

COMPARATIVE STUDY OF TOTAL ORGANIC CARBON (TOC)
METHODS FOR HIGH-LEVEL MIXED WASTE

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COMPARATIVE STUDY OF TOTAL ORGANIC CARBON (TOC) METHODS FOR HIGH-LEVEL MIXED WASTE

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ABSTRACT

Hanford tank waste is a complex, nonhomogeneous sludge, slurry, or salt-cake mixture requiring robust methods for analytical characterization. While numerous total organic carbon (TOC) methods are described in the literature, no single TOC method has been found to be ideal for this caustic, high-salt, sometime high-fluoride matrix. Three TOC methods have been in use at the Pacific Northwest Laboratory, and one complementary method is in place at Westinghouse Hanford Company. All have been found to have strengths and weaknesses when applied to the Hanford tank waste problem. These TOC methods include silver-catalyzed hot persulfate wet oxidation in batch-mode with coulometry detection, two methods for high-temperature furnace oxidation with coulometry detection, and UV-catalyzed persulfate oxidation with nondispersive infrared detection. To provide comparative data on these four methods, a recovery study of carbon compounds, which are relevant to Hanford tank waste, has been performed. One major conclusion is that it is most useful to have multiple methods available for the analysis of this waste material. The comparative study is discussed, operational experience in TOC analysis from these laboratories is described, and strengths and weaknesses in the methods are summarized.

I. INTRODUCTION

The analysis of total organic carbon (TOC) in the high-level mixed waste (HLMW) stored in Hanford

waste tanks has been identified as an important, long-term concern for several reasons. First, a most important reason is tank safety, with carbon materials providing possible fuel for potential exothermic tank reactions. Second, during retrieval and pretreatment of the tank waste, TOC levels will be important due to waste-compatibility concerns, and could impact, if not control, the various pretreatment options, such as sludge washing, organic destruction, or radionuclide removal. Third, during the disposal phase, in which different waste forms are produced for long-term storage and disposal, TOC levels can affect certain performance characteristics of the final product. For example, the leachability of the vitrified glass waste form can be affected by the TOC concentration. Finally, plant design will likely be impacted by total carbon levels in the feed material, and carbon mass balance throughout the process will require TOC and total inorganic carbon (TIC) analysis.

In industry, TOC instrumental methods are usually applied to part-per-million trace analysis of drinking water, marine or lake water, or other industrial process water waste streams.¹⁻⁴ The application of existing TOC methods to a matrix such as the Hanford tank sludge, slurry, and salt-cake wastes, containing up to several percent carbon, is not described in the literature. The tank waste routinely analyzed at Pacific Northwest Laboratory (PNL), in Richland, Washington, and Westinghouse Hanford Company (WHC) usually is a caustic, highly radioactive mixture, generally high in nitrate, nitrite, sulfate, phosphate, and/or fluoride. All of these matrix constituents can present severe operational problems for some methods. The tank

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waste usually contains widely variable organic carbon sources, though the major carbon species present are generally organic salts and complexants from past processing operations. Three independent instrumental methods are in place at PNL and one complementary method is in use at WHC. The extensive, long-term use of all of these methods has provided a good understanding of their strengths and weaknesses.

A comparative study of each of these methods on the recovery of carbon compounds relevant to the Hanford tank wastes has been completed, and the results are discussed. An important conclusion from this work is that no single method for TOC has been found to be ideal for all waste tank matrices. Therefore, the capability of having multiple, complementary methods available is most useful. Generally, the silver-catalyzed hot persulfate method has been found to be the most practical for the routine analysis of Hanford tank waste and sludge.

II. DESCRIPTIONS OF TOC METHODS

The methods in use at PNL and WHC, shown in Table 1, use three different oxidation techniques, combined with two different CO₂ detection methods, and cover the full range of sample type or matrix. These methods include 1) silver-catalyzed hot persulfate wet oxidation with coulometry detection, 2) UV-catalyzed persulfate with nondispersive infrared (NDIR) detection, and 3) high-temperature furnace combustion with coulometry detection. The furnace method in use at WHC is a variation of the PNL high-temperature combustion method.

A. Hot Persulfate Method

This method was originally developed for low-level analysis of organic material in seawater and other natural waters. While it has been shown to be successful for this purpose, it had not previously been extended to analysis of more difficult materials, such as sludges and slurries, containing up to several percent carbon. The use of persulfate as an oxidant of organic compounds has been well-characterized in the literature.^{1-3,5-7} The mechanism for oxidation is free-radical generation and step-wise attack. Peyton⁵ provides evidence and states that the persulfate-based free radical reaction should be able to convert virtually any organic compounds (excluding perhalogenated compounds) to carbon dioxide with essentially 100% efficiency. A variety of conditions can be found in the literature, including uncatalyzed persulfate in water, in base, and in acid, or catalyzed by various metals,

notably Fe(II) and Ag(I), all at various temperatures. Configurations using Ag(I)-catalyzed persulfate in H₂SO₄ have been described, such as flowthrough systems at various temperatures, flame-sealed glass ampoules for heated, pressurized conditions, and an O₂-sparged, enclosed reaction flask operating in batch-mode at near-boiling temperatures. The latter method was determined most amenable for remote operation in a shielded-cell.

The Ag(I)-catalyzed, O₂-sparged hot persulfate method, operating in batch-mode at 92-95°C, is in routine use at PNL on HLMW acid-soluble sludge and slurry samples. It is currently set up in a shielded-cell, in a fume-hood, and on a benchtop. The method, as implemented at PNL, uses a modified, gamma-hardened, acid-digestion unit for the wet-oxidation step and a coulometer detector system for measurement from Coulometrics, Inc. Potassium persulfate is added, in solid form, as preweighed batches directly to the 50 Ml digestion flask to a concentration of 20% in 2M H₂SO₄. The catalyst (0.2 mmol of 1M AgNO₃) is added directly to the flask. The system is closed, inserted into the preheated heater well, and oxidation and release of CO₂ begins, with transport of the released gas to the out-of-cell detector unit located in a fume-hood. Two modes of operation can be used. Normally, the sample is initially reacted only with acid, releasing the carbonate for a measure of TIC. Then the persulfate and Ag are added, and the organic carbon is reacted, released, and measured as TOC. Total carbon (TC) is calculated by summation. Alternatively, all reactants can be added initially for a single measurement of TC. Most of the tank sludge sample material tested to date has been found to be nearly entirely dissolved by this hot sulfuric acid/persulfate treatment. The method is not used for acid-insoluble silica-based solids, such as soils and sand materials.

B. High-Temperature Combustion Furnace Method

This method is also well-described in the literature, with even some comparisons to the hot persulfate method.^{4,8,9} But the application of the method to caustic, high-salt samples such as Hanford HLMW tank sludge or slurry has been discussed little. The method, as implemented at both PNL and WHC, allows for easy shielded-cell installation of the furnace as well as fume-hood installation, with the coulometer either installed in a fume-hood or adjacent. The past experience has been with systems from Coulometrics, Inc., but new systems from ASTRO Corp., using NDIR CO₂ detection, are currently being installed and investigated.

Table 1: TOC Methods in Use at PNL and WHC

| Oxidation Method | Detection Method | Temperature Range | Sample Matrix | Sample Introduction Method/Size | Typical Blank Levels |
|---|------------------------|--|---|---------------------------------------|----------------------|
| Ag(I)-catalyzed hot persulfate, at PNL | Coulometry | 92-95° C | Acid-soluble solids, sludges, slurries, liquids | Weighed boat/up to 10 g sample | 30-50 µg C |
| UV-catalyzed persulfate at PNL | Nondispersive Infrared | 60-65° C | Aqueous only | Syringe injection/up to 1 mL sample | 0.05-0.2 µg C |
| High-temperature combustion by furnace at PNL | Coulometry | 600° C for TOC 1000° C for TC, using different samples | Solids, soils, sludges, slurries, liquids | Weighed boat/up to 200 mg sample | 5-15 µg C |
| High-temperature combustion by furnace at WHC | Coulometry | 800° C for TOC normally after acid-sparge | Aqueous only | Syringe injection/up to 200 µL sample | 5-10 µg C |

The PNL system uses a furnace tube designed for quartz-boat sample introduction of solids and sludges, while WHC uses a different furnace tube designed for aqueous sample injection by syringe. At PNL, furnace operation is at two different analysis temperatures. One sample is analyzed at 600° C and a second sample is analyzed at 1000° C, providing discrimination between TOC and TC, respectively, with TIC determined by difference. At WHC, the method normally involves prior acid-sparging of the sample to remove carbonates, followed by a single analysis temperature of 800° C for TOC analysis.

C. UV-Catalyzed Persulfate Method

This method is also fully described in the literature.^{2,3} The method as implemented at PNL uses a Dohrmann DC-80, with the UV reactor unit and supporting components installed in a fume-hood, and the NDIR detector unit located on the adjacent benchtop. The method involves aqueous sample injection into a flowthrough system with the UV-light catalyzing the oxidation reaction with 3.5% potassium persulfate in 0.2% H₃PO₄ solution. The solution heats

to about 60-65° C during flowthrough. Total carbon is determined with UV-light on, TIC is determined with UV-light off, and TOC is calculated by difference.

This method is generally considered very good for aqueous samples containing no particulates, sludge, or slurry material. Filtered water leach samples of actual HLMW are successfully analyzed by this method.

III. COMPARATIVE STUDY OF CARBON RECOVERIES

To quantitatively compare and evaluate the weaknesses and strengths of each of these four methods, a representative list of carbon compounds, representing various compound categories, was established and analyzed, as far as resources have allowed, using each of the four methods. Many of the compounds on this list, shown in Table 2, were selected due to their known importance to the Hanford waste tank characterization effort. The list comprises 34 compounds representing 12 different categories. The primary goal of this study was to provide a database that would allow an informed comparison of these

Table 2: Tested Carbon Compounds and Recovery (% Rec ± SD) for Each Method

| Type of Compound | Compound Name | PNL Hot Persulfate Method (% Rec) | PNL Furnace Method (% Rec) | PNL UV-Catalyzed Method (% Rec) | WHC Furnace Method (% Rec) ^d |
|--|---------------------------|-----------------------------------|----------------------------|---------------------------------|---|
| organic salts | sodium formate | 93.2 ±1 | 85.4 ±5 ^b | 102 ±1 | 102 |
| | sodium oxalate | 93.4 ±5 | 93.8 ±6 ^b | 97.7 ±1 | 98.8 |
| | sodium gluconate | 85.1 ±5 | 89.8 ±6 | 99.5 ±1 | 101 ±1 |
| | potassium acetate | 95.5 ±1 | 76.9 ±7 ^b | 90.5 ±1 | |
| | ethyl acetate | 17.4 ±2 ^a | 83.3 ±4 | | 88.3 ±1 |
| | potassium acid phthalate | 90.7 ±4 | 90.0 ±5 | 95.0 ±3 | |
| complexants | EDTA | 83.6 ±7 | 74.9 ±9 | 101 ±1 | 96.6 ±5 |
| | HEDTA | 82.9 ±5 | 97.1 ±2 | 102 ±1 | 119 ±1 |
| | NTA | 83.2 ±6 | 98.6 ±1 | 97.6 ±1 | 97.2 ±2 |
| | DPTA | 97.7 ±5 | 107 ±7 | 97.0 ±2 | 96.8 ±2 |
| saccharide | glucose | 95.4 ±3 | 98.5 ±2 | 99.0 ±2 | 101 ±3 |
| aromatic and non-aromatic ring compounds | benzene | 6.3 ±4 ^a | 89.0 ±1 | 45.7 ±1 | |
| | toluene | 8.8 ±4 ^a | 99.0 ±1 | 25.5 ±1 | |
| | pyridine | 6.0 ±2 ^a | 96.9 ±1 | 96.6 ±1 | 93.8 ±1 |
| | cyclohexane | <1 ^a | 80.8 ±2 | 12.3 ±1 | |
| ketones, alkanes, organic acids | MIBK | 22.1 ±4 ^a | 95.9 ±1 | 90.8 ±1 | |
| | dodecane | <1 ^a | 109 ±3 | 12.9 ±3 | |
| | succinic acid | 97.4 ±1 | 104 ±4 | 98.1 ±1 | 99.4 ±1 |
| | glycolic acid | 102 ±1 | 88.8 ±1 | 101 ±1 | 111 ±1 |
| Alcohols, diols | 1-butanol | 58.2 ±9 ^a | 93.3 ±3 | 95.7 ±1 | 103 ±2 |
| | ethylene glycol | 96.0 ±3 | 92.7 ±4 | 96.6 ±1 | 99.9 ±1 |
| | glycerol | 94.0 ±9 | 107 ±7 | 99.4 ±1 | 98.1 ±1 |
| elemental carbon | Graphite | <1 | 2.8 | | |
| | lamp black | 65 | | | |
| Long-chain hydrocarbons | NPH | <1 ^a | 94.0 ±6 | | |
| | Paraffin wax | <1 | | | |
| N-containing organics | hexylamine | 56.1 ±12 ^a | 91.4 ±2 | 90.0 ±1 | |
| | urea | 84.3 ±2 | 99.1 ±3 | 96.3 ±1 | 98.2 ±1 |
| P-containing compounds | tributyl phosphate, TBP | 40.2 ±14 ^a | 100 ±2 | | |
| | dibutyl butyl phosphonate | 74.7 ±2 | 86.6 ±2 | 90.4 ±2 | |
| Cl-containing compound | Chloroform | 9.3 ±5 ^a | ^c | 41.8 ±3 | |
| | Carbon tetrachloride | <1 ^a | ^c | 2.4 ±1 | |
| cyanide compounds | Sodium ferrocyanide | 10.0 ±5 | 61.1 ±9 | | 105 ±1 |
| | Sodium thiocyanate | 35.0 ±5 | 99.7 ±2 | 61.7 ±3 | 74.4 ±2 |

^aDenotes compound is volatile at 90°C and is partially lost during sparged oxidation.

^bThese solid-form organic salts are difficult-to-oxidize. Furnace conditions for these were 850°C.

^cCl-containing compounds caused severe coulometer detector problems.

^dWHC furnace method was performed with and without acid-sparging, for this work. All the listed values shown were obtained with no sparging.

methods for the analysis of Hanford tank waste. Other such informative comparative studies can be found in the literature, comparing at least two of the methods discussed here.^{2,3,6}

A few comments can be made and points summarized regarding the data in Table 2. The hot persulfate method is seen to give good recoveries for the nonvolatile organic salts and complexants, both important constituents of tank waste. The exception regarding organic salts tested was ethyl acetate, which has some volatility at 90°C and was therefore partially lost during sparging. The obvious weakness in this sparged, hot persulfate method is the loss of volatile compounds, explaining most of the low recoveries. Other compounds, such as the inorganic cyanides and elemental carbon, may be difficult-to-oxidize by this method. In contrast, both furnace methods generally show good results across all types of compounds. Some of the alkali-metal organic salts were found to be difficult-to-oxidize in the PNL furnace method. The values shown were for unusual furnace conditions of 850°C, but normal furnace conditions gave results as low as 40-50%. The PNL furnace method used a standard combustion time of ten minutes. Some of the difficult-to-oxidize compounds, such as graphite, ferrocyanide, alkali-metal organic salts, and the carbonates, continue to oxidize and give increasing results in longer times, i.e. 20-40 minutes. The chlorine-containing compounds caused severe coulometer detector problems for the PNL furnace method. Since the procedure for the WHC furnace method required water dissolution of all compounds, the low-solubility compounds were not tested, resulting in blank spaces in the table. As can be seen, volatile compounds gave good recoveries by the furnace methods. The WHC furnace method was performed for this work with and without acid-sparging, to provide additional information. The values shown in Table 2 were obtained with no sparging and, therefore, show no losses due to volatility. The UV-catalyzed persulfate method showed good recoveries for most water-soluble volatile and nonvolatile compounds. Though this method also required water dissolutions of the compounds, the low-solubility organics, such as the ring compounds, were analyzed for information, since water leach treatments of tank waste are performed, resulting in some small dissolution of the low-solubility compounds.

It must be emphasized that the test compounds were analyzed as the pure reagents, without the presence of any caustic or high-salt matrix typical of the tank waste. A pure-compounds study is only a first step in a full

evaluation of these methods. Additional comparison of the methods should involve analyzing the compounds spiked into simulated or real tank wastes. In further distinguishing the four methods, it should be noted that the first two listed methods, the hot persulfate and PNL furnace methods, directly handle tank sludge, as received, while the latter two methods, UV-catalyzed persulfate and WHC furnace methods, handle only the water leached sample, with no solids or sludge present.

IV. ADDITIONAL SUPPORTING STUDIES

Additional tests were completed to provide further evidence of strengths or weaknesses in the various TOC methods. One particular area of concern was the effect of the presence of inorganic carbonates on TOC results from the furnace method, in the absence of an acid-sparge step. The concern is that certain carbonates may partially decompose at 600°C, the temperature at which organic carbon only is expected to oxidize to carbon dioxide. The result would be high-biased TOC values. Table 3 shows the results of these tests. The heavier metal carbonates all show complete decomposition at the TOC analysis temperature of 600°C. The presence of any of these compounds would bias the TOC result high. Even the alkali metal and alkaline earth carbonates show some decomposition at 600°C, ranging from 1% to 17%.

Another area of concern was the possible loss of volatile organic compounds in both the WHC furnace method, which uses a room temperature acid-sparge for removing carbonates, and the PNL persulfate method, which analyzes for TIC by an acid-sparge at >90°C. The data in Table 4 show that lightweight alcohols and ketones, as well as organic volatile salts, all show varying amounts of loss on sparging, up to 96% loss. This fact may not be too significant for many Hanford waste tanks, since the 40-year-old waste is expected to not contain many volatile compounds. But this indicates a weakness caused by the sparging process.

One supporting study providing good comparison and confidence in the accuracy of the three PNL methods was a round-robin test of actual samples containing 450 g/L uranium nitrate, 0.8M nitric acid, and about 0.2 g/L carbon from the 1993 startup of the Hanford UO₃ plant. The results from all three methods were averaged for each of seven samples. The averaged results ranged from 0.16 g/L to 0.28 g/L carbon with relative standard deviations of 3% to 23% over the three methods. None of the methods demonstrated any measurable bias compared to the others.

Table 3: Effect of Furnace Temperature on Carbonate Decomposition

| Carbonate Compound | Percent Recovery at 600° C (0% expected) ^a | Percent Recovery at 1000° C (100% expected) ^a |
|---------------------|---|--|
| Lithium Carbonate | 6 | 94 |
| Sodium Carbonate | 0.7 | 96 |
| Potassium Carbonate | 17 | 88 |
| Calcium Carbonate | 5 | 94 |
| Strontium Carbonate | 5 | 98 |
| Mn(II) Carbonate | ~100 | ~100 |
| Fe(II) Carbonate | ~100 | ~100 |
| Nickel Carbonate | ~100 | ~100 |

^a All results measured after the standard 10 minute combustion period.

A final supporting study providing a comparison between the WHC furnace method and the PNL hot persulfate method was a round-robin test of actual samples from the Hanford 101-SY complexant waste tank analyzed by both of these methods. The measured carbon levels throughout the various strata in the tank ranged from about 1.5% to 2.5% TOC. However, the methods' averages were 20% apart, with the WHC furnace method giving 20% higher results than the hot persulfate method. No specific cause was identified for the 20% difference, though two possibilities were considered: 1) the possible presence of volatile compounds or difficult-to-oxidize compounds causing a low-bias in the hot persulfate method, or 2) a high-bias in the WHC furnace method due to either the possible presence of high levels of nitrate salts, causing overloading of the purification columns, or incomplete removal of carbonates.

V. OPERATIONAL EXPERIENCE

Though a pure-compounds study, as described in this paper, provides extremely useful comparative information, such a study may present a misleading comparison of these four methods by ignoring possible matrix effects, instrumental difficulties, and detector problems when applied to the actual tank waste. Therefore, a summary of the strengths and weaknesses of each method, based upon direct operational experience, is provided here.

Upfront advantages of the hot persulfate method are the ease of installation and of operation within a remote, shielded-cell environment. The wet oxidation reaction minimizes problems with the presence of nitrates, sulfates, fluorides, or caustic. Large sample sizes (1-10 g) can be easily accommodated, providing more representative sampling. The primary organic constituents of many Hanford tanks, organic salts and complexants, give good recovery as seen in Table 2. The major weakness of this method is the poor recovery of volatile compounds due to loss during the heated sparging operations.

An important caveat here is that most of the aged tank waste analyzed to date has shown very little volatile or semi-volatile organic compounds present, as measured by gas chromatography/mass spectrometry methods. In fact, most of the organic carbon in the Hanford waste tanks is expected to be water-soluble complexants introduced during fission-product recovery processes. The possible volatile and semi-volatile organics that may be present would be small quantities of solvents, such as TBP, NPH, HDEHPA, and hexone, used in solvent extraction processes. Significant amounts of these are not expected, in most tanks, due to evaporative waste-concentration operations and aging. For applications where volatile and semi-volatile compounds are expected, the hot persulfate method, as implemented here, would probably be a poor choice.

For the furnace methods, the advantages are clearly seen in Table 2, with good recoveries of most

Table 4: Effect of Acid-Sparge on Loss of Volatile Compounds

| Compound | Recovery with Sparge (%) | Recovery without Sparge (%) |
|----------------------------|--------------------------|-----------------------------|
| Acetone ^a | 56 | 96 |
| 1-Butanol ^a | 99 | 103 |
| 1-Butanol ^b | 4 ^b | 58 ^b |
| Isopropanol ^a | 89 | 95 |
| Ethanol ^a | 89 | 97 |
| Ethyl Acetate ^a | 26 | 88 |
| Pentanol ^a | 67 | 93 |

^a Normal sparge conditions, during WHC furnace method, consisted of acid-sparge at room temperature.

^b Sparge conditions for this sample, during PNL hot persulfate method, consisted of acid-sparge at 90° C.

compounds by both the PNL and WHC furnace methods. The method can be installed in either a remote cell or fume-hood. Disadvantages of this method, particularly in the analysis of HLMW, are a major concern. Some of these disadvantages include severe waste-matrix attack of the quartz apparatus, the labor-intensive process for tube-furnace exchange within a radiation zone or remote cell, and buildup and concentration of radioactive residues within the furnace tube during fume-hood operation. A disadvantage in the use of the furnace's coulometer detector for this HLMW includes significant detector interference problems due to high-temperature combustion of nitrate, nitrite and sulfate salts. The combustion of these salts forms large quantities of acid gases which require removal, and can directly interfere with the coulometer operation. Additional disadvantages are excessive purification column loading from the high-salt matrices and the described problems caused by the presence and decomposition of carbonates. In addition, the absorption of released CO₂ by a caustic sample at 600° C is a matter of concern. All of these can contribute to potentially severe operational problems with the furnace method. One important distinction between the two described furnace methods is that the PNL furnace method is capable of handling tank sludge directly, while the WHC furnace method handles water leach samples only and therefore measures only water-soluble compounds.

For the UV-catalyzed persulfate method, excellent results were obtained for most compounds, within the method's limitations. The method gives good results for essentially all water-soluble carbon compounds. The method is used only on water-leached and filtered samples containing no particulates or other solids. The data in Table 2 show very good recovery for all compounds except for those identified as having limited solubility in water. Though this method is intended to only measure water-soluble carbon compounds with the water-leach procedure, the Table 2 data clearly shows some measurement of the low-solubility compounds.

VI. CONCLUSIONS

The application and extension of TOC methods to Hanford tank waste have been shown to be difficult, requiring a thorough understanding and comparison of each method's strengths and weaknesses. To provide informed input for this comparison, the TOC compounds study was performed, and the accumulated operational experience of the two laboratories was summarized. Based upon this work, the following conclusions can be given.

- 1) Because the methods cover a broad range of sample types and matrices, and because no single method has been found to be ideal for these samples, it is most useful to have multiple methods available for the analysis of Hanford tank waste materials.

- 2) While each method has inherent limitations, advantages, and disadvantages, each also has been shown to be very useful for specific sample matrices. The hot persulfate method is useful for remote operation and for most non-volatile carbon compounds. The furnace method is useful for the presence of both volatile and nonvolatile compounds in non-caustic media. The UV-persulfate method is very useful for aqueous samples.
- 3) While the current procedures in place at PNL and WHC have been found to be adequate for many tank sludge and slurry samples, continued methods development is necessary for reliable and robust measurements over a wider variety of waste tank matrices.

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