

DTIC FILE COPY

UNLIMITED DISTRIBUTION

①



**National Defence
Research and
Development Branch**

**Défense nationale
Bureau de recherche
et développement**

TECHNICAL MEMORANDUM 89/203

January 1989

AD-A206 702

**A STUDY OF FUEL DILUTION OF
DIESEL LUBRICATING OIL BY GAS
CHROMATOGRAPHY/MASS SPECTROMETRY**

J. A. Hiltz - D.E. Veinot - R.D. Haggett

**DTIC
ELECTE
S - 4 APR 1989 D
α E**

**Defence
Research
Establishment
Atlantic**



**Centre de
Recherches pour la
Défense
Atlantique**

Canada

89 4 04 010

DEFENCE RESEARCH ESTABLISHMENT ATLANTIC

9 GROVE STREET

P O BOX 1012
DARTMOUTH, N.S
B2Y 3Z7

TELEPHONE
(902) 426-3100

CENTRE DE RECHERCHES POUR LA DÉFENSE ATLANTIQUE

9 GROVE STREET

C P 1012
DARTMOUTH, N E
B2Y 3Z7



**National Defence
Research and
Development Branch**

**Défense nationale
Bureau de recherche
et développement**

**A STUDY OF FUEL DILUTION OF
DIESEL LUBRICATING OIL BY
GAS CHROMATOGRAPHY/MASS SPECTROMETRY**

J.A. Hiltz - D.E. Veinot - R.D. Haggett

January 1989

Approved by L.J.Leggat

Director/Technology Division

DISTRIBUTION APPROVED BY

D/TD

TECHNICAL MEMORANDUM 89/203

**Defence
Research
Establishment
Atlantic**



**Centre de
Recherches pour la
Défense
Atlantique**

Canada

Abstract

A method for the detection and identification of fuel components in diesel lubricating oil is described. The method uses a capillary gas chromatograph coupled to a quadrupole mass spectrometer to separate, detect and identify diluents in the oil. A typical analysis takes 40 minutes. Accurate determination of the level of fuel dilution of a diesel lubricating oil sample using GC/MS is shown to be dependent upon a number of factors including the source of the fuel, the age of the fuel, the thermal history of the fuel diluted diesel oil sample and the availability of a suitable sample of fuel to prepare standard response versus concentration curves. In contrast to the standard methods of determining fuel dilution in diesel lubricating oil such as ASTM D445-82 (viscosity change), ASTM D92-78 (flash point reduction), and ASTM D3524-78 (packed column gas chromatography with flame ionization detection), this method can identify diluents and contaminants in the diesel lubricating oil. This is extremely important in cases where the standard tests give false negatives or indicate the presence of a diluent but cannot identify the diluent.

CANADA DES

RÉSUMÉ

L'article décrit une méthode de détection et d'identification des éléments de carburant présents dans de l'huile de graissage diesel. Les instruments utilisés sont un chromatographe capillaire à phase gazeuse et un spectromètre de masse quadripolaire; ils séparent, décèlent et identifient les diluants de l'huile. L'analyse prend généralement 40 minutes. La détermination exacte de la quantité de carburant diluant présent dans un échantillon d'huile de graissage diesel, avec ces instruments, dépend d'un certain nombre de facteurs, notamment la source du carburant, son âge, les antécédents thermiques de l'échantillon et la disponibilité d'échantillons de carburant suffisants pour établir une courbe d'étalonnage en concentration. Grâce à cette méthode, on peut déterminer quels diluants et contaminants sont présents dans un échantillon d'huile, contrairement aux méthodes plus courantes de détermination de la dilution de l'huile: ASTM D445-82 (modifications de la viscosité), ASTM D92-78 (réduction du point d'éclair), ASTM D3524-78 (chromatographie en phase gazeuse sur colonne garnie avec détection par ionisation de flamme). C'est un net avantage, car les essais conventionnels donnent parfois de faux résultats négatifs ou des résultats positifs incomplets parce qu'ils n'identifient pas le diluant.

Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

TABLE OF CONTENTS

	Page
1.0 Introduction	1
2.0 Experimental Approach	3
2.1 Equipment - Capillary Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS)	3
2.2 Standard Solutions	3
2.3 Naval Distillate Fuel Aging Study	4
3.0 Results and Discussion	4
3.1 Separation of Naval Distillate from Diesel Lubricating Oil	4
3.2 Quantitative Analysis	5
3.2.1 Response Versus Concentration of Naval Distillate Fuel in Diesel Lubricating Oil	5
3.3 Relative Concentration of the Components of Naval Distillate Fuel	6
3.4 Fuel Aging Studies	7
3.5 Examples of Fuel Dilution of Diesel Lubricating Oil by GC/MS	9
3.6 Identification of Diluents in Diesel Lubricating Oil	11
3.7 Detection Limits of Naval Distillate Fuel	12
4.0 Conclusions	13
Figures	14
References	23

1.0 INTRODUCTION

Accurate monitoring of the level of naval distillate fuel (CGSB 3-GP-11Ma¹) dilution in diesel engine lubricating oil (MIL-L-9000G²) is an important concern in the daily operation of Canadian Forces ships for two reasons. Fuel in the diesel lubricating oil will lower the flash point of the lubricant mixture to below that for the unadulterated oil which presents a safety hazard due to the possibility of explosion in the engine crankcase. Fuel can also act to alter the viscosity of the diesel lubricating oil which may adversely affect its lubricating properties.

Conventionally, the level of fuel dilution of diesel lubricating oil has been determined by two ASTM standard methods, namely, viscosity change³ and flash point⁴ reduction, both of which provide only indirect results for fuel dilution. These methods involve the use of standards (prepared from stock samples of diesel lubricating oil and naval distillate fuel) to prepare calibration curves relating the measured change to the level of fuel dilution of the standards.

The determination of fuel dilution of diesel lubricating oil by viscosity change involves the assumption that the reduction in viscosity of the sample is the result of fuel dilution. However, the reduction in viscosity may result from other factors including dilution of the diesel lubricating oil by any other less viscous solvent or by breakdown of the lubricant itself. Samples that have been in service for a period of time and are contaminated with fuel will likely contain a lower percentage of the more volatile constituents of fuel as a result of in service evaporation of the lighter components. The use of a standard prepared in the laboratory from an unused sample of fuel would have a different composition than the actual sample and this would effect the calculated value of the fuel dilution, e.g., the apparent concentration of fuel determined from the calibration plot may not necessarily reflect the actual level of fuel dilution of the diesel lubricating oil. In other instances the viscosity of the diesel lubricating oil may be increased by a number of factors including polymerization and oxidation of the oil, excessive carbon buildup in the oil, or the addition of the wrong makeup oil to the system. If the oil suffers fuel dilution at the same time, the viscosity of the sample may not reflect the degree of fuel dilution that has actually taken place. Viscosity analysis, does however, provide some useful information regarding the lubricating qualities of the fuel.

Similarly, a change in the flash point of a lubricating

fluid does not necessarily indicate that fuel dilution of the fluid has taken place. Although a decrease in flash point may indicate the presence of a contaminant, it does not indicate the source or nature of the diluent. Flash point analysis does, however, provide an indication of the potential for explosive hazard while using the adulterated sample.

An ASTM method⁵ is in place that utilizes packed column gas chromatography (GC) with flame ionization detection (FID) to quantitatively determine fuel dilution of diesel lubricating oil. This ASTM method utilizes an internal standard (n-decane) in the quantitative step. A series of at least three solutions of fuel in diesel lubricating oil, containing known amounts of fuel and a constant amount of n-decane, are prepared and utilized to plot a calibration curve of the ratio of the area of the fuel peaks to the area of the internal standard peak against the concentration of fuel in the solution. The peaks of the components of the naval distillate fuel are assigned on the basis of their retention times. The sample to be analyzed is then spiked with the internal standard and the ratio of the areas under the fuel peaks and the internal standard are determined. The concentration of the fuel in the sample, i.e., the fuel dilution, can then be obtained from the calibration curve.

As with the methods using the measurement of viscosity and flash point changes, the packed column GC method with FID can not identify the contaminant giving the observed response. If a contaminant is present that has a retention time in the range of the components of naval distillate fuel then it will also be measured as a component of the fuel. Further this packed column method is not able to resolve the individual fuel constituents and the response it provides is from the cumulative total of all of the compounds which elute from the column during a specified time frame.

Capillary gas chromatography/mass spectrometry (GC/MS) has the ability to separate and identify the individual contaminants in a diesel lubricating oil sample. The improved separation realized with a capillary column facilitates quantitative analysis by allowing the quantitative measurement of the individual components of the fuel. Identification of compounds eluting from the column can eliminate false positives caused by contaminants in the sample with retention times similar to the components of the fuel and can also aid in determining the source of the contaminant in the fuel.

This paper describes the development of a capillary GC/MS method for the detection and identification of contaminants in

diesel lubricating oil. Limitations on the quantitative determination of fuel dilution of diesel lubricating oil using this method are discussed at length.

2.0 EXPERIMENTAL APPROACH

2.1 Equipment - Capillary Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS). Capillary gas chromatographic separations using MS detection were carried out on a Finnigan MAT model 9611 gas chromatograph. A 30m long by 0.25mm inside diameter Durabond DB-1 capillary column (5 μ m thick 100% methyl silicone bonded phase) was utilized for all analyses. Injections into the capillary column were 1 μ L in volume and were made in the modified splitless mode, i.e., the split and septum sweep valves were closed until 40 seconds after the injection had been made. Helium was used as the carrier gas at a flow rate of approximately 1.0 mL/min (linear flow 30cm/sec at 40°C).

The GC oven was temperature programmable over the range from ambient temperature to 425°C with ramping rates between 0.1°C and 30°C per minute in 0.1° increments. The temperature program utilized to control the GC oven temperature is listed in Figure 1. It consisted of holding the column at 40°C for 5 minutes, ramping the temperature to 150°C at a rate of 8°C per minute, then ramping the temperature to 300°C at a rate of 10°C per minute, and finally holding the column at 300°C for five minutes. The program took 38.75 minutes to complete.

Detection, identification, and quantitative measurement of naval distillate fuel in lubricating oil was made with a Finnigan MAT 5100 quadrupole mass spectrometer with a SuperIncosTM data system. The data system contained the National Bureau of Standards library of approximately 38,000 mass spectra. The quadrupole mass spectrometer was operated in the full scan mode (0.7 seconds per scan) between 25 and 340 atomic mass units (amu). Typical values of the parameters controlling the electron ionization (EI) source of the quadrupole MS are listed in Table 1.

2.2 Standard Solutions. Samples of naval distillate (3-GP-11Ma) were obtained from HMCS Ottawa, HMCS Gatineau, HMCS Nipigon, and ESSO Petroleum Limited, Dartmouth Refinery. Diesel lubricating oil (MIL-L-9000G) was obtained from the stores system, CFB Halifax. Standards solutions of naval distillate fuel in diesel lubricating oil containing 1, 3, 5, 7 and 9 weight percent fuel were prepared by adding known weights of naval distillate to weighed samples of diesel lubricating oil. These standards were

diluted 1 in 20 in hexane and 40 μ L of internal standard solution was added to each milliliter of the standard solution prior to analysis.

Table 1

Typical values of the parameters used to control the mass spectrometer and electron multiplier electronics.

Electron multiplier voltage	1400volts(-)
Resolution low (RL)	132
Resolution high (RH)	94
Ion energy (IE)	2.51 volts
Ion program (IP)	5.02 volts
Extractor (EX)	2.82 volts
Lens (L)	134 volts(-)
Electrometer range	7

The internal standards; decene, undecene, dodecene, tridecene, and tetradecene, were obtained from Polyscience Corporation, Niles, Illinois. A stock solution of these alkenes containing 6.67% 1-decene, 13.33% 1-undecene, 20.00% 1-dodecene, 26.67% 1-tridecene, and 33.33% 1-tetradecene was diluted 1 part in 100 with hexane to make the internal standard solution.

2.3 Naval Distillate Fuel Aging Study. A sample of new naval distillate fuel was separated into three one litre aliquots. Two of the aliquots were placed in one litre poly bottles, one for storage at 4°C, the other for storage at room temperature and the third one litre portion was transferred to a loosely stoppered flask for placement in a water bath heated to 85°C (185°F) to simulate the operating temperature of a diesel engine. One liter of a 5% (weight/weight) solution of naval distillate fuel in diesel lubricating oil was also placed in the heated water bath. The samples were heated for one month during which time one millilitre samples of the fuel and fuel-diluted oil were taken daily for analysis by GC/MS. One hundred millilitre samples were taken weekly for flash point determination.

3.0 RESULTS AND DISCUSSION

3.1 Separation of Naval Distillate from Diesel Lubricating Oil. The reconstructed ion chromatogram (RIC) of a solution of naval distillate fuel in hexane, acquired using a full scan (25 to 340 amu) and the temperature program listed in Figure

1, is shown in Figure 2a. The peaks corresponding to the various components of fuel eluted from the column between 5 and 35 minutes. The RIC for a solution of diesel lubricating oil in hexane acquired using the same conditions is shown in Figure 2b. The peaks corresponding to the diesel lubricating oil eluted from the column between 25 and 40 minutes. Figure 2c shows the RIC for a 3% solution of naval distillate fuel in diesel lubricating oil. Comparison of the RIC of the mixture with those shown in Figures 2a and 2b indicates that the temperature program and column utilized gave a good separation of the components of the fuel that elute prior to 25 minutes. Although this is not ideal it does provide separation of the majority of the fuel peaks from the lubricating oil. That is, hydrocarbon molecules containing from eight to twenty two carbon atoms, typical of the naval distillate fuel are separated from the diesel lubricating oil. Therefore any of these fuel peaks can be used for quantitative analysis of fuel components in the fuel diluted sample.

3.2 Quantitative Analysis. Internal standards were used to minimize the effect of the variation of detector response and facilitate comparison of results acquired over a period of time. An internal standard should be similar to the component(s) being quantified in both structure and retention time so that the factors affecting a change in response to an internal standard will affect the response of the components of the fuel in a similar way. The internal standards chosen; decene (C-10 or ten carbon atoms), undecene (C-11), dodecene (C-12), tridecene (C-13), and tetradecene (C-14), are similar in structure to the fuel components with the same number of carbon atoms and have retention times that are close to but different from the corresponding alkanes; decane (C-10), undecane (C-11), dodecane (C-12), tridecane (C-13), and tetradecane (C-14), contained in the fuel. As such, these alkenes are excellent internal standards for quantification of the corresponding alkanes in the fuel.

3.2.1 Response Versus Concentration of Naval Distillate Fuel in Diesel Lubricating Oil. To determine if the response of the various components of naval distillate fuel increased linearly with an increase in the concentration of the fuel in the diesel lubricating oil, a series of solutions containing known amounts of fuel in diesel lubricating oil were prepared and a constant amount (40 μ L/mL) of internal standard was added to each solution. The RICs of solutions containing 1%, 3%, 5%, 7% and 9% fuel by weight in diesel lubricating oil, obtained with MS detection, are shown in Figures 3a through 3e. The internal standards; decene, undecene, dodecene, tridecene, and tetradecene, and fuel peaks; decane, undecane, dodecane, tridecane, and tetradecane, used to set up calibration curves are

designated in the chromatograms by S1 through S5 and P1 through P5 respectively.

The ratios of the areas under each fuel peak and the closest internal standard peak are listed in Table 2. Response (ratio of area under peak to that of internal standard) versus concentration curves for each of the five peaks (decane through tetradecane) are shown in Figures 4a through 4e.

Table 2

Data used to plot the calibration curves shown in Figures 4a through 4e.

Peaks	% Fuel Dilution				
	1	3	5	7	9
Ratio of Area (Fuel peak/Internal Standard)					
P1*/S1*	.119	.368	.599	.855	1.032
P2/S2	.093	.222	.428	.602	.623
P3/S3	.054	.153	.261	.414	.427
P4/S4	.048	.130	.201	.271	.351
P5/S5	.063	.162	.320	.419	.507

P1* - fuel peak 1 (decane)

S1* - internal standard peak 1 (decene)

The correlation coefficients (r^2) for these plots varied between 0.98 and 1.00 and indicate excellent correlation between these ratios and the concentration of fuel in the diesel lubricating oil.

3.3 Relative Concentration of the Components of Naval Distillate Fuel. These results indicate that for a particular sample of naval distillate fuel the response of an individual component of the fuel relative to an internal standard increases linearly with concentration. However, naval distillate fuel is a mixture of hydrocarbons, containing for the most part molecules with from eight to twenty-eight carbon atoms, whose relative concentrations may vary depending on a number of factors including the source of the crude oil used to obtain the fuel and the age of the fuel sample.

To determine how the relative concentrations of various components of fuel vary from one sample to another, samples of naval distillate fuel from three ships; HMCS Ottawa, HMCS Gatineau, and HMCS Nipigon, and a sample from ESSO Petroleum Limited, Dartmouth Refinery, were used to prepare 3% by weight standards in diesel lubricating oil and the ratios of five of the fuel peaks to the internal standard peaks were determined. The ratios of the fuel peaks to the internal standard peaks for the four fuel samples are shown in Table 3.

Table 3

Variations in the ratios of areas of fuel peaks to internal standard peaks for 3% solutions of naval distillate fuel (from sources listed) in MIL-L-9000G diesel lubricating oil.

Ratio of Areas (Fuel Peak/Internal Standard)

Peaks	Imperial*	Ottawa	Gatineau	Nipigon
P1/S1	0.481	0.741	0.547	0.510
P2/S2	0.176	0.584	0.411	0.314
P3/S3	0.145	0.287	0.281	0.218
P4/S4	0.102	0.231	0.176	0.187
P5/S5	0.110	0.203	0.190	0.182

* - sample from ESSO Petroleum Limited, Dartmouth refinery.

The relative concentrations of the components in the fuel were found to vary from one fuel sample to another. This indicates that it is not possible to quantitatively determine the level of fuel dilution of a sample of diesel lubricating oil using a calibration plot prepared with fuel from any other source.

3.4 Fuel Aging Studies. The results of the thermal (85°) aging of the naval distillate fuel and the diesel lubricating oil containing 5% naval distillate fuel are shown in Tables 4 and 5. Table 4 shows that the flash point of the naval distillate fuel rose 12.5°C, from 66.5°C to 79.0°C, over the one month test period while the flash point of the 5% fuel diluted sample increased by 10.0°C over the same period of time. It should be noted that the flash points of the fuel and fuel diluted diesel oil were determined by different flash point methods. Conventionally flash point of fluids that flash below 100°C are generally determined by the closed cup method⁶ while the flash points of fluids that flash above 100°C are measured by the open

cup method⁴.

Table 4

Variation in the flash points of naval distillate fuel and 5% naval distillate fuel in diesel lubricating oil with time of exposure at 85°C.

Time at 85°C (days)	Flash Point (°C)	
	naval Distillate ¹	5% naval Distillate ² in Lubricating Oil
0	66.5	197.0
4	71.0	200.0
24	75.5	205.0
32	79.0	207.0

1- closed cup flash point

2- open cup flash point

The increase in the flash points of the fuel and the 5% fuel diluted diesel oil with time indicates that the lighter components in the fuel mixture have volatilized in preference to the heavier components. This is confirmed by the results of the distillation curves shown in Table 5 where the initial boiling point of the sample aged for 4 weeks at 85°C was 20° higher than the new sample or the sample aged at room temperature for 4 weeks which indicates that the lower boiling components of the fuel have been reduced in concentration during the aging process.

Table 5

Distillation curves for samples of naval distillate fuel; 1) unaged sample, 2) sample aged 4 weeks at room temperature, and 3) sample aged 4 weeks at 85°C.

	Unaged Sample	4 Weeks at RT	4 Weeks 85°C
initial boiling point	168°C	168°C	188°C
10% recovery	208	210	220
20% recovery	232	235	238
50% recovery	279	280	279
90% recovery	345	345	348
end point	355	364	353

The aging of samples of fuel and diesel lubricating oil containing 5% fuel dilution were also studied using GC/MS by monitoring the variation in response of the decane, undecane, dodecane, tridecane, and tetradecane peaks of the fuel relative to the internal standards; decene, undecene, dodecene, tridecene, and tetradecene respectively. Unlike the results from the flash point and boiling range studies, the GC/MS results did not indicate a definite trend, that is, a decrease in the relative response of these peaks with aging. This suggests that the change in the flash point and the boiling range of the aged samples is due primarily to the loss of hydrocarbons lighter than decane.

3.5 Examples of Fuel Dilution of Diesel Lubricating Oil by GC/MS. Two examples of determinations of fuel dilution of MIL-L-9000G, the first from the number 1 diesel HMCS Nipigon and the other from HMCS Ottawa, using the GC/MS technique follow. The percent fuel dilution of the samples of MIL-L-9000G from these vessels was determined by viscosity change at 100°C to be 2% and 4% respectively. The RICs of a MIL-L-9000G sample from the #1 diesel generator of HMCS Nipigon and a sample of fuel from its tanks are shown in Figures 5a and 5b. Internal standard was added to both samples. Comparison of the relative response of the fuel peaks in the MIL-L-9000G sample received for fuel dilution analysis and the pure fuel sample to the internal standards indicates that the fuel in the MIL-L-9000G sample has lost some of its lighter components.

A sample of fuel from the HMCS Nipigon was used to prepare a series of standard solutions of fuel in MIL-L-9000G and response versus concentration curves for the quantitation peaks were prepared. The ratios of the areas of the fuel peaks to the internal standard peaks for the standard solutions containing 1%, 3%, 5%, and 7% by weight naval distillate fuel in MIL-L9000G are shown in Table 6. The best fit straight lines for the five fuel peaks are also listed in Table 6. The apparent concentration of fuel in the MIL-L-9000G (% fuel dilution) sample from Nipigon was then calculated for each of the five peaks of the sample submitted for fuel dilution. The apparent fuel dilution varied from less than 1% for the decane peak (P1) to approximately 3.4% for the tetradecane peak (P5).

Table 6

Ratios of the areas (fuel peak to internal standard peak) for solutions of naval distillate fuel from HMCS Nipigon in MIL-L9000G diesel lubricating oil containing 1%, 3%, 5%, and 7% fuel by weight and MIL-L-9000G sample from Nipigon #1 diesel generator.

	Samples				
	1%	3%	5%	7%	#1DG
P1/S1	0.249	0.775	1.362	2.090	0.253
P2/S2	0.234	0.567	0.987	1.371	0.105
P3/S3	0.160	0.377	0.573	0.895	0.149
P4/S4	0.114	0.317	0.415	0.624	0.200
P5/S5	0.092	0.223	0.400	0.649	0.287

Best fit straight lines for the plots of response (ratio of area of fuel peak relative to an internal standard) (P/S) versus concentration of naval distillate fuel (FD) in MIL-L9000G diesel lubricating oil.

P1/S1 = 0.298	FD - 0.085	$r^2 = 1.00$
P2/S2 = 0.192	FD + 0.024	$r^2 = 1.00$
P3/S3 = 0.120	FD + 0.021	$r^2 = 0.99$
P4/S4 = 0.081	FD + 0.042	$r^2 = 0.99$
P5/S5 = 0.092	FD - 0.025	$r^2 = 0.99$

Figures 6a and 6b show the RICs of a sample of fuel and a sample of MIL-L-9000G diesel lubricating oil from HMCS Ottawa. The fuel dilution of the MIL-L-9000G sample from HMCS Ottawa was handled in a similar manner to that from HMCS Nipigon, i.e., a sample of fuel from HMCS Ottawa was used to prepare response versus concentration curves for the fuel peaks and these curves were used to quantitate the fuel in the diesel lubricating oil sample. The data is shown in Table 7 along with the best fit straight lines for the five quantitation peaks. The apparent percent fuel dilution varied from 0.75% to 4.6% for the peaks corresponding to decane and tetradecane respectively.

Table 7

Ratios of the areas (fuel peaks to internal standard peaks) for solutions of naval distillate from HMCS Ottawa in MIL-L-9000G diesel lubricating oil containing 1%, 3%, 5%, and 7% naval distillate by weight and MIL-L-9000G sample from HMCS Ottawa #3 diesel.

Percent fuel dilution (by weight)					
	1	3	5	7	#3DG
Peak	Ratios of areas (fuel peak/internal standard)				
P1/S1	0.266	0.780	1.314	1.894	0.181
P2/S2	0.215	0.622	0.944	1.363	0.211
P3/S3	0.157	0.412	0.717	0.961	0.260
P4/S4	0.115	0.328	0.527	0.699	0.309
P5/S5	0.111	0.312	0.495	0.656	0.444

Best fit straight lines for plots of response (ratio of area of fuel peak to that of internal standard), PS, of naval distillate fuel from HMCS Ottawa versus concentration of naval distillate fuel in MIL-L9000G diesel lubricating oil (FD).

P1/S1 = 0.271	FD - 0.020	$r^2 = 1.00$
P2/S2 = 0.188	FD + 0.033	$r^2 = 1.00$
P3/S3 = 0.136	FD + 0.019	$r^2 = 1.00$
P4/S4 = 0.097	FD + 0.027	$r^2 = 1.00$
P5/S5 = 0.091	FD + 0.030	$r^2 = 1.00$

It is evident from these results that the actual fuel dilution of a sample of diesel lubricating oil will be difficult to determine accurately by any method if it has been in service for a period of time as a result of the preferential and random loss of the more volatile components of a fuel with aging time and temperature. However, the use of this GC/MS method allows the determination of the minimum fuel dilution that has taken place. If the lighter, more volatile components of the fuel have been reduced when in service then this will be evident from the RIC and quantitative analysis will give a minimum fuel dilution level.

3.6 Identification of Diluents in Diesel Lubricating Oil. One of the drawbacks of using viscosity or flash point methods to determine fuel dilution of diesel

lubricating oil is that the change in the measured property is assumed to be caused by fuel dilution. If a diluent other than fuel has caused the change, the ability to identify the diluent will aid in determining its source and allow steps to be taken to stop the ingress of the diluent.

The RIC of a sample of diesel lubricating oil suspected of naval distillate fuel dilution is shown in Figure 7. Analysis at NETE using a capillary GC with flame ionization detection indicated that a diluent other than naval distillate fuel was present in the sample. Comparison of the traces shown in Figure 7 and Figures 2a through 2e confirmed this analysis. The broad peak (retention time approximately 4.5 minutes) was determined to be, on the basis of its mass spectrum, 1,2-ethanediol, a commonly used coolant chemical. This analysis therefore suggested a potential problem related to coolant ingress into the diesel lubricating oil and not fuel dilution existed.

3.7 Detection Limit of Naval Distillate Fuel.

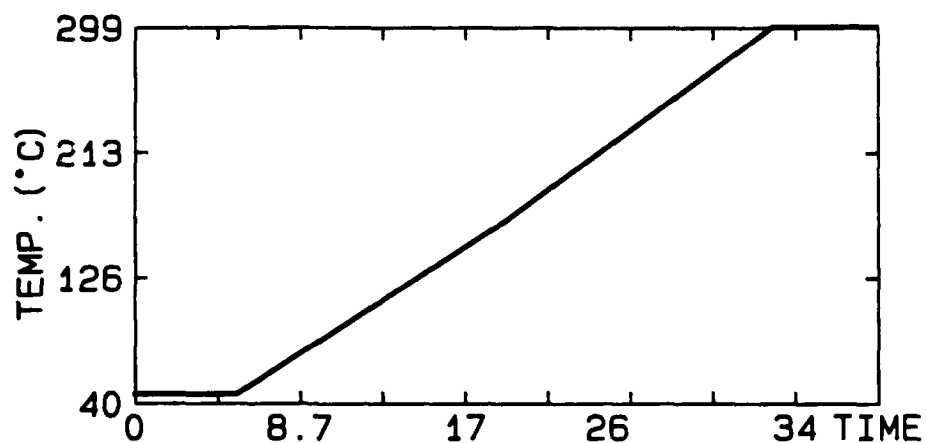
The maximum allowable level of fuel dilution of diesel lubricating oil has been set at 3%. However, the the maximum allowable limit for fuel dilution of diesel lubricating oil is presently under review. The GC/MS method described here has been found to be applicable in the range from 1% to 9%. If it is required to detect naval distillate in diesel lubricating oil at lower levels, this method can be modified to allow detection of fuel dilution at levels below 1%.

Two simple modifications of the method which result in a lower detectable level of fuel are discussed below. The amount of the sample introduced for analysis can be increased. The 20 fold dilution of the sample prior to analysis could be changed to a 10 fold dilution, for instance, which would double the amount of sample introduced onto the column. Alternatively, a 2 μ L injection could be used which would also double the amount of sample introduced onto the column. The sensitivity of the quadrupole mass spectrometer for particular compounds can be increased dramatically through the use of specialized multiple ion detection (MID) sequences. An MID sequence can be designed which would detect only ions that are characteristic of the aliphatic hydrocarbons of the fuel and internal standards. This is in contrast to the full scan used in this study which detects ions between 25 and 340 atomic mass units. Much of the time in each 2 second scan is spent looking for ions that are not characteristic of the compounds of interest. By determining the ions characteristic of the compounds of interest, the detector can be instructed to detect only these ions during each scan. As more time is spent detecting these ions, the sensitivity of the

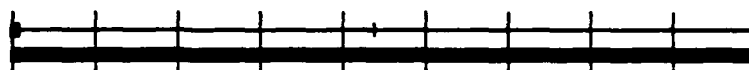
detector increases proportionately.

4.0 CONCLUSIONS

A GC/MS technique for the detection and identification of diluents in diesel lubricating oil has been described. The responses of the various constituents of a typical naval distillate fuel relative to internal standards have been shown to vary linearly with concentration. Accurate determination of the level of fuel dilution of a sample of diesel lubricating oil using a capillary GC has been shown to be dependent upon factors such as the source of the fuel, the age of the fuel and the thermal history of the fuel diluted lubricant sample. These results indicate that GC/MS analysis of diesel lubricating oils can confirm the presence of fuel and separate, detect, and identify other organic-based diluents and act as a useful adjunct to standard tests for fuel dilution such as flash point lowering or viscosity change. However, it appears that the combined use of flash point and viscosity measurements are still the simplest and least expensive means of obtaining the basic desired information regarding potential explosion hazards and lubricity of fuel diluted diesel lubricating oils.



GC VALVES: CLOSE OPEN
 (CV) CAPILLARY 0.0 0.4
 (DV) DIVERT 0.0 38.7



SEQ. #	FROM TEMP (C)	TO TEMP (C)	RATE (C/M)	TIME (MIN)	TOTAL TIME (MIN)
1	40	-	40	-	5.0
2	40	-	150	8.0	13.7
3	150	-	300	10.0	15.0
4	300	-	300	-	5.0
					38.7

FIGURE 1 - Temperature program used to control the gas chromatograph oven.

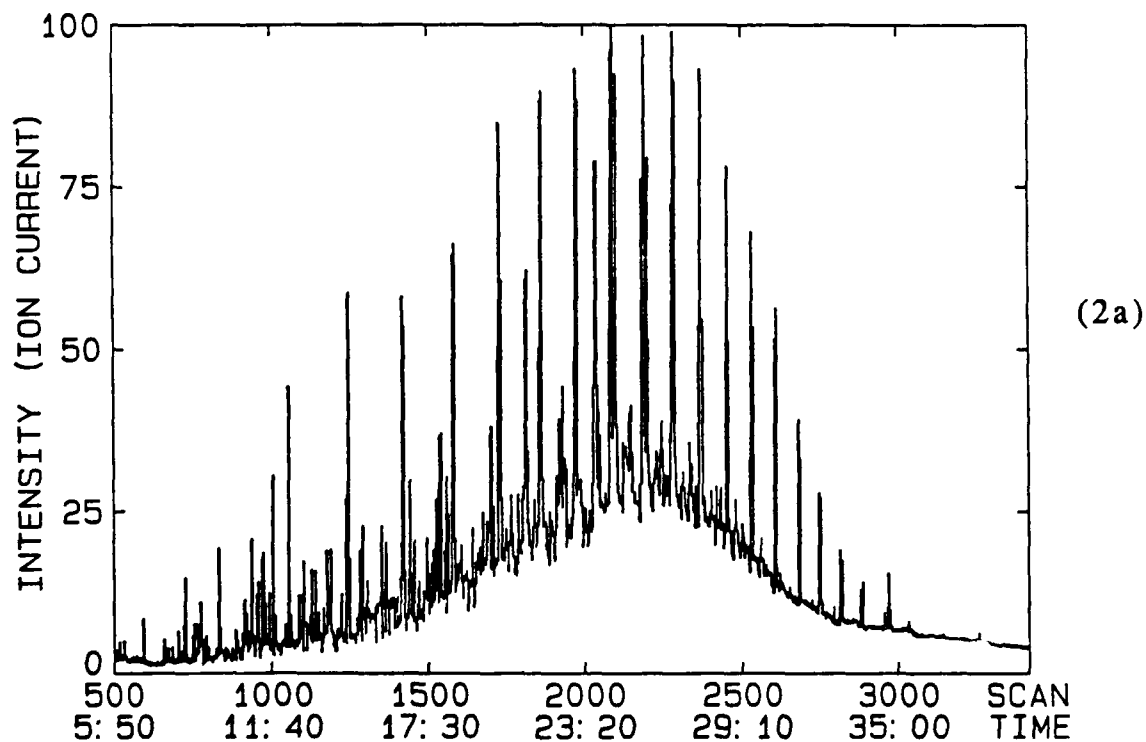


Figure 2 - (a) RIC of a sample of 3-GP-11Ma naval distillate fuel.

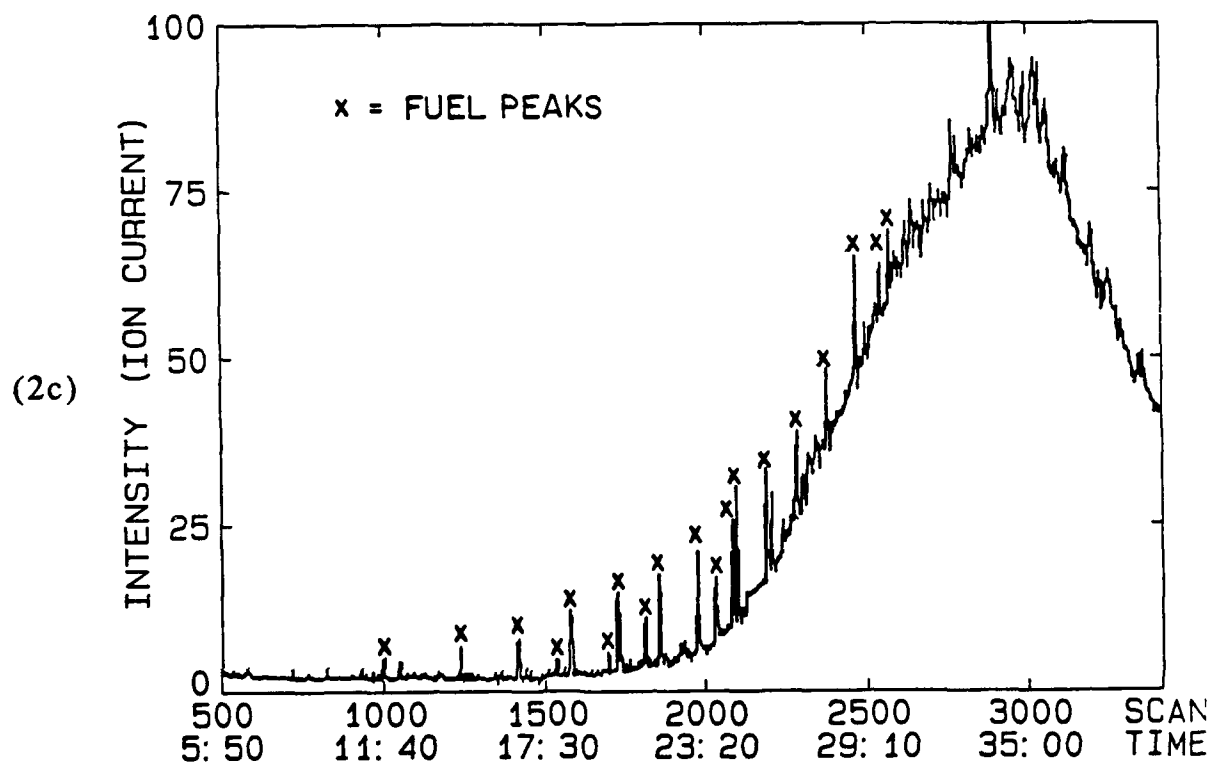
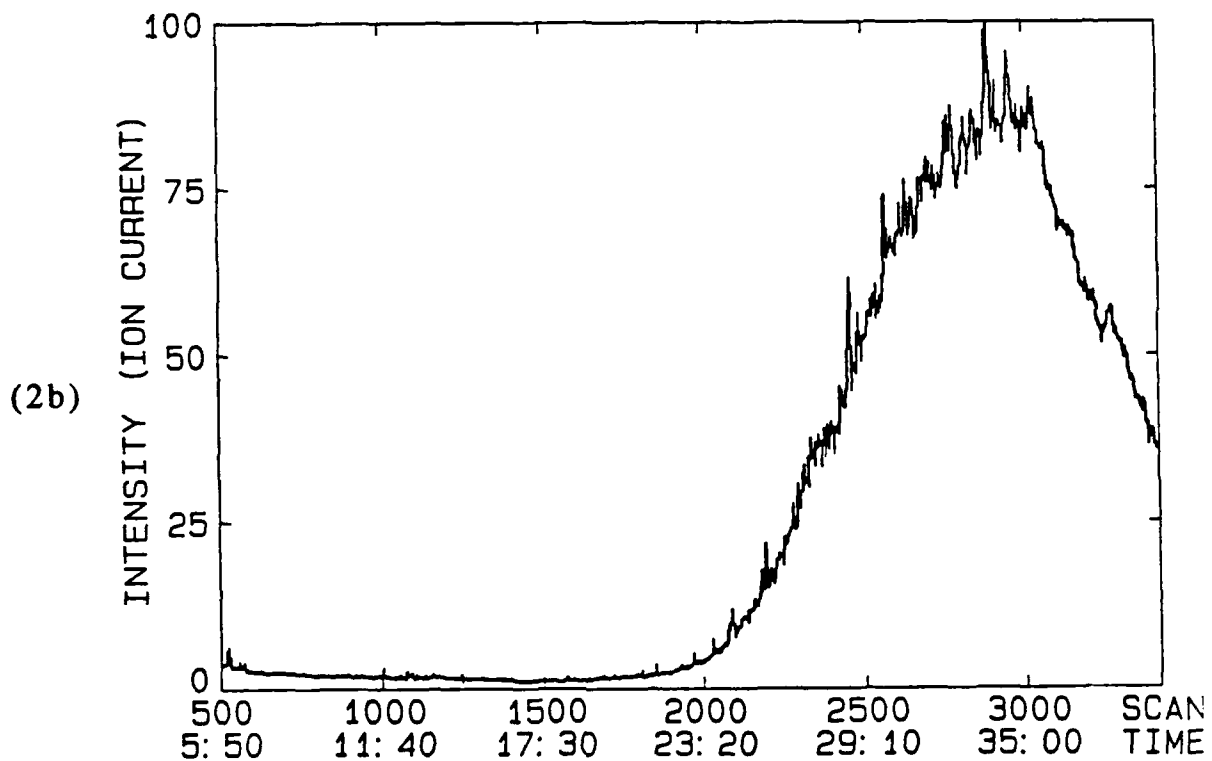


Figure 2 - (b) RIC of a sample of MIL-L-9000G diesel lubricating oil; (c) RIC of a sample of MIL-L-9000G diesel lubricating oil containing 3% 3-GP-11Ma naval distillate fuel.

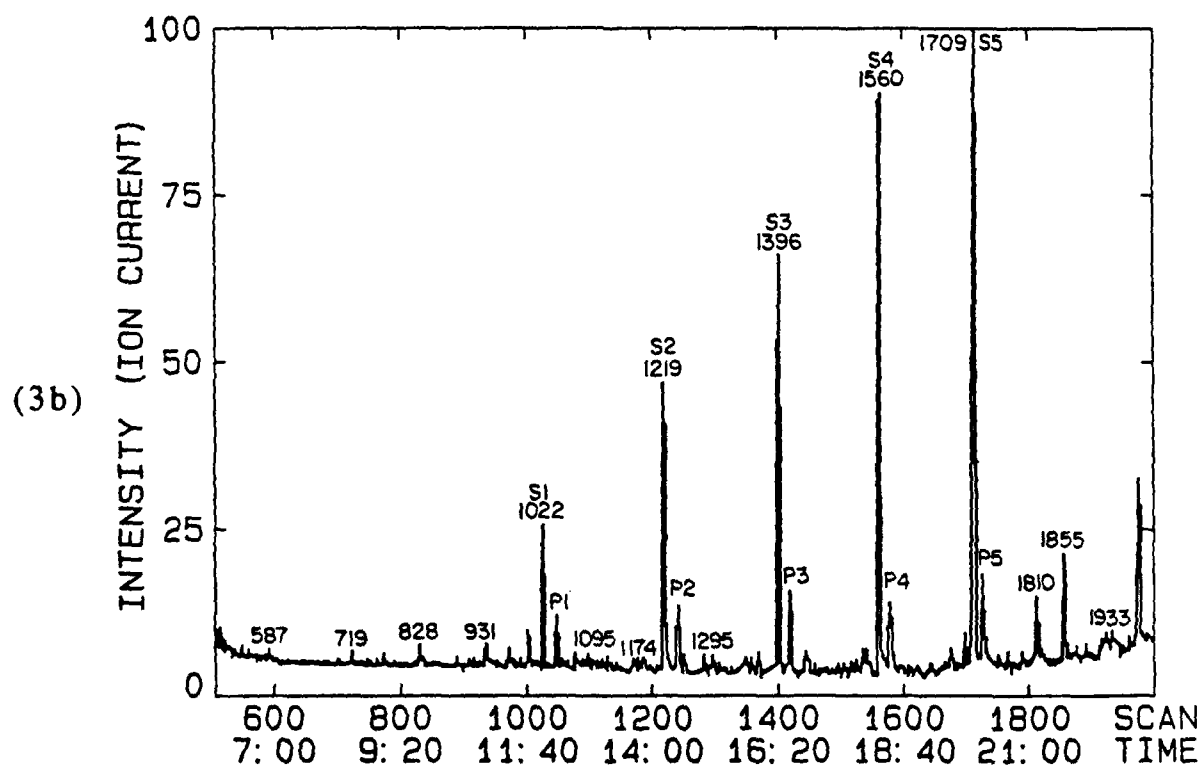
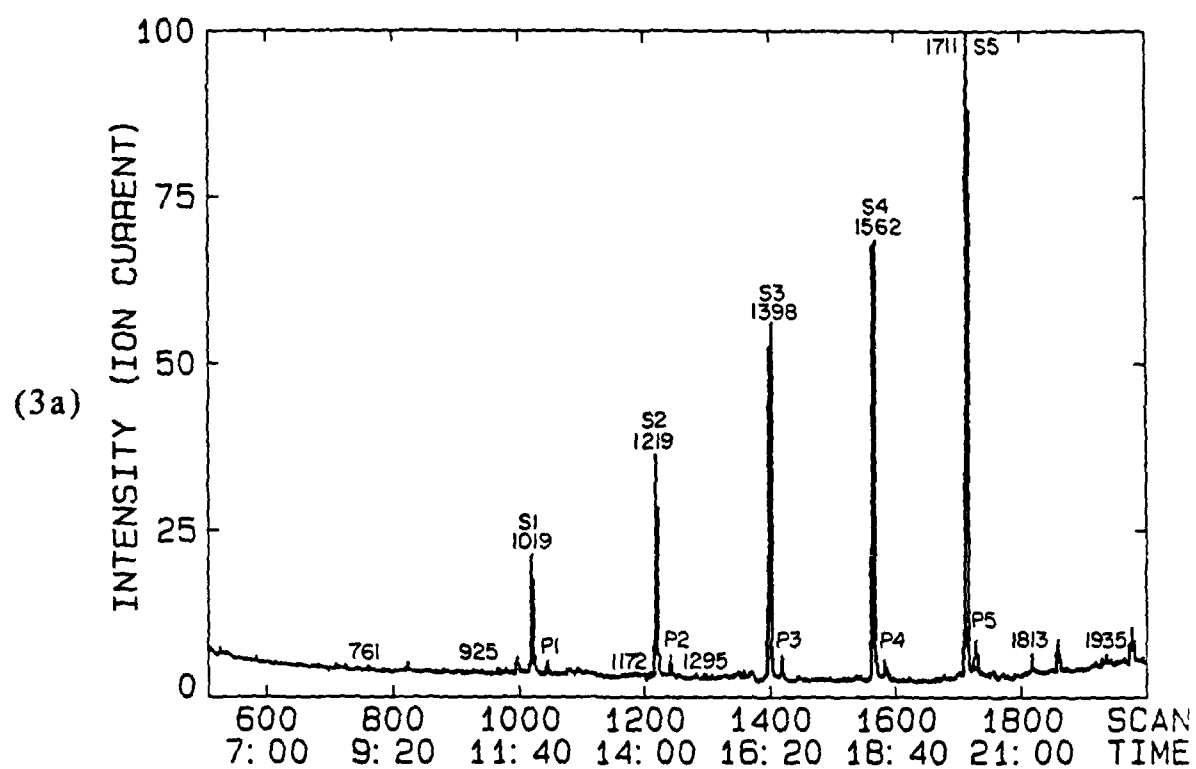


Figure 3 - RIC (scans 500 to 2000) of samples of MIL-L-9000G diesel lubricating oil containing (a) 1% and (b) 3% naval distillate fuel. Samples contain internal standards (S).

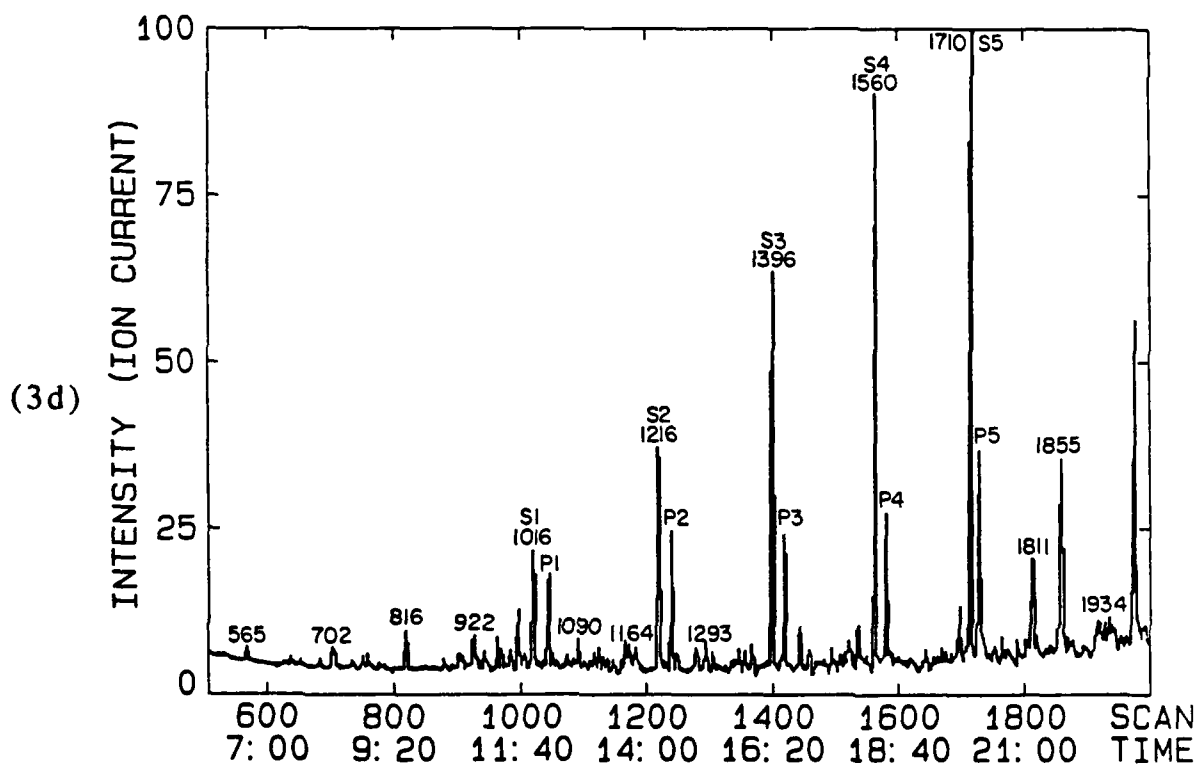
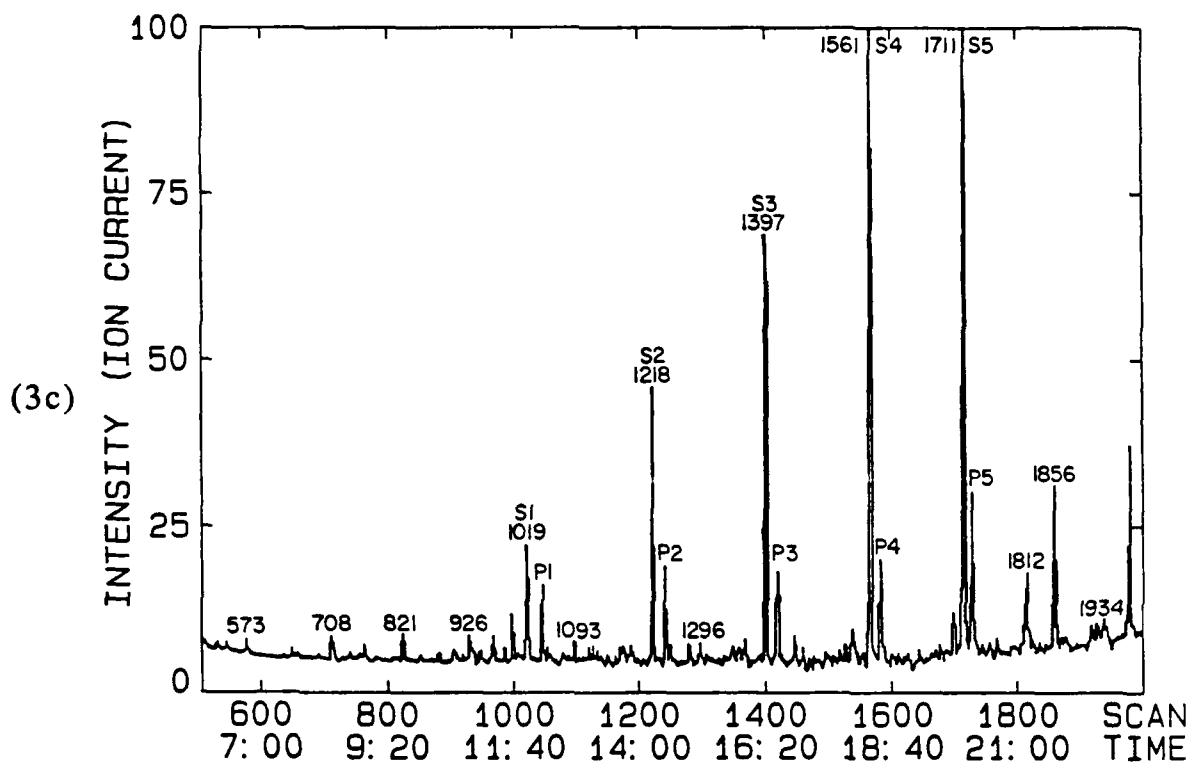


Figure 3 - RIC (scans 500 to 2000) of samples of MIL-L-9000G diesel lubricating oil containing (c) 5% and (d) 7% naval distillate fuel. Samples contain internal standards (S).

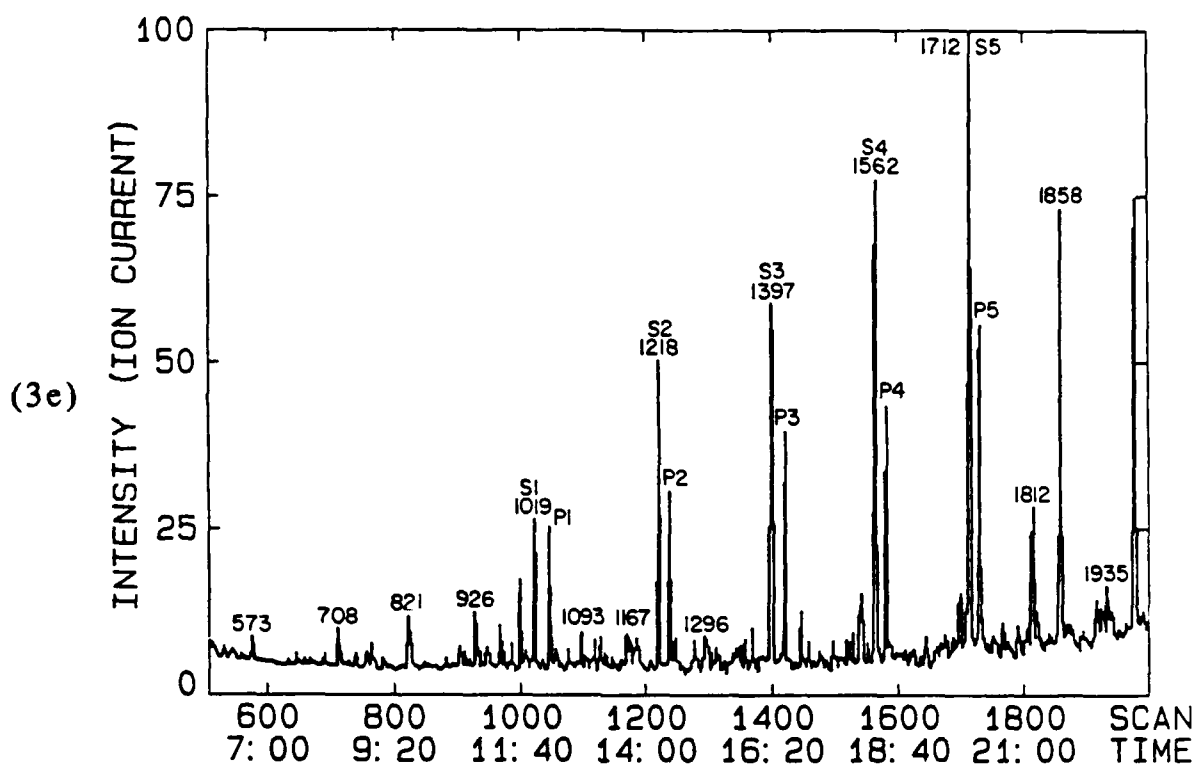


Figure 3e - RIC (scans 500 to 2000) of sample of MIL-L-9000G diesel lubricating oil containing 9% naval distillate fuel. Sample contains internal standards (S).

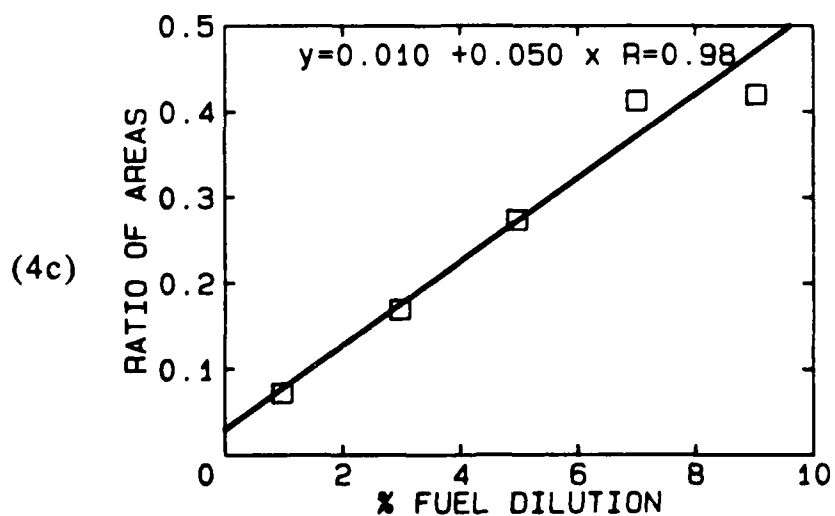
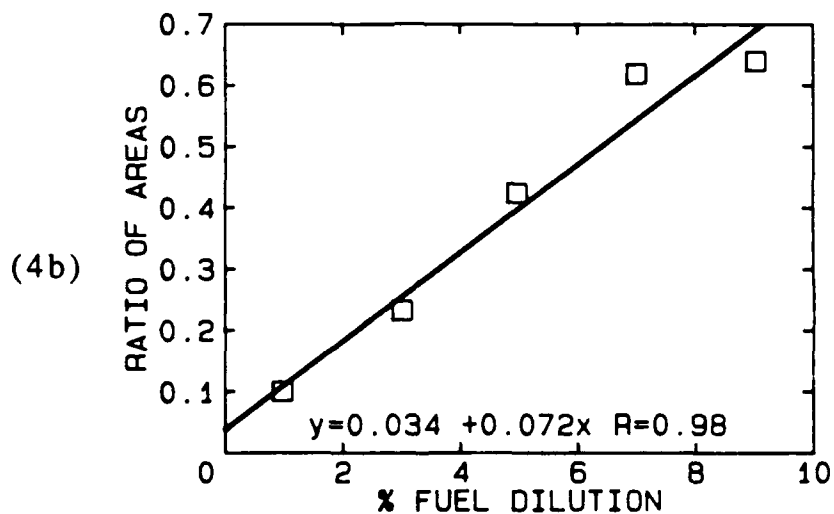
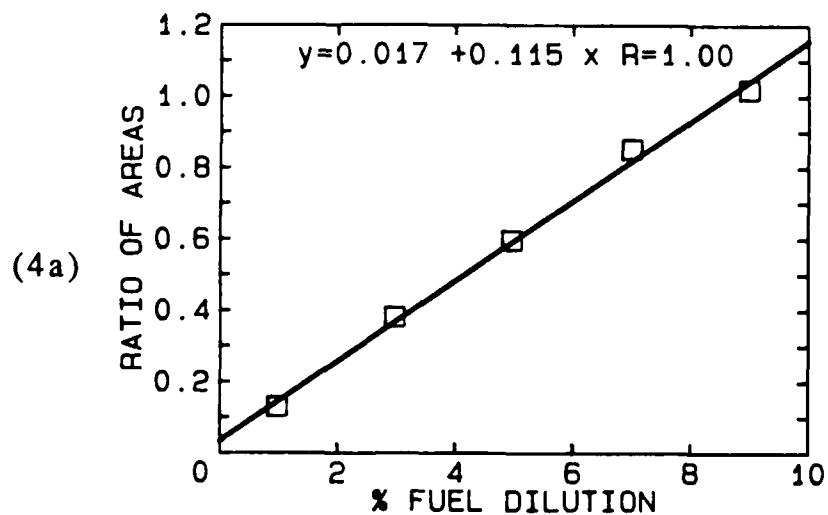


Figure 4 - Plots of the ratios of areas of fuel peaks (P) to internal standard peaks (S) for MIL-L-9000G diesel lubricating oil samples containing from 1% to 9% 3-GP-11Ma naval distillate fuel (a) P1/S1, (b) P2/S2 and (c) P3/S3.

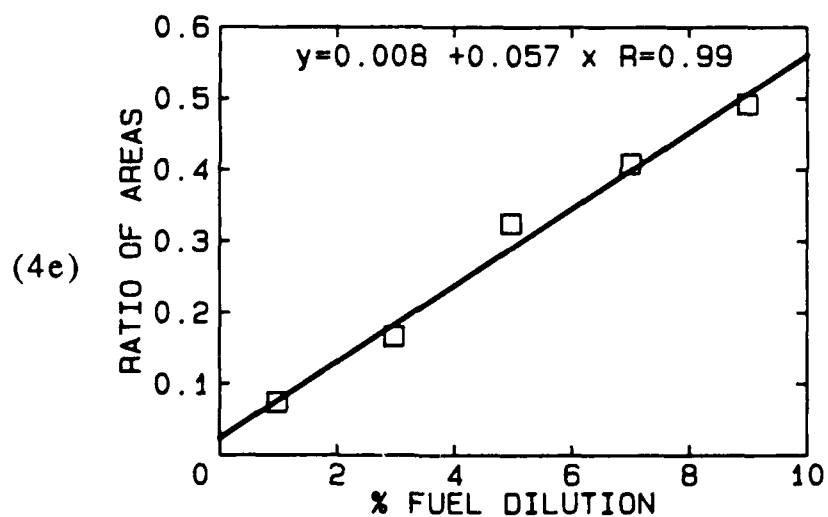
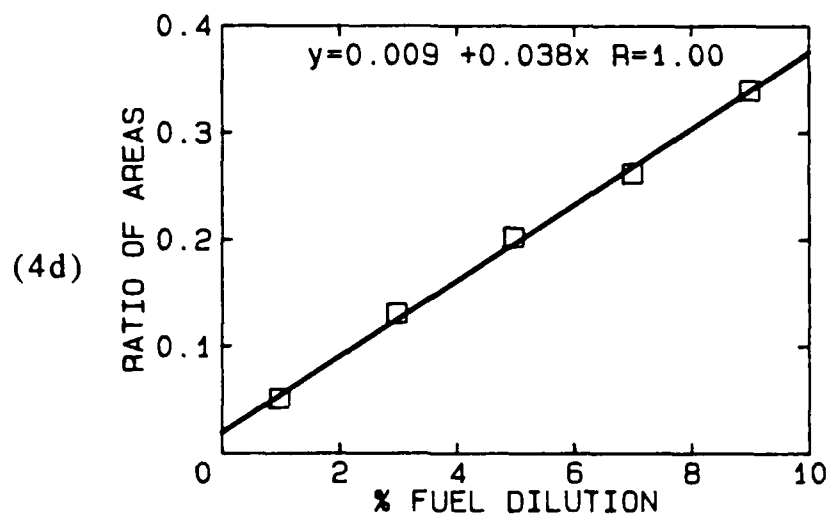


Figure 4 - Plots of the ratios of areas of fuel peaks (P) to internal standard peaks (S) for MIL-L-9000G diesel lubricating oil samples containing from 1% to 9% 3-GP-11Ma naval distillate fuel (d) P4/S4 and (e) P5/S5.

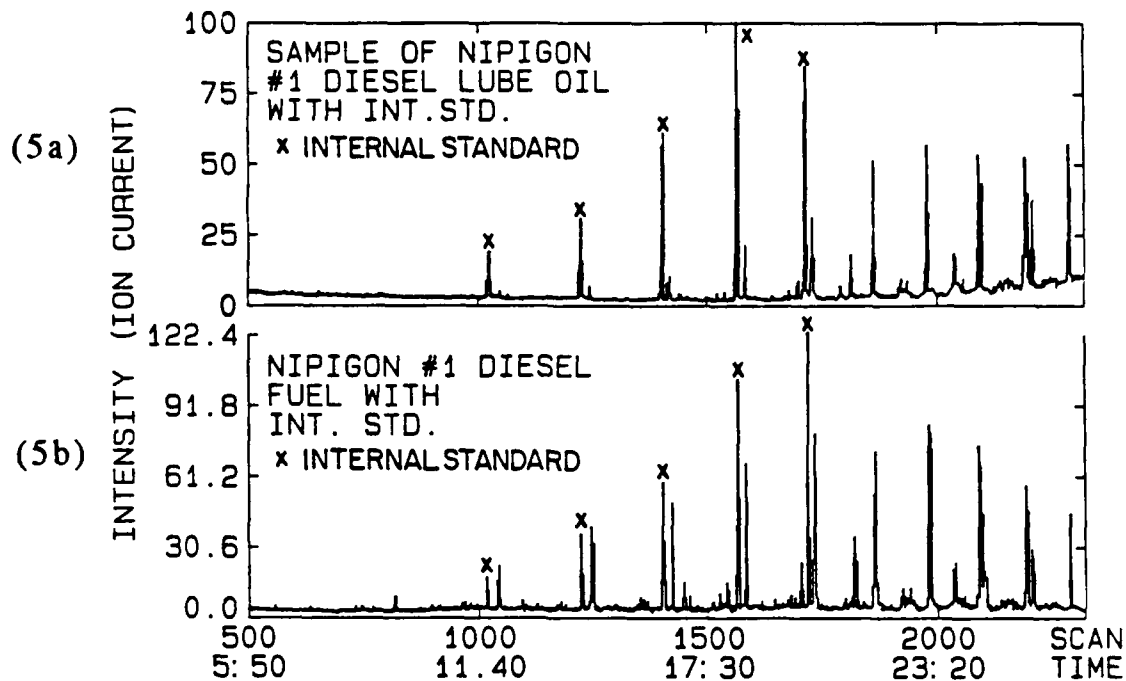


FIGURE 5 - (a) RIC of sample of MIL-L-9000G diesel lubricating oil from #1 diesel, HMCS NIPIGON, containing internal standard; (b) RIC of sample of 3-GP-11Ma naval distillate fuel used in #1 diesel, HMCS NIPIGON, containing internal standard.

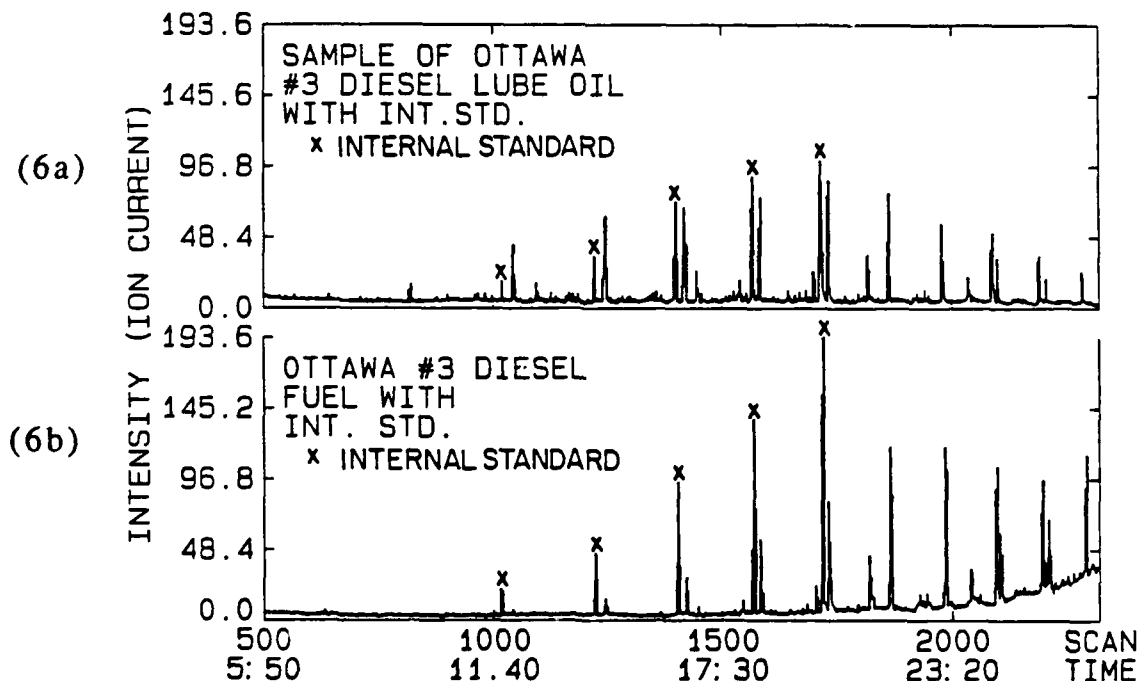


FIGURE 6 - (a) RIC of sample of MIL-L-9000G diesel lubricating oil from #3 diesel, HMCS OTTAWA, containing internal standard; (b) RIC of sample of 3-GP-11Ma naval distillate fuel used in #1 diesel, HMCS NIPIGON, containing internal standard.

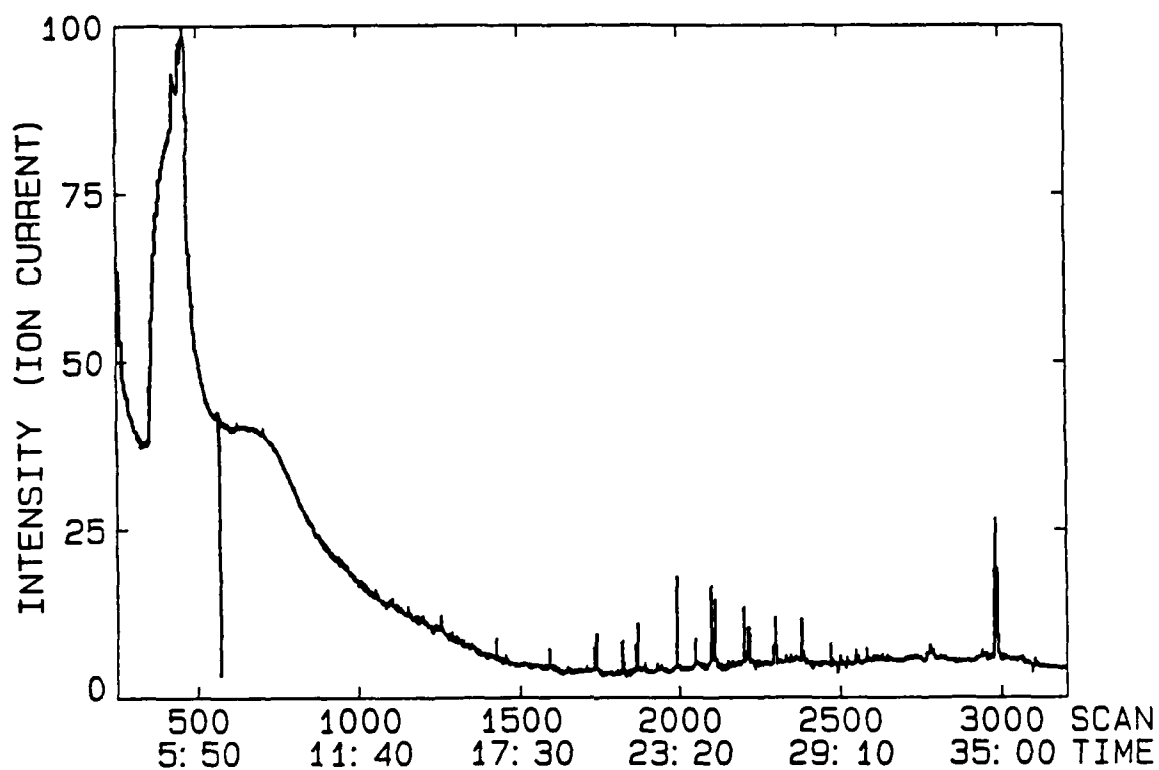


FIGURE 7 - RIC of a sample of MIL-L-9000G diesel lubricating oil suspected of contamination with a diluent other than 3-GP-11Ma naval distillate fuel.

References

1. CGSB Specification 3-GP-11Ma, Fuel, Naval Distillate (-6°C Pour), Canadian Government Specifications Board, Ottawa, Ontario, 1985.
2. Military Specification, Lubricating Oil, Shipboard Internal Combustion Engine, High Output Diesel, 23 March, 1979.
3. ASTM D-445-82, Kinematic Viscosity of Transparent and Opaque Liquids, 1987 Annual Book of ASTM Standards, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania, 1987.
4. ASTM D92-78, Flash and Fire Points by Cleveland Open Cup, 1987 Annual Book of ASTM Standards, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania, 1987.
5. ASTM D3524-86, Test Method for Diesel Fuel Diluent in used Diesel Engine Oils by Gas Chromatography, 1987 Annual Book of ASTM Standards, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania, 1987.
6. ASTM D93-85, Flash Point by Pensky-Martens Closed Tester, 1987 Annual Book of ASTM Standards, American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania, 1987.

UNCLASSIFIED

SECURITY CLASSIFICATION OF FORM
(highest classification of Title, Abstract, Keywords)

DOCUMENT CONTROL DATA		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)		
1. ORIGINATOR (the name and address of the organization preparing the document. Organizations for whom the document was prepared, e.g. Establishment sponsoring a contractor's report, or tasking agency, are entered in section 8.) Defence Research Establishment Atlantic, Dochyard Labboritory, Bldg. D-17, FMO Halifax, N.S. B3K 2X0		2. SECURITY CLASSIFICATION (overall security classification of the document, including special warning terms if applicable) UNCLASSIFIED
3. TITLE (the complete document title as indicated on the title page. Its classification should be indicated by the appropriate abbreviation (S,C,R or U) in parentheses after the title.) A STUDY OF FUEL DILUTION OF DIESEL LUBRICATING OIL BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY		
4. AUTHORS (Last name, first name, middle initial. If military, show rank, e.g. Doe, Maj. John E.) HILTZ, J.A., VEINOT, D.E., and HAGGETT, R.D.		
5. DATE OF PUBLICATION (month and year of publication of document) January 1989	6a. NO. OF PAGES (total containing information. Include Annexes, Appendices, etc.) 29	6b. NO. OF REFS (total cited in document) 6
6. DESCRIPTIVE NOTES (the category of the document, e.g. technical report, technical note or memorandum. If appropriate, enter the type of report, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.)		
8. SPONSORING ACTIVITY (the name of the department project office or laboratory sponsoring the research and development. Include the address.)		
9a. PROJECT OR GRANT NO. (if appropriate, the applicable research and development project or grant number under which the document was written. Please specify whether project or grant) 1AI	9b. CONTRACT NO. (if appropriate, the applicable number under which the document was written)	
10a. ORIGINATOR'S DOCUMENT NUMBER (the official document number by which the document is identified by the originating activity. This number must be unique to this document.) DREA Technical Memorandum 89/203	10b. OTHER DOCUMENT NOS. (any other numbers which may be assigned this document either by the originator or by the sponsor)	
11. DOCUMENT AVAILABILITY (any limitations on further dissemination of the document, other than those imposed by security classification) ☒ (X) Unlimited distribution ☐ () Distribution limited to defence departments and defence contractors; further distribution only as approved ☐ () Distribution limited to defence departments and Canadian defence contractors; further distribution only as approved ☐ () Distribution limited to government departments and agencies; further distribution only as approved ☐ () Distribution limited to defence departments; further distribution only as approved ☐ () Other (please specify):		
12.. DOCUMENT ANNOUNCEMENT (any limitations to the bibliographic announcement of this document. This will normally correspond to the Document Availability (11). However, where futher distribution (beyond the audience specified in 11) is possible, a wider announcement audience may be selected.)		

UNCLASSIFIED

SECURITY CLASSIFICATION OF FORM

DCD03 2/06/87

UNCLASSIFIED

SECURITY CLASSIFICATION OF FORM

13. ABSTRACT (a brief and factual summary of the document. It may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall begin with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (S), (C), (R), or (U). It is not necessary to include here abstracts in both official languages unless the text is bilingual.)

A method for the detection and identification of fuel components in diesel lubricating oil is described. The method uses a capillary gas chromatograph coupled to a quadrupole mass spectrometer to separate, detect and identify diluents in the oil. A typical analysis takes 40 minutes. Accurate determination of the level of fuel dilution of a diesel lubricating oil sample using GC/MS is shown to be dependent upon a number of factors including the source of the fuel, the age of the fuel, the thermal history of the fuel diluted diesel oil sample and the availability of a suitable sample of fuel to prepare standard response versus concentration curves. In contrast to the standard methods of determining fuel dilution in diesel lubricating oil such as ASTM D445-82 (viscosity change), ASTM D92-78 (flash point reduction), and ASTM D3524-78 (packed column gas chromatography with flame ionization detection), this method can identify diluents and contaminants in the diesel lubricating oil. This is extremely important in cases where the standard tests give false negatives or indicate the presence of a diluent but cannot identify the diluent.

14. KEYWORDS, DESCRIPTORS or IDENTIFIERS (technically meaningful terms or short phrases that characterize a document and could be helpful in cataloging the document. They should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location may also be included. If possible keywords should be selected from a published thesaurus, e.g. Thesaurus of Engineering and Scientific Terms (TEST) and that thesaurus-identified. If it is not possible to select indexing terms which are Unclassified, the classification of each should be indicated as with the title.)

FUEL DILUTION
DIESEL LUBRICATING OIL
GAS CHROMATOGRAPHY/MASS SPECTROMETRY
QUANTATIVE ANALYSIS
IDENTIFICATION OF DILUENTS
ETHYLENE GLYCOL
FLASH POINT REDUCTION
VISCOSITY REDUCTION

UNCLASSIFIED

SECURITY CLASSIFICATION OF FORM