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# On-line high-performance liquid chromatography–solvent evaporation–high-performance liquid chromatography–capillary gas chromatography–flame ionisation detection for the analysis of mineral oil polyaromatic hydrocarbons in fatty foods

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**Abstract**

An automated on-line method is described that involves a first LC separation on a large column, evaporation of a 6-ml fraction in an on-line solvent evaporator, a second LC separation using a different mobile phase, fractionating the components of interest and transfer to GC through the in-line vaporiser/overflow interface. The method is designed for the injection of a large amount of food extract (e.g. up to 200 mg of fat) and is applied to the analysis of mineral oil material in a linseed oil.

*Keywords:* Food analysis; Mineral oils; Oils; Automation; Polyaromatic hydrocarbons; Alkanes; On-line coupled chromatography; On-line solvent evaporation

## 1. Introduction

A number of on-line LC–GC methods in routine use involve two step LC for sample preseparation (LC–LC–GC, e.g. [1–3]). Direct LC–LC presupposes, however, that the fraction eluted from the first LC column is focused at the inlet of the second column. This may be achieved by selection of a second LC column with an increased retention power (used for the methods mentioned above) or by on-line dilution of the eluent with a weak solvent [4]. If no such focusing is feasible, reconcentration requires evaporation of the eluent from the fraction of the first column before it is introduced into the second column.

The analysis of mineral oil polyaromatic hydrocarbons in foods is such an application. Many foodstuffs contain mineral-oil-based products used as release agents or lubricating oils. Others are contaminated from packing material or the environment [5]. Concentrations often exceed 100 mg/kg, sometimes even 1000 mg/kg.

Analysis of mineral oil and its products is probably the field that on-line LC–GC is most widely used for [6–14]. Östman et al. [15] analyzed polyaromatic hydrocarbons with at least three rings in urban air, using an aminopropyl silane LC column in normal phase mode. On-line LC–GC for the analysis of natural paraffins in citrus essential oils was described by Micali et al. [16]. A manual method for the analysis of mineral oil contamination in foods was described by Castle et al. [17].

Our previous analyses of mineral oil material in foods were performed using LC–GC–flame ioniza-

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tion detection (FID) [18] or LC–LC–GC–FID. Preseparation at high resolution is essential to this analysis because of the limited selectivity achieved by GC–FID: gas chromatograms usually show a broad "hump" of unresolved material (primarily isoalkanes), often with numerous peaks on top of it. Its capability of separating mineral oil constituents from food components is, therefore, limited. GC–MS cannot be used for identifying the thousands of components involved, nor does it enable selective quantitative analysis because of the lack of standards enabling to determine the response. FID is, in fact, the only way of quantitating hydrocarbons of unknown identity. Hence, preseparation has to make sure that only hydrocarbons reach GC. Up to some 30 mg of fat were injected, resulting in a detection limit of approximately 1 mg/kg [18].

The second LC preseparation step was added in order to remove olefins, such as isomerized squalenes, since these often disturbed analysis (particularly in the instance of samples containing refined olive oils). Following a method developed for the analysis of olefins resulting from food irradiation [1], the hydrocarbons were isolated from the food extract (primarily fat) on the first column and separated according to the number of double bonds on the second column.

Previous methods either analyzed the aliphatic and aromatic mineral oil hydrocarbons together or the paraffins only. They did not enable selective analysis of the aromatic components, which is of interest for legislation, toxicological assessments and for the identification of the mineral oil product or source of contamination. Mineral oil products used in the food industry are usually white oils, i.e. the aromatics have been removed, whereas food contamination, e.g. from jute bags or the environment, mostly includes polyaromatic hydrocarbons.

The method for analyzing polyaromatic hydrocarbons in foods described in this paper is of high complexity; automated on-line LC–solvent evaporation (SE)–LC–GC–FID departing from a crude food extract or edible oil. It involves two-dimensional LC with intermediate eluent evaporation and transfer to GC–FID and is the first application of the solvent evaporator in an on-line system. The solvent evaporator and the optimization of its working environment has been described in [19,20]. It works on the principles of concurrent SE (the solvent being volatilised during its introduction) and vapour overflow (vapours being discharged by their expansion and their own vapour pressure) with the help of a vacuum. Application of the method to various foods will be described in [21].

## 2. Experimental

### 2.1. Instruments and materials

Experiments were performed on an LC–GC instrument (Dualchrom 3000 from Fisons/C.E. Instruments, Milan, Italy), which included an autosampler, two syringe pumps, an UV–Vis detector and three actuators for rotating switching valves in the LC section (ISS 300). A fourth valve (with ten ports) was mounted on the rear of the central actuator, in the software addressed as valve 1 with two time events. The regular valve at the front of this actuator was exchanged for a larger one with 1/8 in. (1 in.=2.54 cm) ports and larger bores (Valco/Vici, Schenkon, Switzerland).

The solvent evaporator was a prototype from Fisons/C.E. Instruments. It consisted of a heating block equipped with heating cartridges and a PT100, and could be thermostatted by the column heater provided with the instrument [20]. A 7 cm×1/16 in. O.D.×1 mm I.D. steel tube served as the vaporising chamber. It was packed with silica gel (35–70 mesh; Fluka, Buchs, Switzerland) that remained above a 0.315-mm sieve (with cotton keeping it in place). The silica gel was silylated with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA)–1% trimethylchlorosilane (Fluka, 20 min at 80°C). A 12 cm×50 μm I.D. fused-silica capillary (Infochroma, Zug, Switzerland) as a restriction at the inlet and a 5 cm×1 mm O.D.×0.5 mm I.D. steel tube (soldered to the chamber) served as the outlet, being connected to the valve with 1/8 in. ports. A regulated water aspirator provided the vacuum (30 Torr; 1 Torr= 133.322 Pa). Dichloromethane (analytical-reagent grade from Merck, Darmstadt, Germany) was purified over alumina (Merck, 1 l passing through 100 g), technical-grade pentane (Siegfried, Zofingen, Switzerland) by distillation.

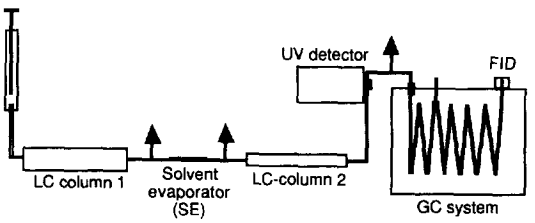


Fig. 1. Overview of the LC–SE–LC–GC–FID system.

## 3. Method

### 3.1. Concept

The first LC column (Fig. 1) was used for isolating the hydrocarbons from the fat extract or edible oil. As this column needed to be large for capacity reasons, the hydrocarbon fraction had a large volume (6 ml). Furthermore, the eluent contained dichloromethane, which could not be tolerated for the second LC separation. This necessitated the evaporation of the eluent from the fraction of the first column before transferring the hydrocarbons into the second column.

At 40°C, on-line SE enabled concurrent evaporation of pentane at rates of up to 1000 $\mu$l/min [20]. This determined the upper limit of the flow-rate for the first LC step. The second LC column separated the paraffins from the aromatic hydrocarbons and split the aromatics into classes according to the number of rings they possessed. This was achieved on an aminosilane column with pentane as the mobile phase, as previously used for the analysis of batching oil for jute fibres [22] and being the standard method for mineral oil analysis. Fractions were transferred into GC by concurrent eluent evaporation using the in-line vaporiser/overflow interface [23].

### 3.2. First LC-column — removal of fat

Adequate sensitivity required that the method enabled the introduction of 150–200 mg of fat or edible oil. The highest capacities for retaining fat have been obtained with silica gel as the packing material [24]. Using a straight alkane as the eluent, a 250×4.6 mm I.D. column (Spherisorb Si, 5 $\mu$m) retained 250 mg of fat with a sufficient safety margin. However, in order to get the largest polyaromatic hydrocarbons of interest eluted within a window of 6–8 ml volume, 10% dichloromethane had to be added to the mobile phase, which reduced the capacity of the column to retain fat. This capacity proved, furthermore, to depend on the method of reconditioning.

After the hydrocarbons of interest had left LC column 1, the fat was removed by backflushing with 10 ml of dichloromethane. Dichloromethane was preferred to, e.g., methyl *tert.*-butyl ether (MTBE) because reconditioning of the column is achieved more rapidly (about 10 min).

The capacity of the column to retain fat was checked gravimetrically: various amounts of fat or edible oil were injected, the fraction of interest collected, the eluent evaporated and the residue weighed. In the course of the experiments, the data shown in Table 1 was obtained. After around 100 injections of 150–200 mg of oils or fat extracts, 200 mg of fish oil were fully retained, whereas 30–36 mg of a linseed oil (non-refined, three years old) broke through the column. Retention of two safflower oils was quite different (with 6 and 48 mg of the 200 mg of oil injected breaking through the column, respectively), suggesting that retention depended on the by-products of an oil (such as free acids, polymerized material) rather than on the type of oil analyzed.

As the capacity seemed to slowly degrade, the column was rinsed with a stronger eluent. A 10-ml volume of isopropanol extracted 97 mg of material, which obviously had not been removed by backflushing with dichloromethane. This treatment brought the column capacity for the linseed oil back to 224 mg.

Table 1
Amounts (mg) of fat or oil breaking through the first column after injection of the amounts (mg) indicated

| Sample | Amount injected | Amount released |
|---|---|---|
| Safflower oil 1 | 200 | 6 |
| Linseed oil 1 | 200 | 36 |
| Safflower oil 2 | 200 | 48 |
| Chocolate fat | 200 | 41 |
| Fish oil | 200 | 0 |
| Linseed oil 1 | 200 | 31 |
| Linseed oil 1 | 200 | 30 |
| Rinse with isopropanol | 97 | |
| Linseed oil 1 | 250 | 26 |

After a further 40 injections of various oils and fats, 150 mg of the linseed oil broke through the column again. This time, isopropanol removed some 70 mg of material.

It was concluded that periodic cleaning with a solvent stronger than dichloromethane is needed and that 150 mg of fat can be injected, whereas 200 mg can be injected only if the column is cleaned frequently. This capacity is in agreement with earlier determinations, taking into account the presence of 10% dichloromethane in the mobile phase [24].

Partial deactivation of the silica gel by injecting large amounts of fat decreases the retention time of the solutes (by about 40% when injecting 150 mg of fat) [24]. Hence, retention times (volumes) of polyaromatic hydrocarbons were determined by spiking a sample, with the amount of fat injected being kept constant in order to achieve stable retention times (except for the paraffins).

The 150 mg of fat or oil were injected as a 500-$\mu$l volume of a 30% solution in the eluent. Smaller volumes with higher concentrations resulted in excessively high viscosity, a strong pressure increase and a reduced column capacity for retaining fat (presumably as a result of channelling).

The flow-rate of the mobile phase was 800 $\mu$l/min, the requirements of the 4.6 mm I.D. LC column, taking into account avoidance of excessively high inlet pressures during injection of the fat and the capacity of the solvent evaporator to vaporise eluent. Under the conditions chosen, the fraction including the hydrocarbons from the paraffins up to perylene had a volume of 6 ml.

### 3.3. Eluent evaporation

Vaporisation of the solvent from the fraction of the first LC column involved the conditions described previously [20]. The eluent was driven into the 5 cm×1 mm bed packed with coarse silica gel by LC pump 1 (800 $\mu$l/min). The silica gel had been deactivated by mild silylation in order to reduce band broadening in LC column 2. This was necessary because the aminosilane column exhibited a lower retention power than did raw silica gel. Stronger silylation had resulted in a decrease in the vaporising capacity [19] (presumably through a less favourable boiling stone effect). A vacuum was applied to the outlet of the vaporising chamber in order to enable evaporation with overflow to occur at a lower temperature (40°C), i.e. to improve retention of the volatile components.

### 3.4. Second LC column: separation of the aromatic hydrocarbons

The analysis of the mineral oil hydrocarbons was performed by the methods previously used for batching oil [21]. The 10 cm×4.6 mm I.D. column was packed with aminosilane-derivatized Spherisorb NH2, 5 $\mu$m. The mobile phase consisted of pentane (600 $\mu$l/min). UV-detection of the aromatic hydrocarbons occurred at 254 nm.

The polyaromatic hydrocarbons were separated using LC column 2 permanently in the forward direction. Fig. 2 shows chromatograms obtained by injection of a mixture of standards either directly into the second column or through LC column 1 and the solvent evaporator (LC–SE–LC–UV). Comparison of the peak shapes indicates that passage through the first column and the solvent evaporator caused some broadening, which is probably the result of the retention power in the solvent evaporator (silica gel) still being somewhat higher than in the amino column.

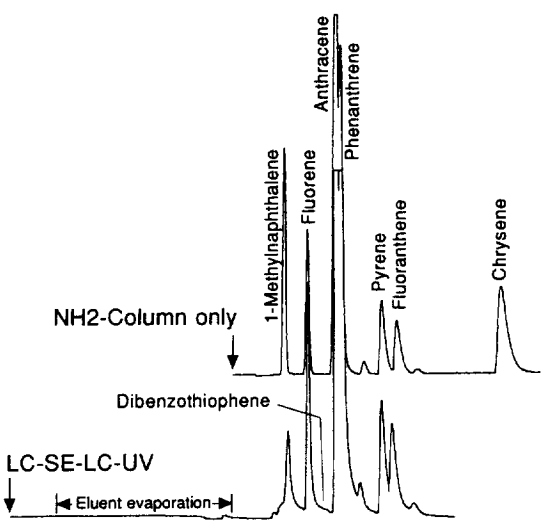


Fig. 2. LC–UV (254 nm) chromatograms of some standards either injected directly into the amino column or passing through the whole LC–SE–LC–UV system.

As described by Beens and Tijssen [14], the separation of highly alkylated benzenes from the paraffins using an aminosilane column remains incomplete. Furthermore, benzothiophenes and biphenyls are largely co-eluted with the naphthalenes. The fraction called "paraffins" does, in fact, include small amounts of olefins and highly alkylated benzenes, whereas the alkylated naphthalenes are the predominating, but not the only, components of the fraction named correspondingly.

For the determination of the proportion of polyaromatic hydrocarbons in mineral oil material contaminating a food sample, the second LC step was performed with backflush: after elution of the paraffins, the column was backflushed and the resulting fraction was analyzed by GC–FID. Backflush was achieved using the additional valve on the actuator carrying valve 1. This configuration, chosen because no fourth actuator was available, caused Transfer Valve LC and Backflush Valve 2 to be actuated at the same time, which was acceptable because switching of the other valve had no negative effect; when making use of the front valve for initiating transfer into the vaporiser, there was only eluent flowing through LC column 2. As the actuator was used for switching the rear valve in order to backflush LC column 2, the front valve switched to vaporisation, but no eluent reached the SE, because Backflush Valve 1 was in the position of backflushing LC column 1 through the waste exit in that valve.

### 3.5. LC–GC transfer and GC analysis

The most volatile components of mineral oil products in foods detected so far were paraffins with 13 carbon atoms and $C_2$-naphthalenes. These components may be partially lost when using concurrent eluent evaporation with the loop-type interface [25]. There is no risk of losing even substantially more volatile compounds when partially concurrent evaporation through the on-column interface is applied. However, this technique becomes tedious when fraction volumes to be transferred exceed 800 $\mu$l. For these reasons, concurrent evaporation through the in-line vaporiser/overflow interface [23] was chosen.

LC pump 2 drove the eluent into the vaporiser thermostatted at 350°C. This vaporiser consisted of a section of the 0.32 mm I.D. fused-silica transfer line with a 5 cm×0.23 mm O.D. wire being inserted. During transfer, the carrier gas supply was stopped. Vapours were discharged by overflow through a 2 m×0.53 mm I.D. retaining precolumn, coated with 0.1 $\mu$m of immobilized PS-255 (a methylsilicone), and escaped through a vapour exit consisting of 0.53 mm I.D. fused-silica. The GC oven temperature was just above the boiling point of pentane at the pressure required for discharge of the vapours. It was determined to be 46°C through the observation that peak splitting occurred at lower temperatures (see Section 4).

Separation was performed on a 15 m×0.25 mm I.D. capillary column coated (in the laboratory) with 0.3 $\mu$m of PS-255, applying 0.7 bar inlet pressure (hydrogen) and a temperature program of 15°C/min to 180°C and of 5°C/min to 300°C.

### 3.6. Analytical procedure

Fig. 3 shows the valve system performing sample preparation. After passing through the Injection Valve, equipped with a 500-$\mu$l loop, the sample passed through Backflush Valve 1 into the large silica

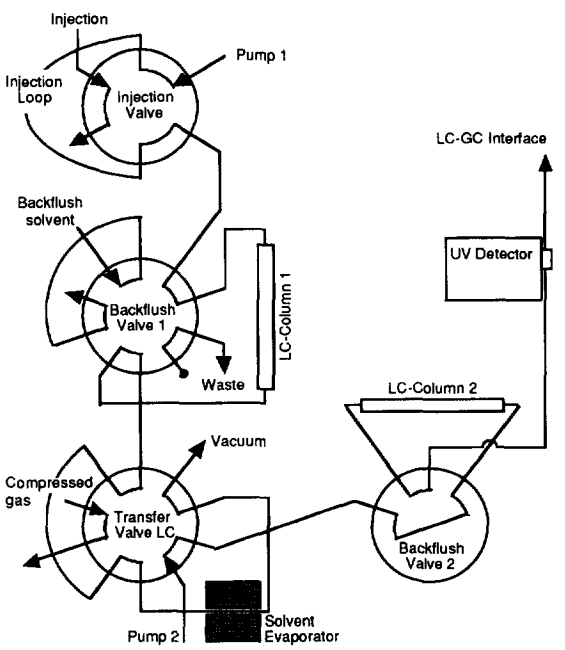


Fig. 3. Valve system for the LC–SE–LC–UV part of the method.

gel column (LC Column 1) for isolating the hydrocarbons from the fat phase. In stand-by, the eluent from LC column 1 went through Transfer Valve LC into the vacuum source. To introduce the fraction of interest into the SE, Transfer Valve LC was switched, first emptying the vaporising chamber by a blow of compressed air (100 $\mu$l, 2 bar) and then feeding the eluent.

At the beginning of the analysis, pump 2 delivered pentane at 20 $\mu$l/min. The flow-rate was increased to 600 $\mu$l/min before eluent evaporation was completed. By returning Transfer Valve LC to stand-by, the hydrocarbons that were reconcentrated in the vaporising chamber were transferred into the amino column (LC Column 2), which was permanently used in the forward direction for group-type analysis. For the determination of the sum of the aromatic hydrocarbons, however, Backflush Valve 2 was switched at the end of the paraffin fraction. The windows for the transfer to GC were determined through the LC–UV chromatograms. Column 1 was backflushed as soon as the hydrocarbons of interest had been eluted. The 10 ml backflush loop was filled with dichloromethane from a pressurised reservoir.

Table 2 shows the sequence of events with the times used for two applications: the determination of the sum of the aromatic hydrocarbons by backflush of LC Column 2 and the analysis of the naphthalenes in the forward elution.

The method was checked by adding 400 mg/kg of the batching oil that had been analyzed previously [22] to a rapeseed oil. Analysis in backflush mode resulted in 15% polyaromatic hydrocarbons, which was in good agreement with the 16% found previously (adding the alkylated benzenes to the paraffins). Agreement was also found for the group-type analysis.

Table 2
Timing of the events

| Time | Event | Function |
|---|---|---|
| 00.00 | Inj. → | Injection |
| 01.00 | Inj. ← | |
| 03.00 | Trf. LC → | Eluent evaporation |
| 10.00 | Trf. LC ← | |
| 10.00 | Pump 2 → | Increase of flow-rate |
| | Bkf 1 → | Cleaning of column 1 |
| 40.00 | Bkf 1 ← | |
| Analysis of aromatics in backflush | | |
| 13.00 | Bkf 2 → | Transfer of aromatics |
| 26.00 | Bkf 2 ← | |
| 14.00 | Carr+Trf GC→ | Transfer to GC |
| 14.00 | Exit → | Release of solvent vapours |
| 16.30 | Carr+Trf GC← | |
| 16.30 | Exit ← | |
| Analysis of naphthalenes | | |
| 13.00 | Carr+Trf GC → | Transfer to GC |
| 13.00 | Exit → | Release of solvent vapours |
| 14.40 | Carr+Trf GC ← | |
| 14.40 | Exit ← | |
| 14.40 | Bkf 2 → | Cleaning of column 2 |
| 30.00 | Bkf 2 ← | |

Injection valve, Inj.
Backflush valves, Bkf.
Transfer valve LC, Trf. LC.
Carrier gas valve, Carr.
Transfer valve LC–GC, Trf LC–GC.
Early vapour exit, Exit. →, actuated; ← return to stand-by.

## 4. Results

### 4.1. Losses of volatile components

Fig. 4 illustrates the performance of the SE and the LC–GC transfer technique, particularly regarding

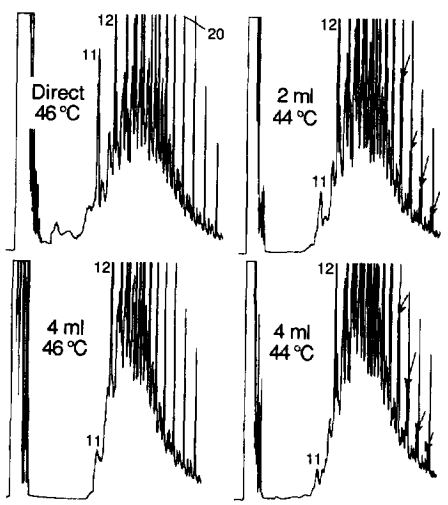


Fig. 4. GC–FID chromatograms of heating oil obtained by injection directly into LC Column 2 (Direct) or by passage through the whole system. Temperatures refer to the oven during transfer, volumes to the eluent vaporised in the SE. Arrows point to peak splitting (chromatograms on the left).

loss of volatile components and typical peak distortion patterns (each of which has previously been studied individually [24,23]). It confirms that $C_{13}$ paraffins are not affected by losses during evaporation, neither by the SE nor by the LC–GC transfer. LC–GC transfer through a vaporiser enabled us to use a lower oven temperature and, due to more efficient phase soaking, provided stronger retention of volatile solutes than can be achieved by the loop-type interface. Heating oil was used as the test sample because it covers the range of critical volatilities. First, a dilute solution (100 $\mu$g/ml) was injected directly into LC Column 2 (through a loop mounted into Backflush Valve 2) and transferred to GC with 400 $\mu$l of pentane (upper left chromatogram). Then the same amount was injected into LC Column 1 and transferred through the whole of the LC–SE–LC–GC–FID system, evaporating 2 or 4 ml of eluent in the SE.

The chromatogram obtained by injection into LC Column 2, merely involving LC–GC transfer, shows a broadened peak of *n*-undecane (11), indicating that the component has been driven rather deeply into the retaining precolumn, i.e. that the latter's retention power was not sufficient to keep the solute as a sharp band in its inlet. Earlier peaks are even broader because the related material was probably spread throughout the precolumn; some of it might have been lost through the vapour exit (as described for concurrent eluent evaporation with the loop-type interface [26]). This tells us that (11) cannot have reached the vapour exit and rules out loss. It is concluded that LC–GC transfer provided the correct results for paraffins with at least eleven carbon atoms.

With the solvent evaporator in the line, components more volatile than (11) were lost completely, (11) to a large extent (coevaporation with the solvent). The peak of *n*-dodecane (12) was reduced by around 15%. Losses depended on the volume vaporised; with transfer of 4 ml, the peak of (11) was less than half the size compared to a 2-ml transfer, but (12) still reached 82%.

The chromatograms at the right were obtained at slightly too low an oven temperature (44°C), causing recondensation in the precolumn and resulting peak splitting (primarily for compounds not migrating at the transfer temperature, indicated by arrows). At a column temperature of 46°C, no such peak splitting was observed.

### 4.2. Mineral oil material in linseed oil

Fig. 5 shows the application of the method to a non-refined linseed oil contaminated with about 300 mg/kg of mineral oil material from an unknown source (sample from the market analysed for normal control). Further investigations showed that the oil seeds, delivered to the mill in paper bags, were already contaminated. A 30-mg amount of oil was injected for the analysis of the paraffins, whereas 150 mg were introduced for analysis of the aromatic hydrocarbons. Hence, GC sensitivity for the aromatic hydrocarbons was five times higher (2.5 times higher for the naphthalenes due to higher attenuation).

The fraction containing the paraffins (with minor amounts of olefins and alkylated benzenes) showed hydrocarbons centred in the range from $C_{15}$ to $C_{23}$. The LC–SE–LC–UV (254 nm) chromatogram (middle at right) shows the presence of a broad range of polyaromatic hydrocarbons, with maxima representing material in the range of the bicyclic hydrocarbons (naphthalenes) and tricyclics (anthracenes

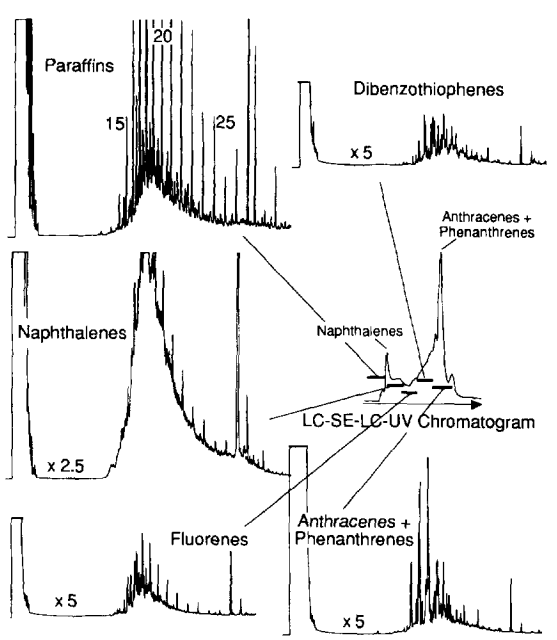


Fig. 5. LC–SE–LC–UV and –GC–FID for the analysis of mineral oil material in a non-refined linseed oil.

and phenanthrenes). Fractions transferred to GC are marked by a bar. GC analysis reveals the presence of a large amount of alkylated naphthalenes (10.1% of the total), less of the fluorene and dibenzothiophenes (1.0 and 0.9%, respectively) and somewhat more of the tricyclics (anthracenes and phenanthrenes, 1.3%). As typical for the aromatic hydrocarbons in mineral oil, the non-alkylated polyaromatic hydrocarbons were hardly detectable.

The presence of large peaks of *n*-alkanes renders contamination by lubricating or hydraulic oils unlikely. It also indicates that the material has not been submitted to biological degradation. The composition of the aromatic hydrocarbons corresponds to a fraction of crude mineral oil, similar to the batching oil used for jute fibres. It could not be ruled out that the linseeds have been transported and stored in jute bags prior to being poured into paper bags.

## 5. Conclusion

Hyphenation in chromatography is far from having reached the limits of its potential. The method described largely eliminates sample preparation (the first LC step isolates the hydrocarbons from a crude extract) and provides preseparation at high efficiency, monitored by the on-line detector. Hence, it saves time for routine analysis, enhances selectivity and provides a means for controlling reliability.

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