

## Systematic Comparison of PeCOD<sup>®</sup> and Dichromate Methods of COD Measurement for a Suite of 34 Organic Species

(Michael Esler, Kumiko Chinen, Heather Higginbotham and Priyanka Reddy; 23 February 2010)

### A. AIM

We wish to systematically compare the basic metrology and response function of two different methods of COD (chemical oxygen demand) measurement: the newly developed PeCOD<sup>®</sup> method and the most commonly used form of the conventional Dichromate method.

This will be achieved by using the two methods in parallel to analyse for COD using standard solutions made from a common set of 34 organic compounds.

### B. SCOPE

The PeCOD<sup>®</sup> method results provided in this report were obtained using several L100 Laboratory COD Analysers. All PeCOD<sup>®</sup> analyses were done using NORMAL + PRECISE mode operation. Non-doped TiO<sub>2</sub> (“white”) sensors were used throughout. It is not anticipated that using the newer doped-TiO<sub>2</sub> (“black”, chloride resistant) sensors would have yielded any different results, however this has yet to be confirmed on a subset of the suite of organic compounds. None of the standard solutions contained a significant quantity (i.e., > 5 mg/L) of chloride ion. Aqua Diagnostic’s standard electrolyte solutions were used throughout, yielding a 1 M electrolyte concentration in the sensor cell. For each organic compound studied, gravimetrically/volumetrically prepared standard solutions were analysed at the following ThOD (theoretical oxygen demand) concentrations, using the following PeCOD<sup>®</sup> measurement ranges:

PeCOD <sup>®</sup> Analyser Measurement Range (mg/L COD)	ThOD concentration of standard solutions (mg/L ThOD)
Green (0 – 150)	0 40 80 120 150
Yellow (0 – 1,500)	0 400 750 1,200 1,500
Red (0 – 15,000)	0 3,750 7,500 11,250 15,000

**Table 1. The measurement ranges of the PeCOD<sup>®</sup> L100 COD Analyser used in this study, and the ThOD concentrations at which reference standard solutions were prepared and analysed.**

The Dichromate method results provided in this report were obtained using, according to the manufacturer’s instructions, a Hach DRB 2000 Reactor Block and 16 mm diameter capped glass vials for closed reflux at 150 °C × 2 hr. The COD vials were commercially supplied “Hach LR” for measurement in the 0 ≤ COD < 150 mg/L range and “Hach HR” for COD measurement in the 150 ≤ COD ≤ 1500 mg/L range. These vials contained conc. H<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (oxidant), Ag<sub>2</sub>SO<sub>4</sub> (catalyst) and HgSO<sub>4</sub> (a chloride complexing agent). The post-reflux solution was analysed using a Hach DR 2800 Portable Spectrophotometer. For analysis of LR vials (0-150 mg/L) DR 2800 stored program #430 was selected, corresponding to a UV absorbance peak of 420 nm to determine the concentration of Cr<sup>6+</sup> remaining. For analysis of HR vials (150-1500 mg/L) DR 2800 stored program #435 was selected, corresponding to a UV absorbance peak of 620 nm to determine the concentration of Cr<sup>3+</sup> produced. For each organic compound studied, gravimetrically/volumetrically prepared standard solutions were analysed at the following ThOD (theoretical oxygen demand) concentrations, using the following Hach measurement ranges:

Hach Dichromate Method Measurement Range (mg/L COD)	ThOD concentration of standard solutions (mg/L ThOD)
LR (0 – 150)	0 50 100 (150)
HR (0 – 1,500)	150 500 1000 1,500

**Table 2. The measurement ranges of the Dichromate method used in this study, and the ThOD concentrations at which reference standard solutions were prepared and analysed.**

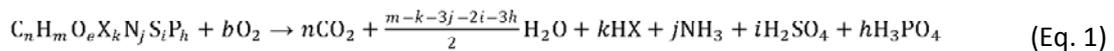
While standard solutions with ThOD = 150 mg/L were analysed using both the LR and the HR Hach vials, the results appeared more reliable for the HR vial analyses, so these have been used throughout rather than the LR vial results.

Note that the COD range covered by the PeCOD<sup>®</sup> analysis was 0-15,000 mg/L, corresponding to the measurement ranges readily available on the L100 and P100 instruments. The Dichromate range was only 0-1500 mg/L, corresponding to the most frequently used Dichromate method vial ranges LR and HR. The Dichromate method has been approved for environmental regulatory compliance reporting by the US EPA only over the COD range 3-1500 mg/L.

The organic compounds used to make the standard solutions were analytical reagent grade throughout. The water used was DI and free of COD (undetectable). Volumetric glassware and a mass balance with resolution 0.1 mg was used to prepare stock solutions from which each standard was prepared by a single dilution step.

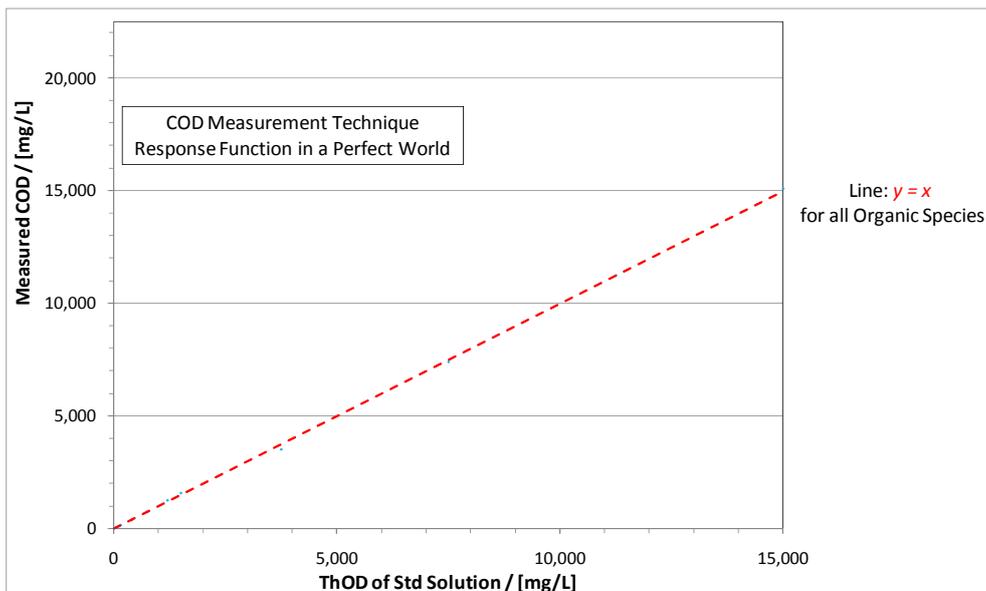
**C. METHOD RESPONSE FUNCTION: THE COD VS. THOD RELATIONSHIP**

The ThOD for complete oxidation of a given organic species can be determined from the stoichiometry of the mineralisation equation:



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

In an ideal world where experiment agreed with theory, a method of COD analysis would conform to the constraint that COD/ThOD = 1. That is, the COD analytical method would provide a reliable estimate of ThOD. In this ideal case, a plot of COD vs. ThOD for any given organic compound would look like Figure 1.



**Figure 1. Ideal world relationship between measured COD and stoichiometrically determined ThOD, y = 1x.**

In the real world, however, a COD measurement method may yield a response function (COD vs. ThOD equation) with a gradient,  $m = \frac{d(\text{COD})}{d(\text{ThOD})}$ , that differs significantly from unity depending on the organic species from which the COD derives. The main results of this study are the measurement of this gradient for each member of a suite of 34 organic compounds, in each of the two distinct COD measurement methods.

It is not necessarily the case that an analytical method's response function can be simply characterised by an equation of the form  $y = mx$ , as is implicitly assumed above. For example, if the response function is a straight line but has a non-zero  $y$ -intercept, then the response function form should be  $y = mx + b$ . Furthermore, nonlinear response functions, for example, would require the inclusion of additional terms in higher powers of  $x$ . Fortunately, in the present case, the response functions of neither method are significantly non-linear, nor do they have  $y$ -intercepts that differ significantly from zero. So, the simplest response function form  $y = mx$  is justified. This means that the single gradient parameter,  $m = \frac{d(\text{COD})}{d(\text{ThOD})}$ , is sufficient to fully characterise the response function of a given COD measurement method for a given organic compound.

#### D. RESULTS

The 34 organic compounds studied using the PeCOD<sup>®</sup> and Dichromate methods are listed alphabetically in the first column of Table 4. Where appropriate both their common and systematic names are given.

The second column of Table 4 indicates the class(es) of compound the species belongs to. These compounds were selected based on them: being representative of the species found in wastewater; having a well-characterised molecular formula; having reasonable solubility in water; and being mentioned in COD journal article literature.

The third column of Table 4 provides the theoretical mass of COD yielded per unit mass of the compound, were the compound to be mineralised according to the stoichiometry of Equations 1 and 2, above. This is the ThOD, (Theoretical Oxygen Demand), of the compound. Note that these ThOD values vary across the range 0.127 mg COD/mg for Oxalic Acid, where the compound is already almost fully oxidised, to 3.073 mg COD/mg for Benzene, where there are many oxidation steps remaining before its complete mineralisation to CO<sub>2</sub> and H<sub>2</sub>O. These values are required in order to properly prepare the standard solutions corresponding to a given ThOD for a given compound.

The experimentally determined response function gradient,  $m = \frac{d(\text{COD})}{d(\text{ThOD})}$ , is given in the fourth and fifth columns of Table 4 for the PeCOD<sup>®</sup> and Dichromate methods, respectively.

Figure 4 presents the data summarised in column 4 of Table 4 in a more graphical format, for the PeCOD<sup>®</sup> method response function. For each of the 34 compounds, the measured PeCOD<sup>®</sup> COD vs. ThOD relationship is plotted across the range 0-15,000 mg/L COD. To the set of measurement points for each compound was fitted a straight line forced through the point COD = ThOD = 0, using linear least squares regression. The gradients of these lines of form  $y = mx$  are noted on the figure and are the same as those listed in Table 4 below. Generally the regression coefficient,  $R^2$ , was >0.998.

Figure 5 presents the data summarised in column 5 of Table 4 in a more graphical format, for the Dichromate COD method response function. For each of the 34 compounds, the measured Dichromate COD vs. ThOD relationship is plotted across the range 0-1,500 mg/L COD. To the set of measurement points for each compound was fitted a straight line forced through the point COD = ThOD = 0, using linear least squares regression. The gradients of these lines of form  $y = mx$  are noted on the figure and are the same as those listed in Table 4 below. Generally, the regression coefficient,  $R^2$ , was >0.998.

Figures 6-8 graphically illustrate, on a single plot, comparisons of the PeCOD<sup>®</sup> and Dichromate response function gradient (i.e.,  $m = \frac{d(\text{COD})}{d(\text{ThOD})}$ ) results. In all three cases, exactly the same data has been plotted, but in a different order in each case. In Figure 6, the  $x$ -axis lists the compounds in alphabetical order. In Figure 7 the compounds are listed in order of increasing PeCOD<sup>®</sup> method response function gradient. Finally in Figure 8 the compounds are listed in increasing Dichromate method response function gradient.

## E. DISCUSSION

The first remarks will be on a few particular compounds that elicited significantly different responses from the two methods, or unexpected responses in either or both methods:

- Nicotinic Acid, Diethylamine and Benzene are observed to give a much lower response in the Dichromate method than in the PeCOD<sup>®</sup> method. The inability of the Dichromate COD method to fully oxidise these compounds (and many others) is well known from the literature ([Baker *et al.*, 1999; Kim *et al.*, 2000] in Section G, below). The oxidation potential of the photocatalytic PeCOD<sup>®</sup> process is +3.1 V; whereas the oxidation potential of the dichromate ion, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, is only half of this at +1.6 V. Thus, it is to be expected that there will be far fewer (if any) organic compounds resistant to oxidation by the photocatalytic PeCOD<sup>®</sup> method than by the conventional chemical method, even when the latter is assisted by the Ag<sub>2</sub>SO<sub>4</sub> catalyst and prolonged reflux at elevated temperature.
- The Dichromate method yields significantly high response gradients for Propionic Acid (1.23 vs. 0.92) and Valeric Acid (1.39 vs. 1.20) relative to the PeCOD<sup>®</sup> method, for reasons as yet unknown.
- The PeCOD<sup>®</sup> method yields a significantly high response gradient for Oxalic Acid (1.29 vs. 1.00) relative to the Dichromate method. The literature suggests that this compound may display current doubling in some photocatalytic systems, where a single UV photon may yield two photocurrent electrons. This is the only compound where we may have observed such behaviour.
- Sodium Acetate gives a very similar response in both methods, with gradients ( $m = \frac{d(\text{COD})}{d(\text{ThOD})}$ ) of ~0.6, much lower than the expected ~1 gradient observed for acetic acid in both methods. Both methods gave gradients of ~1 for both formic acid and its sodium salt. This idiosyncratic sodium acetate behaviour has long been known for the Dichromate method, and is now observed for the PeCOD<sup>®</sup> method. Its source is not well understood, but suggests a significant departure from the stoichiometry of mineralisation provided in Eq's 1 and 2.

With a sample size of  $N=34$  compounds, it is possible to do some simple statistical characterisation of the set of response gradients for the two methods. Table 3 summarises the basic statistical parameters for the PeCOD<sup>®</sup> and Dichromate response gradient results.

	PeCOD <sup>®</sup>	Dichromate
Number of gradients in set, $N$	34	34
Mean gradient, $m$	1.030	0.972
Median gradient, $m$	1.035	1.020
Std Deviation of $m$ values, (absolute)	±0.127	±0.234
% Std Deviation of $m$ values, (relative)	±12.3	±24.1

**Table 3. Mean, Median and Standard Deviation ( $1\sigma$ ) values for the set of PeCOD<sup>®</sup> and the set of Dichromate response function gradients,  $m$ .**

The *median* value of a set of  $N$  values is frequently a better guide to “typical” or “expected” behaviour than is the *mean* value, since the former is considered to be a more “robust” statistic, meaning it is less susceptible than is the mean to the influence of outliers. We observe that the median  $m$  value of the PeCOD<sup>®</sup> method,  $m \approx 1.04$ , is a little greater than the  $m$  value of Sorbitol,  $m = 1.00$  (by our convention), which we use as our primary calibration compound for this method. This suggests that perhaps Sorbitol is not, after all, the best choice as primary calibrant for the PeCOD<sup>®</sup> method. It would be preferable to select a compound which yields an  $m$  value closer to the median value of  $m \approx 1.04$ . Possibilities would include Glucose at  $m = 1.03$  or 1,4-Diaminobutane at  $m = 1.04$ . Alternatively, a weighted mixture of 2 or 3 compounds (e.g. sorbitol and KHP) could be designed such that  $m \approx 1.04$ .

A similar observation could be made for the Dichromate method, for which the median  $m$  value is ~1.02, which corresponds better to the compounds Sucrose or Benzoic Acid than it does to KHP ( $m = 1.00$ , by convention), which is frequently used, including here, as the default calibrant for the Dichromate method. However, the difference is small (only 2%), significantly less than the magnitude of the overall uncertainty

in the Dichromate method itself. In any case, the use of KHP as primary calibrant is so deeply entrenched in the Dichromate user community that this is unlikely to change.

In figure 2 below we have binned the 34  $m$  values for each method into bins of range 0.0-0.1, 0.1-0.2, 0.2-0.3 . . . , 1.5-1.6, then plotted the population of each bin, in terms of a percentage of the population of  $N=34$  results (i.e., each result represents about 3% on the % Frequency axis). This gives a graphical indication of the distribution of gradients seen on Figures 4 and 5 below. We can observe that the distribution is reasonably similar for the two methods. The differences lie mainly in the “outliers” results lying away from the main peak around  $m=1.0$ .

For the PeCOD<sup>®</sup> method, 88% of the  $m$  values lie in the main band centred on  $m = 1.00$ ,  $0.8 < m < 1.2$ . Another 9% lie in the slightly high band,  $1.2 < m < 1.3$ ; and the final 3% in the low band  $0.5 < m < 0.6$  (this is the single idiosyncratic Na-acetate result). This distribution yields an overall standard deviation ( $1\sigma$ ) of  $\pm 12.3\%$ . (We note that if the idiosyncratic Na-acetate result is excluded from the PeCOD<sup>®</sup> results, the overall standard deviation is reduced to  $\pm 9.3\%$ ).

Correspondingly, for the Dichromate method, 82% of the  $m$  values lie in the main band centred on  $m = 1.00$ ,  $0.8 < m < 1.2$ . Another 6% lie in the higher band,  $1.2 < m < 1.4$ ; and the final 12% are distributed across the low ranges  $0.1 < m < 0.7$  (including the idiosyncratic Na-acetate result). This distribution yields an overall standard deviation ( $1\sigma$ ) of  $\pm 24.1\%$ , double that found for the PeCOD<sup>®</sup> method. (We note that if the idiosyncratic Na-acetate result is excluded from the Dichromate results, the overall standard deviation is reduced only to  $\pm 23.2\%$ , now 2.5 times greater than the corresponding result for the PeCOD<sup>®</sup> method).

The results tend to indicate that the Dichromate method will have low  $m$  (i.e.,  $m \ll 1.0$ ) values for considerably more organic compounds than is the case for the PeCOD<sup>®</sup> method. If we accept the proposition that the ideal COD measurement method will give a reliable estimate of ThOD, then it follows that the PeCOD<sup>®</sup> method is demonstrably superior to the Dichromate method in this regard. The PeCOD<sup>®</sup> method is less likely to give an erroneously low estimate of ThOD, and will yield a ThOD estimate with about half the measurement uncertainty of the Dichromate method, all other things being equal.

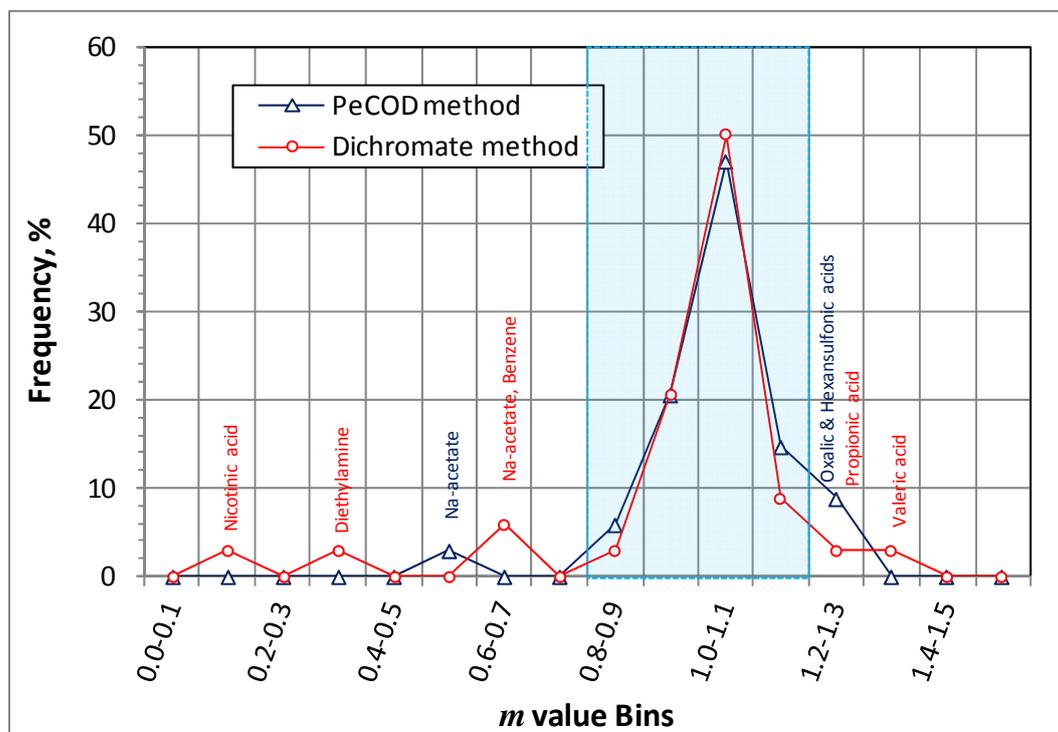


Figure 2. Plot of the frequency with which certain response function gradients,  $m$ , occur amongst the set of 34 organic compounds, for the PeCOD<sup>®</sup> and Dichromate methods.

The tendency for the Dichromate method to have low  $m$  values for a significant proportion of organic compounds has been reported previously in the scientific literature. Janicke [1983] is a book in German

which contains a survey of 565 organic chemicals across 64 classes of compounds. For each compound the ThOD, experimental COD and COD/ThOD ratio (i.e.,  $m$  value) is reported. More accessible is the study by Baker *et al.* [1999] who perform a statistical analysis of Janicke's exhaustive data set. Figure 3 below, plots Janicke's  $m$  value data in the same way as we have plotted ours above.

For Janicke's Dichromate method data ( $N=565$ ), 75% of the  $m$  values lie in the main band centred on  $m = 1.00$ ,  $0.8 < m < 1.2$ . Another 2% lie in the high band,  $1.2 < m < 1.4$ ; and fully 23% are distributed across the low ranges,  $0.0 < m < 0.8$ , strongly biased towards  $m = 0$  with 10 % of  $m$  values in the  $0.0 < m < 0.2$  band. Janicke's data is qualitatively similar to our results for the Dichromate method plotted in Figure 2, with a significant proportion of low  $m$  values.

Janicke identifies the following classes of aromatic and non-aromatic organic compounds as amongst those most likely to yield a particularly low  $m$  value:

Aromatics: benzene, toluene, xylene and derivatives; halogenated aromatics; nitro-aromatics; quinones;

Non-aromatics: pyridine and derivatives (e.g. nicotinic acid); amines (e.g. diethylamine); halogenated alkanes and alkenes; thioethers (e.g. dimethylsulfide); sulfones, sulfoxides (e.g. dimethylsulfoxide) and sulfonic acids.

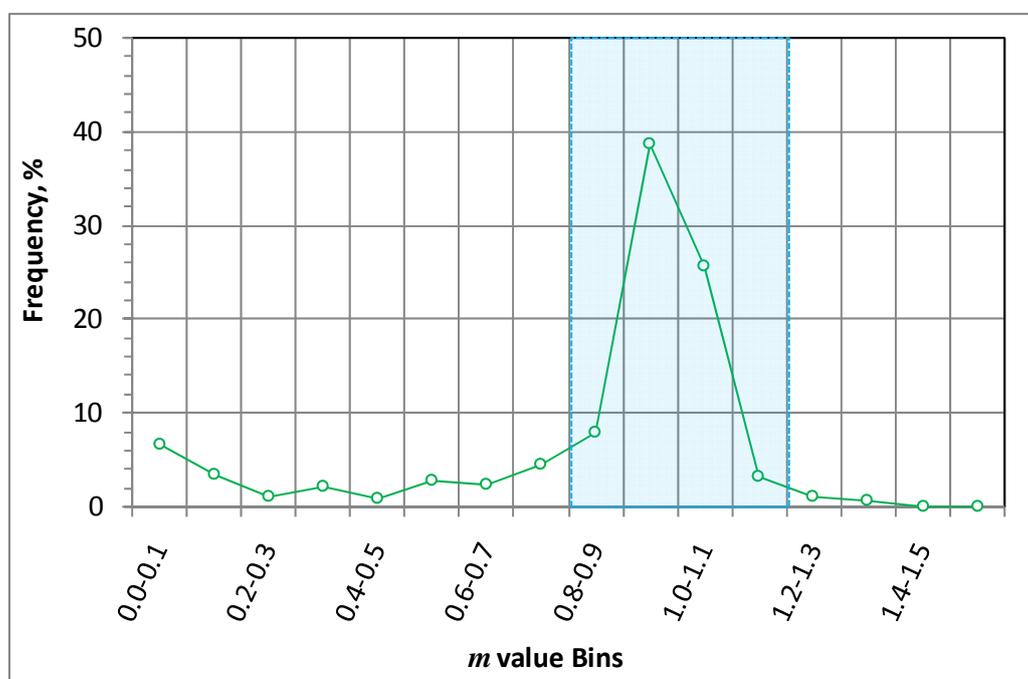


Figure 3. Plot of the frequency with which certain response function gradients,  $m$ , occur amongst the set of 565 organic compounds surveyed by Janicke [1983] using the Dichromate method. Data from Baker *et al.* [1999].

## F. CONCLUSION

The following main conclusions may be drawn from this systematic comparative study of the response functions of the two methods of COD measurement:

- The PeCOD<sup>®</sup> method is a significantly better estimator of ThOD than is the Dichromate method;
- The Dichromate method is much less than 100% sensitive to a significant proportion of organic compounds; this is not the case with the PeCOD<sup>®</sup> method.
- The PeCOD<sup>®</sup> method has approximately half the measurement uncertainty of the Dichromate method.

#### **G. OTHER PUBLICATIONS ON THE RESPONSE FUNCTION OF COD MEASUREMENT METHODS W.R.T. THOD**

Baker, J.R., 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.

Dentel, S.K., Comment on: "Relationship between chemical and theoretical oxygen demand for specific classes of organic chemicals, *Water Research*, **33**(2), 327-334" by J.R. Baker, M.W. Milke, J.R. Mihelcic, *Water Research*, **33**(14), 3220-3222, 1999.

Janicke, W., Chemische Oxidierbarkeit Organischer Wasserinhaltsstoffe. WaBoLu Berichte, Dietrich Reimer Verlag, 1983.

Kim, Y.C., S. Sasaki, K. Yano, K. Ikebukuro, K. Hashimoto and I. Karube, Relationship between theoretical oxygen demand and photocatalytic chemical oxygen demand for specific classes of organic chemicals, *Analyst*, **125**, 1915-1918, 2000.

Organic Compound	Class of Compound	ThOD content of Compound (mg COD/mg)	Gradient of PeCOD <sup>®</sup> Response Function (w.r.t. Sorbitol: $y = 1x$ )	Gradient of Dichromate Response Function (w.r.t. KHP: $y = 1x$ )
Acetic Acid (ethanoic acid)	carboxylic acid, volatile fatty acid	1.066	0.921	1.002
Na-Acetate	Na-salt of carboxylic acid	0.780	0.559	0.610
Acetone (propanone)	ketone, solvent	2.204	0.954	1.078
Aniline (phenylamine)	aromatic, amine	2.405	1.061	1.172
Benzene	aromatic, solvent	3.073	0.840	0.620
Benzoic Acid	aromatic, carboxylic acid	1.965	1.071	1.025
Cadaverine (1,5-diaminopentane)	diamine, animal tissue putrefaction product, foul odour	2.192	0.987	1.088
<i>p</i> -Cresol	aromatic, phenolic	2.515	1.184	1.147
1,3-Diaminopropane	diamine	1.727	0.979	0.900
Diethylamine	secondary amine	2.625	0.880	0.312
Ethanol	alcohol, solvent	2.084	1.071	0.974
Formic Acid (methanoic acid)	carboxylic acid	0.348	1.117	1.031
Na-Formate	Na-salt of carboxylic acid	0.235	1.060	1.023
Glucose	monosaccharide, a sugar	1.066	1.029	0.991
Glutamic Acid	amino acid	0.979	1.076	0.996
Glutaric Acid (pentanedioic acid)	dicarboxylic acid	1.211	1.108	1.013
Glycine	amino acid	0.639	1.119	1.021
Na-Hexanesulfonate (hydrate)	Na-salt of sulfonic acid	1.615	1.209	0.891
Isobutyric Acid	carboxylic acid, volatile fatty acid, foul odour	1.816	1.078	1.093
KHP	aromatic, K-salt of dicarboxylic acid	1.175	1.131	<b>1.000</b>
Lactose	disaccharide, "milk sugar"	1.102	1.022	0.961
Malonic Acid (propanedioic acid)	dicarboxylic acid	0.615	1.003	0.989
MEK (methyl ethyl ketone)	ketone, solvent	2.441	1.022	1.067
Methanol	alcohol, solvent	1.498	0.997	1.103
MTBE (methyl <i>tert</i> -butyl ether)	ether, solvent (in petrol), major soil contaminant	2.721	1.079	1.055
Nicotinic Acid	aromatic, carboxylic acid, "niacin", a pyridine derivative	1.433	0.916	0.143
Oxalic Acid (ethanedioic acid)	dicarboxylic acid	0.127	1.289	0.999
Propionic Acid (propanoic acid)	carboxylic acid, volatile fatty acid, foul odour	1.512	0.921	1.227
Putrescine (1,4-diaminobutane)	diamine, animal tissue putrefaction product, foul odour	1.997	1.041	1.020
Salicylic Acid	aromatic, carboxylic acid, phenolic	1.622	1.015	1.038
Sorbitol	carbohydrate, sugar substitute	1.142	<b>1.000</b>	1.001
Succinic Acid (butanedioic acid)	dicarboxylic acid	0.948	1.076	1.042
Sucrose	disaccharide, "table sugar"	1.122	1.007	1.020
Valeric Acid (pentanoic acid)	carboxylic acid, volatile fatty acid, foul odour	2.037	1.201	1.392

**Table 4. Column 1:** the 34 organic compounds considered in this study; **Column 2:** class of compound; **Column 3:** the ThOD content of the compound, calculated according to the stoichiometry Eq's 1 and 2; **Column 4:** the gradient,  $m$ , of the PeCOD<sup>®</sup> response function, measured COD vs. ThOD, for the organic compound; and **Column 5:** the gradient,  $m$ , of the Dichromate response function, measured COD vs. ThOD, for the organic compound.

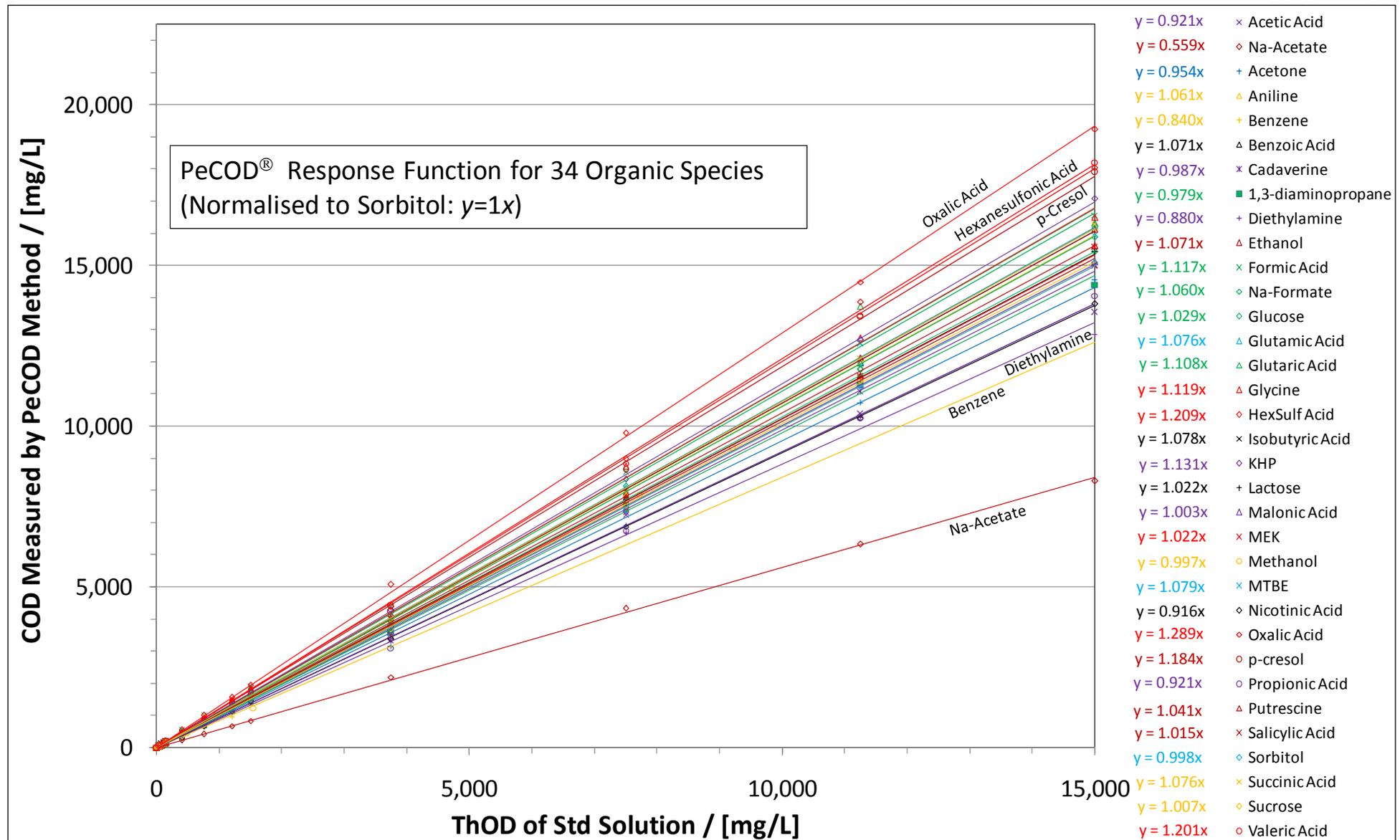


Figure 4. Plot of PeCOD® measured COD vs. ThOD for the set of 34 organic compounds. Experimental data points are shown as symbols. Lines of best fit having form  $y=mx$ , were determined by linear least squares regression.

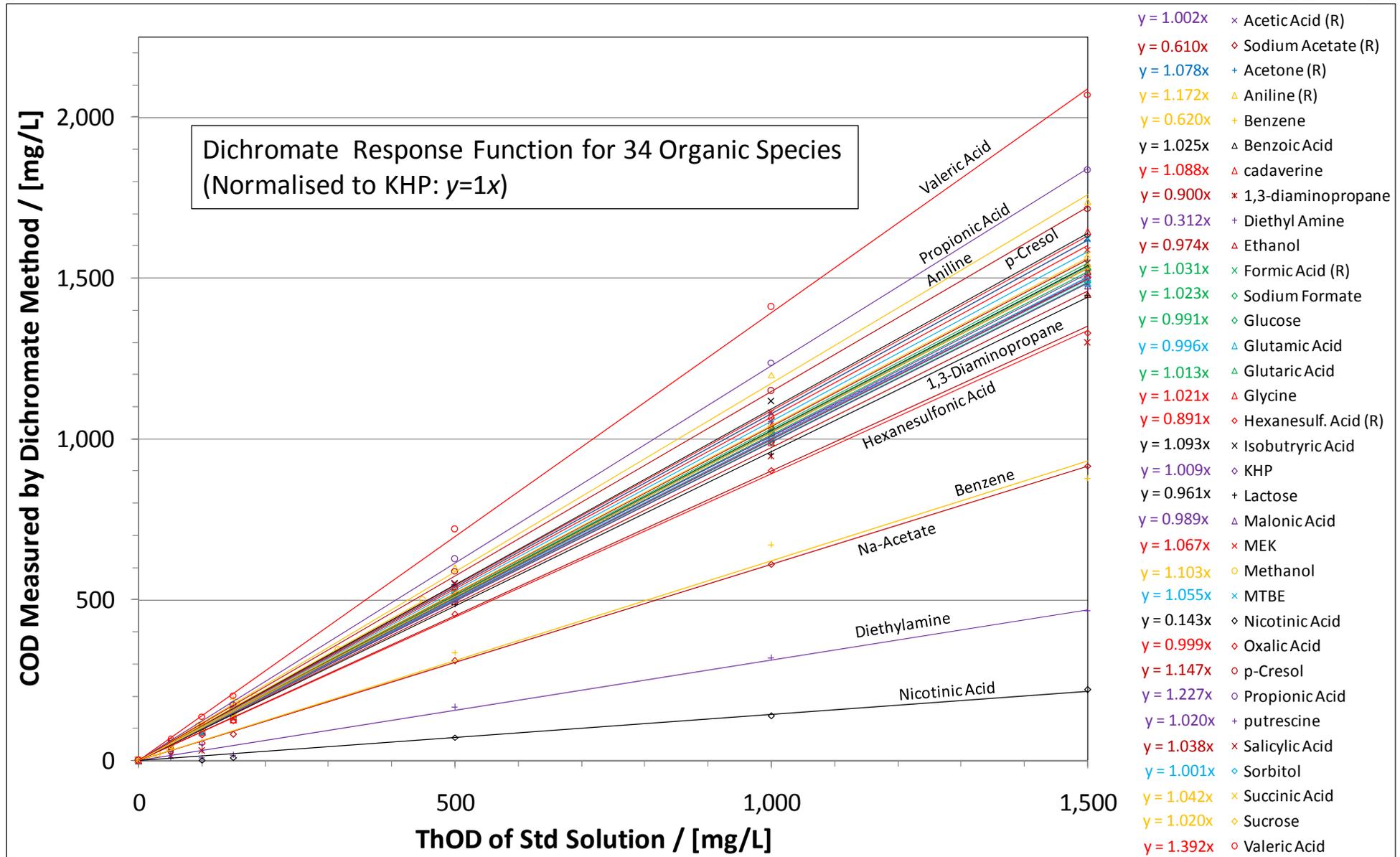


Figure 5. Plot of Dichromate measured COD vs. ThOD for the set of 34 organic compounds. Experimental data points are shown as symbols. Lines of best fit having form  $y=mx$ , were determined by linear least squares regression.

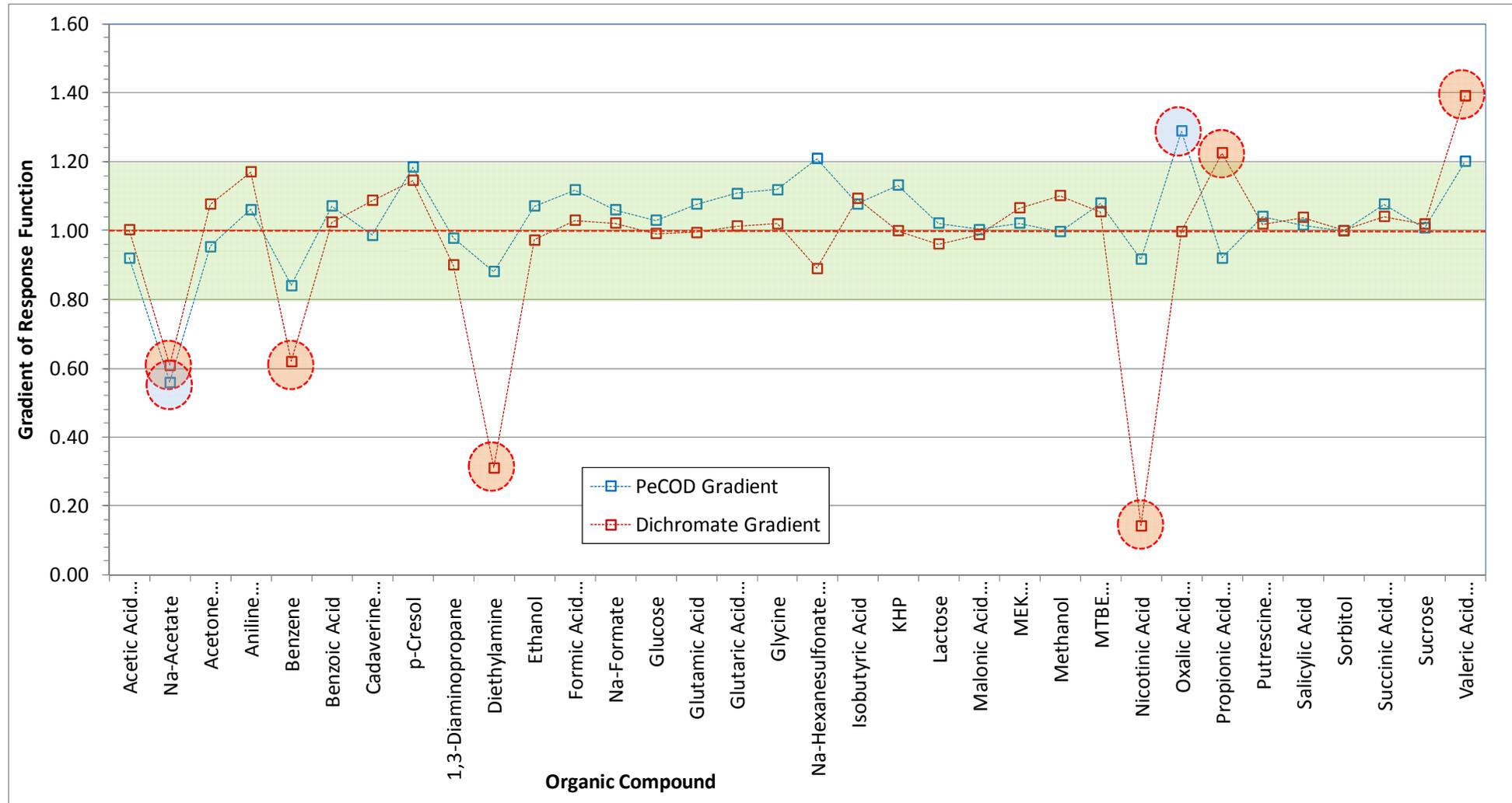


Figure 6. Plot comparing the response function gradients,  $m$ , for the two methods, for all 34 organic species. Here the compounds are listed on the  $x$ -axis in alphabetical order. Possible outliers are indicated by shaded circles.

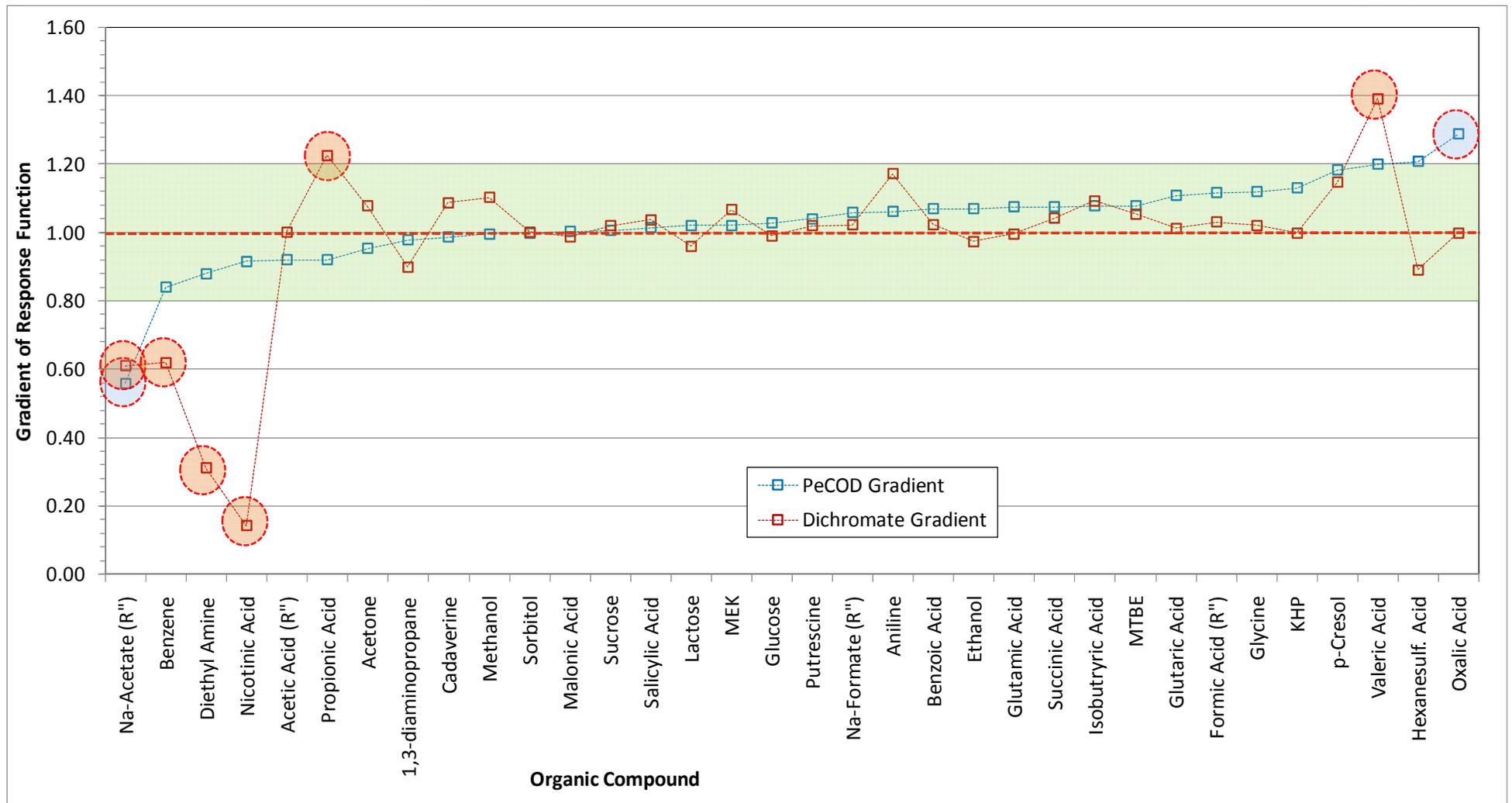


Figure 7. Plot comparing the response function gradients,  $m$ , for the two methods, for all 34 organic species. Here the compounds are listed on the  $x$ -axis in order of increasing PeCOD<sup>®</sup> gradient. Possible outliers are indicated by shaded circles.

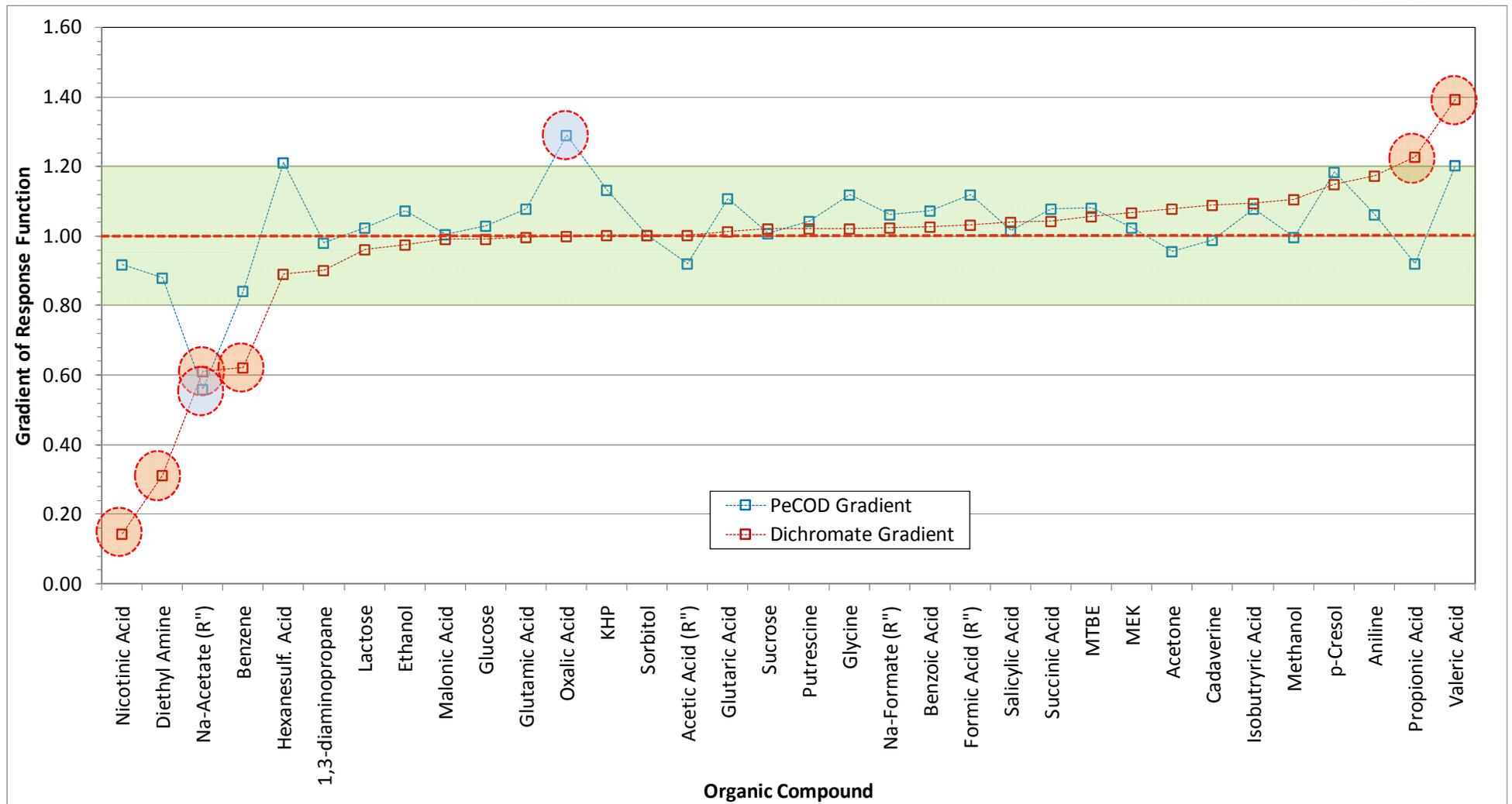


Figure 8. Plot comparing the response function gradients,  $m$ , for the two methods, for all 34 organic species. Here the compounds are listed on the  $x$ -axis in order of increasing Dichromate gradient. Possible outliers are indicated by shaded circles.