

Concerning Recalcitrant/Refractory Organic Species and Chemical Oxygen Demand (COD) analysis by two different methods:

- (a) COD_{Cr} (the dichromate method) and
 - (b) TiO₂/UV photoelectrochemistry (the PeCOD™ method)
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Abstract

While the conventional method of chemical oxygen demand (COD_{Cr}) measurement uses a combination of dichromate, sulfuric acid and heat to oxidise the organics in the water sample, Aqua Diagnostic's PeCOD™ technology oxidises the organics photocatalytically on a UV illuminated TiO₂ surface. Because the two measurement techniques differ in their oxidation method, it is conceivable that this may give rise to corresponding systematic differences between COD_{Cr} and PeCOD™ measurement results on identical samples. In light of this we have conducted a literature search on the subject of organic species which are known to be refractory to oxidation, whether by dichromate, photocatalysis on TiO₂ or by some other oxidative process. The literature unequivocally reports that while there are many species and indeed whole classes of organics that are in varying degrees refractory or entirely resistant to oxidation by dichromate, there are almost none that will not be totally oxidised by photocatalysis on TiO₂. We conclude that: (a) there may be systematic differences between COD_{Cr} and the PeCOD™ measurements on identical samples because the COD_{Cr} method is effectively blind to a range of refractory organic species; and (b) the PeCOD™ method will always give a truer measure of the oxygen depleting potential (i.e. the COD) of water samples than will the COD_{Cr} method. Aqua Diagnostic is in the process of confirming these literature-based conclusions experimentally and will report them separately.

Background

The literature on:

- (a) COD analysis by the conventional dichromate method (COD_{Cr});
- (b) COD analysis based on heterogeneous photocatalysis by illuminated TiO₂; and
- (c) wastewater treatment processes to reduce COD and BOD in effluent streams;

identifies a number of organic species as “recalcitrant” or “refractory” to oxidation. These descriptors seem to be used interchangeably and generally refer to an organic species' resistance to oxidation in the COD measurement process and/or resistance to degradation in oxidative water treatment processes.

Aqua Diagnostic wishes to identify refractory organic species and, to the extent possible, quantify their degree of refractoriness in both the COD_{Cr} process and in the PeCOD™ COD measurement process for the following reasons:

- (a) Regulatory: there may be organic species where PeCOD™'s photocatalytic oxidation process is significantly more efficient than the COD_{Cr} oxidation process, i.e. species which are refractory to COD_{Cr} but not to PeCOD™. This may result in systematic offsets between PeCOD™ and COD_{Cr} measurements of COD for samples containing such organics, with PeCOD™ yielding the higher COD measurements.

We need to be able to justify this systematic difference between PeCOD™ and COD_{Cr} measurements to regulatory bodies. PeCOD™'s photocatalytic oxidation applies an oxidation potential of +3.2 V to the sample, whereas COD_{Cr}'s Cr⁶⁺→Cr³⁺ process applies an oxidation potential of +1.3 V. Thus we expect that PeCOD™'s photocatalytic oxidation is more efficient than COD_{Cr}'s chemical oxidation. This may result in higher PeCOD™ measurements than COD_{Cr} measurements of COD, where refractory organics are present in the sample. This difference may be justified to regulatory authorities in terms of PeCOD™ giving a more accurate

measure of the true organic burden of the sample than does COD_{Cr}. Thus use of PeCOD™ rather than COD_{Cr} may lead to improved environmental outcomes, since effluent samples will be more truly characterised.

- (b) PeCOD™ customer education: the systematic offset between PeCOD™ and COD_{Cr} measurement results, in the case of samples containing refractory organics, will need to be explained to PeCOD™ customers and potential customers.

In the case where the industrial customer is using COD measurement feedback to achieve certain internal process optimisations it will be easy to argue in support of PeCOD™ since the higher measurement (expected from PeCOD™) is a truer measure of the chemical state of the sample stream. In the particular case of COD analysis being used to minimise the loss of expensive organics in the effluent stream, PeCOD™ will clearly represent an opportunity to the customer to make savings, relative to using the COD_{Cr} method.

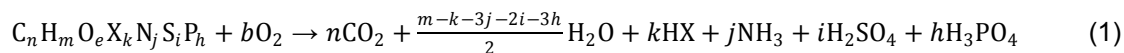
In the case where the industrial customer's primary use of COD analysis is to ensure compliance with regulatory requirements on effluent content, the customer may see use of PeCOD™ technology as disadvantaging them, since it may increase their pre-discharge wastewater treatment burden, and therefore their costs. Obviously there may be resistance to this from customers for whom costs are more important than environmental responsibility. For those customers who do give some weight to responsible environmental citizenship, however, they will consider a more accurate result to be desirable.

In the following sections, we will summarise the initial findings regarding refractory organic species from the literature.

Refractory Organic Species Identified in the COD Analysis Literature

- Moore, Kroner & Ruchhoff, *Anal. Chem.*, **21**(8), 953-957, 1949¹

The nearest we have found to a foundational paper in the area of refractory organics and COD_{Cr} is that published in 1949 by Moore *et al.* of the U.S. Public Health Service. This paper in turn cites Adeney and Dawson, 1926², as one of the first reports of the [dichromate + sulfuric acid + heat] method for producing a rapid chemical equivalent of the BOD measurement. This is essentially the COD_{Cr} method still used today more than 80 years later, except the Ag⁺ catalyst seemed to be absent at that stage. Even by 1949 COD_{Cr} existed as an officially recommended procedure and had been published as such by Standard Methods³. Out of interest, Moore *et al.* attribute the inception of the BOD test to Sir Edward Frankland in 1870 and Dupré in 1884, as reported in Phelps (*ed.*), 1944⁴. Moore *et al.* experimentally considered the efficiency of oxidation by [dichromate + sulfuric acid (50% v/v) + reflux (2 hr)] for about 32 organic compounds of various classes (sugars, aliphatic and aromatic acids, amino acids, alcohols, phenolics and carbohydrates). The oxidation efficiency was quantified as the COD_{Cr}/ThOD ratio, where ThOD (*b* in equation below) is theoretical oxygen demand based entirely on the compound's stoichiometry, according to the following equation:



where X represents the sum of all halogens and

$$b = n + \frac{m-k-3j-2i-3h}{4} - \frac{e}{2} + 2i + 2h \quad (2)$$

At least two replicate measurements were performed on each species, and typically the replicate results differed by less than ~2-3 %. The results are summarised in the Table 1 below.

¹ W.A. Moore, R.C. Kroner and C.C. Ruchhoff, "Dichromate Reflux Method for Determination of Oxygen Consumed: Effectiveness in Oxidation of Organic Compounds", *Analytical Chemistry*, **21**, 953-957, 1949.

² W.E. Adeney and B.B. Dawson, *Sci. Proc. Roy. Dublin Soc.*, **18**, 199-202, 1926.

³ "Standard Methods for the Examination of Water and Sewage", 9th ed., APHA & AWWA, New York, 1946.

⁴ "Stream Sanitation", E.B. Phelps (*ed.*), Wiley & Sons, New York, 1944.

Fully Oxidised (mineralised) (COD _{Cr} /ThOD > 0.95)	Intermediate Oxidation (0.95 > COD _{Cr} /ThOD > 0.80)	Refractory to Oxidation (COD _{Cr} /ThOD < 0.80)
glucose (1.00) lactose (0.97) citric acid (0.97) tartaric acid (0.99) malic acid (0.95) benzoic acid (0.99) salicylic acid (0.98) <i>m</i> -hydroxybenzoic acid (0.99) glycine (0.98) tyrosine (0.98) isopropanol (1.00) catechol (0.97) thymol (5-methyl-2-isopropyl phenol) (0.95) <i>p</i> -cumyl phenol (1.00) 2,4,6-trinitrophenol (0.95) 2-naphthol (0.99) cellulose (1.00)	furan-2-carboxylic acid (0.86) valine (0.81) ⁵ α -amino- isobutyric acid (0.86) glutamic acid (0.85) ⁶ <i>o</i> -cresol (0.90) <i>m</i> -cresol (0.93)	acetic acid (0.05) lactic acid (0.51) alanine (0.32) ⁷ ethanol (0.36) ⁸ benzene (0.09) pyridine (0.00) toluene (0.24)

Table 1. Moore et al.'s division of organics into three groups, according to COD_{Cr}/ThOD ratio, using COD_{Cr} method.

Summarising the results further, sugars, carbohydrates, aromatic acids, branched chain and substituted aliphatic acids and branched chain alcohols are all easily oxidised. With phenols, some are easily oxidised and others (cresols) are only oxidised to an intermediate extent. Similarly, some amino-acids are fully oxidised and others that proceed on oxidation to saturated aliphatic acids (e.g. valine, α -amino-isobutyric acid, glutamic acid, alanine) are not. Furan, pyridine and benzene derivatives as well as straight chain aliphatic acids are resistant to oxidation. Moore et al. also briefly considered the effect on measured COD_{Cr} by chlorides and generally found that they elevate the apparent COD, although the effect was observed to be erratic.

- Baker, Milke & Mihelcic, *Wat. Res.*, **33**(2), 327-334, 1999⁹

The next landmark study of organics refractory to oxidation appears to be that by Janicke, 1983¹⁰, cited extensively in Baker et al., 1999. Baker et al. (and earlier Janicke) considered the COD_{Cr}/ThOD ratio of 565 distinct species in 64 separate classes of organic chemical using the COD_{Cr} method in its modern form, including the presence of a Ag₂SO₄ catalyst. The 64 classes of compound are resolved into 6 groups, summarised in Table 2 below.

For Groups 1 and 2 in Table 2 we can proceed safely on the basis that all members of these chemical classes are easily oxidised in both the COD_{Cr} and PeCOD™ methods and will give COD/ThOD of $\sim 0.97 \pm 0.1$ (1 σ).

For Groups 3 and 4, both COD_{Cr} and PeCOD™ are still on fairly safe ground since the average COD/ThOD for all compounds in these groups (as measured by COD_{Cr}) was ~ 0.92 , however the variance of COD_{Cr}/ThOD within this population was greater, as shown by the larger standard deviation values obtained, typically ± 0.2 (1 σ).

Groups 5 and 6 need to be considered in more detail as these are the classes containing the compounds most refractory to COD_{Cr} and therefore most likely to be refractory to PeCOD™. Note that the methodology for classification used by Moore et al. was quite conservative in the following sense: any class of compounds that had very few of its members (say, <5) analysed was likely to be

⁵ Oxidation of valine hypothesised to proceed to isobutyric acid, which is refractory to COD_{Cr}.

⁶ Oxidation of glutamic acid hypothesised to proceed to propanoic acid, which is refractory to COD_{Cr}.

⁷ Oxidation of alanine hypothesised to proceed to acetic acid, which is refractory to COD_{Cr}.

⁸ Oxidation of ethanol hypothesised to proceed to acetic acid, which is refractory to COD_{Cr}.

⁹ J.R. Baker, M.W. Milke and J.R. Mihelcic, "Relationship between chemical and theoretical oxygen demand for specific classes of organic chemicals", *Water Research*, **33**(2), 327-334, 1999.

¹⁰ W. Janicke, *Chemische Oxidierbarkeit Organischer Wasserinhaltsstoffe*. WaBoLu Berichte, Dietrich Reimer Verlag, 1983 [German].

Group 1: Aromatic class all easily oxidised (5 classes)	# chemicals, mean COD _{Cr} /ThOD, (std. dev.)	Group 2: Non-aromatic class all easily oxidised (7 classes)	# chemicals, mean COD _{Cr} /ThOD, (std. dev.)
<ul style="list-style-type: none"> • sulfonic acids • phenols & phenol ethers • alcohols, aldehydes & ketones • carboxylic acids • amines & nitriles 	N=113 0.98, (0.092)	<ul style="list-style-type: none"> • alcohols • nitrile esters with phosphate, sulfate, silicate substituent • unsaturated carboxylic acids • acetates and acrylates • multi-substituted alcohols and ether alcohols • saturated dicarboxylic acids • carbohydrates • terpenes, sesqui- and di- 	N=97 0.97, (0.082)
Group 3: Aromatic class contains some intermediate or mixed results (2 classes)	# chemicals, mean COD _{Cr} /ThOD, (std. dev.)	Group 4: Non-aromatic class contains some intermediate or mixed results (6 classes)	# chemicals, mean COD _{Cr} /ThOD, (std. dev.)
<ul style="list-style-type: none"> • chloro-, nitro- and amino-phenols • thiocompounds 	N=29 0.93, (0.18)	<ul style="list-style-type: none"> • nitriles • ketones and hydroxyketones • amino acids • diketones • hydroxy di- & tri-carboxylic acids • polycyclic ring structure with N substituted into aromatic ring 	N=38 0.92, (0.23)
Group 5: Aromatic class may contain several or many refractory compounds (8 classes)	# chemicals, mean COD _{Cr} /ThOD, (std. dev.)	Group 6: Non-aromatic class may contain several or many refractory compounds (35 classes)	# chemicals, mean COD _{Cr} /ThOD, (std. dev.)
<ul style="list-style-type: none"> • azo compounds • <i>non-benzene hydrocarbons</i> • hydrocarbons • halogenated hydrocarbons • nitro- & chloro-nitro- hydrocarbons • quinones • triphenylmethane derivatives • condensed ring hydrocarbons 	N=79 0.65, (0.33)	<ul style="list-style-type: none"> • alkanes • alkenes • alkynes • <i>multiple unsaturated hydrocarbon</i> • <i>alkenols</i> • <i>alkynols</i> • ethers, halogenethers, oligoethers • thioalcohol and derivatives • thioethers • nitroalkanes • silicon and metal organics • <i>aldehydes</i> • saturated acids • furan with 2 heteroatoms and derivatives • six-sided ring with heteroatom and derivatives • bicyclic hetero-system • <i>alkaloid</i> • aliphatic halogen alkanes & alkenes • glycerin ester • halogenalcohol, halogenated acid & acid ester • <i>hydroxyacid</i> • <i>aldehyde and ketoacid</i> • <i>unsaturated acid</i> • keto acid & carbon acid derivative • thio-carbon-acid derivative • iso- and thio- cyanate • aliphatic sulphone, sulfoxide, sulfonic acid • aliphatic amines and imines • acyclic cycloalkane and cycloalkene • bicyclic alkanes • <i>steroids</i> • furan & derivatives • condensed rings of furan- thiophene- and pyrrol • derivatives of cycloparafin & olefinin • synthetic polymers 	N=209 0.78 (0.43)

Table 2. Baker et al.'s division of organics into 6 groups of classes, 3 aromatic groups and 3 non-aromatic groups.

placed into Group 5 or Group 6 on the basis of caution. For many of these small classes, the members that were analysed gave COD_{Cr}/ThOD ratios of ~1.0. They have been greyed out and italicised in Table 2 as probably not being priority targets for further investigation on our part, at least in the immediate future.

Observe that *Baker et al.* (where Ag₂SO₄ catalyst was used) found that alcohols, saturated non-aromatic carboxylic acids, amino acids and the hydroxyacid lactic acid were in general easily oxidised, whereas *Moore et al.* (where no catalyst was used) found they were in general refractory. Both report benzene and toluene as being refractory, although *Baker et al.* reports higher COD_{Cr}/ThOD ratios than *Moore et al.* These differences can probably be attributed to the presence of the catalyst assisting the oxidation in the more recent study.

We are still left with 7 classes of aromatic compound in Group 5 and 29 classes of non-aromatic compound in Group 6 likely to contain species refractory to oxidation by COD_{Cr}, if not by PeCOD™. Because these are of particular interest, *Baker et al.* list all the individual compounds which were members of these classes, along with their COD_{Cr}/ThOD ratios. We have taken this list and further selected from it a representative sample of compounds that have both an appreciable solubility in water and a COD_{Cr}/ThOD of significantly less than 1.0. These species, or at least a subset of them, listed in Table 3 below, recommend themselves to us in the first instance for an in-house parallel analysis by the COD_{Cr} and PeCOD™ methods.

Aromatics Classes	Examples from Class	COD _{Cr} /ThOD ratio	Solubility in Water (g/L)
Hydrocarbons	benzene	0.65	0.80
	toluene	0.40	0.47
	ethyl-benzene	0.75	0.15
Halogenated hydrocarbons	chlorobenzene	0.58	0.5
	1,4-dichlorobenzene	0.34	0.08
Nitro & Chloro-nitro hydrocarbons	4-chloronitrobenzene	0.16	0.25
Triphenyl methane derivatives	Rhodamine B	0.82	soluble

Non-Aromatic Classes	Examples from Class	COD _{Cr} /ThOD ratio	Solubility in Water (g/L)
Ether, halogenether, oligoether	diethyl ether	0.81	69
Nitroalkanes	nitroethane	0.63	46
Saturated Acids	pentanoic acid	0.81	10
	hexanoic acid		
Furan with 2 heteroatoms and derivatives	imidazol	1.14	miscible
	1,2,4-triazole	0.03	miscible
Six-sided ring with heteroatom and derivatives	pyridine	0.01	miscible
	isonicotinic acid	0.14	soluble
Halogen alkane & alkene	dichloromethane	0.06	13
	trichloromethane	0.08	8
	tetrachloromethane	0.08	0.8
Halogenalcohol, halogenated acid and acid ester	trichloroacetic acid	0.69	soluble
Thio carbon acid derivative	carbon disulfide	0.21	2
Sulfone, sulfoxide, sulfonic acid	dimethyl sulfone	0.00	miscible
	dimethyl sulfoxide	0.11	miscible
Amines and Imines	dimethylamine	0.03	soluble
	trimethylamine	0.01	soluble
	diethylamine	0.16	miscible

Table 3. Aromatic (top) and non-aromatic (bottom) classes of organics, and example species from each class, that recommend themselves for further analysis by Aqua Diagnostic to assess their refractory nature to oxidation by COD_{Cr} and by PeCOD™.

- Kim *et al*, *Analyst*, 125, 1915-1918, 2000¹¹

Kim et al., perhaps stimulated in part by *Baker et al.*, to which they refer, published a similarly structured paper soon after the latter. It is a much narrower study insofar as it covers only twenty organic species across the four classes: sugars, benzene derivatives, alcohols and carboxylic acids. On the other hand, *Kim et al.* is broader than *Baker et al.* in that the COD/ThOD ratio for three different experimental COD methods is reported. The methods are:

- (a) COD_{Cr}: conventional dichromate/H₂SO₄ digestion with Ag₂SO₄ catalyst;
- (b) COD_{Mn}: alternative method, preferred in Japan and Korea, of permanganate/H₂SO₄ with Ag₂SO₄ catalyst;
- (c) COD_{photo}: a TiO₂ photocatalytic method developed in Kim's laboratory¹². While this method exploits the same photocatalytic oxidation of organics on UV-illuminated TiO₂ as PeCOD™ does, the measurement principle is quite different. In Kim's apparatus an oxygen electrode is used to measure the change in dissolved oxygen concentration in the sample solution due to oxidation of the organics.

The results of *Kim et al.* are easiest to summarise by extracting the key figures from the paper. They are inserted below as Figure 1.

It is clear that while the oxidation efficiency of the COD_{Cr} method is somewhat higher than that of the COD_{Mn} method, neither of these methods comes even close to complete oxidation of the alcohols, saturated carboxylic acids or benzoic acid. On the other hand, all twenty species seem to be completely oxidised in the (TiO₂-based) COD_{photo} method.

Aqua Diagnostic is encouraged by this, as it provides strong evidence that the PeCOD™ method is likely to be similarly efficient in the oxidation of previously refractory organics. In a sense, the *Kim et al.* paper gives us a preview of what we should expect when we do our own analysis of refractory species using PeCOD™.

¹¹ Yoon-Chang Kim, Satoshi Sasaki, Kazuyoshi Yano, Kazunori Ikebukuro, Kazuhito Hashimoto & Isao Karube, "Relationship between theoretical chemical oxygen demand and photocatalytic chemical oxygen demand for specific classes of organic chemicals", *Analyst*, **125**, 1915-1918, 2000.

¹² Y-C. Kim, K-H. Lee, S. Sasaki, K. Hashimoto, K. Ikebukuro & I. Karube, *Anal. Chem.*, **72**, 3379, 2000.

Chemical class	Substrate	b^a	Concentration/ mg L ⁻¹	ThOD ^b / mg L ⁻¹
Sugars	D(+)-Glucose	6	10	10.45
	Sucrose	12	10	11.22
	D(+)-Lactose, 1-hydrate	12	10	10.66
Alcohols	Methanol	3/2	5	5.85
	Ethanol	3	5	8.18
	Propan-1-ol	9/2	5	9.56
	Butan-1-ol	6	5	10.44
Carboxy acids	Formic acid	1/2	10	4.16
	Acetic acid	2	10	11.15
	Propionic acid	7/2	10	14.94
	<i>n</i> -Butyric acid	5	10	17.24
	Isobutyric acid	5	10	17.08
	<i>n</i> -Valeric acid	13/2	10	18.74
Benzene derivatives	Isovaleric acid	13/2	10	18.96
	Phenol	7	5	12.62
	Aniline	7	5	12.23
	<i>o</i> -Cresol	17/2	5	13.04
	<i>m</i> -Cresol	17/2	5	12.87
	<i>p</i> -Cresol	17/2	5	12.88
	Benzoic acid	15/2	5	12.92

^a The values can be obtained from eqn. (2) for each substrate. ^b Calculating equation for the ThOD, (mass in solution × purity × density × 32 × b) / molecular weight

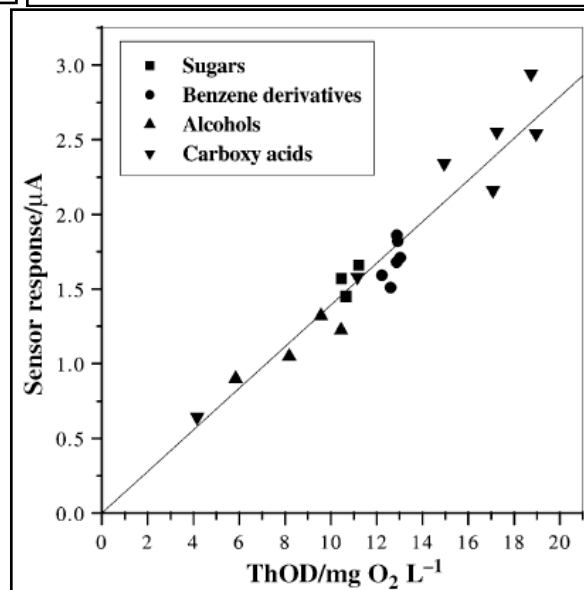
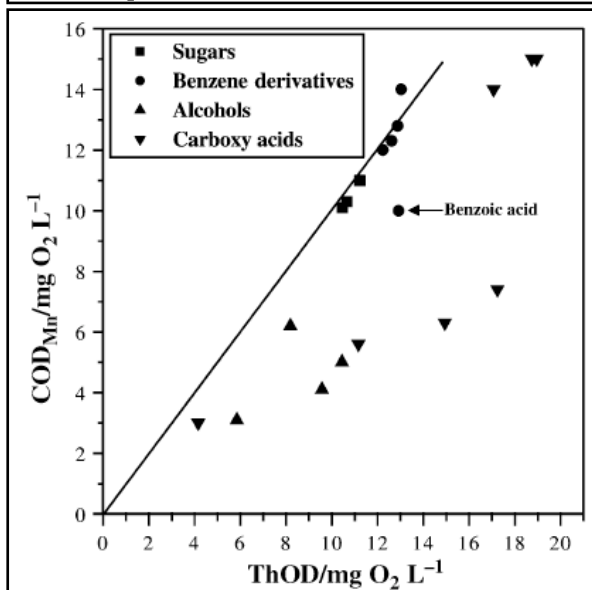
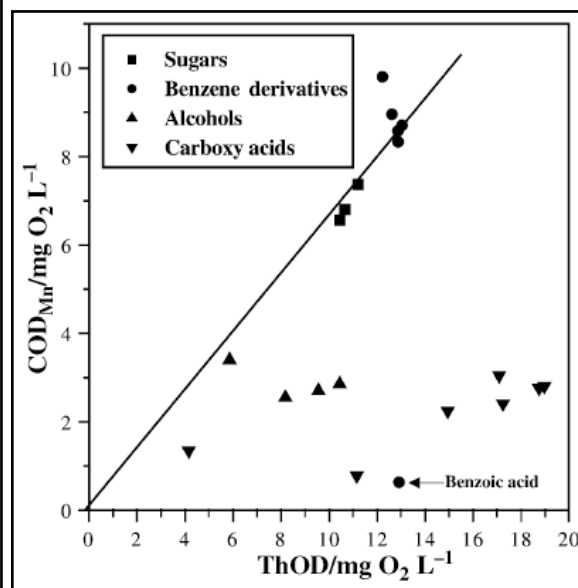


Figure 1. Key results figures extracted from Kim *et al.*

Top Left: Table of ThOD values for the compounds studied.

Top Right: COD_{Mn} vs. ThOD plot for permanganate method.

Bottom Left: COD_{Cr} vs. ThOD plot for dichromate method; (y-axis label is typo in original paper – should read COD_{Cr}).

Bottom Right: COD_{photo} instrument response vs. ThOD plot for Kim's photocatalytic method.

Refractory Organic Species Identified in the Wastewater Treatment Literature

- Ollis, Pelizzetti and Serpone, *Environmental Science and Technology*, **25**(9), 1523-1529, 1991¹³

This article, although now 17 years old, is a broad ranging review article, with 75 references, and is the most relevant review article we have found to date. It addresses specifically the destruction of water contaminants by heterogeneous photocatalysis with TiO₂ as the solid phase. At least some of the chemical findings regarding photocatalytic *destruction* in bulk waters should translate into the area of photocatalytic *measurement* in aqueous microsamples, given that PeCOD™ relies on exhaustive oxidation. The findings of *Ollis et al.* are summarised in the table below. Most, if not all, of the classes and species listed here are highly refractory to chemical oxidation, and certainly to the COD_{Cr} method:

Organics classes where complete mineralisation by TiO ₂ photocatalysis has been demonstrated	Examples from classes	Species shown to undergo incomplete mineralisation by TiO ₂ photocatalysis	Species shown to be resistant to TiO ₂ photocatalysis
Alkanes, alkenes (& their simple and halogenated derivatives)	- dodecane - dodecyl sulfate - 1-bromo-dodecane - bromoform - ethylene dibromide - 1-decanol - tetrachloroethylene	- s-triazine herbicides (e.g., atrazine, simazine, trietazine, prometone, prometryne)	- carbon tetrachloride - cyanuric acid
Carboxylic acids (& chlorinated derivatives)	- decanoic acid - trichloroacetic acid		
Simple aromatics (& halogenated derivatives)	- benzene - chlorobenzenes - chlorophenols - fluorophenols		
Surfactants (anionic, cationic & non-ionic)	- alkyl phenols - nonylphenol ethoxylate		
Herbicides/pesticides	- chlorinated biphenyls - chlorinated dioxins - DDT - 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) - 2,4,5-trichlorophenol (2,4,5-TCP) - 2,4,5-trichlorophenylformate - bentazon		

Table 4. Summary of results from *Ollis et al.* regarding oxidation of organics by TiO₂/UV photocatalysis.

The only two organic molecules identified as being entirely resistant to photocatalytic oxidation were carbon tetrachloride and cyanuric acid. The former, CCl₄, is believed to be resistant because the photocatalytic oxidation process is initiated by abstraction of an organic hydrogen, but CCl₄ contains no hydrogen.

The latter, with formula (CNOH)₃, is a very stable molecule and is quite resistant to oxidation. Cyanuric acid is an industrially useful chemical, used as a precursor or component of bleaches,

¹³ D.F. Ollis, E. Pelizzetti & N. Serpone, "Destruction of Water Contaminants", *Environmental Science and Technology*, **25**(9), 1523-1529, 1991.

disinfectants and herbicides. Fortunately, from an environmental perspective, cyanuric acid itself is non-toxic to the point that it may be added to stockfeed as a nitrogen supplement. The s-triazine herbicides will undergo partial degradation until cyanuric acid is reached as an intermediate, at which point degradation proceeds no further.

Note also that the ThOD for both CCl_4 and $(\text{CNOH})_3$ is exactly zero according to the stoichiometric formulae, (1) and (2) above.

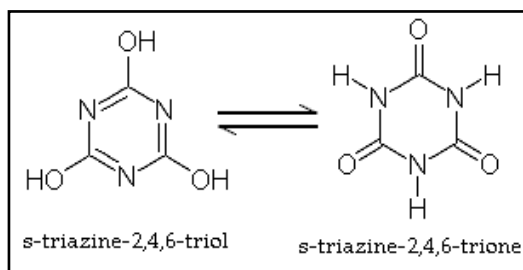


Figure 2. Cyanuric acid structure.

One other observation made by *Ollis et al.* is worth reporting here. ThOD is calculated on the assumption that the oxidation of organic nitrogen proceeds fairly rapidly only to ammonia, NH_3 . In the case of photocatalysis, given enough time because the reaction is relatively slow, NH_3 may be further oxidised to nitrate, NO_3^- , and the measured oxygen demand may be greater than that estimated by use of the usual ThOD formula¹⁴. It is worth noting that those few compounds in *Baker et al.* where a $\text{COD}_{\text{Cr}}/\text{ThOD}$ ratio of significantly greater than 1.0 was observed were N-rich organics (notably, *N*-nitroso-*N*-methylurea with $\text{COD}_{\text{Cr}}/\text{ThOD} \approx 3.3$).

- Gaya and Abdullah, *J. Photochem. & Photobiol. C: Photochem. Reviews*, **9**, 1-12, 2008¹⁵

Class of organic contaminants	Example compounds
Aldehydes	acetaldehyde; formaldehyde
Carboxylic acids	phenoxy acetic acid; 2,4,5-phenoxyacetic acid
Chloroanilines	2-chloroaniline
Chlorocarboxylic acids	monochloro-acetic acid
Chlorophenols	2-chlorophenol; 4-chlorophenol; 2,4-dichlorophenol
Dyes	Acid Orange 8; Acid Red 1; Chrysoidine Y; Acridine Orange; Ethidium Bromide; Methylene Blue; Methyl Orange; Indigo Carmine; Chicago Sky Blue
Ethers	(MBTE) methyl tert-butyl ether
Fluorophenols	4-fluorophenol
Fungicides	fenamidone
Herbicides	isoproturon
Ketones	acetone
Perfluoroaliphatics	trifluoroacetic acid; sulfonic acid of nonafluorobutane; sulfonic acid of heptadecafluorooctane ¹⁶
Phenolics	phenol
Pharmaceuticals	tetracycline; lincomycin
Polymers	(PVP) polyvinylpyrrolidone

Table 5. Refractory species named in *Gaya & Abdullah* which are known to be oxidisable by TiO_2/UV .

¹⁴ See also G.K.C. Low, S.R. McEvoy and R.P. Matthews, "Formation of Nitrate and Ammonium Ions in Titanium Dioxide Mediated Photocatalytic Degradation of Organic Compounds Containing Nitrogen Atoms", *Environmental Science & Technology*, **25**, 460-467, 1991.

¹⁵ Umar Ibrahim Gaya & Abdul Halim Abdullah, "Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: A review of fundamentals, progress and problems", *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, **9**, 1-12, 2008.

¹⁶ While the perfluorinated carboxylic acids were degraded under TiO_2/UV conditions, perfluorinated sulfonic acids were not. These were the only compounds in this table found to be resistant to TiO_2/UV degradation.

This very recent review article is more concerned with the process itself of photocatalysis on TiO_2 , rather than with surveying the generality of its application to myriad particular organic species. However, the paper does at one point list a range of classes and species, normally considered refractory to oxidation, that have been shown to be oxidised by photocatalysis on TiO_2 . The results are summarised in Table 5 above.

Finally a few articles that identified refractory organics in particular types of wastewater sample are mentioned here:

- S. Figaro *et al.*, "Adsorption studies of recalcitrant compounds of molasses spentwash on activated carbons", *Water Research*, **40**(18), 3456-3466, 2006.

Reporting on problems faced in sugar industry process wastewater, specifically MSWD (molasses spentwash after anaerobic digestion), the recalcitrant compounds identified are:

- gallic acid (3,4,5-trihydroxybenzoic acid);
- tannic acid (a polyphenol); and
- melanoidin (brown, high molecular weight heterogeneous polymers that are formed when sugars and amino acids combine).

- P.A. Pekakis *et al.*, "Treatment of dyehouse wastewater by TiO_2 photocatalysis", *Water Research*, **40**(6), 1276-1286, 2006.

Treatment of a dyehouse wastewater stream with TiO_2/UV was found to be capable of completely decolourising the effluent and reducing COD by 40-90%, depending on the operating conditions. Azo-dyes have in the past been identified as refractory species.

- A-M. Enright *et al.*, "Low-temperature anaerobic biological treatment of solvent containing pharmaceutical wastewater", *Water Research*, **39**(19), 4587-4596, 2005.

This report suggests that the solvents prevalent in pharmaceutical wastewaters are propanol, methanol and acetone. There seems to be a lack of consensus in even the recent literature over whether or not the COD_{Cr} method can efficiently oxidise these simple alcohols. On the one hand Baker *et al.* in 1999 reports non-aromatic alcohols as easily oxidised; but on the other hand in 2000 Kim *et al.* reports methanol, ethanol, propan-1-ol and butan-1-ol to be incompletely oxidised by both the COD_{Cr} and COD_{Mn} methods. Certainly, however, alcohols are efficiently oxidised by photocatalysis on TiO_2 .

- D.P. Saroj *et al.*, "Mineralization of some natural refractory organic compounds by biodegradation and ozonation", *Water Research*, **39**(9), 1921-1933, 2005.

This paper, from Indian authors deals with wastewater streams related to wood processing. The refractory species mentioned are:

- gallic acid (3,4,5-trihydroxybenzoic acid);
- tannin (polyphenols); and
- lignin (a complex biopolymer constituting 25-33% of the mass of wood, from the cell walls).

- O. Lefebvre *et al.*, "Halophilic biological treatment of tannery soak liquor in a sequencing batch reactor", *Water Research*, **39**(8), 1471-1480, 2005.

This French/Indian-authored paper observes that a number of industrial processes, including some of those in hide tanning, produce wastewater which is hypersaline (i.e. > 35 g Total Dissolved Solids, mainly NaCl). (I also understand that some textile dyeing processes produce saline wastewater, as the azo-dyes are introduced as Na^+ or K^+ salts, the cation being lost to solution when the dye fixes to the textile). The COD_{Cr} method is incapable of dealing with saline samples, whereas the PeCOD^{TM} method can.

- Z. Arbell *et al.*, "Treatment of high-strength dairy wastewater in an anaerobic deep reservoir", *Water Research*, **40**(19), 3653-3659, 2006.

From Israel, this study of a large industrial dairy found the most problematic (because of malodour as well as COD) species for degradation in dairy wastewater were the acetate and propionate products of lactose fermentation (volatile fatty acids).

- S. Khoufi *et al.*, "Treatment of olive oil mill wastewater by combined process electro-Fenton reaction and aerobic digestion", *Water Research*, **40**(10), 2007-2016, 2006.

In this industry focused paper from Tunisia, the problematic species in olive oil mill wastewater were polyphenols and lipids.

- H.Q. Yu & H.H.P. Fang, "Acidification of mid- and high-strength dairy wastewaters", *Water Research*, **35**(15), 3697-3705, 2001.

From Hong Kong, this paper observes that an acidification step in dairy wastewater processing results in conversion of carbohydrates to volatile fatty acids (acetate, propionate and butyrate), protein to alcohols (ethanol, propanol, butanol) plus *i*-butyrate and other higher VFAs. The wastewater also contained lipids, which were less successfully degraded.

- S. Ledakowicz *et al.*, "Elimination of resin acids by advanced oxidation processes and their impact on subsequent biodegradation", *Water Research*, **40**(18), 3439-3446, 2006.

From a Polish pulp and paper research institute, this paper identifies resin acids and fatty acids as problematic classes of organics in pulp and paper processing wastewater. Resin acids, naturally produced as protectant molecules by conifers, are toxic to aquatic life.

Conclusions

From the literature considered above we are able to draw the following set of conclusions regarding the relative behaviours of the COD_{Cr} and PeCOD™ methods in the case of water samples containing refractory organic species.

- For all species where

$$\{\text{COD/ThOD}\}_{\text{COD}_{\text{Cr}}} \approx 1.0$$

we should expect that

$$\{\text{COD/ThOD}\}_{\text{PeCOD}} \approx 1.0$$

- All organic species are likely to be more completely oxidised by TiO₂/UV photocatalysis than by the COD_{Cr} dichromate process. So we should always find that:

$$\frac{\{\text{COD/ThOD}\}_{\text{PeCOD}}}{\{\text{COD/ThOD}\}_{\text{COD}_{\text{Cr}}}} \geq 1$$

- For the species cyanuric acid and carbon tetrachloride and for the class perfluorinated sulfonic acids we probably should expect that both

$$\{\text{COD/ThOD}\}_{\text{COD}_{\text{Cr}}}$$

and

$$\{\text{COD/ThOD}\}_{\text{PeCOD}}$$

will be either zero or undefined.

- For species that contain a significant amount of organic N (e.g. *N*-nitroso-*N*-methylurea) we should expect that

$$\{\text{COD/ThOD}\}_{\text{COD}_{\text{Cr}}} \gg 1.0$$

and possibly

$$\{\text{COD/ThOD}\}_{\text{PeCOD}} \gg 1.0$$

because of the further oxidation of NH₃ to NO₃⁻. COD_{Cr} is known to be susceptible to this.

PeCOD™ may be less so because of the brevity of the measurement process, but this would need to be confirmed experimentally.

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