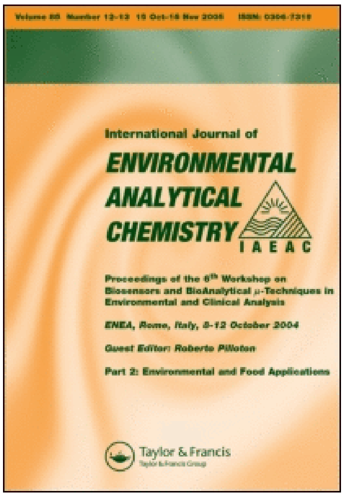

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Comparison of Methods to Determine Oxygen Demand for Bioremediation of a Fuel Contaminated Aquifer

R. M. Powell[a]; R. W. Callaway[a]; J. T. Michalowski[a]; S. A. Vandegrift[a]; M. V. White[a]; D. H. Kampbell[b]; B. E. Bledsoe[b]; J. T. Wilson[b]
[a] Northrop Services, Inc., Environmental Sciences, Robert S. Kerr Environmental Research Laboratory, Oklahoma, U.S.A. [b] United States Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, Oklahoma, U.S.A.

To cite this Article Powell, R. M. , Callaway, R. W. , Michalowski, J. T. , Vandegrift, S. A. , White, M. V. , Kampbell, D. H. , Bledsoe, B. E. and Wilson, J. T.(1988) 'Comparison of Methods to Determine Oxygen Demand for Bioremediation of a Fuel Contaminated Aquifer', International Journal of Environmental Analytical Chemistry, 34: 3, 253 — 263
To link to this Article: DOI: 10.1080/03067319808026842
URL: http://dx.doi.org/10.1080/03067319808026842

Intern. J. Environ. Anal. Chem., Vol. 34, pp. 253–263
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in Great Britain

Comparison of Methods to Determine Oxygen Demand for Bioremediation of a Fuel Contaminated Aquifer

R. M. POWELL, R. W. CALLAWAY, J. T. MICHALOWSKI, S. A. VANDEGRIFT and M. V. WHITE

Northrop Services, Inc., Environmental Sciences, Robert S. Kerr Environmental Research Laboratory, P.O. Box 1198, Ada, Oklahoma, U.S.A.

and

D. H. KAMPBELL, B. E. BLEDSOE and J. T. WILSON

United States Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, P.O. Box 1198, Ada, Oklahoma, U.S.A.

(*Received 21 April 1988*)

Four analytical methods were compared for estimating concentrations of fuel contaminants in subsurface core samples. The methods were total organic carbon, chemical oxygen demand, oil and grease, and a solvent extraction of fuel hydrocarbons combined with a gas chromatographic technique. Presently the most applicable and convenient technique for our purposes, based on greatest apparent contaminant recovery, is the solvent extraction gas chromatographic method. Sample heterogeneity and opportunity for losses due to contaminant volatility require consideration during sample handling, analysis, and when interpreting analytical data.

KEY WORDS: Oxygen demand, bioremediation, subsurface cores, fuel contamination, analyses, methods.

INTRODUCTION

Several conventional analytical methods can be used to determine petroleum fuel constituents in geological material such as soil or sediments. Accurate analytical data for such samples requires minimizing loss of volatile fuel components during sample processing. There are a variety of methods[1–7] to measure fuel constitutents in water and solid wastes, but none of them completely eliminates volatiles losses. Sample storage conditions can also change apparent contaminant concentrations through redistribution, or by actual reduction in contaminant levels due to biological or physical transformation.

Core samples, profiled according to depth, were collected under anaerobic and aseptic conditions at two different drilling sites in a fuel contaminated aquifer.[8] One site consisted primarily of contamination from aviation gasoline, whereas the other was due mainly to JP-4 jet fuel.

Analyses were needed to determine oxygen demand for biorestoration of the sites. Since oxygen demand is due not only to the fuel contamination but also to the naturally occurring organic materials and reduced metals, a variety of techniques were considered. Modifications of standard methods[2–4] for oil and grease (O&G), chemical oxygen demand (COD), and total organic carbon (TOC), along with a fuel hydrocarbon gas chromatographic technique (FC/GC) were developed and used to analyze the aquifer materials. A comparison was then made to evaluate the effectiveness of each method in terms of oxygen demand. This report presents the results of quantitative analyses obtained by each method.

EXPERIMENTAL

The methods were tested and finalized prior to collecting the core samples. Evaluation of method applicability, precision, and accuracy was accomplished by analyzing previously obtained contaminated cores, in addition to generating calibration curves, blanks, and spiked sample analyses.

Sampling

The core samples were received in tightly-capped pint and quart glass jars which were stored at 12 °C. Although the primary matrix constituent was sand, the material within each jar was anticipated to be fairly heterogeneous with respect to distribution of the contaminating fuel as well as widely dispersed particles of kerogen and carbonate minerals. All the samples were wet, with those from below the water table being saturated. To attain representative sampling, longitudinal subsamples from each jar were quickly taken using an 8 mm i.d. tubular paste sampler (Figure 1). The sampler was modified with a Teflon sleeve as a gasket, to minimize the loss of volatiles and water. These subsamples were then transferred to tared tubes or vials. Sample weights obtained using this tool varied from 5 to 14 grams, depending on the length of the plunger stroke and the proportion of water to solids in the sample. The sample containers were capped and weighed.

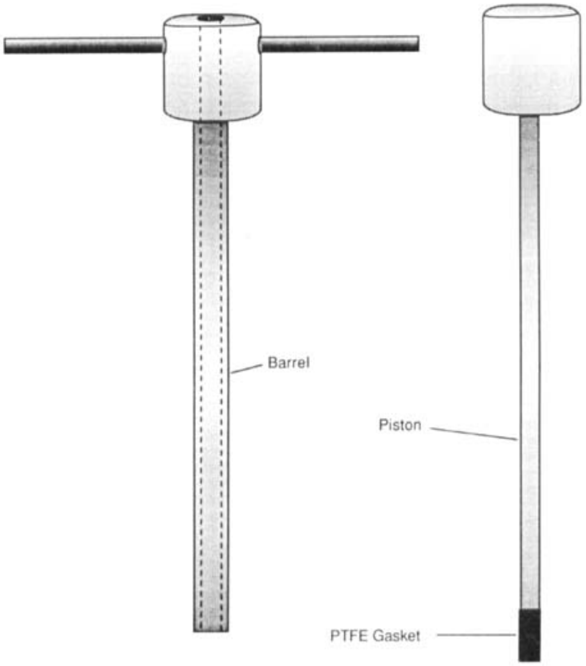

Figure 1 Paste sampler modified to reduce moisture and volatiles loss.

Chemical oxygen demand

Capped, 50-ml glass culture tubes containing approximately 5.0 grams of sample, water blanks, and standards of potassium hydrogen pthalate in water were heated for two hours at 150 °C in a Technicon block digestor (Technicon Instruments, Tarrytown, NY). Prior to heating, 10 mls of water, silver sulfate catalyst and potassium dichromate digesting solution had been added. After cooling, solution absorption was measured spectrophotometrically at 600 nm using a Brinkmann Colorimeter with a single-cell dipping probe (Brinkmann Instruments, Westbury, NY).

Total organic carbon

Due to the presence of volatile components, the TOC procedure normally employed for aquifer materials, which includes acidification (carbonate removal) and subsequent drying at 105 °C, could not be used.[9] Instead, the quantity of total organic carbon was determined as the difference between total (TC) and inorganic (IC) carbonate carbon:

$$\mathrm{TOC} = \mathrm{TC} - \mathrm{IC}.$$

Approximately 50 mg of each sample was weighed into a tared platinum boat and a tared 2-port OIC standardization vial (OI Corp., College Station, TX). The Pt boat was quickly inserted into a Dohrmann DC-80 carbon analyzer (Xertex Corp., Santa Clara, CA) using a sludge-sediment sampling accessory. Carbonaceous constituents were oxidized on a cobalt oxide catalyst at 800 °C. The resultant CO_2 was quantified versus potassium hydrogen phthalate standards by a non-dispersive infra-red analyzer (NDIR), for the determination of TC. To determine IC, the standardization vial was attached to an OIC Model 0524 carbon analyzer. Hot 20% V/V H_3PO_4 was injected through a septum onto the aquifer material and bubbled with N_2 for mixing and analyte purging. Carbon dioxide emitted from the vial was dried with $Mg(CLO_4)_2$ and measured by NDIR. Standardization was accomplished by injecting $CaCO_3$ standards into a vial containing H_3PO_4.

Oil and grease

Core subsamples were placed in 50-ml glass culture tubes with Teflon-lined screw caps, weighed, and just covered with Freon 113 (1,1,2-trichlorofluoroethane, b.p. 48 °C, Burdick & Jackson). Anhydrous magnesium sulfate was added to remove water from the core material and to allow better extraction of the soil with freon. The tubes were filled with freon, tumbled for mixing, and centrifuged. The liquid phase was clarified by centrifugation and the freon volume was determined. Absorbance of the freon fraction was measured by infrared spectrophotometry between 3200 and 2800 cm^{-1} using a Perkin Elmer 521 Grating Infrared Spectrophotometer (Perkin Elmer Coporation, Norwalk, CT). The strongest absorbance peaks for aviation gasoline occurred at 2955 cm^{-1} and for jet fuel at 2955 and 2925 cm^{-1}. Calibration curves for both peaks were prepared from aviation gas and JP-4 stock.

Fuel carbon by gas chromatography

The core subsamples were weighed into 20-ml headspace vials containing 5 ml water.[10] The vials were sealed using aluminium crimp caps with Teflon-lined septa and 3 ml of methylene chloride were injected. The vials were then shaken for 15 minutes and sonicated for a few minutes to break the emulsion layer. One ml of the extract was passed through an anhydrous sodium sulfate micro-column to remove water. One μl of the eluate was injected into the splitless injector of a Hewlett-Packard Model 5880 gas chromatograph (Hewlett-Packard, Avondale, PA) using a 15 m × 0.32 mm i.d., 1.5 μm film thickness, DB-5 capillary column (J. &. W. Scientific, Folsom, CA), flame ionization detector, and liquid N_2 cryogenic cooling. The temperature program was held at 10 °C for three minutes, then ramped 10 °C/minute to 225 °C and held for two minutes. Standards prepared from neat solutions of JP-4 jet fuel and aviation gasoline were also analyzed. Target peak areas were summed for each concentration level to develop a calibration curve. Samples were analyzed in the same manner as the standards. Fuel carbon (FC) was estimated at 85% of the fuel weight (confirmed by elemental analysis), therefore:

$$\mu\text{g FC} = 0.85\,(\text{determined, } \mu\text{g}).$$

RESULTS

Since the goal of this project was to determine the oxygen demand for bioremediation of the aquifer, it seemed reasonable to compare the analytical results on a stoichiometric oxygen demand basis. To accomplish this, it was necessary to determine the carbon and hydrogen contents of the jet fuel and aviation gasoline. Elemental analysis of the fuels were performed using a Carlo-Erba Model 1106 Elemental Analyzer (Carlo Erba, Strumentazione, Buchler Instruments, Saddle Brook, NJ). The results are given in Table 1. The differences in results for the two fuel types, both for carbon and hydrogen, were approximately equivalent to the accuracy and precision errors quoted for the elemental analyzer. Because of this, and since any error introduced would be insignificant compared to error from sample heterogeneity, the values obtained for the two differing fuels were averaged to calculate a single empirical formula of $CH_{2.16}$. Factors were determined to convert the analyses to theoretical oxygen demand (TOD).

Comparative analytical results obtained for 17 sample containers are shown in Figure 2. In nearly every case where a contaminated sample was encountered, the FC/GC method gave the highest oxygen demand results, possibly indicating greater retention of the volatile components by this method than by the others. Oil & Grease, TOC, and COD followed in order of decreasing indication of oxygen demand. This was true even though the FC/GC and O&G methods are incapable of quantifying all naturally occurring oxygen demand from sources such as kerogens and unoxidized metals. Based on the results of these 17 samples, it appears that naturally occurring

Table 1. Elemental Analysis of Aviation Gas and Jet Fuel, Percent

	Nitrogen	Carbon	Hydrogen
Aviation Gas	0.43	84.86	15.24
JP-4 Jet Fuel	0.63	85.36	15.46
	Mean* =	85.11	15.35

*The elemental analysis gives >100% recovery for both fuels

Carlo Erba Model 1106 Specifications:	Accuracy = 0.3 %	Precision = 0.2 %

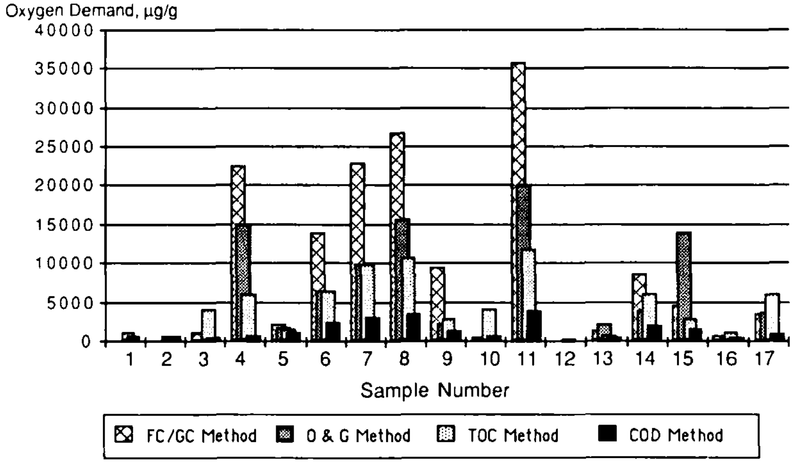

Figure 2 Oxygen demand determination by method for 17 samples of aquifer material.

oxygen demand can be considered insignificant for bioremediation in the highly contaminated zones of the aquifer.

Ideally, both TOC and COD should give oxygen demand results comparable to the FC/GC and O&G methods in a highly contaminated, low natural oxygen demand system but, when examined closely, the results obtained follow a logical pattern associated with handling and treatment, with volatiles losses of

$$\mathrm{FC/GC} < \mathrm{O\&G} < \mathrm{TOC} < \mathrm{COD}$$

for the following reasons:

1) The FC/GC method immediately seals the relatively large, 5–14 g, sample in a closed vial before injection of the extractant, methylene chloride.

2) When the anhydrous magnesium sulfate is added to the culture tube during the O&G analysis an exothermic reaction with the water of the 5–14 g sample occurs, generating enough heat in some instances to cause the freon to boil, resulting in potential loss of analyte.

3) For the TOC method, imprecision and inaccuracy are increased by small sample size. In addition, the small usable sample sizes of 50 mg or less results in a high surface to volume exposure of the sample, with subsequent high probability of volatiles loss.

4) The COD analysis is affected by extremely exothermic reactions and carbonate CO_2 generation, resulting in gas evolution which cannot be adequately contained by the culture tube caps, hence volatiles are lost.

Spike recoveries and precision are summarized in Table 2. Both accuracy and precision would certainly be affected by volatiles loss and subsample heterogeneity. The information presented indicates that the FC/GC method is superior in both these respects. The relative sensitivity curve in Figure 3A illustrates, however, a strong

Table 2. Quality Assurance Data

Replicates of the same sample are separated by a comma (,), differing samples by ellipsis dots(...)

Total Organic Carbon (TOC)

Total (TC)	Range of Coefficient of Variation (CV) = 14.2 - 52.2, where n = 4 Spike Recoveries, Percent: 101...(43, 83)...129
Inorganic (IC)	Worst case sample: CV = 95 % at the 0.09% IC level 13 of 17 samples were < 0.01 % IC, the lower reporting limit

Chemical Oxygen Demand (COD)

Sample Replication as
Oxygen Demand, µg/g: (860, 790)...(880, 830, 670)...(2480, 2320)...(250, 270)

Aqueous Standard Quality Control Samples, COD, mg/L	#1) Actual=84...Determined=95 #2) Actual=331...Determined=315

Oil & Grease (O & G)

Sample Replication as
Oxygen Demand, µg/g: (3830, 3790, 4590)...(20100, 28600, 7830)

Spike Recoveries, percent: (102, 99, 103, 104)...9...27...76...83...76

Fuel Carbon by Gas Chromatography (FC/GC)

Sample Replication as
Oxygen Demand, µg/g: (27000, 29000)...(23000, 25000)...(<66, <74, <53)...(<37, <82, <41)

Spike recoveries, percent: 69...84...99...96...74...77...101

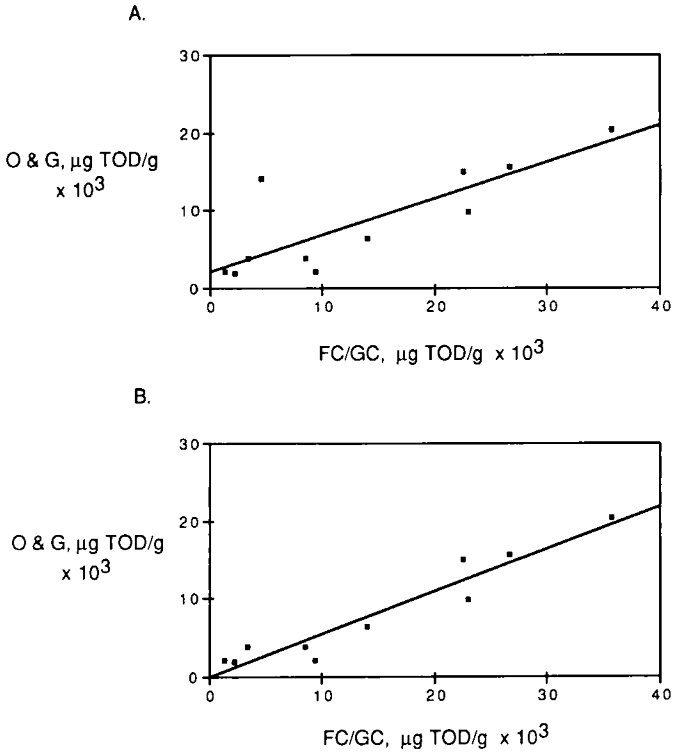

Figure 3 Correlation between FC/GC and O&G results.

correlation between the FC/GC and O&G determinations at all concentration levels of TOD (i.e. above the detection limits of both methods) with the exception of one data pair, sample 15 in Figure 2. The O&G coordinate of this pair is possibly an outlier since correlations of O&G with TOC and COD showed a similar pattern, even though overall scatter was increased. When this point is disregarded, as in Figure 3B, the relationship has a coefficient of determination (R^2) of 0.92 and is linear according to

$$\mu\text{g TOD by O\&G} = 0.55\ (\mu\text{g TOD by FC/GC}) + 93\,\mu\text{g TOD}$$

with the standard error of estimate $= 2025\,\mu$g TOD.

The slope value of 0.55 is due to greater contaminant recovery using the FC/GC method. The linearity and low scatter of this relationship can be interpreted in two ways:

1) Both techniques were consistent with respect to volatiles losses, or

2) Extraction efficiency was more important than volatiles loss for these two techniques.

It should not be assumed from this linearity that the FC/GC value can be calculated from an O&G determination, and vice versa, since the degree of consistency or extraction efficiency would probably vary both by analyst and laboratory.

CONCLUSIONS

Core examples can exhibit a rather large variability due to heterogeneous distribution of fuel components. This might be minimized by compositing subsamples from throughout the volume of each core sample, but volatiles loss during this process would be a major concern. Since longitudinal and lateral diffusion along with biodegradation of the contaminant can occur, sample storage time must also be a consideration. Sample heterogeneity can be partially alleviated by analyzing replicates of subsamples from each core sample.

Minimization of volatiles loss and/or greatest extraction efficiency during sample analysis was demonstrated by the extractive FC/GC method, which gave the highest oxygen demand levels for the contaminated cores. The oil and grease method might be a reasonable alternative when less volatile contaminants are to be determined but may also be limited by extraction efficiency. Our first choice for the aquifer under study was the FC/GC method, due to the greater contaminant recovery obtained.

Plans for future work should include development of techniques to further reduce volatile losses, better evaluate extraction efficiencies of the FC/GC and O&G methods, and improve subsampling of heterogeneous aquifer materials.

Acknowledgements

The authors would like to thank Annette Gavit of Williams Brothers Laboratories, Tulsa, Oklahoma, for the elemental analyses of the fuels.

Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency under contract number 68-03-

3315 to Northrop Services, Inc., Environmental Sciences, and under in-house research programs, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred.

References

1. Total Recoverable Petroleum Hydrocarbons, EPA Method 418.1, *Methods for Chemical Analysis of Water and Wastes* (1979).
2. Total Recoverable Oil and Grease, EPA Method 413.2, *Methods for Chemical Analysis of Water and Wastes* (1979).
3. Chemical Oxygen Demand, EPA Method 410.4, *Methods for Chemical Analysis of Water and Wastes* (1979).
4. Total Organic Carbon, EPA Method 415.1, *Methods for Chemical Analysis of Water and Wastes* (1979).
5. Purgeable Aromatics, EPA Method 602, Federal Register, Vol. 49, No. 209, Friday, October 26 (1984).
6. Static Headspace Analysis of Volatile Organic Compounds in Solids, EPA Method 5020, *Test Methods for Evaluating Solid Waste*, SW-846, 3rd ed., November (1986).
7. Aromatic Volatile Organics Analysis, EPA Method 8020, *Test Methods for Evaluating Solid Waste*, SW-846, 3rd ed., November (1986).
8. L. E. Leach, F. P. Beck, J. T. Wilson and D. H. Kampbell, *Aseptic Subsurface Sampling Techniques for Hollow-Stem Auger Drilling*, Proceedings of the Second National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods (National Water Well Association, 1988), Vol. 1, pp. 31–35.
9. R. M. Powell, B. E. Bledsoe, G. P. Curtis and R. L. Johnson, *Interlaboratory Methods Comparison for the Total Organic Carbon Analysis of Soils*, revised and resubmitted to Environ. Sci. and Technol., August (1988).
10. S. A. Vandegrift, D. H. Kampbell, *Gas Chromatographic Determination of Aviation Gasoline and JP-4 Jet Fuel in Subsurface Core Samples*, in press, J. of Chromatogr. Sci., August (1988).