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Modified APHA closed-tube reflux colorimetric method for TOC determination in water and wastewater

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Abstract The analysis of total organic carbon (TOC) by the American Public Health Association (APHA) closed-tube reflux colorimetric method requires potassium dichromate ($K_2Cr_2O_7$), silver sulfate ($AgSO_4$), and mercury ($HgSO_4$) sulfate in addition to large volumes of both reagents and samples. The method relies on the release of oxygen from dichromate on heating which is consumed by carbon associated with organic compounds. The method risks environmental pollution by discharging large amounts of chromium (VI) and silver and mercury sulfates. The present method used potassium monochromate (K_2CrO_4) to generate the $K_2Cr_2O_7$ on demand in the first phase. In addition, miniaturizing the procedure to semi microanalysis decreased the consumption of reagents and samples. In the second phase, mercury sulfate was eliminated as part of the digestion mixture through the introduction of sodium bismuthate ($NaBiO_3$) for the removal of chlorides from the sample. The modified method, the potassium monochromate closed-tube colorimetry with sodium bismuthate chloride removal (KMCC-Bi), generates the potassium dichromate on demand and eliminates mercury sulfate. The semi microanalysis procedure leads to a 60% reduction in sample volume and ≈ 33.33 and 60% reduction in monochromate and silver sulfate consumption respectively. The LOD and LOQ were 10.17 and 33.90 mg L^{-1} for APHA, and 4.95 and 16.95 mg L^{-1} for KMCC-Bi. Recovery was between 83 to 98% APHA and 92 to 104% KMCC-Bi, while the RSD (%) ranged between 0.8 to 5.0% APHA and 0.00 to 0.62% KMCC-Bi. The method was applied for the UV-Vis spectrometry determination of COD in water and wastewater. Statistics was done by MINITAB 17 or MS Excel 2016.

Introduction

The total organic carbon (TOC) analysis being a non-specific test gives no information about specific species of substances or chemical composition of a sample. It however gives the total carbon associated with organic compounds in the sample or compound (HACH 2015; LaPara et al. 2000; USNRC 1980). Hence,

$$TC = TOC + TIC \tag{1}$$

$$TOC = TC - TIC \tag{2}$$

TC   total carbon
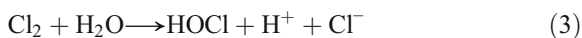TOC   total organic carbon
TIC   total inorganic carbon

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The TOC analysis may be required for a number of reasons including (1) regulatory or process control phenomenon (HACH 2015), (2) monitoring efficiency of processes in municipal and industrial waste control to ensure the discharge of less harmful or harmless waste to the environment, (3) industrial monitoring of corrosion which may increase the cost of production due to redox reaction of some organic compounds, (4) ensuring that microorganisms do not grow in water used for pharmaceutical products (Deborde and von Gunten 2008; HACH 2015; LaPara et al. 2000), (5) screening rocks and underground water for potential petroleum sources (Jarvie 1991), and (6) ensuring microbe-free water for the production of electronic chips.

Another major importance of monitoring TOC is the formation of carcinogenic disinfection by-products (DBPs) during and/or after water disinfection. This is particularly important to ensure safe drinking water in addition to environmental protection and avoiding long range effects when treated water is discharged. Monitoring is necessary to reduce or eliminate organic compounds prior to disinfection (Deborde and von Gunten 2008; HACH 2015).

The formation of DBPs may be understood by, for instance, bubbling chlorine into water. The resulting mixture contains hypochlorous acid and other species some of which are transient (Eqs. 3–5), whose dissociation is pH dependent. The hypochlorous acid and some species being electrophiles react with organic compound by substitution, addition, or oxidation. The products of the substitution and addition mechanisms are harmful chlorinated organic compounds while oxidation produces non-chlorinated organic compounds that can also be harmful (Deborde and von Gunten 2008; USNRC 1980).

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \tag{3}$$

$$HOCl \longrightarrow H^+ + OCl^- \tag{4}$$

$$H_2O + Cl^- \longrightarrow H_2OCl^+ \tag{5}$$

Furthermore, species such as HOCl, OCl^-, Cl_2, H_2OCl^+, and Cl^- ions have the potential to oxidize both iodide and bromide to hypoiodous and hypobromous acids, respectively, a process thought to be particularly responsible for the presence of trihalomethanes (THMs) in disinfected water (Deborde and von Gunten 2008; Golea et al. 2017; USNRC 1980). There are many THMs; the ones of interest are the trichloromethane (TCM),

dibromochloromethane (DBCM), bromodichloromethane (BDCM), and tribromomethane (TBM) because they are more associated with treated water and hazardous. For their cancer risk, the USEPA sets regulation to control the level of THMs in drinking water and water used by the public to a maximum of 80 mg L^{-1} especially for the four THMs of interest (Oram 2014; USEPA 2006). Based on this maximum level risk assessment, studies have been made especially in swimming pools and drinking and pipe bone water. For instance, the predicted cancer and health risks were found to be high in swimming pools (Hang et al. 2016; Hsu et al. 2009; Lee et al. 2009) and shower (Chowdhury and Champagne 2009), and the risk was dependent on conditions such as temperature, number of swimmers (in swimming pools), and the organic matter content of the water. In their study of the characteristics of THM production and associated risk assessment, Lee et al. (2009) treated swimming pools with different disinfection methods and found that the life time cancer risk by dermal contact and ingestion was negligible, but Panyakapo et al. (2008) found a very high cancer risk in another study. Furthermore, a study of swimmers in a swimming pool detected more than 6400 metabolic features in exhaled breathe and 293 were associated with at least one DPB. In the same study of urine or water, a total of 333 metabolic features were associated with at least one DBP (Veldhovena et al. 2018).

The TOC analysis is widely conducted by the American Public Health Association (APHA) closed-tube reflux colorimetric method 5220 (APHA 1995) due to its simplicity both in equipment and reagent requirements. The method determined TOC as chemical oxygen demand (COD) and the digestion reagent has been strong sulfuric acid solutions containing potassium dichromate and silver and mercury sulfates. The principle relies on the release of oxygen by the dichromate when heated and subsequent reaction of the oxygen with carbon associated with organic compounds. The chemistry of process is a redox reaction where hexavalent chromium is reduced to the trivalent specie as simplified in (Eq. 6). The COD is then determined either as the amount of Cr(III) generated or dichromate remaining. The method has tremendous impacts on the environment due to discharge of hazardous elements.

$$2Cr_2O_7^{2-} + 3C + 16H^+ \rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O \tag{6}$$
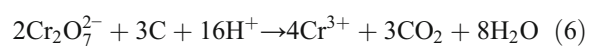
Understanding the behavior of the mono- and dichromates with pH (Eqs. 7–12) was significant in

the method modification process (Brito et al. 1997; Gans 2000).

$$CrO_4^{2-} + H^+ \rightleftharpoons HCrO_4^- \qquad (7)$$

$$K_1 = \frac{[HCrO_4^-]}{[CrO_4^{2-}][H^+]} \qquad (8)$$

$$2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad (9)$$

$$K_D = \frac{[Cr_2O_7^{2-}]}{[HCrO_4^-]^2} \qquad (10)$$

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad (11)$$
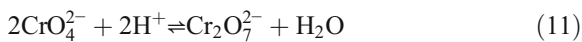
$$K_D^* = \frac{[Cr_2O_7^{2-}]}{[CrO_4^{2-}]^2 [H^+]^2} \qquad (12)$$

The calculated log K_1 and log K_D are 5.89 and 2.05, respectively, and the concentration of the species can be found at various pH levels by means of equilibrium expression (Brito et al. 1997). The total concentration of chromium is the sum of all the species (Eq. 13).

$$[Cr] = [CrO_4^{2-}] + [HCrO_4^- + 2[Cr_2O_7^{2-}]] \qquad (13)$$

A plot of the pCr against pH (Eqs. 14 and 15) gives the predominant diagram (Fig. 1) depicting the conditions of pH and concentration where chemical species have highest concentration in solution with multiple acid-base equilibria (Brito et al. 1997; WFI 2016).

$$pCr = -\log_{10}[Cr] \qquad (14)$$

$$pH = -\log_{10}[H^+] \qquad (15)$$

The lines in the diagram represent points where the opposite species are of equal concentration. However, all species are of equal concentration at point "O". The chromate ion predominates at high pH, but at pH < pK_1 (low pH), the hydrogen chromate ion is predominant in dilute solution while the dichromate ion predominates in concentrated solutions.

From the stand point of the predominance diagram of mono- and dichromates, the latter can be

generated on demand in a strong acid medium (Brito et al. 1997; Gans 2000).

The UV spectra of the chromate and dichromate depicted in Fig. 2 proved the phenomenon in Eq. 6 and Fig. 1 that the monochromate exists as dichromate in strong acid solution.

The APHA method generates and discharges hazardous Cr(VI), Hg(II), and Ag(I) into the environment. To reduce this effect, LaPara et al. (2000) miniaturized the method in a research that reduced the discharge of these substances by > 80%. Nevertheless, the hazard persists.

The major interference in TOC analysis has been chloride (Dobbs and Williams 1963; Miller et al. 2001). Mercury sulfate was incorporated into the digestion mixture for the first time by Dobbs and Williams (1963) to remove chloride interference (Eq. 16) from where the APHA closed-tube reflux colorimetry method evolved. Several other methods have evolved since then and still use potassium dichromate (Abuzaid et al. 1997; Canals and Del Remedio Hernandez 2002; Kayaalp et al. 2010a, b; Vyrides and Stuckey 2009; Zupančič and Roš 2011).

$$Hg^{2+} + 2Cl^- \longrightarrow HgCl_2 \qquad (16)$$

An effort made to eliminate the chloride interference has included the use of sodium bismuthate (Eq. 17) in a TOC analysis (Miller et al. 2001). Bismuth plays a role, an antacid and treatment of gastrointestinal tract infections, thus safer in the environment compare to mercury (Hammond 2004; Kean 2011; Kruger et al. 2003; Parnell 1924).

$$Bi^{5+} + 2Cl^- \longrightarrow Cl_2 + Bi^{3+} \qquad (17)$$
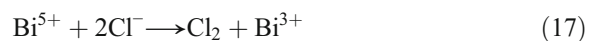
However, Miller et al. (2001) developed a method that used a trivalent manganese oxidant as the digestion reagent with sodium bismuthate for chloride removal preceding digestion. Although the method is green, the chloride removal procedure is complicated and flow of the sample may be difficult to control with multiple cartridges, besides its required 0.5 g sodium bismuthate per cartridge. The design of the chloride removal device used one cartridge at a time, thus not time friendly and may increase incident of sample transfer with shortage of cartridges.

This research modified the APHA closed-tube reflux colorimetry method in two steps. The first step replaces potassium dichromate ($K_2Cr_2O_7$) digestion reagent by

**Fig. 1** The predominance diagram of mono- and dichromate species. Adopted from (Brito et al. 1997; WFI 2016)
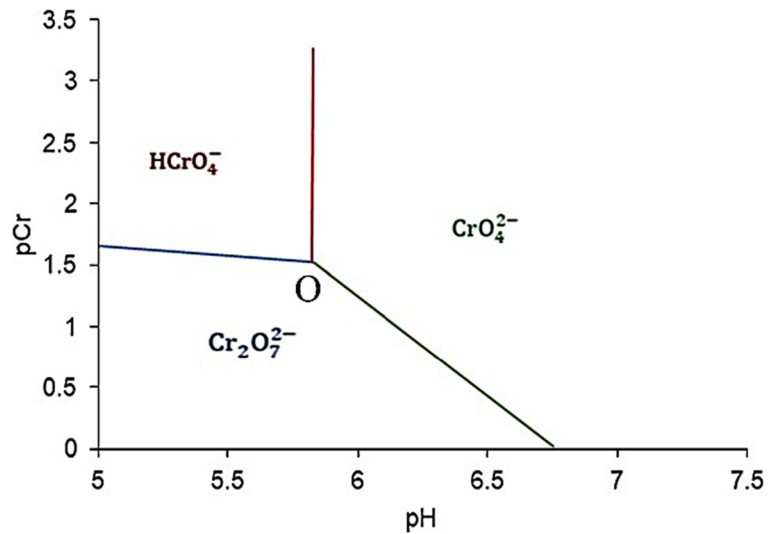
generating it on demand from potassium monochromate (K_2CrO_4). Optimizing this step precedes a second step which eliminates mercury sulfate and introduced sodium bismuthate for the removal of chlorides prior to digestion. The method was simplified by dispersing the sodium bismuthate in the sample instead of using solid phase cartridge. The dispersion procedure reduced the consumption of sodium bismuthate compare to other methods (Miller et al. 2001). A semi microanalysis procedure was adopted, which reduced the consumption of sample, digestion reagent, and catalyst thus further green the method compares to APHA closed-tube reflux colorimetry method. Parameters such as time,

temperature, amounts of catalyst, sodium bismuthate, and potassium monochromate were optimized.

Materials and method

Instrumentation

The UV-Vis analysis was performed on the Shimadzu UV-1800 (Shimadzu, Japan). The digestion process was accomplished on Hanna COD reactor (H1839800, Hanna Inst. Hungary).
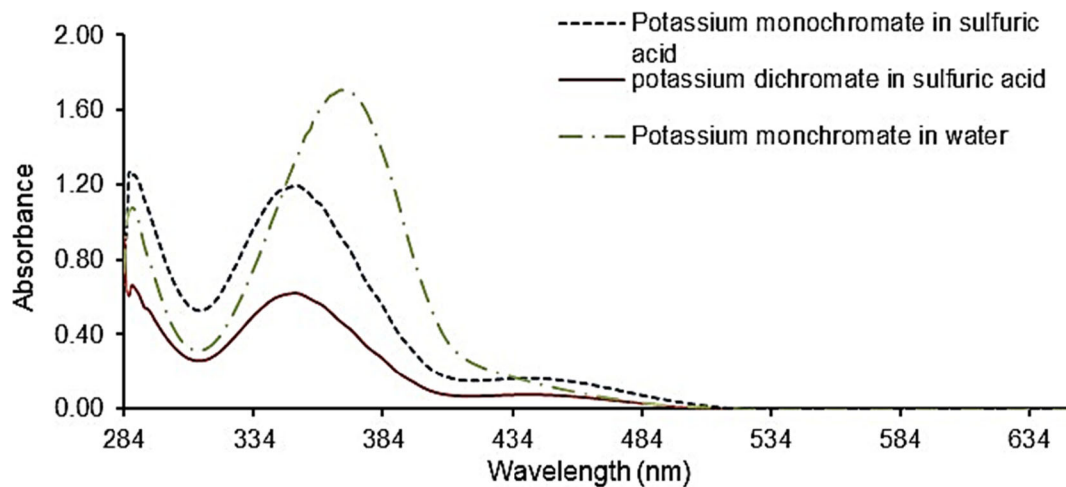
Fig. 2 Spectra of dilute potassium chromate (K_2CrO_4) in water, potassium chromate (K_2CrO_4), and potassium dichromate ($K_2Cr_2O_7$) in concentrated H_2SO_4 at wavelength of 900 to 200 nm

Reagents

All reagents were of analar grade. Digestion reagents (DRs) were prepared according to the APHA method (APHA 1995; LaPara et al. 2000). They were categorized into DR-A, DR-B, and DR-C. The DR-A and DR-B contain dichromate and monochromate respectively in a mixture with mercury sulfate, while DR-C contains only monochromate in sulfuric acid. In brief, 2.6 g $K_2Cr_2O_7$ or K_2CrO_4 and 8.3 g $HgSO_4$ or 2.6 g K_2CrO_4 (Merck, Darmstadt, Germany) were mixed with 100 mL deionized water in a 250-mL volumetric flask and 42 mL of conc. H_2SO_4 was added slowly. The mixture was cooled to room temperature and made up to the mark with deionized water. The reagents were stored in amber screw cap reagent bottles. The catalyst, Ag_2SO_4 (Merck, Darmstadt, Germany), was prepared by mixing 1.4 g of the salt in 250 g conc. H_2SO_4 in a 250-mL beaker, covered with a watch glass, allowed to dissolve for 24 h in the dark, and then stored in an amber screw cap reagent bottle. A 0.077 or 0.085 g potassium hydrogen phthalate (KHP) was dissolved in 100 mL DI water to obtain 900 and 1000 mg L^{-1} COD standards respectively. A 1000 mg L^{-1} solution of chloride ions was prepared by dissolving 1.65 g of the NaCl (Bendoson Lab. Chem., Selangor, Malaysia), in a liter of deionized water.

Sampling and treatment

The samples of hospital wastewater were obtained from Sungai Buloh Hospital, Selangor wastewater treatment plant, while bottled drinking water were obtain in Kamal Agencies, Jalan 17/1A, Flat section 17, Petaling Jaya. The pH measurement was performed with the pH meter (F20, Mettler Toledo FiveEasy, Switzerland). The wastewater samples were filtered through Whatman paper and diluted tenfold before analysis.

Procedure

A 1 mL portion of the sample or standard was dispensed into a centrifuge tube and 50 mg of sodium bismuthate was added and shake horizontally to disperse and allowed to stand for about 10 to 20 s and then centrifuge on the Chinamedevice centrifuge (Chinamedevice 0412-1(80-2), China). The sample was decanted into a chemical oxygen demand (COD), digestion tube (16 × 100 mm, Darmstadt, Japan), and 1.2 mL digestion

reagent (DR-C) was added. A 1.4 mL portion of the catalyst was dispensed carefully into the mixture by the sides of the tube such that it formed a layer. The tube was closed securely with a screw cap cover, swirl gently, and allowed to digest for 2 h at 150 °C on the COD digester block (H1839800, Hanna Inst. Hungary). The tube was removed, allowed to cool to room temperature, and inverted to mix before venting. The digest was transferred into a 2.5-mL polystyrene cuvette and the absorbance was read at 600 nm on a spectrophotometer (Shimadzu UV - 1800 Japan). The procedure was the same for the KMCC method using DR-B, but without chloride removal step and the APHA closed-tube method using with 2.5 mL sample, 1.5 mL digestion mixture (DR-A), and 3.5 mL catalyst, and the results were compared.

## Results and discussion

Developing the method

Spectrometric characterization of the potassium monochromate and dichromate

It was important to ensure that potassium monochromate and dichromate are similar or the same in the reaction medium. The comparative UV-Vis spectra of $K_2Cr_2CO_7$ and K_2CrCO_4 in strong H_2SO_4 solution and K_2CrCO_4 in deionized water are indicated in Fig. 2 and prove the existence of monochromate as dichromate in acid medium in which the digestion is done.

Table 1 Preliminary digestion experiments with the potassium monochromate as the digestion reagent. Experiment A represents the volume of sample and reagents as recommended in the TOC analysis with the APHA standard method. Percentages are the volumes used relative to standard APHA closed-tube reflux method

Experiment	Vol. sample (mL)	Vol. of digestion reagent (mL)	Vol. of catalyst (mL)
A	2.5	1.5	3.5
B	1.0(40%)	0.9(60%)	1.4(40%)
C	1.5(60%)	0.9(60%)	1.4(40%)
D	1.0(40%)	0.6(40%)	2.1(60%)

Fig. 3 Signals from preliminary experiments A to D at 150 °C with 350 mg L^{-1} standard KHP. Absorbance determined at wavelength (λ) = 600 nm (λ^* = read with undigested blank as reference solution)
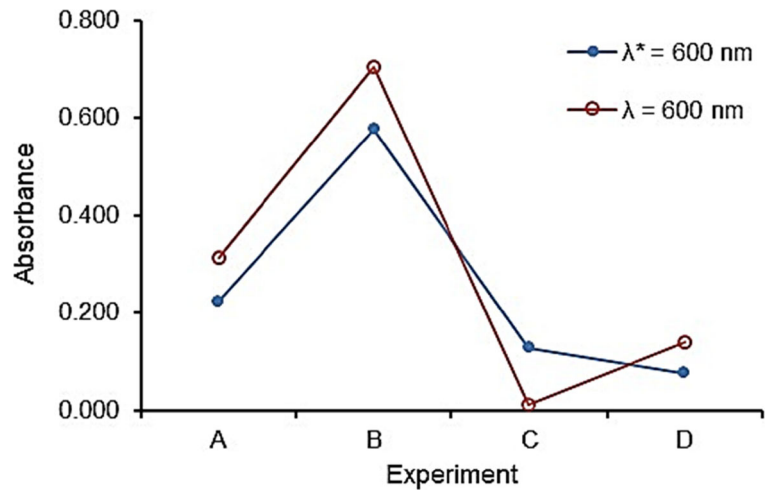

Preliminary investigation

The American Public Health Association (APHA) closed-tube reflux colorimetric method requires 2.5 mL sample, 1.5 mL digestion mixture, ($K_2Cr_2O_4$ and $HgSO_4$), and 3.5 mL catalyst (Ag_2SO_4) solutions in sulfuric acid. The digestion reagent for preliminary digestion was prepared according to the APHA closed-tube method but used potassium monochromate (K_2CrO_4). In Table 1, ratios of the sample and reagents were varied reference to the APHA recommendation, at a constant potassium hydrogen phthalate (KHP) standard. The mixtures were treated according to the APHA closed-tube reflux method (APHA 1995). The curve of the absorbance at wavelength 600 nm against the experiments is presented in Fig. 3. Experiment (B) was

optimized due to the high amount of Cr(III) produced (Eq. 6). The effect of temperature, digestion mixture, catalyst, and chloride ion concentration was examined. The second step of the modification that included the chloride removal step was then introduced and optimized. The calibration linearity studies, LOD, and LOQ as well as the accuracy and precision of the method were performed on the methods.
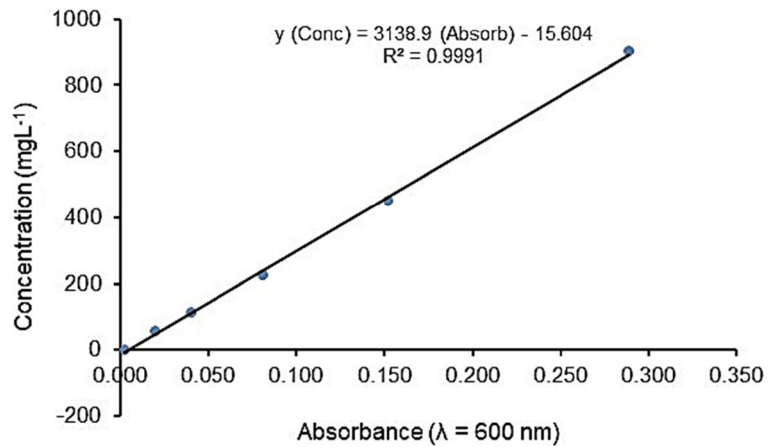
Temperature and time of the digestion

The digestion temperature was studied at 105 and 150 °C, the only temperature levels of the Hanna (H1839800, Hanna Inst. Hungary) digestion block. Portions of a 450 mg L^{-1} KHP standard were digested at these temperature points for 2 h. The UV-Vis analysis in Fig. S1 (Supplementatry) showed that the suitable

Fig. 4 APHA closed-tube colorimetry method calibration curve from standard KHP solutions
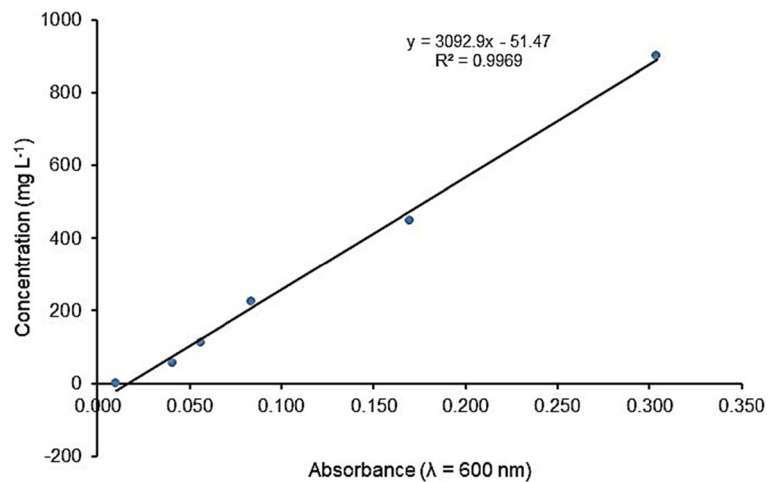
Fig. 5 KMCC closed-tube method calibration curve using standard KHP solutions

digestion temperature is 150 °C. Similarly, the digestion time was monitored by subjecting the same concentration of KHP standard to digestion at different times at 150 °C. The digestion time of 2 h yielded better signals after UV-Vis analysis (Fig. S2 (Supplementary).

Effect of the digestion mixture and catalyst

The volume of digestion reagent required for the digestion was determined by varying the volume of the digestion mixture from experiment B (Fig. 2), at a constant KHP standard solution. Figure S3 (Supplementatry) shows the curve 600 nm and the 1.2 mL of digestion reagent seems better. The catalyst is a substance needed to speed up the rate of a chemical reaction. The effect of increase concentration of a catalyst was monitored at 150 °C and optimized digestion reagent concentration. From the spectrum in Fig. S4 (Supplementatry), 1.4 mL catalyst was chosen as the optimum volume.

Calibration linearity of APHA and KMCC closed-tube reflux methods

A study of the proportional response of both instrument and/or method to changing concentration is termed the calibration studies. The APHA and KMCC closed-tube methods were compared. Concentration of KHP standards ranging from 0 to 900 mg L^{-1} was subjected to both APHA and KMCC closed-tube reflux digestion and absorbance was read at 600 nm. Figures 4 and 5 indicate the linearity, respectively, of both APHA and the KMCC closed-tube reflux colorimetric methods at the given range of KHP standards.

Effect of chloride concentration on APHA and KMCC

To study the effect of chloride, four portions of KPH standard of the same concentration were spiked with 0, 50, 100, and 200 mg L^{-1} sodium chloride solution. The samples were digested as in the procedure and analyzed at 600 nm using DI water as the reference solution.

Table 2 Mean values ($n = 3$) of COD showing the effect of chloride on KMCC method and APHA closed-tube reflux colorimetric method on 400 mg L^{-1} KHP standard

Chloride conc. (mg L^{-1})	Mean COD (mg L^{-1})		COD recovery (%)		RSD(%)	
	KMCC	APHA	KMCC	APHA	KMCC	APHA
0.00	383.67 (4.61)[a]	430.79(7.79)[a]	95.92	107.70	1.202	1.808
50.00	439.56 (9.22)	425.60 (8.99)	109.89	106.40	2.097	2.113
100.00	399.64 (4.61)[b]	542.42 (4.50)[b]	99.91	135.60	1.154	0.829
200.00	423.59 (4.61)[c]	576.16 (4.50)[c]	105.90	144.04	1.088	0.780

Different superscript letters indicate statistically significant

Fig. 6 Mean signal ($n = 3$) from digest of the KMCC and KMCC-Bi closed-tube colorimetric methods at various concentration of standard KHP solution spiked in 200 mg L^{-1} NaCl
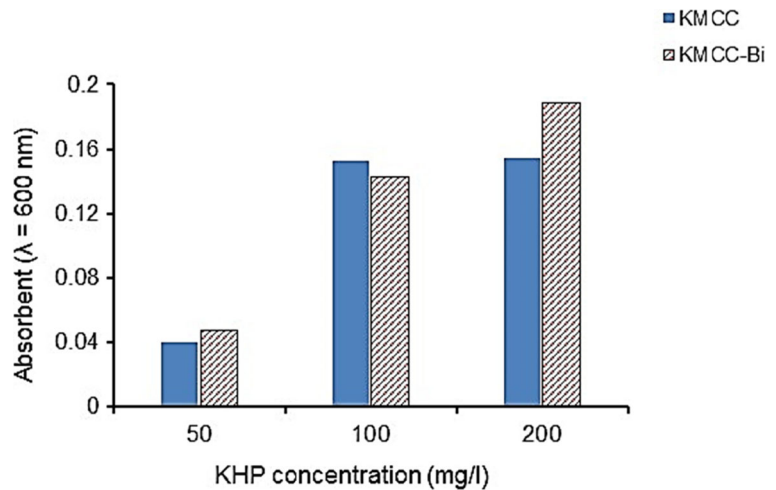

Table 2 bares the effects of chloride concentration on the methods where statistical significance was observed but the recovery indicates that the KMCC seems to endure effect of chloride better at high chloride concentration.

The chloride removal step and calibration of the KMCC-Bi

From the knowledge that $K_2Cr_2O_7$ can be generated on demand from K_2CrO_4 and used as the digestion reagent as shown in the previous step, the second step of the modification was introduced. Blank samples were spiked with various amounts of KHP and constant amount of chloride. The signals (Fig. 6) from the KMCC digest were compared with digest from DR-C (reagent without $HgSO_4$) after $NaBiO_3$ treatment, and the later procedure was named the potassium monochromate closed-tube colorimetry with sodium bismuthate chloride removal, (KMCC-Bi). This step was a prerequisite to further eliminate the $HgSO_4$ from the digestion reagent used in the APHA method, thereby paving the way for the final modification of APHA to KMCC-Bi method. Signal in Fig. 6 indicates the suitability of the H_2SO_4-K_2CrO_4 (DR-C) for COD determination after the removal of chloride interference with sodium bismuthate.

The calibration curve (Fig. 7) for the KMCC-Bi was made for further study of the method. Furthermore, the amount of sodium bismuthate required and the method of chloride removal depicted in Fig. 8 seem to prove the stability of the interference removal by dispersion as compared to elution method as sodium bismuthate concentration increases. Miller et al. (2001) reported that long contact of the sample with the bismuthate could affect the sample. That is probably responsible

Fig. 7 The KMCC-Bi calibration curve using standard KHP solution

$$y \text{ (conc)} = 2479.2x \text{ (Absorb)} - 50.375$$
$$R^2 = 0.9969$$
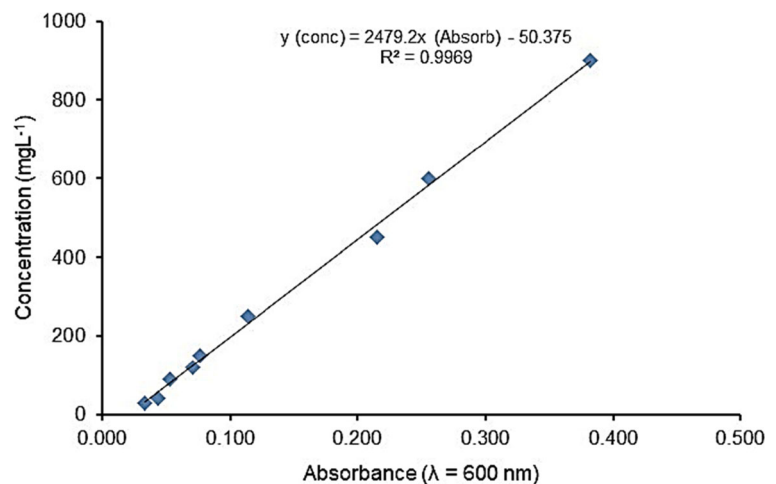
Fig. 8 Comparison of the mean recovery (%) ($n = 3$) of column and dispersion method of chloride interference removal 400 mg L^{-1} sodium chloride and 450 mg L^{-1} KHP
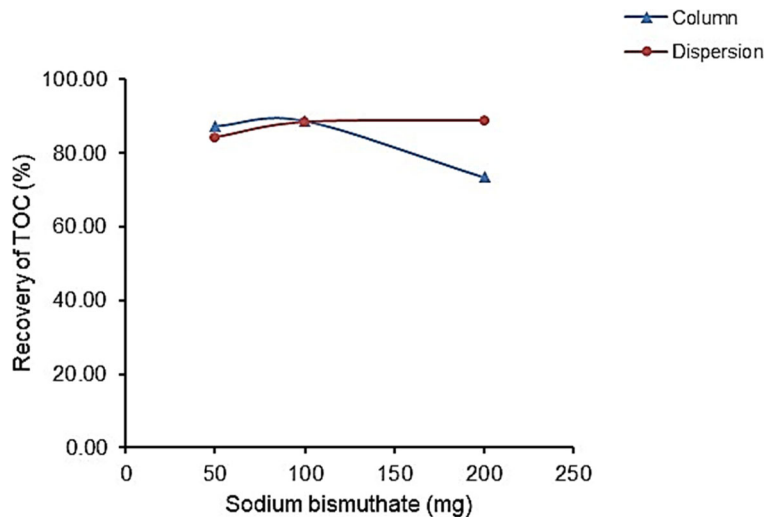
of the 73% recovery at 200 mg sodium bismuthate with the column removal method observed in Fig. 8. On the other hand, the recovery from the dispersion method remains relatively steady with increasing sodium bismuthate.

Limit of detection and limit of quantitation

The concentration of analyte in a matrix, which cannot be reliably quantify, is the limit of detection (LOD) while that which can be quantified with certainty is referred to as the limit of quantitation (LOQ). The signal to noise ratio (S/N), graphical methods, and visual methods are some of the popular methods for the determination of these limits. The graphical method as described by McHale (2012) and Taylor (1987) was employed in this study. The method determines the limits from an SD of a pooled data of different concentrations within the calibration range as shown in Figs. S6, S7, and S8, and Tables S1, S2, and S3 of the Supplementary material.

Briefly, five portions of blank sample were spiked with standard KHP of concentration ranging from 56.25 and 900 mg L^{-1} COD. The series was subjected to either APHA, KMCC, or KMCC-Bi closed-tube reflux colorimetric methods. Analysis was done in triplicate. The mean and standard deviation (SD) of each level of the series were determined. The curves of SD vs theoretical concentration were obtained. The absolute intercept, which represents the pooled standard deviation, was used to compute the limits. The LOD and LOQ were

three and ten times the intercept respectively and are presented in Table 3.

Accuracy and precision

The accuracy and precision were determined following the method described by (Al-Rimawi 2014; Narola et al. 2011). Triplicate analysis of blank samples spiked to 100, 200, 450, and 900 mg L^{-1} KHP standards, and 120, 250, 450, and 600 mg L^{-1} KHP for the KMCC-Bi method previously passed through sample preparation was performed. Absorbance of the digested samples was read at 600 nm. The recovery (%) and relative standard deviation (RSD (%)) of each level were computed (Table 4), and compared with the literature (Narola et al. 2011).

Application to water and wastewater

Total organic carbon of wastewater from Sungai Buloh Hospital, Selangor wastewater treatment plant, and

Table 3 A comparison of the limits of detection and quantitation of the APHA and modified methods

Method	Limits (mg L^{-1})	
	LOD	LOQ
APHA	10.17	33.9
KMCC	6.89	22.95
KMCC-Bi	4.95	16.95

Table 4 Mean values ($n = 3$) of accuracy and precision study of closed-tube reflux colorimetry of APHA, KMCC, and KMCC-Bi at different levels of concentration. Absorbance at $\lambda = 600$ nm

Spiked (mg L^{-1})	Accuracy				Precision	
	Mean recovery (mg L^{-1})		Recovery (%)		RSD (%)	
	APHA	KMCC	APHA	KMCC	APHA	KMCC
100	83.52 (4.014)	93.56 (0.091)	83.52	93.56	4.806	0.097
200	169.21(4.014)	226.25(4.471)	84.60	113.12	2.372	1.976
450	442.96 (7.789)	444.85 (0.054)	98.44	98.85	1.758	0.012
900	840.97 (6.715)	873.08 (5.214)	93.44	97.01	0.798	0.597
KMCC-Bi						
Spiked (mg L^{-1})	Accuracy				Precision	
		Mean(SD)	Recovery (%)		RSD (%)	
120		125.46(0.00)	104.55		0.00	
250		232.22(0.00)	92.89		0.00	
450		483.41(0.00)	107.42		0.00	
600		581.79(3.63)	96.97		0.62	

bottled water from Kamal Agencies, Petaling Jaya, were analyzed. Absorbance was taken at $\lambda = 600$ nm. The result in Table 5 showed some consistency between the modified and APHA closed-tube reflux colorimetry methods. The TOC level of BW2 was < LOD when analyzed with the APHA and KMCC methods while the KMCC-Bi method detected 7.2 mg L^{-1} TOC in the same sample. This could probably prove the sensitivity of chloride removal with the sodium bismuthate. The percentage recovery from spiked samples further shows

some agreement of the method with the standard one. The APHA method recorded 94 to 150% recovery, but the recovery from KMCC and KMCC-Bi was 101 to 168% and 102 to 168% respectively. The mean of TOC in HW1 was significantly different from the other methods. Various levels of significance in the means of TOC were observed in a few other samples compare to the standard method.

The miniaturized APHA conducted by LaPara et al. (2000) and the trivalent manganese with bismuthate

Table 5 Means ($n = 3$), of the result from the modified and the APHA closed-tube colorimetry methods. (Absorbance were read at $\lambda = 600$ nm)

TOC (mg L^{-1})				Spike recovery						
				Added (mg L^{-1})	Found (mg L^{-1})			Recovery (%)		
Sample	APHA	KMCC	KMCC-Bi	KHP	APHA	KMCC	KMCC-Bi	APHA	KMCC	KMCC-Bi
HW1	503.76(78.30)[a]	639.04(0.00)	601.50(0.00)	350	528.27	517.10	505.01	150.93	147.74	144.29
HW2	268.73(0.00)	161.99(0.00)[b]	253.60(31.4)	350	528.27	477.35	463.56	150.93	136.39	132.45
HW3	973.82(0.00)[c]	1195.60(0.00)[c]	1343.77(31.4)[c]	350	457.76	501.20	488.43	130.79	143.20	139.55
HW4	112.05(0.00)	241.50(0.00)[d]	187.03(62.8)	350	524.35	588.66	579.62	149.81	168.19	165.60
HW5	268.73(0.00)	241.50(0.00)	249.83(62.8)	350	473.43	501.20	488.43	135.27	143.20	139.55
BW1	< LOD	< LOD	7.19(4.8)	350	332.41	383.53	379.79	94.97	109.58	108.51
BW2	113.05(0.00)	115.58(3.98)	72.14(0.314)	350	418.59	353.71	357.81	119.60	101.06	102.23
MIN	*< LOD*	*< LOD*	*7.19(4.8)*		*332.41*	*353.71*	*357.81*	*94.97*	*101.06*	*102.23*
MAX	*973.82(0.00)[c]*	*1195.60(0.00)[c]*	*1343.77(31.4)[c]*		*528.27*	*588.66*	*579.62*	*150.93*	*168.19*	*165.60*

The italisized values denote the minimum and maximum values (range), of the given parameter determined with the given method within the column

Note: [a], [b], [c], and [d] indicate means significantly different ($p < 0.05$) from others within the group

chloride removal applied to wastewater and selected organic compounds, Miller et al. (2001) gave consistent result with the standard APHA closed-tube colorimetry method. They observed statistical significance ($p < 0.05$) between some means of TOC from the standard method and modified methods as observed in the present study. However, Canelli et al. (1976) observed no significant difference ($p > 0.25$) in TOC content from wastewater digested with standard method and a developed method which used digestion reagent consisting sulfuric acid, potassium dichromate, silver and mercury sulfates, and sulfamic acid.

Conclusion

As shown by the UV-Vis and the KMCC and KMCC-Bi methods, potassium dichromate was generated from potassium monochromate on demand in strong acid medium and used for TOC analysis in water samples. The chloride removal was effective and the KMCC-Bi method is comparable to the standard method. The developed method was cheaper as it consumes less reagents compare to standard APHA method. The new method leads to a 60% reduction in sample consumption and 33.33 and 60% reduction in monochromate and silver sulfate consumption, respectively, and in addition used ≤ 100 mg $NaBiO_3$ for chloride removal.

The KMCC-Bi is also greener when compared to the standard method due to the elimination of mercury sulfate and semi microanalysis procedure. The LOD and LOQ of the modified method are low compare to the standard method thereby making it more sensitive. Overall, the impact of the discharge of waste from the KMCC-Bi method into the environment is considerably minimized compare to the APHA method.

References

Abuzaid, N. S., Al-Malack, M. H., & El-Mubarak, A. H. (1997). Alternative method for determination of the chemical oxygen demand for colloidal polymeric wastewater. *Bulletin of Environmental Contamination and Toxicology, 59*(1997), 626–630.

Al-Rimawi, F. (2014). Development and validation of a simple reversed-phase HPLC-UV method for determination of oleuropein in olive leaves. *Journal of Food and Drug Analysis, 22*(3), 285–289. https://doi.org/10.1016/j.jfda.2013.10.002.

APHA. (1995). *Chemical oxygen demand. Standard methods for the examination of water and wastewater* (19th ed.pp. 5.12–15.14). Washington, DC: American Public Health Association, Water Environment Federation, and American Water Works Association.

Brito, F., Ascanioa, J., Mateoa, S., Hernandeza, C., Araujoa, L., Gili, P., & Mederos, A. (1997). Equilibria of Cr(VI) species in acid medium and ad initio studies of these species. *Polhedron, 16*(21), 3835–3846.

Canals, A., & Del Remedio Hernandez, M. (2002). Ultrasound-assisted method for determination of chemical oxygen demand. *Analytical and Bioanalytical Chemistry, 374*(6), 1132–1140. https://doi.org/10.1007/s00216-002-1578-2.

Canelli, E., Mitchell, D. G., & Pause, R. W. (1976). An improved determination of chemical oxygen demand in water and wastes by a simplified acid dichromate digestion. *Water Research, 10*(4), 351–355. https://doi.org/10.1016/0043-1354(76)90179-2.

Chowdhury, S., & Champagne, P. (2009). Risk from exposure to trihalomethanes during shower: probabilistic assessment and control. *Sci Total Environ, 407*(5), 1570–1578. https://doi.org/10.1016/j.scitotenv.2008.11.025.

Deborde, M., & von Gunten, U. (2008). Reactions of chlorine with inorganic and organic compounds during water treatment-kinetics and mechanisms: a critical review. *Water Research, 42*(1–2), 13–51. https://doi.org/10.1016/j.watres.2007.07.025.

Dobbs, R. A., & Williams, R. T. (1963). Elimination of chloride interference in the chemical oxygen demand test. *Analytical Chemistry, 35*, 1064–1067.

Gans, P. (2000). A puzzle concerning solution equilibra. *Journal of Chemical Education, 77*(4), 489.

Golea, D. M., Upton, A., Jarvis, P., Moore, G., Sutherland, S., Parsons, S. A., & Judd, S. J. (2017). THM and HAA formation from NOM in raw and treated surface waters. *Water Research, 112*(2017), 226–235. https://doi.org/10.1016/j.watres.2017.01.051.

HACH. (2015). *The importance of measuring total organic carbon: Application to drinking water analysis*. UK: HACH.

Hammond, C. R. (2004). The element. In D. R. Lide (Ed.), *Handbook of chemistry and physics* (81st ed.). Boca Raton: CRC Press.

Hang, C., Zhang, B., Gong, T., & Xian, Q. (2016). Occurrence and health risk assessment of halogenated disinfection byproducts in indoor swimming pool water. *Science of the Total Environment, 543*(Pt A), 425–431. https://doi.org/10.1016/j.scitotenv.2015.11.055.

Hsu, H. T., Chen, M. J., Lin, C. H., Chou, W. S., & Chen, J. H. (2009). Chloroform in indoor swimming-pool air: monitoring and modeling coupled with the effects of environmental conditions and occupant activities. *Water Research, 43*(15), 3693–3704. https://doi.org/10.1016/j.watres.2009.05.032.

Jarvie, D. M. (1991). Total organic carbon (TOC) analysis: Geochemical methods and exploration In R. K. Merrill (Ed.), *TR: Source and migration processes and evaluation techniques*. Oklahoma USA.

Kayaalp, N., Ersahin, M. E., Ozgun, H., Koyuncu, I., & Kinaci, C. (2010a). A new approach for chemical oxygen demand (COD) measurement at high salinity and low organic matter samples. *Environmental Science and Pollution Research International, 17*(9), 1547–1552. https://doi.org/10.1007/s11356-010-0341-z.

Kayaalp, N., Ersahin, M. E., Ozgun, H., Koyuncu, I., & Kınacı, C. (2010b). New approach for chemical oxygen demand (COD) measurement at high salinity and low organic matter samples. *Environmental Science and Pollution Research, 17*(9), 1547–1552. https://doi.org/10.1007/s11356-010-0341-z.

Kean, S. (2011). *The disappearing spoon (and other true tales of madness, love and history of the world from the periodic table of elements)*. New York/Boston: Back Bay Books.

Kruger, J., Winkler, P., Luderitz, E., Lucky, M., & Wolf, H. U. (2003). *Bismuth, bismuth alloys, and bismuth compounds. Ullmann's encyclopedia of industrial chemistry*. Weinheim: Wiley-VCH.

LaPara, T. M., Alleman, J. E., & Pope, P. G. (2000). Miniaturized closed reflux colorimetric method for the determination of chemical oxygen demand. *Waste Management, 20*(2000), 295–298.

Lee, J., Ha, K. T., & Zoh, K. D. (2009). Characteristics of trihalomethane (THM) production and associated health risk assessment in swimming pool waters treated with different disinfection methods. *Science of the Total Environment, 407*(6), 1990–1997. https://doi.org/10.1016/j.scitotenv.2008.11.021.

McHale, W. (2012). A better approach to calculation limits of detection and limits of quantitation. Retrieved from http://www.eraqc.com/Portals/0/PDF%20documents/ERA_LOD-LOQ_White_Paper_R2.pdf.

Miller, D. G., Brayton, S. V., & Boyles, W. T. (2001). Chemical oxygen demand analysis of wastewater using trivalent manganese oxidant with chloride removal by sodium bismuthate pretreatment. *Water Environment Research, 73*, 63–71.

Narola, B., Singh, A. S., Mitra, M., Santhakumar, P. R., & Chandrashekhar, T. G. (2011). A validated reverse phase HPLC method for the determination of disodium EDTA in meropenem drug substance with UV-detection using precolumn derivatization technique. *Analytical Chemistry Insights, 6*, 7–14. https://doi.org/10.4137/ACI.S5953.

Oram, B. (2014, May, 2018). Disinfection by-products trihalomethanes. Retrieved from https://www.water-research.net/index.php/trihalomethanes-disinfection.

Panyakapo, M., Soontornchai, S., & Paopuree, P. (2008). Cancer risk assessment from exposure to trihalomethanes in tap water and swimming pool water. *Journal of Environmental Sciences, 20*(2008), 372–378. https://doi.org/10.1016/S1001-0742(08)60058-3.

Parnell, R. J. G. (1924). Bismuth in the treatment of syphillis. *Journal of the Royal Society of Medicine, 17*(War section), 19–26.

Taylor, J. K. (1987). *Quality assurance of chemical measurement*. Washington DC: Lewis Publishers.

USEPA. (U.S. Environmental Protection Agency). (2006). National primary drinking water regulations: stage 2 disinfectants and disinfection by products rule: final rule. Retrieved from https://www.scribd.com/document/2827547/Rule-Water-supply-National-primary-drinking-water-regulations-8212-Stage-2-disinfectants-and-disinfection-byproducts-rule.

USNRC. (1980). *Drinking water and health (Vol. 2)*. Washington D.C: National Academic Press.

Veldhovena, K. v., Keski-Rahkonenb, P., Barupalb, D. K., Villanueva, C. M., Font-Ribera, L., Scalbert, A., & Kogevinas, M. (2018). Effects of exposure to water disinfection by-products in a swimming pool: a metabolome-wide association study. *Environment International, 111*(2018), 60–70. https://doi.org/10.1016/j.envint.2017.11.017.

Vyrides, I., & Stuckey, D. C. (2009). A modified method for the determination of chemical oxygen demand (COD) for samples with high salinity and low organics. *Bioresource Technology, 100*(2), 979–982. https://doi.org/10.1016/j.biortech.2008.06.038.

WFI (Wikimedia Foundation Inc). (2016, 27/11/2017). Predominance diagram. Retrieved from https://en.wikipedia.org/w/index.php?title=Predominance_diagram&oldid=720029937.

Zupančič, G. D., & Roš, M. (2011). Determination of chemical oxygen demand in substrates from anaerobic treatment of solid organic waste. *Waste and Biomass Valorization, 3*(1), 89–98. https://doi.org/10.1007/s12649-011-9087-1.