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Development of an improved analytical method for the determination of carcinogenic polycyclic aromatic hydrocarbons in transformer oil

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Abstract

Polynuclear aromatic hydrocarbons (PAHs) are natural constituents of transformer oils and are essential in prolonging transformer in-service lifetime. Issues concerning PAH carcinogenicity demand methods that provide qualitative and quantitative information on the PAH composition of new and in-service oils to allow informed operational decisions to be made. However, current analytical methods focus on PAH fingerprinting, as opposed to quantitative analysis and are also cumbersome, relying on the use of large (>100 ml) volumes of organic solvents, some of which are hazardous. This paper reports a method for the improved quantification of carcinogenic PAHs in transformer oils that is both simple and repeatable. The method uses commercially available solid-phase extraction columns and millilitre volumes of relatively non-hazardous solvents. Extraction efficiencies of ≥74% were obtained for the Environmental Protection Agency priority PAHs. The method has potential for automation and high-throughput analysis and thus is of interest to industries that use transformer oils.

Keywords: Polynuclear aromatic hydrocarbons; Solid-phase extraction; Transformer oil

1. Introduction

Mineral oils serve a variety of functions in maintaining healthy transformers including minimisation of heat losses, corrosion and conduction effects. The particular physico-chemical properties of transformer oils is crucial in determining transformer lifetime and efficiency whilst allowing the unit to withstand lightning, over-voltage and overload stresses within the windings. These oils contain polycyclic aromatic hydrocarbons (PAHs), which absorb potentially explosive gases produced ss during transformer operation and extend oil lifetime by acting as natural oxidation inhibitors. In the UK, transformers and other substation equipment are filled with 10^8 l of insulating oil, with a typical high voltage transformer holding 10^5 l.

In addition to gauging gas absorption and anti-oxidant properties, knowledge of the PAH composition of a transformer oil has other benefits. Many PAHs have been labelled as probable carcinogens by the International Agency for Research on Cancer (IARC) [1], thus the identification and quantification of these compounds in oils can provide useful information for health and safety purposes. PAHs have also been identified as the most suitable class of compounds for the fingerprinting of transformer oils [2]. Oil fingerprinting is beneficial for categorising oils with regard to key in-service properties and performance characteristics, notably stability.

A standard method exists for determining the total polycyclic aromatic (PCA) content of an oil, which includes all PAH compounds. BS2000 Part 346 (IP346) is a gravimetric method that equates carcinogenicity to the proportion of the oil soluble in dimethyl sulfoxide (DMSO) [3]. DMSO is a polar solvent that recovers all PAHs and many mono-aromatics, naphthenic rings and hetero-atoms. Those oils having IP346 values ≥3% (v/v) must be labelled under European Union

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legislation [4,5]. PAHs and PCAs are often confused, but differ in that PAHs are solely hydrocarbons that consist of two or more fused benzene rings. It has been suggested that IP346 does not measure PCA, but rather the proportion of a substance soluble in DMSO [6]. However, IP346 is widely accepted due to the correlation between this method and the incidence of skin cancer in mice [7,8].

IP346 is not suitable for determining the PAH content of an oil as it is non-specific and time-consuming, requiring large volumes of hazardous solvents and oils coupled to poor reproducibility. More specific methods exist, based on a combination of liquid–liquid extraction and solid-phase extraction (SPE) techniques coupled to chromatographic fractionation and analysis [2,9–12]. Whilst these methods offer increased specificity, they still require large volumes of hazardous organic solvents (DMSO and dichloromethane). High sample throughput and extraction repeatability is hampered by the non-uniform separation of the extraction solvent from the sample after mixing, a process particularly influenced by the PAH content and oxidative state of the oil.

Wong and Wang [12] propose the use of supercritical fluid extraction (SFE) for the recovery of PAHs from oils. Whilst circumventing the problems of liquid–liquid extraction and benefiting from corresponding improvements in repeatability and extraction efficiency, a SPE step is still necessary coupled to the cost and throughput constraints inherent in the SFE technique.

This paper reports a simple cost-effective method for the quantitative extraction of a range of PAHs from transformer oils with subsequent determination by gas chromatography. Since there are a huge number of possible congeners, the work has focussed on those PAHs designated as both priority pollutants by the United States Environmental Protection Agency (EPA) and probable carcinogens by the IARC. The extraction method involves a three-stage sample clean-up process based on SPE that requires only small volumes of low-hazard solvents. The process is simple to perform, allowing high sample throughput with the potential for automation. Transformer oils with a range of PAH contents were examined and also a highly refined ‘white oil’, selected for its low native PAH content. The method was compared with those of Wilson and Pahlavanpour [2] and Wang et al. [9], the latter being modified to permit the use of less hazardous solvents.

2. Materials and methods

2.1. Reagents and materials

C_{18} cartridges (9000 mg, 1 ml) were purchased from Machery-Nagel (Oxon, UK). PAH HC Isolute SPE columns (1 g, 1 ml) were purchased from Jones Chromatography (Hengoed, UK). Silica gel (60) was purchased from Sigma–Aldrich (Poole, UK). Polypropylene filtration tubes (3 ml) with matching polyethylene frits were supplied by Supelco (Bellefonte, PA, USA). A well-refined mineral oil (‘white oil’) chosen for its very low PAH content, and Nytro10GBN transformer oil, produced by Nynas Naphthenics (Stockholm, Sweden) were supplied by National Grid Transco (NGT). The latter oil was selected since it is the transformer oil most widely used by NGT oils were either extracted as provided, or spiked with 2 $\mu g\,ml^{-1}$ of each of the 16 EPA listed priority PAHs in cyclohexane supplied by QMX Labs. (Essex, UK). All solvents (99+% ACS reagent) were purchased from Fisher (Manchester, UK).

2.2. Extraction

The extraction process comprised a three-step SPE procedure, utilising in sequence a C_{18}, silica (Si) and speciality PAH column. Si columns were prepared in-house by placing a frit in the base of a filtration tube and adding dry silica gel (1.3 g; 2.5 ml) with vortexing to prevent void formation. Commercial silica columns of this sorbent mass are generally supplied in 6 ml capacity columns, which were prone to drying out due to the low rate of solvent elution from the upstream C_{18} cartridge. Rather than increasing solvent volume, the silica columns were prepared in narrower bore 3 ml capacity columns. The column was conditioned with 4 ml cyclohexane ($\sim$5 ml min^{-1}) and then placed at the elution point of the C_{18} cartridge. The C_{18}/Si columns were then conditioned with 8 ml cyclohexane, which was discarded after use. Aliquots (100 μl) of transformer oil were loaded onto the C_{18} column and allowed to interact with the sorbent for 2 min. The C_{18} cartridge was covered to prevent drying out of sorbent. Samples were eluted onto the Si column with 3 ml cyclohexane ($\sim$2 ml min^{-1}). Migration of fluorescent species, including PAHs could be observed using a UV lamp with 366 nm light source. The C_{18} cartridge was discarded and the Si column washed with 5 ml cyclohexane, which was then discarded. Columns were eluted with 6 ml acetone ($\sim$4 ml min^{-1}) and the eluate evaporated to dryness in a fume cupboard at ambient temperature. Samples were re-dissolved in 1 ml cyclohexane and applied to a PAH HC Isolute column, preconditioned with 8 ml cyclohexane. Drainage of the conditioning solvent from the column allowed the sample-bearing solvent fraction to contact the sorbent. The column was washed with 3 ml pentane, which was discarded, and the final extract eluted with 6 ml acetone (4 ml min^{-1}) and analysed using GC–MS. All tests were run six times.

Modifications to the method of Wang et al.: Aliphatic compounds were removed from the Si column using cyclohexane in place of hexane. PAH-rich fractions were eluted in acetone rather than hexane–dichloromethane. The protocol was otherwise unchanged. Substitutions were made to permit the use of less hazardous solvents.

2.3. Spiking experiments

Transformer and white oils were extracted as supplied, or spiked to the 2 $\mu g\,ml^{-1}$ level with each of the 16 EPA priority

PAHs (200 μl EPA standard mixture, containing 10 μg ml^{-1} of each PAH in cyclohexane, was added to 1 ml of oil and the solvent evaporated at room temperature). An experiment was carried out to determine the performance of the assay at varying PAH levels by spiking the white oil with 1, 2, 3 and 4 μg ml^{-1} of phenanthrene, benzo[*k*]fluoranthene and benzo[*a*]pyrene. The steps at which PAHs were lost during the extraction procedure were identified by subjecting the solvents used to wash the Si and PAH HC columns to GC–MS analysis. Additionally, the C_{18} column was washed with 6 ml acetone to recover residual PAH species not recovered by the cyclohexane eluent. PAH losses during the evaporation step were quantified by extracting an unspiked white oil with the C_{18} and Si columns and spiking the extract with the 16 EPA priority PAH mixture (2 μg ml^{-1} of each) followed by evaporation in a fume cupboard at ambient temperature, reconstitution and subsequent extraction using the PAH HC Isolute column. By determining the PAH content of the pentane wash from the PAH HC Isolute columns and the eluted PAH-rich acetone fractions, an estimate of PAH losses due to the evaporation step could be calculated.

2.4. GC–MS analysis

SPE extracts were analysed using a Perkin-Elmer Turbomass GC mass spectrometer with NIST library. Column: Perkin-Elmer Elite series 5MS 30 m × 0.25 mm, 25 μm film thickness with splitless injection. Injection volume was 1 μl and the injector and GC–MS interface temperatures were both 300 °C. The oven temperature was held at 90 °C for 2 min then ramped (30 °C min^{-1}) to 180 °C, then to 310 °C for 5 min at a rate of 30 °C min^{-1}. Mass spectroscopy was performed in electron ionisation (EI) mode (70 eV) and scanned from 30 to 350 atomic mass units for a scan time of 0.2 s in total ion chromatogram (TIC) mode and total run time of 36 min. Source temperature was 230 °C. Selective ion chromatograms were collected for quantitation with a dwell time of 0.1 s. Linear calibration curves were obtained for each of the 16 EPA priority PAHs across the calibration range 0–2 μg ml^{-1} with detection limits varying from 0.006 to 0.2 μg ml^{-1} (based on 3 × SD blank) depending upon the PAH species.

3. Results and discussion

3.1. Qualitative performance of extraction method

The need for sample preparation when analysing transformer oils for PAH content is evident from the TIC of Nytro10GBN with no sample preparation (Fig. 1a). The large number of sample components present results in indistinct chromatograms in which individual oil components cannot be identified. The same oil, when subject to the new C_{18}/Si/Isolute SPE method is shown in Fig. 1b. The presence of individual peaks, equating to naturally occurring PAH species, can clearly be seen.

The mechanism of extraction is that of reverse phase on the C_{18} column and normal phase on the silica and Isolute PAH HC columns. The C_{18} column, being non-polar, results in polar PAHs being washed from the column, even in the presence of non-polar solvents such as cyclohexane, whilst retaining the unwanted non-polar fraction. The Si sorption mechanism retains polar PAHs whilst unwanted components are removed prior to PAHs elution in acetone. The Isolute PAH HC column serves primarily as a purification step, and although the sorbent, and hence sorption mechanism, remains

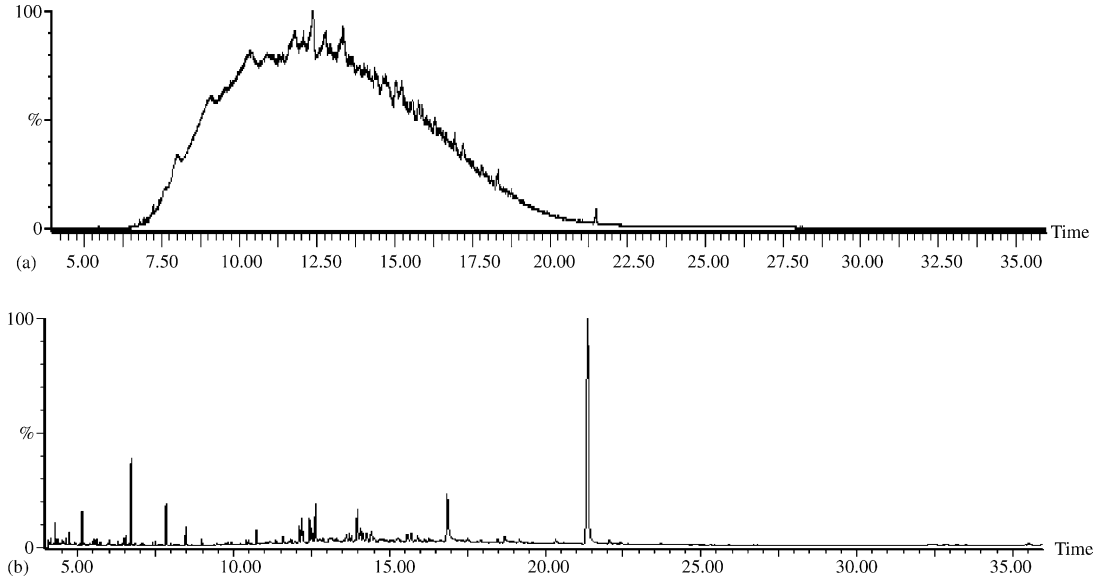

Fig. 1. Total ion chromatograms of Nytro10GBN transformer oil with: (a) no sample preparation and (b) sample preparation using the C_{18}/Si/PAH HC SPE method.

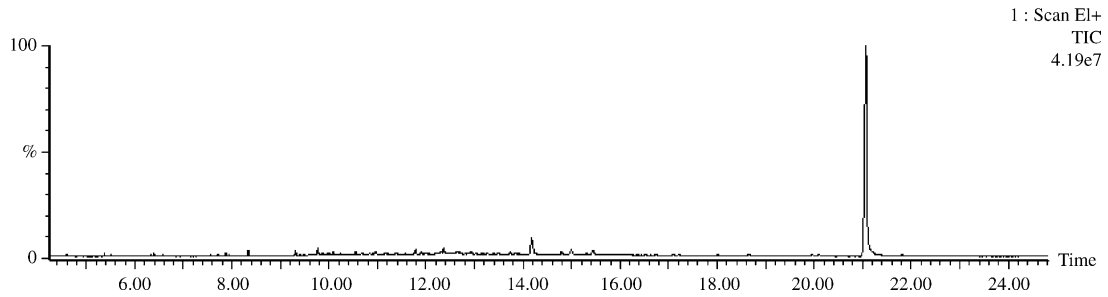

Fig. 2. Unspiked white oil TIC.

as the proprietary information of the manufacturer, it is most probably normal phase, since it retains PAHs until addition of the elution solvent.

Since native transformers have widely varying PAH levels due to the variable composition of the crude oil, the refining process and batch-to-batch production variability, the performance of the extraction procedure was assessed with the aid of spiked oil fractions. Extractions were performed on Nytro10GBN oil, selected due to the widespread usage of this oil within UK electrical plant. Also examined was 'white oil', an oil containing many of the matrix components common to the less highly refined transformer oils, but with a low PAH content.

The TICs of unspiked extracted Nytro10GBN, as shown in Fig. 1b may be compared with that of the white oil (Fig. 2), confirming that the white oil has a low native PAH content and hence is suitable as a 'blank' oil for PAH spiking. The large peak (retention time 21 min) was identified as column bleed from the Isolute PAH HC column. This material was not recognised by the NIST software library, but did not interfere with identification of the 16 EPA priority PAHs. The TIC for the spiked Nytro10GBN oil shows the presence of both the naturally occurring and the spiked PAHs (Fig. 3), indicating the efficacy of the extraction method for the PAH fingerprinting of transformer oils.

3.2. Quantitative performance of extraction method

3.2.1. Extraction efficiencies

Tables 1 and 2 show the concentrations of both naturally occurring PAHs (limited to the 16 EPA priority compounds) and the same PAHs spiked into white oil (Table 1) and Nytro10GBN (Table 2) then extracted. By subtracting the concentration values of the naturally occurring PAHs from the equivalent spiked PAHs, the extraction efficiency of the method for the spiked PAHs can be determined. In this context, extraction efficiency equates to the final concentration of each PAH spiked into the oil (2 $\mu g\,ml^{-1}$) and the concentration of that PAH measured in the final oil extract, expressed in percent terms. The repeatability of the extraction method can be gauged from the recorded relative standard deviation values.

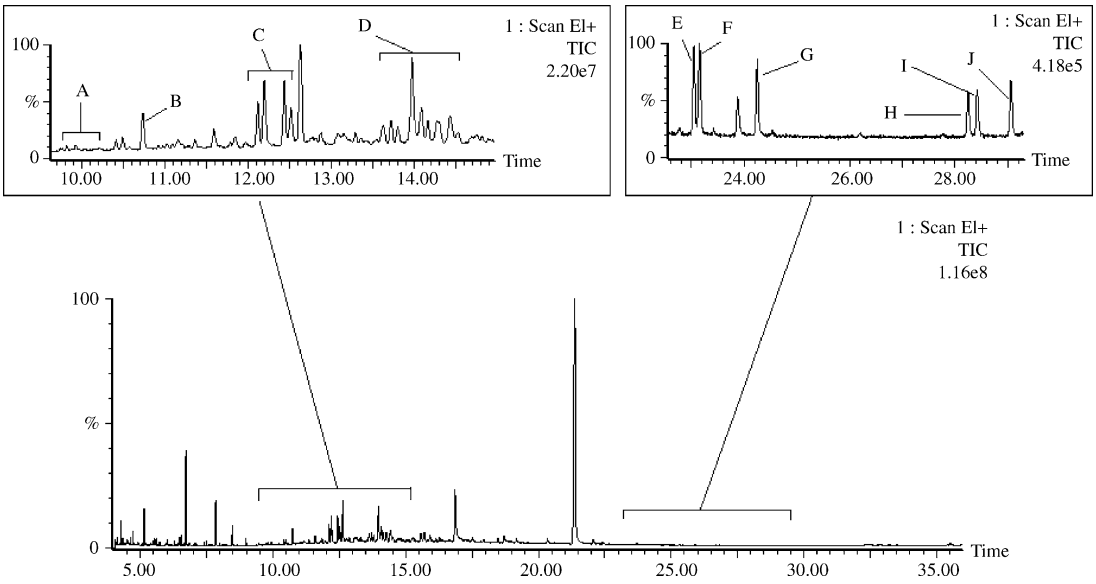

Fig. 3. Total ion chromatogram of a PAH-rich mineral oil spiked with 20 $\mu g\,ml^{-1}$ EPA 16 PAHs: A = methylfluorene isomers; B = phenanthrene; C = methylphenanthrene isomers; D = dimethylphenanthrene isomers; E = benzo[*b*]fluoranthene; F = benzo[*k*]fluoranthene; G = benzo[*a*]pyrene; H = indeno[1,2,3-*cd*]pyrene; I = dibenz[*a,h*]anthracene; J = benzo[*ghi*]perylene. A–D occurs naturally in the oil while E–J were spiked into the oil prior to extraction.

Table 1
Results of extraction of white oil before and after spiking with 2 μg ml^{-1} of each of the EPA 16 priority PAHs

PAH	Naturally occurring PAH in non-spiked extract (μg ml^{-1})	RSD[a] (non-spiked extract)	Total PAH content in spiked extract[b] (μg ml^{-1})	RSD[a] (spiked extract) (%)	Recovery efficiency[c] (%)
Naphthalene	0	–	0.041	–	2.0
Acenaphthylene	0	–	0.067	–	3.3
Acenaphthene	0	–	0	–	0
Fluorene	0.052	–	0.424	0.15	21.2
Phenanthrene	0.063	–	1.166	0.05	58.3
Anthracene	0.068	0.03	0.855	0.18	42.7
Fluoranthene	0.056	–	1.341	0.11	67.0
Pyrene	0.069	0.21	1.208	0.06	60.4
Benzo[*a*]anthracene[d]	0	–	1.672	0.08	83.6
Chrysene[d]	0.051	0.22	1.564	0.07	78.2
Benzo[*b*]fluoranthene[d]	0	–	1.583	0.10	79.2
Benzo[*k*]fluoranthene[d]	0	–	1.617	0.13	80.9
Benzo[*a*]pyrene[d]	0	–	1.660	0.04	83.0
Indeno[1,2,3-*cd*]pyrene[d]	0	–	1.386	0.10	69.3
Dibenz[*a*,*h*]anthracene[d]	0	–	1.639	0.09	82.0
Benzo[*ghi*]perylene	0	0.07	1.303	0.09	65.1

[a] RSD: relative standard deviation.
[b] Total PAH concentration measured in spiked oil minus naturally occurring PAH concentration (column 2).
[c] Recovery efficiency (%) = 100% × known amount of PAH spiked into oil (2 μg ml^{-1})/amount of equivalent spiked PAH in extract (column 4).
[d] Probable human carcinogen (IARC Classification).

The difference in the total (16 priority EPA) PAH content in the white oil and Nytro10GBN oil was found to be 0.64 and 1.20 μg ml^{-1}, respectively. The commonest priority PAHs in the transformer oil were found to be fluorene, phenanthrene, anthracene and pyrene. All of those EPA priority PAHs identified by the IARC [1] as probable human carcinogens were not identified in both the white and transformer oils.

Tables 1 and 2 show that the extraction efficiencies for those EPA priority compounds identified as probable human carcinogens by the IARC, and therefore of most concern to the transformer oil end-user, were ≥77.7% for the two types of oil tested. Of the remaining PAHs, the extraction efficiency varied from 21.2 to 71.4%, except for the most volatile PAHs (naphthalene, acenaphthylene and acenaphthene) where analyte recoveries were ≤3.3%. The similarities in recovery efficiencies within the two matrices indicate that the greater complexity and higher aromatic content of the transformer oil does not greatly affect the quantitative nature of the extraction method. However, of the 13 PAHs quantified, the repeatability of the method was superior for the white oil, in

Table 2
Results of extraction of Nytro10GBN oil before and after spiking with 2 μg ml^{-1} of the EPA 16 priority PAHs

PAH	Naturally occurring PAH in non-spiked extract (μg ml^{-1})	RSD[a] (non-spiked extract)	Total PAH content in spiked extract[b] (μg ml^{-1})	RSD[a] (spiked extract) (%)	Recovery efficiency[c] (%)
Naphthalene	0	0	0	0.00	0
Acenaphthylene	0.066	0.008	0.001	0.36	0
Acenaphthene	0	0	0	0.00	0
Fluorene	0.107	0.14	0.450	0.28	22.5
Phenanthrene	0.128	0.10	1.190	0.08	59.5
Anthracene	0.091	0.17	0.973	0.20	48.6
Fluoranthene	0.070	0.00	1.428	0.15	71.4
Pyrene	0.372	0.41	1.004	0.12	50.2
Benzo[*a*]anthracene[d]	0	0	1.569	0.19	78.5
Chrysene[d]	0.077	0	1.553	0.08	77.7
Benzo[*b*]fluoranthene[d]	0	0	1.630	0.13	81.5
Benzo[*k*]fluoranthene[d]	0	0	1.716	0.10	85.8
Benzo[*a*]pyrene[d]	0	0	1.798	0.13	89.9
Indeno[1,2,3-*cd*]pyrene[d]	0	0	1.493	0.06	74.6
Dibenz[*a*,*h*]anthracene[d]	0	0	1.668	0.15	83.4
Benzo[*ghi*]perylene	0	0	1.377	0.11	68.9

[a] RSD: relative standard deviation.
[b] Total PAH concentration measured in spiked oil minus naturally occurring PAH concentration (column 2).
[c] Recovery efficiency (%) = 100% × known amount of PAH spiked into oil (2 μg ml^{-1})/amount of equivalent spiked PAH in extract (column 4).
[d] Probable human carcinogen (IARC Classification).

Table 3
Percentage PAH lost at each stage of the extraction process during white oil extraction

PAH spiked into oil	Loss of PAHs from C_{18} column (%)	Loss of PAHs from cyclohexane wash (%)	Loss of PAHs from pentane wash (%)	Loss of PAHs during evaporation (%)	Total PAHs accounted for in method (%)
Naphthalene	0	15.2	0	84.8	102.0
Acenaphthylene	0	6.8	0	93.2	103.3
Acenaphthene	0	0	0	100.0	100.0
Fluorene	0	0	8.2	77.0	106.4
Phenanthrene	0	0	0	40.0	98.3
Anthracene	6.8	0	6.1	39.2	94.9
Fluoranthene	7.7	0	0	2	76.8
Pyrene	8.4	0	0	0	68.8
Benzo[*a*]anthracene	0	0	0	0	83.6
Chrysene	10.8	0	0	0	88.9
Benzo[*b*]fluoranthene	0	0	0	0	79.2
Benzo[*k*]fluoranthene	12.4	0	0	0	93.2
Benzo[*a*]pyrene	14.2	0	0	0	97.2
Indeno[1,2,3-*cd*]pyrene	0	0	0	0	69.3
Dibenz[*a*,*h*]anthracene	15.6	0	0	0	97.5
Benzo[*ghi*]perylene	17.3	0	0	0	82.4

which 11 of the 13 relative standard deviation (RSD) values were lower than the corresponding transformer oil values.

A further measure of the quantitative nature of the assay was gauged by determining the extraction efficiency of the method for three representative PAHs across the range 0–4 $\mu g\,ml^{-1}$. The PAHs chosen were phenanthrene, a three-ringed structure with an extraction efficiency of 58.3% in the white oil, and the larger suspect carcinogens benzo[*k*]fluoranthene (five-ring, 80.9%) and benzo[*a*]pyrene (five-ring, 83.0%). Linear relationships were evident for phenanthrene ($y = 3961.3x - 1144$, $r^2 = 0.9858$), for benzo[*k*]fluoranthene ($y = 1499.3x - 5412.1$, $r^2 = 0.9471$) and for benzo[*a*]pyrene $y = 1046.4x - 3998.9$, $r^2 = 0.9344$), where y = area under GC–MS peak and x = PAH concentration in $\mu g\,ml^{-1}$.

3.2.2. Losses of more volatile PAHs

Since none of the spiked PAHs investigated in this study were recovered with 100% efficiency, the amounts of PAHs lost (retained on the column or lost during the evaporation step) at each step of the process were determined. Correspondingly, GC–MS analyses were performed on the solvent washes and the white oil extract immediately after the evaporation/reconstitution step. Results are shown in Table 3.

The C_{18} acetone wash recovered more of the less-volatile PAH species, including appreciable quantities of some of the probable carcinogenic species including chrysene (10.8%), benzo[*k*]fluoranthene (12.4%), benzo[*a*]pyrene (14.2%), dibenz[*a*,*h*]anthracene (15.6%) and benzo[*ghi*]perylene (17.3%). The Si cyclohexane wash recovered the volatile PAHs naphthalene (15.2%) and acenaphthylene (6.8%), but no other priority PAHs. Recoveries of PAHs from the pentane wash were also minimal, with only small amounts of fluorene (8.2%) and anthracene (6.1%) being recorded. The evaporation step was found to be the main reason for the low recoveries of the more volatile PAHs with large amounts of naphthalene (84.8%), acenaphthylene (93.2%), acenapthene (100.0%), fluorene (77.0%), phenanthrene (40.0%) and acenapthene (39.2%) being lost.

Summing the individual losses recorded for each of the extraction steps and combining with the levels of PAHs recovered in the final PAH-rich acetone fraction (Table 1, column 6), a mass-balance for PAH recovery may be made (Table 3, column 6). Those total recoveries significantly lower than 100% (fluoranthene, pyrene, benzo[*b*]fluoranthene, indeno[1,2,3-*cd*]pyrene all gave total recoveries of <80%) were indicative of PAH retention on one or more of the SPE sorbents, possibly the C_{18} sorbent, given the relatively large amounts of the less-volatile PAHs recovered by the acetone wash. Loss of spiked PAHs may have also occurred before the oil was extracted, as oil spiking involved the evaporation of the cyclohexane in the standard EPA 16 PAHs mixture in a fume cupboard at ambient temperature.

3.3. Comparison with other reported methods

The new method may be compared with those other methods reported in the literature for the fingerprinting PAHs in transformer oils. These methods were reproduced in our laboratory with Nytro10GBN oil using the methods of Wang et al. [9] and Wilson and Pahlavanpour [2] and are shown in Fig. 4a and b, respectively. These chromatograms may be compared against that for the new method (Fig. 3) and are shown on the same scale to allow direct comparison.

The new method produces a cleaner extract with more clearly defined PAH peaks when compared to the other methods. Significant matrix effects are apparent using the liquid–liquid/Si extraction procedure (Fig. 4a), whilst the benefits of an additional SPE (C_{18}) clean-up step for PAH fingerprinting are clear from Fig. 4b in which clearly defined peaks are apparent. However, many compounds, including native PAHs, are also lost during the latter extraction proce-

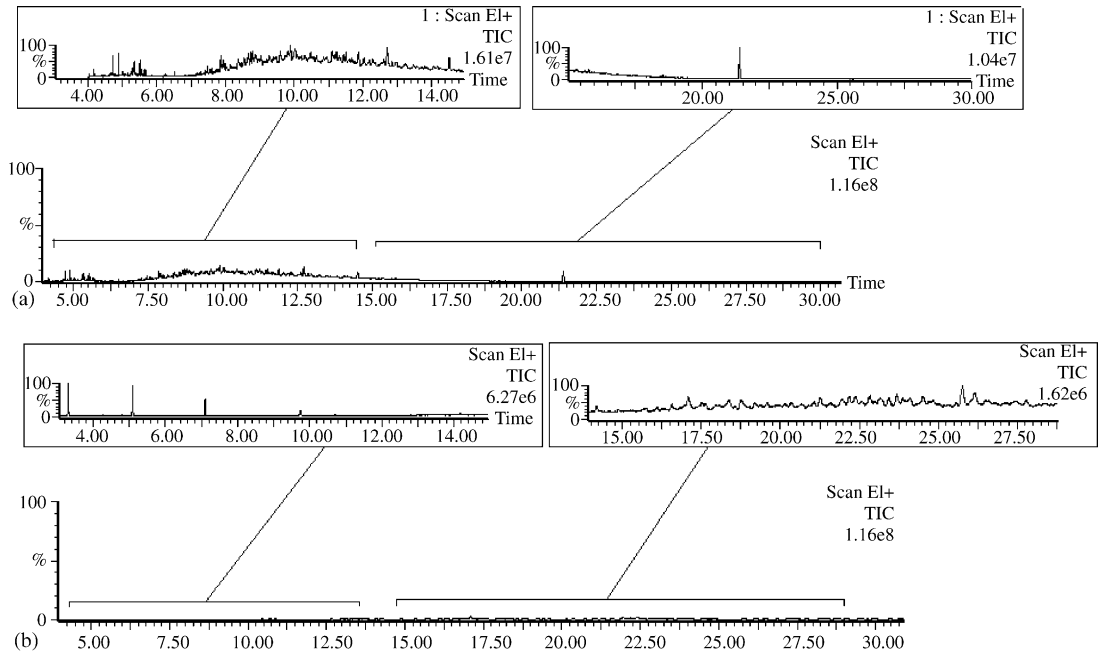

Fig. 4. Chromatograms of transformer oil extracts prepared by the methods of: (a) Wang et al. [9], liquid–liquid extraction followed by Si SPE clean-up and (b) Wilson and Pahlavanpour [2], liquid–liquid extraction followed by Si/C_{18} SPE clean-up.

dure, as evidenced by the overall reduction in the quantity of components retained by the method. The most clearly identifiable PAH peaks are obtained using the new method due to the more selective extraction of the larger carcinogenic PAHs with respect to other oil matrix components.

Examples of other transformer oils extracted with the C_{18}/Si/Isolute SPE method are given in Fig. 5. The oils have been measured for aromatic content using IP346 and the data suggests a possible correlation between the chromatographic and IP346 methods.

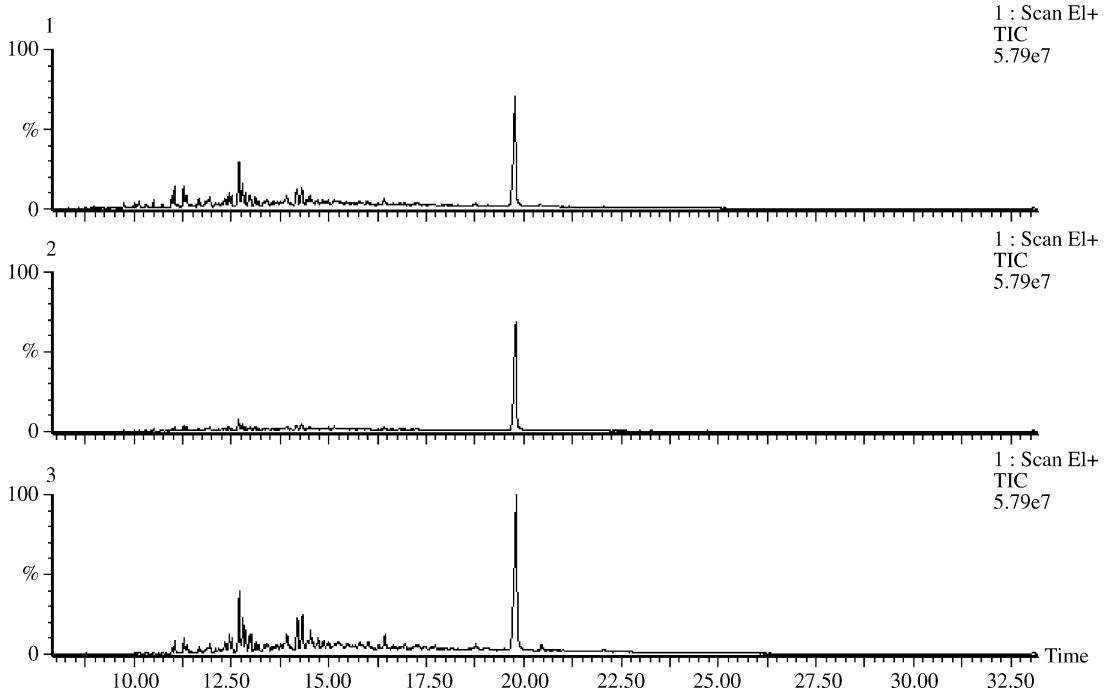

Fig. 5. Total ion chromatogram of three transformer oils extracted using the C_{18}/Si/Isolute SPE method. The IP346 values for the oils are: (1) 2.7%, (2) 1.8%, and (3) 8.9%.

4. Discussion

The method described is able to selectively extract key PAH species with probable carcinogenic properties from transformer oils. In comparison to existing methods, the procedure provides a greater degree of quantitative information regarding individual priority PAHs in the oils using simpler, cheaper, more rapid methodologies, coupled to the use of less hazardous solvents and a reduction in solvent consumption. It is recognised that appreciable amounts of non-carcinogenic PAH species are lost during the evaporative step. This must be weighed against the fact that no existing analytical method is able to provide either quantitative or semi-quantitative information on transformer oil PAH content, leaving the analyst reliant on the low-specificity IP346 method. Furthermore, the identification and quantification of those PAH species considered probable carcinogens is of primary importance from the health and safety perspective.

The method described in Wang et al. [9] suffers less from the loss of volatile PAHs and this may be due to the use of a Rapivap N_2 evaporator. The method of Wilson and Pahlavanpour [2] has only been used qualitatively and the loss of volatiles has not been investigated. However, since sample concentration was facilitated by rotary evaporation, loss of volatiles may be less significant than the method of Wang et al., and may improve volatiles extraction efficiency when used in conjunction with the C_{18}/Si/Isolute SPE extraction method. However, as the aim of this work was to produce a simple extraction method for carcinogenic PAHs that could be automated for high throughput of samples, extra evaporation equipment was not a viable option.

The information provided by the extraction method offers a number of benefits to concerns that are involved in transformer oil handling. Focussing on the qualitative information provided by the new method, the simplicity and reproducibility of the approach provides an improved method for oils fingerprinting with the potential for automation and high-throughput analysis. Fingerprinting is an area of increasing interest to transformer oil users as it allows categorisation of oils which experience has shown to have particularly beneficial or disadvantageous properties.

The more quantitative data provided by the method offers additional benefits to the oil user. Whilst certain PAHs carry a probable carcinogenic threat, the presence of PAH species in transformer oils is beneficial for reasons of stability, anti-oxidant activity and gas absorption properties. Quantitative information regarding the levels of many of these species in oil will aid in the selection of new oils and assessing the state of in-service oils. In-service oils exhibiting a significantly depleted PAH profile may indicate potential catastrophic transformer failure and consequently would be subject to full stability analysis.

Potentially, the improved extraction method may, in combination with other methods, provide a more complete understanding of oil carcinogenicity. IP346 provides an indication of carcinogenicity based on oil solubility in DMSO and previously observed correlation between oil aromaticity and skin cancer in mice [7]. IP346 provides valuable information on the potential carcinogenic threat posed by oil, but is non-specific. By relating the amounts of specific carcinogenic PAHs in oil with IP346 data, conclusions regarding actual carcinogenic PAH levels and risk may be drawn. For example, oil that may be considered non-carcinogenic by IP346 may have high levels of carcinogenic PAHs present. Similarly, it may be shown that oils identified as risk free may have a low overall aromatic content, but a high carcinogenic PAH content and therefore put personnel at risk.

5. Conclusion

A method for the selective extraction of those PAHs defined as probable carcinogens by the IARC, and listed as priority pollutants by the EPA, from a range of commonly used transformer oils has been described. Recoveries of these compounds are >74%, with relative standard deviation values of <20% ($n = 6$), allowing the analyst to make informed deductions regarding the quantitative presence of these individual compounds in transformer oils. Whilst many of the more volatile IARC recognised non-carcinogenic PAHs are lost during the evaporation step, this approach represents a considerable advance over previous PAH extraction methods which do not claim to be quantitative and are primarily used for PAH fingerprinting and other qualitative purposes.

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