Spectroscopic detection of PCB

Feasibility Report

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Contents

1. Introduction

This report describes the activity and findings from the RAL Space Spectroscopy Group during a scoping study for polychlorinated biphenyl (PCB) analysis. This work was undertaken under a contract with Willow Innovation Ltd.

1.1. Background on the prospective application

The Stockholm Convention on Persistent Organic Pollutants (POPs) came into force in May 2004 and covers 22 chemicals, including polychlorinated biphenyls (PCBs). EU directive 96/59/EC adopted the Convention and provides for the phasing out of all equipment containing PCB materials at levels greater than 50 ppm by mass by 2025. As far as is known, no distinction is made amongst the 209 PCB congeners for regulatory purposes.

Transformers in electricity networks contain mineral oil as a dielectric, which may contain PCBs either through leaching of material added to electrical components as a fire-retardant, or through unintentional contamination. The UK electricity distribution network includes ~ 350,000 transformers, of which ~ 220,000 are overhead. Replacement of the entire collection would cost ~ £2 billion.

The Environment Agency (EA) is the body responsible for enacting the requirements of 96/59/EC in the UK and maintains a register of assets that may reasonably be suspected of exceeding the permitted levels of PCBs. All assets on the register are assumed to exceed the limit unless proven otherwise. Any assets which cannot be demonstrated to be below the limit by 2025 must be regarded as hazardous waste and disposed of as such. The EA places the responsibility for demonstrating compliance on the national Distribution Network Operators (DNOs). The means of demonstrating compliance with the 50 ppm limit must be approved by the EA.

As far as is known, analysis has only ever been performed on potentially contaminated liquid oil samples, rather than the vapour. BS EN 61619 relates to determination of PCB contamination in insulation liquids by capillary column gas chromatography. A cohort analysis method, approved by the EA, applied to the analyses suggest that ~ 1 % of the transformer population contain PCB levels in excess of the 50 ppm limit, corresponding to ~ 3500 units. Although the cohort analysis has been approved by the EA, DNOs would like a means of determining compliance of the transformer population in order to limit replacement only those necessary under the terms of 96/59/EC.

1.2. Understanding of the requirements

It is understood that the DNO desired requirements are for a solution capable of :

(i) PCB detection with an accuracy relevant to 96/59/EC requirements (10 ppm in liquid),

(ii) On-site real-time reporting of PCB level (30-minute overall test time),

(iii) Deployment & operation by a single operative,

(iv) Operation from ground level to a height of 5 metres,

(v) Power autonomy during the test process,

(vi) Operating in a typical range of UK outdoor conditions of temperature & humidity,

(vii) Conforming to PCB workplace exposure limits,

(viii) Partial detection of a limited number of PCBs is in scope for screening purposes.

Fig. 1.1 : A typical pole-mounted transformer showing the head-space vent

Fig. 1.1, supplied by Western Power Distribution, shows a typical pole-mounted transformer including the breather tube fitted to allow the headspace to remain at atmospheric pressure and the sight-glass indicating the oil level. It is understood that there is typically a mesh barrier in the region where the breather tube joins the body of the transformer and so any access to the headspace through the breathing tube would require a means of temporarily displacing the mesh.

1.3. Document scope

The study focuses on optical spectroscopic detection techniques, with emphasis on the mid-infrared (mid-IR) wavelengths (2 to 20 µm). General advantages of mid-IR spectroscopic methods and instrumentation relevant to the intended application include :

- Sensitive detection as a result of strong interaction of molecules with mid-IR light
- Limited interference from atmospheric water vapour
- Reliable quantitative measurement method
- Ready identification of chemical identity via the mid-IR ‘fingerprint’
- Discrimination between congeners
- Stand-off detection capability
- No major consumables
- Frequent calibration unnecessary

Additional potential advantages of spectroscopic instruments based on quantum cascade lasers (QCLs), a type of semiconductor chip laser, include :

- Devices can be compact & rugged
- Low power requirements
- Mid-IR QCL systems are generally eye-safe

The study consists of an analysis of the state of the art on PCB analysis as publicly available. The case of gas phase and liquid phase detection and quantification are considered. A first estimate of instrumental requirements is derived, followed by a short review of possible technologies and implementation approaches to consider.

1.4. RAL Space Spectroscopy Group expertise & technologies

RAL Space Spectroscopy Group has 15 years' experience of developing a range of high-sensitivity molecular spectroscopic sensing techniques, primarily based on QCLs, and in developing laboratory Fourier Transform Spectroscopy (FTS) studies. In developing laser-based analytical technologies and instruments, the group typically focuses on TRL 1 to 6-7.

The group is composed of ~10 full time scientists with backgrounds in physical chemistry, physics, photonics, instrumentation and physical modelling. Electronic, mechanical and thermal engineering expertise can be brought in from the RAL Space engineering division.

The group develops novel spectroscopic sensing concepts, new sensing technologies and prototypes. It also actively develops software and models for spectrometers data simulation, interpretation and error budget analysis. The Group operates three state-of-the-art laboratories in spectroscopic sensing R&D:

1) the laser spectroscopy laboratory, where novel laser sensing solutions are actively developed,

2) the high-resolution spectroscopy facility, where high-performance reference spectroscopy can be conducted for spectroscopic data interpretation,

3) the high-resolution atmospheric observatory, where high accuracy transmittance spectra of the atmosphere can be recorded and analysed.

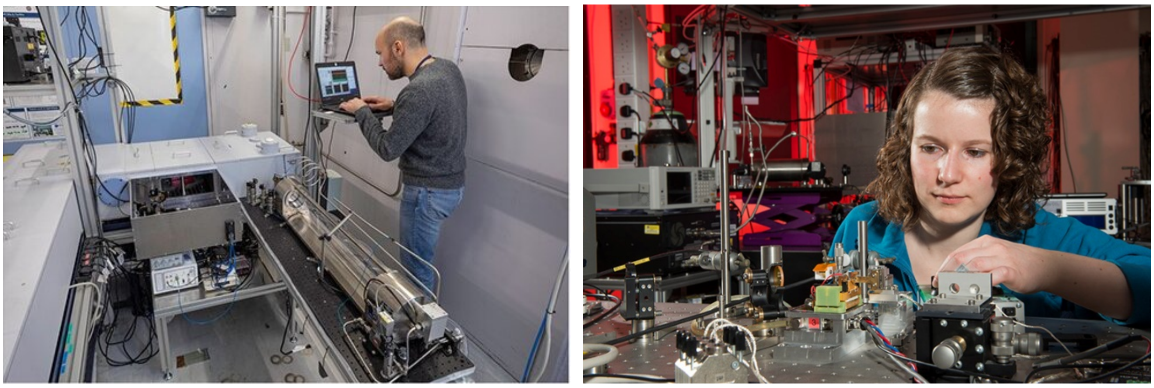


Fig. 1.2 : Left : Spectroscopy Group IFS125 FTS spectrometer in use ; Right : an instrument bench-top demonstrator in the Laser Spectroscopy Laboratory

2. State of the art on PCB spectroscopic data

The two principal optical spectroscopy techniques relevant to identification and quantification of large unsaturated organic molecules such as PCBs are ultraviolet (UV) and infrared (IR) absorption spectroscopy. In this section, the results of literature surveys of both techniques are reported, with emphasis on the availability of quantitative, congener-specific spectral data which is key to the use of spectroscopy as a quantitative tool.

The UV method generally enjoys advantages of high absorption coefficients and low-noise detectors, allowing high detection sensitivity; however, UV absorption spectra of large molecules often lack distinctive structure and so cannot readily discriminate between members of a set of chemically similar compounds such as the PCBs. UV spectroscopy therefore lacks the chemical selectivity required of methods for detecting trace compounds. Infrared methods, in contrast, record the 'fingerprint' region of molecular spectra and so offer very high species selectivity. Although infrared detectors exhibit inherently lower sensitivities that those of their shorter-wavelength counterparts, the disadvantage can be mitigated through use of either multiplex spectroscopic techniques (Fourier-transform infrared spectroscopy, FTIR) or spectrally bright sources such as tunable diode lasers (TDL) to perform tunable laser spectroscopy (TLS).

For simplicity of reference, the 209 PCB congeners were each designated an index (the BZ number) by Ballschmiter and Zell (Ballschmiter and Zell, 1980). A list of PCB BZ numbers and the corresponding IUPAC names can be found in the International Agency for Research on Cancer (IARC) Monograph 107 (Hasemann et al., 2016).

2.1. Review of PCB spectroscopic studies - methods based on infrared absorption

Quantitative analytical methods for PCB congeners, or similar materials such as chlorinated dioxins and furans, reported in the period approximately 1980-2000 are overwhelmingly based on gas chromatography (GC) using either flame ionisation (FI) or electron-capture detection (ECD) for quantification. The results therefore apply to PCBs in the gas phase. More recently, mass spectrometry (MS) has been used as the means of quantification.

FTIR has been deployed in many of these studies, but with the purpose of obtaining the characteristic spectral pattern (a 'fingerprint' spectrum) for specific congeners separated from a PCB mixture by the GC process ; the spectra were intended to allow identification rather quantification of individual PCBs. The FTIR spectra were obtained of samples either trapped by the matrix isolation technique or isolated in a 'light pipe' incorporated into the GC elution tube. In neither case is sufficient information made available on sample concentration and path length to allow a quantitative absorption cross-section to be determined. Bush et al. (Bush and Barnard, 1995)report spectra for all 209 PCB congeners which, whilst not useful for quantitative purposes, may have value in determining spectral regions to be targeted in any proposed practical sensing device.

More recently (since ~ 2010) mid-IR quantum cascade laser (QCL) sources have been commercially available which offer certain advantages over FTIR. However, QCL devices appear not to have been widely deployed as a means of detecting and quantifying PCBs and related materials. For those studies seeking to obtain fingerprint spectra, FTIR is a more logical choice as it offers coverage of the entire mid-IR spectral range (500 – 4000 cm^{-1}), whereas QCLs, even when deployed in an external cavity (EC-QCL) can typically only offer ~ 100 cm^{-1} coverage. Siciliani de Cumis et al. (Siciliani De Cumis et al., 2013) report measurements on chlorinated dioxins and furans using a pair of EC-QCLs with a combined wavenumber coverage of some 360 cm^{-1}.

The publications surveyed for quantitative PCB infrared spectral data are listed in Table 2.1. Table 2.2 lists spectral atlases and databases for which a similar survey was carried out.

Authors	Remarks
(Nyquist et al., 1983)	DRIFTS on pentachlorobiphenyl isomers. Spectral assignments but no quantitative spectral information. Link
(Gurka et al., 1985)	GC / FTIR diffuse reflectance of tetrachlorodibenzodioxins. Spectra used for isomer discrimination. Absorption not calibrated. Link
(Schneider et al., 1985)	GC / matrix isolation FTIR. Spectra used for isomer discrimination. Absorption not calibrated. Spectral assignments questionable. Link
(Schneider et al., 1986)	Comparison of lightpipe method to Schneider at al. 1985. Link
(Gurka and Pyle, 1988)	Application of GC / FTIR lightpipe method. No quantitative spectral information. Link
(Wurrey et al., 1989)	GC/MI/FTIR of chlorinated dioxins & furans. No quantitative spectral data. Link
(Doumenq et al., 1992)	GC/FTIR of selected PCBs ; transition assignments. Link
(Hembree et al., 1993)	GC/MS/FTIR with matrix isolation. No quantitative spectral data. Link
(Bush and Barnard, 1995)	GC / FTIR of all 209 PCB congeners using GC / FTIR lightpipe. Gas phase, absorption not calibrated. Link
(Mhin et al., 2001)	Computational chemistry study of group frequencies of polychlorodibenzodioxins. Link
(Siciliani De Cumis et al., 2013)	EC-QCL / FTIR on dioxins & furans. Example spectrum 1000-1500 cm^{-1} of dioxin/CCl$_4$ solution from which cross-section can be derived. Link
(Patrizi et al., 2014)	Dioxin/furan mixture analysis by FTIR. Link

Table 2.1 : Journal publications surveyed for PCB cross-section data in the mid-IR..

The databases have a general shortcoming for current purposes in that their compilation has been motivated by the need in the field of organic chemistry for a means of compound and structure identification rather than quantification. The path length and concentration information necessary to infer cross-section data from the absorption spectra is rarely provided.

Source	Comments
Sadtler Handbook of Infrared Spectra, ed. W. Simmons, Heyden (1978) ISBN 978-0845600344	Includes spectra for 2- and 4-chlorobiphenyl, in neat & melt form respectively. Quantitative data cannot be inferred as no path length information is given.
Aldrich Library of FTIR Spectra ISBN 978-1-119-37679-8	No data on PCBs
Merck FTIR Atlas ISBN 978-3527264599	In British Library but unavailable for ILL. Inspection possible in person only.
EPA FTIR Reference Spectrum database https://www3.epa.gov/ttn/emc/ftir/refnam.html	No data for PCBs. Gas phase quantitative data for analogous 1,4-dichlorobenzene and 2,4,5- & 2,4,6-trichlorophenols
NIST Webbook https://webbook.nist.gov/	Absorbance for PCBs 1 & 3 in solution, and PCBs 2, 3 & 15 in gas phase. Data are cited as not quantitative but concentration and path lengths are given for liquid phase.
(Brauer et al., 2014)	No data for PCBs. Gas phase quantitative data for analogous dichlorobenzenes and dichlorotoluenes. Link
Bio-Rad spectral library software utility	Data obtained from free 14-day trial subscription. Spectra not downloadable ; screen-shots taken for 1-, 2- & 3-chloro, 4.4'dichloro- and decachloro congeners

Table 2.2 : Infrared spectral databases searched for PCB cross-section data in the mid-IR.

2.2. *Review of PCB spectroscopic studies - methods based on ultra-violet absorption*

As with the majority of reported mid-IR studies, those using UV/visible techniques have focused on compound identification rather than quantification. Andersson et al. (Andersson, Patrick L., Haglund, Peter, Tysklind, 1997) report UV/visible spectra of all 209 PCB congeners in the range 200-300 nm but use them via principal component analysis to relate spectral features to molecular structure for use in structure-property and structure-activity studies.

Publications surveyed for quantitative PCB UV/visible spectral data are listed in Table 2.3. Relevant spectral atlases and databases are listed in Table 2.4

Authors	Remarks
(Tysklind et al., 1993)	UV absorption of chlorinated dioxins & furans. Liquid phase molar extinction coefficients of band maxima & sketches of spectral envelope
(Funk et al., 1995)	UV absorption and LIF on chlorinated dioxins & furans. Gas phase ; peak absorption cross-section data
(Andersson, Patrick L., Haglund, Peter, Tysklind, 1997)	UV absorption spectra of all 209 congeners. PCA analysis. No quantitative spectral data.

Table 2.3 : Journal publications surveyed for PCB cross-section data in the UV/visible.

The following spectral atlases & databases were surveyed for quantitative PCB UV/visible spectral data.

Source	Comments
NIST Webbook https://webbook.nist.gov/	UV/vis spectrum of PCB 4 in the region 218 – 284 nm ; absorption units not clearly defined

Table 2.4 : Infrared spectral databases searched for PCB cross-section data in the UV/visible.

2.3. *Summary of quantitative data - infrared*

Characteristic ('fingerprint') infrared spectra are available for all 209 PCB congeners but are not useful for quantitative purposes. The availability of quantitative spectroscopic data in the infrared appears limited to just two PCB congeners in the liquid phase, as described below.

The NIST Webbook database lists IR spectra for PCBs 1 & 3 in the liquid phase and measurement conditions from which cross-section data can be inferred, as summarised in Table 2.5. The data are taken from the Coblentz Society IR spectral collection (Lemmon et al., 2017).

Compound	**Molecular mass** $g.mol^{-1}$	**Phase**	**Concentration** $\mu mol.cm^{-3}$	**Resolution** cm^{-1}	**Path length** cm
PCB 1	188.5	Liquid	843.5	4	0.011
PCB 3	188.5	Liquid	843.5	4	0.011

Table 2.5 : Quantitative infrared spectral data for PCBs 1 and 3.

2.4. *Summary of quantitative data – ultra-violet*

No quantitative UV spectral data for PCBs were found.

2.5. *Key conclusions on spectroscopic data*

- Availability of quantitative spectroscopic data for PCBs appears extremely limited, such that a necessary first step in the development of any spectroscopic analysis device would be a laboratory measurement campaign to obtain quantitative spectra of ideally all 209 PCB congeners, or at least a significant subset of these known to be spectrally distinguishable.

- The UV absorption method has poor congener selectivity and so is not considered further.

3. Quantitative absorption cross-section data

In Section 2 it was reported that quantitative spectroscopic data could only be found for two PCB congeners, and only in the liquid phase. In order to extend the present study to an assessment of viable PCB detection options, a means of deriving semi-quantitative data for a wider range of PCBs, and for the gas phase, is necessary ; the approach used is described in this section.

First, Section 3.1 lists a number of general points regarding PCB spectroscopy, useful in understanding how a quantitative proxy could be derived to obviate the lack of spectroscopic data. Section 3.2 then addresses the question of estimating quantitative gas-phase spectroscopic data from the limited available quantitative liquid-phase data. Finally, Section 3.3 presents a means of generating approximate, yet justifiable, quantitative data from the relatively wide range of qualitative spectroscopic data available.

The methods are not rigorous, making use instead of empirical data and observations, but are sufficient for the present feasibility study. The results derived are not a substitute for the quantitative spectroscopic data identified as necessary in the previous section.

3.1. General features of PCB IR spectra

Spectrum assignment

The infrared spectrum of a specific chemical compound is determined by its chemical structure through the vibrational modes of its constituent chemical bonds. PCB infrared transitions (which are the origin of the distinctive spectral features observable for each compound) are assigned to particular types of molecular bond as derived in a number of references. These are listed in Table 3.1.

Spectral region / cm^{-1}	Functional group and mode	Reference
700-900	C-H out-of-plane bend	(Schneider et al., 1985)
1000-1150	C-Cl	
1400-1600	C-C stretch	
3000-3100	C-H stretch	
< 900	C-Cl stretch	(Bush and Barnard, 1995)

Table 3.1 : Classification of PCB spectral features.

There is disagreement in the assignments of Schneider et al. (Schneider et al., 1985) and Bush et al. (Bush and Barnard, 1995) regarding the position of spectral features attributable to the presence of Cl atoms. A comparison of the liquid-phase spectrum of the unchlorinated biphenyl with those of a range of some 12 PCBs supports the view of Schneider et al (Schneider et al., 1985) that the features of the spectral region 1000-1150 cm^{-1} are attributable to the presence of Cl atoms. The point is illustrated in Fig. 3.1 which compares the spectrum of biphenyl to those of PCBs 1 and 3 ; the strong features in the PCB spectra in the 1000-1150 cm^{-1} range are not seen for biphenyl.

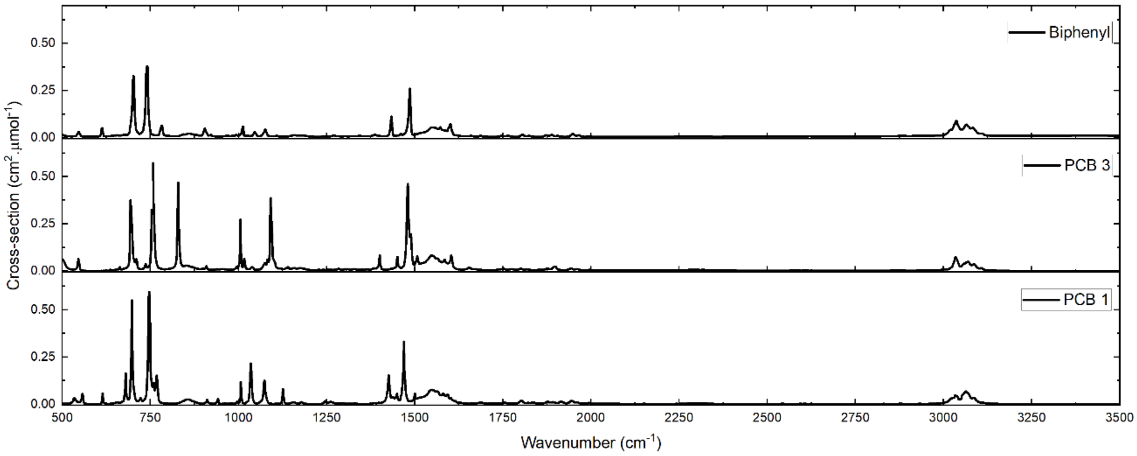


Fig. 3.1: Comparison between spectral features of liquid biphenyl and PCBs 1 and 3.

Band shifts

Bands (spectral features) may shift occur depending on nature of sample (vapour, neat, melt or in solution). The reference spectrum measurement campaign identified as a requirement in the previous section should therefore be carried out at representative concentrations (tens of ppb) in a solvent relevant to the mineral oil present in a typical transformer. A long-chain hydrocarbon liquid at ambient temperature such as dodecane would be suitable.

3.2. *Derivation of gas-phase spectra*

First, the quantitative liquid-phase spectra for PCBs 1 and 3 identified in Section 2.3 are presented. The concentrations for the liquid samples in Table 2.5 are stated as ‘10 % in CCl_4’. Notes for the Coblentz collection Coblentz Society Desk Book of Infrared Spectra, p. 15 (Smith, 1982) refer to sample concentrations in ‘% weight per volume’, which is taken to mean the fraction of PCB by mass present in a given volume of CCl_4. Concentration in the more useful units of µmol.cm^{-3} have been derived in Table 2.5 using the density of CCl_4 of 1.59 g.cm^{-3}. The resulting spectra are shown in Fig. 3.2.

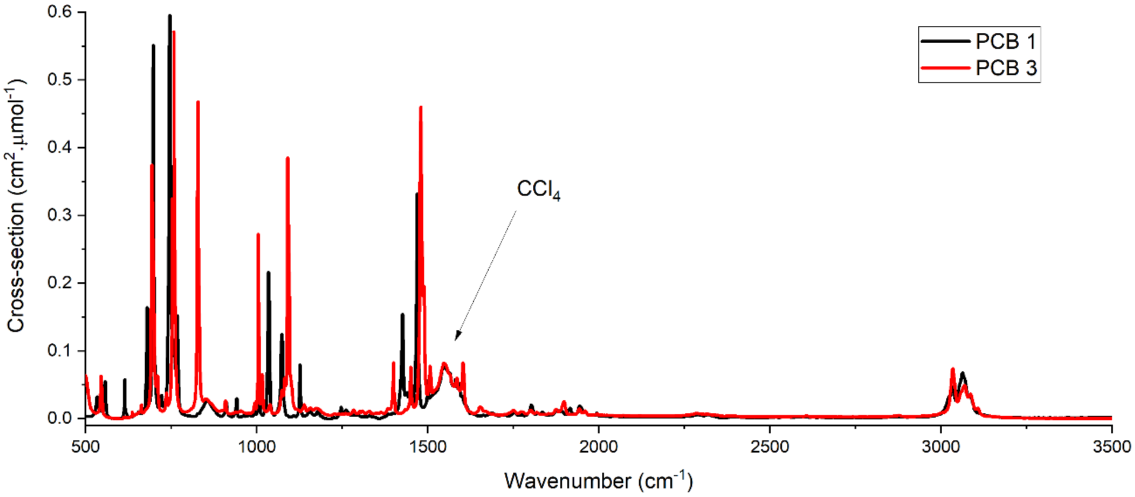


Fig. 3.2 : Quantitative liquid-phase spectra for PCBs 1 and 3.

Proxy compounds

In the absence of reference data, it is necessary to devise a physically reasonable empirical means of relating the unknown gas-phase spectra of PCBs 1 and 3 to the known liquid-phase spectra of Fig. 3.2. The method chosen is to compare spectra of sets of the analogous compounds dichlorobenzene and chlorotoluene, for which quantitative data for both liquid and vapour phase are available, to determine the ratio of cross-sections between the two phases for each compound. The same ratio, amounting to a conversion factor, is assumed to be applicable to the liquid-phase spectra of PCBs 1 and 3, on grounds of similarity in their chemical composition and structure.

Spectra of each of the three isomers of dichlorobenzene and chlorotoluene are shown in Figs. 3.3 and 3.4, from which, as expected on grounds of molecular structure, a similarity in spectral structure to the PCB spectra of Fig. 3.2 is evident.

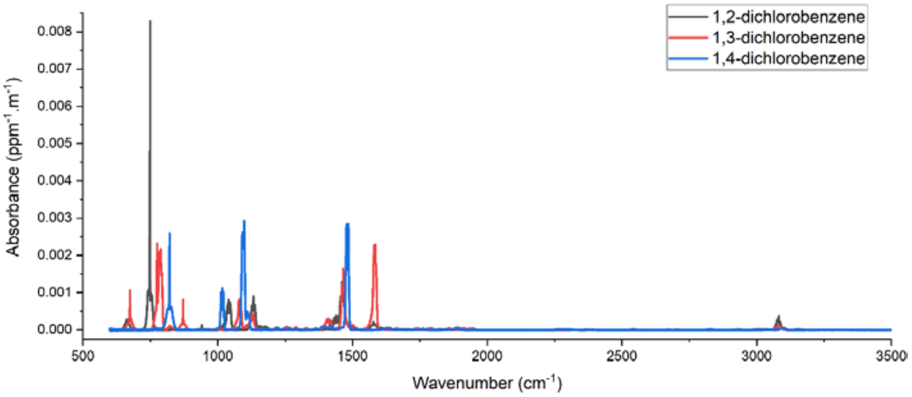


Fig. 3.3 : PNNL dichlorobenzene spectra, gas phase. Resolution 0.15 cm^{-1}.

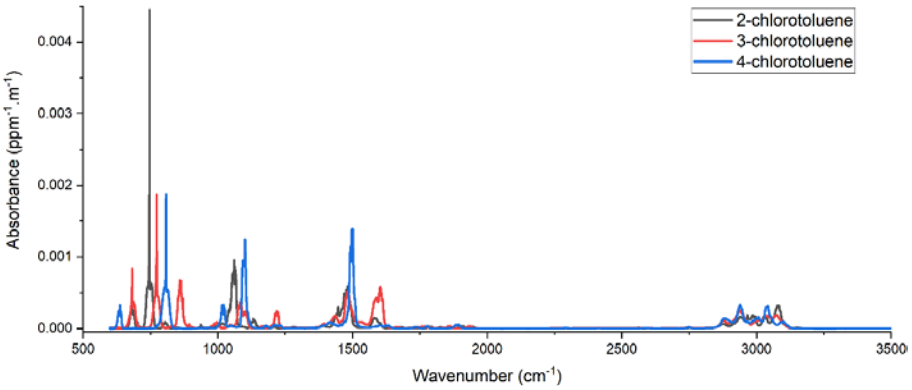


Fig. 3.4 : PNNL chlorotoluene spectra, gas phase. Resolution 0.15 cm^{-1}.

Fig. 3.5 now compares the proxy compound gas-phase data of Figs. 3.3 and 3.4 with the corresponding liquid-phase spectra. Cross-section data for the liquid-phase have been inferred from sample information provided in the NIST database alongside the spectral data. The purpose of the comparison is twofold: first, to determine if major differences in spectral structure exist between the phases, and second, whether the cross-section ratio between phases is consistent. If both the conditions are fulfilled, an empirical conversion factor can justifiably be applied to liquid-phase data in order to derive a model gas-phase spectrum.

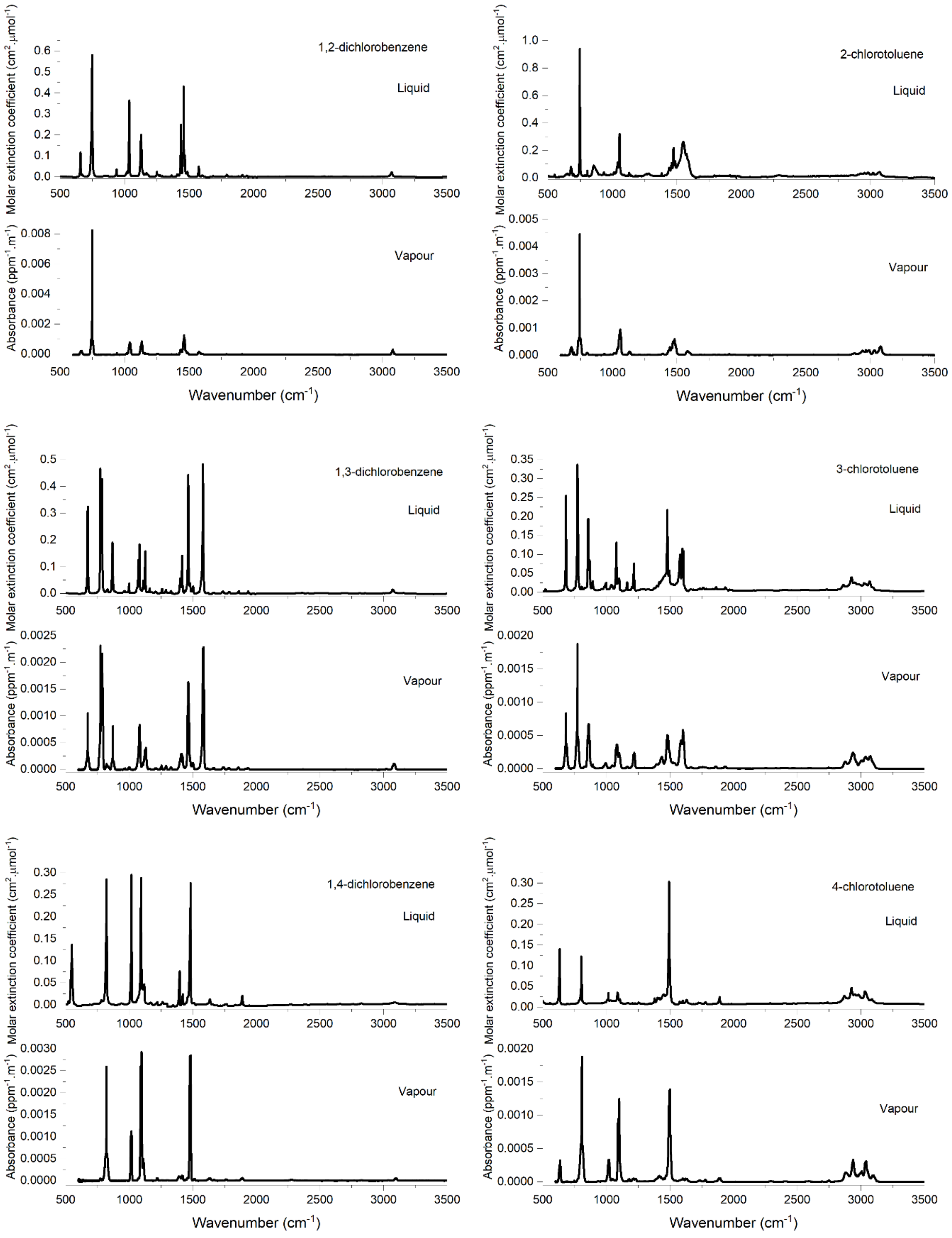


Fig. 3.5 : Comparison of liquid- and gas-phase spectra for the PCB-related compounds dichlorobenzene and chlorotoluene.

With the exception of 1,2-dichlorobenzene, the relative intensities of spectral features for a given compound do not vary dramatically according to physical state, so the use of the suitably-scaled PCB liquid-phase spectra as model for the gas-phase is reasonable. To determine a cross-section scaling factor, the integrated absorption coefficients of the major spectral features for each compound and phase were determined. For these six model compounds, the ratio of molar extinction coefficient (liquid phase) to absorbance (gas phase), in units of $cm^2.\mu mol^{-1}.ppm.m$, is 193 ± 54 1σ.

Using this ratio, approximate model gas-phase absorbance spectra for PCBs 1 and 3 are obtained from the liquid phase spectra. The resulting spectra are shown in Fig. 3.6.

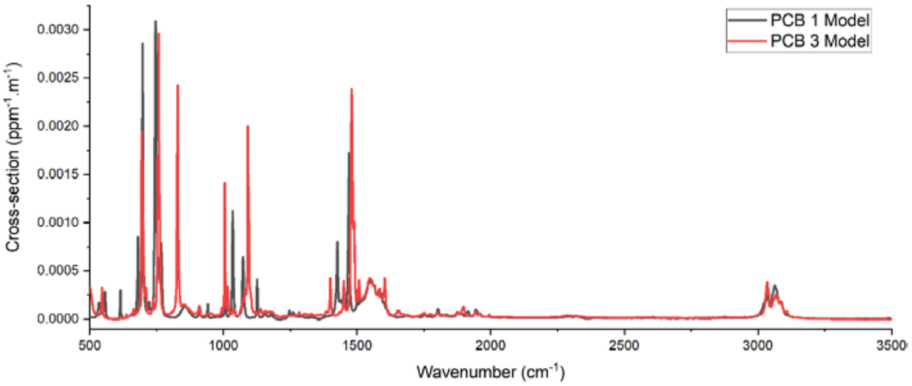


Fig. 3.6 : Semi-quantitative model gas-phase spectra for PCBs 1 and 3 obtained by scaling of the liquid-phase spectra. These data are to be used in the rest of the report for deriving performance estimates.

3.3. *Empirical calibration of liquid phase PCB absorption coefficients*

Now that we have a quantitative estimate for two PCBs, we use it as a reference to derive second order estimates for the other congeners. As noted in Table 2.5, calibrated spectra of liquid-phase PCBs were only found for PCB-1 and PCB-3. It is desirable to find a reasonable means of assigning an empirical absorption coefficient to the numerous uncalibrated spectra of other PCB congeners available in the literature, using the existing data for PCBs 1 and 3.

The approach used is to use the integrated absorption coefficient over a portion of the spectrum characteristic of PCB as a metric. A comparison of liquid-phase PCB spectra with that of the unchlorinated biphenyl indicates that the majority of the spectral features of these compounds in the region 700-1900 cm^{-1} is attributable to the presence of chlorine in the molecules. However, the manner in which this metric might vary between congeners remains to be resolved. In order to proceed, existing data for polychlorinated ethanes is used.

Fig. 3.7 shows on the left the calibrated spectra of 7 polychlorinated ethanes in the 700-1900 cm^{-1} region. On the right, the Figure shows the integrated absorption coefficients in the same region, which appear to a reasonable approximation to scale directly with the chlorine atom count, at least as far as the tetrachlorinated ethanes.

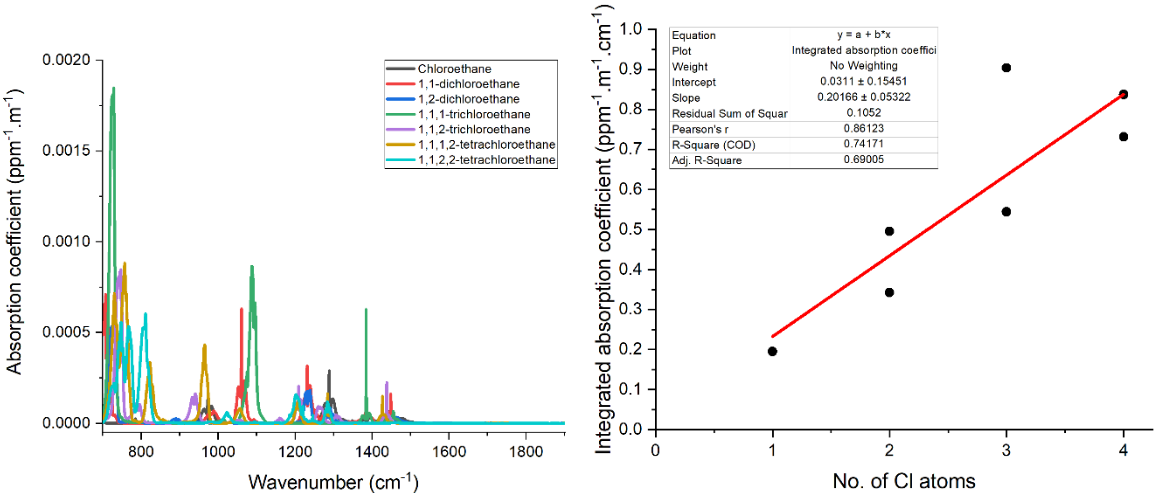


Fig. 3.7 : Spectra (left) and integrated absorption coefficients in the range 700-1900 cm^{-1} for mono- to tetrachloroethanes.

The empirical approach adopted for the current work to generate quantitative model PCB spectra is therefore:

- Normalise qualitative spectra to the mean of the integrated absorption coefficients in the region 700-1900 cm-1 of the two quantitative monochloro-PCBs found in the literature.
- Scale the resulting spectra to the number of chlorine atoms present.

3.4. Summary of model spectrum generation process

Sections 3.2 and 3.3 have described empirical methods for generating model PCB spectra for both phases from the two quantitative liquid-phase PCB spectra and those of proxy compounds available in the literature.

The first method relates vapour-phase cross-sections to liquid phase absorption coefficients; the second relates the intensities of spectra in the liquid phase through the chlorine atom count and the spectral intensity in a spectral region characteristic of the presence of chlorine.

The two processes are illustrated as a flow diagram in Fig. 3.8.

We wish to emphasize that the confidence in the accuracy of the data hence derived is low and would require validation. These data are not suitable to be used in an operational PCB spectroscopic analyser. However, these estimates are judged good enough to derive information on limit of detection and predict the coarse performance of spectroscopic detection methods.

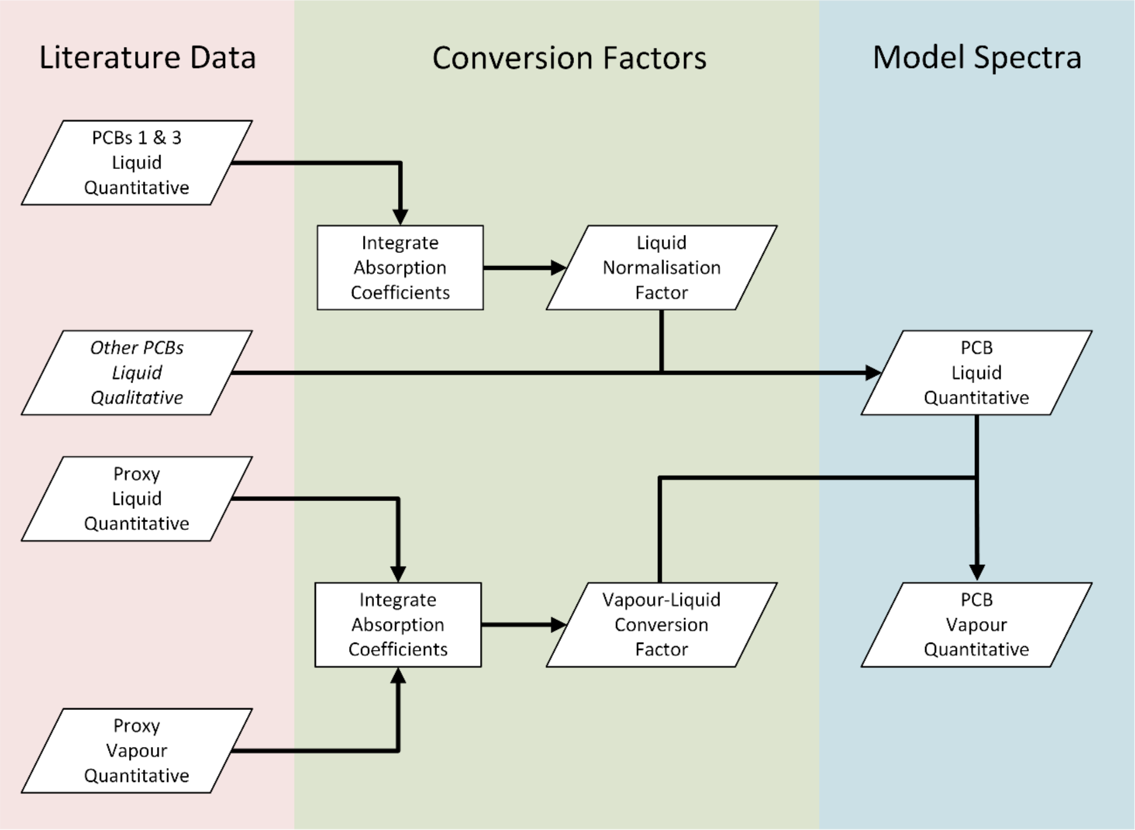


Fig. 3.8 : Flow diagram illustrating the derivation of quantitative model PCB spectra for both phases from literature data.

3.5. *Model spectrum status*

Table 3.2 summarises the status of PCB spectra obtained for the purposes of this paper study using the empirical calibration method described above. The first two columns list the PCBs for which spectral data has been obtained, either in digital or scanned form. The second column indicates whether the data are quantitative at source, or modelled using the methods described earlier in this section. The fourth column indicates those PCBs for which the cross-sections are available digitally (those which are not remain to be digitised manually) and the final column indicates the spectral range over which the digitised data exist.

The corresponding spectra are shown overlaid in Fig. 3.9.

PCB BZ	PCB name	Calibration	Digitised	Range / cm^{-1}
1	2-chlorobiphenyl	Quantitative	Y	450-3790
2	3-chlorobiphenyl	Modelled	Y	550-3846
3	4-chlorobiphenyl	Quantitative	Y	450-3744
4	2,2’-dichlorobiphenyl	Modelled	Y	700-1900
9	2,5-dichlorobiphenyl	Modelled	Y	700-1900
15	4,4’-dichlorobiphenyl	Modelled	Y	450-3960
16	2,2’,3-trichlorobiphenyl	Modelled	Y	400-2000
87	2,2’,3,4,5’-pentachlorobiphenyl	Modelled	N	
88	2,2’,3,4,6-pentachlorobiphenyl	Modelled	N	

90	2,2′,3,4′,5-pentachlorobiphenyl	Modelled	N	
91	2,2′,3,4′,6-pentachlorobiphenyl	Modelled	N	
92	2,2′,3,5,5′-pentachlorobiphenyl	Modelled	N	
95	2,2′,3,5′,6-pentachlorobiphenyl	Modelled	N	
97	2,2′,3,4′,5′-pentachlorobiphenyl	Modelled	Y	400-2060
99	2,2′,4,4′,5-pentachlorobiphenyl	Modelled	N	
101	2,2′,4,5,5′-pentachlorobiphenyl	Modelled	N	
104	2,2′,4,6,6′-pentachlorobiphenyl	Modelled	Y	400-2000
115	2,3,4,4′,6-pentachlorobiphenyl	Modelled	Y	400-2050
116	2,3,4,5,6-pentachlorobiphenyl	Modelled	Y	400-2000
119	2,3′,4,4′,6-pentachlorobiphenyl	Modelled	N	
121	2,3′,4,5′,6-pentachlorobiphenyl	Modelled	Y	400-2055
209	Decachlorobiphenyl	Modelled	N	

Table 3.2 : Summary of surveyed PCB spectra.

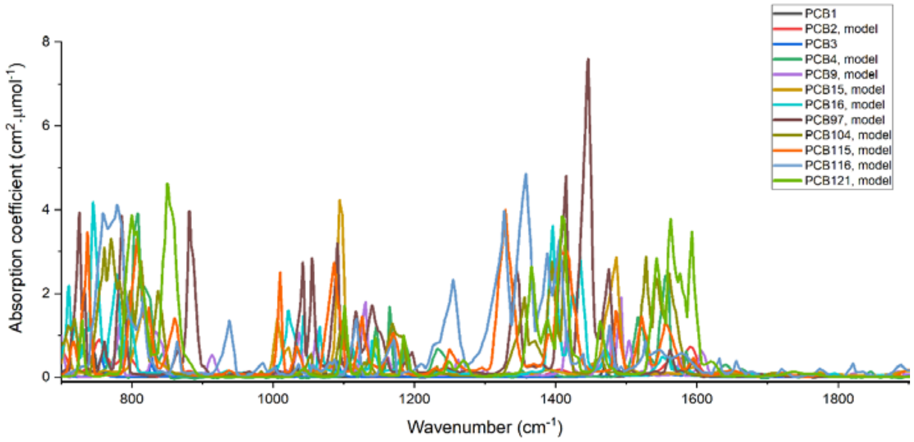


Fig. 3.9 : Absorption coefficients of PCBs in the liquid phase derived from literature.

3.6. *Key conclusions on cross section data*

- Availability of quantitative PCB spectroscopic data is extremely limited ; in order to enable PCB detection performance assessment, empirical methods have been established to derive semi-quantitative model spectra for a representative range of 12 PCBs in both vapour and liquid phase from the very limited set of quantitative spectroscopic data found in the literature.
- Absorption coefficients of model spectra have been generated, which provide the data required to estimate the minimum detectable quantity of PCB in a given sensing scenario.
- The positions of congener spectral features have been established, which, together with a knowledge of the spectral characteristics of the mineral oil or its vapour, informs the choice of spectral window for a sensing device.

4. Physical & chemical properties of PCBs

This section presents relevant physico-chemical properties of PCBs and the implication those properties have for assessing the feasibility of different detection methods.

4.1. General properties

PCBs are generally inert, resisting both acid and alkali and being thermally stable ; they are relatively insoluble in water but freely soluble in non-polar organic solvents and lipids. Liquid PCBs are combustible, producing polychlorinated dibenzodioxins and polychlorinated dibenzofurans which are generally even more toxic than the PCBs themselves.

4.2. Vapour pressure

The vapour pressure of a material is a measure of its volatility, and is a key quantity in this context as it influences the concentration of PCB vapour expected in a transformer head-space for a given concentration in the liquid phase. Vapour pressures for a range of PCB congeners are reported in the International Agency for Research on Cancer (IARC), Monograph 107 (Hasemann et al., 2016). The left-hand plot of Fig. 4.1 shows data from IARC 107 for pure PCB BZ numbers 1, 7, 18, 49, 95, 153 & 171, being a series of PCBs containing an increasing number of Cl atoms from 1 to 7 inclusive. The vapour pressures are for 25 °C. A range in vapour pressure according to number of chlorine atoms of $\sim 10^4$ is evident.

The data of the left-hand plot of Fig. 4.1 relate to pure PCBs. In the context of the application underpinning this study, PCBs are highly unlikely to be encountered in pure form. The vapour pressure exerted by a dilute solution of PCB in transformer oil can be calculated from Raoult's Law, which relates the vapour pressure over the mixture P_x to the concentration x and the vapour pressure of the pure compound P^0 by :

$$P_x = x\,P^0 \qquad \text{Eq. 2.1}$$

The ideal thermodynamic behaviour assumed by Raoult's Law is likely to be followed to a very good approximation in these cases owing to the very dilute nature of the PCB solutions.

The right-hand plot of Fig. 4.1 shows the vapour pressures expected using Raoult's Law for the same PCBs in solution, again at 25 °C. The vapour pressures expected for a solution of 50 ppm in the liquid are shown. For simplicity, the variation in mole fraction with molecular mass for a given mass fraction for the different congeners has been neglected, and since the RMM of a typical paraffin constituent (~ 300 g.mol^{-1} assuming a C-20 hydrocarbon) is similar to the range of congener RMM (200 – 500 g.mol^{-1}), the mole fraction is taken to be identical to the mass fraction. The effect of this approximation is to reduce the spread of modelled vapour pressure by a factor ~ 3 across the conger range from Cl-1 to Cl-10, leaving the values for the mid-range congeners (Cl-5 and Cl-6) largely unchanged.

Although the data presented in this section relate to the range of mono- to heptachloro- PCBs reported in the literature, the linear trend in molar enthalpy of vaporisation seen in Fig. 4.2 can be used to extrapolate vapour pressure data for the higher congeners. The conclusion from that extrapolation is that the vapour pressure for the decachloro-PCB is a factor of ~ 100 lower than that of the heptachloro-PCBs, as indicated by dashed lines in Fig. 4.1. We can therefore estimate the expected concentration in the gas phase above a 50 ppm PCB liquid mixture to be between <1 part per billion at best, for ambient pressure and temperature.

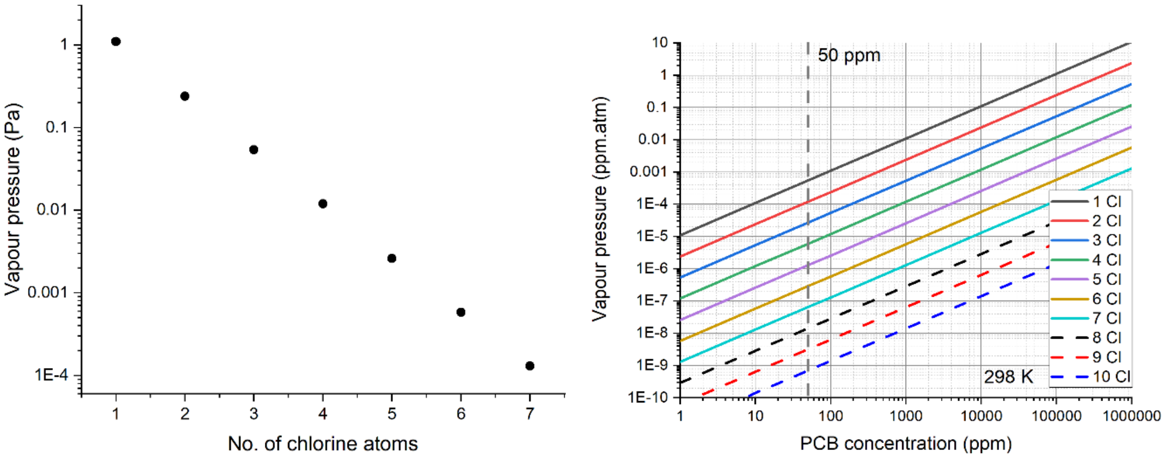


Fig. 4.1 : Left : vapour pressures of a series of mono- to deca-chloro PCBs in the pure state ; Right : head-space vapour pressures for the same PCBs at 50 ppm concentration in the liquid. Dashed lines indicate extrapolated data.

4.3. Vapour pressure variation with temperature

The vapour pressure P of a material varies with temperature T according to the Clausius-Clapeyron equation, in which a key parameter is that material's molar enthalpy of vaporisation $\Delta H_{vap,m}$:

$$P(T) = P(T_0)exp\left[\frac{-\Delta H_{vap,m}}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \qquad \text{Eq. 2.2}$$

Puri et al. (Puri et al., 2001) report molar enthalpies of vaporisation for 16 PCBs in the monochloro- to heptachloro- range as shown in the left-hand plot of Fig. 4.2. The enthalpy data allow the vapour pressures of PCBs to be calculated as a function of temperature, the results of which are shown in the right-hand plot of Fig. 4.2 for pure PCBs over the range 0 – 100 °C for the sub-set with BZ numbers 1, 7, 18, 49, 95, 153 & 171. The upper temperature limit of 100 °C was chosen in view of the typical flashpoint of mineral oil of 140 °C.

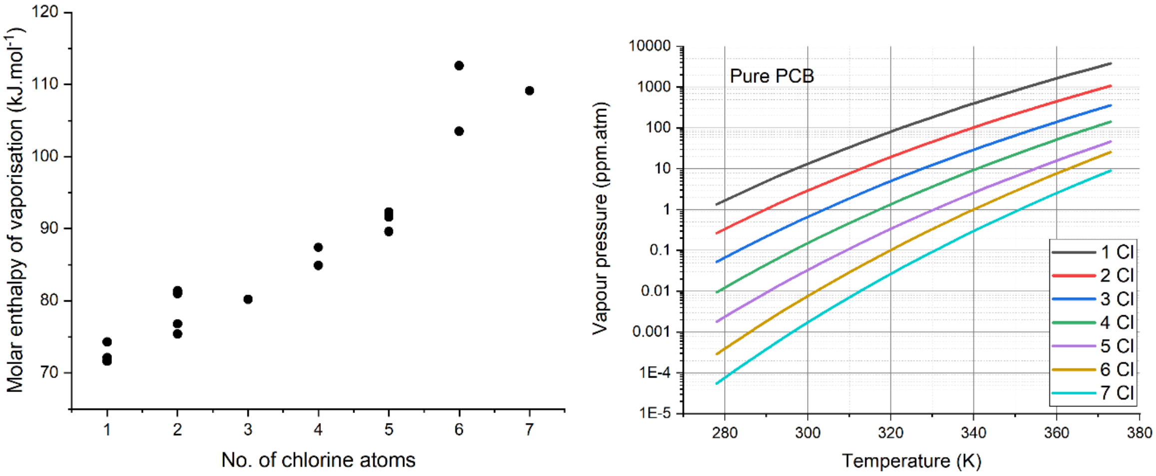


Fig. 4.2 : Vaporisation enthalpies and vapour pressure curves for Cl-1 to Cl-7 PCB congeners

A significant feature evident from Fig. 4.2 is that the vapour pressure of a PCB mixture will vary by a factor of ~ 10 for a 20 °C variation in temperature. For a vapour concentration measurement to be related to the liquid concentration, therefore, a measurement of the transformer oil bath temperature accurate to a few degrees would be necessary.

4.4. Key conclusions on PCBs volatility

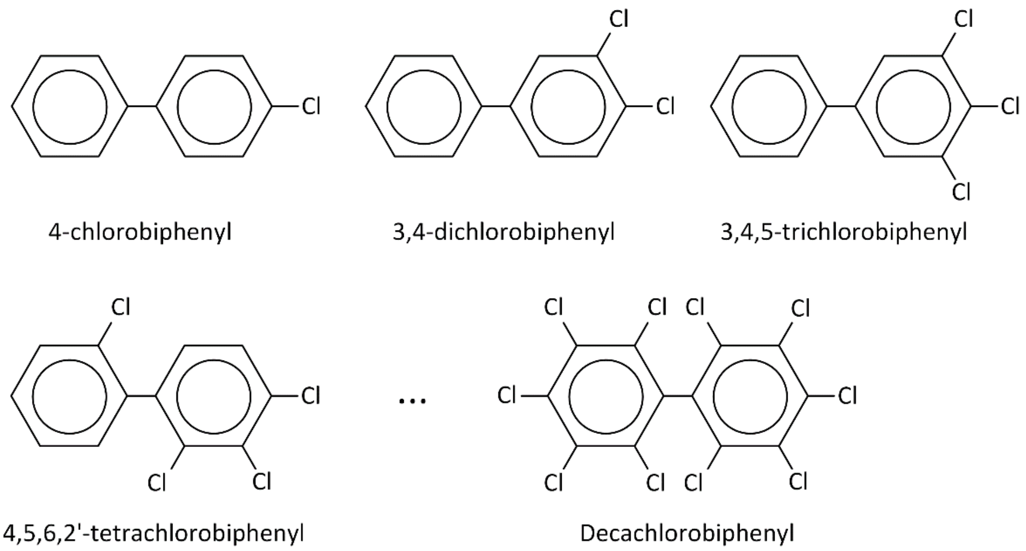
- The low volatility of PCBs in general limits the concentration of PCB to be expected in a transformer headspace. At room temperature, the headspace above an oil sample containing 50 ppm of the most (monochloro-) and the least (decachloro-) volatile PCBs would show concentrations of ~ 1 ppb and ~ 0.001 ppt respectively.
- The gas phase PCB concentration in the transformer headspace increases approximately 10-fold for a temperature increase of 20 °C. Local heating of the transformer is a way to increase vapour phase sensitivity of a detection technique.
- For a detection technique to have equal sensitivity to all PCB congeners for a given concentration in the liquid, a dynamic range of 6 orders of magnitude would be required.
- The conversion factor relating a given concentration of PCB in the vapour to that of the same PCB in the liquid phase varies from $\sim 10^5$ to $\sim 10^{11}$ for the most and least volatile congeners respectively. In consequence, even very low concentration measured in the gas phase implies a concentration between a million and a trillion times larger in the liquid phase.
- The ability accurately to relate a PCB concentration measured in the gas phase to that in the liquid phase would require knowledge of the temperature of the transformer oil bath to within a few degrees C.
- The ability accurately to relate a PCB concentration measured in the gas phase to that in the liquid phase would in addition require knowledge of the enthalpy of vaporisation of each PCB congener to within a few kJ.mol^{-1}, information which is not generally available. Experimental determination of vaporisation enthalpies would be a non-trivial task, especially for the higher homologues.

5. Composition of PCB mixtures

Given the existence of 209 individual PCB congeners, each of which has its own unique spectrum, a knowledge of the likely composition of a typical PCB mixture in a transformer is useful in determining possible detection strategies. For example, do we need to know about all the 209 PCBs or is there a subset of these that is prevalent, on which one can focus ?

5.1. Composition of trade PCB formulations

PCBs are composed of 10 homologues, each corresponding to the degree of chlorination from mono- to decachlorobiphenyl, within which physical properties such as melting point an enthalpy of vaporisation are similar. Fig. 5.1(a) shows examples of the homologues from mono- to tetrachloro-, and decachlorobiphenyl. Each homologue consists of a range of congeners, varying in number from 1 for decachlorobiphenyl to 46 for pentachlorobiphenyl. Fig. 5.1(b) shows the three congener members of the monochloro-PCB homologous set. There are a total of 209 PCB congeners, each having its own IR spectrum. It is not known at this stage the degree to which homologue compounds may share spectral similarities.



4-chlorobiphenyl

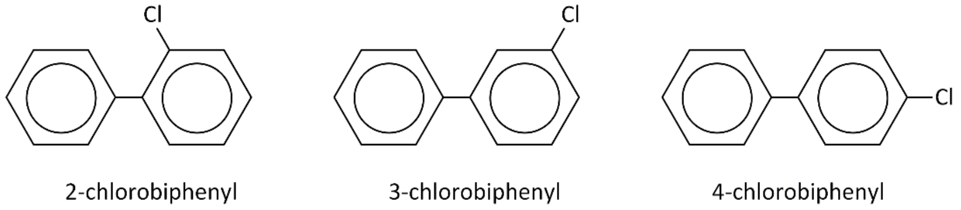
3,4-dichlorobiphenyl

3,4,5-trichlorobiphenyl

4,5,6,2'-tetrachlorobiphenyl

Decachlorobiphenyl

Fig. 5.1(a) : Examples of the first four, and the final, PCB homologues



2-chlorobiphenyl

3-chlorobiphenyl

4-chlorobiphenyl

Fig. 5.1(b) : the three congeners of the monochloro-PCB homologue

There exists a wide variety of PCB formulation trade names for industrial application, listed in Appendix 11.1, whose formulations in general appear only to be available when determined and reported in the scientific literature. Composition determination was carried out using gas chromatographic techniques. Two such cases are ‘Fenclor’ and ‘Aroclor’ whose compositions have been determined by De Voogt & Brinkman (De Voogt and Brinkman, 1989) and by Nyquist et al. (Nyquist et al., 1983), Frame et al. (Frame et al., 1996) & Mayes et al. (Mayes et al., 1998) respectively. Fenclor is reported to be 100 % decachloro-biphenyl. Aroclor has been produced in a range of different formulations each designated by a four-digit code. The primary manufacturing process for Aroclor is reported to consist of reacting biphenyl with chlorine under conditions (for example reaction time) selected according to the extent of chlorination required. Unless subsequently fractionated, therefore, each Aroclor formulation is expected to show a range of PCB homologues (PCBs with the same chlorine atom count) and to show a range of congeners within each homologue. The reported Aroclor compositions are tabulated and illustrated in the remainder of this section.

Compound	Abundance, (Nyquist et al., 1983).	Fraction of total chlorinated content	
		(Nyquist et al., 1983).	(Frame et al., 1996)
Biphenyl	20.7	-	-
2-chloro	38.4	75.8	60.1
3-chloro	3.3		
4-chloro	18.4		
2,2′-dichloro	5.2	22.8	33.4
2,4-dichloro	2.3		
2,4′-dichloro	8.4		
4,4′-dichloro	2.2		

Table 5.1 : Distribution (%) of congeners in trade formulation Aroclor 1221 reported by Nyquist et al. (Nyquist et al., 1983).

Mayes et al (Mayes et al., 1998) report that for Aroclors 1242, 1254 and 1260, the chlorination reaction was stopped when the weight percent of chlorine in the PCB had reached 42, 54 and 60 % respectively. Aroclor 1016 was prepared by fractional distillation of Aroclor 1242, which excludes the higher-boiling, more highly-chlorinated congeners.

Compound	Aroclor 1016	Aroclor 1242	Aroclor 1254	Aroclor 1260
Monochloro-	0.8	0.1	0.0	0.0
Dichloro-	17.6	14.5	0.1	0.2
Trichloro-	55.0	42.8	0.7	0.5
Tetrachloro-	25.8	33.5	19.7	2.4
Pentachloro-	0.7	6.6	45.3	12.0
Hexachloro-	0.0	1.7	31.4	39.3
Heptachloro-	0.0	0.1	2.8	36.4
Octochloro-	0.0	0.0	0.1	7.7
Nonachloro-	0.0	0.0	0.0	1.6
Decachloro-	0.0	0.0	0.0	0.1

Table 5.2 : Compositions (%) of Aroclor formulations reported in Mayes et al. (Mayes et al., 1998)

Frame et al. (Frame et al., 1996) report Aroclor composition by PCB homologue (degree of chlorination) (see Table 5.3) for 9 Aroclor mixtures, and in addition the composition by individual congener for 7 Aroclor mixtures (see Fig. 5.3 – the vertical bars and top axis labels indicate the zones occupied by each PCB homologue). In cases where two compositions are reported for the same Aroclor same designation, the data relate to two different batches of that Aroclor.

Homologue	Aroclor formulation							
	1016	1221	1232	1242	1248	1254	1254	1260	1262
$C_{12}H_9Cl$	0.7	60.1	27.6	0.8	0.1	0.0	ND	0.0	0.0
$C_{12}H_8Cl_2$	17.5	33.4	26.8	15.0	1.6	0.1	0.2	0.1	0.3
$C_{12}H_7Cl_3$	55.7	4.2	25.6	44.9	21.3	0.4	1.3	0.2	1.0
$C_{12}H_6Cl_4$	22.1	1.2	10.6	20.2	32.8	4.9	10.3	0.4	0.5
$C_{12}H_5Cl_5$	5.1	1.2	9.4	18.9	42.9	71.4	59.1	8.7	3.4
$C_{12}H_4Cl_6$	ND	ND	0.2	0.3	1.6	22.0	26.8	43.3	26.4
$C_{12}H_3Cl_7$	ND	ND	0.0	ND	0.0	1.4	2.7	38.5	48.5

$C_{12}H_2Cl_8$	ND	ND	ND	ND	ND	ND	0.0	8.3	19.7
$C_{12}HCl_9$	ND	ND	ND	ND	ND	0.0	0.0	1.0	1.7

Table 5.3 : Compositions (%) of Aroclor formulations reported in Frame et al. (Frame et al., 1996).

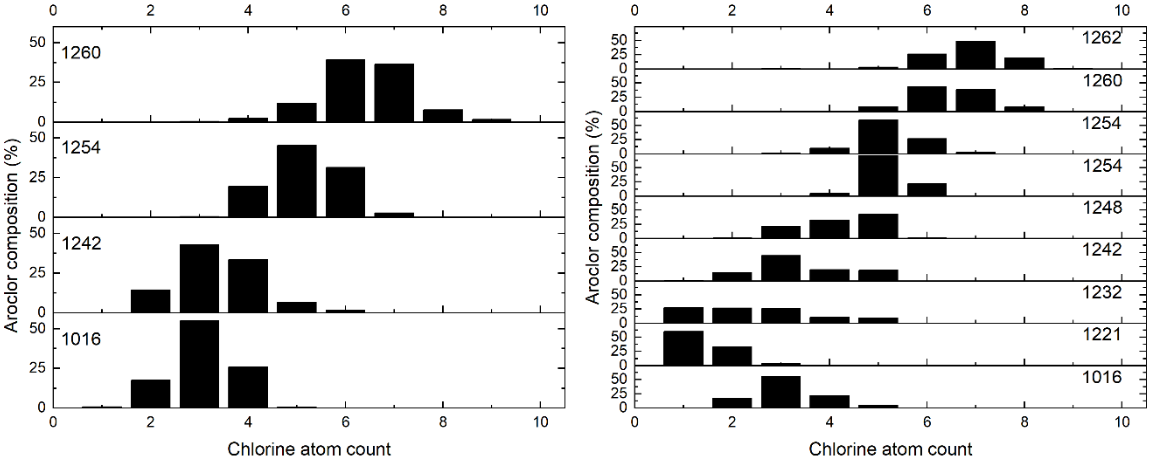


Fig. 5.2 : Histogrammes of Aroclor homologue compositions reported by Mayes et al. (Mayes et al., 1998) (left) and Frame et al. (Frame et al., 1996) (right).

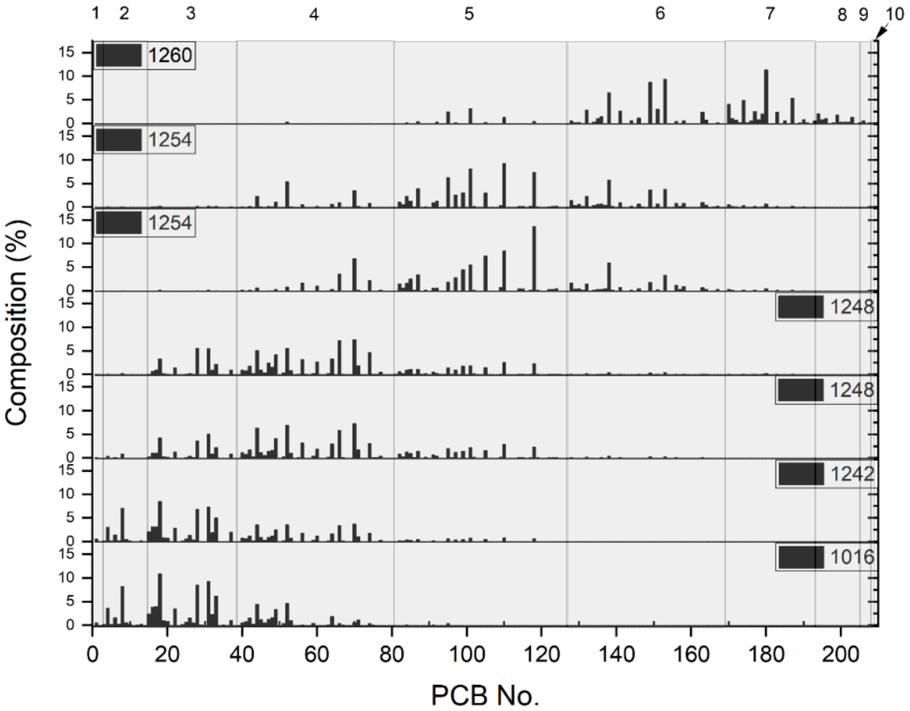


Fig. 5.3 : Histogramme by PCB congener of data reported by Frame et al. (Frame et al., 1996) for a variety of Aroclor formulations.

The degree of diversity of the PCB component distributions for the above mixtures can be assessed by sorting the contributions by decreasing abundance and taking the cumulative distribution function (CDF).

The results are shown in Fig. 5.4 for each of the 7 Aroclor formulations, and for the mean composition of the entire set. The distributions for the 'pure' formulations show that in each case, ~ 90% of the PCB content is composed of a set of ~ 30 congeners, though the composition of each set varies between formulations. In view of the assumption that any mineral oil sample may have contributions from a number of different PCB formulations over time, the CDF was also computed for the mean of the 7 formulations. The number of congeners making up ~ 90 % of total PCB content increases to 60 as a result.

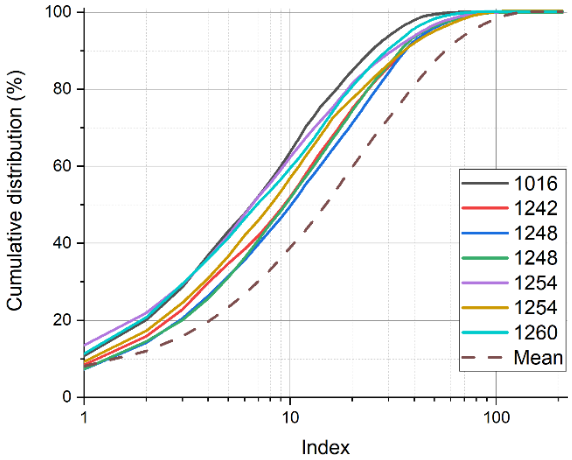


Fig. 5.4 : Cumulative distributions of PCB components in Aroclor mixtures by decreasing order of abundance

5.2. *Key conclusions on PCB mixture composition*

- For the data limited to the Aroclor trade product, the composition at congener level of each formulation is complex, and not entirely reproducible between different batches of the same formulation. We anticipate this situation to be the general case across the industry.
- For present purposes it must be assumed that any of all 209 congeners may be present at significant levels in a sample of transformer oil, and would each contribute to the total concentration of 50 ppm in liquid phase.
- The requirement for PCB congener spectral reference data is especially acute, given the diversity of composition expected.
- Analysis based on gas phase samples would provide information primarily on the less heavily chlorinated, more volatile, PCBs, which, whilst unable to give reliable total PCB quantification, may nevertheless be useful for screening purposes.

6. Spectroscopic detection methods

On the basis of the findings from the previous sections, section 6 first considers instrumental aspects relevant to implementation of spectral detection of PCBs. These include spectral window selection, likelihood of spectral interference, spectral resolution and dynamic range requirements. Once these requirements are established, a range of relevant spectroscopic detection technologies are reviewed. The section concludes with a comparison of instrument concepts and a recommendation of the most appropriate technology.

6.1. Requirements

Spectral window selection

Spectral window selection refers to the choice of region of the mid-IR spectrum in which a proposed detection device is to operate. The selection of spectral window is driven by a number of factors:

- The target molecule should show a strong signal in the selected spectral window to ensure sensitivity of detection.
- The spectral window should be relatively free from signals from other materials potentially present ('interference') to ensure selectivity of detection.
- Suitable technology must be readily available operating in the desired spectral window.

To illustrate the requirements on spectral window selection, the left hand side of Fig. 6.1 shows the mean absorption coefficient of all the PCB spectra of Fig. 3.9 along with that of a quantitative paraffin spectrum derived during an earlier Spectroscopy Group project on detection of contamination in clean rooms. The paraffin spectral signature is assumed to be close to that of the mineral oil in which PCBs are mixed. On the right hand of the figure is also shown the expected absorption coefficient of the trade compound Aroclor, in which the place of the 2,4- and 2,4'- components, for which spectra could not be found, is taken by the 2,5- congener which the data of Bush et al. (Bush and Barnard, 1995) show is a reasonable proxy in the 9 µm region.

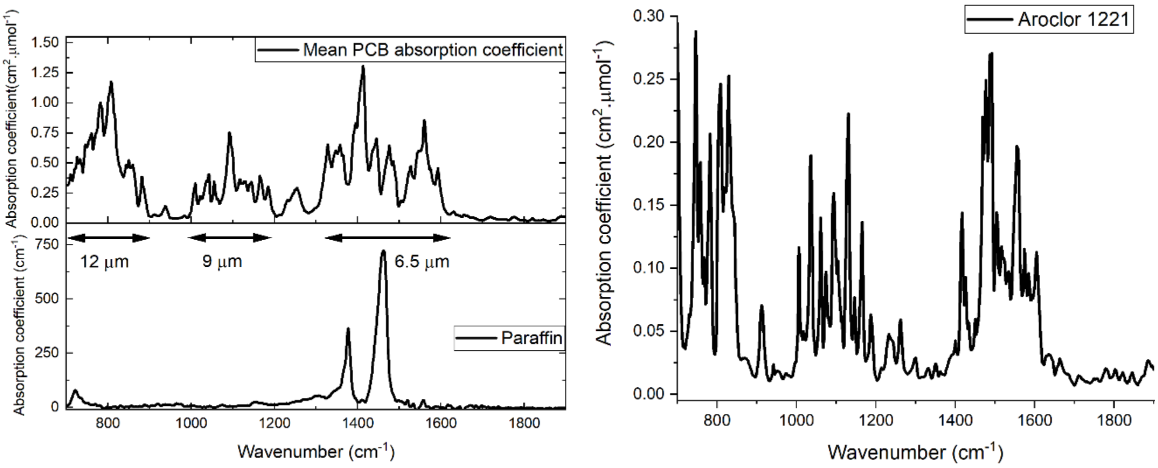


Fig. 6.1 : Left : Mean PCB absorption coefficient compared to paraffin absorption. Right : Computed absorption coefficient of Aroclor 1221, a typical PCB trade formulation, according to Nyquist et al. (Nyquist et al., 1983)

The left-hand plot of Fig. 6.1 shows three regions of the mid-IR in which PCBs in general show strong spectral features. An additional feature around 3 µm (not shown) is discounted as it is weak, and not specific to PCBs. As previously noted, the region around 9 µm has been identified by Schneider et al. (Schneider et al., 1985) as attributable to the presence of chlorine atoms in PCBs. On these grounds, the 9 µm region appears the optimum choice of spectral window, especially that atmospheric water vapour does not interfere in this region. Ideally, based on the proxy data we derived, the spectral coverage required to capture unambiguously the global PCB signature is 300 – 400 cm^{-1}.

Spectral interference

The largest spectral interference in this context is undoubtably from the mineral oil content of the transformer bath. Discrimination against the large mineral oil background absorption is likely to be a major challenge, applying to both liquid and vapour phase, as mineral oil is expected by analogy with pentadecane to have a vapour pressure of ~ 0.5 Pa at ambient temperature. The mineral oil spectrum shown in the left-hand plot of Fig. 6.1 indicates that the 12 and 6.5 μm bands of PCBs are near-coincident with features in the oil spectrum, whereas the 9 μm band is less affected. However, more accurate absorption data in this region for representative mineral oil would be necessary to assess the level of interference.

In the liquid phase, there also exists potential spectral interference from 'fault gases', small molecules which can be generated by a variety of transformer faults and remain dissolved in the oil (https://en.wikipedia.org/wiki/Dissolved_gas_analysis). The principal gases which are infrared active are CO, CO_2, acetylene, ethylene, methane and ethane. Of these, it is only the last four may interfere owing to the wide range of possible combination and overtone bands. A degassing stage in the oil sampling process may be necessary to remove interferences from these sources. It is also possible that concentration of the sample by extraction of oil vapour may increase sensitivity of detection in the liquid, though an assessment of the quantity of PCB also lost would be needed. A form of differential measurement may be feasible by measuring spectra at differing levels of concentration; to a first approximation, the PCB concentration will increase while that of the oil will remain unchanged, assuming no fractionation of oil components.

In the gas phase, in addition to the presence of the fault gases described above, it may also be necessary to discriminate against interference from water vapour and possibly overtones of other atmospheric constituents.

Spectral resolution

The spectral resolution of an instrument refers to its ability to distinguish a number of closely-spaced sharp lines such as those seen in the 9 μm region of Fig. 6.2 (right). An instrument of sufficiently high resolution can correctly reproduce the true structure of the spectral region. A lower-resolution instrument will record a spectrum in which the lines are narrower, and ultimately merge into a single broad feature.

High resolution in this context is clearly desirable as it permits specific congeners to be identified and quantified through their characteristic fingerprint spectrum pattern. However, there is a trade-off between resolution and signal-to-noise ratio (SNR). In order to record spectra with the highest SNR without degrading spectral structure, a resolution of ~ 10% of a typical linewidth is usually used.

Spectral linewidths in liquid phase tend to be broad, as the molecular absorptions are perturbed by collisions with the dense environment of other molecules. Linewidths of liquid-phase spectra reported here are ~ 5 cm^{-1}, and are likely to be partly determined by the resolution of the spectrometer. Nonetheless, such a resolution is clearly capable of generating distinctive spectra for the range of congeners. In the gas phase, linewidths are typically much narrower (~0.2 cm^{-1}) but the density of lines for large molecules such as PCBs is such that relatively broad features are observed even at high resolution. The distinctive structures of gas-phase spectra of PCBs found in this study (typified by the gas-phase spectra of the PCB analogues in Fig. 3.5) recorded at 1 or 4 cm^{-1} resolution demonstrate that, as for the liquid phase, high spectral resolution is not a prime requirement and 0.5 – 1 cm^{-1} would be suitable.

Dynamic range

The dynamic range of a sensing instrument refers to the ratio of the largest and smallest quantities it can reliably detect. Devices based on technologies that have linear response to the concentration of target molecule, such as laser-induced fluorescence (LIF) or the recently-developed chirped laser dispersion spectroscopy (CLaDS), can achieve dynamic ranges of $10^5 – 10^6$ (Wysocki and Weidmann, 2010), whereas techniques whose response is non-linear, such as absorption spectroscopy, typically only achieve ranges of $\sim 10^2$ - 10^3.

In the current context, liquid-phase detection techniques require a modest dynamic range, as (to a first approximation) all PCB congeners have an equal absorption strength. A weak absorption feature that falls outside the instrument's dynamic range is relatively insignificant, as it is generated by a small quantity of PCB that makes only a minor contribution to the total PCB detected. A dynamic range of $\sim 10^3$ is likely to be adequate. Gas-phase detection techniques however require a much higher dynamic range, at least equal to the difference in vapour pressures of the most and least volatile congeners, a factor of $\sim 10^6$, and ideally 2-3 orders of magnitude greater, in the case of transformer oil at ambient temperature. The required dynamic range is reduced to $\sim 10^4$ if the oil sample is at 100 °C.

Sensitivity

The expected degree of absorption in the vapour for congener samples at 50 ppm in the liquid assuming a 1-metre absorption path length and a representative absorption cross-section of 0.002 $ppm^{-1}.m^{-1}$ can be determined by combining the spectral and physical chemical data from Sections 4.2 and 4.3. The results are summarised in Table 6.1 assuming two limiting-case liquid temperatures of 25 and 100 °C ; the latter temperature is selected in view of the typical flashpoint of 'transformer oil' of ~ 140 °C. The analysis is restricted to congeners Cl-1 to Cl-7 owing to availability of vapour pressure data ; however, from the trends observable in the existing data it seems that detection of the congeners Cl-8 and above in the vapour phase is even more challenging than for the Cl-1 to Cl-7 congeners. Vapour pressures of the higher congeners can be estimated using reasonable extrapolations of vapour pressure and enthalpy of vaporisation data available for Cl-1 to Cl-7 and are also shown in Table 6.1 with an asterisk indicating an estimated value.

No. of chlorine atoms	Vapour pressure / ppm.atm 50 ppm liquid , 25 °C	Absorption	Vapour pressure / ppm.atm 50 ppm liquid , 100 °C	Absorption
1	5.5×10^{-4}	1.1×10^{-6}	0.19	3.8×10^{-4}
2	1.2×10^{-4}	2.4×10^{-7}	5.5×10^{-2}	1.1×10^{-4}
3	2.7×10^{-5}	5.4×10^{-8}	1.8×10^{-2}	3.6×10^{-5}
4	6.0×10^{-6}	1.2×10^{-8}	7.2×10^{-3}	1.4×10^{-5}
5	1.3×10^{-6}	2.6×10^{-9}	2.3×10^{-3}	4.6×10^{-6}
6	2.9×10^{-7}	5.8×10^{-10}	1.3×10^{-3}	2.6×10^{-6}
7	6.5×10^{-8}	1.3×10^{-10}	4.6×10^{-4}	9.2×10^{-7}
8*	1.4×10^{-8}	2.8×10^{-11}	1.6×10^{-4}	3.3×10^{-7}
9*	3.2×10^{-9}	6.4×10^{-12}	6.0×10^{-5}	1.2×10^{-7}
10*	7.1×10^{-10}	1.4×10^{-12}	2.2×10^{-5}	4.3×10^{-8}
* : data obtained by extrapolation				

Table 6.1: Absorption of PCB Cl-1 to Cl-7 congener vapour assuming 50 ppm in the liquid phase, 1 m path length and cross-section 0.002 $ppm^{-1}.m^{-1}$.

Assuming a 1-metre interaction length between the light and the PCB vapour, Table 6.1 suggests that the instrument signal to noise ratio must be at the very least ~10,000 in the best case scenario (1 Cl atom, 100 °C).

A similar evaluation can be made for absorption by a 50 ppm PCB sample in the liquid phase. Assuming a hypothetical path length of 1 cm, and a molar extinction coefficient of 0.5 $cm^2.\mu mol^{-1}$. Results are shown in Table 6.2. In this case, signal to noise ratio of ~1000 is adequate to quantify PCB congeners up to 10 Cl atoms.

No. of chlorine atoms	Concentration / $\mu mol.cm^{-3}$ 50 ppm by mass in oil	Absorption 1-cm path length, 0.5 $cm^2.\mu mol^{-1}$
1	0.282	0.131
2	0.230	0.108
3	0.195	0.092
4	0.168	0.081
5	0.148	0.071
6	0.133	0.064
7	0.120	0.058
8	0.109	0.053
9	0.101	0.049
10	0.093	0.045

Table 6.2 : Absorption of Cl-1 to Cl-10 PCB congeners in liquid phase, assuming 50 ppm in the liquid, 1 cm path length and cross-section 0.5 $cm^2.\mu mol^{-1}$.

6.2. Spectroscopic detection technologies

This section briefly reviews a number of existing sensor technologies, focussing on their potential sensitivity and any particular features relevant to the intended manner of field deployment. The survey is based partly on a limited literature survey, the results of which are tabulated for ease of reference in Appendix 11.4.

Fourier -Transform Infrared (FTIR)

FTIR is a well-established method for laboratory analytical spectroscopy with a wide range of commercial instruments available of which the smaller, lower-resolution models may be suitable for field deployment. It is typically implemented as an absorption technique, where light traverses the sample to be analysed, either in the vapour or the liquid phase. Compared to some of the techniques described later it is not especially sensitive but has the advantage that the entire mid-IR spectrum is acquired, in contrast to laser-based techniques.

The absorption sensitivity of an FTIR at low (1 cm^{-1}) resolution is typically ~ 10^{-4}. RAL Space Spectroscopy Group have recently modified a compact commercial FTIR to detect trace contaminants on surfaces with an absorption sensitivity of ~ 5 x 10^{-5} corresponding to a contaminant loading of ~ 10^{-8} $g.cm^{-2}$. Spectroscopy Group also have also applied a least-squares forward-model algorithm to derive contamination loading levels and their associated uncertainties.

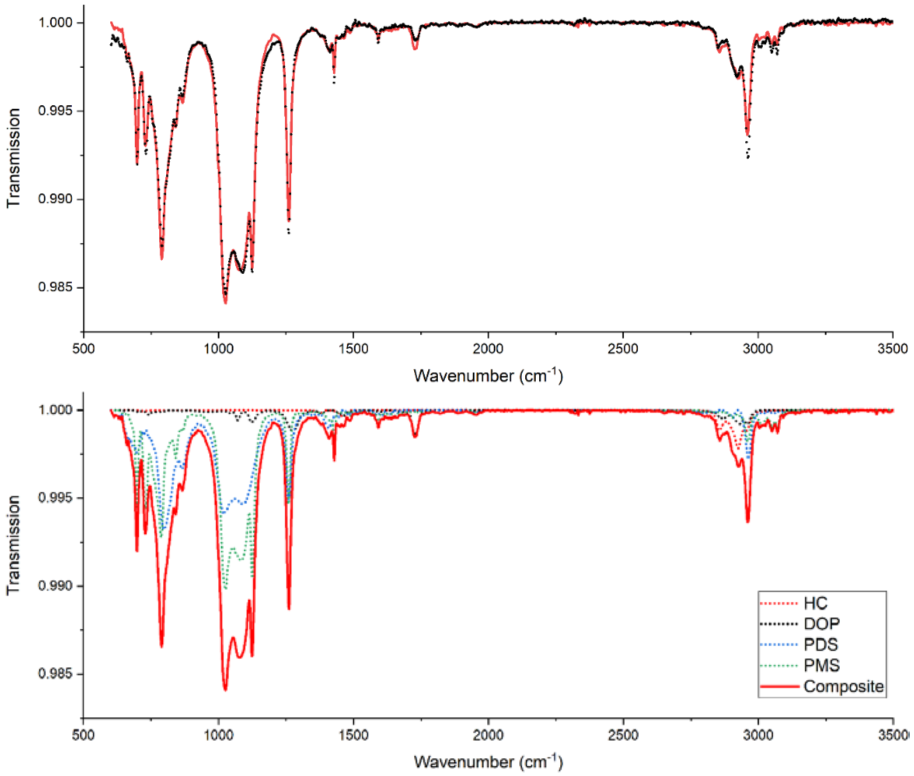


Fig. 6.2 : Top : composite spectrum of a sample of 4 common clean room contaminants and the least-squares fit to the data ; Bottom : spectra of the fitted individual components (dashed lines) and the total (solid line).

The process is illustrated in Fig. 6.2, which in the upper frame shows the spectrum of a synthetic mixture of trace quantities of four common clean room contaminants (known by acronyms HC, DOP, PDS and PMS) prepared on an infrared-transparent plate. Also shown is the fit to the data generated by the fitting algorithm using the calibrated reference spectra of the four contaminants. The lower frame shows the contributions to the overall fitted spectrum of each component. The fit also reports the concentration of contaminant associated with each spectral component.

A typical commercial low-resolution FTIR instrument would meet the current requirements of spectral range and resolution ; certain models are sufficiently compact to be field-deployable in a car or light van. The typical sensitivity is expected to be adequate for use on liquid-phase samples, but not for vapour in the absence of sensitivity enhancement techniques such multi-pass absorption. The mid-IR radiation sources typical of FTIR instruments are less well-suited to compact multi-pass applications than the corresponding laser sources.

Commercial FTIR systems would have the advantage of being off-the-shelf detection solutions, requiring little adaptation for use in this application.

Tunable Laser Absorption Spectroscopy (TLAS)

In TLAS, a laser source of well-defined wavelength is scanned over the absorption region of interest. The laser intensity transmitted through a sample (either in vapour or liquid phase) is recorded as a function of laser wavelength to produce an absorption spectrum. It is an inherently high-resolution technique capable of absorption sensitivity of ~ 10^{-4} which can be extended to ~10^{-5} by use of wavelength-modulation techniques (WMS).

In the current context, TLAS would be performed using a laser source based on external cavity QCL lasers (EC-QCLs), in which the tuning range of a distributed-feedback QCL laser of ~ 1 cm^{-1} is extended by placing it in a tunable external cavity Depending on manufacturer, these can cover a spectral range of 200 to 600 cm^{-1} in the mid-IR region, which is adequate for this application's spectral coverage requirement. Although the typical resolution of QCL sources of ~ 10^{-4} cm^{-1} far exceeds the current requirements, some degradation of effective resolution such as mode-hopping can occur in the external cavity configuration. Nonetheless, the effective resolution is expected to remain ample for this application. An example of previous Spectroscopy Group activity in the TLAS class of techniques is shown below, in which an EC-QCL device was used to test the concept of an open-path laser spectrometer deployed in a typical public space environment to test the ambient air for trace quantities of a target molecule (Macleod et al., 2015). The particular technique is known as 'ACLaS'. In this case the compound dichloroethane (DCE) was used as the target, being a broad-band absorber with a spectrum representative of large volatile organic molecules. Small quantities of N_2O were added to the DCE sample to simulate the presence of spectral interference, as described previously; given that the device operated in ambient air, interference from water vapour was also present. Fig. 6.3 shows examples of spectra recorded and the residuals from the fitting process to be described in Section 7, which indicate reliable retrieval of DCE concentration. From the observed noise levels, a detection sensitivity of 300 ppm.m.$Hz^{-1/2}$ for DCE was determined ; a device using a 1-metre sample path length and 100 second acquisition time would thefore have a detection limit of 30 ppm. The detection limit could be further reduced using multipass techniques as described in the next section.

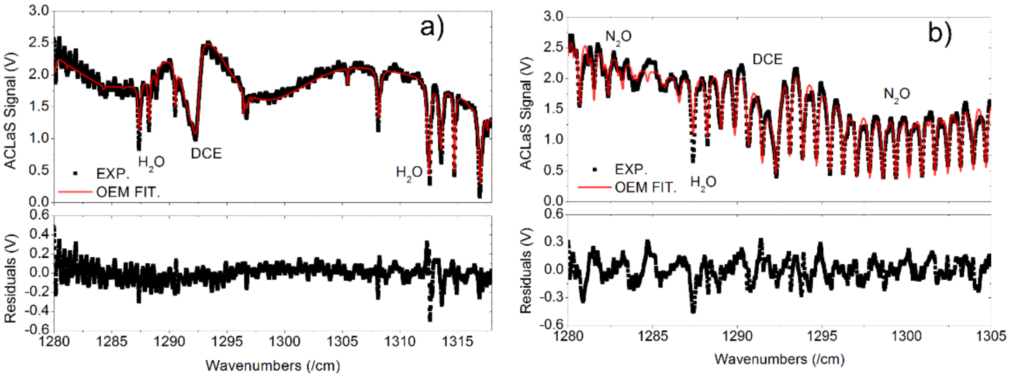


Fig. 6.3: Example of TLAS spectra of a cell containing a) dichloroethane (DCE) and (b) containing DCE and N_2O. The upper panel shows the experimental trace (black dots) and the fitted trace (red). The bottom panel shows the fit residuals.

In the present context, the TLAS technique would be well-suited for liquid-phase detection. Vapour-phase detection is feasible for the lower homologues (having higher vapour pressures), but would require ambitious levels of sensitivity enhancement for detection of higher homologues.

Multipass absorption spectroscopy

Multipass absorption spectroscopy is used to enhance the sensitivity of an existing detection technique by passing its radiation source multiple times through a sample chamber equipped with reflective surfaces at each end, thus increasing the interaction length of sample and radiation and therefore the extent of absorption. A number of designs exist, including White, Herriott and astigmatic multipass absorption (AMAC) cells which can achieve interaction path lengths of typically 50-200 metres. The Spectroscopy group has developed a proprietary multipass system to maximize the gain:volume ratio of a multipass cell.

In the current context, multipass techniques would not be useful for liquid phase detection, as absorption coefficients are much stronger than for gas phase; here the challenge is instead to discriminate small PCB signals against a potentially strong background absorption from mineral oil.

The potential utility of multipass methods in vapour-phase detection varies according to congener. From the illustrative expected levels of absorption shown in Table 6.1, and assuming an absorption sensitivity of 10^{-5} for WMS-enhanced TLAS, path lengths of ~10 and ~ 10^{7} metres would be required for the lowest and highest homologues respectively. Existing multipass techniques might therefore be of use to detect mono- and dichloro-PCBs, but for higher homologues an alternative means of sensivity enhancement would be necessary.

Cavity-enhanced absorption spectroscopy (CEAS)

Instead of enhancing sensitivity by means of a folded light path as previously described, there exist a number of cavity-enhanced absorption techniques by which radiation from a laser is coupled to a high-reflectivity resonant cavity, as a result of which effective interaction path lengths on the order of kilometres can be achieved (Taubman et al., 2005, 2003).One of the first cavity-enhanced techniques to be developed is cavity ring-down spectroscopy (CRDS) in which the decay time of a short laser pulse propagating in the cavity is used to infer information about the absorbing medium in the cavity. Effective path lengths of ~ 1 km and absorption sensitivities of ~ 10^{-7} are achievable. CRDS has the advantage of being immune to pulse energy fluctuations. However, it requires costly high-reflectivity mirrors not readily available in the mid-IR and which are highly sensitive to misalignment and reflectivity degradation in a field environment. In addition, there is a stringent requirement to match cavity length to laser wavelength, which may prove challenging in an application requiring tuning over a range of ~ 200 cm^{-1}.

More recently-developed techniques include Off-axis Integrated Cavity Output spectroscopy (OA-ICOS) and Noise-Immune Cavity-Enhanced Optical Heterodyne Molecular Spectroscopy (NICE-OHMS). NICE-OHMS combines the advantage of cavity-enhanced methods with that of wavelength modulation spectroscopy and has less stringent cavity locking requirements compared to other methods. To date it remains relatively under-developed as a technique for trace gas detection, but is regarded as being the CEAS technique with greatest potential for high sensitivity. Despite the high effective path length of CEAS techniques, OA-ICOS suffers from low transmitted signal levels, though broadband RF perturbation has been used to give a ten-fold improvement in sensitivity.

Although suitable for liquid phase measurements, CEAS techniques are significantly more complex than the simpler FTI and TLAS techniques which offer adequate performance at lower complexity. From the data of Table 6.1 it appears that a technique based on CEAS might feasibly be sufficiently sensitive to the higher congeners in the vapour phase for insulating oil temperatures approaching 100 °C. However, this observation should be qualified by the previous observations (Section 4.4) regarding the importance of accurate temperature and vaporisation enthalpy data for reliable interpretation of results.

Chirped laser dispersion spectroscopy (CLaDS)

CLaDS is a technique developed by RAL Space Spectroscopy Group. In the context of PCB detection, it offers two additional benefits compared to TLAS already described :

- The technique has a high dynamic range compared to absorption methods.
- The technique is largely immune to fluctuations in transmitted laser intensity.

The latter feature could be advantageous in a liquid-phase application in cases in which the transformer oil is turbid as a result of particulates in suspension, for example generated by transformer faults.

However, the current implementation of CLaDS in the mid-IR is not ideally suited to record spectra with the relatively large linewidths (a few cm^{-1}) typical of condensed phase materials, and is therefore likely to suffer from lack of sensitivity The technique also remains to be validated using the widely-tunable laser sources such as EC-QCLs required in this application.

Attenuated Total Reflection (ATR)
ATR is a sampling technique used together with infrared spectroscopy, particularly FTIR, especially suited to direct sampling of liquid or solid materials with potential for *in-situ* sampling of the transformer oil.

However, despite instrument manufacturers' readiness to provide software utilities to do so, conversion between spectra acquired using ATR and those using conventional absorption spectroscopy is not necessarily reliable. For ATR to be used reliably, therefore, a measurement campaign of PCB ATR spectra would be required. The technique is therefore classed as beyond current scope.

6.3. Key conclusions on detection methods

- The optimum spectral window is ~ 1000-1200 cm^{-1} (9 μm).
- The level of spectral interference from mineral oil around 9 μm remains to be quantified.
- The level of spectral interference in the liquid phase from dissolved fault gases and in the gas phase from fault gases and other atmospheric constituents remains to be quantified. In the case of the liquid phase, interferences might be mitigated by a degassing step in the sampling process.
- A spectral resolution of a few cm^{-1} is likely to be adequate for congener identification.
- For measurements on liquid-phase samples, a dynamic range of ~ 10^3 is required. Owing to the wide variation of vapour pressure of the PCB homologues, a dynamic range for measurements in the gas phase of significantly better than 10^6 is required for room temperature transformer oil, reducing to better than 10^4 for a temperature of 100 °C.
- For samples of 50 ppm of the most volatile PCB in oil, a detection limit in the vapour phase of 5.5×10^{-4} ppm is required at ambient temperature and 0.19 ppm at 100 °C. For samples of 50 ppm of the least volatile PCB in oil, a detection limit of 7.1×10^{-10} ppm is required at ambient temperature and 2.2×10^{-5} ppm at 100 °C.
- Allowing for a measurement time limited by typical instrument stability, the detection limits reported in the survey of Appendix 11.5 range between 2.25×10^{-2} and 2.5×10^{-6} ppm.

The summary of this section can be organized as in Table 6.3 showing the key requirements for the addressing the PCB detection problem and how these are addressed by the different spectroscopic detection method considered. The assessment is twofold:

- addressing the need for full PCB analysis at a 10 ppm liquid concentration level sensitivity, being the baseline as described in the requirements,

- a special column entitled “Screening (vap.)”, indicates the requirements for “screening” only of PCBs. Only the monochlorinated, most volatile, congeners are in the scope of the analysis, and only the vapour phase is considered. The method does not constitute a full analysis; instead, it can provide a lower limit on the total PCB content. A positive test result would indicate the presence of a certain minimum total level of PCB level; however, a negative result could not be used to assert that the asset does not contain less volatile PCBs.

Detection method	Spectral Window 950 – 1250 cm^{-1}	Spectral resolution 1 cm^{-1}	Dynamic range			Absorption sensitivity		
			10^3 (liq.)	10^7 (vap.)	Screening (vap.)	10^{-3} (liq.)	10^{-9} (vap.)	Screening (vap.)
FTIR	🟩	🟩	🟨	🟥	🟩	🟨	🟥	🟥
TLAS	🟩	🟩	🟩	🟥	🟩	🟩	🟥	🟥
TLAS multipass	🟩	🟩	🟩	🟥	🟩	🟩	🟥	🟩
CLADS	🟨	🟩	🟩	🟨	🟩	🟩	🟥	🟨
CEAS	🟨	🟩	🟩	🟨	🟩	🟩	🟨	🟨
ATR	🟩	🟩	🟨	🟨	🟨	🟨	🟨	🟨

Table 6.3 : ‘Traffic-light’ classification of suitability of spectral detection techniques reviewed. The “Screening (vap.) column refers to partial screening of most volatile PCBs and is not a full content analysis method.

7. Data reduction & measurement error

7.1. Data inversion

The optical spectrometers considered so far output a transmission spectrum containing fingerprint signatures from the presence of PCBs. However, these raw spectral data need to be processed in order to derive the information required by the end user, namely: 1) the total concentration of PCBs in the liquid phase, 2) a robust estimate on the quality of the data provided by the measurement system. This part of the solution. This section described the processing algorithms and methodology used to extract the information from spectra.The technology developed in the spectroscopy group for the identification and quantification of complex chemical mixtures from spectroscopic data relies on the construction of a mathematical model of the instrument and the measurement method, known as the forward model. This model allows simulation of the expected data output from the measurement system, including noise.

Based on this forward model, Bayesian statistics can be used to infer concentration information about the chemical mixture, as well as diagnostic information on the data inversion. The latter is critical as it allows a metric on the overall measurement process to be constructed, and a confidence metric on the output data, which is crucial to the user.

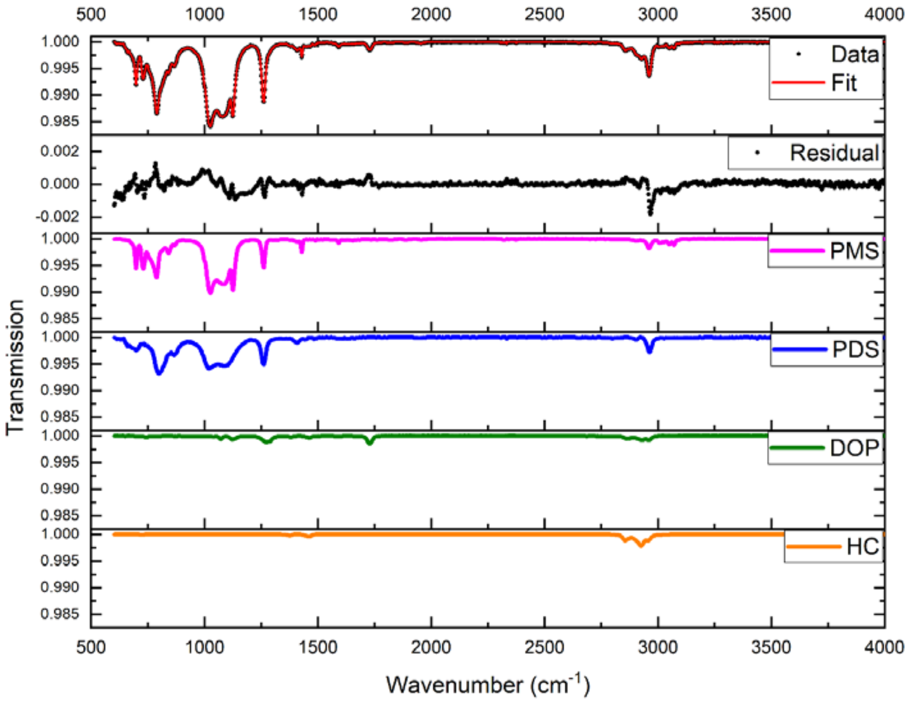


Fig. 7.1 : Illustration of application of the forward model to experimental data, by which the spectra of individual components and their associated concentrations are retrieved

Fig. 7.1 illustrates the process by more detailed reference to the data presented earlier in Section 6.2. A synthetic mixture of trace quantities of four common clean room contaminants (known by acronyms HC, DOP, PDS and PMS) was prepared on an infrared-transparent plate. The spectrum of the contaminated plate and the fit generated by the fitting algorithm are shown in the top panel. The residuals, being the deviation of the fit from the data, are shown in the panel below and give an indication of the reliability of the fit and the associated retrieved contaminant concentration values. Table 7.1 lists the concentrations retrieved for each contaminant along with the associated uncertainties.

Compound	Retrieved concentration / g.cm^{-2}	Uncertainty / g.cm^{-2}
Hydrocarbon (HC)	8.27 x 10^{-9}	2.22 x 10^{-10}
Ester (DOP)	5.51 x 10^{-7}	1.8 x 10^{-8}
Dimethyl silicone (PDS)	1.46 x 10^{-7}	1.7 x 10^{-9}
Methylphenyl silicone (PMS)	4.46 x 10^{-7}	3.12 x 10^{-9}

Table 7.1 : Trace contaminant concentrations retrieved from the experimental spectrum by the fitting algorithm

For this data reduction method to give accurate results, PCB reference spectra are essential to guarantee the quality of the data output.

7.2. Preliminary error analysis

Ultimately the error analysis is embedded in the inversion algorithm briefly described above. However, to assess a suitable spectroscopic detection method, a preliminary error budget analysis is required. The following error propagation analysis is based on the (realistic) assumption that any combination of the 209 PCB congeners may be present in the sample oil.

Liquid phase

The model liquid phase spectrum to be fitted to the experimental spectrum is:

$$\hat{S}(\overline{\upsilon}) = \sum_{i=1}^{209} a_i\, S_i(\overline{\upsilon}) + P(\overline{\upsilon}) \qquad \text{(Eq. 7.1)}$$

in which $P(\overline{\upsilon})$ represents a polynomial background. The fit returns the estimated concentration a_i of each PCB in the basis set together with an uncertainty δ_i for that component.

The total estimated PCB concentration A and, assuming uncorrelated uncertainties δ_i, its uncertainty Δ is given by:

$$A = \sum_{i=1}^{209} a_i \quad ; \quad \Delta = \left[\sum_{i=1}^{209} \delta_i^{\,2}\right]^{1/2} \qquad \text{(Eq. 7.2)}$$

The assumption of uncorrelated uncertainties is a working assumption, but is highly unrealistic. In reality, it is highly likely that the spectral identification will only allow to separate a subset of congeners. Therefore, the concentration data inferred will be compounded concentrations with fully correlated errors. Making the reasonable simplifying assumption that $\delta \equiv \delta_i$, Eq. 7.2 implies $\Delta \sim 14.5\ \delta$. Applying in addition the regulatory requirement that $\Delta < 50$ ppm implies the requirement that individual congeners are to be measured with $\delta \sim 3$ ppm at 1σ confidence level, or ~ 1 ppm at the 3σ level. Again, this is an unrealistic worst-case scenario giving an absolute lower bound on the detection accuracy ; more work is needed to derive a more robust error analysis.

Vapour phase

The model vapour phase spectrum is analogous to Eq. 7.1 in which prime notation is used to refer to quantities relating to vapour phase.

$$\hat{S}'(\bar{\upsilon}) = \sum_{i=1}^{209} a_i'\, S_i'(\bar{\upsilon}) + P'(\bar{\upsilon}) \qquad \text{(Eq. 7.3)}$$

The estimated total PCB concentration in the liquid derived from the estimate of concentration in the vapour phase, and its uncertainty, are now given by :

$$A = \sum_{i=1}^{209} a_i'\, T_i \quad ; \quad \Delta = \left[\sum_{i=1}^{209} (\delta_i'\, T_i)^2\right]^{1/2} \qquad \text{(Eq. 7.4)}$$

where T_i is the transfer function relating concentration of PCB in the liquid to that in the vapour. Fig. 4.1 shows that T_i varies from ~ 10^5 for Cl-1 congeners to ~ 10^9 for Cl-7, and by extension to ~ 10^{11} for decachloro-PCB. Again assuming $\delta' \equiv \delta'_i$, and with the same caveat regarding the highly unrealistic assumptions underpinning this early analysis, Eq. 4.4 shows that the uncertainty in total concentration will be dominated by the term due to decachloro-PCB, giving $\Delta \sim 10^{11}\delta'$. For the requirement $\Delta < 50$ ppm, the measurement uncertainty δ' required in the vapour phase is then ~ 10^{-10} ppm.

7.3. *Key conclusions on data reduction*

- A robust framework for data interpretation and quantitative measurement of complex chemical mixtures exists and can be applied to the case of spectroscopic PCB measurements.
- Early error propagation analysis suggests that accuracy requirements for the vapour phase analysis are several orders of magnitude more demanding than for liquid phase analysis, and far from what any realistic analytical techniques can provide.

8. Conclusion and recommendation

- The regulatory requirement of < 50 ppm of PCB applies to liquid phase samples, irrespective of the actual composition of PCB congeners. Using vapour phase measurements to infer PCB concentrations in the liquid requires an accurate way to relate vapour phase to liquid phase concentrations, which requires an accurate knowledge of temperature of the mixture and the enthalpies of vaporisation of PCB congeners.
- The variability in composition of PCB trade formulations and the possibility that the oil in a transformer may have been supplied from a variety of uncontrolled sources means that any detection technique must allow for the presence of the full range of all 209 congeners if the total 50 ppm in liquid phase analysis is required.
- The requirements for vapour phase detection and quantification are extremely demanding, especially for the heavier, more chlorinated congeners. The outcome of this study suggests the practical solution should focus on liquid analysis, which has implications for the practical implementation of the solution and particularly on the method of obtaining samples.
- Vapour phase solutions are realistic only when applied to volatile monochlorinated PCB congeners. This would allow the development of a screening solution but not a full quantification solution.
- Using liquid phase analysis, mid-infrared spectroscopic analysis will fulfil the requirements, based on the partial knowledge we have and the assumptions we made at the time of this study.

The following recommendations can be made following this initial study to strengthen the core of the proposed solution:

- There is a considerable lack of reliable data. First, almost no quantitative spectral data on PCB congeners could be found. We conducted this study based on realistic assumptions and proxy methods. We would recommend conducting laboratory work to consolidate the required dataset required for quantitative spectroscopic detection of PCBs. We recommend focusing on the liquid phase data if a full quantification solution is required, or on volatile PCBs congeners if only screening is required.
- During analysis, PCB spectral features must be distinguished against a background of mineral oil signatures. We could not find sufficiently accurate data to assess the impact of the mineral oil background. We would recommend conducting laboratory work to capture these data in addition to the PCB reference data mentioned above.
- We would recommend analysing real-world transformer oil samples in the laboratory to validate the assumptions made during this study and gather real data.
- The liquid-phase analysis could be conducted using either of two core technologies: Fourier transform spectrometry, or widely-tunable laser absorption spectroscopy. We would recommend conducting a proof-of-concept to demonstrate and evaluate both approaches.
- If the screening method is of interest, we would recommend conducting a widely tunable laser absorption spectroscopy multipass proof-of-concept in the laboratory.
- After reference data have been produced, we would recommend running a proof-of-concept focusing on the data reduction and qualification methodology to validate the proposed mathematical approach to data analysis.

9. Prospective possible implementation

From the study and from the interaction with Steve Pinkerton-Clark during a review meeting at RAL on the 10th of February, we see two different approaches:

- Developing a solution for fast partial screening based on gas sniffing,
- Developing a solution for full systematic quantification against the 50 ppm in liquid phase requirement for total PCB content.

9.1. Screening approach

We anticipate the screening solution to focus on the most volatile congener of PCBs and to work using a gas phase sample. Again, it is important to note that this approach will allow to identify some transformers contaminated by PCBs, but it will not permit to conclude that the ones negative with this test are not contaminated.

The approach is conceptually seen as the following:

- An operator drives to the transformer location.
- Using a long pole, perhaps aided with a camera providing visual feedback, he couples the extremity of the pole to the transformer breather tube.
- The gas in the head space above the oil bath in the transformer is flushed into the analysis cell. This cell could be either at the tip of the pole, or on the ground close to the operator and connected to the tip of the pole via tubing.
- The system runs the vapour phase analysis on the sample collected and provides a YES/NO screening output. This information is logged, time stamped, and geolocated.
- The operator wraps up equipment and drive to the next one.

The possible contamination of the sampling equipment by PCBs and exposure of the operator will need to be considered.

9.2. Full PCB quantification

The requirement for full quantification of PCBs calls for the liquid phase analysis approach, which critically requires obtaining a liquid phase sample of the oil bath. Two liquid sampling approaches are being considered:

- A long pole enabling the operator to perform a sponge wipe of the oil residue in the vicinity of the breather tube. The impregnated sponge is then brought down to ground level and used to provide a smear over a test plate for analysis using a system in the car's luggage space.
- A long pole equipped with a liquid sampling system penetrating the transformer reservoir via the breather tube, similar to an endoscope probe. The system would allow collection of a ~1 ml sample of oil to be brought to ground level and inserted into an analyser in the luggage space of the operator's car.

The rest of the procedure would be similar to that described in the case of the screening approach.

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11. Appendices

11.1. Acronym description

GC	Gas chromatography
MS	Mass spectrometry
FTIR	Fourier-transform infrared
DRIFTS	Diffuse reflectance infrared Fourier-transform spectroscopy
UV	Ultraviolet
QCL	Quantum cascade laser
EC-QCL	External cavity quantum cascade laser
BZ	Ballschmiter & Zell
IUPAC	International Union for Pure & Applied Chemistry
DL	Diode laser

11.2. Trade names or descriptions of PCB fluids

These are used by manufacturers of transformers, switch gear and insulating mineral oil.

Name	PCBs	Name	PCBs	Name	PCBs
Abestol		Ducanol		Orophene	
Aceclor		Duconol		PCB	
Apirolio		Dykanol		PCBs	
Areclor		EEC-18		Phenoclor	
Aroclor	Various	Elaol		Plastivar	
Arubren		Electrophenyl		Polychlorinated Bipl	
Asbestol		Elemex		Polychlorobiphenyl	
Askarel		Eucarel		Prodelec 3010	
Auxol		Fenchlor		Pydraul	
Bakola 131		Fenclor	Pure Cl-10	Pyralene	
Biclor		Fenocloro		Pyranol	
Chlorextol		Gilotherm		Pyroclor	
Chlorinated Biphenyl		Gyvol		Saf-T-Kuhl	
Chlorinated Diphenyl		Hivar		Santosol	
Chlorinol		Hydol		Santotherm	
Chlorobiphenyl		Hvvol		Santotherm FR	
Chlorphen		Inclor		Santovac 1 and 2	
Clophen		Inerteen		Siclonyl	
Clophenharz		Kanechlor		Solvol	
Cloresil		Kaneclor		Sovol	
Delor		Kennechlor		Sovtol	
Delorene		Leromoll		Terphenychlore	
Diaclor		Montar		Therminmol	
Dialor		Nepolin		Therminol FR	
Disconon		No-Flamol		Turbinol	
DK		Olex-SF-D			

Table 11.1 : Trade names and compositions where known of commercial PCB products

11.3. Number of congeners by Cl atom count

Table 11.2 lists the number of PCB congeners by the number of chlorine atoms.

PCB homolog	CASRN	No. of Cl substituents	Number of congeners
Biphenyl	92-52-4	0	1
Monochlorobiphenyl	27323-18-8	1	3
Dichlorobiphenyl	25512-42-9	2	12
Trichlorobiphenyl	25323-68-6	3	24
Tetrachlorobiphenyl	26914-33-0	4	42
Pentachlorobiphenyl	25429-29-2	5	46
Hexachlorobiphenyl	26601-64-9	6	42
Heptachlorobiphenyl	28655-71-2	7	24
Octachlorobiphenyl	55722-26-4	8	12
Nonachlorobiphenyl	53742-07-7	9	3
Decachlorobiphenyl	2051-24-3	10	1

Table 11.2: PCB homologues and their compositions

11.4. Molar mass of congeners

The molar mass of a congener is important if converting between mol.cm^{-3} or ppmv and ppm by mass. For the purposes of this study it is assumed that concentration measures such a '50 ppm' refer to parts by mass, as per 96/59/EC, rather than mole fraction. The molar mass of PCBs varies by a factor of ~ 3 from the monochloro- to the decachloro- congeners.

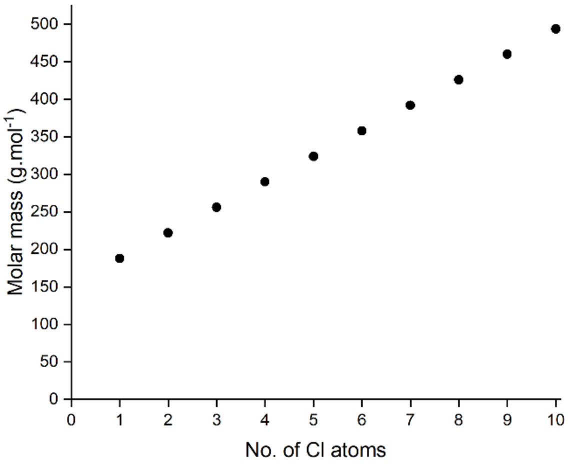

Fig. 11.1 : Molar masses of PCB homologues

No. of Cl atoms	Molar mass	Concentration at 50 ppm (1)
	g.mol^{-1}	μmol.cm^{-3}
1	188	0.231
2	222	0.196

3	256	0.170
4	290	0.150
5	324	0.134
6	358	0.122
7	392	0.111
8	426	0.102
9	460	0.095
10	494	0.088

(1) By mass, in mineral oil assuming 0.87 g.cm^{-3}

Table 11.3 : Molar masses of PCB homologues and corresponding concentrations in μmol.cm^{-3} at concentration 50 ppm by mass

11.5. Summary of laser spectroscopic detection methods surveyed

LOD refers to Limit Of detection and NEAS to Noise-Equivalent Absorption Sensitivity

Lead author	Reference	Technique	λ	Molecule	LOD	LOD in 100 s	NEAS	Sensitivity
			μm		ppb.Hz$^{-½}$	ppb	ppb.cm^{-1}. Hz$^{-½}$	ppm.m.Hz$^{-½}$
Manne	(Manne et al., 2010)	ICOS/CEAS	10.3	Ammonia	45	4.5	0.006	3
Bakhirkin	(Bakhirkin et al., 2004)	ICOS/CEAS	5	Nitric oxide	8	0.8	40	-
Arslanov	(Arslanov et al., 2011)	ICOS/CEAS	3-4	Ethane	0.025	0.0025	-	-
Parameswaran	(Parameswaran et al., 2009)	ICOS/CEAS	3.3	Ethane	0.5	0.05	-	-
Wang	(Wang et al., 2019)	ICOS/CEAS	1.65	Methane	60	6	5	-
Moyer	(Moyer et al., 2008)	ICOS/CEAS	6.7	Water	-	-	0.024	-
Centeno	(Centeno et al., 2014)	ICOS/CEAS	11	Ethylene	100	10	15	-
Lang	(Lang et al., 2016)	ICOS/CEAS	7	Methane	0.28	0.028	3.6	-
Bergin	(Bergin et al., 2013)	ICOS/CEAS	5.5	Nitric oxide	7	0.7	24	-
Manne	(Manne et al., 2006)	CRDS	10.3	Ammonia	225	22.5	-	-
Nelson	(Nelson et al., 2002)	Multipass	5.3	Nitric oxide	0.12	0.012	-	0.025
Roller	(Roller et al., 2007)	Multipass	5.2	Nitric oxide	1	0.1	-	0.11
Ghorbani	(Ghorbani and Schmidt, 2017)	Multipass	4.7	Carbon monoxide	2	0.2	-	-
Dong	(Dong et al., 2015)	Multipass	3.6	Formaldehyde	0.6	0.06	-	-
Nadeem	(Nadeem et al., 2019)	Multipass	7.7	Nitrous oxide	47	4.7	6	-
Weibring	(Weibring et al., 2007)	Multipass	3.5	Formaldehyde	0.11	0.011	-	-
Manne	(Manne et al., 2011)	Multipass	10.3	Acrylonitrile	6	0.6	-	-
Daghestani	(Daghestani et al., 2014)	CLaDS	7.8	Methane	20	2	-	0.1

Table 11.4 : Summary of performance metrics for laser spectroscopic methods surveyed.