standard technique.

1.3 PROBLEM DESCRIPTION

The main method utilised within the Netherlands for water quality testing, of discharge water, is the COD method that employs Potassium Dichromate. This test however incorporates substances such as Mercury and Potassium Dichromate itself which are potentially harmful to the environment (Yao et al, 2014; Esteves et al, 2015 and Gutiérrez-Capitán et al, 2015). As a result of its toxicity the EU will enforce a ban in September 2017 on potassium dichromate, (Annex XIV of Regulation (EC) No 1907/2006 REACH regulation (Commission Regulation No 348/2013 of 17 April 2013 amending Annex XIV to REACH)). This means that from this date, general usage of Potassium dichromate is prohibited. There is however a Scientific research and development (SR&D) clause which encompasses the COD analyses. This clause sanctions the use of Potassium Dichromate for purposes of any scientific experimentation, analysis or chemical research carried out under controlled conditions in a volume of <1 tonne/year/legal entity (REACH 2015). So encompassing monitoring of effluent waters. The effects of this ban are as of yet unknown however it is highly probable that the price and supply of Potassium Dichromate will be effected. Consequently this may lead to the need to replace the Potassium Dichromate-COD test with an alternative method.

Past studies focusing on alternative test methods to the Potassium Dichromate-COD as possible replacements, have advised the continuation of COD due to its superior performance (Morrison, 1998). However the effects of the ban on Potassium Dichromate may force a change therefore creating the potential to impact the following features, if a suitable alternative is not found. Even with a suitable alternative the following features need adaptation.

- **Taxation;** currently based on the polluter pays principle, with both the level of purification and pollution being determined on the basis of the amount of COD in the waste water. When COD, due to the ban on potassium dichromate, can no longer be used for the analysis, it will not be possible to impose the current taxation method.

- **Licensing;** in many water permits the quality norm is given as a measure of COD. This is in accordance with applicable laws and regulations, such as the water regulations (waterregeling Article 7), Waste Water Directive, activity based decisions (activiteitenbesluit) etc. When COD amounts cannot be verified due to the ban on potassium dichromate, the current permits will be null and void.

- **Enforcement;** this applies in regard to the monitoring and maintenance of the standards listed under the water permits. When no more analyses can be carried out on the COD standard outlined within the water permits, it will not be possible to monitor nor maintain this standard, thus making it unenforceable.

This will, in turn, affect the following organizations as it will impact their activities (Rijkswaterstaat 2014):

- **Rijkswaterstaat:** In the form of the authority of the Water Act (licensing, enforcement and pollution tax) and as debtor for the pollution.
- **Water Boards:** In the form of the authority of the Water Act (licensing, enforcement purification and pollution tax) and as debtor for the pollution.
- **Environmental Services:** In the form of the authority of the Water Act (licensing and enforcement) – water permit obligations (companies, individuals, etc.)
- **Other Organisations:** persons liable for the purification and / or pollution levies (companies, individuals, etc.).

As a result of this upcoming ban there is a need for more research into the possible alternative methods that are available to replace the Dichromate-COD test (CEN 2014).

1.4 AIM

The aim of this paper is to conduct a review of alternative organic content based test methods, to that of the Potassium Dichromate-COD test, due to the prohibition of Potassium Dichromate. It aims to identify a suitable replacement by evaluating a variety of alternatives to the current method of water quality analysis of effluent waters, and to indicate benefits and drawbacks of these alternatives, using the current method as a baseline.

1.5 RESEARCH QUESTION

What is the best alternative to the Potassium Dichromate-COD test, for the purpose of monitoring, licensing, taxation and enforcement of effluent waters?

I. What is a suitable criteria list to assess and compare possible alternatives to the Potassium Dichromate-COD test?

II. Which organic content based methods are currently used worldwide as alternatives, for pollution monitoring and control as well as for taxation purposes?

III. What additional organic content based alternative test methods, not currently being utilised for pollution monitoring and control as well as for taxation purposes, are there?

IV. What are the benefits and limitations of these methods in comparison with the Potassium Dichromate-COD test?

2 METHOD

Research into the alternative test methods for the Potassium Dichromate-COD which are centred on the organic content of water was carried out. This paper sought to achieve this by firstly answering sub-research question (I), providing a basis for what information was most suitable to assess the alternative test methods and consequently, providing a basis for comparison and rejection of the alternative methods. This was followed by research into the currently used alternatives along with other possible alternatives as per sub-research question (II and III). This was all achieved by conducting three main steps. In each step relevant information, in the pursuit of finding an answer to the research question was sought, meaning that data from actual tests carried out by RWS or other organisations, were obtained and used, and backed by literature where possible. Alternatively wherever test results were unavailable

the data/information was drawn from the literature, when accessible. The three main steps are outlined below:

2.1 Literature Review

An extensive literature review was carried out utilising Google scholar, Scopus and Web of Science, along with other search engines and RWS archives. The main aim of reviewing the available literature is to identify possible alternative methods to the current Dichromate-COD test as well as checking methods used in other countries, as these are possibly the better options for an alternative method. This was motivated in response to, research sub question (II and III). Comparisons between the identified methods and that of the current method, were also searched for within the literature review to help provide information relating to answers to sub question (IV), thus helping to provide a better understanding of the relationship between the methods. The literature review was also important in the accumulation of data necessary for the assessment step, including the creation of the criteria list, in response to sub question (I) e.g. Costs, results and methodology practices. Once the criteria list was created (Results 3.1) it was possible to start eliminating those options that did not meet with or did not achieve one or more of the criteria thresholds.

The literature review consisted of approximately seventy five percent of the time spent on data collection. This included research into and creation of the criteria list along with research into alternative methods. This time period also includes the time spent on reviewing information received through consultations.

2.2 Consultation

Consultations were made with relevant parties to discuss the current practices of the Dichromate-COD test. This enabled a better understanding of how the different parties involved currently utilise the COD test and how it fits in with the daily business. It indicated the needs and wants of the party in question, thereby helping to develop the assessment criteria for alternative methods. The opinions and views regarding the alternative test methods, were also discussed regarding the perceived advantages and disadvantages of the different alternative methods, (in relation to sub-research questions (I and IV)). Additional alternative methods were also investigated (as per sub-research question (III).

The three organisations involved with maintaining good water quality, within the Netherlands; RWS, the water boards and the environmental services (Omgevingsdiensten), as well as companies who manufacture and/or use water quality test equipment were consulted. The companies/organisations contacted can be seen in Table 2 below. The parties were consulted by means of telephone, email and/or face to face interviews. In many cases a combination of the three were used, as most consultations involved pre-interview contact along with follow-up calls or emails. This organisation and participation of consultations along with follow-ups accounted for approximately twenty five percent of the data collection time.

Table 2: Companies and Organisations consulted.

Company/Organisation	Role (Department)
Aqualab	Laboratory operating COD and other water quality testing
AVR	Waste Processing and energy Company
AWWA	American Water Works Association a non-profit, scientific and educational association dedicated to managing and treating water
European Commission (REACH)	REACH Helpdesk
HACH LANGE GMBH	Manufacturer of laboratory equipment
Hanna Instruments	Manufacturer/Retailer of laboratory equipment

Lar AG	Manufacturer of laboratory equipment, especially TOC
ManTech and Camlab	Manufacturer of PeCOD
NEN	Netherlands Standard Institute
Oasen	Water Company
RealTech Inc.	Manufacturer of laboratory equipment, especially UV sensors
Rijkswaterstaat	Authority of the Water Act (licensing, enforcement and pollution taxation)
UK Environment Agency	Authority over water management in the UK
US Environmental Protection Agency (EPA)	Governing Authority over the environment (Water Quality)
Vitens	Water Company
WaterNet	Water Company
Waterproof	Laboratory operating COD and other water quality testing
wln	Laboratory operating COD and other water quality testing

2.3 ASSESSMENT

This stage of the paper was based on a comparison of the alternative methods to the baseline (the current Potassium Dichromate-COD test). This comparison was achieved through the development of a criteria list in response to sub-research question (I). The criteria were derived from the literature review as well as responses from consultations. The information regarding the alternative methods gathered from the literature review and through consultations was compared to the criteria list and in each phase if one or more of the criteria were found to be significantly inadequate then that alternative did not successfully progress to be included in the final assessment, e.g. the need for precious metals or jewels leading to unrealistic running costs.

The criteria chosen were based on research results, from both the literature and consultations. The first criteria was chosen from a business perspective. All consultations indicated that expensive alternatives would be unacceptable, therefore an '***Economics***' criteria with thresholds for investment of €100,000 (based on previous investment for analysis by RWS) and cost per test of around €25-30 was created. It was highlighted throughout the research that the uncertainties associated with the alternative test methodologies and their results was important leading to '***Quality'*** as a criteria. The thresholds for this criteria were set at 10 and 15 percent respectively, for accuracy and reproducibility. It was also judged that any alternative method with a reporting limit considerably higher than 5 mg/l was not satisfactory. Consequently any alternative that could not detect pollution within these boundaries were rejected before the final assessment.

The ability to compare present results with historical results was also seen as advantageous, for the purpose of assessing progress of policy/strategy decisions. On this basis the '***Continuity'*** criteria was incorporated into the research. The duration of the test is very important in pollution control. The current method has a digestion time of two hours though the full testing time is around three hours (ISO 6060). Thus a '***Time'*** criteria was made with a threshold of three hours for acceptance into the final assessment. Another criteria used was '***Green Test***' and any alternative method not meeting this was not included within the final assessment. This was incorporated to attempt to avoid this same situation occurring in the future. Additionally during the consultation phase it was identified that there are a large diversity of stakeholders involved, meaning large differences in capabilities thus leading to a '***Feasibility***' criteria. If the alternative methods are not possible for all stakeholders then they were not included in the final assessment. There was also the '***Standardised'*** criteria which focused on whether the test methodology follows a consistent technique, which has been standardised, reducing uncertainties associated with mass usage along with ease of implementation. The above criteria are discussed further in sections 3.1 and 4.1.

The results of this research which are based on the criteria are displayed in easy to read Figures and Tables. However within some of the assessment criteria there are measures of uncertainty which must be acknowledged. Thus only exact values are used where appropriate and when available, and the uncertainties are outlined and shown where appropriate and possible. Once this has been completed there will be an indication of a potentially suitable replacement, to the current Dichromate-COD test, in response to the research question. A suitable replacement will have approximately the same, if not better, results for each of the criteria, as the current Potassium Dichromate-COD test.

3 RESULTS

3.1 CRITERIA

In order to judge and achieve the comparison of the alternative methods a criteria list was made. This is due to the fact that all the alternatives looked at, throughout this research were based on organic content, each of the alternatives reveals a different portion of the water matrix, as can be seen in Figure 2. The alternatives show overlap, but subsequently represent different portions of the sample water, consequently creating the need for comparison to identify the best currently available alternative. The conditions and data required for each of the criteria to achieve this comparison are outlined here;

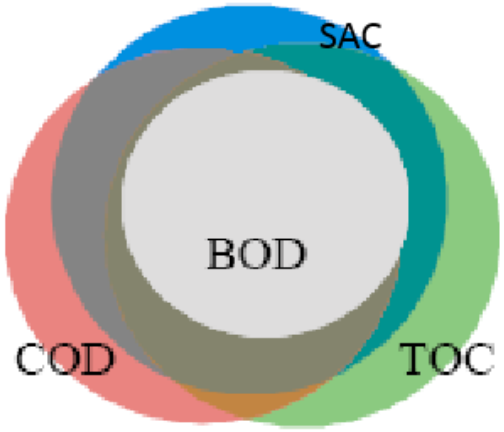

Figure 2: Relationship and cross-over between COD, BOD, TOC and UVAS results (Source: HACH LANGE GMBH 2015)

~ ***Economics*** – This refers to the costs incurred due to the employment of the test. Including the initial investment cost along with the cost per test. Therefore information was required on the costs of: necessary equipment for each test method, any outsourced tests, replacement parts/consumables and labour. The results were comprised as follows. The initial investment cost was specified by the price range from basic to top end (incorporating fully automated systems) equipment (Although it must be noted that with economies of scale and market factors this investment range may vary). This is accompanied by the cost per test associated with the methods. This is only available if the method is currently commercially available. The cost per test is calculated from the cost and life span of replacement parts/consumables, when conducting 10,000 tests per year, the approximate number of tests RWS conducts per year. The prices identified for outsourced testing and labour costs were also incorporated, when available.

~ ***Quality*** – This criteria is derived from the accuracy, reproducibility and the reporting limit of the methods. The required information was obtained from literature and supported by data and information received from consultations, as it was often exaggerated within the literature. This criteria focuses on how reliable and accurate the test is. Therefore, it was divided into: accuracy in relation to the current method or the Theoretical Oxygen Demand (ThOD) (ThOD is explained invAppendix 8.1), and reproducibility of results represented as the standard deviation spread from the mean) and the reporting limit (the lowest detection limit).

~ ***Continuity*** – It is important to find trends and monitor progress when looking at policy implementation. This criteria refers to this, hence data for the same sample tested by the alternative methods was needed. This was only available for those test methods in common usage, otherwise the data (if available), was derived from the literature review, consequently providing the correlation

between the methods. This was conducted utilising results from testing the same water samples with the alternative methods, and was only possible when the test methods were in combined usage.

~ ***Feasibility*** – This criteria needed information regarding, the implementation, as well as how simple the test is to administer and maintain, e.g. online options or complicated chemical processes requiring technically trained staff.

~ ***Time*** – An assessment of the time from the start of the test till the result is derived. Data concerning how long until the results can be obtained was desired. Some data was available in the literature however in practice it is not always alike. Therefore information regarding actual testing times was compiled from both users and suppliers of test equipment. Some time was also included for preparation time before the test methods could begin. The preparation time did show differences between the consultations and literature thus there may be variations in the times specified.

~ ***Green Test*** – Considering whether the test is environmentally friendly. This was typically found within the literature and was judged by the test methodology and if there were any environmentally harmful chemicals or processes used.

~ ***Standardised*** – Has the test methodology been standardised by a relevant organisation? This indicates whether the test methodology follows a consistent technique. This was obtained through literature and consultations.

~ ***Other barriers/constrains/difficulties the Netherlands face in implementing one of these new test*** – Information concerning the alternative techniques was discussed with all parties contacted. The aim of this was to identify any other criteria or other obstacles, associated with the alternative methods which led to the creation of the standards criteria. The 'standards' criteria as seen in Table 4, was thus created. The importance of this was identified by NEN but was not agreed upon by all the stakeholders consulted.

3.2 SUMMARY OF ALTERNATIVES

Table 3 below provides a quick overview of the main alternatives identified throughout the research, indicating in which stage of the research they were rejected (if the reason for rejection was situated within literature or due to information obtained through consultations), along with the main criteria responsible for the rejection. The criteria refer to those above, derived in response to sub research question (I). The first column within the Table identifies a method of testing. This is followed by sub methods which utilise the same principles as the other methods within the respective group, but vary on one or more point (e.g. biosensors with different bacteria, electrode material variations and alternative chemicals).

The table furthermore shows the results to sub research question (II and III). In the third column the table identifies that Potassium Permanganate, UVAS and TOC are currently used as alternatives. Potassium Permanganate is currently being used in Japan as a replacement to the Dichromate-COD (MANTECH INC. 2015), where the poorer oxidizing power of Potassium Permanganate reduces the methods accuracy (incomplete oxidation of various chemicals), and where as well as a digestion time of 2-4 hours is accepted. Thus any developments in the methodology improving the quality of the test should be monitored. In India the CPCB (Central Pollution Control Board) have recognized UVAS as an acceptable parameter for monitoring COD and BOD in their waste water effluents (RealTech, 2015). Several Nordic countries have chosen to replace COD all together by TOC (Rijkswaterstaat, 2015). More background and information relating to some of the rejected alternatives shown in Table 3 can be found in Appendix 8.3.

Table 4 which is directly below Table 3 (page 16 & 17), shows the results of the final assessment and the 4 final alternatives which were judged according to the criteria list to be the most suitable options, thus revealing the results of the comparison to that of the baseline with the aim of providing an answer to the research question.

Table 3: Overview of main possible alternatives assessed and there progression through the research, along with the chief rejection criteria.

Method	**Sub Method**	**Currently Utilised as an alternative**	**Rejected**			**Reason**		
			Step 1 (Literature Review)	*Step 2 (Consultancy)*	*Step 3 (Assessment)*	*Economic*	*Quality*	*Time*
Biological Oxygen Demand (BOD)					✓			✓
Biosensors e.g.	*Ferricyanide-Mediated BOD Sensor*		✓			✓	✓	
	Hybrid Material for BOD Sensor		✓			✓	✓	
	Mediated BOD Sensor		✓			✓	✓	
	Multi-Species-Based BOD Sensor		✓			✓	✓	
COD Sensors and electrodes (Photo-electro-catalytic and Electrochemical) e.g.	*Pt/PbO_2 Ring-Disc Electrode*		✓			✓	✓	
	Fluoride-Doped PbO_2-Modified Electrode		✓			✓	✓	
	Rhodium Oxide–Titanium Electrode		✓			✓	✓	
	Boron-Doped Diamond Electrode		✓			✓	✓	
	Nano Copper-Modified Electrode		✓			✓	✓	
	Activated Glassy Carbon Electrode		✓			✓	✓	
	Cobalt Oxide-Modified Glassy Carbon Electrode		✓			✓	✓	

	Nickel Nanoparticles		✓			✓	✓	
	Nickel-Copper Alloy Electrode		✓			✓	✓	
	PeCOD,							
COD utilising alternative Oxidising agents	*Potassium Permanganate,*	✓		✓			✓	
	Manganese III,			✓			✓	
	Cerium(IV) oxide (CeO_2),		✓				✓	
	Hydrogen Peroxide,		✓				✓	
	Oxygen		✓				✓	
Nitrogen Kjeldahl			✓				✓	
Optical Sensors	*UVAS*	✓			✓			
Sensor arrays			✓			✓	✓	
Total Organic Carbon (TOC),		✓						
QuickCODultra				✓		✓	✓	
Total Oxygen Demand (TOD),				✓			✓	
Total Suspended Solids			✓	✓				
Virtual Sensors / Modelling	*Artificial Neural Networks (ANN)*		✓	✓			✓	

3.3 FINAL ASSESSMENT

3.3.1 Overview

Table 4: Overview of the assessment of the final alternatives.

	Criteria									
	Economic		***Time (min)***	***Quality***				***Continuity***	**Standardised**	**Green Method (Y/N)**
Method	**Investment Cost (€)**	**Cost per test (€)**	**Duration of test**	**Reporting Limit (mg/l)**	**Accuracy % of ThOD**	**Reproducibility % difference between Repetitions**	**Relative Standard Deviation (%)**	**Correlation Factor**		
Potassium Dichromate COD (Baseline)	2000 - 15000	3.45 - 10.5	121 - 180	5	104	8	5 - 10	N/A	NEN-ISO 15705:2003, NEN 6633:2006/A1:2007, N6634, DIN 38409, Teil41/43/44, ISO 6060, EPA 410.4, DIN ISO 15705	N
Biological Oxygen Demand (5 day)	1750 - 3500	4.84 - 16.8	7200	1	90	12	5 - 15	1.3 – 2	ISO 5815-1:2003 ISO 5815-2:2003 NEN-EN 1899-1:1998 NEN-EN 1899-2:1998 ISO 5815-1:2003 ISO 5815-2:2003 NEN-EN 1899-1:1998 NEN-EN 1899-2:1998 NEN-EN 1899-1:1998, NEN-EN 1899-2:1998, ISO 5815-1:2003, ISO 5815-2:2003, N1899_2, DIN EN 1899-1, DIN EN 1899-2, ISO 5815, EPA 405.1, Standard Method 5210B	Y

Total Organic Carbon	20,000 - 70,000	6.12 - 17.76	13 - 30	0.1	96	10	5 - 10	2.41 - 9.21	NEN-EN 1484:1997, NEN-EN 15936:2012, NWIP (NP 20236), N1485, Standard Method 5310B, EPA 415.1, EPA 9060A, ASTM D2579, ISO 8245, EN 1484 (replace of the DIN 38409-3)	Y
PeCOD	*14,000 - 70,000*	< 1.4	7 - 10	0.2	Not enough data	Not enough data	Not enough data	C/D*	Non-Known	Y
UVAS	6,000 - 7,500	0.006 -0.14	>4	>0,1	Not enough data	Not enough data	Not enough data	C/D*	Non-Known	Y

Table 4: Key

Investment Cost (€)	Cost per test (€)	Duration of test	Reporting Limit (mg/l)	Accuracy % of ThOD	Reproducibility % difference between Repetitions (R^2)	Relative Standard Deviation (%)	Correlation Factor	Standard	Green Method
A range of costs for a selection of different equipment types and setups.	A Range of costs per test, showing the differences between equipment types as well as in house and external testing	How much time does the test take	The minimum detectable limit in milligrams per litre. Each method does have a maximum limit but samples can be diluted to overcome this. Thus not reported in the Tables and Figures.	The accuracy of the method for a particular substance. (Expressed as a percentage, the optimum value is 100%)	Relative within laboratory reproducibility. The spreading (inaccuracy) of results from the method. (Expressed as a percentage, the optimum value being 0%)	The Standard Deviation given as a percentage	There is historical data concerning the water quality. Is it possible for this method to compare with this data	Has the Method been standardised and what is the standard	Is the Method Environ-mentally friendly? Does it utilise hazardous chemicals, with the potential to cause environmental damage.

***C/D = Calibration Dependent**
. = Best result

3.3.2 Economic

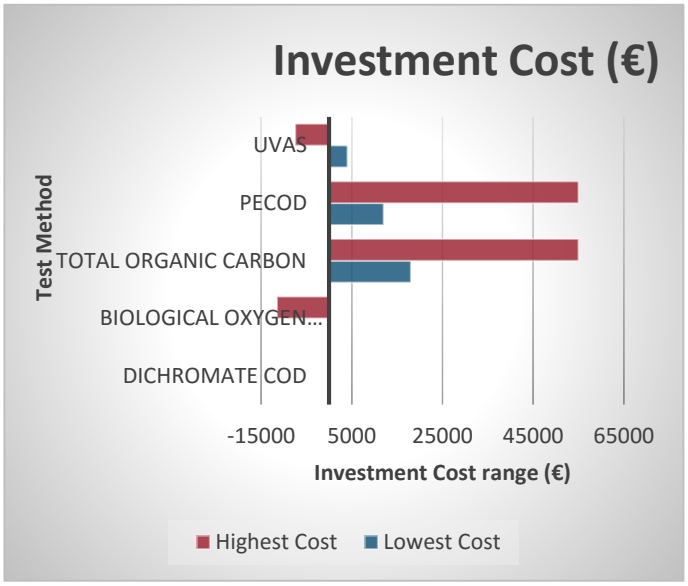

Figure 3: The Investment costs (€) for the final alternatives relative to Potassium Dichromate-COD

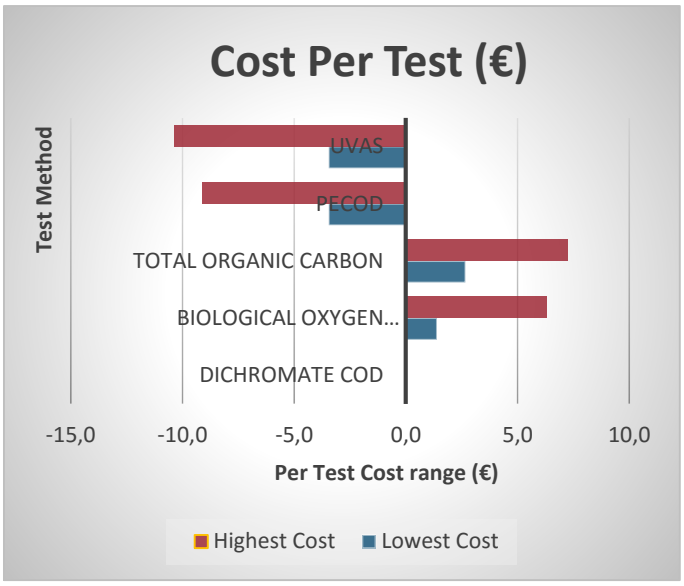

Figure 4: Cost per test (€) for the final alternatives relative to Potassium Dichromate-COD

(Pricing Data was Sourced from: Camlab, 2015 (PeCOD); Process Instruments Pi, 2015; RealTech Inc., 2015; HACH LANGE GMBH, 2015 and Hanna Instruments, 2015 (UVAS); HACH LANGE GMBH, 2015; Hanna Instruments, 2015 and Rijkswaterstaat 2015 (COD, BOD and TOC))

It can be seen from the results (Table 4) on investment costs that, in comparison to the Dichromate-COD, only UVAS and BOD have the potential to be cheaper than the Current method. Figure 3 shows the results for the range of investment costs for each of the assessed alternatives minus that of the Dichromate method, thus any presenting a negative value is a cheaper alternative. This confirms that the BOD and UVAS are the cheaper options, with TOC and PeCOD having the potential to be just as expensive. Figure 4 on the other hand depicts the associated cost range associated with the tests, hence the difference in cost per test, based on 10,000 samples tested per annum. This shows that although BOD is potentially the cheapest investment it has one of the highest costs per test. Figure 3 reveals that UVAS and PeCOD are the cheapest two alternatives assessed.

3.3.3 Testing Time

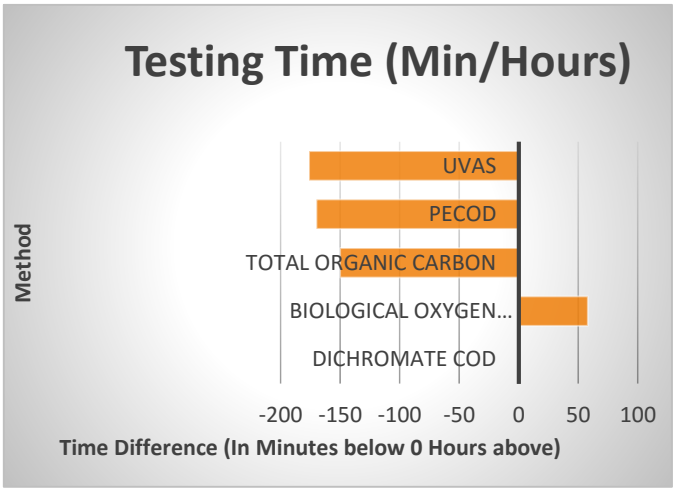

Figure 5: Duration of the test, in comparison to the current Dichromate-COD test (Data Sourced from: Camlab, 2015 (PeCOD); RealTech Inc., 2015 and HACH LANGE GMBH, 2015 (UVAS); NEN, 2015 and Rijkswaterstaat 2015 (COD, BOD and TOC)).

Figure 5, illustrates the difference in the testing times. The Figure shows the duration of the test and does not include sampling, transportation or preparation time. It must be noted that all negative numbers are in minutes whereas the positive numbers are in hours. This is due to the large time period required for BOD_5. The figure identifies UVAS as the fastest option closely followed by PeCOD.

This is owing to the fact UVAS is an online meter, where light absorption is measured and translated into the sum of pollution, thus making it a very quick test method. If however this was implemented in a laboratory then the testing time would be the same but preparation time would increase, nevertheless it would still be the fastest method. The PeCOD is a close second based on the testing time, however it must be noted that there can be a large delay caused by preparation time needed to adjust samples and equipment. However the time required to perform the PeCOD analysis has recently been reduced by extensive automation of the sample preparation and introduction procedures (Rijkswaterstaat 2015). TOC is shown to be in third place as it turns out to be slower than the UVAS and PeCOD methods but significantly faster than BOD. However when the preparation time is included TOC may be a quicker alternative than PeCOD, depending on the equipment setup used.

3.3.4 Quality

Table 5: Quality Criteria for the final Alternative Methods (Data Sourced from: Camlab, 2015 (PeCOD); RealTech Inc., 2015 and HACH LANGE GMBH, 2015 (UVAS); NEN, 2015 and Rijkswaterstaat 2015 (COD, BOD and TOC))

	Quality			
Method	**Reporting Limit (mg/l)**	**Accuracy % of ThOD**	**Reproducibility % difference between Repetitions**	**Relative Standard Deviation (%)**
Dichromate COD (Baseline)	5	104	8	5 - 10
Biological Oxygen Demand (5 day)	1	90	12	5 - 15
Total Organic Carbon	0.1	96	10	5 - 10
PeCOD	0.2	Not enough data	Not enough data	Not enough data
UVAS	<0,1	Not enough data	Not enough data	Not enough data
. . = Best result				

Table 5, shows the results for the quality criteria of the final alternatives in relation to the accuracy and reproducibility of each test. The table indicates the accuracy of the method. This is expressed as a percentage, consequently the optimum value is 100. The accuracy can be over 100 percent due to the fact that it is based on the ThOD. The ThOD is the calculation of the amount of oxygen required to oxidize organic compounds to CO_2 and H_2O (further information in Appendix 8.1). If a test oxidises more than would theoretically be oxidized in the sample, the result is over 100 percent. Table 5, shows that the current Dichromate-COD is one such method, with an accuracy result of 104 percent of the calculated ThOD. While TOC is reported to have results indicative of 96 percent of the ThOD, BOD has a result around the 90 percent margin. Therefore TOC is shown to be as accurate as Dichromate-COD, due to the fact that they both give results that deviate from the ThOD by around 4 percent.

As can be seen from Table 5, Dichromate-COD has an 8 percent spread, between results of the same sample. TOC has a larger spread by 2 percent, therefore being less precise, thus reproducible. BOD has another 2 percent from TOC and so 4 percent less reproducible in comparison to the Dichromate-COD. The last column in Table 5 states the standard deviation from the mean for the results of the alternatives given as a percentage. This is given as a range as it differs in relation to water type. This shows yet again that the TOC is equal to the Dichromate method, with BOD having a wider spread.

Unfortunately there was not enough data available for good estimations for the PeCOD and UVAS as they are not currently in standardised use. However it is indicated that the accuracy of UVAS for COD readings is dependent on the correlation with the Potassium Dichromate-COD (RealTech Inc**.,** 2015). This in turn depends on calibrations which are recommended to be site specific. This is subject to the variations in the water matrix of different industries waste water discharges, so the accuracy and reproducibility are not well known without implementation. The PeCOD is currently on trial at RWS and as a result more data regarding this method should soon be available.

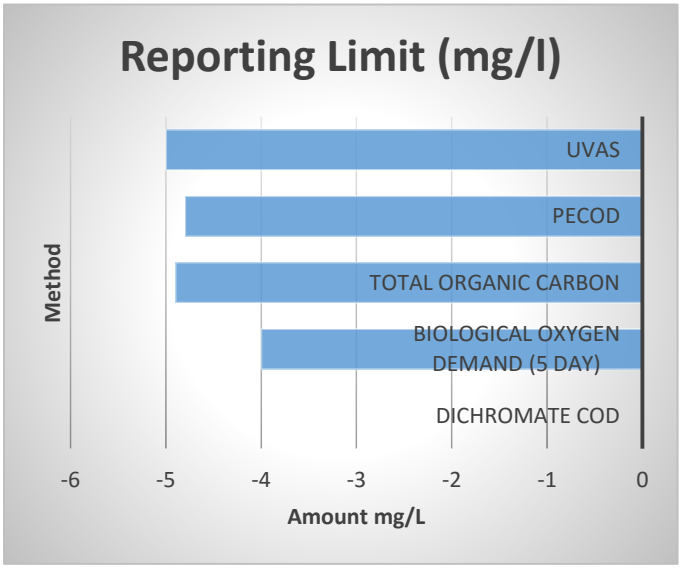

*Figure 6: Detection Limit of the Final alternatives in relation to Dichromate-COD (Data Sourced from: Camlab, 2015 (PeCOD); RealTech Inc**.,** 2015 and HACH LANGE GMBH, 2015 (UVAS); NEN, 2015 and Rijkswaterstaat 2015 (COD, BOD and TOC)).*

Figure 6 shows the minimum Reporting limit of the methods which is also shown in table 5 above. However the figure shows a comparison between the alternative methods and that of the Dichromate-COD test.

The results reveal that the UVAS has the lowest reporting limit as it measures absorbance, demonstrating it has the potential to identify the presence of even the smallest amounts (<0,1mg/l), of pollutants. This is followed by TOC which also has a very low detection limit. Figure 6, shows that out of four final methods the BOD_5 has the highest detection limit. This can vary with the sample water matrix and seed/method used. The detection limit is generally reported as no lower than 1mg/l.

It must be noted though that the baseline method is known to be susceptible to interference by chloride and bromide ions. This interference is especially prone when levels of chloride top the COD level by a factor of 100. The stated sensitivity can be strongly reduced and will not allow the determination of COD beneath 30 mg/l. The BOD, TOC and UVAS methods are not or to a much lesser degree affected by high chloride and bromide levels.

3.3.5 Continuity

The results in this section are focused on the possibility of correlating the results from the different alternatives to the historical pollution data, which consist of the results from Dichromate-COD testing. This then provides the ability to continue monitoring the effects of pollution control measures.

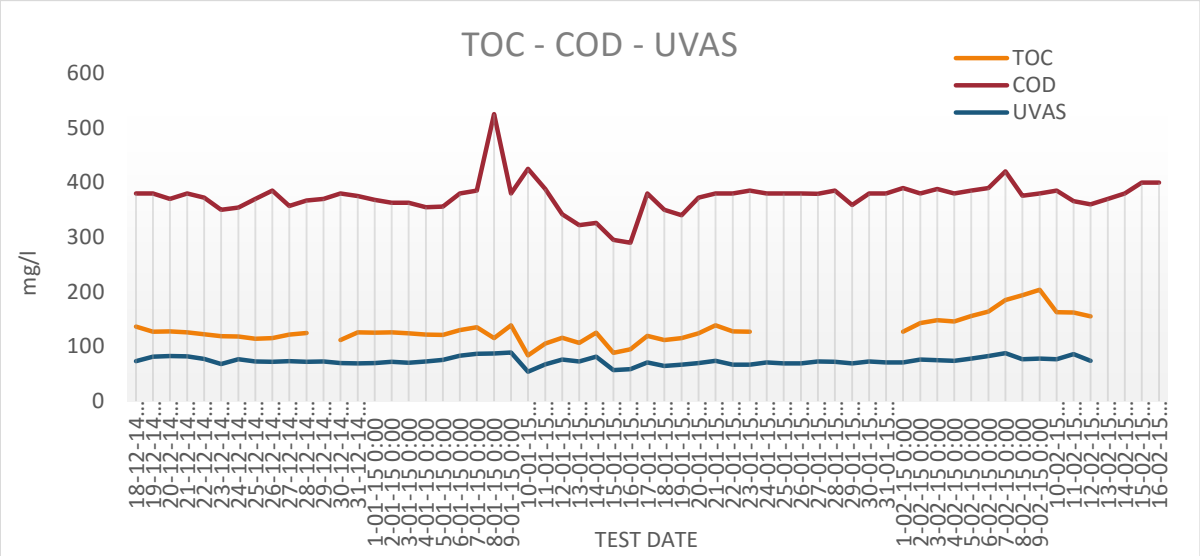

Figure 7: Comparison of Dichromate-COD, TOC and UVAS test results from over a 3 month period (Data scoured from Rijkswaterstaat, 2015).

Figure 7 above, represents the pollution level results for a company's discharged water, measured by RWS, over a 3 month period. The results are for Dichromate-COD, TOC and UVAS. There are two periods without TOC data as there was a problem with the sampler. From the above figure the relationship between the three indicators looks good. The Dichromate-COD has the highest values, which is as expected, but the other two although being lower show the same pattern. Nevertheless it is too early to judge and there is not enough data for a conclusion. Therefore in Figure 8 below the ratios between these results are shown.

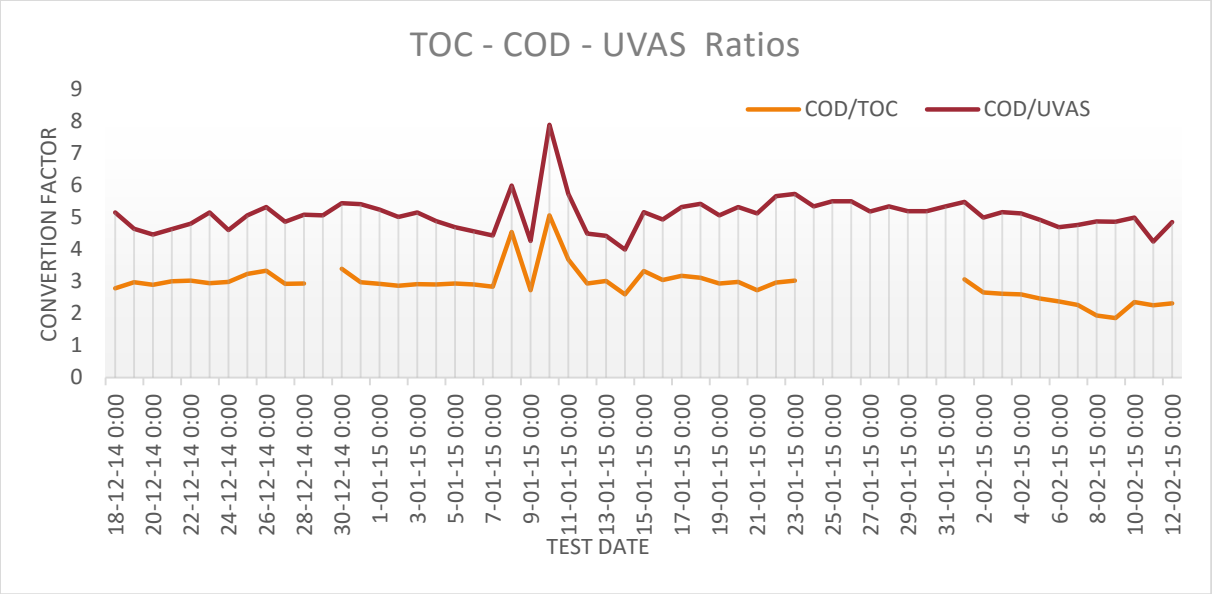

Figure 8: ratios between the results in Figure 7 (Data scoured from Rijkswaterstaat, 2015).

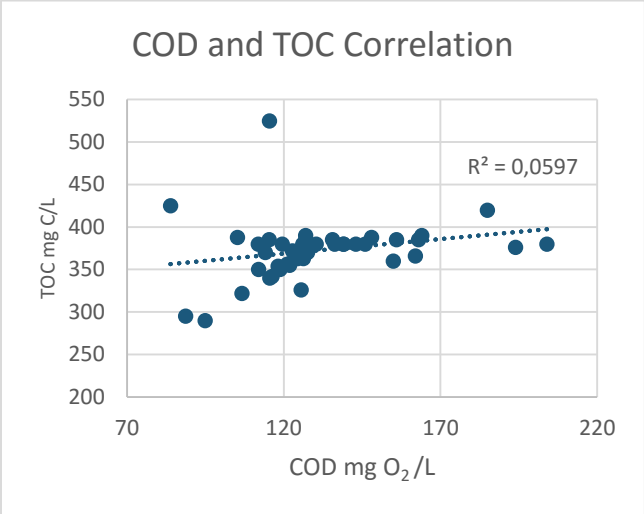

Figure 9: COD and TOC Correlation for one company over a three month period (Data sourced from Rijkswaterstaat, 2015).

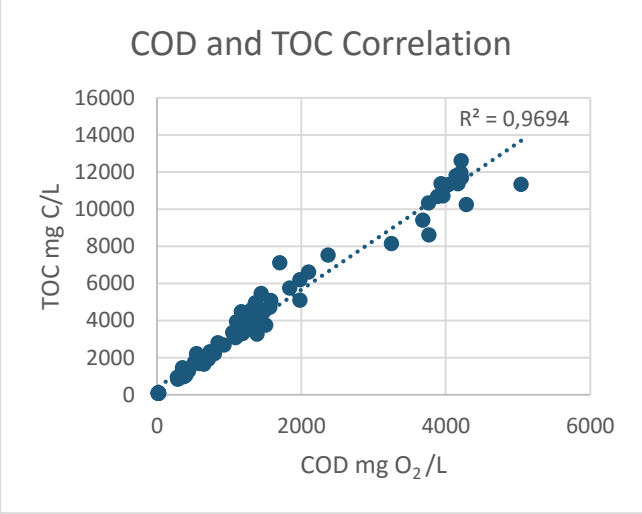

Figure 10: COD and TOC Correlation for ten different companies (Data sourced from STOWA and Aqualab Zuid B.V. 2015).

At first the results depicted in Figure 8, appear good as they both show the same pattern. However this is not the case. This graph reveals the fluctuations in the ratio between the different methods. Over this 3 month period there is a maximum ratio for TOC of 5.07 and 7.91 for UVAS. The lowest ratios identified were 1.86 and 4 respectively, with the means being 2.94 and 5.1. This is further seen in Figure 9, which identifies the correlation between the Dichromate-COD and TOC methods. The data is derived from the same company as in Figures 7 and 8. In Figure 9 an extremely small R^2 value is seen (0, 06), revealing an undeniably very poor correlation. UVAS had a better R^2 (0.15) for the same correlation as in Figure 9 (Figure 12, in Appendix 8.4), however it was excluded from further correlation owing to insufficient data.

Figure 10, illustrates the correlation between Dichromate-COD and TOC, showing data from ten different companies. This correlation shows that with the inclusion of more data points representing a broader

sample matrix a better correlation (R^2 = 0.97) can be obtained. This indicates the evaluation period of three months used appears to be insufficient to achieve a good correlation.

4 DISCUSSION

As stated earlier this research started with the development of a criteria list in which to compare and assess alternative test methods. The criteria list is the first point of discussion. This will be followed by a brief discussion on the results along with any additional considerations regarding the final alternatives. This will then be followed by recommendations.

4.1 CRITERIA

The criteria list was created with the purpose of providing a basis of comparison for the alternative test methods as well as the foundation in which to choose the alternatives to be assessed. The choice of a suitable alternative based on these criteria depends on the requirements of the implementing body and the weighting they associate with each of the criteria.

4.1.1 Economics

This criteria was comprised of two parts. Firstly that of investment cost and secondly the cost per test. This is the most important criteria from a business perspective due to the large effect on potential users. With this consideration in mind, an investment cost limit of around €100,000 was used as the criteria for acceptance into the final assessment, alongside a cost per test limit of €25-€30. However, the guiding principle from all consultations was the cheaper the better. Thus any alternative found or judged to be in excess of these limits was rejected and not included in the final assessment.

The results for this criteria are given as an estimated price range for each of the alternatives, for both investment and cost per test, as each one has differences in the equipment set-up, thus affecting costs. There are certain factors to be considered, which may cause deviations in the costs. Firstly that of economies of scale. The prices obtained are based on one equipment set, thus for larger companies or organisations requiring multiple sets this may lead to a reduction in the cost. The supplier also must be noted as prices vary between brands and suppliers.

The equipment size and test methodology is also important, as there is often a choice to be made. The choice concerns how many sample sets are required to be tested, as smaller sets are naturally cheaper. Also as can be seen in Table 4, from the standards some of the alternatives have different standardised methodologies. Thus all of these values are subject to change creating uncertainty. The reason for giving a range of costs was to try to reduce the level of uncertainty within this criteria.

However it must be noted that the higher BOD price can be double that of what is stated, due to the fact that the €3500 listed is for a 6 sensor table top laboratory unit. The equipment is also available with 12 sensors for double the price. The costs associated with PeCOD have a large range for investment, due to the differences in options. The basic bench top unit is around €14000, the online version is just under €40000. There is then the option of adding other parameters and features such as; pH, phosphate, and nitrogen, along with the possibility of automation for multiple samples increasing the cost up to around €70,000, which is also the case for TOC. Depreciation associated with the investment costs, was not assessed within this research because of the large variations in testing schedules of the involved parties. The differences in testing timetables, the wear and thus the depreciation associated with the testing equipment has the potential to differ greatly between companies, creating a large amount of uncertainty. It would be impossible to give an accurate prediction as it can only be achieved with acceptable uncertainty levels on an individual basis.

The cost per test was calculated from the calibration solutions required and consumables (e.g. replacement bulbs for UVAS) divided over the lifetime of the consumable and 10000 tests a year. This however is an estimation and therefore contains uncertainty. The UVAS is mainly an online (constant in-situ monitoring) method with cost per test differences being mainly due to the light source as each bulb has a different life span and cost. The cost per test, for all alternatives was calculated in this way and included all consumables but it does depend on how often the calibration and test sets are run which provides more uncertainty within the results for this criteria.

4.1.2 Quality

This criteria is derived from the accuracy, reproducibility and the reporting limit of the alternatives. As can be seen from Figure 11, both accuracy and precision (reproducibility) are required together. Precision is designated in Table 5 as the reproducibility between repetitions, alternatively known as the relative within laboratory reproducibility. Thus the reproducibility is how precise the method is, and so in the context of this quality criteria it is interchangeable as it represents the spreading (inaccuracy) of results from the method which is stated as a percentage, the optimum being zero percent. Therefore the accuracy represents the closeness of the result to the true value, and the precision/reproducibility represents the difference in the results when assessed under the same conditions.

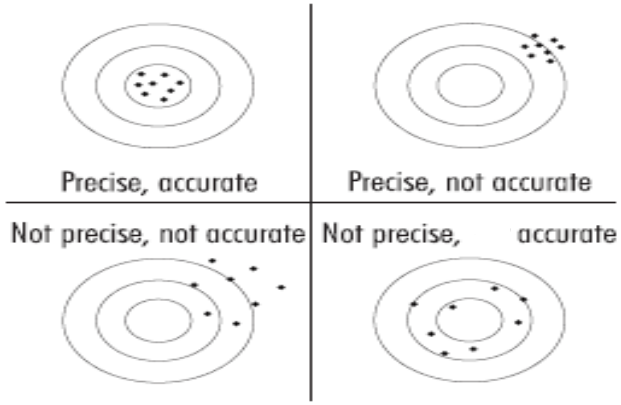

Figure 11: Difference and relation between Precision and Accuracy (Source: Hanna interments 2015)

Consequently indicating how reliable the test results are. This criteria in this way looks at the uncertainty of the results given by the alternative test methods, with the thresholds being set at 10 and 15 percent respectively, for accuracy and reproducibility. As seen in Table 5, BOD was at the criteria threshold.

All of the methods included in step 3 have a detection limit below that of the current method, as it was judged that anything much higher than 5 mg/l was not satisfactory. Consequently any alternative that could not detect pollution levels around 5 mg/l or lower were rejected within the literature review or consultancy phases. This can be seen with TOD in Table 3 the reporting limit was judged too high. The standard for TOD stated that lower detection limits were possible but at the cost of accuracy and reproducibility. Thus it was rejected after consultancy with NEN and Aqualab Zuid B.V.

All the data for this criteria was found within standards where possible. If there was no standard for the test methods other literature was used or the manufactures were consulted. However the data collected for PeCOD and UVAS was judged to be insufficient to include. The data for accuracy and reproducibility that was obtained was constructed from a small data set and therefore the uncertainty was too large to be reliably included within the assessment (standard deviations based on two data points etc.). The data for the current Potassium Dichromate COD, BOD and TOC are included because they are well documented so reducing the uncertainty around these methods.

4.1.3 Continuity

It is important to find trends and monitor progress when looking at policy implementation, especially when looking at water pollution. The continuity criteria is based on this and to assess the possibility of a correlation between the alternative methods and that of the Potassium Dichromate COD test. As shown in chapter 3, the determination principle of each alterative test method is different. It identifies and highlights different portions of the water sample which is influenced by the diverse compounds in the wastewater they measure. Due to this, a simple conversion factor from one parameter to another is difficult to derive,

with the relationship between many of the alternative methods being empirical. Precise values depend on the matrix influence, molecular structure and potential of oxidation.

The correlation factor associated with UVAS will depend on the particular organic water quality matrix being measured. This means that correlations are site and application specific and so the correlation factor must be determined at the measurement site. The correlation for UVAS showed a better initial correlation with the Potassium Dichromate-COD, than TOC in the results, but was not tested further due to insufficient data. Nevertheless it has been shown that municipal waste water as well as most natural water sources such as raw water for drinking water have a good correlation between COD and UV254 absorption. Numerous investigations have demonstrated the comparability between UVAS and COD, such as Baumann & Krauth, 1994, who observed a R^2 value of 0.94 between COD and UVAS from measurements in a primary settling tank (HACH LANGE GMBH, 2015 and RealTech, 2015).

The Correlation between TOC as seen in chapter 3 is uncertain but shows a good potential to have a good correlation over effluent waters as a whole. This however does lead to a choice that needs to be made. The decision on whether to opt for a single conversion factor, one figure applying to all effluent waters or multiple correlation factors based on water type. In order for the right decision to be made further research is needed with a larger data set in order to reduce the uncertainty around the correlation factors.

4.1.4 Feasibility

This criteria was mainly utilised within the first two phases of this research. Any alternative test method had to be possible in order to reach the final assessment phase. Thus any alternatives that could not be easily implemented were rejected. This included highly complicated test methodologies or methods incorporating rare materials etc. like e.g. diamond electrodes (Wang et al 2012a and Yu et al, 2007), though it must be noted that synthetic diamond significantly reduces cost, and diamond does have high durability.

4.1.5 Time

The duration of the test is very important in pollution control. The quicker a monitor knows that they are over the water permit levels, the faster the response time. The current method has a digestion time of two hours though the full testing time is around three hours (ISO 6060). Three hours were used as a guide for the time criteria for acceptance into the final assessment. An exception was made for BOD due to its long history and wide spread use as a pollution indicator. There is now however, a move to online testing which enables a shorter response time. On-line equipment is an in-situ measurement which is directly converted to a result, whereas laboratory testing needs a sample to be taken, transported to a laboratory and analysed. This may add a large amount of time to the testing procedure. For the purposes of this research only the testing time was incorporated within the results section. The sampling transportation and waiting times as well as the preparation times varied considerably from place to place causing the uncertainty in calculating a reliable time frame without actual testing to be too great. It must be noted that TOC, PeCOD and UVAS are all available as on-line methods, consequently the decision to only directly compare the testing time was taken, to remove some of the uncertainty.

4.1.6 Green Test

To achieve acceptance into the final assessment it was deemed necessary that the alternative method being assessed, must be a green method. As it was judged necessary in order to attempt to prevent the same scenario occurring in the future. Hence why all the alternative methods in the final assessment are shown as being green methods. It must be noted though that the UVAS method which was reported as a

Green method, indicating that it is environmentally friendly can however in some of the equipment sets, have the option to use mercury bulbs. Hence it is suggested that an alternative bulb be used or appropriate disposal/recycling of old bulbs is implemented to ensure a green method, if this alternative is utilised.

4.1.7 The Final Alternatives and Any Additional Considerations

4.1.7.1 BOD

Biological oxygen demand (BOD) also known as the Biochemical oxygen demand is still based on the same concept as when it was established in 1908. BOD was the first test for organic pollution in rivers (Ingols & Murray, 1948). It is perhaps the most important oxygen demand measurement for the analysis of the organic content of effluents and receiving waters (Boyles 1997 and Young et al, 2003).There are a variety of BOD techniques, in all cases the test sample should be at a temperature of 20 ± 2°C and in case of aeration the sample should stand for approximately 15 min to help remove air bubbles and possible super-saturation of oxygen. The main BOD_5 test can be carried out in an undiluted method or in a diluted method with added seed (ISO 5815-1:2003).

The BOD method has been the most widely used method to measure organic pollution in water samples and is still commonly used today as a pollution indicator. This is because of its broad applicability to different types of samples as well as its simplicity (Liu, 2014), since it requires no expensive equipment. Consequently BOD has the lowest investment cost of the final options.

Due to the prolonged incubation time, it is not suitable for the monitoring or control of wastewater treatment systems where fast feedback is necessary (Raud et al, 2012b and Pittman et al, 2015). This coupled with, the fact that BOD is less accurate and precise than TOC (Roeleveld & Van Loosdrecht, 2002), it is not recommended as a suitable alternative. It was included however because it remains a prominent and important pollution indicator.

4.1.7.2 PeCOD

The photo-electro-chemical oxidative degradation principle is commercially available as the PeCOD system. This nanotechnology based approach is currently deployed at nearly 100 sites around the world and used in a variety of sectors including regulatory agencies, academic laboratories, industrial facilities, food and beverage producers and municipal water treatment facilities (Camlab, 2015).

This approach is recorded in the results as having an analysis time of 7-10 minutes, a significantly reduced time to that of the dichromate-COD. However it must be noted that there is a long preparation time consequently extending the working time of this method. The preparation time may be reduced with the incorporation of the automated equipment setup, but this leads to a higher end regarding investment cost.

There was inadequate data to satisfy the quality criteria though there is a trial currently being run at RWS. At the end of this trial period (2015/16) there should be sufficient data to fill the criteria specified within this paper, which will help to reduce the large amount of uncertainty involved with this method.

4.1.7.3 TOC

Several Nordic countries have chosen to replace in legislation the determination of COD altogether with TOC (Rijkswaterstaat, 2015). Despite the fact that TOC is a convenient and direct expression of total organic content, TOC does not entirely provide the same information as COD. TOC is, unlike COD, not dependent on the oxidation state of the organic matter, neither is it a measure for other organically bound elements, such as nitrogen and hydrogen and inorganics that would contribute to the oxygen demand measured.

Total Organic Carbon (TOC) is an indirect measure of organic molecules present in water and measured as carbon. Organic molecules are introduced into the water from the source water, from purification, and from distribution system materials (Rand et al, 1976). TOC is measured for both process control purposes and to satisfy regulatory requirements such as the European Drinking Water Directive. The Directive is intended to protect human health by laying down health and purity requirements which must be met by drinking water within the EU. The directive applies to all water intended for human consumption apart from natural mineral waters and water which are medicinal products. The European drinking water directive includes the category of indicator parameter value specifications of which TOC is one. However it has not been assigned a limiting value or criterion but can be considered as a cautionary warning for action under unusual circumstances (Schumacher, 2002).

This method shows a range of possible costs for the different methodologies. There are differences between the High Temperature and Wet-Chemical Oxidation methodologies, the laboratory table top or online equipment and the cuvette option. This alternative has the potential to be more costly than the current Dichromate method, for both investment and per test. However it is stated in the standards to be just as accurate if only a little less precise than the current method (NEN-EN 15936:2012). TOC has the second lowest detection limit of the finalists and is much faster than the current method.

4.1.7.4 UVAS

Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to the absorption spectroscopy (UVAS) or reflectance spectroscopy in the ultraviolet-visible spectral region. It is also known as SAC (spectral absorption coefficient). This method uses light in the visible and adjacent wave lengths. The absorption or reflectance in the visible range directly affects the perceived colour of the chemicals involved. (RealTech Inc., 2015 and HACH LANGE GMBH, 2015).

Absorption measurements are very common in the laboratory and in the field since absorbance at a given wavelength is proportional to the concentration of any substances in the water that are known to absorb light at the given wavelength. UV_{254} refers to the UVAS measurement utilising the light wavelength of 254nm. Light at the 254nm wavelength is of particular interest since it is a wavelength that is very readily absorbed by organic matter present in water. Since the UV_{254} absorbance method is proportional to the concentration of organics in the water, it is a simple process to determine a linear correlation factor (R^2), relating to the Dichromate-COD test (RealTech Inc., 2015 and HACH LANGE GMBH, 2015).

The application of UVAS is attracting a lot of interest lately, especially in India with the CPCB (Central Pollution Control Board) which has recognized UV as an acceptable parameter for monitoring COD and BOD in its waste water effluents (RealTech Inc., 2015). Unfortunately the accuracy of the UV method depends on the calibration set used. Consequently it is necessary to use the COD test to initially calibrate the instrument followed by periodic checks of the instrument and calibration. To help improve the accuracy and precision, there is the option to test with more wavelengths.

For very complex water (i.e. Industrial processes) RealTech Inc., recommend their PL-series as it provides more stability in the measurements. For basic applications and general indications of changes, the M-series maybe enough. The main difference is that the M-series uses a single UV wavelength (254nm) and the PL-series uses the full UV and Visible light spectrum (700+ wavelengths). The equipment type, affects the cost, however the costs associated with this method are one of the lowest out of the final alternatives, which is due to the simple equipment needed.

4.2 RECOMMENDATION

From an economic perspective the results indicate that the PeCOD and UVAS methods are the most desirable in the long run due to the low running costs. However the available data regarding the quality criteria for these two methods is insufficient. Also they have not been standardised which is a long process (5-10 years by NEN). A consequence of implementing a method without a standard is the creation of the possibility of different methodologies being used with variations in results. Thus for the governing body trying to enforce restrictions, this may become difficult. Therefore these two methods cannot be recommended. Also UVAS is site and water matrix dependent, requiring periodic recalibration, making UVAS unsuitable for use by RWS, as it is unrealistic to calibrate for every discharger monitored.

Due to the fact that the PeCOD and UVAS cannot be recommended at this point, TOC is the last alternative as BOD is not suitable for monitoring or control of wastewater treatment systems where fast feedback is necessary (Raud et al, 2012a and Pitman et al, 2015). Also BOD is less accurate and precise than TOC (Roeleveld & Van Loosdrecht, 2002) and is not recommended as a suitable alternative.

TOC has a lower detection limit than the current method which is a prerequisite for recommendation as TOC-values will in all cases turn out lower than corresponding COD-values by a factor of 2 to 4. Moreover TOC is just as accurate, if not a little less precise/reproducible. It is standardized, environmentally friendly and available in different equipment sets. It also has a greater versatility and fits into current processes easily and is not hampered by high loads of salt. Therefore, the feasibility of implementation is very good. This method is also specified and in use due to the European Drinking Water Directive, meaning most laboratories currently working with water will already have the equipment needed to perform this test. It has also been shown that a correlation with the Potassium Dichromate-COD can be made. Concluding that at this point out of the assessed alternatives this is the recommended method.

4.2.1 Next Step

The PeCOD shows a great deal of promise. The main reason it was not recommended was owing to a lack of reliable data, though early indications are good (MANTECH Inc. 2014; Camlab, 2015 and Rijkswaterstaat, 2015). PeCOD is currently on trial at RWS, after which time there should be more data available for further assessment. Therefore this method cannot yet be dismissed until this further assessment has been completed.

The correlation between TOC must be assessed further. As shown in the results section, when looking at one company over a short time period, the correlation is not great. However the correlation improves vastly with the size and diversity of the data set used. An accurate data set for correlation must be created, and assessed, to ensure an even and fair transition of taxation schemes.

An assessment on which TOC methodology to implement must be completed. Although the current methodologies have a good correlation (Rijkswaterstaat, 2015), NEN is currently reviewing a new TOC standard, which may influence the methodology and so will need to be evaluated.

5 CONCLUSION

In recent years some interesting new organic pollution test methods have surfaced, along with alterations of older methods, in the pursuit of improvement. This report has reviewed some of these alternative methods. Methods such as the Potassium Permanganate (Lie et al, 2003 and Zenki et al, 2006), and UVAS (RealTech, 2015), which are currently used for monitoring and enforcement purposes in Japan and India respectively, along with TOC which is used in some Nordic countries as an alternative pollution control and monitoring test, to that of the potassium Dichromate COD.

Additional potential alternatives were also identified throughout the research, such as the QuickCODultra, or methods using Biosensors or the use of alternative Oxidising agents e.g. Manganese III, Cerium (IV) oxide or Hydrogen Peroxide. Some showed promise however there is a general need for further research on these methods as they are far from being a suitable replacement as they all failed on one or more aspects within the criteria. These included limitations in detection limits, accuracy, reproducibility and time issues (Liu & Mattiasson, 2002; Raud et al, 2012a & b; Lagarde & Jaffrezic-Renault, 2011; Moretto & Kalcher, 2014 and Ponomareva, 2011). BOD being an example of a method being rejected due to an extended testing time.

Out of the four finalists assessed on the criteria as per the research question, the top candidate was TOC. This is due to its accuracy, its present wide spread use and its extended state of Standardisation. The PeCOD method is a strong contender but still lacks sufficient data. The same can be said for UVAS. Due to the ease of implementation and low cost, it would be another viable option, if not for the site specific and periodic calibrations needed. So it is important to find a good correlation between methods. The measurement of each alternative method is different however, influenced by the diverse compounds of the wastewater measured. Due to this fact deriving a simple conversion factor from one alternative to another is difficult, with the relationship between many of the alternative methods being empirical. Precise values depend on the matrix influence, molecular structure and potential of oxidation. Thus further assessment and research into the correlation of specific standardised methods is necessary and to ensure the selection of the most suitable method, the results of the PeCOD study when finished, should also be taken into account.

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7.1.2 Standards

All standards used where obtained though NEN and Rijkswaterstaat.

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8 APPENDIX

8.1 THEORETICAL OXYGEN DEMAND (THOD)

When looking at the amount of oxygen required to oxidize organic compounds to CO_2 and H_2O, it is possible to calculate the theoretical amount provided the exact composition of the water is known. This theoretical amount will therefore not be assessed within this paper as a possible replacement for the Dichromate-COD test, as the samples would require full chemical analyse to identify every substance and the quantity thereof within the sample. This is not a realistic perspective due to cost and time factors. However it is noted due to the fact that the Industry Standard COD testing is based upon the theoretical amount of oxygen required to oxidize organic compounds, as well as most of the other oxygen demand testing procedures (Rijkswaterstaat, 2015 and waterregeling Article 7). It is also regularly used as a means to assess accuracy of the tests, by means of identifying a percentage of the ThOD identified by the test.

When calculating the theoretical oxygen demand it is normal to use a standard solution with a known compound. This can be achieved with a variety of substances such as glucose ($C_6H_{12}O_6$) or the most commonly used standard Potassium Hydrogen Phthalate (KHP) ($C_8H_5KO_4$). This being the standard used as a calibration check in the NEN-ISO 15705:2003, which is a source of the baseline used within this paper. The theoretical oxygen demand of KHP is calculated as follows:

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

As shown 7.5 molecules of oxygen, oxidise one molecule of KHP. So, the theoretical oxygen demand for KHP on a weight basis is: 1.175 mg O_2 per mg KHP. The test results are expressed in these terms, as mg/L COD or mg/L O_2. Thus the results being expressed in equivalence.

8.2 CHEMICAL OXYGEN DEMAND

The Chemical Oxygen Demand (COD) test uses a strong chemical oxidant in an acid solution and heat to oxidize organic carbon to CO_2 and H_2O. By definition, chemical oxygen demand is *"a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant."* (Rand et al, 1976) However more recently the International Standards Organisation (ISO), has set the standard COD test as that of the Dichromate-COD test, in the ISO 6060. This has the accepted definition of COD as the *"mass concentration of oxygen equivalent to the amount of dichromate consumed by dissolved and suspended matter when a (water or sludge) sample is treated with that oxidant under defined conditions."* (ISO 6060)

8.2.1 History of COD

In 1908, BOD was the test for organic pollution in rivers. A time period of 5 days was chosen as an appropriate test period because this is supposedly the longest time that river water takes to travel from

source to estuary in the UK (Ingols & Murray, 1948). However there was a demand for a test with a shorter time period.

For more than 150 years efforts to anticipate and quantify the oxygen reduction effects of organic wastes on receiving water have been continuing. This has led to the launch of the development of methods to determine COD. The earliest attempts to examine the oxygen consumption in water and wastewater caused by pollution used a permanganate test. This was achieved by mixing a permanganate solution with sample water with the observation of the resulting colour changes representing (Miller et al, 2001). However, the permanganate test does not directly correlate with the results of the BOD test partly due to a lack of oxidation power of permanganate, in many cases BOD measurements were often much greater than results from COD measurements (Moore et al, 1951)

The first attempts to use dichromate instead of permanganate to oxidize organic matter date from the period 1925 to 1930 (Adeney & Dawson, 1926). In 1949 Moore *et al,* applied the dichromate COD test to wastewater analysis. This allowed the oxidation of many more compounds to be obtained by boiling samples with dichromate under reflux in a 50% sulphuric acid solution, at a temperature between 145-150 ºC for 2 hours. Using this procedure approximately 90% of the organic matter present could be oxidized as well as essentially all of the chloride, the latter for which would be corrected for (Moore et al, 1949).

The next step was in 1951 by Moore *et al* with the addition of a small amount of silver sulphate to the test mixture to help catalyse the oxidation. Consequently obtaining nearly quantitative results even with several relatively inert compounds like carboxylic acids and aliphatic alcohols present. Dobbs *et al.* 1963 took the next step to deal with the oxidation of chloride. This was with the introduction of mercuric sulphate to eliminate the chloride interference. From that time a separate chloride analysis was no longer necessary.

8.2.2 Dichromate-COD

COD relies on chemical oxidation with a strong oxidizer. Dichromate has been used to oxidize organic matter for more than 70 years. It has been preferred over other oxidants because of its superior oxidizing ability on a large variety of samples, and for its ease of use (Pisutpaisala & Sirisukpocac, 2014). The test measures the oxygen equivalent of the amount of organic matter oxidized by potassium dichromate in a 50% sulphuric acid solution. A silver compound is added as a catalyst to promote the oxidation of certain classes of organic compounds. A mercuric compound may be added to moderate the interference from chloride ion oxidation. The sample is heated for two hours in which time the oxidisable organic compounds react reducing the dichromate ion to the green chromic ion.

There are two main digestion methods used in the COD test: the older Macro Digestion Method, and the Micro Digestion Method. The Macro Digestion Method requires a considerable amount of space, equipment and volume of reagents for each test. Each set-up includes a flask, a glass condenser with hose, a hot plate, a laboratory stand, and clamps. Sample volumes are also relatively large. Because of these inconveniences, the macro method has been virtually replaced by the micro method (Rand et al, 1976). The Micro Digestion Method minimizes reagent consumption and reduces the required space and equipment to one reactor block that will digest up to 25 samples at one time. Each test set-up is a self-contained disposable vial, which is inserted into a block heater. Reagent and sample volumes are considerably smaller, which decreases reagent cost and waste volume.

The two-hour digestion time can be reduced if caution is observed. Many types of waste are digested completely in 30 minutes or less at 150 °C (ISO 6060), the normal operating temperature. The time of complete digestion can be recognized through experience, or by using a colorimetric reading with the micro method discussed later. In this approach, many consecutive readings are taken on a single sample,

allowing a final determination of when the reaction is complete. After the oxidation step is completed, the amount of dichromate consumed is determined titrimetric-ally or colorimetric-ally. Either the amount of reduced chromium or the amount of unreacted dichromate can be measured. End products of the reaction are CO_2 and H_2O, and various states of the chromium ion. In all cases the results are given in milligrams of O_2 consumed per litre of sample water.

8.2.2.1 Dichromate-COD Result determination

When organic matter is oxidized by dichromate in sulphuric acid, most of the carbon is converted to CO_2. Hydrogen present is converted to H_2O. The reaction is illustrated below, as it was for the ThOD above, using the primary KHP standard:

$$2\ KC_8H_5O_4 + 10\ K_2Cr_2O_7 + 41\ H_2SO_4 \longrightarrow 16\ CO_2 + 46\ H_2O + 10\ Cr_2(SO_4)^3 + 11\ K_2SO_4$$

Dichromate ions ($Cr_2O_7^{-2}$) form orange-coloured solutions. However when dichromate is reduced to chromic ions (Cr+3), the solution becomes green. Intermediate states can also occur, and this is the bases for the results of the COD test. The standard reduction potential, E° (25 °C vs Normal Hydrogen Electrode, pH = 0) is approximately 1.36 volts. The actual potential will vary in accordance with temperature, pH, and the ratio of dichromate to chromic ion concentrations according to the following equation:

$$E = E° + \frac{0.0001983\ T}{6} \log \frac{[H+]\ [Cr_2O_7^{-2}]}{[Cr^{+3}]^2}$$

However as stated above there are two methods utilised for the determination of results for the COD test. Firstly the Titrimetric determination will be outlined followed by the colorimetric method.

8.2.3 Titrimetric Technique

To begin with the inside walls of the testing tube containing the digested sample must be rinsed with less than 1 ml of water complying with Grade 3 from ISO 3696:1987, otherwise, quantitatively transfer to another suitable container. Once this is complete add one drop of Ferroin indicator into the container whilst swirling the sample. If there is a direct colour change from blue-green to orange-brown, the COD value of the original sample is higher than the range of the method. Therefore the sample must be diluted and the digestion step repeated. However if the colour remains lime green, titrate whilst swirling the solution with ammonium iron(II) sulphate Solution (FAS) (as described in NEN-ISO 15705) until the sample changes from a greenish-blue colour to an orange-brown. The volume of FAS required (V_2 ml) needs to be recorded. Following this a digested blank using water instead of a test sample must be titrated, with the volume of FAS required (V_1 ml) also recorded. Once this is finished it is then possible to calculate the COD, expressed in milligrams of oxygen per litre, using the equation:

$$COD = \frac{8\,000\ c(V_1 - V_2)}{V_0}$$

Where

- 8 000 is the molar mass of ½ O_2 (i.e. O), in milligrams per mole (mg/mol);
- V_0 is the volume of the test portion before dilution (if any), in millilitres (ml);
- V_1 is the volume of ammonium iron (II) sulphate used in the titration against the blank, in millilitres (ml);
- V_2 is the volume of ammonium iron (II) sulphate used in the titration against the test portion, in millilitres (ml); and
- c is the concentration of the ammonium iron(II) sulphate in moles per litre (mol/l), as calculated by;

$$c = \frac{0{,}5 \times 0{,}1 \times 6}{V} = \frac{0{,}3}{V}$$

Where

- V is the volume of ammonium iron (II) sulphate solution consumed, in millilitres (ml);
- 0,5 is the volume of dichromate solution, in millilitres (ml);
- 0,1 is the concentration of dichromate solution, in moles per litre (mol/l);
- 6 is a factor: 1 mole of dichromate is equivalent to 6 moles of ammonium iron (II) sulphate hexahydrate.

8.2.4 Colorimetric Technique

If the cooled digested samples show no visible turbidity, the results can be directly read from a spectrophotometer or by comparison against a calibration graph as outlined in NEN-ISO 15705. This is achieved by measuring the absorbance of the digested sample at 600 nm using a spectrophotometer. Conversely if any of the cooled digested samples appear to be turbid, they should be centrifuged at 4000*g* ± 200*g* for 5 min ± 0, 5 min. If the digestion solution is no longer turbid, the measurement of the absorbance at 600 nm using the photometer can be carried out. The results should be recorded and if any results are outside the working range, the analysis must be repeated with a dilution of the original sample. Calculate the COD, expressed in milligrams of oxygen per litre, up to three significant figures as read off from the calibration graph, depending upon the concentration found if however the solution is still turbid, or if the digest possesses an abnormal colour, it is recommended to follow the titration method.

8.3 Eliminated Alternative Methods

8.3.1 Biosensors, Sensor arrays and Artificial Neural Networks.

A biosensor by definition is: ‘a self-contained integrated device capable of providing specific quantitative analytical information’. Biosensors consist of a biological recognition element (Luong et al, 2008; Lagarde & Jaffrezic-Renault, 2011 and Su et al, 2011), combined with a suitable transducer e.g. electrodes (Thévenot et al, 2001 and Xu & Ying, 2011). The biological component produces a biochemical signal

which is then converted into an electronic signal. It is the sensitivity of the biological constituents utilised such as enzymes, antibodies or whole microbial cells that are responsible for the selectivity and sensitivity of the assessment.

The first BOD biosensor was reported by Karube et al in 1977. This included a dissolved oxygen electrode and a membrane infused with the yeast. Since then, many BOD biosensors based on various measurement principles and biological sensing elements have been reported. (Liu & Mattiasson, 2002; Raud et al, 2012a & b; Lagarde & Jaffrezic-Renault, 2011 and Ponomareva, 2011). Microorganisms originally were and still are employed as a single pure culture. More recently mixtures of several pure cultures, or mixed cultures, such as activated sludge or the BODSEED culture have also been used (Tan & Wu, 1999 and Rastogi et al, 2003). Biosensors comprised of only one microbial strain have relatively good stability and a long service life (Kim et al, 2006), however the BOD value is limited due to the narrow spectrum of the chosen strain (Liu & Mattiasson, 2002 and Raud et al 2010), which may lead to an underestimation of BOD. In order to construct a BOD biosensor with a wider substrate spectrum, mixtures of several microbial strains or mixed cultures have been used (Suriyawattanakul et al, 2002).

Unfortunately when compared to single strain biosensors, mixed culture biosensors have decreased stability and a shorter service life. This is due to the different life-spans and growth rates of various microorganisms used in association (Liu & Mattiasson, 2002). Thermally killed cells have been used to overcome the instability of microbial groups and to achieve a longer service life for biosensors (Ponomareva, 2011).

The principle of sensor-arrays is based on an analogy to the olfactory and taste systems of mammals. According to the IUPAC (The International Union of Pure and Applied Chemistry) definition, ‘an electronic tongue is a multisensory system, which consists of a number of low-selective sensors and uses advanced mathematical procedures for signal processing based on pattern recognition and/or multivariate data analysis’ (Vlasov et al, 2005 and del Valle et al, 2010). This first started in 1943 when the idea of artificially replicating the response of a human to environmental stimuli, was first published (Vlasov et al, 2005). It was not until the 1960’s though, that the first attempts to design an artificial olfactory system for smell were made (Vlasov et al, 2008). Non-specific sensor arrays became commercially available in the mid-1990s (Bourgeois et al, 2003). Now arrays based on gas sensors are termed ‘electronic noses’ while arrays of liquid sensors are referred to as ‘electronic tongues’ (Escuder-Gilabert & Peris, 2010).

Each sensor in an array produces an individual signal. These signals are then gathered and analysed by means of statistical multivariate analysis, consequently generating qualitative and quantitative information about the samples. The main characteristics shared by electronic nose and tongue systems is that an array of low selective and cross-sensitive sensors is created with data processing and pattern recognition methods (Vlasov et al, 2008). Cross-sensitivity in this situation refers to the ability of a sensor to respond to a number of different compounds in a solution and produce a stable response in the sample (Vlasov et al, 2005). So, when the sensors are responding to several different substrates, a chemical image of the sample or a signal pattern is created (Hruškar et al, 2010).

In recent years, much attention has been given to electronic tongue applications regarding industrial and environmental monitoring, and quality control (Vlasov et al, 2008), because electronic tongues are capable of fast, inexpensive, automated and on-line control (Witkowska et al, 2010). However each sensor in an array produces an individual signal which may not always correlate with the samples’ composition, possibly leading to false or inaccurate results. Also sensor drift remains a big problem with sensor-arrays. It may be caused by the ageing of a sensor, temperature or pressure changes, or the ageing of the biological recognition element (Bourgeois et al, 2003). Achieving a longer and more stable service life for biological recognition elements, guaranteeing easy and effective maintenance of the measurement system, and overcoming the toxic effect of samples to microorganisms are just a few of the challenges needing to be addressed. This means the method has to be rejected at the outset. If these issues are addressed however, biosensors and sensor arrays may well be an option in the future.

Another option that was rejected was that of Artificial Neural Networks (ANN) (Patra, 2015 and Abyaneh, 2014). This however is based on the sensors discussed above. A difference is that the ANN system utilises a computer software package designed to learn the consequences of a change in other parameters e.g. PH and Temperature. This means that the sensor array monitors COD on the bases of a modelled response curve. This is why this was rejected as a forecasted pollution amount would be difficult to enforce.

8.3.2 COD utilising alternative Oxidising agents.

As stated previously, COD relies on chemical oxidation with a strong oxidizer. And has been used to oxidize organic matter for more than 70 years however the earliest attempts to examine the oxygen consumption in water and wastewater caused by pollution used a permanganate test. This was achieved by mixing a permanganate solution with water samples with the observation of colour changes representing the results (Miller et al, 2001). However, the permanganate test does not directly correlate with the results of the BOD test partly due to a lack of oxidation power of permanganate, and in many cases BOD measurements were often much greater than results from COD measurements (Moore et al, 1951)

Since then, there have been tests using other oxidising chemicals, some of which are: Manganese III, Cerium (IV) oxide and Hydrogen Peroxide. Korenaga et al, 1993 tried used cerium (IV) sulphate as oxidizing reagent, utilizing a flow injection system and absorbance detection of 320 nm which resulted in a high degree of sample oxidation under mild operating conditions. The detection limit and relative standard deviation of the method was 0.5 mg/L and 0.6% respectively. Chloride was tolerated up to a concentration of 30000 mg/L without any masking agents and 20 samples could be analysed per hour. COD values for various types of wastewater samples correlated well with those obtained by standard methods

There has also been a good procedure developed with the use of Manganese III COD Reagent where calibration is linear over the range from 0 to 1000 mg/L COD. The working range however, of the test is 20 to 1000 mg/L COD. The reagent has an oxidation efficiency of about 80%, and has a limited digestion temperature (Boyles, 1997). Zhanga et al (2004), also showed similar limitations, therefore with the reporting limit criteria set at around 5 mg/l, along with the low accuracy, this was not included in the final assessment.

The effort to develop a more effective potassium permanganate method is still ongoing. Tian & Wu, 1992, tried a segmented flow-injection with potassium permanganate oxidation with spectro-photometric detection. The procedure has the advantage of high sample throughput (80/h), high sensitivity and precision with low interference. Chloride concentrations up to 1500 mg/L is achievable. Unfortunately many classes of organic compounds are stable towards permanganate. Moreover reaction of permanganate with compounds that are readily attacked gives rise to the formation of manganese dioxide which catalyses the decomposition of permanganate. This subsequently magnifies the actual extent of consumption of the permanganate.

It must be noted that some companies are carrying out more research into new methods with old oxidants such as Potassium Permanganate (Korenaga, 1980 and Fujimori & Maeda, 1998), while others are investigating the possibility of other oxidants such as Peroxydisulfate (Aqualab Zuid B.V. 2015). However companies are reluctant to share this information until there is a commercially prepared setup. Consequently the flow injection and permanganate oxidation method with e.g. luminol-H_2O_2-chemiluminescence detection remains an option (Li et al, 2003). There is still a lot of work needed on the method e.g. the concentration of permanganate or other reagents like luminol, H_2O_2 and/or acidity have to be optimised e.g. the flow-rate of the sample has to adjusted and interferences of metals such as Cu (II), Co (II) and Cr (III) have to be overcome. The drawback of this FIA method is the high consumption of reagents. However a Potassium Permanganate COD test is currently being used in Japan as a replacement to the Dichromate-COD (MANTECH INC. 2015), where the poorer oxidizing power of

permanganate reduces the methods accuracy (incomplete oxidation of various chemicals), along with a digestion time of 2-4 hours is accepted. Thus any developments in the methodology should be observed.

8.3.3 COD Sensors and electrodes (Photo-electro-catalytic and Electrochemical)

Applying more instrumental techniques rather than chemical techniques in COD determination from an environmental viewpoint has a pronounced drop in the use of toxic chemicals. In the last decade the interest in photo-catalysis and electrochemical techniques has grown exponentially (Dan, 2005; Kim et al, 2000a & b; Li & Song, 2009; Moretto & Kalcher, 2014; Zhang et al 2006; Zhang et al, 2003; Zhang et al, 2004; and Zhang et al 2009). Photo catalysts have the ability to convert light into chemical energy through a series of electronic processes and surface reactions. Among them TiO2 is used most frequently. In an excellent review paper by Hernández-Alonso *et al,* 2009 the pros and cons of TiO2 and alternative photo catalysts are described. Hydroxyl radicals (OH•) are considered the key intermediate in the photo oxidation reactions with TiO2.These entities readily react with organic molecules resulting in oxidative degradation, *e.g.* OH• +organics = CO2 + H2O

A number of alternative methods based on photo catalytic or electrochemical principles have been proposed and investigated. Although these methods have a number of advantages over the Dichromate-COD method, they are far from perfect. The main drawback of processes based on the phenomenon of photo catalysis, such as those that employ discrete TiO2 particles and TiO2-coated Nano films, is their low efficiency, owing to the ready recombination of the photo generated electrons and holes in the particles and Nano films (Wang et al, 2010). In the case of electrochemical methods, numerous sensors, including copper electrodes (Silva et al 2009) nano-PbO2-modified electrodes (Ai et al, 2004), F-doped PbO2-modified electrodes (Li et al, 2005) RhO3/Ti electrodes (Li et al, 2006), boron-doped diamond electrodes (Wang et al 2012 and Yu et al, 2007), rotating Pt ring–Pt/PbO2 disc electrodes (Westbroek & Temmerman, 2001), and cobalt oxide-modified glassy carbon electrodes (Wang et al, 2012a) have been employed for determining the COD. The main advantages of electrochemical COD methods are the following: a wide linear range, low cost, simplicity, short response time, and ease of automation. However, unstable background currents in the electrodes or the low oxidation capabilities of the chemicals involved, owing to which organic pollutants remain in the wastewater, can lead to poor accuracy and reproducibility (Han et al, 2011). We have developed a thermal biosensor for use in COD determination. The biosensor measures the amount of heat released during the oxidation of organic compounds in the test water samples (Xie el al, 2000 and Chen et al, 2013). The flow injection analysis (FIA) technique is normally used along with the assay (Decristoforo & Danielsson, 1984). Therefore, the amounts of the carrier solution and the test water sample can be readily controlled using this continuous analysis technique (Mishra et al, 2010), The height of the thermometric peak is proportional to the change in the enthalpy of the organic content in the test water sample (Ramanathan & Danielsson, 2001 and Lerchner et al, 2006), In contrast to other devices used for COD measurements, the thermistor is insensitive to the optical, electrochemical, and other material properties of the test sample. Therefore, the degree of interference owing to the characteristics of the test sample is extremely low, and the obtained COD values are highly accurate (Zheng et al, 2004), In addition, the detection efficiency of the thermistor is very high.

A rotating ring-disc electrode was used in an amperometric method by Westbroek & Temmerman 2001. The method produced COD values within a minute, once calibration of the system is complete. Different calibration curves were obtained for low and high COD values. Also in 2009, Silva et al did a study on a copper electrode as an electro catalytic sensor. The linear range was 50-2800 mg/L and the procedure is applicable for “soft” wastewater samples. No toxic reagents are used in this method.

A comparison of a photo-catalytic sensor combined with TiO_2 and an oxygen electrode with both the permanganate and dichromate method, was conducted by Kim et al, 2000b. The response values of the photo-catalytic COD sensor were found to be extremely good for all 20 compounds investigated.

Zhang et al 2007a used ion chromatography to analyse COD. In a photo catalytic oxidation system including Nano TiO_2-$K_2S_2O_8$ all organic compounds were degraded while $S_2O_8^{2-}$ was deoxidized to SO_4^{2-} that is determined by ion chromatography. Chloride is separated in the chromatographic system but is still present in the oxidation step. No indication of chloride interference was given in this paper.

Li et al, 2006, used Nano particles TiO_2 as a photo-catalyst and cerium sulphate as oxidizing agent. The fluorescence intensity of Ce3+ was detected. The method is linear in the 0-100 mg/L COD range. No chloride interference up to 2000 mg/L was found in this rapid and apparently accurate method. One problem encountered was the fineness of the powder of Nano particles which was so high that catalyst recovery proved difficult. On the other hand a photo- electro-chemical method based on direct quantitation of the extent of electron transfer on a TiO_2 Nano-porous film electrode with a thin layer photo electrochemical cell was developed by Zhao et al 2004. The linear range was between 0-200 mg/L and the procedure requires just 5 minutes per sample and a very little reagent. It shows good agreement with a standard dichromate method was achieved. The method stated an ability to overcome matrix interferences, though no indication of chloride interference was presented.

Nowadays the photo-electro-chemical oxidative degradation principle is commercial available as the PeCOD system. This system was judged to be the better of the options assessed and so was the one chosen to be assessed in step 3.

8.3.4 Total Suspended Solids (TSS)

The aim of wastewater treatment is to remove contaminants from wastewater using physical, chemical and biological processes. Wastewater can contain solid wastes (organic and inorganic), organic material which consumes oxygen (BOD), nutrients, greases and oils, metals, different kinds of chemicals, and microorganisms. Wastewater treatment usually involves three different stages called the primary, secondary and tertiary treatment. In primary treatment, the influent wastewater is strained to remove all large objects that are deposited in the sewer system. Secondary treatment is designed to substantially degrade the biological content of the wastewater (biological treatment), whereas tertiary treatment provides a final stage to raise the effluent quality before it is discharged to the receiving environment. (Moel et al, 2006)

When consulting with representatives from waste treatment plants it was stated that the amounts of the TSS is vastly reduced and that even though there is a good correlation and a large quantity in post treatment wastewater, in the discharged waters there is significantly less. This was also reinforced in the literature, with Stephenson & Duff (1996), reporting up to 98% removal. Also in discharged water with high TSS it is presently being tested for. Therefore TSS did not progress further than step 2. (WaterNet, 2015: Oasen, 2015 and Rijkswaterstaat, 2015)

8.3.5 Total Oxygen Demand (TOD),

TOD is a measure of the oxygen demand of wastewater by injecting a small volume of the sample into oxygen containing carrier gas and passed through a catalyst bed. The carbon, nitrogen, and many minerals are converted to their oxides by consuming oxygen from the carrier gas, the amount of gaseous oxygen consumed is measured and given as the TOD of the sample in mg oxygen/litre of wastewater (Young et al, 2003).

Even in the 1970s online analysers for the determination of TOD were available. After the rise in popularity of the COD-dichromate method the TOD had been suppressed in many countries as the COD prevailed in analysis of waste water. However, the total oxygen demand is a reliable and reproducible parameter to indicate the oxygen demand of water. In the United States it is standardized with the ASTM D6238 and was thought to be commonly used. The TOD correlates easily to the COD, and up until this point was a forerunner. However within step 2 communication with the US Environment Protection Agency (EPA) revealed that this test is not widely used due to a high detection limit. A limit of 0ppm is specified, though the lower limits are only available at the expense of accuracy and

reproducibility. The test also states an inaccuracy of 2-5 percent, which in the lower detection limits also increases. Moreover, a large interference is generated by urea. Therefore the method is unsuitable for municipal wastewater treatment plants (EPA, 2015; Aqualab Zuid B.V. 2015 and ASTM D6238). Consequently it is not in the assessment in step 3.

8.3.6 QuickCODultra,

QuickCODultra is a detection technique very similar to the TOC high temperature method. The investment costs are a little higher than those of TOC. However the running costs are extremely low, and is a good option as a replacement as long as the required detection limit is higher than 10 mg/L. It is the high detection limit that prevented this method progressing.

8.4 UVAS/COD CORRELATION

Figure 12 below is the same as figure 9 in chapter 3 and shows the results of a correlation between results from UVAS and Potassium Dichromate-COD testing.

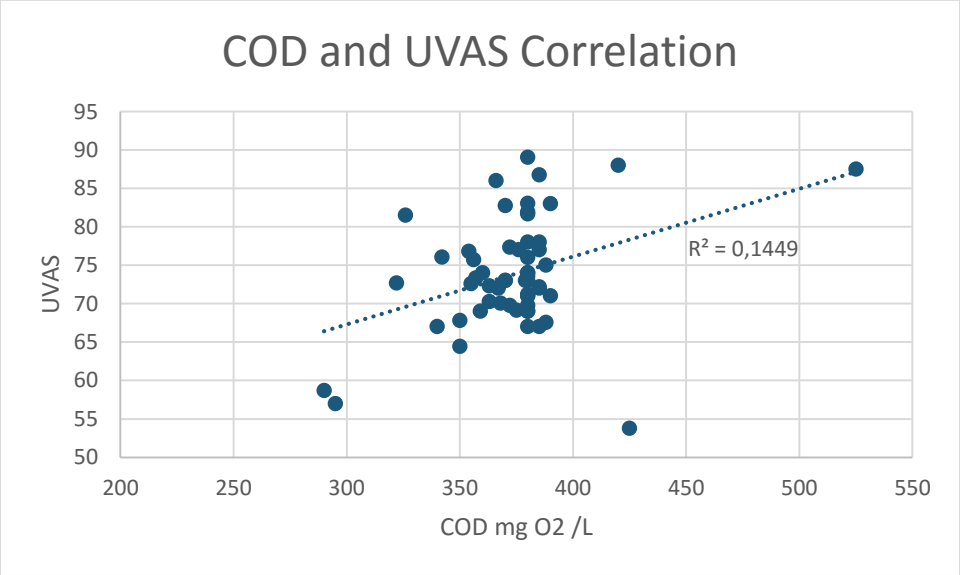

Figure 12: COD and UVAS Correlation for one company over a three month period (Data sourced from Rijkswaterstaat, 2015).