Evaluation of Carbon Disulfide as an Alternative to Carbon Tetrachloride for the Determination of Hydrocarbon Oils in Water by Infra-Red Spectrophotometry

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EVALUATION OF CARBON DISULFIDE AS AN ALTERNATIVE TO CARBON TETRACHLORIDE FOR THE DETERMINATION OF HYDROCARBON OILS IN WATER BY INFRA-RED SPECTROPHOTOMETRY

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The replacement of carbon tetrachloride as an extraction solvent for the determination of hydrocarbon oils has been investigated. A detailed comparison of the performance of carbon tetrachloride and carbon disulfide has been undertaken using sets of homogeneous artificial seawater samples spiked with three different oils (gas oil, medium fuel oil and Forties field crude oil) at varying levels. An initial study of two sets of samples spiked with gas oil at different concentrations indicated problems with the homogeneity of the samples. A multiple interleaved run-off technique for sample preparation was therefore developed and this was found to significantly improve the sample homogeneity. A further three sets of samples spiked with gas, fuel and crude oil were prepared using this technique. In total, five sets of samples were analysed. In all cases, there was no significant difference between the variation in the results obtained for each solvent. In three cases the means of the results obtained using the two solvents were found to be significantly different. For the samples spiked with fuel oil and the lowest level of gas oil, the results obtained using carbon disulfide were significantly higher than those obtained using carbon tetrachloride. For the samples spiked with crude oil the carbon tetrachloride results were significantly higher, however the difference was not as great as in the other cases. It is concluded that carbon disulfide could be used as a replacement for carbon tetrachloride in the analysis of hydrocarbon oils in water by infra red spectrophotometry. However, there is some evidence that current regulatory limits based on carbon tetrachloride extraction may require re-evaluation, especially for specific oil types, if identical rather than similar overall effects in enforcement are to be achieved.

Keywords: Hydrocarbon oils; solvent replacement; carbon tetrachloride; carbon disulfide; infra red spectrophotometry

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INTRODUCTION

Carbon tetrachloride is a commonly used solvent in analytical chemistry. The AOAC methods book[1] lists approximately 46 methods in the fields of food and agriculture that specify the use of this solvent, and a survey of methods in our laboratory identified a further 10 methods.[2] There is increasing pressure on industry and analytical laboratories to reduce the amounts of chlorinated solvents used due to concerns about their impact on the environment. The most well known and far reaching example of controls on the use of chlorinated solvents is the Montreal Protocol on substances which deplete the ozone layer. The signatories to the protocol agreed to restrict the production and use of certain ozone depleting substances, including the common laboratory solvents carbon tetrachloride and 1,1,1-trichloroethane. Within the European Union the protocol is enforced by Regulation 594/91 as amended by 3952/92.[3,4] The phase-out date for carbon tetrachloride was 1 January 1995. However, a number of exemptions were agreed for certain "essential uses". One such exemption was for laboratory and analytical uses. However, as the requirements of the protocol begin to take effect, production of such solvents will decrease, leading to an increase in price and a reduction in availability. Therefore, in spite of the exemption, supplies to analytical laboratories cannot be guaranteed and it is prudent to seek alternatives.

One common use of carbon tetrachloride in analytical chemistry is the extraction of oil and grease from water samples for quantification by infrared spectrophotometry, and in particular for the determination of hydrocarbon oils in tanker ballast water. Hydrocarbon oils are economically important and the regulation of this discharge has correspondingly wide economic effects. The current methods are typically similar to that described by Simard *et al*[5] and use approximately 100 ml carbon tetrachloride per sample, plus 600 ml for the preparation of standards. The aim of this study was to identify a replacement solvent for carbon tetrachloride and evaluate its performance against the chlorinated solvent.

Choice of solvent

A number of criteria had to be met by possible alternative solvents. The solvent must be immiscible with water; be transparent to infrared in the region 2700 to 3200 cm^{-1}; be at least as efficient as carbon tetrachloride at extracting oil from water samples; should not be prohibitively expensive and have minimal environmental impact. It was decided to exclude chlorinated solvents from the study. Although not all chlorinated solvents are covered by the Montreal Protocol, there is a general move to reduce the use of such solvents. The infra red transparency criteria ruled out solvents containing C—H bonds. Perfluorinated solvents were

considered, including perfluoro(methyl cyclohexane) and perfluoroheptane. Although infrared and miscibility criteria were met, the solubilities of a number of different oils in the perfluorinated solvents were found to be unsatisfactory and the cost high. However, the results obtained for carbon disulfide were more encouraging. It was therefore decided to carry out a direct comparison of the performance of carbon disulfide and carbon tetrachloride for the extraction of three different oil types at different concentrations from specially prepared spiked samples.

EXPERIMENTAL

Reagents

The solvents used were carbon tetrachloride, 99.8%, (BDH) and carbon disulfide, 99.99%, (Fisher Scientific). Pentadecane, 2,2,4-trimethylpentane and benzene were supplied by Aldrich Chemical Co. Sea water corrosion test mixture to DEF 1053/BS 3900/BS 2011 supplied by BDH (360 g) was dissolved and diluted to 10 litres with demineralised water. Fully rebated gas oil, Medium fuel oil and Forties field crude oil were obtained from the laboratory reference collection.

Linearity check

Two sets of calibration standards were prepared, one in carbon tetrachloride and the other in carbon disulfide, using a synthetic oil standard containing 37.5 % 2,2,4-trimethylpentane, 37.5 % pentadecane and 25 % benzene (v/v). The standard concentrations were in the range 0 to 750 mg l^{-1}. Each standard was scanned twice from 3200 cm^{-1} to 2700 cm^{-1}, and the peak height at 2930 cm^{-1} recorded, in a dual beam infra red spectrophotometer, Perkin Elmer model 882.

Preparation of spiked samples

To compare the performance of the two solvents, sets of four homogeneous spiked samples were required. Two of the samples in each set were extracted with carbon tetrachloride and the remainder with carbon disulfide.

Method 1: Single run-off

The method used to prepare the samples was a modification of that described by Gruenfeld.[6] 1.5 litres of synthetic seawater was placed in a 2 litre separating

funnel and an appropriate amount of gas oil added (see Table I). The mixture was then shaken vigorously to disperse the oil in the water. After shaking, the mixture was allowed to stand for approximately 15 minutes. Four 250 ml portions of the lower layer were placed in separate sample bottles. A further 750 ml synthetic sea water and 5 ml of 1:1 hydrochloric acid (v/v) were then added to each sample. Each bottle was then shaken vigorously to thoroughly mix the contents. The samples were labelled A to D. Samples A and C were analysed using carbon tetrachloride as the extraction solvent whilst samples B and D were analysed using carbon disulfide, according to the extraction procedure given below. The procedure was repeated six times at each concentration.

TABLE I Approximate weights of oil added to 1.5 litre of synthetic seawater for the preparation of homogeneous spiked samples

Type of oil	Method of sample preparation	Approximate weight of oil (g)	Predicted concentration (mg l^{-1})
Gas oil	Method 1	0.15	25
Gas oil	Method 1	0.25	42
Gas oil	Method 2	0.45	75
Fuel oil	Method 2	0.45	75
Crude oil	Method 2	0.45	75

Method 2: Multiple interleaved run-off

The required amount of oil (see Table I) was added to 1.5 litres of the synthetic sea water in a 2 litre separating funnel. The mixture was shaken vigorously to disperse the oil in the water and then allowed to stand for 15 minutes. The first 50 ml of the water layer was run off and discarded. Four 250 ml samples (A to D) were then taken from the water layer using the scheme presented in Table II. 50 ml portions were run into the sample bottles A to D in the order ABCD, DCBA, ABCD ...... (note the reversal on each pass) until 250 ml had been delivered to each bottle. A further 750 ml synthetic sea water and 5 ml of 1:1 hydrochloric acid (v/v) were then added to each sample. Each bottle was then shaken vigorously to thoroughly mix the contents. For each oil and spiking level, six sets of four samples were prepared. The samples were analysed using either carbon tetrachloride or carbon disulfide according to the plan given in Table II.

TABLE II Sampling of 250 ml spiked water samples from 1.5 litres synthetic seawater and order of extraction

	Volume of water layer taken			
	Sample A	Sample B	Sample C	Sample D
	50 ml	50 ml	50 ml	100 ml
	100 ml	50 ml	50 ml	←
	→	50 ml	50 ml	100 ml
	100 ml	50 ml	50 ml	←
	→	50 ml	50 ml	50 ml
Total	250 ml	250 ml	250 ml	250 ml

	Extraction solvents to be used for each batch of samples			
Batch No.	Sample A	Sample B	Sample C	Sample D
1	CC_4	CS_2	CS_2	CCl_4
2	CS_2	CCl_4	CCl_4	CS_2
3	CS_2	CS_2	CCl_4	CCl_4
4	CCl_4	CCl_4	CS_2	CS_2
5	CCl_4	CS_2	CCl_4	CS_2
6	CS_2	CCl_4	CS_2	CCl_4

Extraction and quantitation

The oil is extracted into carbon tetrachloride or carbon disulfide and the maximum infrared absorbance in the range 3200 cm^{-1} to 2700 cm^{-1} is recorded. Calibration standards are prepared from a synthetic oil mixture as the exact nature of the oil present in contaminated waters is generally unknown.

The sample was transferred to a 2 litre separatory funnel and successively extracted with three portions of solvent (50 ml, 20 ml and 20 ml) by shaking vigorously for 2 minutes and then allowing the solvent layers to separate. Before being added to the sample in the separatory funnel, the solvent aliquots were used to rinse the sample bottle. The extraction solvents were passed through a funnel plugged with cotton wool covered with a layer of sodium sulphate, collected in a 100 ml volumetric flask and then made up to volume. Calibration was by means of six standards prepared from the synthetic oil standard dissolved in the extraction solvent and made up to 100 ml. The approximate concentrations of the standards were 30, 90, 150, 300, 450 and 600 mg l^{-1}. Calibration curves of peak height at 2930 cm^{-1} against standard oil concentration in mg l^{-1} were prepared.

RESULTS AND DISCUSSION

Both calibration curves were visually linear over the range examined and the fit good ($R^2 = 0.9999$ and 0.9997 for CCl_4 and CS_2, respectively). It was found that carbon disulfide produced a baseline disturbance which resulted in a negative reading for the blank standard. The readings for subsequent standards and samples were corrected for this blank reading. The baseline disturbance made it slightly more difficult to record the peak heights for the low level standards, compared to when carbon tetrachloride was used. However, it was possible to read a 10 mg l^{-1} standard in carbon disulfide, which corresponds to a concentration of 1 mg l^{-1} for a 1 litre water sample. The reason for the disturbance is at present unknown.

The results from the analysis of the samples spiked with gas oil prepared using method 1 are presented in Figure 1a and Figure 1b. The means and variances of the data and the results of the statistical analyses are summarised in Table III. The results obtained for all the samples were significantly lower than the target concentrations. It is likely that this is mainly due to the limited solubility of the oil in water. During preparation of the samples a film of oil was observed on the surface of the 1.5 litres of water in the separating funnel, indicating that not all of the oil added had gone into solution. The samples with a target concentration of 25 mg l^{-1} were found to contain approximately 11 mg l^{-1} using CS_2 as the extraction solvent, whilst the "40 mg l^{-1}" samples were found to contain approximately 20 mg l^{-1}.

TABLE III Summary of statistical analysis of results from spiking studies

	Mean concentration (mg l^{-1})			Difference between sample pairs		Variance		
Oil	*CCl_4*	*CS_2*	*Two-factor ANOVA significant at 95%*	*Two-factor ANOVA significant at 95%*		*CCl_4*	*CS_2*	*F-test significant at 97.5%*
Gas	6.5	9.9	Yes	No		0.49	1.13	No
Gas	19.8	19.4	No	Yes		3.45	8.94	No
Gas	17.8	18.9	No	No		9.08	12.41	No
Fuel	6.8	12.1	Yes	No		1.34	2.03	No
Crude	14.0	11.8	Yes	Yes		0.60	0.70	No

For the samples containing approximately 20 mg l^{-1} gas oil, two-factor ANOVA indicated no significant difference between the results obtained for the two extraction solvents at the 95% confidence level. However, a significant difference between the results obtained for the sample pairs was observed. It was noted that results obtained for sample C in each batch were consistently lower than those obtained for sample A, and those obtained for sample D were lower than those obtained for the sample B. A typical result is shown in Figure 1a.
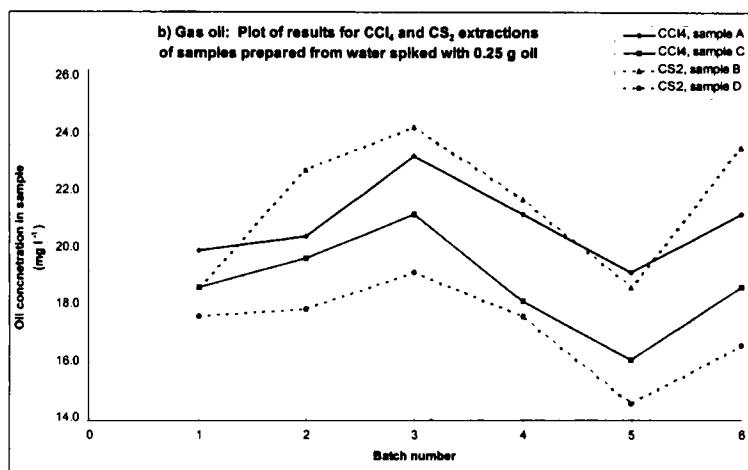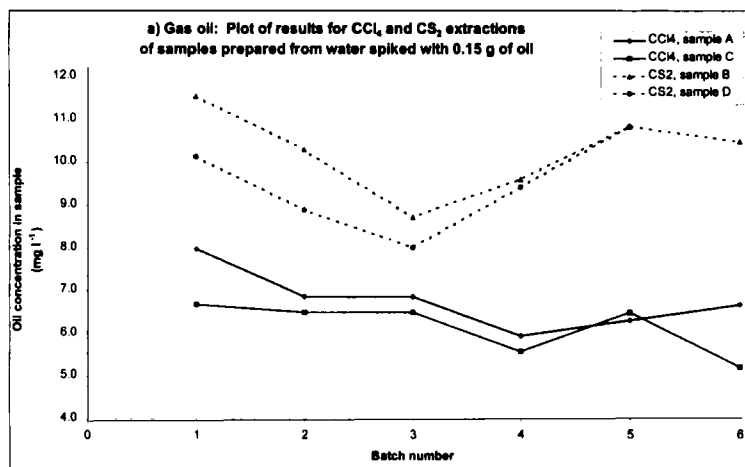

FIGURE 1 Comparison of results obtained using carbon tetrachloride and carbon disulfide as extraction solvent

At the 11 mg l^{-1} level, two-factor ANOVA indicated a significant difference between the results obtained for the different solvents, with carbon disulfide producing consistently higher results. No significant between sample variation was observed but a similar trend was noted across the A, C and B, D sample pairs as for the 20 mg l^{-1} samples.

The results indicated that the samples were probably heterogeneous. The concentration of oil in each sample appeared to decrease from A to D. A plot of the difference in concentration observed for the sample pairs for each solvent is presented in Figure 2a. All except one of the differences have the same sign indicating a consistent drop in oil concentration across the pairs. As problems with sample homogeneity could mask the effect of changing the extraction solvent, the remainder of the spiking studies were conducted using a multiple interleaved run-off technique (method 2).
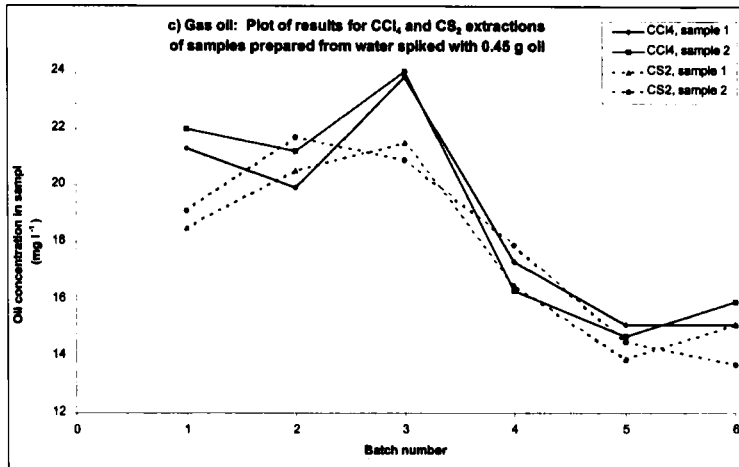

FIGURE 1 Continued

The results obtained for the three sets of samples prepared using the multiple interleaved run-off technique are presented in Figure 1c to Figure 1e . The data and results of the statistical analyses are summarised in Table III. Two-factor ANOVA was applied to the three sets of results. For the samples spiked with gas oil, no significant between sample pair or between solvent variation was observed at the 95% confidence level. In the case of the samples spiked with fuel oil, a significant between solvent variation was observed, with carbon disulfide producing higher results than carbon tetrachloride. The between sample pair var-

iation was not significant. The analysis of the results obtained for the samples spiked with crude oil indicated significant between solvent and between sample pair variation. In this case carbon tetrachloride produced the higher results. The significant between sample variation (p = 0.0253) can probably be attributed to an unexpectedly low result for the second sample extracted with carbon tetra-chloride in the first batch (but not sufficiently low to be considered an outlier in this data set). The results should accordingly be viewed with caution.
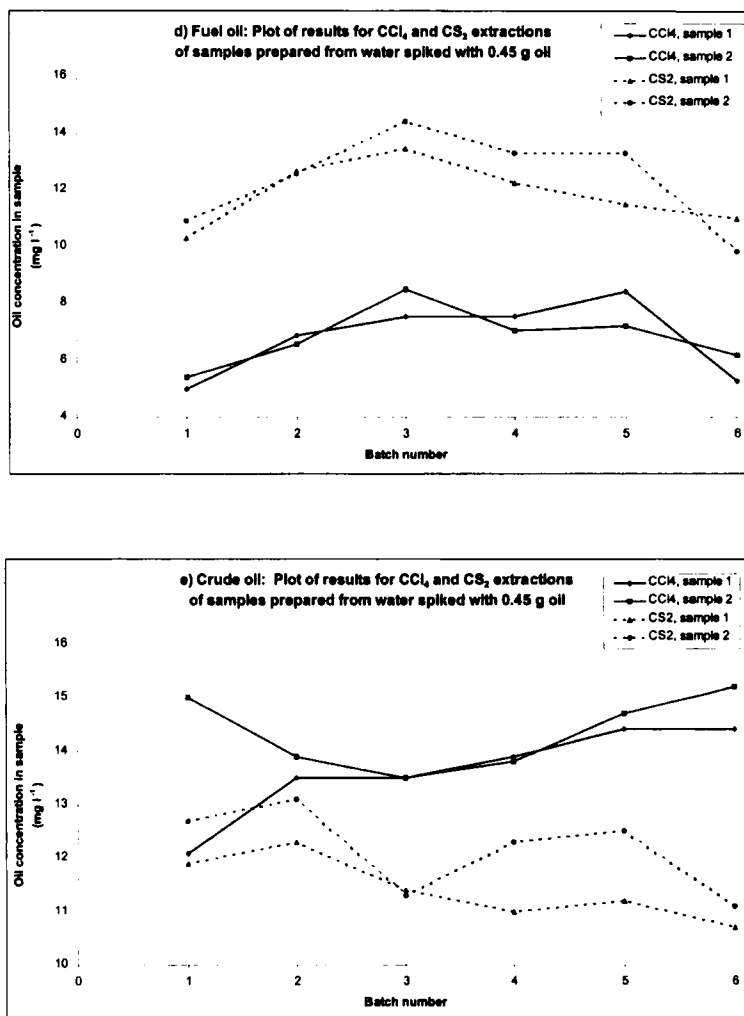

FIGURE 1 Continued

The reason for the differing performances of the oils is unclear. It is possible that differing oil compositions could produce selective extraction effects, but comparison of the IR spectra of the extracts showed no significant differences in aromatic/aliphatic content.
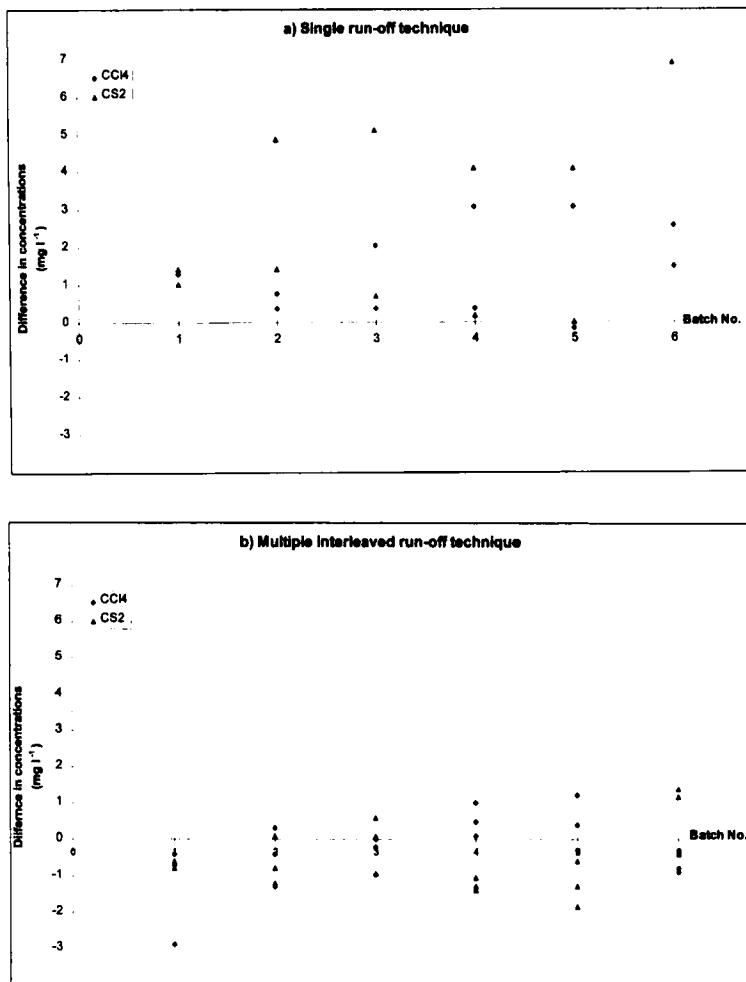

FIGURE 2 Plot of differences in concentrations observed for sample pairs prepared using the two different run-off techniques

The effect of multiple interleaved run-off sample preparation is shown in Figure 2b which presents a plot of the difference in concentration observed for the sample pairs for each solvent. In contrast to the results obtained using

method 1, the differences are now spread about the zero difference line indicating no clear trend in concentration change across the sample pairs. This method is to be recommended in preference to a single run-off technique.

Tests for homogeneity of variance showed no significant difference (95% one tailed F test) between carbon tetrachloride and carbon disulfide in any cases.

In addition to its technical performance, there are other pros and cons associated with the use of carbon disulfide as a replacement solvent. Carbon disulfide is a relatively inexpensive solvent which is readily available. Table IV presents a comparison of the hazards associated with each solvent. The most significant difference between the two solvents is the high flammability of carbon disulfide. In addition, carbon disulfide is a very volatile solvent which requires careful handling. Due to these factors, carbon disulfide may not be an ideal solvent to use in the large volumes required by the method. However, the choice of possible alternative solvents is very limited and the advantages of carbon disulfide, in terms of its performance in the method, outweigh the disadvantages.

TABLE IV Physical properties and hazards associated with carbon tetrachloride and carbon disulfide

	Carbon Tetrachloride	Carbon disulfide
Boiling point (°C)	76.1	46.3
Flammability	Non-flammable	Highly flammable
Hazards	Toxic by inhalation, in contact with skin and if swallowed. Danger of serious damage to health by prolonged exposure through inhalation. Possible risk of irreversible effects.	Toxic, danger of serious damage to health by prolonged exposure through inhalation. Irritating to eyes and skin. Possible risk of impaired fertility, possible risk of harm to the unborn child.

Based on the results of this study it is concluded that carbon disulfide could be used as a replacement for carbon tetrachloride in the analysis of hydrocarbon oils in water by infra red spectrophotometry. However, there is some evidence that current regulatory limits based on carbon tetrachloride extraction may require re-evaluation, especially for specific oil types, if identical rather than similar overall effects in enforcement are to be achieved.

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