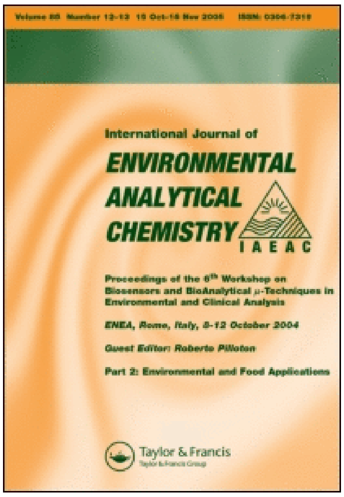

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A MERCURY-FREE MICROWAVE METHOD FOR THE CHEMICAL OXYGEN DEMAND ANALYSIS OF SEWAGE

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A COD (chemical oxygen demand) method involving dichromate oxidation in a digestion bomb heated in a microwave oven, was developed and tested for sewage samples. Oxidation was complete within 2 min and the method gave comparable results to more conventional open reflux and closed tube methods, which require a 2 h oxidation. Lower sulphuric acid concentrations were required for full sample oxidation under pressurised microwave conditions which reduced interference from chloride oxidation to a tolerable level. Lowered chloride interference meant that a mercury-free microwave method could be developed for sewage samples with chloride concentrations less than 250 mg l^{-1}. This seems timely in view of increasingly stringent controls on mercury usage in the laboratory.

KEY WORDS: COD, sewage, microwave, mercury.

INTRODUCTION

Chemical oxygen demand (COD) is a base parameter in assessing the environmental consequences of bulk organic substances discharged from sewage treatment plants, combined sewer overflows and stormwater and industrial outfalls. The accepted definition of COD is the mass concentration of oxygen equivalent to the amount of dichromate consumed by dissolved and suspended matter when a water sample is treated with that oxidant under defined conditions.[1] COD analysis usually involves oxidation of organic substances with boiling dichromate in concentrated sulphuric acid for two hours under reflux followed by titrimetric detection of residual dichromate. Introduction of the closed tube method, with colorimetric detection of formed Cr(III), has provided the advantage over open reflux of minimisation of dichromate waste and simplified apparatus and experimental procedure,[2–6] although the usual digestion time of two hours is not reduced. Although open reflux is generally considered the definitive method, in reality the closed-tube method may prove more reliable due to minimisation of sample contamination risk and handling of reagents.[5]

Besides the time-consuming aspect of COD, the method also involves the addition of $HgSO_4$; usually 0.4 g in the standard reflux method and 50 mg in the closed-tube method. The large amount of waste dichromate and Hg from COD analysis poses a potential environmental problem in itself. As COD waste is processed it is known that approx.

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1000 kg of COD closed tubes are recycled for Hg in Sweden each year, which is equivalent to about 25 kg Hg. It is further possible to estimate that COD analysis contributes in the order of 0.1–0.5% of the total Hg usage in Sweden. Pending increasingly stringent controls on Hg usage in industry and dentistry, it does not seem unlikely that this percentage will increase in the near future.

As chloride interferes with the standard COD analysis, reliable open reflux and closed-tube[1] methods depend on the addition of $HgSO_4$ to complex chloride and thereby minimise the oxidation of chloride by the boiling potassium dichromate/sulphuric acid mixture. Although Hg-free methods, which include the addition of $AgNO_3$[7] and Cr(III),[8] are available they are not generally regarded as satisfactory surrogates in series of samples where the salt content varies considerably. Due to its toxicity the addition of Ag, even if it can be shown that it is usually recycled, will eventually succumb to the same toxicity argument as Hg avoidance. The addition of Cr(III) prevents the use of colorimetric detection. Not surprisingly most standard methods still prefer a more reliable Hg addition.[1,17,18]

Microwave heating has been shown to be effective in drying, extraction and digestion procedures.[9–12] Therefore, it is possible to reduce digestion time by the introduction of a COD method with microwave digestion.[13–15] Although organic substances oxidise under short microwave digestions, it is not known whether chloride oxidises under the same conditions.

In this article a Hg-free microwave COD method is introduced and tested which gives comparable COD results, for sewage samples, to the reflux and closed-tube methods.

EXPERIMENTAL

COD methods. The developed method is reported below, followed by the reflux and closed tube methods. Please note that all microwave procedure development was done in sealed containers as acid fumes may damage the microwave oven, leading to safety problems. The open reflux method was at no point done in the microwave oven and is for comparison only.

Microwave method. 18 M H_2SO_4 (140 ml) was added carefully to ultrapure water (60 ml). After cooling the mixture was added to 0.17 M $K_2Cr_2O_7$ (100 ml). The reagent is stable for up to one month and is equivalent to a 60% dilution of the open reflux digestion mixture in terms of H_2SO_4 concentration. Sample (4 ml) was added to a Parr 45 ml PTFE cup, followed by reagent (6 ml). The final H_2SO_4 concentration was therefore 4.8 M. The cup was sealed in a Parr 4782 digestion bomb and placed in a household microwave oven at 80% effect for 2 min. The microwave oven was calibrated[16] and 80% effect was found to be equivalent to 550 W. After cooling in an ice bath for at least 10 min the digestion bomb and PTFE cup were opened carefully and the digestion solution diluted to volume (25 ml). One blank with ultrapure water was run with each series of four bombs. Absorbance (585 nm for produced Cr(III) and 500 nm for unreacted dichromate) was measured in a Philips PU 8620 spectrophotometer with a 1 cm quartz cuvette. Absorbance was compared to oxalic acid standard solutions, usually in the range 100–1250 mg O_2 l^{-1}.

Open reflux method. The Swedish standard open reflux method,[17] which is comparable to other international standard methods,[1,18] was used. Sewage sample (10 ml) was mixed with 0.4 g $HgSO_4$ in a round-bottomed flask (250 ml). 0.04 M $K_2Cr_2O_7$ (5 ml) was added, followed by a mixture of 17 M H_2SO_4 and 0.03 M Ag_2SO_4 (15 ml). The final H_2SO_4 concentration was therefore 8 M. The sample was digested under reflux for 2 h and, after cooling and rinsing with ultrapure water, residual dichromate was back-titrated with 0.07 M $Fe(NH_4)_2(SO_4)_2 . 6H_2O$ and ferroin indicator. COD was calculated from the difference in titration values between the sample and the blank.[1,18] Two blanks with ultrapure water were run with each series.

Closed-tube method. The commercial closed tube method was a Dr Lange cuvette LCK 114 (150–1000 mg O_2 l^{-1}). Sample (2 ml) was added to the cuvette and heated for 2 h in a LASA Aqua LTK 031 thermostat. The cuvette contains 3 ml of 92% H_2SO_4 with 40 mg $HgSO_4$. The final H_2SO_4 concentration is therefore 9.9 M. Formed Cr(III) was measured in a LASA pocket photometer with filter 114. A HACH system was also tested which has similar reagent concentrations and oxidation and measurement conditions. The HACH tubes contain slightly more $HgSO_4$ (50 mg).

Samples. Untreated sewage was collected from the inlet to the Ryaverket sewage treatment plant in Göteborg, (Sweden). The treatment plant receives domestic sewage, stormwater and industrial discharge. Sewage sample (100 ml) was stabilised with 4 M H_2SO_4 (1 ml) and stored at 4°C. Before analysis the sample was treated with a sonic probe for 1 min to disperse the solids. After dispersion and before removal of sample aliquots, the solids were kept in suspension by stirring. All COD analyses were carried out at least six times for sewage samples.

Safety. The Parr digestion bombs allow the buildup of high temperature and pressure in the PTFE cup during microwave exposure. Should the pressure become too great then a safety screw is released and the hot acid fumes may damage the microwave oven. It is therefore recommended that the microwave is always turned off prior to opening the unit. It is further recommended that the microwave oven is calibrated[16] and the time for exposure adjusted accordingly. Laboratory microwave units are available which exhaust acid fumes and therefore completely avoid potential safety risks.

RESULTS AND DISCUSSION

The aim of developing a microwave method was to minimise analysis time and $HgSO_4$, while retaining oxidation efficiency of tested model compounds and samples. The method was optimised for variations in reaction time, H_2SO_4 concentration and organic concentration. At the same time the extent of chloride interference was studied.

Reaction time. The degree of oxidation of model compounds, starch and oxalic acid, and sewage was followed with time of microwave exposure. Figure 1a demonstrates an effective oxidation of both oxalic acid and starch at 50 s. However sewage proved to be more refractory with two oxidation steps (Figure 1b). The first oxidation is in cold dichromate representing readily oxidisable organics. In the samples studied this fraction represented 54–77% of COD. A complete oxidation, compared to the open reflux method, was not achieved until 2 min. Similar experiments with variation of reaction volume instead of time showed an optimum of 10 ml for a 45 ml PTFE cup.

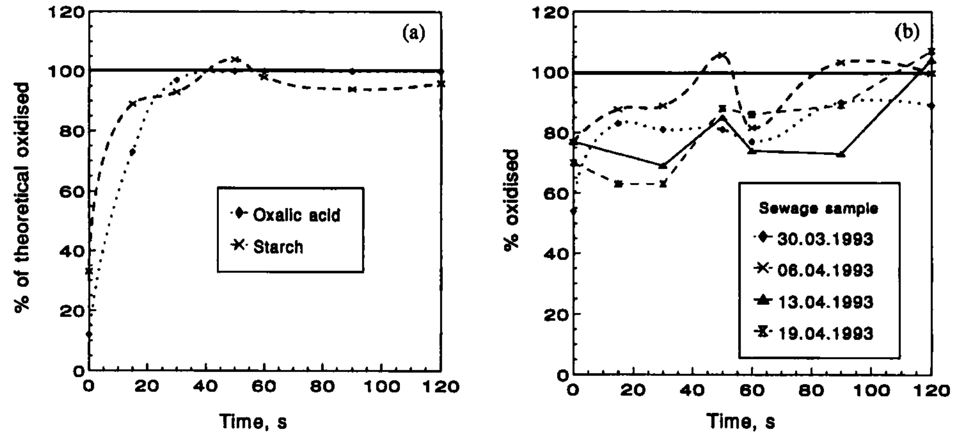

Figure 1 Effect of oxidation time on microwave oxidation of (a) oxalic acid (625 mg O_2 l^{-1}) and starch (606 mg O_2 l^{-1}) compared to theoretical oxygen demand and (b) sewage samples compared to open reflux values (i.e. open reflux is assumed to be 100% oxidation).

Variation of H_2SO_4 concentration. Microwave oxidation of oxalic acid and starch were tested under final concentrations of H_2SO_4 between 1.7 and 5.5 M (Table 1). A H_2SO_4 concentration of 5.5 M gave variable and unreliable results (high for oxalic acid and low for starch) due to a crystalline product occasionally forming during microwave heating. This product also formed during solution storage. All concentrations of H_2SO_4 tested gave reasonable oxidation, although 4.8 M H_2SO_4 was chosen to ensure a high acid concentration for sewage samples. Lower sulphuric acid concentrations lead to some decrease in efficiency of oxalic acid oxidation.

Chloride interference. The microwave method gives a similar response to chloride as the open reflux and closed tube methods. Following the absorbance at 585 nm with time, with 3125 mg l^{-1} chloride and no organic material, shows that chloride interference is negligible until 50–60 s (Figure 2). At this point oxalic acid and starch are fully oxidised (Figure 1a) and their oxygen demand can therefore be detected even in the presence of

Table 1 Oxidation of oxalic acid and starch at different H_2SO_4 concentrations.*

	Oxidation efficiency, (% of theoretical)			
	Oxalic acid, mg O_2 l^{-1}			*Starch, mg O_2 l^{-1}*
H_2SO_4,(M)	*320*	*640*	*960*	*638*
1.7	90	92	93	84
3.5	100	98	98	88
4.2	94	96	95	86
4.8	100	100	100	93
5.2	100	101	99	89
5.5	111	112	112	45

* Microwave oxidation was 2 min at 80% (550 W).

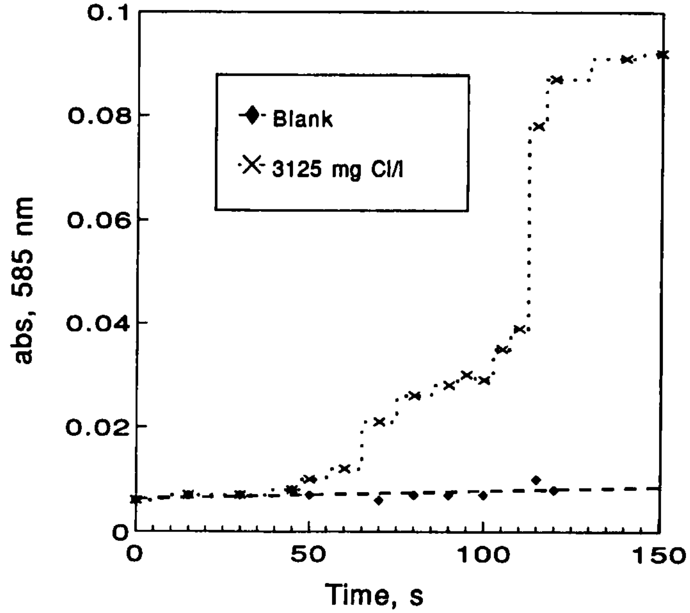

Figure 2 Effect of chloride on absorbance at 585 nm with time of microwave heating.

high salt concentrations. After 60 s, Abs_{585} increases following an S curve with a maximum at 120 s (Figure 2). Unfortunately, this is the oxidation time that is necessary to completely oxidise sewage samples (Figure 1b).

At lower chloride concentrations (250–1500 mg l^{-1}) chloride interference is less marked and provides a positive error of less than 10% under 500 mg l^{-1} (Figure 3). The reason for such a low error is the lower sulphuric acid concentrations that can be used due to the more effective sample heating in the microwave method. Higher pressure in the digestion bomb used increases the boiling point for H_2SO_4 and therefore allows the solution to reach a high enough temperature for effective oxidation, but at a lower H_2SO_4 concentration. This phenomenon is well known, for example, the heated temperature of nitric acid increases from 120°C at room pressure to 176°C at an effective pressure in the vessel of 5 atm,[20] giving substantial increases in oxidation potential. In an experiment where the microwave digestion reagents was used in the closed tube method with a 2 h digestion only 83% digestion of sewage samples was found, compared to complete digestion after 2 min in the microwave vessel. For the microwave method presented here the increase of temperature in the bomb can be calculated.[20] The controlled boiling point[17] for the open reflux method is 148°C and it can be calculated that this temperature should be reached in the microwave digestion bomb within approx. 18 s. This explains the rapid oxidation of oxalic acid and starch found in Figure 1a.

Although dichromate is a powerful oxidant, it does not oxidise chlorides in aqueous solution. It is known that, in the presence of sulphuric acid, CrO_2Cl_2 (chromyl chloride) is formed:[19]

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 = 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O \quad (1)$$

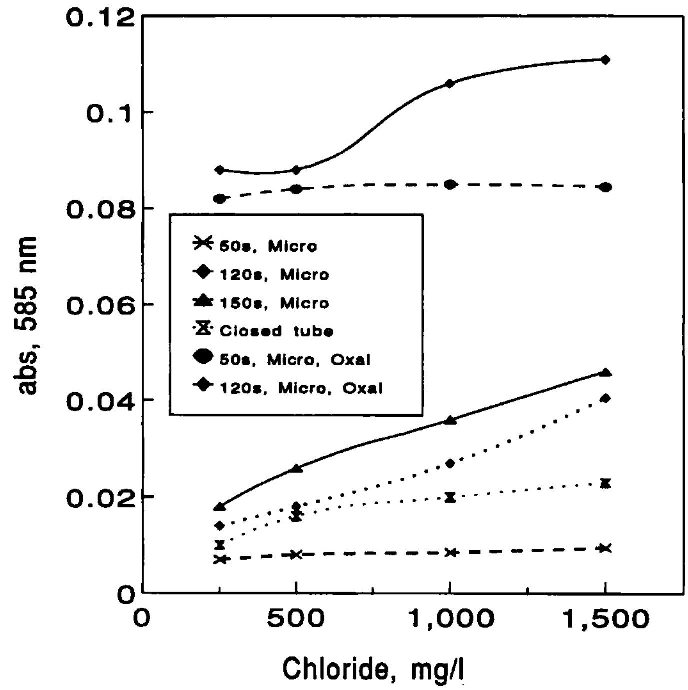

Figure 3 Effect of variation of chloride concentration on absorbance at 585 nm at different microwave heating times and in the closed tube method. The effect of the presence of oxalic acid (625 mg O_2 l^{-1}) is provided for comparison.

It is also known that during the 2 h dichromate oxidation of organic compounds, chloride is oxidised to chlorine:[8]

$$Cr_2O_7^{2-} + 6Cl^- + 14H^+ \rightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O \qquad (2)$$

It follows that minimising sulphuric acid concentration through microwave heating under pressure should reduce chloride interference. In addition, in the microwave method samples are heated through, whereas the open reflux and closed tube methods rely on heating the sides of the containing flask. The sample probably remains in a more dispersed, readily oxidised, form in the microwave method.

The presence of organic material appears to affect the extent of chloride interference (Fig. 3). In the presence of oxalic acid (625 mg O_2 l^{-1}) interference due to 500 mg l^{-1} chloride is effectively suppressed. Chloride interference is usually reported to decrease with increasing COD on the basis of formed Cr(III) complexing chloride, indeed addition of Cr(III) is the basis of a Hg-free method.[8] Chloride interference was found here to be suppressed by the presence of organics and it may be the case that, for sewage samples known to contain high concentrations of readily oxidisable organics, the microwave method could be used for chloride concentrations of up to 500 mg l^{-1}. However, in many cases concentrations of readily oxidised organics may be too variable in sewage samples to allow a reliable assessment of suppression in routine analysis.

For sewage samples with a chloride concentration of less than 250 mg l^{-1} interference will be negligible; this is demonstrated for a sewage sample diluted and adjusted to approx. 170 mg l^{-1} chloride in Table 2. At this chloride concentration no significant difference was found between the open reflux method with $HgSO_4$ added and the

Table 2 Effect of sewage organics on chloride interference.*

		COD, mg $O_2\,l^{-1}$	
Original sample (%)	*Final measured chloride, (mg l^{-1})*	*Open reflux*	*Microwave*
100	173	443 ± 2.5%	460 ± 11%
67	160	316 ± 1.3%	292 ± 8%
50	165	212 ± 1.9%	182 ± 2.5%
33	175	125 ± 0%	126 ± 9.5%
13	175	58 ± 16%	63 ± 19%

* Sample 21.04.1993 was diluted and chloride concentration adjusted.

Table 3 Percentage of the theoretical oxygen demand of model compounds achieved by the three COD methods tested.*

Sample	*Percent of theoretical oxygen demand*		
	Open reflux	*Closed tube*	*Microwave*
Glucose	90	95	97
Nicotinic acid	3	3	3
Oxalic acid	100	100	100
Pot. hyd. phthalate	96	101	99
Starch	109	86	93
Triton X-100	72	83	58

* Concentrations as substance tested were (theoretical value, g O_2 g^{-1}); glucose, 6.5 x 10^{-4} – 6.5 x 10^{-3} M (1.07); Nicotinic acid, 1 x 10^{-4} M (2.01); Oxalic acid, 8 x 10^{-3} – 8 x 10^{-2} M (0.13); Potassium hydrogen phthalate, 5.2 x 10^{-4} – 5.2 x 10^{-3} M (1.18); Starch, 6.2 x 10^{-4} – 6.2 x 10^{-3} M (1.19); Triton X-100, 5.1 x 10^{-3} M (2.92).

microwave method with no $HgSO_4$ addition. In addition, the samples fall within the usual 10% standard deviation found for sewage samples. Further dilution of the sewage leads to a poorer standard deviation due to the heterogeneous nature of the samples, but again, no significant effect of chloride interference can be found.

It is accepted practice to include interference from inorganic reducing agents (nitrites, sulphides, iron(II)) in the COD value.[1]

COD for model compounds. The three COD analysis methods were compared for model compounds which had varying degrees of resistance to oxidation. The degree of oxidation is expressed as a percentage of the theoretical oxygen demand in Table 3.

Readily oxidisable compounds, such as glucose, oxalic acid and potassium hydrogen phthalate gave close to, or exactly, the correct theoretical value for all three methods of analysis. Nicotinic acid was resistant to oxidation for all COD methods tested.

Starch gave reliable values for the open reflux and microwave methods. The higher value for the open reflux method may be due to the uncertain purity of the starch used, which made it difficult to exactly calculate the theoretical oxygen demand. The closed

Table 4 Comparison of COD values for open reflux (including an independent laboratory), closed tube and microwave methods for sewage samples

		COD, mg O_2 l^{-1}				
Sampling Date	*Chloride (mg l^{-1})*	*Open reflux*		*Closed tube*		*Microwave*
		*A**	*B**	*C**	*D**	*E**
16.03.1993	202	425	380	433	394	447
23.03.1993	178	450	450	431	419	451
30.03.1993	166	596	371	566	686	531
06.04.1993	200	435	376	435	377	360
13.04.1993	173	443	425	475	388	460
20.04.1993	130	390	330	408	-	372

* A, own laboratory; B, independent certified laboratory; C, Dr Lange method, own laboratory; D, HACH method, treatment plant laboratory; E, own laboratory.

tube method gave consistently lower COD values for starch, even when tested over a range of concentrations.

Sewage samples. Similar values for COD in sewage were obtained using the microwave, open-reflux and closed-tube methods (Table 4). Values for one sample (30.03.1993) differ significantly for the methods not done in our laboratory. Analyses B and D were not subjected to sonic pretreatment to disperse solids and the inaccurate values can be attributed to analysis of a non representative aliquot. Generally, though, agreement between all methods tested can be considered reasonable. The microwave photometric method reported here gives a standard deviation of ± 4.7% for sewage from the Ryaverket treatment plant, which was as precise as for the open reflux method. The source of deviation here is sample preparation as sewage is heterogenous, even after sonication.

The major differences between the conventional open reflux/closed tube and the microwave methods are sulphuric acid concentration and time of oxidation. The 2 h digestion time and strong sulphuric acid required for full oxidation of resistant organic material leads to interference from chloride oxidation, thereby necessitating the addition of $HgSO_4$. Effective oxidation at a lower sulphuric acid concentration in the microwave method reduces chloride oxidation and therefore provides a Hg-free alternative.

Volatile hydrophobic substances may be lost through evaporation in the reflux method, but are probably retained and oxidised in the closed tube and microwave methods.

CONCLUSIONS

The microwave method presented here is reliable and precise for sewage samples. In terms of accuracy, microwave gives comparable values to the open reflux and closed tube methods. The lower sulphuric acid concentration required minimises chloride interference and therefore allows the use of a Hg-free method. The microwave method can be routinely used on samples known to be consistently below 250 mg l^{-1} chloride.

The method presented here utilises neither $HgSO_4$ nor Ag_2SO_4. While $HgSO_4$ is normally added to mask chloride interference, Ag_2SO_4 is added both for the latter purpose and to catalyse the oxidation of alcohols and low molecular weight acids. In this study problems were found with precipitation when silver was added and, as comparable results to the open reflux method were found without silver addition, a simpler dichromate/sulphuric acid mixture was used.

Two variations for the microwave COD method immediately spring to mind. Firstly, at low organic (COD) values but in the presence of high salt concentrations, a completely chloride-interference-free oxidation method with 50 s heating would give a measure of readily oxidisable COD. Although a compromise to the usually required 95% oxidation for COD analysis, the method would open the possibility for the analysis of highly saline seawater and industrial discharge samples. Secondly, at high organic (COD) values and with low salt concentrations (i.e. under 250 mg l^{-1}), 2 min heating would give a COD value comparable to present day methods and without the need for Hg addition. The exact heating times should be adjusted depending on microwave effect, but this can be readily calibrated[16] and tested against the results presented here.

A recap on the methods for the removal/minimisation of chloride interference is worthwhile here, because the literature is, quite frankly, confusing. To achieve complete organic oxidation, sulphuric acid concentration is usually kept as high as possible. This increases the boiling point and therefore the oxidation efficiency by chromic acid. Under these conditions, chloride interference is maximised and is then treated by one of three approaches.

Firstly, add $HgSO_4$,[1,17,18] $AgNO_3$,[7] Cr(III)[8] or a combination thereof.[6] This is the traditional approach which minimises, rather than completely removes, chloride interference. Strangely, a lowered organic oxidation efficiency cannot be accepted, yet some degree of chloride interference can. This dilemma has been some-what reconciled by limiting the method to samples with a chloride concentration of less than 1000 mg l^{-1},[1] previously 2000 mg l^{-1} was accepted.[4]

Secondly, measure chloride concentration and provide a correction to the final COD value. This method is complicated by correction dependence on COD, although because this is thought to rely on rapid Cr(III) formation due to readily oxidised organics[4] the correction may be sample dependent. Consequently, this approach is not only inconvenient but probably unreliable.[21]

Thirdly, the oxidised form of chloride is collected in acid potassium iodide and the extent of interference titrimetrically quantified.[22] This method, applicable to highly saline waters, still relies on the addition of $HgSO_4$.

The philosophy presented here is to start with the basic dichromate/sulphuric acid system and no fussy additions of mercury or silver salts. Chloride interference is completely removed through minimisation of sulphuric acid concentration. It is then possible to work towards a complete oxidation by optimising dichromate concentration and by raising the temperature/pressure in the microwave digestion bombs. Continuous measurement of these parameters would be clearly desirable.[23] This is the basis of our continuing research.

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