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Utilization of the spent Caustics generated in the Petroleum Refineries in the Crude Distillation Unit.

G. N. Sarkar

Indian Oil Corporation Ltd., Gujarat Refinery, P.O. Jawaharnagar,
Vadodara - 391 320, India

Abstract:

Generally 2 to 3 mg caustic per Litre of Crude Oil is used in the desalting Unit to take care of the acid generated from the Calcium and magnesium chlorides present in the crude Oil. Another 7-8 mg caustic is again added per litre of crude Oil to take care of the residual chlorides left over after desalting in the atmospheric distillation column.

The spent caustics from the refineries contains a considerable amount of free sodium Hydroxide along with the pollutants like Sulphides, Phenolics and Mercaptides.

The various distillation cuts contain considerable amount of Phenols, thioPhenols, Mercaptans etc. and can sustain with the finished streams from them with the stipulated specification.

In the present work it is shown that the addition of this spent caustic in the crude oil will not only save the consumption of fresh caustic but will also solve the disposal problem which is major concern for pollution and at the same time will not deteriorate the products as well as equipments.

Introduction:

Refineries uses caustic solutions of strength varying for the removal of hydrogen Sulphide, Mercaptans and Phenolics from streams like LPG, naphtha, ATF etc. These caustic solution loses their absorbing capacities after absorption still these remains adequate quantity of unused caustic.

These spent caustic could be easily added in the crude oil instead of fresh caustic in the desalting unit.

The quantitative addition of these spent caustic will increase the various pollutants like thenols, thioPhenols and Mercaptans already present in the streams in a very small amount which will be taken care by itself. This process of recycling and reusing of spent caustics is very interesting phenomenon and experimentally estimated with various typical types of crude oil processed in the Haldia Refinery.

Experimental:

Crude oil samples from various sources as available in the Haldia Refinery are atmospherically distilled by ASTM distillation and distillates as normally collected from the atmospheric distillation unit were collected and analyzed for Phenols, ThioPhenols, Mercaptans etc. using UOP method No. 262-91. Using UV 160 spectrophotometer chemito 2500 and Automatic Titrator using chemito 120.

The results are tabulated in table No. 1 for the characterization of the crude oil taken for experimentation and table No 2 for the distilled products from the corresponding crude oil.

Table No. 1.

Characteristics of the crude oils

Sl No	Types of crude	Arrival date at HR	Density @ 1.5°C gm/ml.	API	Sulphur % W	Salt content 1b/1000 brls.
1.	Iran mix.	23.6.92	0.8603	32.9	1.88	3.1
2.	Upper Zakum	03.6.92	0.8544	34.1	1.70	3.2
3.	Kuwait export	05.6.92	0.8655	31.9	1.84	3.2
4.	Arabian Blend	11.6.92	0.8660	31.8	1.94	3.2
5.	Gulf of Suez-mix crude	08.7.92	0.8746	30.2	1.50	4.2
6.	Arab Mix	11.7.92	0.8665	31.8	1.90	4.1
7.	Lavan Blend	20.2.92	0.8535	34.2	1.84	3.4
8.	Dubai crude	14.12.91	0.8676	31.5	2.0	7.0
9.	Arab Medium	01.3.92	0.8755	30.05	2.24	4.2
10.	Iranian Blend	19.4.92	0.8579	33.36	1.82	3.0

Table No. 2.

Characterization of the Distilled products

Sl No	Types of Crude Oil	Dist. cuts.	Yield % V	Phenol ppm	Thiophenol ppm	Mercaptans ppm
1.	Iran Mix	IBP-90°C	4.0	88	76	330
		90°-140°C	10.5	288	675	142
		140-270°C	25.0	12910	500	100
		270-340°C	8.0	12780	2230	88
		340-365°C	20.0	14200	1020	62
		365+°C	32.5	—	—	—
2.	Upper Zakum	IBP-90°C	4.0	90	86	316
		90-140°C	10.0	300	730	120
		140-270°C	24.5	13000	580	100
		270-340°C	8.5	12800	2245	80
		340-365°C	20.0	14000	1100	48
		365+°C	33.0	—	—	—
3.	Kuwait Export	IBP- 90°C	4.1	102	92	282
		90-140°C	10.0	312	680	100
		140-270°C	24.3	12224	560	96
		270-340°C	9.0	10460	1540	82
		340-365°C	20.2	13632	1082	42
		365+°C	32.4	—	—	—
4.	Arabian Blend	IBP- 90°C	3.9	92	90	244
		90-140°C	10.1	300	802	108
		140-270°C	25.0	12600	532	92
		270-340°C	9.1	14020	2400	82
		340-365°C	20.1	13298	1082	44
		365+°C.	31.8	—	—	—

Following experiments were carried out:

Spent caustic solution were added in the increasing order in the crude samples mentioned and allowed to interact for 2 hrs. This mixed crude oil is again distilled by ASTM distillation and each distillation cuts were estimated for the components like Phenols Thiophenols and Mercaptides, etc. Results are tabulated in table No. 3 for the quality of the spent caustics generally generated in the refineries and table No. 4 and 5 for the quality of the products after addition of spent caustics.

Table No. 3.

Characteristics of spent caustics

Sl No	Sources	Free Caustic % W	Phenols ppm	Sulphides as "S ppm	Mercaptans ppm
1.	Merox Unit	11.0-13.0	$(1.2\text{-}9.5) \times 10^3$	$(1.5\text{-}14.0) \times 10^3$	—
2.	ATF Extractor	12.0-14.0	30-60	$(0.2\text{-}1.8) \times 10^3$	—
3.	LPG Prewash	7.0-16.0	20-60	$(0.2\text{-}5.0) \times 10^6$	$(20\text{-}60) \times 10^5$
4.	Caustic Prewash VBN/A+F	5.0-17.0	$(8.0\text{-}9.0) \times 10^6$	$(0.6\text{-}2.0) \times 10^6$	—
5.	Caustic Settler	5.0-7.0	—	$(0.1\text{-}1.8) \times 10^6$	10-30

Table No. 4.

Characteristics of products after addition of spent caustics:
(4 mg spent caustic per litre of crude oil)

Sl No	Type of crude	Cuts	Before Addition			After Addition		
			Phenols ppm	Thiophe. ppm	Mercap ppm	Phenols ppm	Thiophe. ppm	Mercap. ppm
1.	Iran Mix crude	C5- 90	88	76	330	92	78	332
		90-140	288	676	142	290	678	144
		140-270	12910	500	100	12920	510	100
		270-340	12780	2230	88	12782	2232	88
		340-365	14200	1020	62	14020	1022	64
		365+	—	—	—	—	—	—
2.	Upper Zakum crude	C5- 90	90	86	316	92	88	318
		90-140	300	730	120	312	732	122
		140-270	13000	580	100	13012	584	102
		270-340	12800	2245	80	12802	2248	82
		340-365	14000	1100	48	14020	1102	50
		365+	—	—	—	—	—	—
3.	Kuwait Export	C5- 90	102	92	282	104	94	284
		90-140	312	680	100	316	684	120
		140-270	12224	560	96	12230	564	98
		140-340	10460	1540	82	10462	1542	82
		340-365	13632	1082	42	13640	1090	44
		365	—	—	—	-	-	—

Table No. 5.

Characteristics of products after addition of spent caustics:
(8 mg spent caustic per litre of crude oil)

Sl No	Type of crude	Cuts	Before Addition			After Addition		
			Phenols ppm	Thiophe. ppm	Mercap. ppm	Phenols ppm	Thiophe. ppm	Mercap. ppm
1.	Iran Mix crude	C5-90	88	76	330	96	80	336
		90-140	288	676	142	292	682	148
		140-270	12910	500	100	12925	506	102
		270-340	12780	2230	88	12784	2234	90
		340-365	14200	1020	62	142025	1024	64
		365+	—	—	—	—	—	—
2.	Upper Zakum crude	C5-90	90	86	316	94	88	322
		90-140	300	730	120	308	734	124
		140-270	13000	580	100	13014	584	104
		270-340	12800	2245	80	12804	2252	84
		340-365	14000	1100	48	14024	1104	52
		365+	—	—	—	—	—	—
3.	Kuwait Export	C5-90	102	92	282	104	96	290
		90-140	312	680	100	314	686	120
		140-270	12224	560	96	12230	568	100
		270-340	10460	1540	82	10464	1544	88
		340-365	13632	1082	42	13642	1090	46
		365	—	—	—	-	-	—

Observations:

From the experimental results as depicted in the table No. 4 and table No. 5 it is very clear that the increase is added constituents popularly known as pollutants is very negligible in comparison with the already present, approximately varying from 0.60% to 4.5% for 4 mg spent caustic addition and little more in the case of 8 mg sodium hydroxide in the range 1.2% to 8.2%. The total effect of 10 mg spent caustic addition per litre will increase the major pollutants by 1.5% to 3.0%.

The quality of the each products remains almost some in terms of critical quality check by BIS requirement.

It appears that in case any typical crude oil demands more caustic due to the presence of excess salts, the same could be accommodated by the addition of little more spent caustics and still the product quality may not vary considerably.

Conclusion:

There are reasonable difference between the actual plant operation and laboratory experimentation in which many finer points must have been omitted. In order to implement it a test run cum plant trial with the addition of spent caustic into crude desalter unit is suggested for its critical review in terms of feasibility and inspection for the equipment corrosion rate etc. because the spent caustic is more corrosive. The product quality so generated should be checked critically.

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ANALYSIS OF SULFUR-ORGANIC COMPOUNDS IN JET FUEL BY CHROMATOGRAPHIC SNIFFING AND GAS CHROMATOGRAPHY WITH ATOMIC EMISSION DETECTOR

Per-Åke Skoog

Celsius Materialteknik AB
Box 13 200
S-580 13 Linköping
Sweden

ABSTRACT

When the Swedish Air Force changed fuel from Jet B to Jet A-1 during 1991-1992, a working environmental problem was reported from the military air force bases. The symtoms were unpleasant odour, headace and indisposition. This problem arose from some batches of the new fuel, Jet A-1. In order to investigate the compounds in the fuel which gave rise to this problem a chromatographic sniffing technique (sensory analysis) was used.

The identification of the compounds from the sniffing analysis was done with a atomic emission detector for gas chromatography. The problem stemmed from relatively volatile sulfur-organic compounds. An interesting question is if these compounds also are strongly involved in the fuel system deposit formation.

This presentation shows this new analysis technique and the complex pattern of sulfur-organic compounds related to fuels from different refinery processes.

INTRODUCTION

During 1991-1992 the Swedish Air Force changed fuel from Jet B to Jet A-1. Several workers at the air force bases who had close contact with the new fuel expressed obvious problems in the form of unpleasant odour, headace, indisposition etc.

An investigation was instigated in 1993 for the purpose of defining the source of the working environmental problem. This paper deals with the chemical analytical part of that investigation.

EXPERIMENTAL

Samples were chosen from the the periodical samples from an air force base, i.e. samples which are regularly taken from the long-term storages and tested. In addition some reference samples were chosen from the ordinary delivery.

All samples were taken during Aug 1993. The periodical samples had then a storing time of one year, while the references were fresh fuel from the supplier.

The samples are given in table 1. They had a pungent, awful-smell.

Table 1

Problem samples	Mercaptan (Doctor's Test)	Refinery process
654	Pos	Modified Merox (Alkaline wash)
644	Pos	"
908	Neg	"
Reference samples		
1054	Neg	Mixed i.e. Merox, Hydrotreated and Hydrocracked
1196	Neg	"

Chemical analysis

In order to detect possible differences in chemical composition between the problem fuels and the references a comprehensive investigation was carried out.. Since Jet A-1 is composed of hundreds of different hydrocarbons, a gaschromatographic separation has been performed. The different compounds have then been analysed with respect to hydrocarbons and sulfur-organic compounds. The analysis was performed with a gaschromatograph connected to a atomic emission detector, figures 1. The results from the sulfur-organic analyses are evident from the figures 2-6.

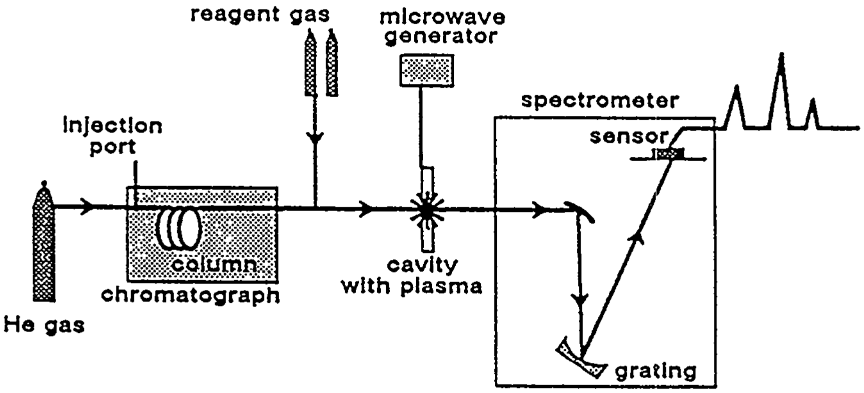

Fig 1 GC-AED Block diagram

In order to investigate if the analytical differences between samples and references concerning sulfur-organic compounds also give differences concerning odour, a sensory analysis has been carried out (sniffing analysis). The GC capillary column was led through copper tubing to a sniffing funnel outside the chromatograph, figure 7. A trained observer recorded the retention time and assessed the odour intensity and the odour chararcter of each odourous compound in the column effluent. Assessments of odour intensity were according to a 3-grade scale, with weak, medium and strong. Sensory analysis was carried out for sample 644 and reference 1054, table 2-3 and figures 8-9.

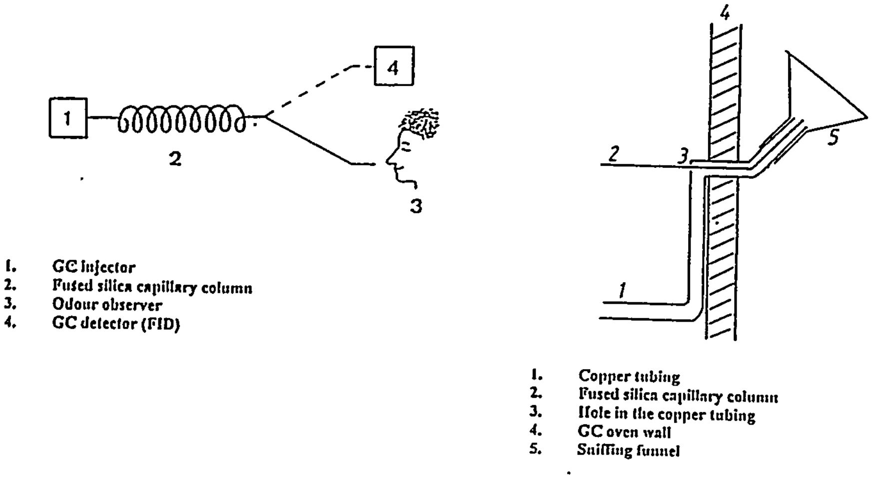

Fig 7 Chromatographic sniffing device

Gas Chromatographic Parameters

Atomic Emission Detector (AED):	Hewlett-Packard 5921A for Gas Chromatograph - Carbon and Sulfur registrations.
Gas Chromatography (GC):	Hewlett-Packard 5890A
Column:	Hewlett-Packard Ultra 1, 50m x 0.32mm, 0.17µm
Temperature programme:	250°C, 30°C(5min), 5°C/min, 250°C(10 min)
Chromatographic Sniffing GC parameters	Fig 1) The same as GC/AED)

RESULTS AND DISCUSSION

The chromatograms fig 2-6 reveal the sulfur-organic compounds in the samples. The samples 2-4 contain sulfur-organic compounds in excess of the references, fig 5-6. The sulfur-organic compounds in the samples exist in the whole destillation interval. In the references the sulfur-organic compounds are distributed at a higher boiling point.

The sensory analysis table 2-3 and figures 8-9 have weak odour-registrations omitted. Sample 644 gives a greater and stronger odour detections than reference 1054. Particularly annoying is the detection with retention time 10.47 min. No estimation of structure concerning this compound has been appropriate to execute within the scope of this project.

CONCLUSION

Our tests indicate that the smell deviations in the fuel do not arise from the main components in the fuel. The reason for the problem is instead trace components of sulfur-organic compounds.

This investigation indicates:

- The samples contain sulfur-organic compounds in excess of the references.
- The samples contain sulfur-organic compounds in the whole destillation interval. In the references the sulfur-organic compounds are distributed at a higher boiling point.
- According to the sensory analysis the samples afforded strongly smelling compounds during the first part of the destillation interval, while the references did not give any remarkable smell deviations.

To eliminate this problem one ought to have a low mercaptan content (Neg Doctor´s test) and the distribution of the sulfur compounds in the fuel ought to have a special pattern.

For controlling or modifying the caustic wash process, this analysis technique can be a useful tool e.g. for characterizing the complex pattern of the sulfur-organic compounds in jet fuels and selectively finding unacceptable compounds.

A further subject for investigation could be whether or not these unacceptable compounds are also especially active in the fuel system deposit formation.

ACKNOWLEDGEMENT

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Fig 2 Sulfur-organic compounds

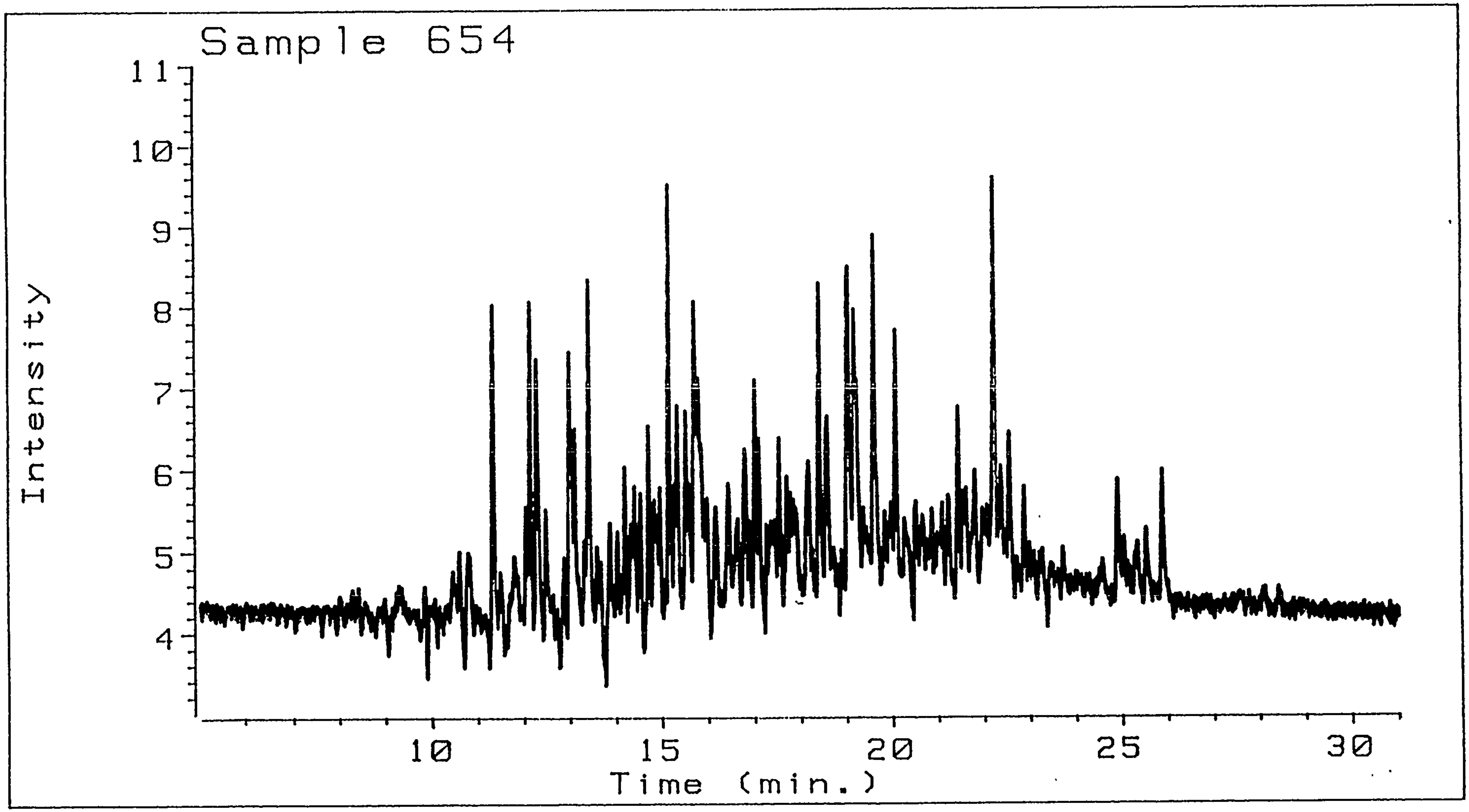


Fig 3 **Sulfur-organic compounds**

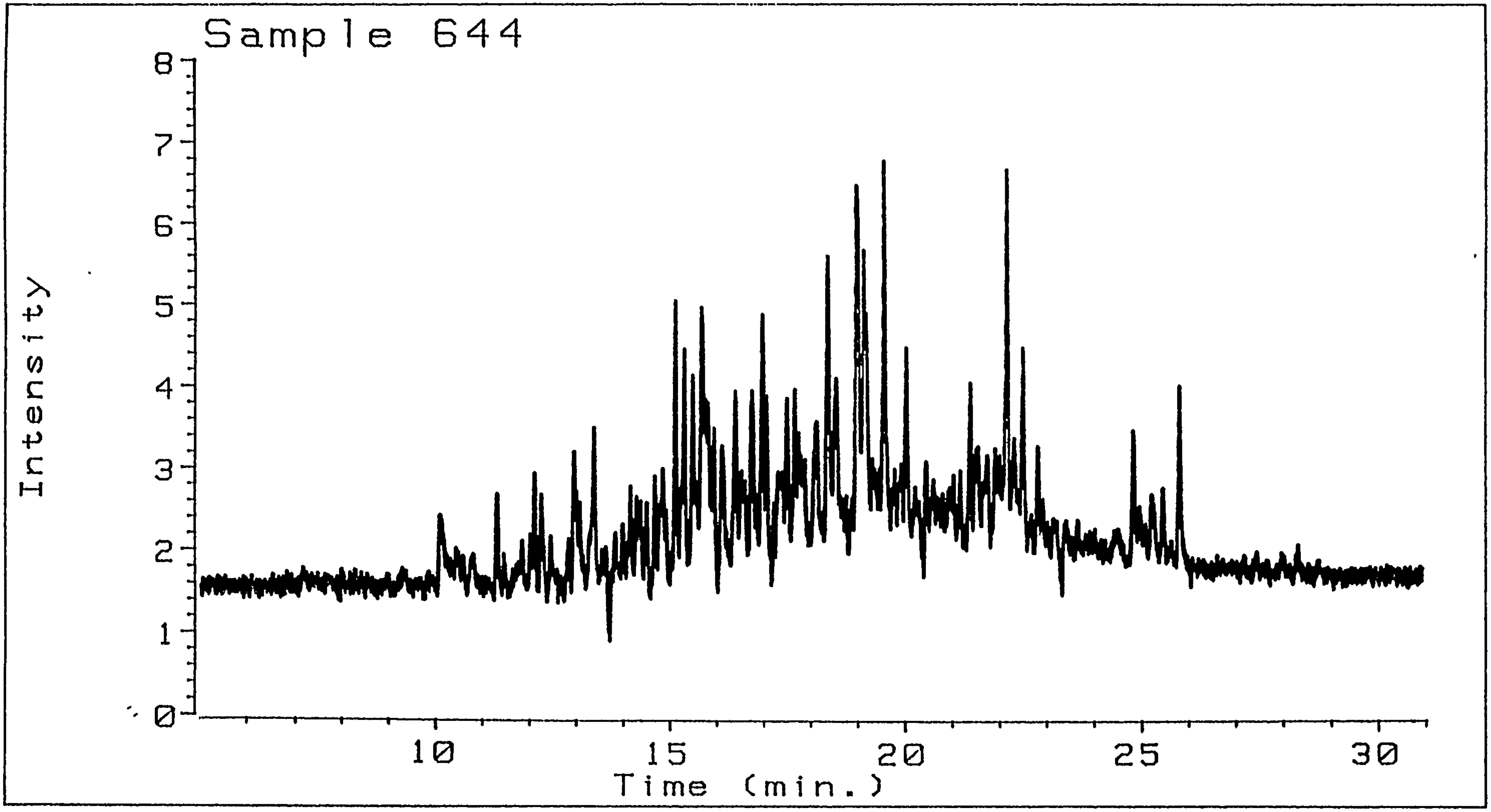


Fig 4 **Sulfur-organic compounds**

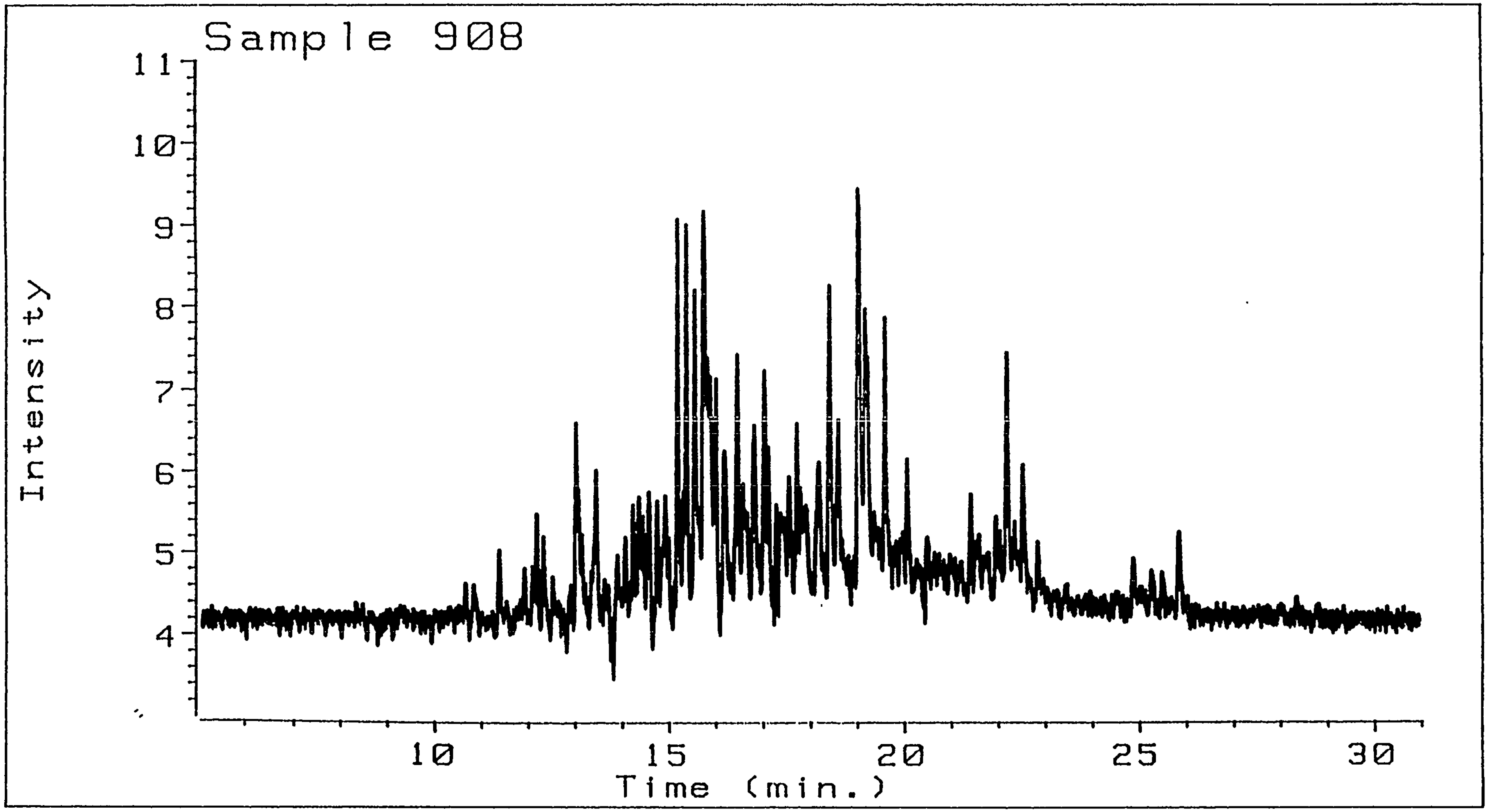


Fig 5 Sulfur-organic compounds

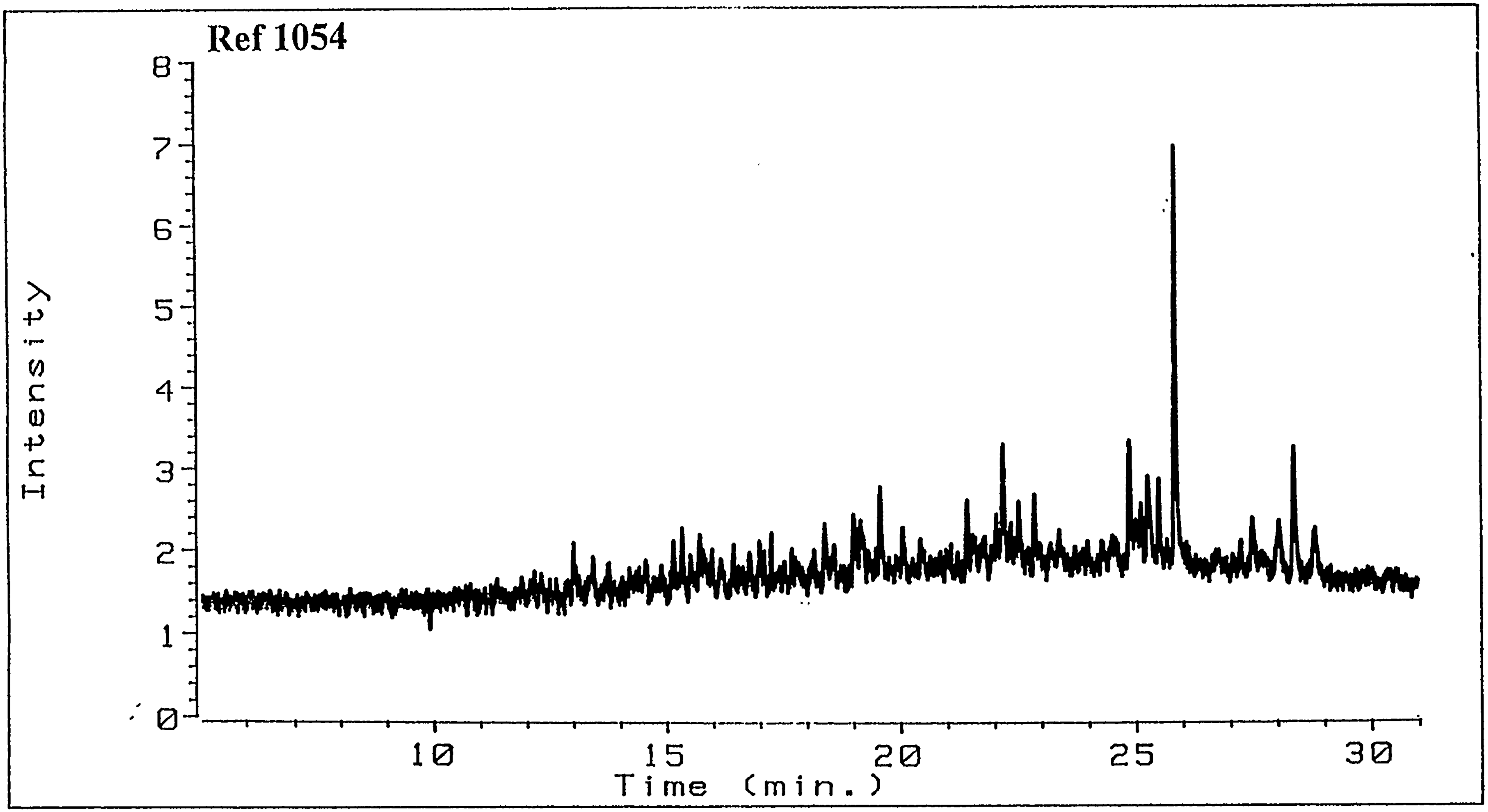


Fig 6 Sulfur-organic compounds

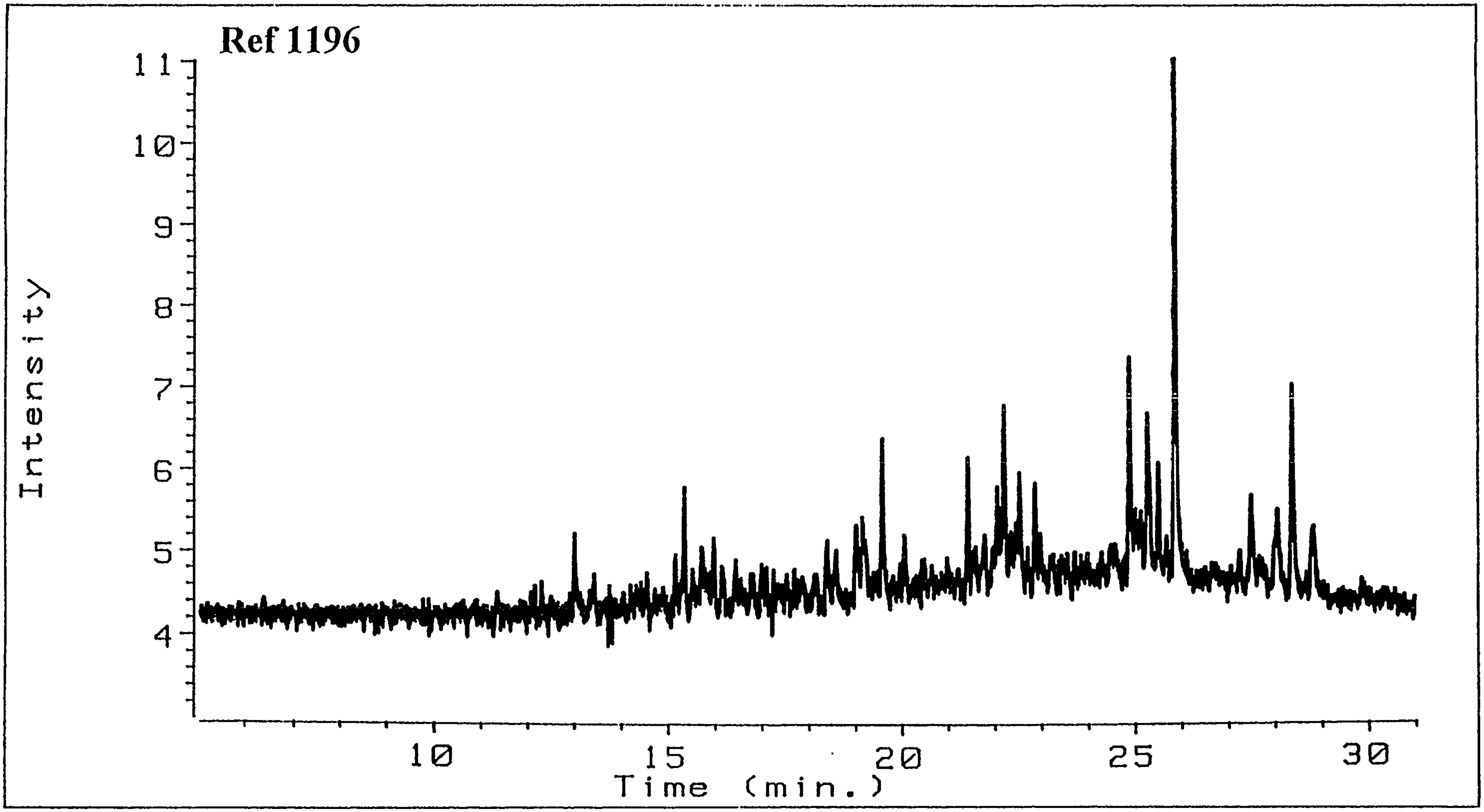


Fig 8 **Sulfur-organic compounds**

Enlargement of chromatogram, fig 5 "odour area"

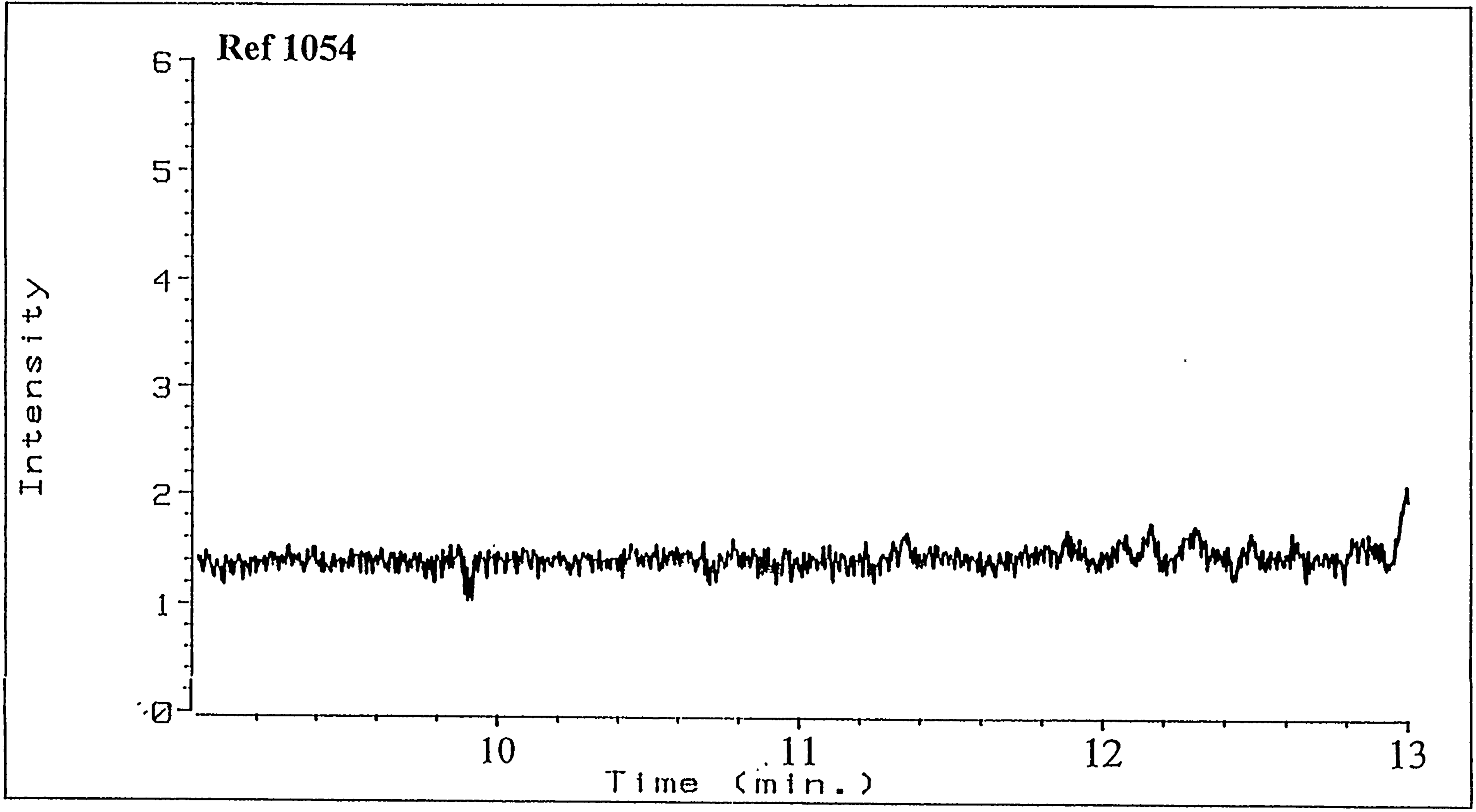
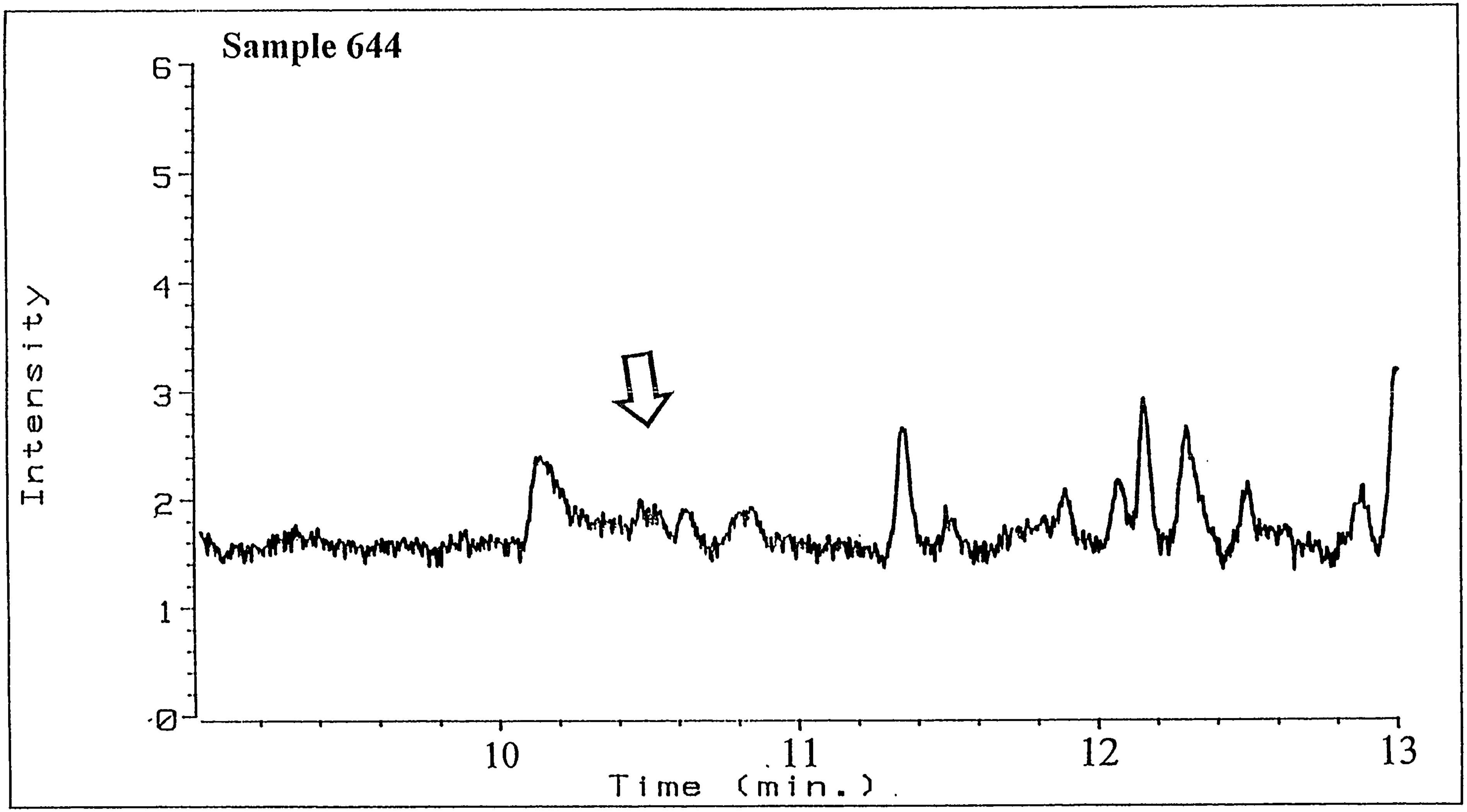


Fig 9 **Sulfur-organic compounds**

Enlargement of chromatogram, fig 3 "odour area"



The arrow in fig 9 points out compounds with extremely strong odour intensity

Table 2 Sensory (sniffing analysis)

Reference 1054

Retention time [min]	**Odour intensity**	**Odour character**
11,37	weak-medium	rosy
11,72	medium	terpene, dormant
13,47	weak-medium	terpene, dormant
14,97	medium	terpene, dormant
15,15	weak-medium	sweet
16,68	weak-medium	rosy
16,88	weak-medium	insecticide
18,45	medium	short, pungent
18,87	medium-strong	moldy, nasty smell
19,17	weak-medium	fresh
19,70	medium	potato
21,27	weak-medium	-
21,92	medium	anise
22,28	weak-medium	-
23,35	medium	sweet, dormant
26,58	medium	smoke

Table 3 Sensory (sniffing) analysis

Sample 644

Retention time [min]	**Odour intensity**	**Odour character**
9,58	medium	resin acids
10,47	strong	pungent, awful-smell, sulfur
11,78	medium	resin acids
12,87	medium	awful-smell, pungent
13,38	weak-medium	org solvent, evil
14,93	weak-medium	nasty-smell
15,15	weak-medium	liquorice, fresh
16,72	weak-medium	earthy
18,23	weak-medium	sweet, dormant
18,47	medium	fungus, earthy
18,87	medium-strong	moldy
19,65-19,83	weak-medium	fresh, dormant
20,20-20,32	weak-medium	fuel, dormant
21,27	weak-medium	-
21,65	weak-medium	earthy
22,27	medium-strong	earthy

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AUTOMATED DEPOSIT-MEASURING DEVICE (ADMD)

Leo L. Stavinoha* and Lona A. McInnis

Southwest Research Institute, U.S. Army Belvoir Fuels and Lubricants Research Facility, P.O. Drawer 28510, San Antonio, TX 78228-0510, USA

ABSTRACT

The Automated Deposit-Measuring Device (ADMD) was developed and fabricated for the evaluation of lacquer-type fuel and lubricant deposits on Jet Fuel Thermal Oxidation Test (JFTOT), ASTM D 3241, heater test tubes. The ADMD employs commercially available components that provide enhanced speed and accuracy of data acquisition as well as improved maintainability, as compared to the prototype Deposit-Measuring Device (DMD) developed in an Army/Navy program. Application of power to the ADMD automatically brings up an operator selection menu on the vacuum fluorescent display. One of five modes of operation can be selected, including both short and long JFTOT tube length and transference of data from random access memory (RAM) to a personal computer (PC) diskette, if the ADMD is already attached to a PC. Maximum breakdown voltage for the DMD is 1,500 volts, compared to 1,372 volts in the ADMD. This difference in voltage will affect maximum measurable volume of deposit, causing the ADMD to sometimes yield a smaller total volume than the DMD. This fact is a problem only with the thicker deposits. The repeatability of the ADMD is at least as reliable as that of the DMD. Comparison of the ADMD values with the old and current values of the DMD reveals a compatibility between the two devices. The correlation between the volume of deposit of the ADMD and carbon burnoff is superior to the correlation between the volume of deposit of the DMD and carbon burnoff. The ADMD is a viable and reliable instrument for measuring deposit on JFTOT standard and long test tubes. This report describes the ADMD features and compares correlations to DMD data and carbon burnoff data. Advantages and limitations of ADMD-derived data are demonstrated and discussed.

INTRODUCTION

The Jet Fuel Thermal Oxidation Test (JFTOT), ASTM D 3241, has been used for many years to evaluate thermal stability of aviation fuels. Available ASTM methods for rating deposits on JFTOT test tubes consist of a subjective visual rating method which attempts to match the deposit to one of five color standards. A photo-optical approach--the tube deposit rater (TDR)--is also used. The TDR measures attenuation of a beam of light that passes through the deposit, is reflected by the tube's surface, exits through the deposit, and is then detected by a photocell.

Modifications of the JFTOT apparatus and procedure to evaluate thermal stability of diesel fuels and crankcase lubricants have expanded the utilization of this expensive apparatus. However, the standard deposit-measuring devices are quantitatively inadequate. The essential problem results from the fact that diesel fuels and lubricants form immensely thick deposits that the visual rating and TDR systems are unable to measure effectively.

In a 1983 cooperative U.S. Army/U.S. Navy project, a unique, nondestructive deposit thickness-measuring technique was devised in support of the diesel fuel injector/thermal fouling bench test development.[1-6] Based on an excellent correlation of 350 volts (dielectric breakdown) with a 1.0-µm deposit thickness for a 1-percent sulfur referee fuel, this technique was applied to deposits from other test fuels and used to calculate deposit thickness and volume. This test methodology was incorporated into a prototype deposit-measuring device comprised of several dissociated components wired together. This Deposit-Measuring Device (DMD), actuated by a manually operated switch, gently lowers the electrode onto the deposit, applies increasing voltage, detects dielectric breakdown, displays the detected voltage, and lifts the electrode off the manually indexed test tube. In 1988, U.S. Patent No. 4,791,811, "Deposit Thickness Measurement," was awarded to Southwest Research Institute for this design.[6]

In a follow-on Army project in 1988, further modifications to the DMD included the following:

- new ramping electronics, including assembly language programming, allowing ramping at rates of one millisecond to ten seconds over a range of 0 to 1,500 volts;

- an outboard DMD electrode module used to evaluate deposits on pintles from injectors subjected to injector fouling bench tests.

An IBM-compatible computer has been interfaced to the control circuits of the DMD and is used to extract breakdown voltage data from the DMD. The computer then performs calculations to produce volume of deposit as well as the maximum thickness of the deposit. The results are then printed in a report format. However, the present DMD requires manual guidance to each test location and, as a breadboard system over 5 years old, requires continual maintenance and cannot be marketed to outside organizations interested in the methodology.

This modified version of the DMD continues in use for Army projects. It provided DMD data reported by the Navy's Morris and Hazlett in 1989, showing a good correlation to carbon burnoff values and deposit volumes calculated by an interferometry technique. Based on deposit density calculations, assuming that a density value of 1.0 to 1.5 g/cm^3 is reasonable, deposit volumes greater than 0.0800 mm^3 and ranging to 0.6365 mm^3 by DMD seem most reliable in this work. These DMD deposit volumes correspond to carbon burnoff values of 95 to 877 μg of carbon, respectively.

The DMD promises to be an invaluable tool for research studies of deposit formation. Experiments that were previously difficult to evaluate, due to the inability to quantitate results, can now be performed with relative ease. Such tests can include studies of fuel additive effects, reaction kinetics, effects of tube metallurgy and surface finish, and the effects of fuel flow rates or residence time on deposit formation.

A final report--BFLRF No. 205[1], dated February 1986--covering early accomplishments in DMD testing and development has been distributed to the U.S. military under the Defense Technical Information Center Accession Number AD A173850. Test data extracted from this report have been presented and favorably received at American Society for Testing and Materials, Coordinating Research Council, and international conferences.[1-5]

The DMD continues to provide valuable data in Lubricant Thermal Oxidation Tester (LUBTOT), JFTOT, and Hot Liquid Process Simulator (HLPS) analyses supporting development of advanced high-temperature lubricants and defining fuel requirements for Army advanced integrated propulsion system engines.

The DMD currently in use is the property of the U.S. government. In addition, it has remained in a developmental stage since 1988, with no further action taken to bring it to final production status until IR & D Project No. 02-9628, "Development of an Automated Deposit-Measuring Device,"[7] that began in October 1990. While this status is acceptable for a developmental project or proof of concept, it does not lend itself well to continuous use as a standard method.

TECHNICAL APPROACH AND RESULTS

A two-task program was required to develop an automated DMD (ADMD). **Task 1** involved the design and construction of the apparatus, and **Task 2** verified that the new system accurately measures the deposits.

Task 1 – Automated DMD Prototype Design and Fabrication. ***Brief Design Overview.*** The ADMD was manufactured with special attention to the following factors:

- the device must be economically reproducible, using readily available components when possible;
- custom fabrication should be employed only when no such component exists on the market;
- any custom-designed components incorporated must be economically reproducible by any general machine or fabrication shop from standard drawings.

To this end, a knowledge base must exist that identifies the manufacturers providing the best selections concerning capability, quality, price, and availability of each required component. Added to these requirements is the need for compatibility between all the major pieces of equipment, which will be interfaced to an onboard computer and contained within one instrument case. Finally, the operator must be able to verify that the unit's major components are working correctly. These major components are described below.

- Three independent stepper motor-drives precisely handle tube motions and probe activity.
  - Test tube rotating fixture and stepper motor drive, with live and dead end chucks, is a keyed (pin and groove) index that ensures accuracy and zero play without dependency on hand-scribed indices and ambiguity of set screws. Unfortunately, the test tube still must be hand-scribed to mark the 0°-test position before JFTOT testing, and the keyed index on the ADMD is on the wrong end for reliable alignment. However, this fixture does allow instant spring-loaded interchange of long and short tubes without any adjustments or realignments.

- Probe translation stage stepper motor driver moves the high-voltage probe along the length of the tube at 2-mm intervals, providing testing at each interval for 0- to 1,500 volts. Hall effect devices are incorporated to ensure absolute repeatability and positional accuracy with any tube for repeat tests.

- The heart of the entire system is the probe, which comes in very light contact with the test tube. Too little contact pressure can cause inconsistent readings along the length of the tube as well as between repeat tests over time. Too much pressure can result in a low false reading, and more significantly, damage to the thin varnish deposit. Inconsistent probe pressure between points 2 mm apart can cause the same undesirable results. The probe mechanism must be free from friction to eliminate inconsistencies throughout the probe travel. The probe force must remain constant even if the test tube is warped. This requirement precludes the previous design on the DMD that was predicated on fixed travel using a spring-type stylus that depends on the tube always being straight.

  A design using a tone arm principle is feasible. However, time and dust accumulation on bearings will disturb the repeatability of the tone arm, especially at very low gram forces. The tone arm also requires extensive design to provide zero play bearings with zero friction and all the support structure. However, a miniature ball bearing slide lends itself well to the needs of a tone arm probe. Still, a mechanism is needed to repeatedly provide the proper force. Since force based on fixed travel and position cannot be implemented with bent tubes, a method must be used to maintain constant force.

  In larger systems, reactive torque of motors is easily measured by using a simple cantilever beam force transducer with mounted strain gages, providing a linear repeatable analog output of force scaled in inch-pounds. For this tone arm, the placement of a strain gage on a 0.020-mm diameter probe would be a formidable task. Consequently, a simple solution is to reverse the process and mount the probe properly by welding it onto a strain gage substrate (stainless steel). The unique, force-sensitive probe design performs as smoothly as its larger counterparts on a smaller force scale. This probe has a mass of 1 gram. A nominal force of the probe on the test tube is in the realm of 0.3 to 0.5 grams consistently, which approximates the force on a tone arm system. The computer will easily detect the force that is incremented by a linear stepper motor.

The probe is calibrated using a simple gram gage, and since the ball bearing slide is lightly spring loaded, all inconsistencies are eliminated from the entire probe motion mechanism. This design will result in repeatable performance. However, the very delicate probe should be enclosed in a protective cage when it is not in use.

- A front panel-mounted printer records the data as the deposit tube undergoes ADMD evaluation.

- A high-voltage AC-DC power supply is ramped from 0 to 1,500 volts by a DAC (digital-to-analog convertor) and contained within the computer.

- A high-voltage comparator board detects the voltage at the point of deposit breakdown, indicated by electrical current flow, and sends a signal to the computer to stop the ramp and acquire data.

- The single-board computer controls the ramping of the high-voltage power supply as well as the printer and the three stepper motor functions, along with a vacuum fluorescent display that shows the test status as it progresses.

  The computer interrogates the high-voltage comparator looking for the signal that indicates deposit breakdown and then reads the ADC (analog-to-digital convertor) to obtain the exact voltage at breakdown. The raw data acquired by the ADC are then converted to engineering units using a prescribed equation, and the final data are printed on the built-in, front panel printer. Operator interface to the built-in computer is via an RS-232 keyboard terminal built into the ADMD instrument. The built-in computer is also capable of transmitting test data to any remote computer via a standard RS-232 communication link. The "Write Data File" mode on the menu display is used to transfer the measured breakdown data from the ADMD RAM to a PC diskette using the PCSmartLINK III software from Octagon Systems Corporation. The code is written in CAMBASIC II, which is the Octagon System version of the BASIC computer language. This allows the data to be obtained in a readable form, in addition to the thermal printer tape that is made during a test. The data then may be loaded into a data base and organized as needed.

The ADMD Measurement Cycle. A selected JFTOT tube is first placed in the tube tray of the ADMD in the horizontally mounted fixture. The tray is shut and the probe is automatically extended until a preset force is obtained. After the high voltage is scanned from 0 volts to the dielectric breakdown voltage, the probe is retracted to an intermediate position. The high-voltage range is then scanned using 0.671 volt-steps, which is the maximum resolution of the DAC used to program the high-voltage power supply.

When the voltage is raised to a sufficient value for deposit breakdown to occur, the deposit can no longer remain an insulator. Current flows through the breakdown point, which is detected by the resistor network in the high-voltage comparator. This breakdown results in a current flow output signal. Recognizing that the last voltage increment resulted in deposit breakdown, the computer stores that value in memory under Row No. 1, Position No. 1. High voltage is shut down immediately to prevent undue influence on the adjacent varnish from continued current flow. The probe is retracted in preparation for its move to the next position.

Since this test point is now complete, the probe horizontal motion stepper motor moves the probe to Position No. 2, still on Row No. 1. The cycle repeats incrementing the voltage up to the point of breakdown. When all four positions in Row No. 1 have been tested and recorded, the testing of Row No. 2 is initiated.

As the test progresses, the vacuum-fluorescent (green) readout under computer control displays the row number, position number, and voltage at breakdown of present position. The operator may abort the test at any time. The display resets to a menu when the test is complete. Meanwhile, the data printout is available from a slot in the front panel of the printer. The data printout includes an average of the voltage from each row, and a total of the averages.

Accuracy, Resolution, and Repeatability. Accuracy, resolution, and repeatability relate directly to the reliability of the ADMD instrument. These three factors are determined by the areas described below.

1) The high-voltage AC-DC convertor, the high-voltage comparator, and the computer convertors (ADC and DAC) section comprise both analog and digital components. The

AC-DC convertor throughput accuracy is not critical since the breakdown voltage will be read from the output rather than being inferred from the binary DAC input. Thus, the possible accuracy detractors from both conversions are eliminated. The ADC accuracy can be verified by the operator from an onboard DC voltage reference, validating the varnish breakdown voltage readings.

The high-voltage comparator is comprised of highly accurate resistors from either Caddock or Micro-Measurements, and a strobe comparator from Maxim with its own DC voltage reference on the circuit board.

Both the ADC and DAC are 12-bit convertors with an accuracy of one part in 4,096 (0.000244, or 0.02 percent), but total accuracy will be a function of all accumulated system errors.

2) The rotation motion control section consists of one rotary stepper motor that can have a resolution of 800 steps/revolution, which is 360°/800 for 0.45°-resolution (0.12 percent). Only four rows are defined around the tube at 90°-intervals; therefore, the computer issues a stream of pulses numbering 200 for each 90°-interval. An absolute zero reference will ensure that the tube always starts its test at 0° and that there is no cumulative error between tests. A stepper responds to a pulse from a computer, i.e., one pulse, one step. Since there are no positional ambiguities as found in feedback servo systems, the stepper is rudimentary to implement and verify.

3) The horizontal motion control section consists of one linear stepper motor that can have a resolution of 3,000, 4,500, 6,000, or 7,500 steps/inch. Three thousand steps/inch results in 0.03 percent when specified in millimeters. Therefore, horizontal resolution is 0.008 mm, and accumulated error after 30 test points (60-mm total travel) is 0.056 mm. A resolution of 3,000 steps/inch (3,000 steps/25.4 mm) requires 118.11 steps/mm. However, since the stepper will advance only 118 discrete steps for each millimeter and not 118.11, there will be an error accumulation after 60 mm of only 0.056 mm, or 0.09 percent of 1 mm (0.002 in.), an easily acceptable error.

Task 2 – Verification of the ADMD. The ADMD tests were verified by comparing the deposit analysis obtained using the manual prototype DMD with those obtained by the ADMD using archived JFTOT test tube deposits. TABLE 1 is a summary of the 304 stainless steel tubes used for comparison of the DMD with itself and with the ADMD.

A linear regression analysis was performed on the new values of the DMD versus the ADMD measurements listed in TABLE 1. The total of the average dielectric breakdown voltage measurements were converted to volume of deposits (mm^3) by multiplying each value by 0.000057 as established in previous work with the DMD.[1-5] A coefficient of determination (R^2) equal to 0.9484 was calculated from this regression model, shown in Figure 1. Figure 2 is a linear regression analysis of the original values of the DMD versus the new values of the DMD listed in TABLE 1. A coefficient of determination (R^2) equal to 0.9418 was calculated from this representation. The patterns of the ADMD are consistent with the DMD configurations, and the new pattern of the DMD closely reproduces the original model.

TABLE 2 includes the aluminum JFTOT test tubes used to test the repeatability of the ADMD, as shown in a linear regression plot in Figure 3. A coefficient of determination (R^2) equal to 0.9615 was determined.

TABLE 3 is a list of the 304 stainless steel tubes that generated carbon burnoff correlations. The tubes were tested in duplicate to enable comparison of the carbon burnoff data in another Army-sponsored program. Set 1 was evaluated earlier by carbon burnoff, and Set 2 was saved for this current SwRI program. A linear regression analysis was performed on the original DMD values of Set 1 and Set 2. The coefficient of determination (R^2) equal to 0.8944 was calculated. However, the coefficient of determination (R^2) equal to 0.7756 was calculated for the carbon burnoff values of Set 1 and Set 2. A coefficient of determination (R^2) of only 0.6079 was calculated for the DMD values versus carbon burnoff of Set 1, and the $R^2 = 0.6718$ for the DMD values (original) versus carbon burnoff of Set 2. Comparing the ADMD values versus the original DMD values, the current DMD values of Set 2, has $R^2 = 0.5588$ for the old values, and 0.7109 for the current values. A coefficient of determination was also calculated for the current values of DMD versus carbon burnoff values of Set 2, with the results of $R^2 = 0.7159$. The best coefficient of determination of $R^2 = 0.9008$ was obtained for the ADMD values versus carbon burnoff values.

The tubes mentioned above were all standard size JFTOT test tubes. One research (long size) JFTOT test tube was tested on the ADMD. This tube has no previous DMD history because the earlier tested long tubes were not kept at SwRI but returned to the project sponsor. The long tube will not fit in the DMD unless both ends of the research tube are cut very short. The long tube will fit in the ADMD without any more problems than those experienced with the standard size test tube.

DISCUSSION AND CONCLUSIONS

The Automated Deposit-Measuring Device compares favorably with the manual Deposit-Measuring Device. More time is required by the ADMD to measure the deposit than is required by the DMD, particularly if the deposit is thick. However, since the ADMD is automated, it does not require as much operator time as does the DMD. The keyed index cap used on the JFTOT test tube in the ADMD is a nuisance. Occasionally, several caps must be tried before one will fit the tube adequately. If the cap does not fit **perfectly**, it could stick in the tube holder of the ADMD, requiring considerable time to remove. A tool should be constructed to allow easier removal of this cap. The ADMD is easier to troubleshoot and repair than the DMD. This can be attributed, in part, to the modular design of the ADMD, as well as having more accurate documentation. Also, it is programmed to display a message on the digital readout that references the problem. It is then a simple matter of checking the documentation to interpret the message. The ADMD is also portable, while it would take a significant endeavor to move the breadboard-prototype DMD.

Application of power to the ADMD automatically brings up an operator selection menu on the vacuum fluorescent display. Five modes of operation are available for selection: three modes are on the initial menu, and two modes are on the second menu. Pushing number "1" on the keypad while the initial or second menu is displayed causes the tray to be opened, while number "2" on both menus will close the tray. Short tube measurement corresponds to "3," while long tube measurement is "4". Pushing "5" on the keypad causes the data to be transferred from RAM to a PC diskette, if the ADMD is already attached to a PC.

Maximum breakdown voltage for the DMD is 1,500, while the ADMD has a maximum breakdown voltage of 1,372. This difference in voltage will affect maximum measurable volume of deposit, causing the ADMD to occasionally yield a smaller total volume than the DMD. This fact is a problem only with the thicker deposits.

The repeatability of the ADMD is at least as reliable as that of the DMD, and ADMD values are compatible with the old and current values of the DMD. The correlation between the volume of deposit of the ADMD and carbon burnoff is superior to the correlation between the volume of deposit of the DMD and carbon burnoff. The ADMD is a viable and reliable instrument for measuring deposit on JFTOT standard and long test tubes.

ACKNOWLEDGEMENTS

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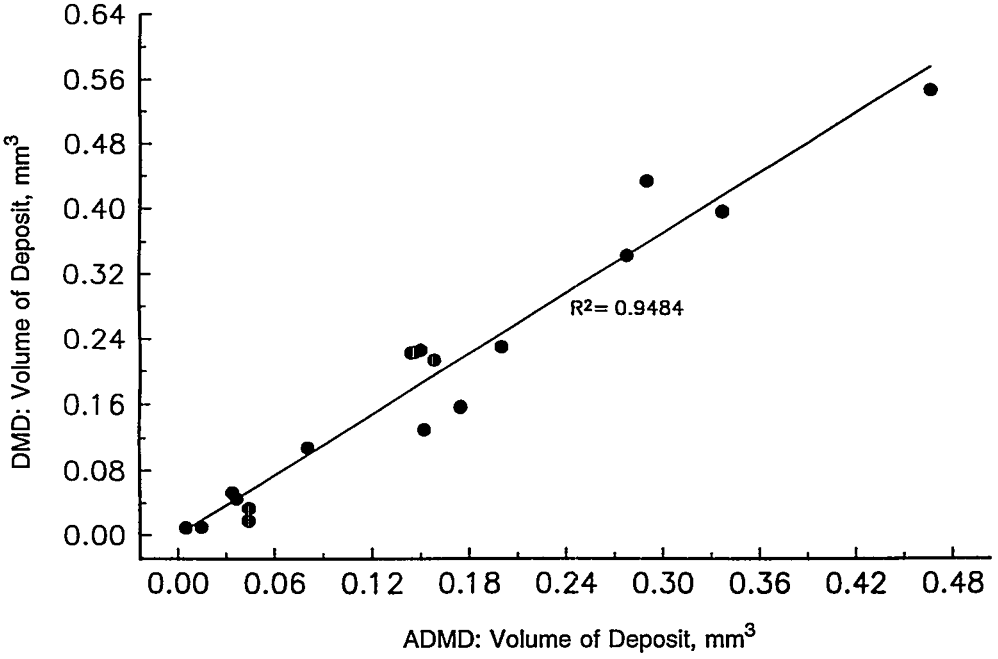
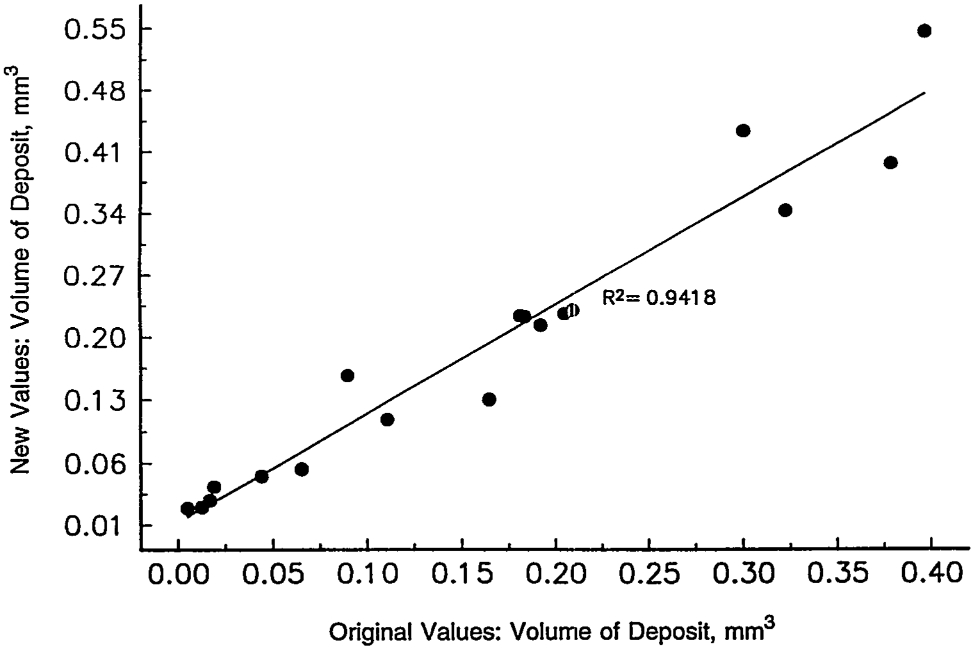


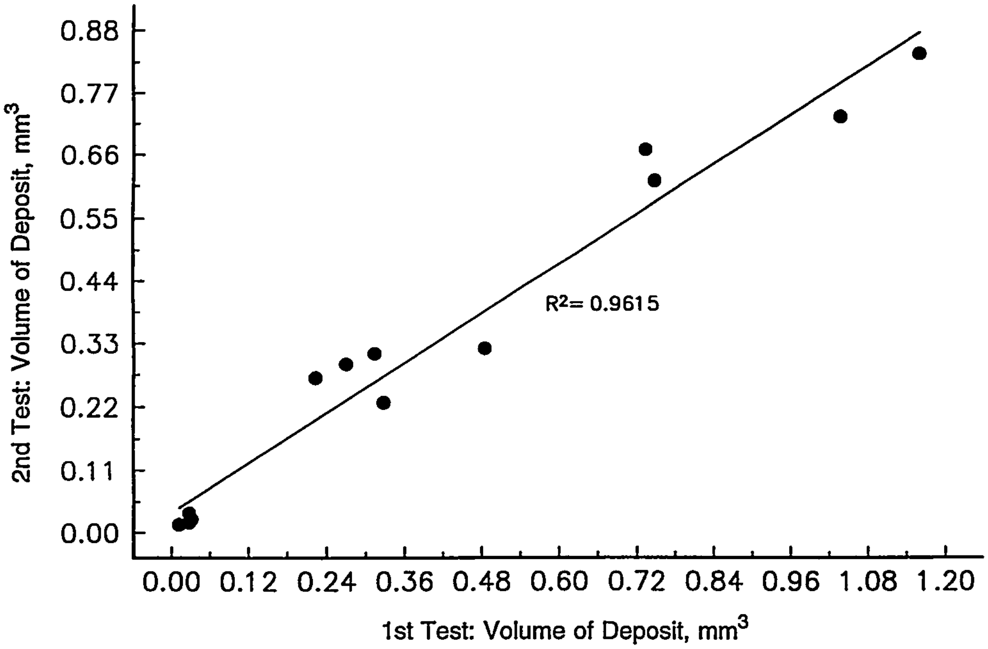
(ADMD vs. DMD: 304 stainless steel JFTOT test tubes tested same day on both instruments)

Figure 1. Regression analysis of ADMD



(DMD original values vs. DMD new values: 304 stainless steel JFTOT test tubes)

Figure 2. Regression analysis of DMD



(Aluminum JFTOT test tubes)

Figure 3. Regression analysis of repeatability of ADMD

TABLE 1. Comparison of DMD and ADMD Using 304 Stainless Steel JFTOT Tubes

Test Fuel	Test No.	Test Date	DMD, mm^3, Original	DMD, mm^3, Repeat	ADMD, mm^3
Jet A	253-H	07-25-89	0.3785	0.3952	0.3368
	254-H	07-26-89	0.3000	0.4328	0.2898
	255-H	07-27-89	0.3226	0.3421	0.2777
	258-H	08-04-89	0.3968	0.5450	0.4664
	259-H	08-15-89	0.0439	0.0458	0.0366
	260-H	08-15-89	0.1835	0.2224	0.1436
	261-H	08-16-89	0.0652	0.0533	0.0338
	262-H	08-16-89	0.2092	0.2298	0.1995
	280-H	08-01-90	0.0893	0.1569	0.1747
	283-H	08-07-89	0.2048	0.2259	0.1498
	284-H	08-08-89	0.1919	0.2131	0.1581
	287-H	08-30-90	0.1810	0.2234	0.1462
	288-H	09-26-90	0.1645	0.1301	0.1523
Reference No. 2	71-B	10-24-90	0.1107	0.1082	0.0808
Jet A-1	292-H	06-07-91	0.0050	0.0092	0.0050
	293-H	06-10-91	0.0168	0.0181	0.0440
	294-H	06-11-91	0.0190	0.0336	0.0441
	300-T	11-27-91	0.0125	0.0103	0.0146

TABLE 2. Repeatability of ADMD Using Aluminum JFTOT Test Tubes

Test Code	Test No.	Test Date	ADMD, mm^3, First Test*	ADMD, mm^3, Second Test*
AL-19647-F	291-H	06-04-91	0.0268	0.0185
AL-19854-F	297-T	11-13-91	0.3130	0.3120
AL-19471-F	304-H	10-29-91	0.0306	0.0242
AL-19540-F	305-H	10-30-91	0.0267	0.0351
AL-15542-F	307-H	11-08-91	0.0113	0.0145
AL-19636-L	L-139-H	04-04-91	0.7476	0.6129
AL-19637-L	L-140-H	04-09-91	1.0368	0.7255
AL-19660-L	L-141-H	04-15-91	0.7326	0.6675
AL-19639-L	L-143-H	04-18-91	1.1607	0.8376
AL-19640-L	L-144-H	04-23-91	0.2229	0.2699
AL-19665-L	L-145-H	05-20-91	0.4841	0.3207
AL-19666-L	L-146-H	05-21-91	0.3276	0.2277
AL-19667-L	L-147-H	05-24-91	0.2693	0.2934

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* Tubes tested at same location.

TABLE 3. Duplicate 304 Stainless Steel JFTOT Test Tube Evaluations

Test Fuel	Test No.	Test Date	DMD, Volume, mm^3	ADMD, Volume, mm^3	Carbon, microgram
Jet A	280-H	08-01-90	0.0892	0.1747	289
	281-H	08-02-90	0.0701	Not Tested	223
Jet A	282-H	08-03-90	0.1576	Not Tested	206
	283-H	08-07-90	0.2048	0.1498	283
Jet A	284-H	08-08-90	0.1918	0.1581	271
	285-H	08-09-90	0.1899	Not Tested	249
Jet A	287-H	08-30-90	0.1809	0.1462	334
	290-H	10-08-90	0.1411	Not Tested	289
Jet A	288-H	09-26-90	0.1645	0.1523	326
	289-H	10-05-90	0.1395	Not Tested	205
Reference No. 2	275-T	10-22-90	0.1279	Not Tested	216
	71-B	10-24-90	0.1107	0.0808	170
Jet A-1	300-T	11-27-91	0.0125	0.0146	21
	314-H	12-17-91	0.0174	Not Tested	11

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INVESTIGATION OF SENSITIVITY TO MICROBIAL INFECTION OF DIESEL FUEL AT THE REFINERY STAGE

Eric Støttrup Thomsen and Simone Petersen

Søren Schierbeck & Co. ApS, Sabroesvej 15 A 2, DK-3000 Helsingør, Denmark

Resumé:

In the practice of a company dealing with microbial problems of infected fuels it was possible to use associations of microorganisms in research. These associations of "wild" microorganisms appeared succesful in the environment of ship's fuel tanks, causing severe problems at the consumer level. Fresh "raw" diesel fuel was inoculated with the cultures to investigate the sensitivity of the fuel to microbial infection at the refinery stage. The fuel samples received from Danish refineries were specified as free of any additives or biocides. Before inoculation the samples were tested for prescence of inhibiting substances or infection. Samples of "raw" fuel was added 1/10, 1/100 and 1/1000 of infected fuel, incubated at 27 °C and observed for 14 days. Other samples were incubated at 5 °C and combinations of periods at 5° and 27 °C. In the abscence of water or nutrients the inoculum did not appear to survive and colonize the "raw" fuel, although one sample did produce microbial growth in an order of magnitude corresponding to common definitions of fuel infections. The ability of the two relevant associations of "wild" microorganisms to infect the "raw" diesel fuel was not clearly demonstrated at this point.

Keywords:

Diesel Fuel, Infection, Wild Cultures, Refinery.

Background:

Microbial contamination of fuels, especially diesel fuel, is a wide spread problem (1,2). Usually this kind of problem is recognized at the consumer level when filter blocking and resulting engine failure is investigated (3). Other problems are corrossion of steel and yellow metals (4,5). In the distribution chain the problem occurs at service stations (6), bunker stations (7) etc. and it is of considerable interest to establish at which point the contamination arises and what factors govern the development (8). The purpose of this experiment is to investigate the sensitivity of raw diesel fuel at the refinery level.

Materials and methods:

Samples of raw diesel fuel were kindly donated by Danish refineries and checked for microbial contamination and presence of biocides before starting the experiement.

The samples were "raw" meaning that they were specified as taken from the refinery tower sampling point before any addition of additives and preservatives.

Both were specified as "light diesel fractions" with the properties stated in Table 1 below.

Each of the two diesel samples were experimentally inoculated with two different "wild type" associations of microorganisms. "Wild Type" means that both cultures were obtained from consumer problems encountered in our practice and thus relevant for the experiement.

Type A originated from a small costal tanker that bunkered what was specified as "gas oil" in Rotterdam in May 1994. The vessel experienced heavy clogging of filters (change of 18 filters in 24 hours, filter MANN BS 1018-1 30 micron). The gas oil appeared dark, with asphalthenes and some water. The culture was predominantly yeasts and fungi, in the range of 10-30 org/ml upon culture.

Type B originated from a pleasure craft in Greenland that bunkered "marine diesel" from the local onshore storage tank at the village harbour. This microbial contamination was a problem over a number of years for the owner of the vessel, and was treated repeatedly with biocides delivered from the fuel supplier, but without success. It was isolated in May 1994, and showed a broad-specter culture dominated by aerobic bacteria and yeasts, both in the range of 10^5 org/ml and with 3 org/ml of fungi upon culture.

A small sample of the contaminated fuel was inoculated into the raw diesel samples, 1:10, 1:100 and 1:1000 and shaken to obtain a good mixture. From these mixtures small samples were inoculated onto TTC and ROSE BENGAL agar (EASICULT, Orion Diagnostics) and incubated at 27 °C and observed twice daily for two weeks. The inoculated samples were also kept at 27 °C and inoculation onto agar dip-slides done again seven and 14 days later. These dip-slides were incubated and observed in the same manner.

Table 1. Specifications for "raw" refinery diesel fuel samples

	Refinery I	Refinery II
Type	Middle Destilate Diesel Oil	Middle Destillate Diesel Oil
Origin	Denmark	Denmark
Water	120 ppm	> 100 ppm
Specific gravity	0,8490	0,8120-0,8130
Sulphur	0,050 % w/w	0,050 % w/w

Source: Specified by the refineries

Before inculation the two diesel samples were tested for the prescence of microorganisms in the same manner as described above and for biocides using a biological biocide test kit utilizing a biocide sensitive marker organism (Biocide Monitor, ECHA Microbiology Ltd.).

None of the raw diesel samples were contaminated and no prescence of biocides could be detected in the water phases.

Results:

The results for the incubation of the 1:10 samples are shown below in Table 2.

The results from the higher dilutions, 1:100 and 1:1000 are omitted here as they showed only slight growth.

TABLE 2: Incubation results with raw diesel samples inoculated with a relevant culture associations isolated from the consumer level, called "Type A". Type A was domminated by associations of yeast and fungi. The incubation on Easicult Dip Slides was started immediatly after inoculation. The temperature of incubation was 27 °C. Every day the tubes were obseverd for their total colony counts on Total Bacterial Count agar (TTC) and Rose Bengal agar (RB).

	-------- Inoculation culture **Type A** ------------ (Total colony counts)											
	Refinery I						Refinery II					
	Test Tube						Test Tube					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	2	8	2	6	4	6	-	-	-	-	-	-
3	9	13	10	10	11	18	-	-	1	2	1	1
4	10	13	10	10	12	20	2	3	8	5	5	7
5	12	13	11	10	13	20	3	8	8	5	5	7
6	15	16	15	16	14	35	3	8	8	5	5	7
7	15	16	15	17	14	35	3	10	12	7	6	7
8	16	16	15	17	15	35	3	10	12	7	6	7
9	16	17	15	17	15	36	3	10	12	7	6	7
10	16	17	17	24	15	36	3	10	12	7	6	7
11	16	17	17	24	15	36	3	10	12	7	6	7
12	16	17	17	24	15	36	7	12	12	11	6	7
13	16	17	17	24	16	36	8	12	12	12	7	7
14	16	17	17	24	16	36	8	12	12	12	7	7

Inoculation Day 7

Type A

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	1	3	1	-	-	2
6	-	-	-	-	-	-	1	4	1	-	-	2
7	-	-	-	-	-	-	1	4	1	-	-	2
8	-	-	-	-	-	-	1	4	1	-	-	2
9	-	-	-	-	-	-	1	4	1	-	-	10
10	-	-	1	-	-	-	1	4	1	-	-	10
11	-	-	1	-	-	-	1	4	1	-	-	10
12	-	-	1	-	-	-	1	4	1	-	-	10
13	-	-	1	-	-	-	1	4	1	-	-	10
14	-	-	1	-	-	-	1	4	1	-	-	10

Inoculation Day 14

Type A

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	1	1	-	-	-
6	-	-	-	-	-	-	-	1	1	-	-	-
7	-	-	-	-	-	-	-	1	1	-	-	-
8	-	-	-	-	-	-	-	1	1	-	-	-
9	-	-	-	-	-	-	-	1	1	-	-	-
10	-	-	-	-	-	-	-	1	1	-	-	-
11	-	-	-	-	-	-	-	1	1	-	-	-
12	-	-	-	-	-	-	-	1	1	-	-	-
13	-	-	-	-	-	-	-	1	1	-	-	-
14	-	-	-	-	-	-	-	1	1	-	-	-

Inoculation Day 0

Type B

	Refinery						Refinery					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	3	2	3	5	5
13	-	-	-	-	-	-	2	7	4	7	5	5
14	-	-	-	-	-	-	2	7	6	9	5	6

Inoculation Day 7

Type B
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	10^2	10^2	10^2	10^2	10^2	10^2
6	-	-	-	-	-	-	10^3	10^2	10^2	10^2	10^2	10^2
7	-	-	-	-	-	-	10^3	10^3	10^2	10^2	10^2	10^2
8	-	-	-	-	-	-	10^3	10^3	10^2	10^3	10^3	10^2
9	-	-	-	-	-	-	10^3	10^3	10^2	10^3	10^3	10^2
10	-	-	-	-	-	-	10^3	10^3	10^2	10^3	10^3	10^2
11	-	-	-	-	-	-	10^3	10^3	10^3	10^3	10^4	10^4
12	-	-	-	-	-	-	10^3	10^3	10^3	10^3	10^4	10^4
13	-	-	-	-	-	-	10^4	10^4	10^4	10^4	10^4	10^4
14	-	-	-	-	-	-	10^4	10^4	10^4	10^4	10^5	10^4

Inoculation Day 14

Type B
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-	-	-	-	-
13	-	-	-	-	-	-	-	-	-	-	-	-
14	-	-	2	-	-	-	-	-	-	-	-	-

Inocculation day 0,
incubation at a low temperature (5 °C).

Type A
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	1	-	-	-	-	-	-	-	-
12	2	-	5	1	2	2	-	-	-	-	-	-
13	3	1	13	5	3	7	-	-	-	-	-	-
14	3	2	16	10	9	7	-	-	-	-	-	-
15	12	2	21	12	12	12	-	-	-	-	-	-
16	16	2	21	16	15	10^2	-	-	-	-	-	-
18	16	2	24	18	18	10^2	-	-	-	-	-	-

Inocculation day 0,
incubation at a low temperature (5°C).

Type B
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
Day												
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	10^2	10^2	10^2	10^2	10^2	10^2
13	-	-	-	-	1	-	10^2	10^2	10^2	10^2	10^2	10^2
14	-	-	-	-	1	-	10^2	10^3	10^2	10^3	10^2	10^3
15	-	-	-	-	1	-	10^2	10^3	10^2	10^3	10^2	10^3
16	-	-	-	-	1	-	10^2	10^3	10^2	10^3	10^2	10^3
18	-	-	-	-	1	-	10^2	10^3	10^2	10^3	10^2	10^3

Inccolation day 0,
changing temperatures, five days incubation at 5°C followed by one days incubation at 27 °C.

Type A
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
Day												
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	18	7	5	5	10	6	-	-	-	-	-	-
7	18	8	6	5	11	6	-	-	-	-	-	-
8	22	9	6	5	11	7	-	-	-	-	-	-
9	22	10	7	7	13	9	-	-	-	-	-	-
10	22	10	7	9	13	15	-	-	-	-	-	-
11	22	10	7	9	13	15	-	-	-	-	-	-
12	22	12	10	11	18	15	1	2	-	-	3	9
13	22	12	10	12	23	15	1	6	4	10^2	3	12
14	22	16	10	13	23	20	2	7	5	10^2	4	14

Inocculation day 0,
changing temperatures, five days incubation at 5 °C followed by one days at 27 °C.

Type B
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	1	2	-	-	-	-	-
13	-	-	-	1	-	1	2	5	-	3	4	10^2
14	-	-	-	1	-	1	6	10^2	1	3	10	10^2

Inocculation day 0,
changing temperatures, two days incubation at 27 °C followed by two days incubation at 5 °C.

Type A
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	2	4	9	4	12	4	-	-	-	-	-	-
3	3	11	9	6	12	5	-	-	-	-	-	-
4	3	11	9	6	12	5	1	3	-	-	-	-
5	3	11	9	6	12	7	3	4	3	2	4	3
6	4	12	12	7	14	7	3	4	3	2	4	3
7	4	13	12	7	14	7	9	5	9	4	12	3
8	4	14	12	8	15	7	9	5	9	4	12	3
9	4	14	12	8	15	8	9	5	9	4	12	3
10	4	14	12	8	19	8	9	5	9	4	12	3
11	4	20	12	8	19	8	9	5	9	4	12	3
12	4	20	12	9	19	8	9	7	9	4	15	9
13	4	20	12	9	19	8	10	7	9	8	15	13
14	4	20	12	9	19	8	10	12	10	11	17	25

Inocculation day 0,
changing temperatures, two days incubation at 27 °C, followed by two days incubation at °C.

Type B
(Total colony counts)

	Refinery (I)						Refinery (II)					
	--1---		--2---		--3---		--1---		--2---		--3---	
Day	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB	TTC	RB
1	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	5	-	-
6	-	-	-	-	-	-	-	-	-	5	1	-
7	-	-	-	-	-	-	4	1	6	7	8	5
8	-	-	-	-	-	-	4	1	6	7	8	5
9	-	-	-	-	-	-	4	1	6	7	8	5
10	-	-	-	-	-	-	4	1	6	7	8	5
11	-	-	-	-	-	-	4	1	6	7	8	5
12	-	-	-	-	-	-	4	3	6	11	12	11
13	-	-	-	-	-	-	7	8	6	27	15	12
14	-	-	-	-	-	-	10	8	11	30	18	15

Results:

The culture **Type A**, predominantly yeast and fungi association, was detectable af inoculation at Day 0 and observed for 14 days in the seeded fuel mixture from Refinery I, but not in the seeded fuel mixture from Refinery II.

After seven days at 27 °C a second inoculation was made from the fuel mixtures. For the culture **Type A** and this time nearly no growth was observed in the fuel mixture from Refinery I, but a slight growth was observed in the fuel mixture from Refinery II.

After 14 days at 27 °C a third inoculation was made from the seeded fuel mixtures, and for culture **Type A** no growth was observed in the fuel from Refinery I and only slight growth was observed in the fuel from Refinery II.

The culture **Type B**, a broad spectrum aerobic bacteria and yeast association with a few fungi, did not show growth when inoculated at Day 0 and observed for 14 days in the seeded fuel mixture from Refinery I. In the fuel mixture from Refinery II a slight growth was observed only from the 13.day of observation in one of the tubes.

After seven days a second inoculation showed no growth in fuel from Refinery I. In the fuel mixture from Refinery II, however, a growth corresponding to a "fuel infection" as defined by Dr. E.C. Hill (   ) was observed from the 5th day an onwards. The growth observed was both aerobic bacteria and yeast and fungi.

After 14 days a third inoculation was made and apart from a single observation in fuel from Refinery I, but only from the 14th days of observation, no growth was observed in the fuel mixtures.

Discussion:

A number of factors are to be considered when discussing a microbial fuel contamination: starting dose, type of microorganism, water availability, temperature and nutrient supply (8).

The typical fuel infection problem arises at the consumer level, where it causes f.i. filter blocking and engine failure. But considerable effort and expense is directed at the various stages of distribution by the oil companies to control microbial infection.
It is of interest to both the consumer and the distributor to know the infective dose required to transmit and infection to an unaffected fuel tank or vehicle.

The infective dose shown here are 1:10 of the original strength of the "wild" infection as present in their own "adjusted" diesel fuels, but 1:100 and 1:1000 were also inoculated, incubated and observed.

Two types of "wild" organism associations have been included in the experiment, both being relevant as having caused severe problems at the consumer level.

No attempt has been made to isolate and identify the microorganisms observed. The visual observation seems to show the same general picture of the culture associations.

In this experiment we have not yet added other factors to the fuel mixture.

In another experiement the degradability of the fuel from <u>Refinery I</u> was tested with a standard culture association but with the addition of water, 0%, 10% and 20% by volume. In this experiment the degradability of the fuel was established in the presence of water (9).

When incubating other inoculated tubes at other temperatures (not shown here) - a stable 5 °C and variations of 5°C and 27 °C - no materially different observations were made. At constant low temperature only a delay was observed in the growth pattern.

Ideally this experiment should be continued for a longer period of time, in order to establish any influence the variation in origins of the crude oil or f.i. the season of the year has on the sensitivity of the "raw" diesel fuel to microbial infection.

The culture methods used are relatively simple methods that can be applied for quality control at various stages in the distribution of diesel fuel (10,11). In our experience they are quite useful to monitor fuel infections, as long as no inhibiting substances are present in the fuel.

To test for the abscence of such inhibiting substances a simple test utilizing a biocide sensitive microorganism was used (BIOCIDE MONITOR, ECHA Microbiology Ltd.). There was no indication of any inhibiting substances.

Conclusion:

The ability of two types of relevant "wild" associations of microorganisms to infect "raw" diesel fuel in the abscence of water and nutriets was not established at this point. Both cultures had caused significant problems at the consumer level. One culture association has survived in the fuel tank of a pleasure craft for a number of years. Further experiments are necessary to demonstrate, if addition of water and nutrients or size of infective dose was the reason for the "failure" of the cultures to rapidly colonize the "raw" diesel fuel.

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PREDICTING STABILITY AT THE REFINERY USING SMORS

Margaret A. Wechter[1] and Dennis R. Hardy[2]

[1]The University of Massachusetts-Dartmouth, N. Dartmouth, MA 02747
[2]Naval Research Laboratory, Code 6180, Washington DC 20375-5342.

Abstract

Previous work has described the relationship between the methanol extractable, hexane insoluble material isolated from aged fuel stocks and storage instability. A predictive test for stability which uses this relationship has been suggested for field use. This paper presents results derived from refinery fresh fuel stocks upon being subjected to a standard storage stability test (ASTM D 5304) and subsequent isolation and quantification of SMORS from the filtered product. Additional evidence which links the extractable material (SMORS) with insoluble sediment formed during long term storage is also presented. The authors suggest a predictive test for fuel stability which might be used as early as the refinery and which might serve as a basis for recommending storage terms for fuel stocks.

Introduction

It has been previously reported(1) that extraction with methanol will improve storage stability characteristics for mid distillate diesel fuel. Moreover, a potential relationship between the methanol soluble, hexane insoluble extractible material and the thermally induced precipitate (TIP) which forms in some fuels under accelerated aging conditions which simulate long term ambient storage, has been suggested.(2,3) Fuel stability is currently assessed through the use of an accelerated aging procedure.(4) However, the procedure or procedures used require substantial commitments of laboratory time and resources and they are necessarily limited to predicting over the relatively (1 - 2 years) short term. A predictive stability test which could serve for field use, or which would require a sufficiently short turnaround time to make it attractive for procurement use is highly desirable. This is particularly true when circumstances require that the fuels may be stored for extended periods.

Fuels which have been aged by ambient storage in the laboratory or field show a very linear relationship between the solids produced by methanol extraction and subsequent precipitation with hexane (EIP - extraction induced precipitate), and solids, or insolubles, formed during the stress, or accelerated aging process (TIP).(3) Thus, for these fuels, the extractibles yields can be used as a predictive test for storage stability. When these aged and thermally stressed fuels are extracted with methanol after filtration for TIP, the yield of extractible solids is typically found to be no more than a few percent higher than the EIP isolated from the unstressed fuel. We propose that, for those cases where the post-stress extractibles (PEIP) yields are about equal to the pre-stress yields (EIP), there is an equilibrium concentration of distributed soluble macromolecular material (which we have previously called SMORS).(2,3,5,6) Examples of fuels which have been aged to equilibrium are found in Table 1.

Fuels which are refinery fresh, or are not aged to equilibrium either because they have been stored under non-oxidative conditions (inert atmosphere, freezer conditions) or their ambient storage times are too short, will frequently show very different extractibles yields before and after accelerated aging. Until these fuels are aged to equilibrium there is no consistently useful relationship between EIP and TIP to obviate the need for a stress test. Some examples of pre (EIP) and post (PEIP) stress extractibles yields for some fresh fuels are also found in Table 1.

Because accelerated aging tests for new fuels do not generally permit storage stability prediction beyond a year or so under ambient conditions and because they are not always reliable, we are suggesting that a stress test in combination with a post stress determination of extractibles will serve to better identify fuels which are likely to develop undesirable storage characteristics over time. This test could serve as the basis for deciding which fuels could be safely stored for additional extended periods, and which should be used promptly. We also provide additional experimental evidence to link the extractible material (SMORS) with insoluble sediment formed as a result of ambient storage.

Experimental

The fuels used in this work were refinery fresh fuels which were tested for EIP and TIP (insolubles) as soon as they reached the Laboratory. They included two light cycle oil (LCO) stocks and two straight runs (SR). For experimental purposes, the fuels tested were the two LCOs and 80%/20% blends of the SR/LCO pairs. Designations for the experimental fuels are found in Table 2.

All fuels involved were tested for pre and post stress extractibles (EIP/PEIP) as soon as they were received and at later intervals, ranging between one and nine months, as well. They were tested for insolubles using the 16 hour ASTM D 5304 - 92 procedure at those same times. All fuel aliquots were prefiltered through two thicknesses of 0.8u 47mm nylon filters (MSI, Westboro,MA) using a water aspirator. Aliquots were 100 mL each; separate aliquots were used for the EIP and for the TIP/PEIP determinations. Stress conditions were 16 hrs., 90°C, 690 kPa oxygen overpressure. Post-stress samples were first filtered for TIP, then subjected to extraction for the determination of PEIP.

For the insolubles (TIP) determination: samples were filtered using glass fiber filters and the procedure described in detail elsewhere.(4) For the extractibles determinations: prefiltered aliquots were extracted (separatory funnel; shake 90 sec.) with 40 mL reagent grade methanol. The methanol phase was rotary evaporated for 30 minutes at 58-63°C. After cooling, 50 mL of reagent grade hexane was added to induce precipitation. The resulting precipitate was filtered (nylon filters) and dried at 70°C to remove any traces of hexane before weighing.

An experimental series was performed to test possible effects of a tertiary amine additive on insoluble sediment (TIP) formation and on post stress extractibles (PEIP) formation. The amine additive has been tested in this laboratory and elsewhere and is known to reduce insolubles formation in some fuels.(7) Light cycle oil samples (Fuels B, D) were doped with the additive in varying concentrations (6 - 890 ppm w/v) and tested, along with control samples, using the same procedures previously described for the TIP and PEIP determinations. All samples were run in duplicate and the aliquot size was 100 mL.

Results and Discussion

Aging (Stress) and Extractibles Testing

Table 3 provides a summary of ambient storage times, pre- and post-stress extractibles levels (EIP and PEIP) and total insolubles/100 mL following the standard 16 hour LPR test (ASTM D 5304 - 92). Fuel A, tested at monthly intervals from 1-3 months passes the LPR test (current pass/fail criterion is 3 mg/100 mL). Pre- and post-stress extractibles levels indicate no tendency for the fuel to degrade over time with respect to insolubles formation and suggest this fuel could be safely stored for extended periods. Fuel B is a light cycle oil and thus might be considered a potential "worst case" fuel. During the time interval between 0 and 3 months of ambient storage the fuel passes the LPR test. The pre-stress extractibles are low, but the post-stress extractibles are increasing to the point where their level suggests that this fuel is not a candidate for long term storage. By 8.5 months of ambient storage LPR insolubles (TIP) and extractibles levels have increased to the point where they support an argument for prompt use. In particular, the post-stress insolubles yield has increased to a level which suggests the fuel is likely to deteriorate badly in the near term.

Fuels C and D are an interesting pair; fuel D being a light cycle oil and C a blended fuel comprised of 20% D and 80% straight run stock. Fuel D fails the LPR test badly on initial testing. Moreover, the post-stress extractibles level (41 mg/100 mL) is high and supports the conclusion that this is a "bad" fuel. As time passes and the fuel is subjected to ambient storage conditions, the condition of the fuel actually improves as noted by TIP (ASTM D 5304) and PEIP (or post-stress extractibles) levels. Note that this LCO, even at 6 months, is not aged to equilibrium and so pre-stress extractibles levels are not as effective predictors of future behavior as are the post-stress levels. By 12 months of ambient storage the fuel has improved to where it passes the LPR. The PEIP has declined as the pre-stress extractibles level has increased. If the existing extractibles (EIP) are subtracted from the PEIP one obtains a measure of the "aging tendency" during the stress test. For this LCO the trend is toward improvement. The relationship between TIP and PEIP formed during accelerated aging is striking: at 0 months of ambient storage TIP is 8.3 mg/100 mL and PEIP is 40.9 mg/100 mL; at 12 months the numbers have fallen to 1.6 and 13.8 mg respectively.

Fuel D is an unusual LCO in that its storage stability with respect to insolubles formation improves as it ages under ambient conditions. However, if criteria we have proposed for aged LCOs using a 24 hour modification of the LPR stress test (TIP ≥ 6 mg/100 mL; extractables ≥ 32 mg/100 mL)(3) are adapted to the 16 hr test, predictions for future storage behavior can be made. Based on post-stress extractibles yields (which must be used rather than pre-stress yields until the fuel is aged to equilibrium) we would predict that, at equilibrium, the pre- and post-stress yields would be roughly equivalent. This fuel is clearly "limited" with respect to the total insolubles it can form during its lifetime prior to use. It apparently forms insolubles rapidly, then levels out to become a rather benign fuel with respect to insolubles formation. While this fuel obviously improves with age, it is not a suitable candidate for procurement on the basis of its poor initial extractibles/aging tests. Moreover, even if it were to be held in storage to equilibrium, there would be so much particulate matter suspended in this fuel as to present filter problems. Thus, this fuel is not a candidate for procurement. Fuel C, the blended stock, is a likely storage candidate on the basis of its extractibles and TIP yields. On the basis of its consistent PEIP and stress test behavior and on its fuel D LCO content, this fuel appears to be a suitable candidate for storage and makes a case for safe storage and use of cracked stock blends.

Effect of Additives

Tables 4 and 5 present results obtained for the two light cycle oils that were tested with the tertiary amine additive (additive #1). Fuel B was also tested using another additive, a hindered phenol (additive #2), for purposes of comparison. Table 4 summarizes additive testing for fuel B. Insolubles (TIP) formation tendency for this fuel is not reduced with either additive. Indeed, it might be argued that TIP increased somewhat on addition of the tertiary amine. PEIP yields for all samples were comparable. Thus, fuel B appears to be one of those fuels that is not affected by tertiary amine additive treatment.

Fuel D, on the other hand, is responsive to additive #1. As was the case with fuel B, additive #2 had no effect on this fuel. Table 5 shows the reduction in insolubles (TIP) that occurs when fuel D is subjected to the 16 hour LPR test after treatment with varying levels of additive #1. A corresponding decrease in PEIP levels is also observed. The fact that additive #1 reduces PEIP levels as it reduces TIP provides additional evidence for a relationship to exist between extractibles levels and the tendency toward insoluble sediment formation in diesel fuels.

Summary

A relationship between extractibles levels before (EIP) and after (PEIP) accelerated aging and insolubles formation tendency has been found to exist in fuels that have not been aged to equilibrium. Additional evidence for the relationship between these entities has been provided by the comparable effect of a common stability additive on post stress extractibles and insoluble sediment. Thus, we propose that a combination of the LPR (ASTM D 5304) stress test and extraction of the filtered, stressed fuel with subsequent precipitation of the hexane insoluble fraction, may serve as a basis for a predictive test for storage stability. This test would enable better decisions to be made as regards the candidacy of fuels for long term storage as opposed to their candidacy for prompt usage. Moreover, for cases where storage is required, this test combination might serve as a reasonable basis for procurement.

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Table 1. Weight of Solids Isolated from the Pre- and Post-Stress Hexane-Insoluble Fraction of the Methanol Extracts of Five Aged and Three Fresh Light Cycle Oil Diesel Fuels[a]

fuel code	EIP: mg/100 mL	PEIP: mg/100mL	aged,A or fresh,F
LCO-1	112	116	A
LCO-2	14	17	A
LCO-3	53	63	A
LCO-4	27	40	A
LCO-5	92	114	A
LCO-12	1	14	F
LCO-13	2	101	F
LCO-14	2	58	F

[a] Storage stress test was for 24 h at 90°C and 690 kPa of oxygen.

Table 2. Experimental Fuel Designations.

Fuel	Type	Legend
A	Blend	80% 91-34(SR)+20% 91-35(LCO)
B	LCO	100% 91-35(LCO)
C	Blend	80% 92-1(SR) + 20% 92-2(LCO)
D	LCO	100% 92-2(LCO)

Table 3. Summary of Test Fuel Results

fuel	Months of Storage time (ambient)	TIP (mg/100mL)	EIP (mg/100mL)	PEIP (mg/100mL)
A	0	1.3	0.23	0.16
A	1	0.4	0.05	0.26
A	2	0.8	0.3	2.5
A	3	0.7	0.6	2.5
B	0	1.9	0.29	6.8
B	1	1.3	0.17	7.8
B	2	1.6	0.3	12.5
B	3	1.9	2.3	28.1
B	8.5	2.3	5.0	45.8
B	14	1.4	13	34.6
C	0	1.8	0.09	6.6
C	0.5	2.2	0.15	5.4
C	1.5	2.5	0.7	5.6
D	0	8.3	0.22	41.1
D	0.5	7.6	0.19	40.6
D	1.5	5.2	2.1	28.0
D	6	4.4	7.3	34.9
D	12	1.6	16.2	30

Table 4. Additive studies for fuel B at 8.5 months ambient storage

Sample tested	mg TIP	mg EIP	mg PEIP
Fuel	2.3	5.0	48.8
Fuel + 24ppm #1	3.3	-	39.3
Fuel + 24ppm #2	2.5	-	42.6
Fuel + 24ppm # 1,2	3.2	-	47.2

Table 5. Studies for fuel D at 6 months ambient storage using additive #1.

Sample tested	TIP	EIP	PEIP
Fuel	4.4	7.3	34.6
Fuel + 6ppm	1.3	-	17.5
Fuel + 24ppm	1.1	-	16
Fuel + 890ppm	1.7	-	22.6