Evaluation and Optimization of the Oxidation efficiency of a UV-Persulphate-Oxidation Toc-Analyzer for the Determination of Oil Contamination from Forestry in Ground Water

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EVALUATION AND OPTIMIZATION OF THE OXIDATION EFFICIENCY OF A UV–PERSULPHATE-OXIDATION TOC-ANALYZER FOR THE DETERMINATION OF OIL CONTAMINATION FROM FORESTRY IN GROUND WATER

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Different chain oils (tall, rape seed and mineral oils) have been used as model compounds to evaluate and optimize the applicability of UV–persulphate TOC-analyzer for quantitative determination of forestry oils and to follow the progress of their biodegradability. It was shown, that $K_2S_2O_8$–UV-oxidation method is not sufficient to oxidize chain oils completely. There were differences in oxidation efficiency between different oils, changing from about 46% measured for tall oil to about 25% observed for rape seed chain oil. The addition of Triton X-100 surfactant up to 2% (w/w) was observed to increase the oxidation efficiency, e.g. to 75% for tall oil. The observations can be explained by assuming that in the presence of surfactant the emulsions are more homogeneous and stable. Optimization using two-level full factorial design (temperature of the oxidation chamber and the amount of persulphate) was studied. The results show that the UV–persulphate-oxidation TOC-analyzer is not suitable method to monitor biodegradability of chain oils.

Keywords: Forestry oil; Chain oil; TOC analysis; Ground water; Biodegradability

INTRODUCTION

The environmental issues are very important in Finnish forestry. It is calculated that there were about 3500 harvesters and 3000 forwarders working in Finnish forests in 2001. The proportion of mechanical forest operations is about 90%. In addition, the annual amount of chain oils discharged into the Finnish forest environment is estimated to be about a total of 2 million litre. The gross revenue of the forestry branch was over 500 million €. Most of the forests have been certificated, i.e. wood procurement

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is based on sustainable forestry. There have been demand for the use of biodegradable oils in the forest machines. There have been, however, damages in hydraulic systems of forest machines when using biodegradable oils. Thus, also the interests on the possible harmful effects of the biodegradable oils on forest environment have been discussed [1]. Therefore, the protection of forestry soil and ground water areas against contamination with oil hydrocarbons is an important issue today because pure ground water is one of our most important natural resources.

The environmental effects of oils on forests and ground water are not widely studied or well known. In our earlier investigations during the last years, we have studied the biodegradability and environmental effects of forestry oils (mineral, tall and rape seed oils) in Finnish forest soils [1–3]. There is also an obvious need to study the effects of forestry oils in ground water. The biodegradability rate of the oils can be monitored, if there is a reliable method which can be used to analyze the total organic carbon content in ground water.

Total organic carbon (TOC) is an important non-specific water quality indicator. It can be used to determine the effectiveness of waste water-treatment procedures and to measure organic pollution. Total organic carbon consists of particulate organic carbon (POC) and dissolved organic carbon (DOC). DOC can be separated out by filtration through a 0.45 μm filter [4]. Volatile organic carbon (VOC), a very current concept in environmental studies today, can also be specified as the part of TOC that is volatile in specified conditions. Nowadays TOC analyses are usually performed using fully-automated instruments based on different oxidation methods.

TOC concentration of forestry oil polluted ground water is an ideal parameter to monitor if the biodegradability of oil is in focus. TOC concentration is directly proportional to hydrocarbon concentration of water. TOC-analyzers are also readily available in many laboratories. They are easy to use, quite fast and operating costs are low. However, incomplete oxidation of the sample components may affect the reliability of TOC concentration determined in ground water.

Using different chain oils as model compounds the aim of this study was to evaluate and optimize the applicability of a $K_2S_2O_8$–UV-oxidation TOC-analyzer for quantitative determination of forestry oils so that it could be used to follow the progress of their biodegradability. It is very important to evaluate the applicability of the method when it is applied to new sample types. Otherwise results from biodegradability study might be systematically wrong. It cannot be automatically assumed that oils are easy to oxidize even if they are biodegradable. For example, it has been mentioned in an extensive publication, that certain substances occurring in seawater samples are resistant to the combined $K_2S_2O_8$–UV-oxidation, even though they are biodegradable [5]. Hence there is a obvious need to study the possibility to use $K_2S_2O_8$–UV-oxidation based TOC-analyzer to analyse the carbon concentration of forestry oils in water phase.

EXPERIMENTAL

Instrumentation

In modern TOC-analyzers, organic compounds are first oxidized to carbon dioxide, then the CO_2 released is measured quantitatively, typically by an IR-detector. The oxidization method used is one of the most important factors that determine the accuracy

of TOC-analysis. The methods used can be classified in three different groups: chemical oxidation, photochemical oxidation and high temperature catalytic oxidation. The first two can be combined to enhance oxidation efficiency. If the oxidation efficiency is not high enough, TOC-results are systematically too low. In some cases, i.e. study of the biodegradability, this can lead to false conclusions.

In chemical oxidation several different reagents are used. The most typical are $K_2S_2O_8$, $K_2Cr_2O_7$ and $KMnO_4$. The oxidation efficiency is increased in the order $KMnO_4 < K_2Cr_2O_7 < K_2S_2O_8$ [6]. Thus, persulphate is the recommended oxidation reagent. It is usually used in elevated temperature (70–90°C). In photochemical oxidation, organic compounds are oxidized using high energy UV light. The most common UV light source is a mercury lamp. The oxidation efficiency can be enhanced by using an appropriate catalyst, e.g. TiO_2. In high temperature oxidation, organic compounds are oxidized at 700–900°C. Also, a catalyst is used, hence the abbreviation of the method, HTCO (High Temperature Catalytic Oxidation). When different oxidation methods have been compared the following efficiency order has been observed: $HTCO > UV > K_2S_2O_8 > K_2Cr_2O_7 > KMnO_4$ [6].

The ASTRO 2001 System 2 TOC-analyzer equipped with an auto-sampler was used in this study. In this analyzer, the combined $K_2S_2O_8$–UV-oxidation method is used to oxidize organic carbon to CO_2. The persulphate solution used was 1.5 M. The carrier gas is oxygen. Released CO_2 is measured by an IR-detector. Before the analyses, the analyzer was calibrated using standards prepared from potassium hydrogen phthalate (the recommended reagent according to ISO standard [4]). Stock solution (TOC concentration 1000 mg/L) was prepared by dissolving 0.5317 g of potassium hydrogen phthalate (dried in 110°C) to 500 mL water. Other standards were diluted from this solution. The surfactant used in the experiments was TRITON X-100. All reagents described above were *pro analyse*-grade. Water used in the experiments was purified using the Aquatron A4S-distillating system.

In the ASTRO analyzer, the TOC concentration of a sample is measured in eight different ranges, depending on TOC concentration of the sample. Each range has recommended upper and lower limits to which the TOC concentration of sample should be matched. Sample volume is different in each range, so that for higher TOC concentrations smaller sample volume is used. Also IR-absorption is measured at different wavelengths depending on range. Oxidation efficiency can be evaluated qualitatively by inspecting the output graph of the measurement. In the ideal case when oxidation efficiency is good, a Gaussian shaped peak should be observed (Fig. 1). When the sample is difficult to oxidize, tailing (Fig. 2) is observed. It was known from our preliminary observations, that oxidation efficiency varied only slightly in different ranges.

The total carbon contents of oils studied were determined using the Perkin Elmer Series II CHNS/O Analyzer 2000. In this analyzer, a 2 mg sample is weighed into a tin capsule and oxidized at a very high temperature (> 1000°C). The results obtained (Table I) were taken as reference values when the oxidation efficiency of the ASTRO TOC-analyzer was evaluated. Because CHNS/O analyzer used measures the total carbon content (both total organic (TOC) and total inorganic carbon (TIC)), it was not suitable for biodegradability studies. In addition analytical costs are quite high, the instrument used is slow to use and is not well suited for water samples.

A Bruker IFS 66 IR-spectrometer (Bruker Analytische Messtechnik GMBH) was used to analyze hydrocarbon concentrations from CCl_4 extracted samples according to the Finnish standard SFS 3010 [7].
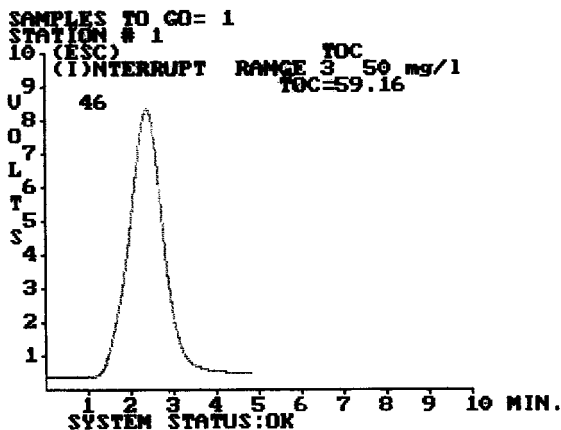
FIGURE 1   The output graph from the TOC analyzer for a potassium hydrogen phthalate measurement. The peak shape is Gaussian, which indicates that oxidation efficiency is high.
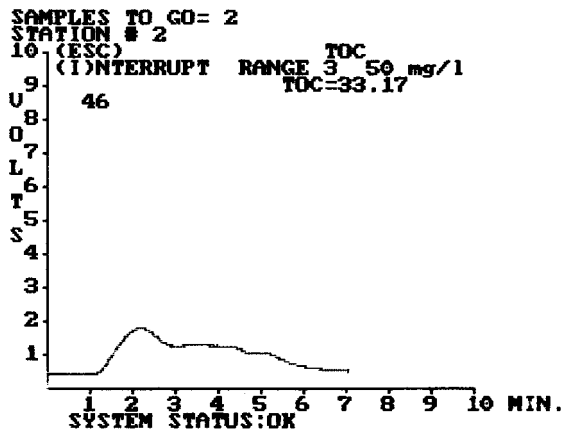
FIGURE 2   The output graph from the TOC-analyzer for a tall chain oil measurement. Peak tailing is observed, which indicates that oxidation efficiency is low.

TABLE I   Carbon content of different forestry oils determined by a Perkin Elmer Series II CHNS/O Analyzer 2000 ($n = 2$)

Type of oil	C (%)	Type of oil	C (%)
Mineral chain oil	85.9	Tall chain oil (ester)	79.2
Mineral hydraulic oil	85.7	Rape seed chain oil	76.0

Preparation of Samples

Simulated ground water samples were used. The samples were prepared by weighing an appropriate mass of oil in water to get solution where the concentration of oil was 2000–3000 mg/L. Then the samples were shaken for half an hour using a mechanical shaker. After that all the samples were diluted with water (1 : 50 dilution) and measured immediately. The TOC-concentration of the distilled water was negligible compared to that of the samples studied, and no blank correction was needed.

Special analytical challenges were the homogeneity of the sample and its adsorption on the glass containers used. These subjects were studied first to ensure the reliability of the results obtained from the oxidation efficiency studies.

The solubility of oils in water range from less than one mg/L level to several milligrams per liter. The content of dispersed oil might be more than one hundred milligrams per liter. A homogeneous sample is required if good accuracy and precision are expected in TOC experiments. Thus the homogeneity problem of the sample had to be studied first, since only a limited sample volume can be used with an ASTRO 2001 analyzer. The homogeneity of the water–oil mixture was studied by preparing samples containing no TRITON X-100 surfactant and samples containing increasing amounts of surfactant. Five replicate samples were prepared. The purpose of TRITON X-100 was to homogenize and stabilize the samples. TRITON X-100 was added to samples as 1% (m/v) solution to get the desired surfactant concentration and the samples were prepared as previously described.

Adsorption of the oil on the inner surface of glass containers is possible. This will cause a negative bias on the results. This possibility was studied by adding tall chain oil to water using two glass containers. TRITON X-100 was added to the other container. Samples were shaken for half an hour. The containers were then emptied and rinsed three times with 10 mL of distilled water. Finally 10 mL of CCl_4 was added to both container and they were again shaken for half an hour. The hydrocarbon content of CCl_4 was measured by FTIR-spectrometer according to the standard SFS 3010 [7].

Optimization of Oxidation Efficiency Using Two-level Full Factorial Design

The aim of the study was to improve the oxidation efficiency by optimizing two instrumental parameters (the temperature of the oxidation chamber and the amount of persulphate). Full two-level factorial design was used for this purpose. The basic principles of factorial designs can be found from textbooks [8,9]. Measurement data was analyzed using MODDE 3.0 statistical software (Umetrics, Sweden).

The oxidation efficiency of the instrument was studied using two measuring ranges and two oil type (tall chain oil and rape seed chain oil). The factorial designs used and the results obtained are presented in Tables IV and V.

RESULTS AND DISCUSSION

Homogeneity of the Sample

Results from homogeneity study are given in Table II. Oxidation efficiency is calculated by comparing the results from TOC-analyses to the results from CHNS/O analyzer. The oxidation efficiency was low for all three oils and depended strongly on the oil type. The highest oxidation efficiency was observed for tall chain oil (about 46%) and the lowest for rape seed chain oil (about 25%). At that time it was not clear whether the low oxidation efficiency was due to sample non-homogeneity or the low oxidation efficiency of the instrument.

The results obtained after addition of TRITON X-100 surfactant (0.5% w/w of oil mass) are shown in Table III. It was clear that the results obtained were closer to the expected values than without the surfactant. The observation can be explained by

TABLE II   Studies on the homogeneity of the oil distribution in the samples

Sample	Tall chain oil		Rape seed chain oil		Mineral chain oil	
	TOC (mg/L)	Oxidation efficiency (%)	TOC (mg/L)	Oxidation efficiency (%)	TOC (mg/L)	Oxidation efficiency (%)
1	16.7	47.5	11.9	27.2	13.4	30.7
2	17.8	50.8	10.6	24.3	12.1	27.7
3	15.7	44.8	10.8	24.8	12.4	28.4
4	16.1	45.9	10.6	24.2	*	
5	14.7	41.8	11.0	25.2	*	
Avg	16.2	46.2	11.0	25.1	12.6	28.9
Sd	1.2	3.3	0.5	1.2	0.7	1.6
RSD (%)	7.2	7.2	4.9	4.9	5.4	5.4

*Outlier (detected using Dixon's Q test).

TABLE III   Studies the homogeneity of the oil distribution in the samples in the presence of 0.5% (w/w) Triton X-100

Sample	Tall chain oil		Rape seed chain oil		Mineral chain oil	
	TOC (mg/L)	Oxidation efficiency (%)	TOC (mg/L)	Oxidation efficiency (%)	TOC (mg/L)	Oxidation efficiency (%)
1	31.3	67.7	24.9	53.9	13.2	26.7
2	29.7	64.2	25.1	54.3	15.2	30.7
3	30.8	66.6	23.6	51.1	15.2	30.5
4	30.2	65.2	22.3	48.2	*	
5	30.6	66.2	22.7	49.0	*	
Avg	30.5	66.0	23.7	51.3	14.5	29.3
Sd	0.6	1.3	1.3	2.8	1.1	2.3
RSD (%)	2.1	2.1	5.4	5.4	7.8	7.8

*Outlier (detected using Dixon's Q test).

assuming that emulsions were more homogenous and stable and so the apparent oxidation efficiency was increased. Again the highest oxidation efficiency was obtained for tall chain oil (about 66 %), but the order of two other oils was reversed.

The effect of increased TRITON X-100 content in the tall chain oil samples is shown in Fig. 3. The results demonstrated that when the TRITON X-100 content was over 2% (w/w of oil mass) the apparent oxidation efficiency was rather constant (about 75%). The same effect was observed for other oils. Hence it was concluded that the homogeneity problem was solved and the low oxidation efficiency was due to the inability of the method to oxidize completely the oil types studied. This was ensured by increasing the TRITON X-100 content in the samples. No further improvement in oxidation efficiency was observed. The TRITON X-100 concentration of 2% (w/w of oil mass) was selected for use in further studies.

Adsorption to Glass Walls

The results showed clearly that oil was adsorbed to the inner walls of containers unless the surfactant was present. Hydrocarbon concentration measured by IR was under the
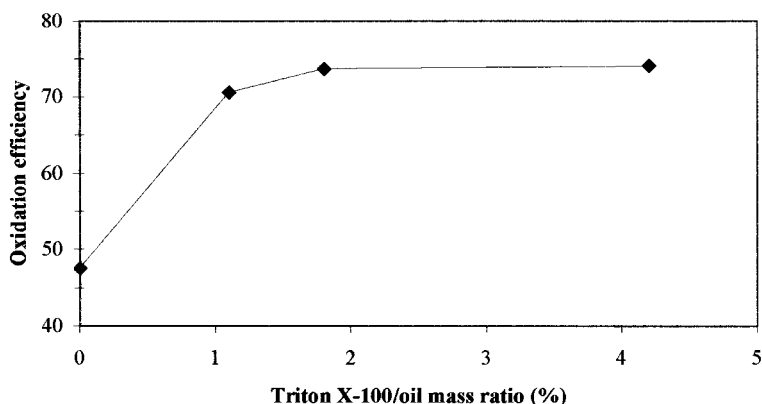
FIGURE 3 The effect of Triton X-100 concentration on the oxidation efficiency. Studied oil is tall chain oil.

TABLE IV Full 2-level factorial design used to optimize oxidation efficiency. The factors studied were the temperature of the reactor and the addition time of persulphate

Experiment	Temperature of reactor (°C)	Addition time of persulphate (s)	Oxidation efficiency of tall chain oil (%)	Oxidation efficiency of rape seed chain oil (%)
1	75	20	85.3	63.5
2	85	20	93.7	75.4
3	75	26	84.7	64.8
4	85	26	88.0	68.1
5	80	23	92.0	67.2
6	80	23	85.2	62.2
7	80	23	86.0	62.0

TABLE V Full 2-level factorial design used to optimize oxidation efficiency. The factors studied were the temperature of the reactor and the addition time of persulphate

Experiment	Temperature of reactor (°C)	Addition time of persulphate (s)	Oxidation efficiency of tall chain oil (%)	Oxidation efficiency of rape seed chain oil (%)
1	75	20	73.6	70.8
2	91	20	69.3	72.5
3	75	28	75.1	71.3
4	91	28	76.4	75.6
5	83	24	72.7	73.9
6	83	24	70.8	72.5
7	83	24	75.7	74.2

limit of detection. In principle surfactant is an detergent. So it 'washes' the walls and eliminates adsorption problems.

Optimization of the Oxidation Efficiency

A first order model with interaction terms was fitted to both sets of data in Tables IV and V using MODDE. ANOVA (Analysis of Variance) showed that models were statistically non-significant. Representative ANOVA results for the tall chain oil and the rape seed oil (Table IV) are in Tables VI and VII, respectively. Same kind of results

TABLE VI Results from ANOVA for the tall chain oil optimization study (Table IV)

	df	SS	MS	F	p
Total	6	78.332	13.055		
Regression	3	50.642	16.881	1.829	0.316
Residual	3	27.69	9.23		

TABLE VII Results from ANOVA for the rape seed oil optimization study (Table IV)

	df	SS	MS	F	p
Total	6	132.131	22.022		
Regression	3	85.247	28.416	1.818	0.318
Residual	3	46.884	15.628		

were obtained for a second optimization study (Table V). The results were interpreted to mean that the factors studied have no effect on the oxidation efficiency of the factor range studied.

CONCLUSIONS

The results obtained in this study showed that the oxidation efficiency of combined $K_2S_2O_8$–UV-oxidation method is not sufficient to oxidize chain oils completely. Oils are designed to be durable in extreme conditions prevailing in engines. So they are not easily oxidized and more efficient oxidation methods are obviously needed to get correct results. Oxidation method used should be always critically evaluated. Otherwise the results might be systematically too low. Sample homogeneity is also important subject when oils are analyzed. Surfactant should be used to homogenize sample. Surfactant also decrease adsorption problems.

It can be assumed that biologically the most easily available part of an chain oil is biodegradated first when the oil is decomposing in the environment. Probably the same part is also oxidized when an TOC-analyzer is used. So it might be assumed that oil is decomposing to certain limit and then the decomposing is stopped when biodegradability is monitored using TOC-analyzer even if some of the oil components are still left. Thus there is a risk that wrong conclusions are drawn from the results. But on the other hand TOC-analyses can give some valuable information, e.g. the biodegradability of an oil mechanism when combined with other methods.

Preliminary studies have shown that the respirometric BOD Oxitop method is a promising method for evaluating the biodegradability of oils in ground water [3]. Further results will be published in the near future.

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