

# Detection of and Countermeasures to Chemical Spills at Sea

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## SUMMARY

A wide range of sensors has been developed to detect crude oils and oil-type products. These are listed and their characteristics described briefly. Normally these are mounted in aircraft, hence "remote sensing". Several European countries carry out aerial surveillance for marine pollution using various combinations of the sensors but this paper concentrates on the instrumentation and response actions in the UK. The IMO Manual on Chemical Pollution<sup>1</sup> infers that the containment and recovery of chemical spillages will bear marked similarities to the recovery of spilled oil. The response options and the equipment are discussed briefly and related to a genuine ships manifest to demonstrate the variety of chemicals that could be encountered in one incident.

## INTRODUCTION

### The Procedure for Countering a Chemical Spillage in UK Waters

Any chemical spillage at sea in UK waters should be reported immediately to Her Majesty's Coastguard (HMCG), who notify the Department of Transport's Marine Pollution Control Unit (MPCU) in Southampton. The Director of Marine Emergency Operations (DMEO) then takes responsibility for dealing with the incident if it is beyond the capabilities of the ship's captain and crew.

The MPCU team gathers information about the fugitive chemicals. They assess from the ship's manifest (see the example in Figure 1) the nature of likely "cocktails" that might be formed and may mobilise a chemical spillage strike team and response package. Local area interests are kept fully informed and possibly involved.

### Packaged Chemicals

For packaged chemicals (Marpol 73/78 Annex III)<sup>2</sup> lost at sea, the response would be primarily a search and rescue operation on the containers, conducted by HMCG. Some packages (Category 1) demand prompt response action<sup>3</sup>

because of the nature of their contents and the likelihood of their being ruptured; others (Category 2) could require similar action but the remainder (Category 3) require notification and monitoring only. All options are directed by the MPCU. In the interests of the health of a ship's crew (in case of leakage), it is agreed internationally that certain packaged hazardous chemicals should be transported on deck. These are therefore the most likely to be lost overboard in a freak storm or very heavy seas.

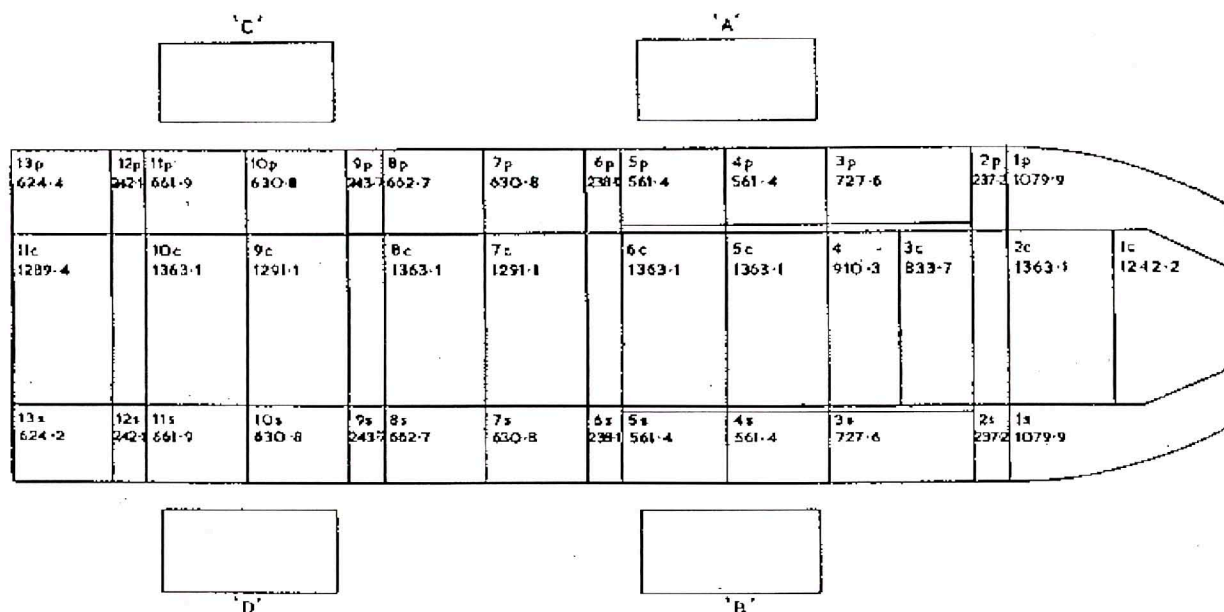
### Bulk Chemicals

Fugitive bulk chemicals (Marpol 73/78 Annex II)<sup>2</sup> may be thought of in much the same way but noting now that each product (pollutant) falls into one or more physical groupings or some combination of them, although in practice this seemingly convenient classification is misleadingly simple:

- Floaters (F)** these are rarely totally insoluble and non-volatile.
- Sinkers (S)** these are unlikely to reach the bottom of the sea without some dispersion - some might possibly reach a level of neutral buoyancy and remain in suspension, raft-like, spreading and breaking up gradually.
- Evaporators (E)** these are unlikely to "boil instantly", but may come very close to doing so.
- Dissolvers (D)** these may take some time to disperse completely.

The above definitions have been included in the modelling studies which have been developed within the EC, eg in EUROSPILL<sup>4</sup> and OSIS<sup>5</sup>, although in OSIS some are given a subordinate role. The more useful physical properties (eg vapour pressure, density and solubility) have been modelled using readily available data sources, such as product data sheets or health and safety literature.

Besides the materials covered by the above definitions the



CAPACITIES GIVEN BELOW TANK NUMBERS ARE IN M<sup>3</sup>

Fig. 1 - Individual Capacities of Cargo Tanks.

lost cargo could include containers of gases which might be harmless but could be toxic, asphyxiating, corrosive or explosive. The acquisition of a copy of the ship's manifest giving full details of the cargo is therefore an urgent requirement at the start of the operation.

From the safety aspect the detection of atmospheric pollution resulting from a chemical spill is an important consideration which is outside the scope of this paper.

**REMOTE SENSING OF CHEMICALS**

Unlike unrefined oils, the majority of chemicals are colourless, rendering them relatively difficult to detect by eye. Like the oils, however, the "floaters" spread easily over the surface of water to form monolayer films, which may pro-

duce a rainbow sheen. They may dampen capillary waves, often producing a mirror-like reflective surface.

Visual detection of either an oil or a chemical film requires an adequate level of ambient light and good weather conditions.

A wide range of sensors has been developed to detect crude oils and oil-type products. These are listed and their characteristics described briefly in Tables 1 to 3. They are usually mounted in an aircraft to carry out this task effectively. Chemicals in general do not lend themselves so readily to detection and identification.

Table 1 lists the types of sensors, whether they are active or passive and the type of properties they detect. They are constantly under development and their sensitivities and detection capabilities improve with technological advances. The types of video camera/recorder available to store data

Table 1: Remote Sensing Detection Systems

SENSOR	TYPE	INDICATION
Side-Looking Airborne Radar (SLAR) Synthetic Aperture Radar (SAR)	Active	Capillary wave damping (surface roughness) Infrared Line Scanner (IRLS) Thermal Imaging Camera
Ultra-Violet Line Scanner (UVLS) Ultra-Violet Imaging Camera	Passive	Reflectance in UV
Microwave Radiometer (MW or MWR) Passive Temperature Laser Fluorosensor (LF)	Active	UV Fluorescence
Forward-Looking InfraRed (FLIR)	Passive	Advance remote sensing systems (as opposed to downward-looking ones)
Forward-Looking Airborne Radar (FLAR)	Active	
Cameras (Still)	Passive	Visual
Cameras (Video)	Passive	Visual

for subsequent analysis are described in Table 2 and the different detection systems are compared in Table 3.

The observer can estimate the area of a slick by eye, given the ground speed of the aircraft, but the mechanical or electronic systems require recorded data on aircraft position and altitude so that the recorded image can be scaled and analysed subsequently. Infra-red and microwave imagery indicate relative differences in thickness of oil and can be calibrated so that estimates of quantity can be made.

## BACKGROUND INFORMATION

Many chemicals are unloaded in North Sea ports. Table 4 lists these, giving the approximate quantities involved and their IMO pollution categories.

Some of the chemicals listed in a typical, genuine ship's manifest (the *MV Post Challenger*, illustrated in Figure 1) are given in Table 5. This table includes data from Sandness et al<sup>6</sup> on their responses to the remote-sensing systems available in 1976. Data were not available for all the chemicals listed in the manifest but it is apparent that, except for five chemicals which are possibly detectable visually or by ultra-violet sensors, they appeared to be detectable only by Raman scattering, one of the sensing functions of the laser fluorosensor. According to this table, none of the chemicals

listed was detectable by thermal infra-red or passive microwave sensors.

[The manifest of the *MV Post Challenger* is used as an example of the sort of chemicals which could be spilled were she to be involved in a collision. Her cargo comprised five products which sink, ten which dissolve instantly with five more dissolving less rapidly, four which would evaporate fairly quickly, leaving two possibly suitable for recovery action at sea - styrene and dodecylbenzene. The former was in tank 7C and the latter in 9S, making it the more likely to be released after collision. Experiments at WSL have shown that application of Type III dispersant enhances the concentration of styrene in water.]

## EXPERIMENTAL WORK BY WARREN SPRING LABORATORY<sup>7</sup>

Sea trials had shown that some chemicals, eg dioctyl phthalate, nonyl acetate and oleyl alcohol, could be detected easily by the SLAR. This initial testwork led to the experiments reported here, to see whether chemicals could be detected by other sensors and whether they could be identified by this means.

Small-scale and pilot-scale experiments were carried out at the laboratory and also sea-trials using thermal (infra-red)

**Table 2: Types of Video Camera**

CAMERA	DESCRIPTION
VHS (Standard or Camcorder)	The simplest, cheapest and easiest to obtain.
S-VHS (Super VHS or Separated VHS)	More data are recorded per unit length of tape, producing a better-quality image, also the audio and video signals are recorded separately.
U-matic video	The magnetic tape is wider than that of the VHS systems and the recording density is greater, giving a very high-quality image.
SLOS (Stabilised Long-range Observation System)	A gyro-stabilised TV camera with a very long focal length lens, capable of receiving images at the maximum range of the SLAR.
LLTV (Low-Light-Level Video)	Ultra-sensitive video system.

**Table 3: Comparison of Different Detection Systems**

DETECTION SYSTEM	INFORMATION			OPERATION			
	Dimensions	Thick-ness	Type of Oil	Long Range	All Weather	Day/Night	Real Time Display
Eye (visual)	Yes <sup>A</sup>	Yes <sup>D</sup>	No	Yes <sup>E</sup>	No	No	Yes
Camera (still)	Yes <sup>A,B</sup>	No	No	Yes <sup>E,F</sup>	No	No	No
Video	Yes <sup>A,C</sup>	No	No	Yes <sup>E,F</sup>	No	No	Yes
LLTV	Yes	No	No	Yes <sup>E</sup>	No	No	Yes
IRLS	Yes	Yes <sup>G</sup>	No	No <sup>L</sup>	No	Yes	Yes
UVLS	Yes	No	No	No <sup>L</sup>	No	No	Yes
MW (MWR)	No <sup>H</sup>	Yes <sup>I</sup>	No	No	Yes	Yes	Yes
LF	No	Yes <sup>K</sup>	Yes	No <sup>M</sup>	No	Yes	No
SLAR (SAR)	Yes	No	No	Yes <sup>N</sup>	Yes	Yes	Yes

**Table 4: Quantities and IMO Categories of Chemicals unloaded in North Sea Ports.**

<i>Chemical</i>	<i>IMO Pollution Category</i>	<i>Scaborne Imports (tonnes x 10<sup>3</sup>)</i>
Acetic Acid	D	86
Acetone	-	132
Acrylonitrile	B	45
Alcohols (C <sub>4</sub> - C <sub>8</sub> )	D	33
Alkylbenzene	D	66
Aniline	C	49
Benzene	C	812
Butyl Acetate	C	15
Chlorobenzene	B	15
Citric Acid	D	30
Cyclohexane	C	227
Cyclohexanone	D	22
Dichloromethane	D	38
Dichloroethyl ether	B	18
Di(2-ethylhexyl) Phthalate	-	54
Di-isononyl Phthalate	D	20
Dodecylbenzene	-	35
Ethyl Acetate	D	30
Ethyl Benzene	C	69
Ethylene Dichloride	B	94
Ethylene Glycol	D	70

<i>Chemical</i>	<i>IMO Pollution Category</i>	<i>Scaborne Imports (tonnes x 10<sup>3</sup>)</i>
Formaldehyde	C	12
Hydrochloric Acid	D	36
Hydrogen Peroxide	C	34
Isopropylbenzene	B	86
Methacrylic Acid	D	44
Methylethyl Ketone	-	13
Nitric Acid	C	61
Octanol	C	28
Perchloroethylene	B	17
Phenol	B	151
Phosphoric Acid	D	724
Propyl Alcohol	-	108
Potassium Hydroxide	C	15
Sodium Hydroxide	D	403
Styrene Monomer	B	470
Sulphuric Acid	C	466
Toluene	C	239
Trichloroethylene	B	17
Vinyl Acetate	C	81
Xylenes	C	922
-	-	-

imaging cameras and selected chemicals. Fourteen chemicals were selected to cover a range of physical and chemical characteristics. They were tested individually, quantities up to 50 millilitres being added to samples of clean, fresh water in the containers. The temperatures of the water and the chemicals were equilibrated previously to ensure that differences in emissivity rather than temperature were detected by the scanner. Table 6 gives the properties of these chemicals.

**Small-Scale Chemical Trials.** These trials utilised several small containers located within the confines of a concrete-lined test-tank, 20 metres long, five metres wide and two metres deep, sunk into the ground, and a Barr and Stroud IR-18 thermal imaging scanner. This operated in the 8-12 micron range of the electromagnetic spectrum. The imagery was recorded on a video recorder for subsequent replay and analysis. The temperatures of the water and chemicals were equilibrated carefully prior to recording the imagery. The results of these trials were used to plan the pilot-scale trials.

**Pilot-Scale Chemical Trials.** Fifteen chemicals were selected. For the tests each one was poured onto synthetic sea water within a freely floating corral one metre square to depths ranging from one to five millimetres. This time the imagery was recorded by a Rank Taylor Hobson thermal

imaging camera similar to that mounted in the Cessna 404 aircraft. Hard copies of typical imagery are shown in Figures 2 and 3.

The thermal imaging response varied from definite but weak for di-iso octyl phthalate, nonyl acetate and xylene to strong and dark for benzene, cyclohexane, 4-methyl pentan-2-one and toluene, whilst amyl acetate and octan-1-ol showed very little in the thermal imagery. When added to the water the methanol became turbid briefly, appearing light to the thermal imaging camera.

**Full-Scale Chemical Trials at Sea.** The chemicals chosen for the sea trials were Cyclohexane, Styrene and Toluene, which were expected to form easily-detectable slicks and give strong thermal imagery; Nonyl Acetate, expected to give weak thermal imagery; Methanol for its solubility and tendency to form white turbidity in sea water, thus behaving differently from other chemicals, and lastly Paraffin Liquid, which had not been tested during the pilot trials but was included in the list for sea trials as being of possible interest. The chemicals were released as slicks and as continuous discharges. In practice the chemicals tested previously behaved as anticipated. Figures 4 and 5 and show airborne infra-red imagery (from the Cessna 404 at 160/170 feet) of the continuous discharges of Cyclohexane and Nonyl Acetate respectively. The infra-red, ultra-violet and visual im-



## NOTES: Fluo/Ram = Fluorescence/Raman scattering

Ref. 3 Scale: 0, 1, 2, 4:

0 indicates that identification/quantification is unlikely.

1 or 2 indicates that identification/quantification may be possible under certain circumstances.

4 indicates that identification/quantification is probable.

For explanation of IMO Category, see Ref. 1.

OLS = Other Liquid Substances (not categorised currently in Annex II but listed in Appendix III).

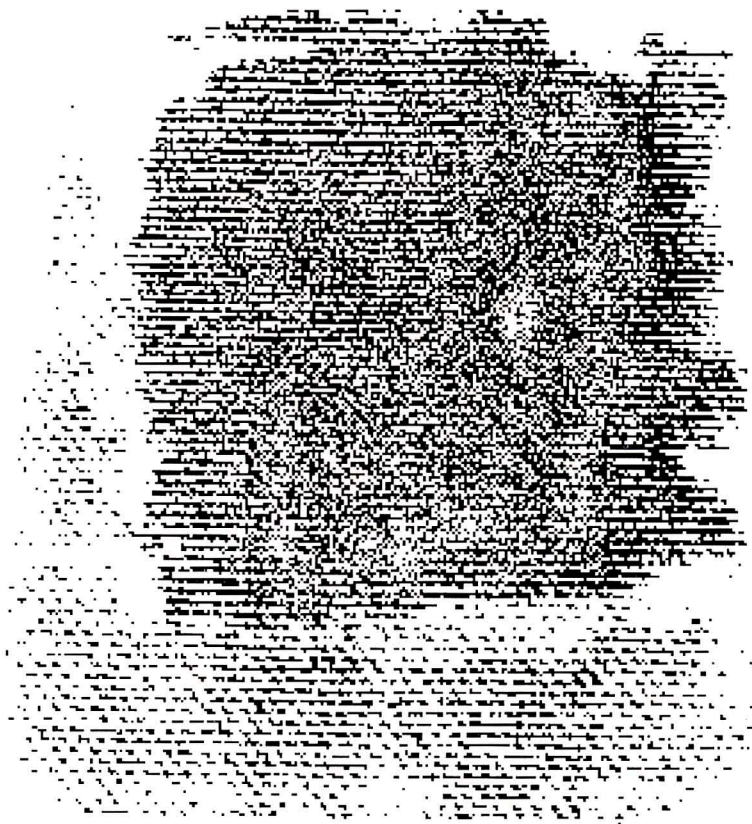
\* = not listed currently in Annex II.

\$ = "Detergent Alkylates" are commercial blends of isomeric, predominantly monoalkyl, benzenes with saturated side chains averaging 12 carbon atoms, prepared by the alkylation

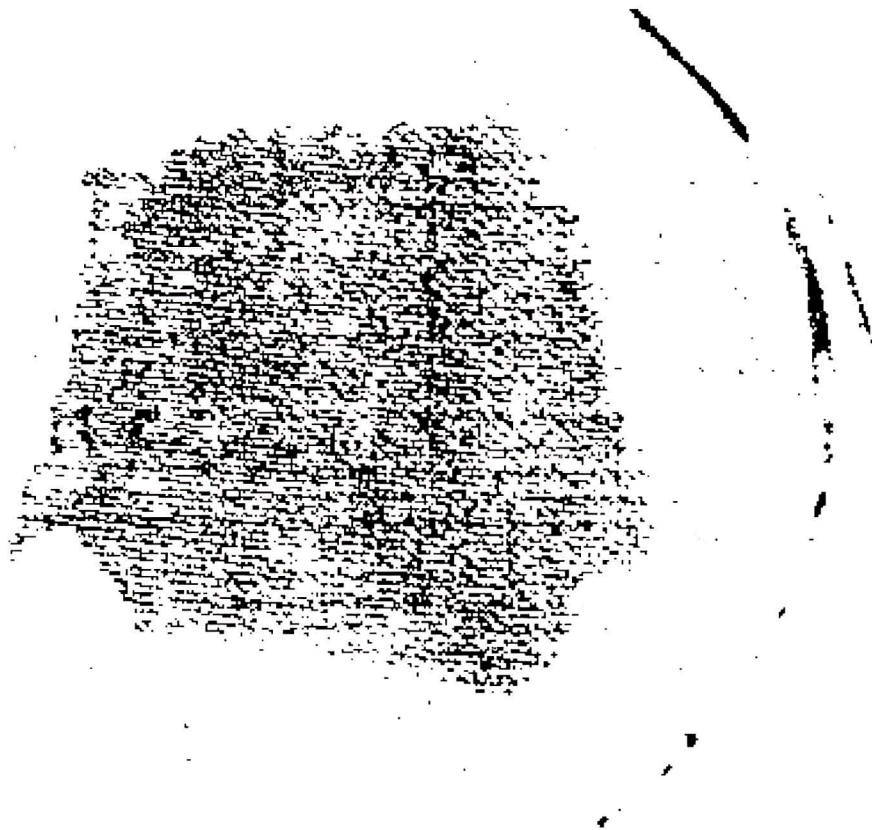
of benzene with isomeric dodecanes (eg Dodecylbenzene) (Ref. 10).

# = additives imparting different properties to lubricating oils. They include butene polymers, metallic stearate soaps, calcium stearate and silicone compounds (Ref. 10).

The ships' names appearing against certain cargo items refer to ships bearing that cargo which have been involved in pollution incidents<sup>11</sup>.



*Fig. 2 - Pilot-Scale Testwork - Imagery of Cyclohexane 2mm Thickness.*



*Fig. 3 - Pilot-Scale Testwork - Imagery of Xylene 5mm Thickness.*

**Table 6: Some Properties (at 293°K) of Chemicals used in WSL Trials.**

Chemicals	Solubility in Water	Specific Gravity	Vapour Pressure	Dielectric Constant	Surface Tension	Viscosity	Thermal Conductivity
	Kg/m <sup>3</sup>	Kg/m <sup>3</sup>	millibars		N m <sup>-1</sup> (x10 <sup>-3</sup> )	mPa s	Wm <sup>-1</sup> K <sup>1</sup>
Amyl Acetate	2.5	880	6	4.75	24.7	NA	0.13
Benzene	0.7	880	100	2.28	28.9	0.65	0.14
Cyclohexane	insoluble	780	102	2.02	25.5	NA	NA
Cyclohexene	v sl sol	810	94	2.22	NA	NA	NA
Di-iso Octyl Phthalate	NA	990	1	NA	NA	NA	NA
Ethyl Acetate	85	900	100	6.02	23.9	NA	0.15
Glycerol	∞	1260	<1	42.5	63	1500	0.27
Hexane	insoluble	660	133-160	1.89	18.4	NA	0.15
Methanol	∞	790	127	32.6	22.6	0.59	0.20
4-Methyl Pentan-2-one	20	800	6	NA	NA	NA	NA
Nonyl Acetate	0.5	870	1	NA	NA	NA	NA
Octan-1-ol	0.5	830	1	10.3	27.5	NA	NA
Paraffin Liquid	NA	800	NA	NA	26	1000	0.15
Propan-2-ol	∞	790	19	18.3	23.8	NA	0.15
Styrenev	sl sol	910	6	2.43	NA	NA	NA
Toluene	insoluble	870	29	2.38	28.4	0.59	0.13
Xylene	insoluble	880	13	2.57	28.9	NA	0.11

NA = information not available.

ages of the continuous release of toluene are reproduced alongside each other in Figure 6.

The discharge rates are given in Table 7, which also summarises the observations made at close hand, from the deck of *MV Seaspring*.

The results of all the trials are summarised in Table 7 and the observations from the deck of the *MV Seaspring* during the sea trials in Table 8.

exceed 1 knot. During the recovery of low viscosity products even this estimate could be optimistic.

**Most skimmers** work best in deep pools of freely-flowing liquids. Most chemicals would be freely flowing, because they have low viscosities and do not usually form emulsions.

**Suction or absorption devices** might be a better option, if suitable ones are available. Wool, straw and other types of matting and mops have been used successfully to absorb oil

**Table 7: Sea Trial - Summary of Observations from the *MV Seaspring*.**

Chemical	Discharge Rate (litres/minute)	Observations from the Deck of <i>Seaspring</i>
Cyclohexane	90	Colourless slick, easily visible, up to 7m wide.
Toluene	50	Colourless trail of Toluene with edges coloured due to refracted light. Up to 4m wide.
Nonyl Acetate	100	Clear, colourless slick, up to 3m wide.
Methanol	100	White turbidity lasted 2-3 minutes before disappearing.
Paraffin Liquid	110	Opaque, white, semi-solid appearance - looked as though it would be very slow to disperse.

## RESPONSE OPTIONS

The IMO Manual on Chemical Pollution<sup>1</sup> refers to the containment and recovery equipment normally deployed to counter oil pollution<sup>8</sup>. Various types of booms and skimmers are available and the choice of a suitable combination would depend on the circumstances<sup>9</sup>.

**Sweeping and recovery operations** are notoriously difficult and slow. Vessels using sweeping booms can rarely

but whatever methods are used it is desirable, although perhaps not always possible, that these devices or materials should not be corroded by or react with the chemicals being retrieved.

Some important points to remember are that (a) any containment and recovery team needs to know where to go and how safe it is to go there; (b) essential portable equipment for the teams to take would be air monitoring instruments and an explosimeter; (c) flash point determination is relatively easy



**Table 8: Summary of Detectability of Chemicals during WSL Trials.**

Chemicals	Thermal Imaging Testwork		Sea Trials							
	Small Scale	Pilot Scale	Cessna 402				Cessna 404			
			IR	UV	SLAR	Visual	IR	UV	SLAR	Visual
Amyl Acetate	1	1	-	-	-	-	-	-	-	-
Benzene	3	3	-	-	-	-	-	-	-	-
Cyclohexane	3	3	2	1	φ	2	3	2	φ	2
Cyclohexene	3	3	-	-	-	-	-	-	-	-
Diesel Oil	4	4	-	-	-	-	-	-	-	-
Di-iso Octyl Phthalate	φ	2	-	-	-	-	-	-	-	-
Ethyl Acetate	3	3	-	-	-	-	-	-	-	-
Glycerol	NA	φ	-	-	-	-	-	-	-	-
Hexane	3	3	-	-	-	-	-	-	-	-
Methanol	4	4	NA	NA	NA	NA	2	φ	NA	φ
4-Methyl Pentan-2-one	NA	3	-	-	-	-	-	-	-	-
Nonyl Acetate	φ	2	2	φ	NA	φ	2	φ	NA	φ
Octan-1-ol	φ	1	-	-	-	-	-	-	-	-
Paraffin Liquid	NA	NA	φ	φ	NA	φ	2	φ	NA	φ
Propan-2-ol	4	4	-	-	-	-	-	-	-	-
Styrene	1	NA	NA	NA	NA	NA	3	4	NA	4
Toluene	3	3	3	2	NA	2	3	4	φ	2
Xylene	φ	2	-	-	-	-	-	-	-	-

KEY: φ = Not detected      1 = Possible imagery      2 = Definite but weak imagery  
 3 = Strong dark imagery      4 = White imagery      NA = Not attempted

SLAR monitoring of the discharge was limited by adverse weather conditions.

but portable instruments could be expensive; (d) oxygen meters could be employed to give useful information; (e) everything should be intrinsically safe.

## CONCLUSIONS

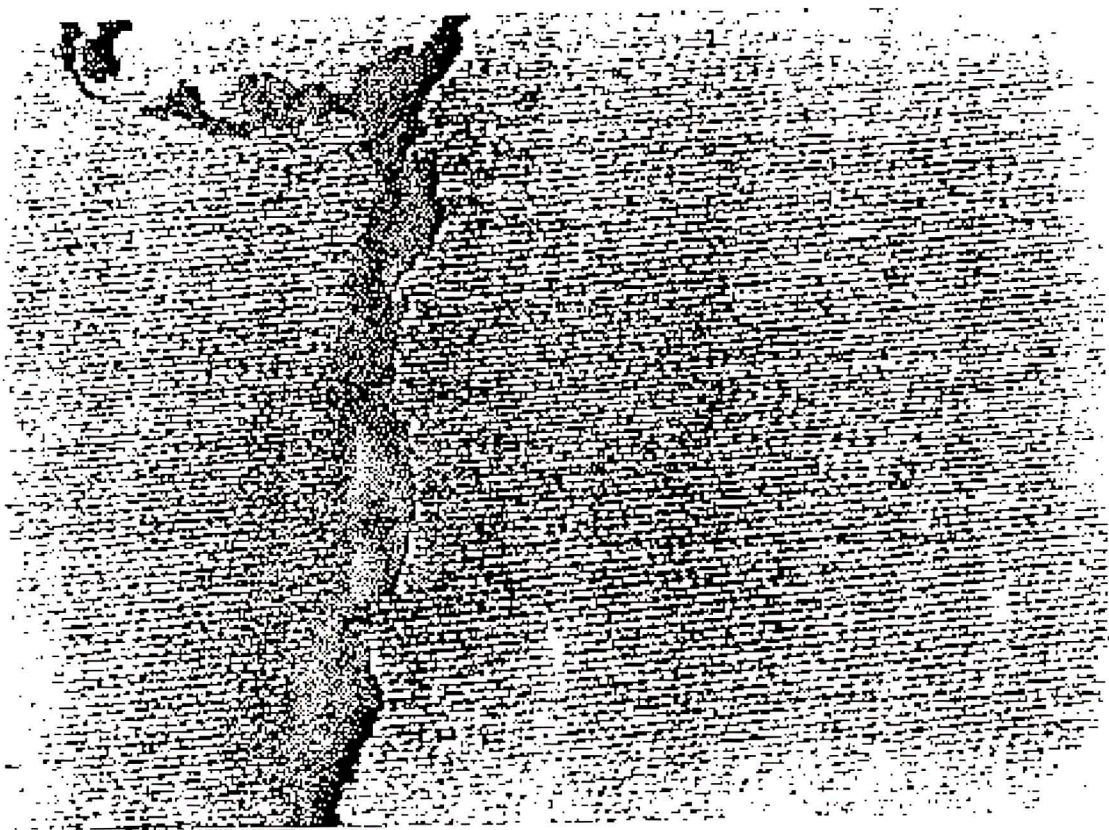
For recovery operations on chemicals on the sea surface, suitably selected containment and retrieval devices of the kind used for oil recovery could be employed, according to circumstances.

The experimental work carried out by Warren Spring Laboratory indicates that several chemicals can be detected by thermal imaging remote sensors and some by SLAR imagery. More extensive sea trials on these chemicals using all available types of sensor could well lead to a means of identifying, if not quantifying, a chemical slick of unknown origin as the detection systems become increasingly sophisticated.

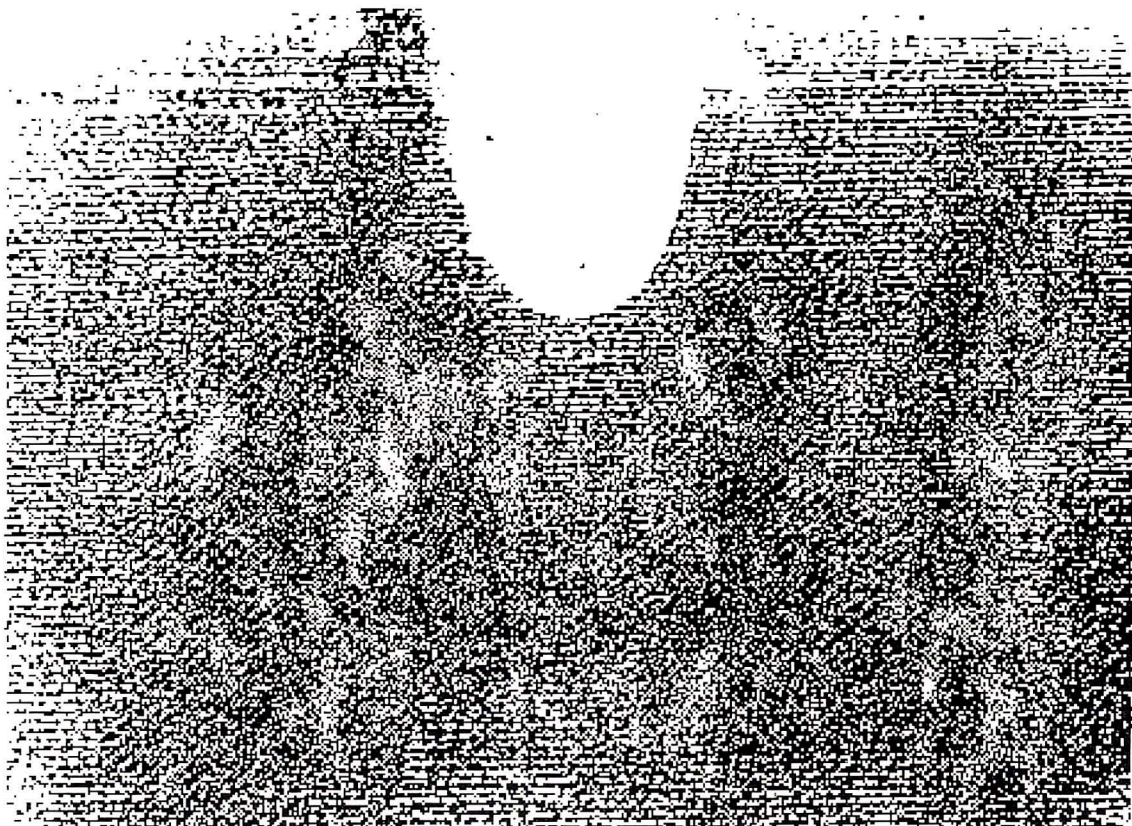
Although experienced observers can assess a situation on the spot and advise on the action to be taken, recorded imagery is very valuable, not simply as a record of the event but also for the development of new analytical techniques.

There are now several software packages available to convert video to digital imagery and then to measure areas and differentiate between areas of different densities and gradually these are being incorporated into on-board computers. The work carried out at Warren Spring Laboratory on the detection of chemicals was essentially a preliminary investigation, limited to thermal infra-red because that equipment was the most readily available and considered from past experience to be likely to produce imagery of some chemicals.

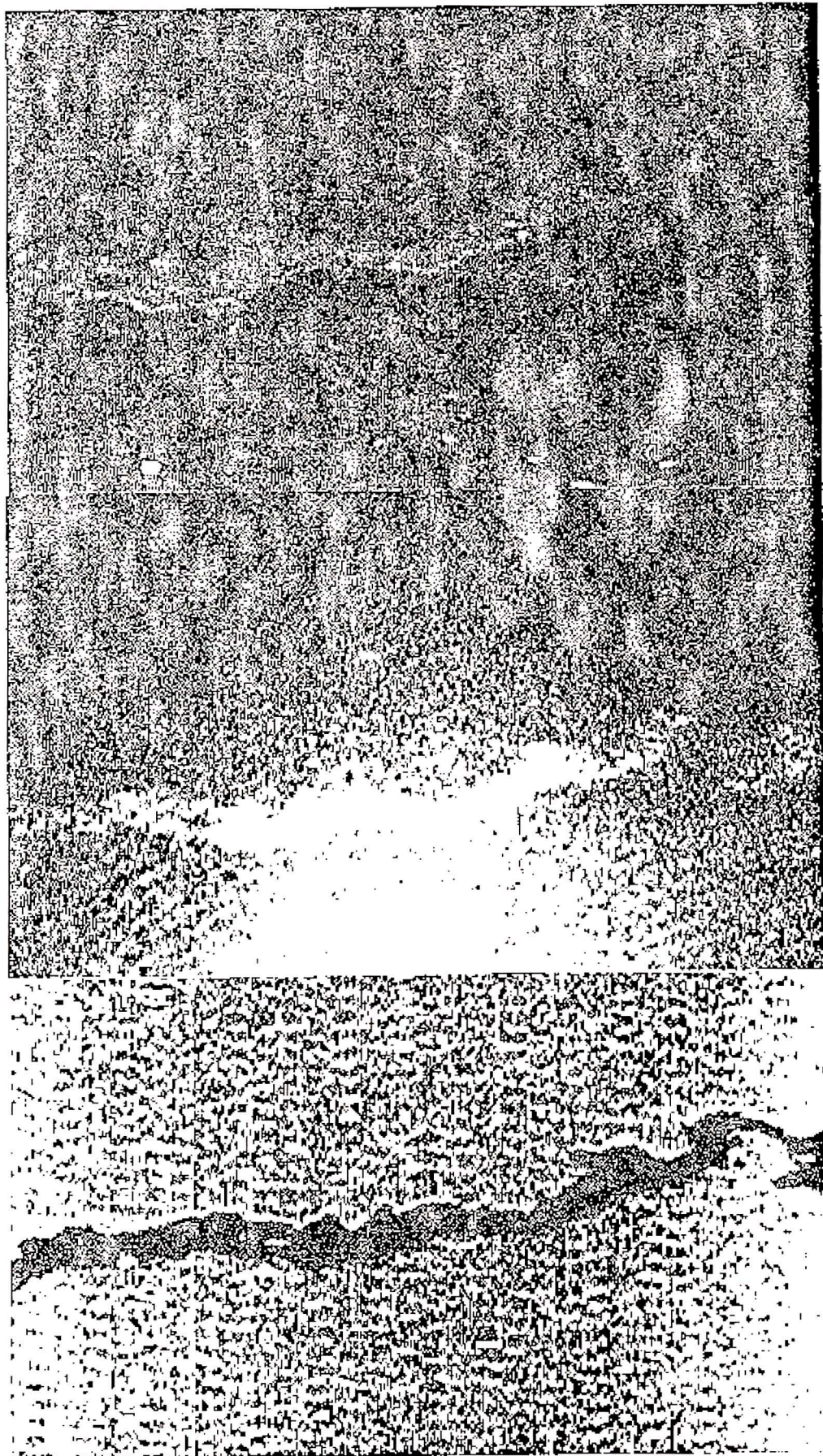
Other sensors may detect different ranges of chemicals thus enabling a number of the chemicals to be identified. Between them the Bonn Agreement and other EC countries have a wide range of airborne sensors. The in-depth investigation of the ability of these sensors to detect chemicals would be an expensive operation, in terms of manpower, transport, equipment and materials, for any one country. Ideally a series of pilot-scale trials could be set up, involving all interested European nations, to examine the responses of different sensors to various chemicals. Where these trials yield positive results they could be followed up by sea trials. In this way each interested nation could participate in the investigation and the cost would be shared.



*Fig. 4 - I-R Imagery of Cyclohexane from Cessna 404 at 170 Feet.*



*Fig. 5 - I-R Imagery of Nonyl Acetate from Cessna 404 at 170 Feet.*



VISUAL

UV IMAGERY

IR IMAGERY

*Fig. 6 - Imagery of Toluene Slick from Cessna 404 at 510 Feet.*

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**NOTES:**

- A. Dimensions can be obtained by timing aircraft flights over major axes of slick if the ground speed of the aircraft is known.
- B. Provision may be made for the recording of position and altitude data, etc, on a specialised data-back camera.
- C. Provision may be made for the display (on the monitor) and recording of position and altitude data, etc.
- D. Thickness can be evaluated subjectively using colour tables.
- E. Depends on visibility and viewing angle.
- F. Range depends on altitude and the acceptance angle of the camera/video lens.
- G. IR indicates different relative thicknesses.
- H. MW footprint is too narrow to allow assessment of slick width.
- J. Calibration is not unambiguous in systems currently in use. This is a field in which developments are taking place and it is anticipated that much greater accuracy can be achieved in the near future.
- K. LF sensors under development are forecast to be able to detect thickness.
- L. Generally 1.5 times the altitude.
- M. Assumed to be 0.5 times the altitude.
- N. Generally up to 20 kilometres (can be extended to 40 km but beyond 20 km little or no detail can be distinguished in the imagery).