APPLICATION OF GAS CHROMATOGRAPHY USING NITROGEN-SELECTIVE DETECTION TO OIL SPILL IDENTIFICATION

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SUMMARY

The use of a gas chromatograph employing a 36-m SE-30 glass SCOT column with dual flame-ionization–nitrogen–phosphorus detection (NPD) for oil identification is described. A rapid extraction and concentration procedure for increasing the size of NPD peak patterns from oils of low N-content and eliminating spurious peaks due to excess aliphatic hydrocarbons is presented. Studies of artificially "weathered" oils indicate that the gas chromatographic–NPD fingerprint of light distillate oils is lost, but that of heavier oils is unchanged. The capabilities and limitations of the gas chromatographic–NPD fingerprints for oil identification are illustrated with reference to real spill case samples.

INTRODUCTION

Gas chromatography (GC), with its unparalleled separation efficiency, is especially suitable for forming a fingerprint of the complex mixtures of compounds which make up petroleum oils. Such fingerprints can be used to match an oil spilled on water to its source in order to assist in establishing legal responsibility for the consequences of the spill. By splitting the effluent from the GC column to a flame-ionization detector (FID) and a flame-photometric detector (FPD) tuned to respond to organic sulfur-containing compounds, we have been able to acquire two independent GC fingerprints simultaneously[1]. Another element often found in some oils is nitrogen[2,3], and thus a thermionic nitrogen-selective GC detector would provide yet another oil fingerprint from a GC effluent. The operation and applications of the newer forms of such nitrogen–phosphorus detectors (NPD), which employ independently heated rubidium glass beads, are described by Kolb and co-workers[4,5].

Lee *et al.*[6] described the use of the NPD with glass capillary columns for the forensic analysis of used engine oils. They observed many NPD peaks which appeared to result from nitrogen compounds produced in the oil by the operation of the engine and whose patterns depended on the particular engine and its operating conditions. Glajch *et al.*[7] have employed the NPD for the characterization of coal tar and petroleum pitches by pyrolysis GC. We have previously described our preliminary evaluation of the NPD for GC oil fingerprinting[8,9]. Using packed OV-101

columns we found that one must use dual FID–NPD detection to assess the contribution of spurious FID response from the NPD due to high concentrations of simultaneously eluting hydrocarbons. There was some question of the value of the NPD fingerprints for oil identification since oils of similar geological origin displayed very similar NPD patterns. To address this latter problem we surveyed over 70 different crudes, distillates, lube oils and synthetic oils from both similar and different geological sources, using dual FID–NPD detection with a 15.75-m Dexsil-300 SCOT column operating under conditions specified for the U.S. Coast Guard's oil spill identification system[1]. The chromatograms of this survey have been published along with an alumina adsorption column procedure for isolating and concentrating the compounds producing the NPD patterns[10]. The data in that report supported the conclusion that there is sufficient variability among high resolution GC–NPD patterns of oils to warrant the use of the NPD for oil fingerprinting.

The purpose of this paper is to present NPD fingerprint data obtained from artificially weathered oils and real spill cases and to assess the usefulness of such fingerprints in oil identification. We also present a new extraction procedure to concentrate the N-containing oil fraction to enhance the GC–NPD patterns of oils of low nitrogen content, and describe some of the problems inherent with the application of the NPD to oil identification.

EXPERIMENTAL

Chromatography parameters

Chromatograms were obtained with a Perkin-Elmer 990 GC equipped with an AS-41 automatic, solvent-free, capsule injection system. The column was a 36 m × 0.5 mm SE-30 glass SCOT manufactured by Scientific Glass Engineering (North Melbourne, Australia). For the period covered in this work we calculated a theoretical plate value of 35,000 for hexadecane run at 180° and a resolution value of 21 for the hexadecane–octadecane peaks. The column was pressure controlled to give a flow-rate of 4 ml/min at room temperature for helium. The column oven temperature was programmed from 75 to 300° at 8°/min and held for 16 to 32 min for light and heavy oils, respectively. These flow and temperature conditions sacrificed some resolution to attain more rapid sample throughput of the heavier oils. The injector temperature was 250° and the manifold and detector blocks were at 325°. Helium carrier make-up gas was supplied at 40 ml/min to the column effluent and this was then split in a ratio of 1:1 to the FID and NPD.

Detector parameters

The FID was operated to produce a maximum response with a hydrogen flow-rate of 21.6 ml/min and an air flow-rate of 353 ml/min. Note that FID curves are displayed inverted above the NPD curves in this paper.

The response of the Perkin-Elmer NPD was a complex function of carrier, hydrogen and air flow-rates as well as the heating current supplied to the rubidium silicate bead. We optimized the response according to the manufacturer's instructions to give a selectivity ratio of 10^5:1 for N,N-dimethylaniline *vs.* light *n*-alkanes. This was achieved with an air flow-rate of 100 ml/min and a hydrogen flow-rate of 2.8 ml/min. Some sensitivity was sacrificed by using a power supply potentiometer

setting of 560 corresponding to a heating current of 2.8 A through the bead. This setting was used to prolong the bead life, and it kept the NPD sensitivity relatively constant over a period of six months. Lubkowitz et al.[11] have recently discussed the effects of these parameters on NPD response reproducibility.

In our previous work with this NPD, we reported that an electrode polarity setting of 2 on the detector power supply module gave much better selectivity for nitrogen compounds at the cost of some sensitivity. Consequently, all work in this report was done at the same setting. It was later discovered that with the SCOT column flow parameters used in this work, the higher sensitivity polarity setting 3 would produce the more selective response. This behavior is consistent with the change in carrier flow parameters when switching from packed column to SCOT column operation[12]. More recent NPD designs have dispensed with the polarity variation as an unnecessary complexity.

Oil sample preparation

Heavy oils were pentane-deasphalted, dried over anhydrous $MgSO_4$ and stripped of pentane (DDS), according to the procedure in ref. 1. With heating of the sample when necessary, quantities of less than 1.0 μl were dispensed from a syringe into the injection capsules. Lighter oils were loaded into the capsules without treatment (NEAT).

Methanol extraction procedure

Weigh 0.2 g of DDS or NEAT oil into a 16 × 125 mm disposable culture tube and add 1.0 ml of pentane and 5.0 ml of a solution 10% (v/v) of water in methanol. Vortex 30 sec, centrifuge if necessary to separate phases, remove the pentane layer and transfer the methanol–water layer to a 10-ml conical-bottom centrifuge tube. Evaporate the solution to dryness under nitrogen flow at 100°, re-constitute the dried sample with 100 μl of toluene and transfer 5.0 μl of this solution to a GC injection capsule and allow the toluene to evaporate under a gentle stream of nitrogen before sealing the capsule. The NPD pattern of such a sample is ap-proximately equivalent to that from a 12-μl injection of the NEAT or DDS oil with almost complete elimination of spurious FID response peaks.

RESULTS AND DISCUSSION

The FID and NPD curves labeled A in Fig. 1 are from the injection of 0.2 μl of NEAT API No. 2 fuel oil. The NPD curve illustrates several general features of NPD oil fingerprints. The majority of the small peaks appearing before 20 min result from the spurious FID response of the NPD to the much higher concentration of aliphatic hydrocarbons eluting during this time. Note the apparent reflection of the upper, inverted, highly attenuated FID curve above the NPD curve.

The peaks labeled X and Y are frequently seen contaminants in our oil samples which are not of petroleum origin. We suspect that they originate from containers in which the oils are shipped as their concentrations are erratic and variable among samples of the same oil and often increase with time. Such contaminant artifacts are often unavoidable with detectors of such great sensitivity as the NPD and the analyst must become familiar with their appearance in order not to be confused in
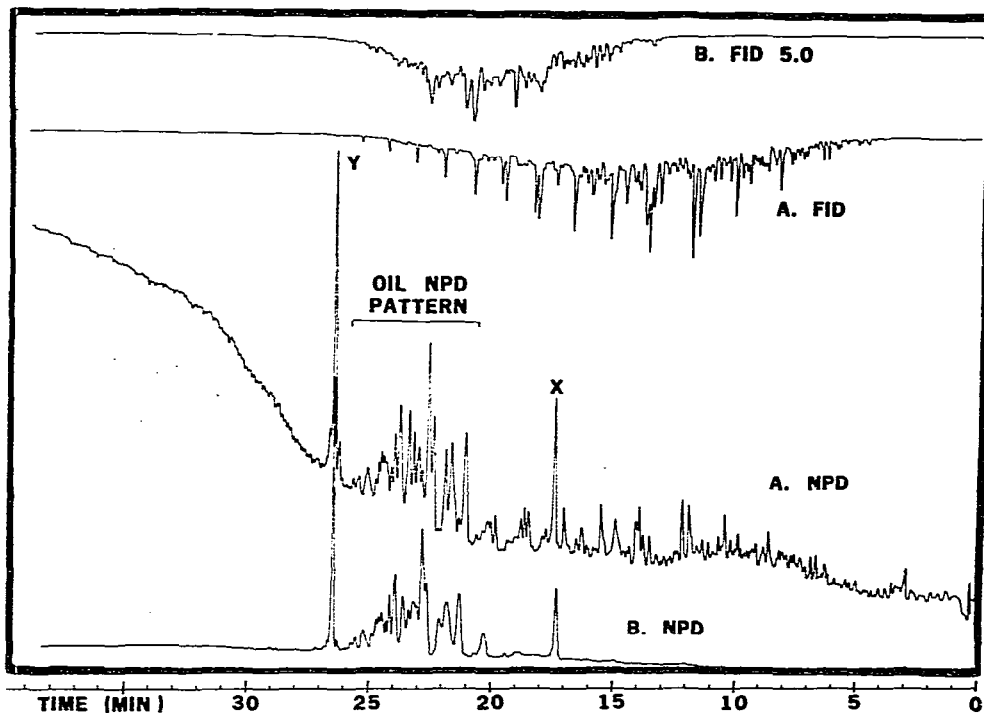
Fig. 1. Dual FID–NPD GC curves of NEAT and methanol extracted API No. 2 oil. (A) 0.25 μl NEAT oil, FID ×3200, NPD ×2; (B) 5.0 μl of toluene-reconstituted methanol extract, FID ×3200, NPD ×32.

the interpretation of the fingerprint. Another source of NPD contaminant patterns (illustrated in ref. 10) is the Apiezon M grease used as a lubricant in the AS-41 capsule injection system. These latter patterns can be eliminated by careful cleaning of the system and the use of Dow Corning silicone grease on the capsule holding magazines. Chromatographers using syringe injection techniques will need to investigate the contribution of septum bleed to the NPD peak patterns.

The apparent column bleed in the NPD curve, for times greater than 26 min, is often observed at high sensitivity. It does not result from decomposition of the stationary phase or from the light oil injected, but is the prolonged tail of the unresolved envelope of nitrogen compounds from the preceding GC analysis of a very heavy residual oil with a high nitrogen content. Such an artifact is not noticed when many such heavy oils are run in succession, but it will be evident in the NPD curves of immediately succeeding light oils. It can be eliminated by cycling the GC through several temperature programs before examining a series of light oils.

The resolution of the NPD peaks displayed in Fig. 1 is not as complete as that seen in earlier work (cf. ref. 10, Fig. 6). It is adequate, however, to produce a distinctive NPD fingerprint, and most importantly, this fingerprint will display the same pattern if the oil is repeatedly analyzed over a period of one to two weeks. As is the case with other GC oil fingerprinting methods, we recommend that oils to be matched by GC–NPD patterns be analyzed in a continuous sequential series on the same column.

We have observed[10] that many oils contain such small NPD patterns when analyzed NEAT or DDS that a concentration procedure for the nitrogen compounds which also removes the bulk of the hydrocarbons producing the spurious FID response is required. We previously described[9,10] such a procedure employing adsorption of the oil on a 5% water-deactivated alumina column followed by elution with pentane and benzene and concentration of the benzene effluent. While it is effective, it is cumbersome and time consuming to apply it uniformly to all the samples of a large spill case. Simple extraction procedures involving vortexing and pipet transfers between tubes are more suitable for large sample loads. Lee et al.[6] recommended nitromethane to extract the NPD fingerprints of used engine oils, but this solvent presents problems of toxicity and flammability. Saner et al.[13] have demonstrated that methanol successfully extracts most of the heavier aromatic compounds from oils for HPLC–fluorescence analysis. As we expected that most, if not all, of the NPD peaks we observe in the characteristic oil patterns result from large N-heterocycle compounds, we developed the simple methanol extraction and concentration procedure described in the experimental section. The combined effects of the variables of each solvent concentration as well as the percentage of water in the methanol solvent were optimized using a three dimensional, two level, factorial design. The optimized procedure was then tested by triplicate extractions for each of four different oils. The NPD fingerprints of the replicated extracts were indistinguishable. Fig. 2 shows the NPD patterns of 3 successive extractions of both
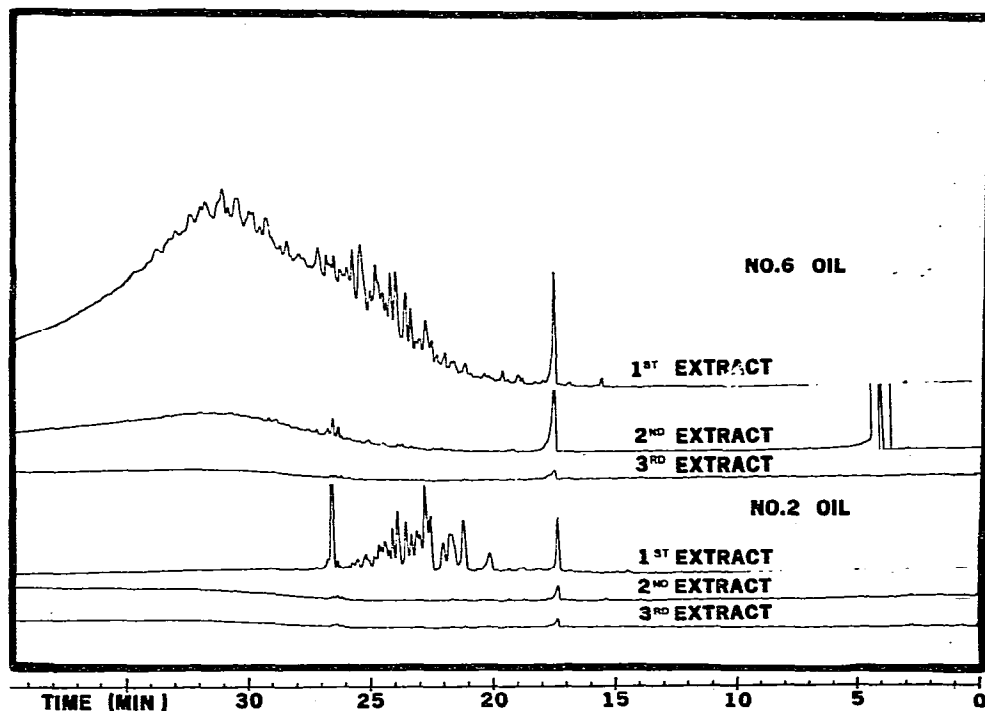

Fig. 2. GC–NPD curves of 5.0 µl of toluene-reconstituted successive methanol extractions of No. 6 and No. 2 oils. NPD ×32.

heavy and light distillate oils. These data as well as identical experiments on crudes indicate that the single step extraction recovers at least 90% of the compounds producing the NPD pattern.

Curves B of Fig. 1 display FID and NPD patterns of the methanol extracts of the same API No. 2 oil as the NEAT curves A. The FID pattern illustrates the loss of n-alkanes and is likely to be composed mostly of the more polar compounds extracted into the methanol. The NPD pattern is similar to that of the NEAT sample of curve A, but the larger attenuation used illustrates the concentration factor attained. Note the degraded resolution of the early NPD peaks and the shift in peak retention times of the extract curve relative to the NEAT curve. This behaviour was consistently observed with the methanol extracts of light oils, and this chromatogram displays the worst instance of the phenomenon we have observed. This may be associated with an unusually large amount of co-eluting aromatic compounds which are seen in the FID curve to have been extracted from this light distillate. However, the altered NPD patterns observed from the extracts of such oils were consistently repeatable, and this is the prime criterion of an identification method. On the other hand, the NPD patterns of the extracts of heavier oils and crudes were indistinguishable from the NPD patterns of DDS samples except in magnitude.

The NPD fingerprint pattern of an oil spill may differ from the original source oil if some of the nitrogen compounds evaporate, dissolve into the water column, biodegrade or are photochemically altered. Such weathering (WX) effects distort the fingerprints observed with other analytical methods as well. To study this problem, a series of 4 different oils were subjected to controlled simulated weathering conditions in tanks of sea water at the Research Institute of the Gulf of Maine (TRIGOM), and the changes in the GC–FID oil fingerprints resulting from this treatment have been described[14]. We used the same TRIGOM weathering series sample set to evaluate the effects of weathering on GC–NPD fingerprints.

Fig. 3 displays the effect of weathering on two light oils. Curves A and B indicate that the NPD pattern of a No. 2 oil is degraded immediately. and after 4 days of weathering it had disappeared completely. The pattern of a No. 4 oil was stable for one day, but 4 days weathering also eliminated its NPD fingerprint. From these data and other cases we conclude that GC–NPD patterns are unsuitable for fingerprinting spilled light distillate oils, after weathering has occurred.

Fig. 4, curve A displays the NPD curve of a DDS sample of the unweathered TRIGOM crude. This oil is a Louisiana crude with a very low content of nitrogen compounds, and the peaks seen in curve A are either contaminants or spurious FID response. This oil requires the use of the methanol extraction procedure to produce usable NPD fingerprints, as illustrated in curves B through D. These NPD curves show that the patterns of this crude are unaffected by weathering. The NPD pattern of the methanol extract of a different Louisiana crude is displayed in curve E. Because of its similar geological origin, this oil has an NPD pattern very similar to that of the TRIGOM crude, but the enhancement of the patterns produced by the extraction and concentration procedure can allow the possibility of distinguishing the oils.

Fig. 5 displays the NPD patterns of the weathering series of a heavy residual oil, and the curves illustrate the excellent stability of the nitrogen fingerprint with respect to weathering for such oils. The compounds forming many of the peaks of
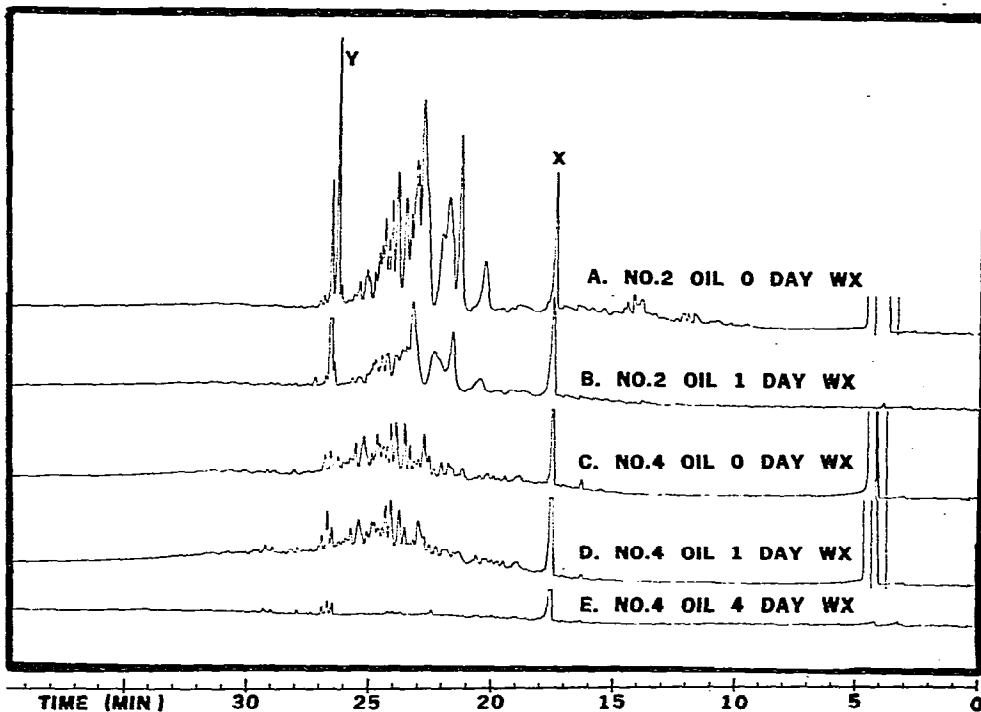
Fig. 3. GC–NPD curves of 5.0 µl of toluene-reconstituted methanol extracts of TRIGOM light distillate oils weathering series. NPD ×32.
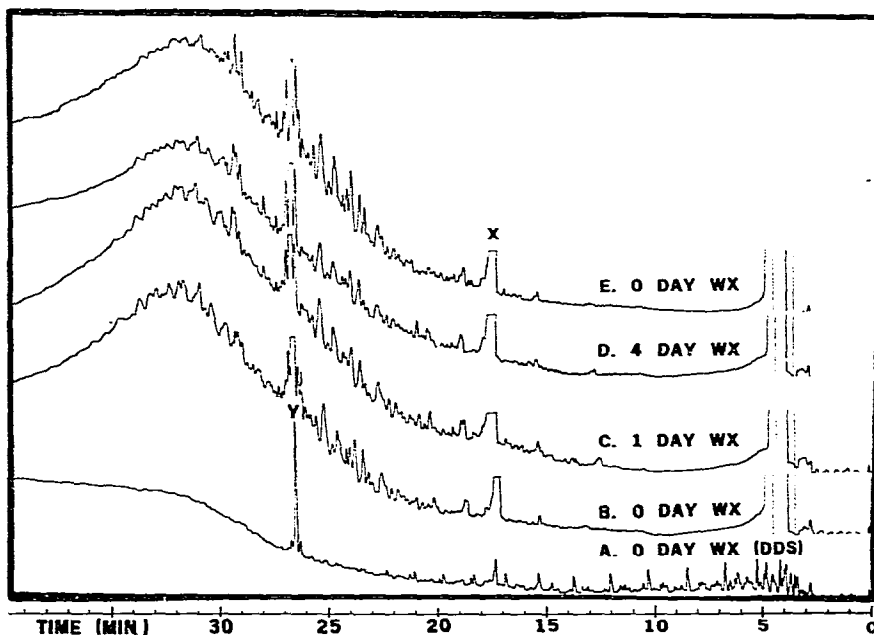

Fig. 4. GC–NPD curves of weathered TRIGOM crudes, NPD ×4. (A) 0.5 µl DDS unweathered; (B) 5.0 µl methanol concentrate unweathered; (C) 5.0 µl methanol concentrate 1 day WX; (D) 5.0 µl methanol concentrate 4 days WX; (E) 5.0 µl methanol concentrate unweathered S. La. crude.
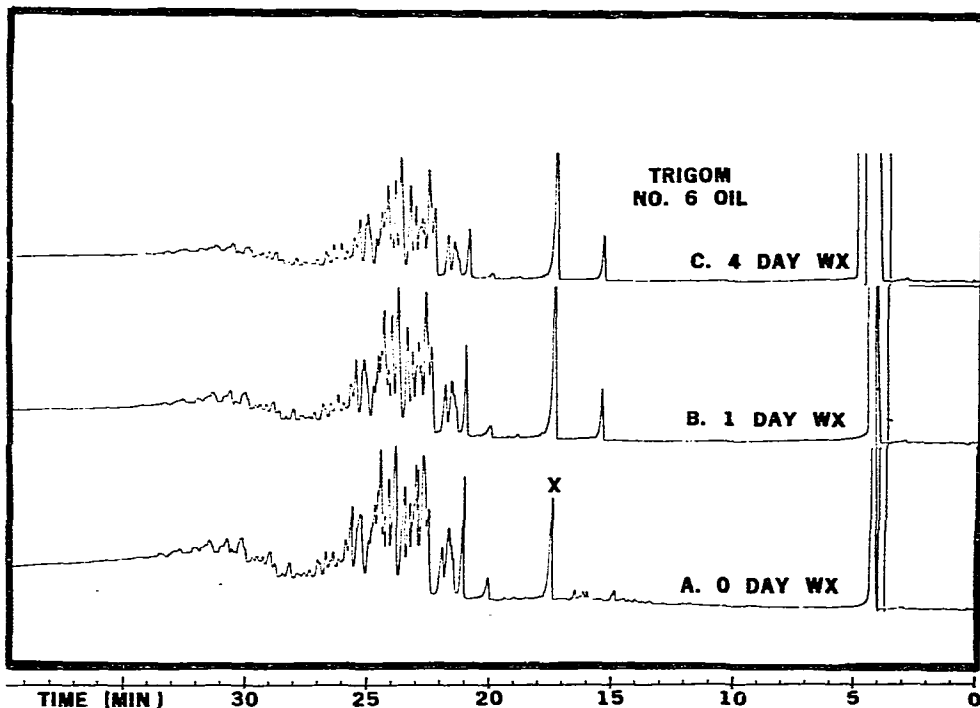
Fig. 5. GC–NPD curves of 5.0 µl of toluene-reconstituted methanol extracts of TRIGOM No. 6 oil weathering series. NPD ×32.

the NPD patterns are likely to be the same in both heavy and light oils, since there are often similarities in the patterns and retention times which are observed[10]. In view of the long retention times of characteristic NPD peaks seen in petroleum oils, the compounds forming them probably have limited volatility at ambient temperature and are polar in nature. It is therefore likely that the primary mechanism for the weathering losses of most of these compounds is dissolution into the underlying water, and this process is likely to proceed less efficiency from the more viscous heavy oils.

Fig. 6 displays the NPD chromatograms of spill and source oils from two spill cases in which positive matches had been previously obtained by the U.S. Coast Guard's four-method (GC, thin-layer chromatography, IR and UV fluorescence) oil identification system[1]. The methanol extract GC–NPD patterns of case 1 also match excellently. The peak patterns of the DDS samples of case 2 also tend to confirm the match in that case. The spill samples display variable quantities of some NPD peaks in the latter parts of the chromatograms. This behavior indicates that the spill samples may have been slightly contaminated with small variable amounts of NPD-responsive compounds, which, however had no effect on the fingerprints of the other methods. The appearance of this type of contamination lessens the usefulness of the NPD fingerprint.

Such small contaminant NPD peaks have been seen in other spill samples, and we believe then to be due to compounds of biological origin which have been
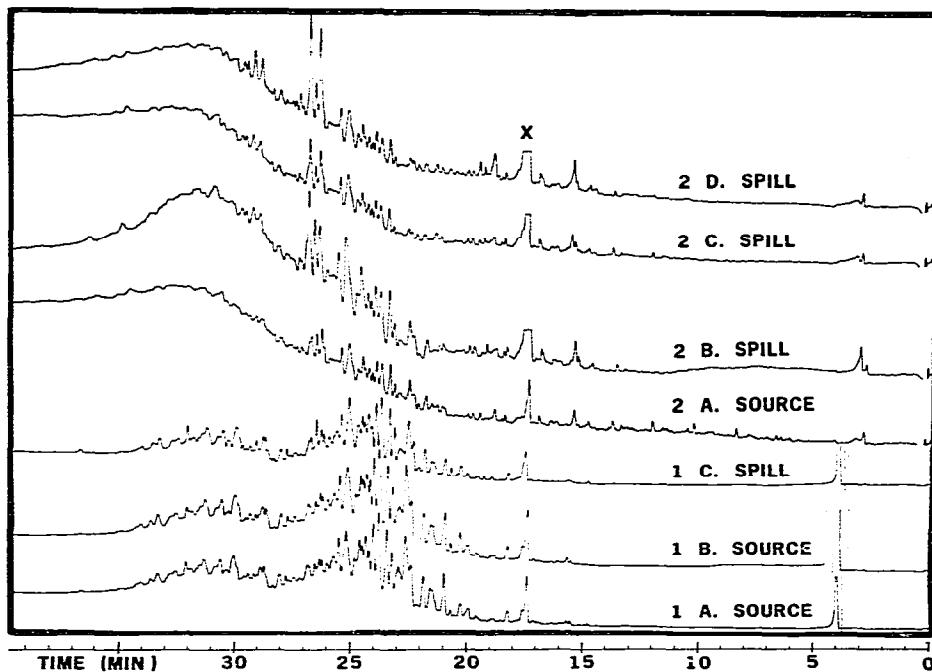
Fig. 6. GC–NPD curves of matched source and spill samples from two real spill cases. Case 1, 5.0 μl methanol concentrates NPD × 32; case 2, 0.5 μl DDS NPD × 4.

picked up by the spilled oil during its movement on the water. Our more time consuming alumina adsorption concentration procedure[9,10] has often succeeded in removing such contaminant peaks without affecting the NPD peak pattern of the oil fingerprint. Our experience with a KOH–methanol saponification and extraction procedure for removing contaminants of this type[15] indicates that the methanol extraction procedure for NPD pattern concentration would have carried along these contaminants.

There is no evidence of weathering degradation of the NPD fingerprints in either case, despite the fact that the FID curves showed that weathering occurred on the case 2 spill samples.

Fig. 7 displays an unusual dual FID–NPD trace from a real spill sample. The FID pattern is characteristic of a lube oil, and unused lube oils are generally found to be free of NPD peaks[10]. The very large, complex NPD pattern displayed in this sample bears no relation to any patterns we have seen which originate from petroleum products[10]. The peaks may have been generated during engine operation in the manner described by Lee et al.[6]. The source sample was matched by the four method technique[1], and while the relative NPD peak heights differed substantially between the source and the spill, the same unusual series of peaks appeared in both samples. Thus it is possible that the NPD can be used to advantage for fingerprinting spilled lube oils if a sufficiently unique series of NPD peaks appears in both the source and spill oils, even though weathering effects may change the relative peak heights.

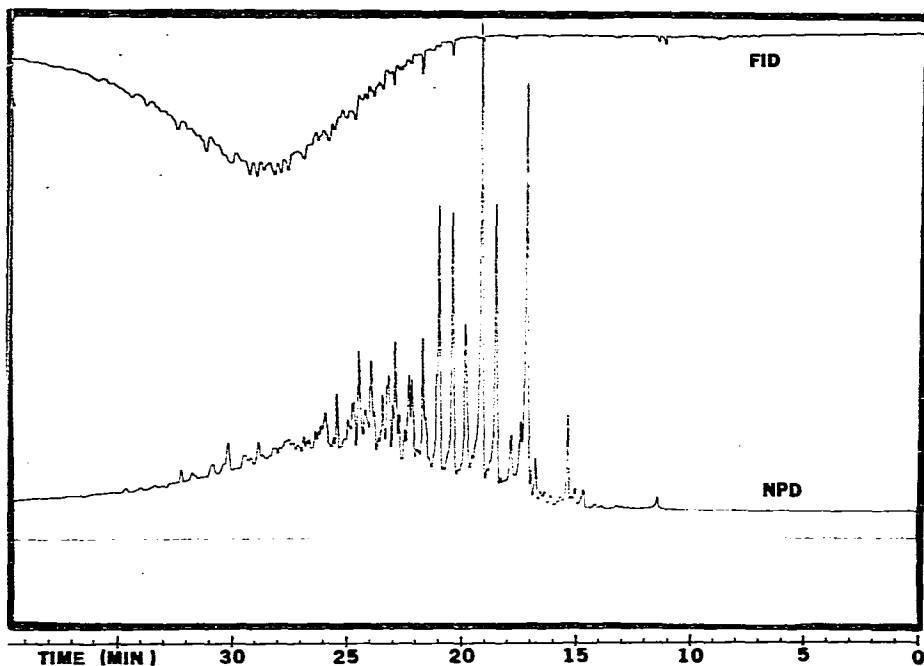Fig. 8 illustrates both favorable points and disadvantages of the use of GC–

TIME (MIN)   30   25   20   15   10   5   0

Fig. 7. Dual FID–NPD GC curves of 0.5 μl DDS lube oil spill sample. FID ×1600, NPD ×128.

TIME (MIN)   30   25   20   15   10   5   0
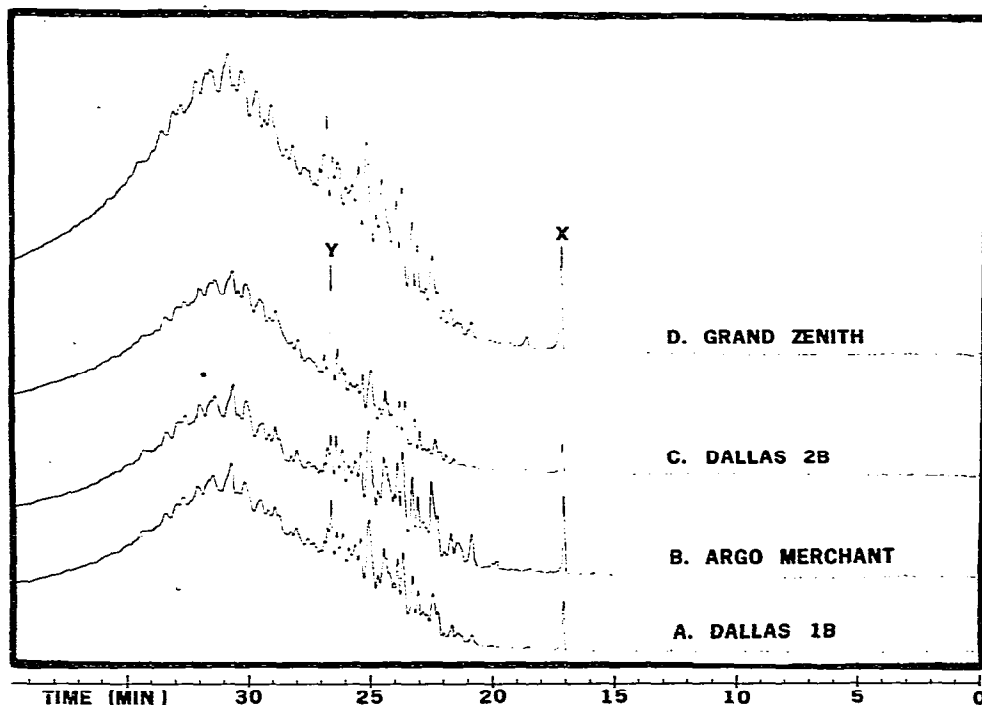
Fig. 8. GC–NPD curves of 5.0 μl of toluene-reconstituted methanol extracts of two matched source-spill pairs. NPD ×32. (A) 1st spill sample taken by Cutter *Dallas*; (B) *Argo Merchant* cargo sample; (C) 2nd spill sample taken by Cutter *Dallas*; (D) *Grand Zenith* cargo sample.

NPD fingerprints of heavy residual oils. Curves B and D are from samples of the cargos of the grounded tanker *Argo Merchant* and the missing tanker *Grand Zenith*, respectively. Curve A is from an oil slick picked up by the USCG Cutter *Dallas* three weeks after the *Argo Merchant* grounding over 320 nautical miles distant. The four-method oil identification system positively matched samples A and B, and it is thus satisfying to see how well the NPD fingerprints match even after the long exposure of the spill sample to weathering conditions. Curve C is from another oil slick sampled by the *Dallas* which was positively matched by the four-method system to sample D. Again the NPD patterns are also matches except for some easily recognized contaminants. The problem arises from the fact that all 4 NPD fingerprints are sufficiently similar that the spills could not be distinguished from the two possible sources or from each other. However, when the other 4 fingerprinting methods were applied to these pairs of matching spills and sources, there was no problem distinguishing them from each other. This demonstrates the advantages of using multiple identification techniques. Our atlas of dual FID–NPD chromatograms of oils[10] contains additional instances of dissimilar oils which possess very similar NPD fingerprints, and this circumstance increases the probability of obtaining an indeterminate result or a false identification with GC–NPD fingerprints unless other fingerprinting methods are also applied to the samples.

CONCLUSION

The GC–NPD fingerprints of oils can provide useful additional information for the identification of oils spilled on water subject to the following qualifications.

(1) The NPD patterns of light distillate oils are likely to be distorted or removed by weathering effects and must be used with caution for fingerprinting.

(2) Additional fingerprinting methods must be applied to the oils to allow for the possibility that the NPD patterns of some different oils may appear identical. Thus the GC–NPD fingerprint serves, at best, as a confirming analysis, not as a primary identification method.

(3) Oils of low nitrogen content require the use of an extraction and concentration procedure to produce NPD patterns of a size adequate for fingerprinting. The NPD patterns of such extracts are sufficiently reproducible for this purpose.

(4) The high sensitivity of the NPD detector, combined with the small quantity of nitrogen compounds forming the NPD pattern of an oil, renders the GC–NPD fingerprint more susceptible than the GC–FID fingerprint to contaminants and other artifacts. Our experience shows that these can be recognized by the analyst or eliminated by additional sample preparation.

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