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Determination of aldehydes in used engine oils by liquid chromatography with chemiluminescence detection

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Abstract

Straight-chain aliphatic aldehydes (C_6–C_{14}) were selectively derivatised in oxidised engine-oil dialysates with the fluorophore 3-aminofluoranthene. The derivatives were separated by reversed-phase liquid chromatography on a mid-bore (3.2 mm I.D.) column and detected by monitoring the chemiluminescence emission from a post-column reaction with bis-(2,4,6-trichlorophenyl)oxalate and hydrogen peroxide. Calibrations for the aldehydes in an oil matrix ($0–5.0 \cdot 10^{-4}$ mol l^{-1}) were linear ($0.9980 < r^2 < 0.9997$) with limits of detection ($S/N = 3$) in the range $3.0 \cdot 10^{-7}$–$3.4 \cdot 10^{-6}$ mol l^{-1} (0.7–75 fmol on-column). Analysis of oil samples taken from an engine test at different times (0, 16, 24 and 32 h) showed that the concentration of aldehydes increased throughout the duration of the test.

1. Introduction

The oxidation of oils in engines results in the formation of polar oxidation products including alcohols, aldehydes, ketones, carboxylic acids and water [1]. These species undergo further reactions to form sludges which degrade the performance of the oil. Characterisation and measurement of the polar oxidation products is therefore useful in monitoring the degradation of engine oils and elucidating the oxidation pathways.

Procedures for the determination of carboxylic acids in used engine oils by liquid chromatography (LC) with chemiluminescence (CL) [2] and fluorescence detection [3] have been described. As aldehydes are intermediate in the oxidation process it would be advantageous to monitor them in conjunction with the carboxylic acids in order to obtain a greater understanding of the oxidation process.

Ultraviolet (UV) absorbing [4,5] and fluorescence [6–9] labels based on nucleophilic addition to the aldehyde with nitrogen containing nucleophiles, e.g. oximes, hydrazines and semicarbazides, have been used for the pre-column derivatisation of aldehydes and photo-initiated peroxyoxalate CL has been applied to the detection of dansylhydrazone derivatives of airborne aldehydes [10]. However, all of these reactions were carried out in aqueous conditions which are incompatible with a used oil matrix.

A procedure for the labelling of aldehydes and ketones, based on reaction with 3-aminofluoran-

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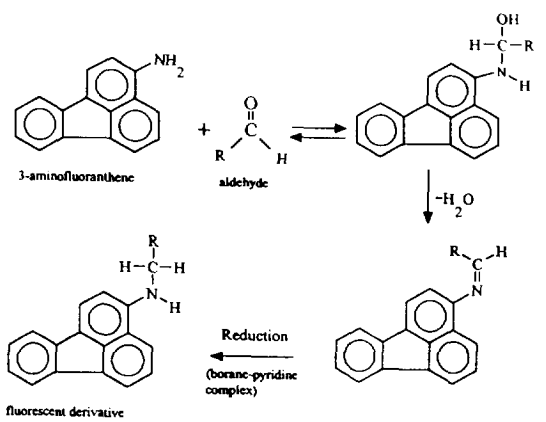

Fig. 1. Reductive amination of aldehydes with 3-aminofluoranthene in the presence of borane–pyridine complex as a reducing agent. R = aliphatic or aromatic substituent.

thene in non-aqueous media, followed by fluorescence and peroxyoxalate CL detection, has been reported [11]. The reaction scheme involved reductive amination of an aldehyde with 3-aminofluoranthene in the presence of a reducing agent (borane–pyridine complex) and is shown in Fig. 1. The high CL efficiency of amino polycyclic aromatic hydrocarbons (amino-PAHs), including 3-aminofluoranthene, has been studied and used to quantify amino-PAHs in shale and coal oils [12]).

This paper describes a procedure for the determination of aliphatic aldehydes (C_6–C_{14}) in oxidised engine oils by off-line derivatisation with 3-aminofluoranthene followed by removal of excess label by solid-phase extraction and isocratic reversed-phase LC with post-column peroxyoxalate CL detection. Results are presented for a series of oxidised oils sampled from a test engine after different periods of operation (0, 16, 24 and 32 h) using the optimised procedure.

2. Experimental

2.1. Reagents

High quality de-ionised water from a Milli-Q system (Millipore, USA) and analytical grade reagents were used unless otherwise stated. Acetonitrile (ACN), tetrahydrofuran (THF), hexane, ethyl acetate and toluene were of HPLC grade (Rathburn, UK).

Solutions of 3-aminofluoranthene (Janssen, Belgium) were prepared daily in acetic acid (glacial, BDH, UK)–toluene (2:7, v/v). The borane–pyridine complex (BAP, Aldrich, UK) was used as the liquid. Solutions of hexanal (C_6), octanal (C_8) (both Aldrich), decanal (C_{10}), dodecanal (C_{12}) and tetradecanal (C_{14}) (all Fluka, UK) were prepared in toluene. All aldehydes were of reagent grade.

Imidazole buffer ($3.0 \cdot 10^{-2}$ mol l^{-1}, pH 7.5) was prepared by dissolving imidazole (Fluka) in water; the pH was adjusted with nitric acid (0.1 mol l^{-1}, Merck, UK). Mobile-phase solvents were degassed in an ultrasonic bath for 10 min immediately before use. A mixed CL reagent of bis-(2,4,6-trichlorophenyl)oxalate ($1.3 \cdot 10^{-3}$ mol l^{-1}; TCPO, Fluka) and hydrogen peroxide ($8.8 \cdot 10^{-2}$ mol l^{-1}; Fluka) was prepared by dissolving 0.120 g TCPO in 198 ml acetonitrile, adding 2.0 ml of 100 volume (30%, m/v) stock hydrogen peroxide solution and mixing the combined solution in an ultrasonic bath for 15 min. This mixed reagent solution was left to stand for 45 min before use. Fresh CL reagents were prepared daily.

The oil samples were initially fractionated using a continuous dialysis system as described previously [3]. A solution of oil was dissolved in light petroleum spirit (b.p. 60–80°C) and contained in a semipermeable membrane (the molecular mass cutoff was M_r 1000) around which warm petroleum spirit (b.p. 60–80°C) was continuously circulated, allowing low molecular mass material to diffuse through the membrane for 24 h. This was done to remove polymeric additives, organometallic oxidation products and solid debris which could interfere with the pre-column derivatisation.

2.2. Off-line derivatisation

The reaction was carried out at room temperature using the following reaction conditions unless otherwise stated.

Aldehyde standards in toluene, oil dialysate samples and oil dialysates spiked with aldehyde standards (50 μl) were added to a mixture of 3-aminofluoranthene ($1.0 \cdot 10^{-3}$ mol l^{-1} in glacial acetic acid–toluene (2:7, v/v), 2 ml) and BAP (5 μl). Toluene (195 μl) was added to bring the final volume of the reaction mixture to 2.25 ml. The reaction mixture was shaken and an aliquot (100 μl) removed after 3 min for solid-phase clean-up.

Neutral alumina Sep-Pak Plus cartridges (Waters, USA) were used to remove the excess 3-aminofluoranthene before LC analysis of the aldehyde derivatives. Each cartridge was pre-cleaned with 10 ml hexane. A 100-μl sample, dissolved in the reaction solvent mixture, was loaded on the alumina cartridge and the aldehyde derivatives eluted with 15 ml of 20% (v/v) ethyl acetate in hexane. The solvent was removed by rotary evaporation and the residue redissolved in 10 ml acetonitrile–tetrahydrofuran (4:1) prior to LC analysis.

2.3. Instrumentation

A schematic diagram of the instrumental configuration is given in Fig. 2. Samples (5 μl) were injected (Rheodyne Model 7010) into a mobile phase of ACN–THF–imidazole buffer (75:15:10, v/v) pumped at 0.5 ml min^{-1} (Model 9012 inert quaternary pump, Varian, USA). Separation was achieved using a stainless-steel column (250 × 3.2 mm I.D.) packed with Spherisorb S5 ODS2-5 (5 μm, Phenomenex, UK). A Spherisorb S5 ODS2-5 cartridge guard column (Hichrom, UK) was also used. The post-column CL reagent was pumped at 1.0 ml min^{-1} by a peristaltic pump (Gilson Minipuls 2, France) fitted with silicone pump tubing (Labsystems, UK) and merged with the column eluate at a low dead volume stainless-steel T-piece (Anachem, UK) before passing into a photodiode-based CL detector (Camspec CL-1, Camspec, Cambridge CB2 4BG, UK) fitted with a specially designed 120-μl flow cell.

Polyetheretherketone (PEEK) tubing (0.5 mm I.D., 1.6 mm O.D.) was used for all of the connections between the LC pump and the analytical column; polytetrafluoroethylene (PTFE) tubing (0.8 mm I.D.) was used for all other connections. The length of tubing between the T-piece and the flow cell was kept as short as possible (4 cm). The output from the detector was recorded on a strip chart recorder (Chessell BD 4004, UK) and a PC-based integration system (Nelson PC integrator, Perkin Elmer, USA).

Signals were measured manually as peak heights and noise measured as the amplitude of the baseline on the chart recorder. Response factors were determined as the signal-to-noise ratio from the chart recorder and peak areas from the integrator were used for quantitative analysis.

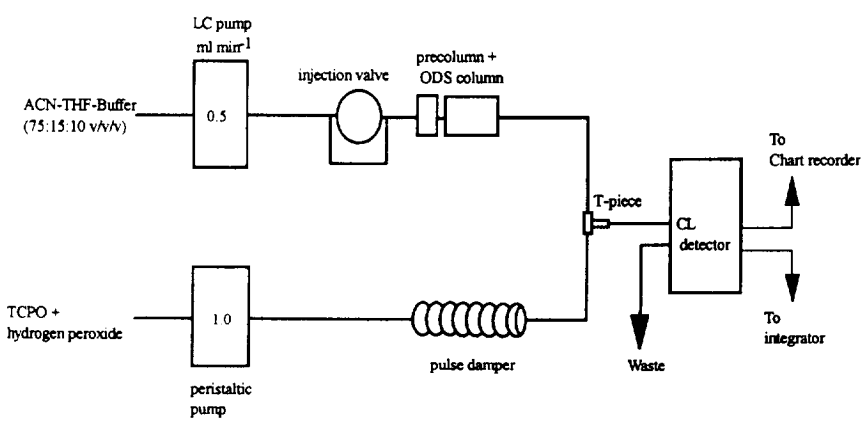

Fig. 2. LC–CL manifold for the determination of aldehydes in a non-aqueous medium.

3. Results and discussion

All concentrations quoted relate to the original sample.

3.1. Off-line derivatisation

Aliphatic aldehydes do not possess a strong chromophore or fluorophore and therefore derivatisation is needed to achieve the required selectivity and sensitivity. The most common derivatising reagent for aldehydes is dinitrophenylhydrazine, which produces strongly UV absorbing hydrazones [4,5]. This method has found wide application in environmental analysis, e.g. automobile exhaust gas [5], indoor and outdoor air [13], and sea and river waters [4]. Fluorescence derivatisation reagents that have been applied to the determination of aldehydes include benzofurazans [6], cyclohexanediones [7], quinolizinocoumarins [8], quinoxalinones [9] and dansylhydrazine [10]. These reagents were unsuitable for application to the analysis of used oils in a process environment because the reaction conditions were either incompatible with the used oil matrix (non-aqueous) or the procedures were lengthy and complex and, in most cases [6–9], the derivatising agent needed to be synthesized and purified prior to use.

Amino-substituted polycyclic aromatic hydrocarbons are amongst the most efficient sensitisers for peroxyoxalate CL [12] due to their low oxidation potentials and high fluorescence quantum yields. Aldehydes and ketones can be labelled with the amino-PAH 3-aminofluoranthene in a non-aqueous medium, which is compatible with the oil matrix, by acid catalysed reduction of the aldehydes in the presence of BAP [11]. Aldehydes react immediately with 3-aminofluoranthene in the presence of BAP, whilst ketones require heating for up to 14 h. Therefore, if no heating is applied, this procedure is selective for aldehydes.

Hexanal ($5.0 \cdot 10^{-4}$ mol l^{-1}) was derivatised with varying concentrations of 3-aminofluoranthene (0–$4.0 \cdot 10^{-3}$ mol l^{-1}) to determine the optimum concentration of the label. The yield of the reaction, measured by the signal-to-noise ratio, was directly related to the concentration of label. However, a large (160 ×) molar excess of the label (ca. $2 \cdot 10^{-3}$ mol l^{-1}) resulted in early breakthrough during solid-phase clean-up due to overloading of the Sep-Pak Plus cartridge. A concentration of $1.0 \cdot 10^{-3}$ mol l^{-1} gave the best compromise between sensitivity and the solid-phase clean-up efficiency.

In a similar manner, the volume of BAP (0–100 μl) added to the reaction mixture was varied using hexanal as the model compound. When no catalyst was present, the derivatisation product was not detected. The optimum level of BAP was 5 μl (the smallest volume that could be added accurately) because volumes of BAP greater than 5 μl decreased the yield of the derivative. This decrease was probably due to the increased formation of non-fluorescent by-products, as no additional peaks were observed in the chromatogram.

The recovery of the aldehyde derivatives (C_6–C_{14}) spiked on a 0-h oil matrix from an alumina Sep-Pak Plus cartridge was in the range 97–100% (duplicate analysis). In addition, the solid-phase extraction procedure removed excess 3-aminofluoranthene label (thus minimising the possibility of further reactions during storage), a compound in the 0-h oil matrix that interfered with the octanal derivative peak and many other compounds in the oil matrix, e.g. phthalate esters which would otherwise accumulate in the LC column. Separation was achieved by greater retention of the more basic components on the alumina cartridge.

3.2. Liquid chromatography

Aryl oxalate esters and solvents are relatively expensive and therefore an LC procedure that reduces CL reagent and LC solvent consumption would be advantageous. This is realised using mid-bore (3.2 mm I.D.) columns, the diameter necessary to reduce the flow-rate of a conventional column (4.6 mm I.D.) by half and still retain an equivalent linear velocity. Furthermore, improved sensitivity for the same injection volume is possible as the peak volumes are lower, leading to less dilution of the injected

sample by the mobile phase, and specialised pumps, fittings or flow cells are not required [14,15]. Use of a larger sample volume with a conventional column would degrade resolution and column lifetime due to the nature of the oil matrix.

For the CL detection procedure reported here, a mixed TCPO-hydrogen peroxide post-column reagent was used, allowing for simpler instrument geometry than is possible with other peroxyoxalates (with the exception of bis[-4-nitro-2-(3,6,9-trioxadecyloxycarbonyl)phenyl]oxalate (TDPO) [16]). The other commonly used aryl oxalate bis(2,4-dintrophenyl)oxalate (DNPO) is unstable in the presence of hydrogen peroxide [17] and therefore cannot be used in this manner. The stability of the mixed reagent (TCPO and hydrogen peroxide concentrations of $1.0 \cdot 10^{-3}$ mol l^{-1} and 0.1 mol l^{-1}, respectively) was assessed by replicate injections of a solution of 3-aminofluoranthene ($1 \cdot 10^{-6}$ mol l^{-1}) in acetonitrile over a period of 8 h. The decrease in signal-to-noise ratio over this time period was less than 5%.

Mann and Grayeski [11] did not remove the excess label prior to LC separation. However it was partially separated from 3-aminofluoranthene derivatives of C_6–C_{10} straight-chain aldehydes on a C_{18} column using a mobile phase of ACN–aqueous tris(hydroxymethyl)-aminomethane buffer ($4.0 \cdot 10^{-3}$ mol l^{-1}, pH 7.5, 85:15, v/v) [11]. In the work reported here, the excess 3-aminofluoranthene was completely removed using solid-phase extraction and 3-aminofluoranthene derivatives were then separated on an ODS2-5 column with a mobile phase of ACN–THF–imidazole buffer ($3.0 \cdot 10^{-2}$ mol l^{-1}, pH 7.5). The inclusion of THF ensured that the mobile phase was compatible with the derivatised oil dialysate samples [2]. Imidazole not only acts as a buffer but also has a marked catalytic effect on the kinetics of peroxyoxalate CL reaction leading to enhanced CL response [18].

THF is relatively non-polar compared with the other mobile phase components and increasing its relative concentration increases the eluting power of the mobile phase for the aldehyde-3-aminofluoranthene derivatives. However, increasing the THF concentration also results in quenching of the CL emission, which in turn decreases the signal-to-noise ratio [2]. Using a mixture of hexanal- and octanal-3-aminofluoranthene derivatives, the ACN–THF ratio was therefore varied from 80:10 to 70:20 whilst keeping the imidazole buffer constant at 10% v/v. The optimum mobile phase composition for separation was ACN–THF–imidazole buffer (75:15:10, v/v). A mixture of straight-chain aliphatic aldehydes (C_6, C_8, C_{10}, C_{12} and C_{14}) dissolved in toluene and spiked on the 0-h oil matrix was derivatised and separated using this mobile phase. Retention data and capacity factors for the aldehydes in toluene and in 0-h and 32-h oil dialysate matrices are given in Table 1 and a chromatogram of the separation is shown in Fig. 3.

Table 1
Capacity factors for synthetic mixture of aldehyde derivatives in toluene and spiked on 0-h and 32-h oil dialysates and concentrations of aldehydes in the 32-h used oil dialysate

Aldehyde	Capacity factor (k')[a] in toluene matrix	Capacity factor (k')[a] in 0-h oil dialysate matrix	Capacity factor (k')[a] in 32-h oil dialysate matrix	Concentration in 32-h used oil dialysate (nmol ml^{-1})
Hexanal	1.9	2.1	2.2	46
Octanal	3.0	3.2	3.4	15
Decanal	4.8	5.0	5.3	66
Dodecanal	8.0	8.0	8.6	77
Tetradecanal	13.3	12.8	13.8	186

[a] $t_0 = 2.0$ min.

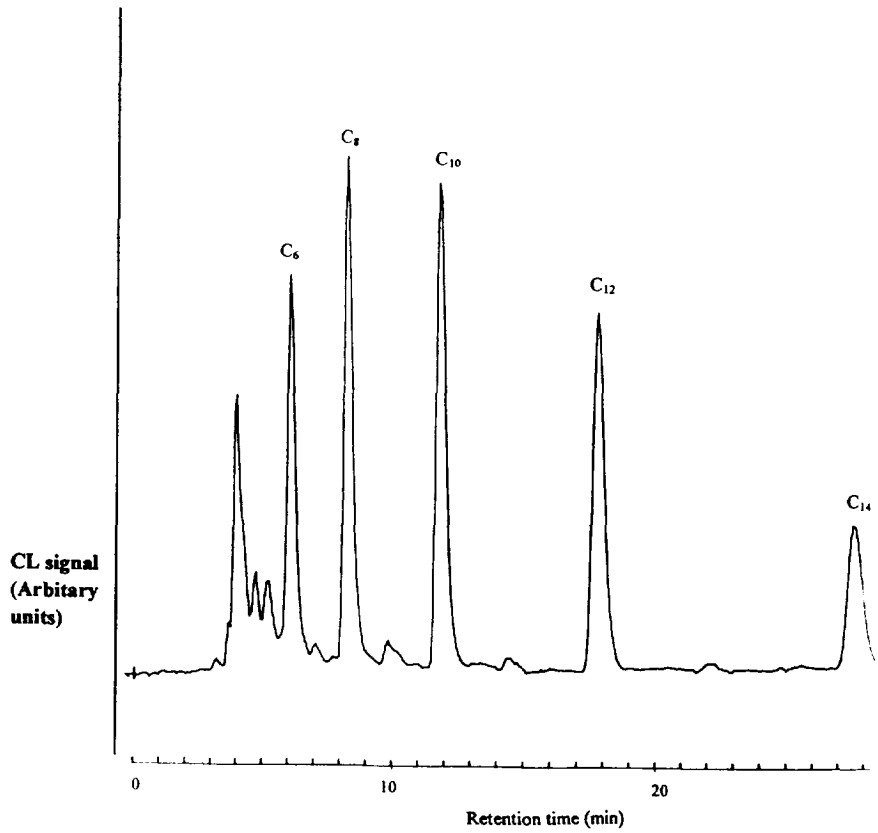

Fig. 3. Chromatogram of aliphatic straight-chain aldehyde-3-aminofluoranthene derivatives of C_6–C_{14} aldehydes spiked on a 0-h oil matrix.

3.3. Chemiluminescence detection

CL reagent flow-rate and concentration were investigated using the hexanal derivative as a model compound. The CL emission intensity was directly related to reagent flow-rate up to 1.0 ml min^{-1}. Higher flow-rates led to lower observed CL emission intensities as the maximum intensity occurred after the analyte had passed through the flow cell. The CL emission intensity was also directly related to the concentrations of TCPO and hydrogen peroxide which are limited by the solubility of TCPO in water.

The optimum conditions, which were used in all subsequent experiments were: TCPO $1.3 \cdot 10^{-3}$ mol l^{-1}, hydrogen peroxide $8.8 \cdot 10^{-2}$ mol l^{-1}, CL reagent flow-rate 1.0 ml min^{-1}. Using these conditions the mixed CL reagent was stable for a period of 24 h, but degraded thereafter and could not be used after 48 h.

3.4. Calibration data

Calibration data for straight-chain aliphatic aldehydes (C_6, C_8, C_{10}, C_{12} and C_{14}) spiked on the 0-h oil matrix were all linear over the range from the detection limit to $5.0 \cdot 10^{-4}$ mol l^{-1} ($0.9980 < r^2 < 0.9997$). The limits of detection ($S/N = 3$) were in the range $3.0 \cdot 10^{-7}$ (C_6)–$3.4 \cdot 10^{-6}$ (C_{14}) mol l^{-1} (which includes the derivatisation step) and is equivalent to 0.7–75 fmol on-column (5-μl injection). These results are an order of magnitude lower than those reported previously [11].

Recoveries were in the range 83–104% for a mixture of straight-chain aliphatic aldehydes (C_6,

C_8, C_{10}, C_{12} and C_{14}) derivatised at the $2.5 \cdot 10^{-4}$ mol l^{-1} level in toluene. The precision (relative standard deviation) of the complete analytical procedure for a mixture of decanal and dodecanal ($2.5 \cdot 10^{-5}$ mol l^{-1}) was 5.6% and 7.1% ($n = 6$), respectively.

3.5. Oil analysis

An oil was sampled from the sump of a car engine after 0, 16, 24 and 32 h of continuous running. Analysis of the 32 h used oil dialysate by LC with fluorescence detection [3] showed the presence of an homologous series of straight-chain aliphatic acids, with hydrocarbon chain lengths from C_7 to C_{22}.

The oil dialysates sampled from the car engine were derivatised with 3-aminofluoranthene and analysed using the optimum conditions described above. Two distinct series of peaks first appeared in the 16-h used oil dialysate and their peak heights increased in magnitude in the 24-h and 32-h used oil dialysates (Fig. 4). These two series are labelled * and Ø on the chromatogram of the 24-h used oil dialysate (Fig. 4). Several peaks of the series labelled * were identified as straight-chain aldehydes by capacity factors in the 32-h used oil dialysate (Table 1). This was confirmed by spiking the used oil dialysate with a mixture of the aldehydes prior to derivatisation.

A plot of log (capacity factor of the aldehyde-3-aminofluoranthene derivatives) against carbon

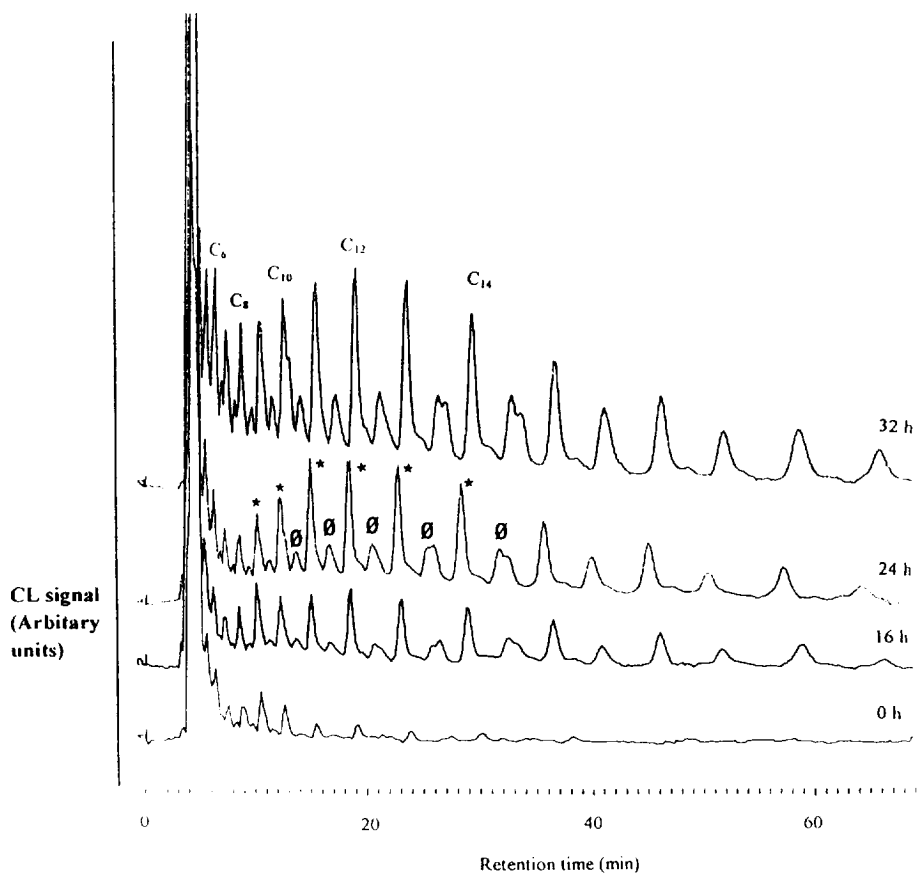

Fig. 4. Chromatograms showing the formation of aldehydes in an engine oil over the 32-h time course of an engine test The chromatogram of the 24-h used oil dialysate shows homologous series of aliphatic straight chain aldehydes (*) and unidentified derivatives, possibly branched-chain aldehydes (Ø).

Table 2
Identification of aldehydes in the 32-h used oil dialysate derived from the equation: $\log(k') = 0.09985$ (number of carbon atoms) − 0.2640

Capacity factor (k')[a]	Calculated number of carbon atoms	Aldehyde
2.73	7.0	heptanal (C_7)
4.25	8.9	nonanal (C_9)
6.76	10.9	undecanal (C_{11})
10.88	13.0	tridecanal (C_{13})
17.57	15.1	pentadecanal (C_{15})
22.41	16.2	hexadecanal (C_{16})
28.72	17.2	heptadecanal (C_{17})

[a] $t_0 = 2.0$ min.

number of the aldehydes (C_6–C_{14}) was linear (equation of line of best fit: $\log(k') = 0.09985$ (number of carbon atoms) − 0.2640) with a correlation coefficient (r^2) of 0.9994. This is characteristic of a homologous series and can be used to predict the capacity factor of any member of that series when using isocratic elution [19]. The aliphatic straight-chain aldehydes observed in the chromatogram shown in Fig. 4 were identified using the equation above and are listed in Table 2. A second series of peaks (Ø) has been tentatively identified as branched-chain aliphatic aldehydes. The formation of aldehydes in the oil is directly related to the length of the engine test, as shown graphically in Fig. 5.

4. Conclusions

Straight-chain aliphatic aldehydes (C_6–C_{14}) in non-aqueous media can be rapidly determined by selective derivatisation with 3-aminofluoranthene and reversed-phase LC with CL detection. A single stream CL reagent line containing mixed TCPO–hydrogen peroxide reagent can be used. Calibration data over the range from the detection limit to $5 \cdot 10^{-4}$ mol l^{-1} were linear ($0.9980 < r^2 < 0.9997$) and limits of detection ($S/N = 3$), including the derivatisation step, were in the range $3.0 \cdot 10^{-7}$–$3.4 \cdot 10^{-6}$ mol l^{-1} (0.7–75 fmol on-column). Analysis of oil from an engine test showed that straight-chain aliphatic aldehydes (C_6–C_{14}) are formed during the oxidation of engine oils and that their concentration increases with running time. Bis-(2-nitrophenyl)oxalate would be an attractive alternative to TCPO because the solubility is relatively high and it can also be mixed with hydrogen peroxide but this reagent is much more difficult to obtain from commercial sources.

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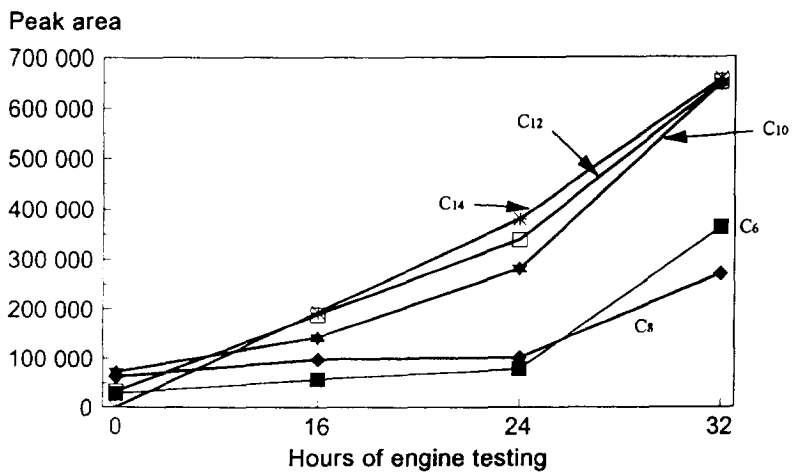

Fig. 5. Graph showing the rate of increase of the individual aldehydes in an engine oil during the course of an engine test.

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