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Isotopic Tracers for Combustion Research

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ABSTRACT

This review article deals with the use of isotopic tracers in the field of combustion science. A number of researchers have reported the use of isotopic techniques, which have been employed to solve a wide range of combustion problems. Radioactive and stable isotopes have been utilized as tracers, including isotopes of carbon (^{13}C and ^{14}C), oxygen (^{18}O), and deuterium (D). One of the main applications has been to quantitatively determine the propensity of a molecule in a mixture, or specific atom within a molecule, to form pollutant emissions. Tracer studies have also been used for the elucidation of combustion reaction pathways, and kinetic rate constant determination of elementary reactions. A number of analytical techniques have been used for isotope detection; and the merits of some of the different techniques are discussed in the context of combustion research. This article concludes by exploring emerging methods and potential future techniques and applications.

Introduction

The isotopic ratios of a number of elements are routinely measured by techniques such as isotope ratio mass spectrometry (IRMS), including elements of carbon ($^{13}C/^{12}C$ or $^{14}C/^{12}C$), nitrogen ($^{15}N/^{14}N$), oxygen ($^{18}O/^{16}O$), sulphur ($^{34}S/^{32}S$), and hydrogen ($D/^1H$). The ability to precisely measure the isotopic abundance of samples has a wide variety of applications, including dating, metabolic flux analysis, chemical mechanism analysis, atmospheric source apportionment studies, and medical diagnostic tests.

The purpose of an isotope tracer experiment is to allow specific molecules, or specific atoms within molecules, to be followed through a reaction or sequence of reactions. Detection of the isotopic marker in the reaction products by isotopic analysis allows the source of the products to be unequivocally determined, since they are derived from atoms that are isotopically distinguishable. Isotope tracer experiments are therefore useful in situations where a species of interest can be derived from a number of sources. Consider particulate matter (PM) collected from the exhaust of a diesel engine vehicle; the PM will contain carbon derived from both the fuel being burned and the engine lubrication oil. In order to discriminate between carbon in the PM derived from the two sources, an isotope labeling experiment is a direct way of measuring the relative contributions. For example, in one such study, Mayer et al. (1980) calculated the fractions of the PM in diesel engine exhaust that originated from the fuel and oil, in an experiment that used lubrication oil

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(15W40) that was enriched with ^{14}C-labeled compound and fossil diesel fuel of natural isotopic composition. By measuring the isotope ratio of the PM, it was calculated that the engine lubrication oil accounted for between 1.5% and 25% mass of the PM carbon, dependent on the engine speed and load. The percent of contribution generally decreased with engine load, and increased with speed. Other studies that have involved apportionment of fuel and lubrication oil contributions to exhaust PM will be discussed in greater detail in the following section.

A further and relevant example is the use of isotopic measurements for the source apportionment of environmental pollutants, such as polycyclic aromatic hydrocarbons (PAHs). PAHs are a product of incomplete combustion, and some of them are known to be mutagenic and carcinogenic (Nisbet and Lagoy, 1992). The major source of PAHs in the environment is from the combustion of carbon-containing fuels, with commercial and residential burning of biomass accounting for an estimated 60.5% of the total global PAH emissions and vehicle tailpipe emissions accounting for some 12.8% (Shen et al., 2013). Compound-specific isotope analysis (CSIA) of combustion-generated PAHs shows that the isotopic signatures of both carbon ($\delta^{13}C$) and hydrogen (δ^2D) are dependent on the fuel source and of the combustion conditions employed (Mcrae et al., 1996, 2000; Sun et al., 2003a); and researchers have used this to aid the identification of the sources of PAHs in the environment. For example, Sun et al. (2003b) demonstrated the use of CSIA to identify the origins of PAHs extracted from soil samples taken from a contaminated site. Heavy contamination of the site from diesel fuel was suggested from the identities of mono- and di-aromatic compounds, and had an isotopic signature close to those expected for diesel fuel (with $\delta^{13}C$ values from –28‰ to –29‰). In addition, some of the larger PAHs with 5–6 rings were consistent with being derived from coal burning by industrial/domestic combustion, and had an isotopic signature that was isotopically 'heavier' than the compounds identified as diesel components (with a $\delta^{13}C$ value of about –25‰). For further information on the topic of environmental sources of PAHs, the review paper of Lima et al. (2005) is recommended, and Buczyńska et al. (2013) have reviewed analytical methods for environmental PAH CSIA.

Despite the widespread application of isotopic techniques in fields such as physiology and atmospheric science, they have not been as widely deployed in fundamental combustion and pyrolysis research. A survey of the literature has identified a number of studies that have employed isotopic tracers; these are listed in Table 1, which is organized by application. The purpose of Table 1 is to classify the various uses of isotope labeling in combustion science, and to demonstrate the variety among the different methods. It is seen that a number of atomic tracers have been used for different purposes since the 1950s, and a range of analytical techniques have been used for isotope detection, including accelerator mass spectrometry (AMS), mass spectrometry (MS), IRMS, radioactive decay counting techniques (such as liquid scintillation counting), and laser techniques. Selected examples from the literature are discussed in this article, and attempts are made to illustrate how isotope-labeling experiments have been employed to solve a range of problems. The majority of the research has involved the tracing of isotopes of carbon (either the stable isotope ^{13}C or radioactive ^{14}C) from the fuel, oil, or additive to the combustion products, including CO, CO_2, and PM. Therefore, the majority of this article is concerned with the isotopic tracing of carbon.

Table 1. The application of isotopic tracing experiments relating to combustion science, as reported in the literature.

Application	Experimental system	Tracer isotope	Detection technique	Isotopically measured species	Reference(s)
Determination of engine lubrication oil contribution to exhaust PM	Diesel engine	^{14}C	Scintillation counter	PM (bulk)	Mayer et al. (1980), Hilden and Mayer (1984)
	Diesel engine	^{14}C	Unspecified	PM (bulk)	Burley and Rosebrock (1979)
	Diesel engine	^{14}C	AMS	PM (bulk, and non-volatile organic fraction)	Buchholz et al. (2003), Jones et al. (2005)
	Diesel engine	D	GC/MS	PM (volatile organics/PAH)	Buttini and Manni (2001), Lombaert et al. (2006), Zielinska et al. (2008)
	Diesel engine	^{13}C	IRMS	PM (bulk, and non-volatile organic fraction)	Eveleigh et al. (2016)
Quantifying of the formation of in-cylinder deposits	Spark-ignition engine	^{14}C	Vibrating reed electrometer	In-cylinder deposits	Sechrist and Hammen (1958)
	Spark-ignition engine	^{14}C	AMS	In-cylinder deposits	Shore and Ockert (1958)
Determination of the conversion rate of fuel molecules or atoms to combustion emissions	Diesel engine	^{14}C	AMS	In-cylinder deposits	
	Diffusion flame	^{14}C	Scintillation counter	Soot	Lieb and Roblee Jr. (1970), Homan and Robbins (1986), Sorek et al. (1984), Sorek and Anderson (1985, 1986), Schmieder (1985)
	Premixed flames	^{13}C	Spectroscopic intensity	C_2 radical species	Ferguson (1955)
	Combustion bomb	^{13}C	MS	Soot, and various gaseous species (CO, CO_2, CH_4, etc.)	Ferguson (1957), Ferguson and Yokley (1958)
	Tube reactor and diesel engine	^{13}C	IRMS	PM (bulk)	Eveleigh et al. (2014, 2015), Eveleigh (2015),
	Diesel engine	^{14}C	AMS	PM, CO_2, in-cylinder deposits	Buchholz et al. (2004), Eveleigh et al. (2016), Buchholz et al. (2002)
	Diesel engine	^{14}C	AMS	CO_2	Mack et al. (2005a, 2005b)
	Tube reactor	^{13}C	GC/MS	PAHs, alkyl-PAHs	Lea-Langton et al. (2013)
	Diesel engine	^{13}C	GC/MS	PAHs, alkyl-PAHs	Lea-Langton et al. (2015)
	Diesel engine	^{14}C	Radio-GC	PAC	Petch et al. (1990), Rhead et al. (1990)
	Diesel engine	^{14}C	Radio-HPLC (scintillation counter)	PAHs	Rhead and Trier (1992), Tancell et al. (1995a, 1995b), Rhead and Pemberton (1996), Rhead and Hardy (2003)
	Spark ignition engine	D	GC/MS	Unburned hydrocarbons	Bennett et al. (1996), Gregory et al. (1999)
Combustion chemical mechanism analysis/ kinetic rate constant determination	Shock tube	^{18}O	Laser absorption	^{16}OH and ^{18}OH	Stranic et al. (2013, 2014)
	Reaction vessel	^{14}C	Decay counting	CO	Cullis et al. (1958)

	Reactor	Isotope	Method	Species	References
	Reaction vessel	^{14}C	Decay counting	Ketones	Cullis et al. (1959, 1962, 1963a, 1966)
	Reaction vessel	^{14}C	Radio-GC (proportional detector)	Gaseous species (C_2–C_5)	Berry and Cullis (1970), Berry et al. (1970), Cullis and Hirschler (1978)
	Tube reactor (pyrolysis)	^{14}C	GC, radiochemical assay	PACs, PAHs, alkyl-PAHs	Badger and Kimber (1961), Badger et al. (1962), Badger and Novotny (1963), Badger et al. (1964, 1966a, 1966b, 1967a, 1967b)
	Tube reactor (pyrolysis)	^{14}C, ^{3}H	Radio-GC	H_2, C_1–C_4, PAHs	Cypres and Bettens (1986)
Reaction pathway analysis: catalytic combustion	Plug-flow microreactor	^{13}C, ^{18}O, D	GC/MS	CO, CO_2, C_3H_8, C_3H_6	Chen et al. (1999)
	Tube reactor	^{16}O, ^{18}O	GC/MS	CO, CO_2	Ciuparu et al. (2001)
	Tube reactor	D, ^{18}O	GC/MS	Light gaseous species	Au-Yeung et al. (1999)
Visualization of flame structure and distribution of reacting species	Premixed flame	D	PLIF	OH, OD	Katoh et al. (2006a, 2006b, 2006c)
	Diffusion flame	D	PLIF	OH, OD	Kajimoto et al. (2013)

In nature there are three isotopes of carbon, these are ^{12}C, ^{13}C, and ^{14}C, and their natural abundances are around 98.89%, 1.11%, and 0.0000000001%, respectively. ^{12}C and ^{13}C are both stable isotopes, which means that they do not undergo radioactive decay. ^{14}C is a radioactive nuclide and undergoes radioactive beta decay, a process that has a half-life of 5730 years; the half-life being the time taken for the radioactivity of a sample to fall to half of its original value. Despite the differences in stability and mass, the isotopes of carbon are practically identical in terms of their reactivity. Physical differences and kinetic isotope effects (KIEs) between different isotopologues (molecules containing atoms of a specified isotopic composition), are in most cases negligible for the purpose of isotopic tracing, or can be corrected for. Due to the relatively larger difference in mass between hydrogen/deuterium, kinetic isotope effects occur to a greater extent than for heavier atoms, such as oxygen or carbon (Criss, 1999). The substitution of hydrogen for deuterium in closed constant volume experiments has a marked effect on measured flame speeds, with deuterium flames burning slower, principally due to differences in diffusivity and KIEs (Gray et al., 1970; Koroll and Kumar, 1991). However, most researchers report negligible isotopic effects for carbon and oxygen (e.g., Schmieder, 1985; Stranic et al., 2013).

Isotope studies of soot and PM formation

One of the earliest examples of the use of isotope labeling in combustion was carried out by Ferguson (1957), and used a ^{13}C-labeling technique. The aim of the study was to identify whether soot was preferentially produced from a C_2 fragment of propane by scission of carbon atoms from the end of the C_3 propane chain. If this were the case, then the central carbon atom would be preferentially converted to soot with respect to the two carbon atoms at the ends of the three-carbon chain. Combustion of propane-2-^{13}C (labeled at the central carbon) was carried out in a combustion vessel, and soot samples were collected for isotope analysis by mass spectrometry. Analysis of the soot $^{13}C/^{12}C$ ratio indicated that the three carbon atoms in propane contributed equally to soot formation. Similarly, measurement of residual carbon monoxide, acetylene, and methane showed a random distribution of ^{13}C; this indicated that these species were derived equally from the three carbon atoms of propane.

Instead of using ^{13}C, the majority of the work described in the literature during the 1950s to 1980s involved the use of ^{14}C as a tracer. Two different detection methods have been used for detecting ^{14}C: due to the fact that ^{14}C is radioactive, one detection method involves counting the rate of decay of a sample as a measure of the $^{14}C/C$ rate in the sample; and the second method involves the spectrometric counting of individual ^{14}C atoms. Most of the earlier research using ^{14}C involved the decay counting method. Lieb and Roblee Jr. (1970) published work that described a ^{14}C labeling experiment, which used decay counting to quantify the conversion of carbon atoms in ethanol to soot. In turn, ethanol-1-^{14}C (where the carbon atom next to the hydroxyl group was ^{14}C labeled) and ethanol-2-^{14}C (where the methyl carbon contained ^{14}C) were burned in a diffusion flame and soot was extracted from the flame using a sampling probe. It was concluded that the methyl carbon atom contributed the majority of carbon to the soot, and a conversion ratio of 2:1 methyl-to-hydroxyl carbon atoms was identified.

Also using the decay counting method, Schmieder (1985) investigated a wider range of hydrocarbons that were selectively labeled with ^{14}C, to determine the conversion

probability of carbon atoms to soot in diffusion flames. To assess the probability of a labeled carbon atom converting to soot, a parameter termed R was used. R was defined as the ratio of the actual probability of incorporating of a labeled atom(s) into soot to the statistical probability (assuming all carbon atoms contribute to soot equally). For example, in a fuel where all of the carbon atoms contribute equally to soot formation $R = 1$; or where the specified carbon atom is more (or less) likely than its statistical likelihood to be incorporated into soot $R > 1$ (or $R < 1$). Schmieder investigated the conversion of carbon atoms in single-component fuels of benzene, cyclohexane, toluene, benzoic acid, and 1-butanol; and large differences in the conversion rates of carbon atoms were found, dependent on local molecular structure of the fuel. For example, the methyl group of toluene was found to convert to soot at a rate ($R = 0.80$ to 0.85) that was lower than that of carbon atoms that were in the aromatic ring. And in the case of 1-butanol, it was found that the hydroxyl carbon atom (next to the OH) converted to soot at a rate ($R = 0.51$) that was around half of that of the 'alkyl' carbon atoms. For the molecules benzene and cyclohexane, each of the carbon atoms are in a chemically equivalent environment, which is to say that due to the symmetry of the cyclic molecules all of the carbon atoms are 'the same'. R-values of 1 ± 0.03 and 0.98 ± 0.03 were obtained for benzene and cyclohexane respectively, meaning that the ^{14}C-labeled atoms in these molecules converted to soot at the same rate as the ^{12}C atoms. This demonstrated the effectiveness of the method and showed that kinetic isotope effects between ^{14}C and ^{12}C during soot formation is negligible.

The examples discussed so far have involved the combustion of single-component fuels, where single atoms within a molecule were traced through to the combustion products. It should be noted that binary and multicomponent mixtures have also been studied where one of the compounds is either entirely or site-specifically labeled and the other component is unlabeled. For instance, Sorek and Anderson (1985) investigated the conversion of binary mixtures of various radiolabeled compounds (^{14}C labeled methanol, ethanol, octanol, acetone, and cyclohexane) blended into toluene and traced to soot in diffusion flames. An interesting result was that of the binary mixtures of toluene and cyclohexane, where the cyclohexane component of the fuel was gradually increased. The results showed that the soot was derived disproportionally from the toluene component for a variety of mixtures, and the aromatic toluene converted to soot with an R value of around 1.65 compared to cyclohexane.

The disadvantage of using decay counting as a technique is that it is inefficient at detecting small changes in the ^{14}C abundance. Short-lived radioisotopes can be efficiently detected by decay counting, but longer-lived radioisotopes are not, and ^{14}C has a half-life of 5730 years. During the time available to carry out an experiment only a small number of the ^{14}C atoms will decay; Buchholz et al. (2002) pointed out that in order to measure 0.1% of the decay of a sample containing ^{14}C, it would require uninterrupted sampling for 8.3 years. In order to compensate for the poor sensitivity at low levels of ^{14}C enrichment, relatively high concentrations of molecules with enriched levels of ^{14}C are required to improve resolution of the decay counting method. As a result, relatively large quantities of ^{14}C containing molecules must be synthesized or acquired from commercial suppliers in order to carry out such investigations, and doing so can be prohibitively expensive. Furthermore, due to the high levels of ^{14}C required, precautionary measures must be implemented to work with materials that have levels of radioactivity in excess of the

natural background, and disposal of the radioactive waste that is produced adds a further restriction of the use of the technique.

The second isotope ratio measurement technique that has been used to measure ^{14}C abundance, which does not rely on decay counting, is AMS. AMS is a highly sensitive technique that involves the counting of individual nuclei, rather than relying on radioactive decay. AMS was developed during the 1970s for the purpose of carbon dating, and has also been widely used in the earth sciences and archaeology. Due to the fact that AMS is a much more sensitive technique, Buchholz et al. (2002) introduced a tracer method that does not require a test sample with molecules that are artificially enriched with ^{14}C. Instead, the method relies on differences in the natural variation of ^{14}C rates between different fuel sources, to trace a given component through combustion. ^{14}C is formed in the atmosphere, and occurs when cosmic rays collide with nitrogen. The newly formed carbon-14 is quickly oxidized to CO_2, where it enters the carbon cycle and therefore becomes incorporated into plants and animals; this means that living things are composed of about 1.2 parts of ^{14}C per 10^{12} C atoms. Biologically derived fuels are formed from processes that incorporate atmospheric CO_2, and as a result contain atmospheric levels of radiocarbon. Fossil fuels, however, are essentially ^{14}C free since they have been isolated underground for >60,000 years, a period of >10 half-lives. The relative absence of ^{14}C in fossil fuels means that there is a very low ^{14}C background, while biofuels have around three orders of magnitude more ^{14}C. This means that biofuels are naturally ^{14}C labeled relative to fossil fuels. Buchholz et al. (2002) made use of this natural label by adding bioethanol to fossil diesel; the elevation of ^{14}C rate arising from the biofuel was sufficient to trace the fate of labeled fuel through the combustion process to the emissions, using AMS as the detection method. They investigated fuel blends of ethanol-in-diesel, with varying ethanol content and using either an emulsifier (SPAN 85) or co-solvent (*n*-butanol). In one experiment, a 9.5% (v/v) blend of bio-ethanol in fossil diesel with the emulsifier was combusted in a compression-ignition engine; in order to assess the contribution of the ethanol component to PM, CO, and CO_2. It was calculated that overall only 2.4% of carbon in the exhaust particulate matter was derived from the ethanol component, while ethanol constituted 5.7% of the carbon mass in the fuel. This means that relative to fossil diesel, carbon atoms in ethanol were found to convert to particulate matter at a much lower rate than the fossil components of the diesel fuel. In addition, it was shown that of the particulate collected, which comprised of a non-volatile organic fraction (NVOF) and an absorbed volatile organic fraction (VOF), carbon derived from the ethanol component was more likely to be found in the VOF than the NVOF. Carbon from the ethanol comprised 3.4% of the NVOF, whereas it comprised 2.4% of the overall PM (NVOF + VOF).

Further work by the same group expanded the concept by using compounds synthetically enriched with ^{14}C at specific molecular positions to investigate the relative contribution of individual carbon atoms within a molecule to PM (Buchholz et al., 2004). Dibutyl maleate (DBM) was investigated, which has a number of interesting molecular features, such as a double bond, ester groups, and alkyl chains. Specific carbon atoms involved in the various functional groups were selectively ^{14}C labeled at the positions indicated in Figure 1. Even though the investigation involved the addition of synthetically enriched ^{14}C molecules, the level of enrichment did not exceed the natural abundance range, and therefore was not 'radioactive' above normal background levels. The
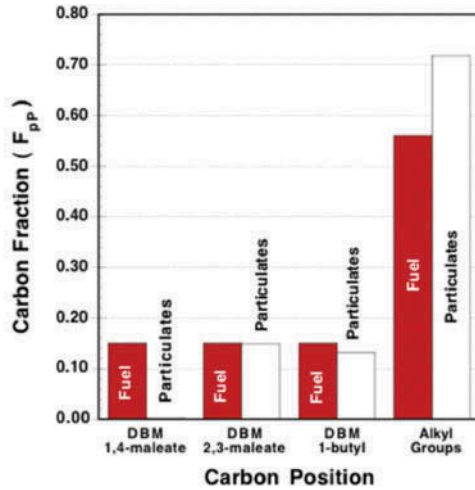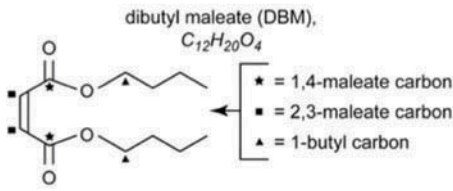
Figure 1. Molecular structure of dibutyl maleate (DBM) and positions of ^{14}C labels, and chart showing the relative contributions of the labeled positions to particulate matter. [Reprinted from Buchholz et al. (2004) with permission from SAE International.]

isotopologues of DBM were combusted in turn in a diesel engine and their relative conversion rates to both the NVOF and VOF fractions of exhaust PM and in-cylinder deposits were assessed. Figure 1 shows the fraction of carbon in the initial fuel at the indicated molecular locations, and the fraction of carbon in the exhaust PM derived from those locations. Significantly, it was shown that the carbon atom attached to the two oxygen atoms ('1,4-maleate' position) in DBM did not contribute to PM emissions or in-cylinder deposits. In addition, the double bonded carbon atoms (2,3-maleate carbon) did not contribute more than the average carbon atom in the DBM molecule to the NVOF and VOF emissions; this was contrary to the prediction of numerical simulations, which indicated that higher levels of C=C conversion could be expected.

The ability to trace the origins of combustion products has also proved useful for quantifying the extent of engine lubrication oil contribution to particulate emissions. As it was discussed in the introduction, Mayer et al. (1980) developed a technique based on ^{14}C labeling of the lubrication oil, where isotopic measurements were made by a decay counting method to identify the portion of particulate matter derived from lubrication oil. Using the same technique, Hilden and Mayer (1984) published further work on the contribution of engine oil, where they examined the contribution of the oil to the total particulate emissions and to the soluble fraction of the particulate, carried out in a range of light-duty diesel engines and using a range of oil formulations. They identified that the oil contribution was in the range of 7–14% of the total particulate emissions. Between 14% and 26% of the total particulate mass in the exhaust was extractable by solvent extraction, of which between 30% and 50% of the extractable fraction was derived from the engine oil. They showed that, generally, there were only minor effects of engine design and oil formulation on the observed oil contribution to PM. The fact that the majority of the oil derived contribution to PM was in the solvent extractable fraction indicated that the engine oil had little to do with the early formation and growth process of soot particles, which implied that the oil does not undergo pyrolysis to the point that it is available to be

incorporated into nascent particles. The authors acknowledged that the oil adsorption onto the particle surface could occur in the exhaust, or even as an artefact of filter-based particulate sample collection as oil vapor passes through the filter.

Using the more efficient AMS detection method Buchholz et al. (2003) investigated the contribution of engine oil to PM in a direct injection diesel engine run on 100% biofuel (with an atmospheric level of ^{14}C) and conventional lubrication oil (^{14}C depleted) derived from fossil sources. They estimated the oil contribution based on the depression in the ^{14}C level in the soot with respect to the biofuel, since engine oil derived from fossil sources has ^{14}C levels that are three orders of magnitude lower than the biofuel. It was estimated that only 4% of carbon in the non-volatile fraction of the particulate matter originated from the engine oil. Jones et al. (2005) carried out further work using this method, and identified the sources of particulate emitted from a heavy-duty diesel engine fueled by natural gas (^{14}C depleted) and pilot-ignited with a biodiesel blend (with a higher ^{14}C content than fossil diesel fuel). It was found that the relative contribution of the sources (i.e., natural gas, pilot fuel, and lubrication oil) to the exhaust PM varied widely depending on the engine operating conditions. For example, the contribution of the biodiesel pilot fuel contribution to PM varied between 4% and 40%; accordingly, the combined contribution of the natural gas and lubricating oil varied in the range of 60–96%. The natural gas contributed to soot formation most at high engine load with EGR, and under these conditions was the main source of the exhaust soot emissions, while the pilot source contributed to the soot emissions most at low engine load without EGR.

A recent ^{13}C labeling technique applied to PM measurement provides a practical alternative to using ^{14}C, and requires only low levels of ^{13}C enrichment at around natural abundance levels, which is ~1% on earth (Eveleigh, 2015). Detection of ^{13}C was carried out by IRMS. The high precision of IRMS, and the technique itself, which reports relative differences between a sample of interest and a known standard reference material, make it suitable for tracer studies. For measurement of ^{13}C/^{12}C by IRMS the sample must first be converted to CO_2, for this, an elemental analyzer (EA) is usually employed, which involves the rapid combustion of the sample to CO_2 in a high-temperature reactor in the presence of excess O_2; the overall technique is therefore referred to as EA-IRMS. For EA-IRMS, a sample containing only about 70 μg of carbon is required for measurement, which is in a similar range to that required for AMS (typically ~200 μg).

The ^{13}C method with IRMS detection was used in an investigation to quantify the conversion rate to PM of individual, site-specific, labeled carbon atoms in a range of molecules (Eveleigh et al., 2014). The conversion rate of carbon atoms was assessed for the molecules: ethanol, n- and i-propanol, ethyl acetate, and toluene. The experimental method required only low levels of ^{13}C enrichment, and taking ethanol as an example, only 45 μL of ethanol-1-^{13}C (with labeling only at the hydroxyl carbon atom) was required to enrich 100 mL of otherwise unenriched ethanol. Continuing the example for ethanol enriched at the hydroxyl atom, its pyrolysis under oxygen free-conditions resulted in PM of which approximately 27% of the carbon was derived from the hydroxyl carbon atom ('a' in Figure 2), and the remainder from the methyl carbon atom 'b'. Figure 2 shows that this result for ethanol—where the majority of the resulting PM was derived from the methyl carbon atom (~70%)—was the same for all pyrolysis temperatures in the range of 1200–1450°C. The result that the methyl-to-hydroxy carbon conversion ratio was about 2:1, was consistent with the earlier results of Schmieder (1985) and Lieb and Roblee Jr. (1970) obtained using the ^{14}C method, as discussed above.
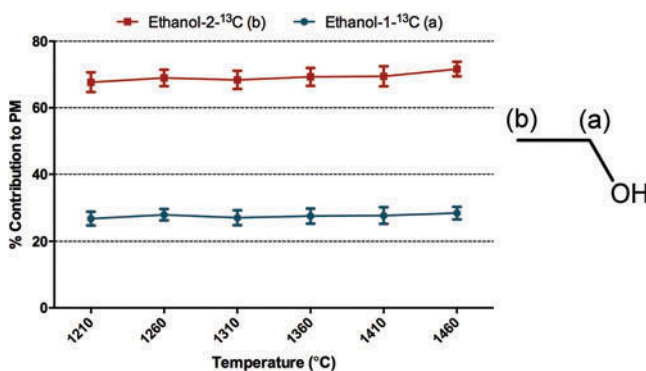
Figure 2. Percentage of PM derived each of the carbon atoms in ethanol (atoms labeled 'a' and 'b'). The PM was generated by ethanol pyrolysis at temperatures in the range of 1200–1450°C. Calculated from isotopic measurements by EA-IRMS. [Reprinted from Eveleigh et al. (2014).]

The results for ethanol, *n*- and *i*-propanol, ethyl acetate, and toluene showed that the conversion rates to PM of specific carbon atoms varied widely depending on the local molecular structure.

Using the same ^{13}C technique, tracer studies were also carried out using both the tube reactor and a direct injection compression ignition engine (Eveleigh et al., 2015, 2016). In the first study, the engine was fueled with labeled single-component oxygenated fuels, a free fatty acid (oleic acid), and a fatty acid methyl ester (methyl oleate; Eveleigh et al., 2015). The results showed that the carbon atoms directly bonded to the two oxygen atoms in methyl oleate and oleic acid were not found in the exhaust PM, suggesting that the carbon atoms are not available for particulate formation. The double bonded carbon atoms in oleic acid did contribute to PM formation, but at a similar rate as the average alkyl chain carbon atom; suggesting no extra contribution of the double bonded carbon atoms to particulate formation. In the second study, a range of molecules (ethanol, *n*- and *i*-propanol, acetone, and toluene) were blended in binary mixtures with *n*-heptane (to 10 mol%) and the contribution of individual carbon atoms to PM was assessed (Eveleigh et al., 2016). One of the interesting results from this study was that in the engine, the aromatic toluene component of the binary mixture contributed disproportionately to the formation of PM, which was consistent with the result of Sorek and Anderson (1985) obtained in a diffusion flame (discussed above).
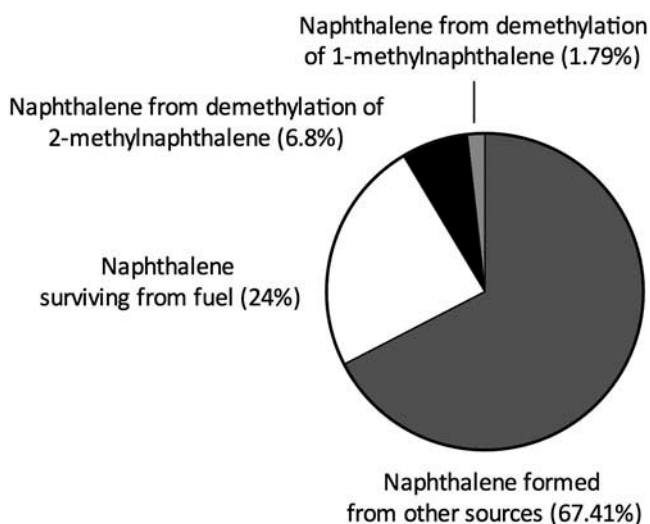
PAHs

The formation and emission of PM is closely related to the formation and emission of PAHs. PAHs are produced during the incomplete combustion of organic fuels, and they are also precursors that are involved in the formation of soot. As mentioned earlier, some of the PAHs are mutagenic and carcinogenic. For these reasons, a large amount of research has been carried out to better understand the origins of PAHs and the mechanisms leading to their formation.

PAHs that are found in diesel engine exhaust are usually a mixture of newly pyro-synthesized PAHs and those that survived combustion unburned and originating from the

fuel or lubrication oil. This means that diesel engine exhaust PM contains pyrosynthesized compounds that are indistinguishable from those originating in the unburned fuel and oil. Therefore, a simple examination of the composition and relative amounts of the PAHs present in the PM, only reveals a limited amount of information about their origins. This problem lends itself readily to isotope tracing.

A comprehensive series of investigations by Rhead and colleagues involved the detection of specific compounds extracted from diesel exhaust PM. They carried out tests where the engine was fueled with conventional diesel fuels to which were added small amounts of ^{14}C labeled compounds, including: alkyl PAHs (Rhead and Pemberton, 1996), and a series of PAHs (Rhead and Hardy, 2003; Rhead and Pemberton, 1996; Tancell, 1995; Tancell et al., 1995a, 1995b). The techniques of radio-high-performance liquid chromatography (radio-HPLC), and radio-gas chromatography (radio-GC), were developed for the measurement of radioactivity in individual PAH compounds and their derivatives that were present in diesel engine exhaust (Tancell and Rhead, 1996). In both techniques, detection of the level of ^{14}C activity for individual compounds eluting from GC or HPLC was by means of a scintillation counter, which measured the rate of radioactive decay.

A study was carried out by Rhead and Pemberton (1996) in order to quantify the rates of PAH pyrosynthesis and survival during combustion. ^{14}C labeled naphthalene, and 1- and 2-methyl-napthalene were added individually in separate experiments to class A2 diesel fuel, which was combusted in a medium duty direct injection compression ignition engine. Figure 3 shows that under operation of the diesel engine at an intermediate speed and load, the majority of the naphthalene in the exhaust (67.14%) originated from unidentified fuel components, presumably formed by pyrosynthetic reactions. A significant amount of the exhaust naphthalene (23%) was derived from naphthalene in the fuel that had survived combustion, with significant contributions also arising from de-alkylation of 1- and 2-methylnaphthalene. Overall, it was calculated that the percentage of naphthalene surviving combustion was 0.484%.

Figure 3. Sources of naphthalene in DI diesel engine exhaust, operated at 2500 rpm and 50 Nm. Adapted from Rhead and Pemberton (1996).

Further investigations studied the survival of the PAHs naphthalene, flourene, fluoranthene, and pyrene, under a range of engine operating conditions (Rhead and Hardy, 2003). It was found that the extent of PAH survival and pyrosynthesis was dependent on the engine operating conditions. For each of the four PAHs investigated there was evidence for pyrosynthesis, and for most cases pyrosynthesis was the main source of PAHs recovered from the exhaust. Significantly, when the engine was operated at an intermediate speed and load, a correlation was found between the rate of PAH survival and the energy level of the lowest unoccupied molecular orbital (LUMO), which is a parameter that is related to chemical reactivity. They concluded that this correlation indicated that the survival of the PAH during combustion was dependent on the chemical kinetics of the oxidative reactions occurring in the combustion chamber, rather than on the thermodynamic stabilities of the PAHs.

A study by Lombaert et al. (2006) investigated whether the presence of PAHs in fuel promoted the formation of PAHs that were extractable from diesel engine exhaust PM. Deuterated naphthalene ($C_{10}D_8$) was added to the fuel to act as a tracer at a level of 1000 ppm. PM was collected from the exhaust onto a filter, and the PAHs were extracted into a solvent. The extract was analysed by GC/MS in order to identify the PAHs and their deuterated isotopologues. The presence of naphthalene did not have an appreciable influence on the total particulate mass, or quantity of the soluble fraction (which accounted for ~14% of total PM mass). Analysis of the mass spectra showed that only deuterated and semi-deuterated pyrene and phenanthrene, and residual deuterated naphthalene were detectable in the soluble extract; they therefore concluded that naphthalene present in the fuel promotes the formation of larger PAHs.

In a related study, Lea-Langton et al. (2013) used ^{13}C labeling to determine the pyrolysis products of methylphenanthrene, which is a component present in diesel fuel. Methylphenanthrene was labeled on the methyl carbon atom with an isotopic enrichment at that location of 99%. Pyrolysis was carried out in a cell-flow reactor with helium as the carrier gas at temperatures of 800°C and 900°C, and analysis of the effluent gas was carried out using GC/MS. The major product of pyrolysis was found to be the parent PAH phenanthrene, which did not contain ^{13}C; this confirmed that dealkylation was a dominant pyrolytic reaction under the conditions employed. A number of other methylated-PAHs were detectable including 1-^{13}C- and 2-^{13}C-methylnaphthalenes, with the ^{13}C label shown to reside in the methyl position, suggesting that re-alkylation of pyrolysis-formed PAHs occurred. Follow-up work investigated the decomposition of methylnaphthalene and methylphenanthrene in a compression ignition engine and a flow cell reactor (Lea-Langton et al., 2015). Similar results were obtained in both systems, which showed that dealkylation was the predominant reaction.

Recent work demonstrated that high-resolution gas chromatography-combustion-isotope ratio mass spectrometry (GC/C/IRMS), could be used for the isotopic analysis of specific PAHs extracted from soot that was formed by the pyrolysis of ethanol (Eveleigh, 2015). This indicates that detection by GC/C/IRMS could be used as a high-resolution alternative to GC/MS for the isotopic measurement of PAHs isolated from combustion products. This would allow even smaller quantities of the tracer compound to be used in the fuel. However, a benefit of GC/MS compared to GC/C/IRMS, is that it can provide information as to the sub-molecular distribution of ^{13}C; this is because mass spectrometry (MS) involves the detection of molecular fragments, and their respective isotopologues.

GC/C/IRMS on the other hand involves conversion of the compounds eluted from the GC into CO_2 before detection by IRMS, and therefore does not give information as to the local molecular distribution of ^{13}C. In addition, GC/C/IRMS generally suffers from broadening of the chromatographic peaks compared to GC/MS, due to the additional components required for interfacing the GC to the combustion reactor and isotope spectrometer. However, a number of methods have been described that provide adequate compound separation and allow for the measurement of individual PAHs, using PAH samples obtained from the environment (Buczyńska et al., 2013).

Reaction pathway analysis and kinetic rate determination

Isotope labeling has also proved useful for the identification of individual reaction pathways involved in the formation of combustion products, and of the measurement of elementary reaction rate constants. There are many examples of this application, which have been carried out in a range of experimental systems, high and low temperature conditions, and for catalytic combustion. Some of the examples described in previous sections of this article are clearly also relevant to this discussion, for example, the study of the thermal degradation of methylated PAHs by Lea-Langton et al. (2013). However, this section is primarily concerned with isotope studies of reaction rate, and of the elucidation of the mechanisms of formation of species other than PAH and soot.

Determinations of pseudo-first order reaction rate of OH + stable species are usually carried out by reacting a stable species of interest with OH at high temperatures (typically 900–1400 K) behind reflected shock waves, in a shock tube, and using laser adsorption to measure OH concentration history (Hanson and Davidson, 2014). In such experiments, OH is produced almost instantaneously by the high temperature decomposition of *tert*-butyl-hydroperoxide (TBHP), yielding OH, CH_3, and acetone. Experimental conditions where only low concentrations of OH (~20 ppm) and excess of the reactant (usually 200–2000 ppm) are employed, with reactant-to-OH concentration greater or equal to 10; this gives rise to OH concentration time histories with an exponential decay (pseudo first-order kinetics) with sensitivity to only the reaction of interest (Pang et al., 2011).

Clearly, in such experiments, the OH concentration time-history may also be influenced by secondary reactions that are either OH-consuming or OH-producing. For example, for alcohols, the OH concentration is influenced by the removal of the hydroxyl group from the alcohol, which produces OH that is indistinguishable from that produced by the TBHP; therefore, the simultaneous production OH from the alcohol would cause the consumption rate to appear much lower. Take for example the reaction of ethanol with OH, the reaction scheme in Figure 4 shows the major reaction pathways. There are three reaction pathways, one of which produces ethylene and OH. To overcome this issue, Stranic and colleagues used ^{18}O-substituted ethanol (Stranic et al., 2014) and *tert*-butanol (Stranic et al., 2013) as reactants, which produce ^{18}OH that is spectroscopically distinguishable from ^{16}OH. That is to say, that by isotopic labeling of the alcohol molecules with ^{18}OH, the alcohols produce ^{18}OH that can be differentiated from the ^{16}O produced from the TBHP (see Figure 4); thereby removing the secondary reaction interference, of the OH reformation from the alcohol, on the apparent OH consumption rate. Stranic and colleagues used narrow-linewidth laser absorption (near 307 nm) as a means to measure the concentration of ^{16}OH, which showed negligible sensitivity to ^{18}OH.
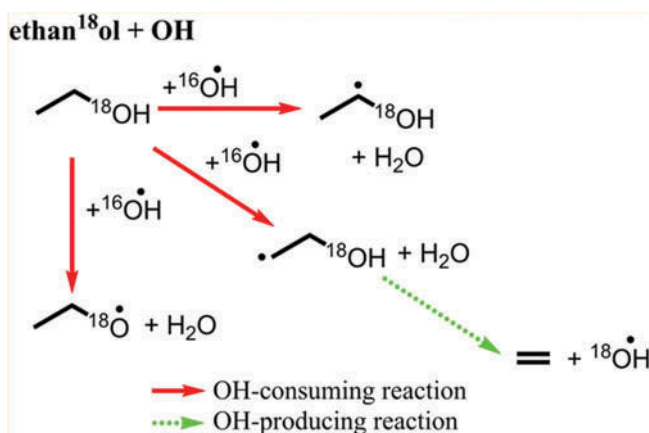
Figure 4. Main reaction of pathways of ethan[18]ol reaction with OH. [Reprinted with permission from I. Stranic, G.A. Pang, R.K. Hanson, D.M. Golden, and C.T. Bowman, Shock tube measurements of the rate constant for the reaction ethanol + OH, *J. Phys. Chem. A*, vol. 118, pp. 822–828. Copyright 2014 American Chemical Society.]

Rate constant measurements of alcohols + OH contributes substantially to the accurate modeling of their combustion, with the deployment of the labeling technique, discussed above, being critical for accurate experimental determination of the rate constants of reaction of alcohols with OH. Similar methodologies may also be used for other reactions, not necessarily limited to alcohols or the measurement of OH, where it is desirable to eliminate interference from secondary reactions on the measurement of a given species.

Cullis carried out a comprehensive series of experiments in the 1950s to 1970s, using radiocarbon (^{14}C) as a tracer. The main use was for the investigation of individual reaction pathways involved in the combustion and thermal decomposition of a range of hydrocarbon molecules, including: 2-methyl-but-2-ene (Cullis et al., 1962), isobutene (Cullis et al., 1963a), tert-butyl hydroperoxide (Cullis et al., 1966), *n*-butane in the presence of butenes (Berry and Cullis, 1970; Berry et al., 1970), and pentanes in the presence of pentenes (Cullis and Hirschler, 1978). Radiolabeling experiments were also used to determine the most probable points of oxidative attack for hydrocarbon molecules. For instance, Cullis et al. (1958, 1959) investigated the slow combustion of 2-methylpentane, which was labeled in turn at each skeletal position. Isotopic measurements were made of the carbon monoxide and ketone emissions, which are stable products of rich combustion. 2-Methylpentane contains primary, secondary, and tertiary C–H bonds, and the relative frequency of initial oxidation at each of the carbon atom centres was determined, and was found to be in the order: tertiary > secondary > primary. The results showed that carbon monoxide was derived from all of the carbon atoms; however, the ketones were derived exclusively from the tertiary carbon atom, which became the ketone carbonyl group. It was found that the oxidation of primary and secondary C–H centers gave rise to aldehydes, which are more effective chain-branching agents than the stable ketone products formed from the oxidative attack at tertiary C–H centers; this means that aldehydes promote the oxidation of the unreacted initial fuel molecules. They concluded that while the tertiary C–H centers are the most frequent point of hydrocarbon oxidative attack during slow combustion, the secondary centers were nevertheless the more effective point of attack. An earlier review article by Cullis et al. (1963b) describes these seminal works in greater

detail, and primarily deals with the use isotopic carbon to elucidate chemical mechanisms of combustion.

The investigation of Buchholz et al. (2004), mentioned in the section"Isotope Studies of Soot and PM Formation," demonstrated that the data acquired from isotopic studies could be used to help strengthen the validation and refinement of detailed chemical kinetic models. The experimental results of the combustion of labeled DBM (see Figure 1 for structure) showed that the ester structure tended to directly produce CO_2 about 90% of the time. This was compared to the numerical predictions of Mueller et al. (2003), which indicated that the DBM ester structure would directly produce CO_2 about 75% of the time. The model assumed C–H bond strength at the 1-butyl carbon atom of DBM to be lower than of other alkyl carbon atoms due its proximity to the ester moiety; this assumption resulted in a higher rate constant of H-atom abstraction from the 1-butyl position of DBM compared to other alkyl sites. The numerical model was subsequently adjusted so that the 1-butyl C–H bond strength was the same as that of the secondary C–H groups of the alkyl chain. The adjusted model predicted that the ester structure would directly convert to CO_2 80% of the time, which was within the experimental error bars of the experimentally obtained value (90%). The authors concluded that the direct formation of CO_2 from the ester group was unfavorable, since this meant that nearly half of the oxygen in the DBM molecule is essentially 'wasted' for the purpose of attenuating soot formation. By contrast, the compound tri-propylene glycol methyl ether (TPGME) has oxygen mainly present in ether moieties, which is a more favorable distribution of oxygen since all of the oxygen is available for soot reduction (Mueller et al., 2003).

Experiments to determine flame structure

Katoh and coworkers applied a laser technique, which they called isotope shift/planar laser induced fluorescence spectroscopy (IS/PLIF), in order to visualise the distribution of various isotopes in flames. For example, the OH radical species has a distinct excitation wavelength, which is different to that of its deuterated analogue OD. When steam produced from water is added to flames, OH radicals are formed by the dissociation of water (i.e., H_2O -> OH + H). Katoh et al. (2006c) demonstrated that it was possible to distinguish and visualize the difference between OH radicals formed by combustion reactions and those formed by dissociation from steam generated from deuterated water. This has given some useful insights into the observed behavior of steam addition to flames, which can be useful to dilute oxygen concentration and thereby suppress formation of NO_X. Other examples published by the same research group can be found in the following references (Kajimoto et al., 2013; Katoh et al., 2006a, 2006b).

Emerging methods

To the best of the authors' knowledge, nuclear magnetic resonance (NMR) spectroscopy has not yet been used as a detection technique for isotope tracer studies in combustion science. NMR is a technique that exploits the magnetic properties of atomic nuclei that have an odd atomic mass number, such as ^1H or ^{13}C. Dependent on the local molecular structure of the molecule, these nuclei give rise to a unique signal in the NMR spectrum. Analysis of complex mixtures by 1D NMR methods, such

as ^{1}H and ^{13}C NMR, can be a problematic task due to spectral overlap from the various components; and combustion emissions such as those present in diffusion flames and diesel engine exhaust typically contain a highly complex mixture of molecules that are not easily isolated. 1D ^{1}H NMR experiments have been widely used to broadly characterise the chemical composition of fuels that contain a complex mixture of components, such as gasoline (Burri et al., 2004), diesel, and biodiesel blends (Diehl and Randel, 2007); this approach usually involves assigning chemical shift regions of the NMR spectra to aromatic, olefinic, and aliphatic protons exclusively. However, the issue of spectral overlap has in some instances been overcome using multidimensional NMR experiments, such as maximum-quantum (MaxQ), or diffusion ordered spectroscopy that can be used to identify and quantify individual components in complex mixtures, without requiring extensive sample pre-treatment. For example, the applicability of MaxQ NMR to determine the concentration of each PAH in a mixture containing 16 PAHs has been demonstrated by Reddy and Caldarelli (2012). Additionally, Snape et al. (1986) showed that 2D NMR experiments ([1]H-^{13}C HETEROCOR, and ^{1}H-^{1}H COSY) could be used to unambiguously identify a range of compounds including mono- and di-aromatic compounds contained in a mixture obtained from a coal liquefaction solvent. While spectral overlap can be reduced or eliminated using multidimensional experiments, accurate quantification is more difficult to achieve than for monodimensional experiments.

The NMR studies discussed so far have involved the measurement of PAHs with only a natural isotopic abundance of carbon and hydrogen; however, experiments utilizing NMR spectroscopy can also be for tracer studies employing isotopically enriched compounds (e.g., Blake et al., 2003). It was described previously in this article that Radio-GC, Radio-HPLC, GC/MS, and GC/C/IRMS techniques have be used to detect the isotopic composition of individual molecules. These techniques can only be used to determine the average isotopic composition of whole molecules, or in the case of GC/MS molecular fragments within a molecule. NMR, on the other hand, can be used to assess the level of isotopic enrichment (of ^{13}C for example) at a specified carbon atom site within a molecule, with respect to another site in the same molecule. An isotope tracer study could be envisaged where NMR would be employed as a detection technique to elucidate the origins of individual carbon atoms within PAHs. This could be carried out by enriching a given hydrocarbon component of the fuel with ^{13}C, and using NMR to ascertain whether the ^{13}C-labeled fuel molecule is preferentially incorporated into specific sites in the PAH molecules that result from combustion. This approach could provide new insights into the origins and chemical mechanisms involved in the formation of PAHs and other combustion-generated species.

Another avenue for future work could be the use of isotopic data to assist the development and verification of numerical models; and an example of how this has been implemented was described above (see the third section). In the future, as detailed kinetic models become more refined, isotopic tracer experiments could become used more widely to provide additional constraints for the verification of numerical models. Recent work by Laurent et al. (2016) reported the use of a numerical algorithm that allows the tracking of specifically 'labeled' atoms during the chemical kinetic simulation of combustion reactions. The algorithm, which automatically formulates tracking equations, has the capability to provide the concentration of 'labeled' atoms at any location in any given species

involved in the chemical mechanism (at any given point in the time evolution of the simulation).

Additionally, predictive models of the sooting tendency of molecules have also been developed, which are based on group additivity, e.g., Pepiot-Desjardins et al. (2008) and Barrientos et al. (2013). The group additivity method was initially developed in order to estimate thermodynamic properties of molecules for which data was not available (Benson and Buss, 1958), and is based upon the division of compounds into smaller units where each unit has a numerical contribution to the property being estimated. Since tracer techniques can be used to reveal the direct contribution of individual atoms or groups to soot emissions, the results of tracer experiments could be used to validate the basis of such models and to develop further their predictive ability.

Discussion

The usefulness of isotope tracing is clear, particularly for the purpose of source apportionment of particulate matter, or for elucidating mechanistic details of PAH pyrolysis, and can be used to provide verification of detailed combustion models. The literature shows that a range of isotope techniques have been used to solve a variety of problems, yet, overall, isotope techniques have not become widely adopted. There are a number of factors that may have prevented isotope techniques being more widely used. First, as it has already been discussed, ^{14}C tracer experiments are expensive to carry out if used at high enough levels of enrichment for decay counting to be used as a detection technique. Additionally at high enrichment levels safety issues relating to the use of radiocarbon need to be considered, the safety precautions can be both expensive and impractical to implement. The more recent implementation of ^{14}C tagging that has employed AMS detection has greatly improved the economic and practical viability of such ^{14}C studies, especially as it reduces or eliminates the need to acquire ^{14}C-enriched compounds. Globally there are a number of laboratories that have AMS capability, for instance in the UK there are four such facilities registered in a directory kept by the journal *Radiocarbon* (Radiocarbon, 2014). However, the cost of AMS analysis itself, and acquiring even small quantities of site specifically enriched ^{14}C compounds, at low enrichment levels are still expensive to synthesize or source. The examples of ^{14}C labeling that have been discussed have generally been conducted at well-resourced national laboratories; for isotope labeling techniques to become more widely used in combustion science, both cost-effectiveness and availability of measuring equipment is required.

In certain situations carbon-13 or deuterium labeling experiments with detection by GC/MS are advantageous, and the relatively high levels of isotopic enrichment required are not always a restriction. For instance, in labeling experiments where isotopic measurements of soot or PM are required, pyrolysis experiments carried out in a flow reactor can yield large quantities of PAHs and soot, and only require a few millilitres of fuel. The main benefit of GC/MS as a method is that it can provide information as to the local distribution of isotopic markers. However, the main disadvantage is the higher levels of isotopic enrichment required; for example, the operation of a diesel engine or even a diffusion flame for long enough to generate sufficient quantities of PM sample for analysis requires significantly more fuel, since the majority of fuel is efficiently combusted to CO_2. The high levels of ^{13}C enrichment required for GC/MS analysis is therefore likely to have been a

factor preventing its use in some situations, such as for the analysis of PM or other minor combustion products or intermediates for the purpose of their source apportionment.

Highly sensitive and routine isotopic measurements by IRMS appear to provide an alternative in such cases. IRMS measurements are considerably less costly to conduct than those by AMS; AMS measurements are usually about 50 to 100 times more costly than those with IRMS. The low levels of ^{13}C enrichment that have been used mean that the combustion experiments are cost-effective, but also give adequate resolution owing to the high precision of IRMS. In any case, laboratories that measure ^{13}C abundances by IRMS are generally reluctant to measure samples highly enriched with ^{13}C, greatly in excess of natural abundance, since this would pose a risk of contamination to the highly sensitive equipment. The relatively low cost of routine isotope measurements by IRMS, and the availability of 'off-the-shelf' commercially produced ^{13}C-labeled compounds, used at low levels of enrichment, thus provides a high-precision yet relatively economical means of tracing ^{13}C. This could mean that the use of ^{13}C labeling, with detection by IRMS, could become more widely used as a diagnostic tool in combustion research.

In recent years, practical measures have also been implemented to extend the economic viability of conducting engines experiments using high-cost fuels (Hellier et al., 2012). Conventional direct injection diesel fuel circuits usually require several litres of fuel to operate. Due to the high cost associated with isotopically enriching large volumes of test fuel, several researchers have used specially designed fuel delivery systems to allow the operation of the engine with only small fuel volumes (~100 ml), see, for example, Trier et al. (1991) and Schönborn et al. (2009). Such innovations extend further the feasibility of isotope labeling experiments carried out in practical combustion systems, where the species of interest (e.g., PM) is only a minor product and most of the test fuel is combusted to CO_2 and H_2O.

Nomenclature

AMS	accelerator mass spectrometry
^{13}C	carbon-13
^{14}C	carbon-14
COSY	correlation spectroscopy
CSIA	compound specific isotope analysis
D	deuterium
$\delta^{13}C$	isotopic signature, a measure of the ratio $^{13}C{:}^{12}C$
DBM	dibutyl maleate
EA	elemental analysis
EGR	exhaust gas recirculation
GC	gas chromatography
GC/MS	gas chromatography mass spectrometry
GC/C/IRMS	gas chromatography–combustion–isotope ratio mass spectrometry
HETCOR	herteronuclear correlation spectroscopy
HPLC	high-pressure liquid chromatography
IRMS	isotope ratio mass spectrometry
IS/PLIF	isotope shift/planar laser induced fluorescence
KIE	kinetic isotope effect
LUMO	lowest unoccupied molecular orbital
MS	mass spectrometry
NMR	nuclear magnetic resonance

NVOF	non-volatile organic fraction
^{18}O	oxygen-18
PAC	polycyclic aromatic compounds
PAH	polycyclic aromatic hydrocarbon
PM	particulate matter
TBHP	*tert*-butyl-hydroperoxide
TPGME	tri-propylene glycol methyl ether
VOF	volatile organic fraction

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References

Au-Yeung, J., Chen, K., Bell, A.T., and Iglesia, E. 1999. Isotopic studies of methane oxidation pathways on PdO catalysts. *J. Catal.*, **188**, 132–139.

Badger, G., Jolad, S., and Spotswood, T. 1966a. The formation of aromatic hydrocarbons at high temperatures. XXV. The pyrolysis of [3-14C] indene. *Aust. J. Chem.*, **19**, 85–93.

Badger, G., Jolad, S., and Spotswood, T. 1966b. The formation of aromatic hydrocarbons at high temperatures. XXVI. Pyrolysis of [1-14C] styrene. *Aust. J. Chem.*, **19**, 95–105.

Badger, G., Jolad, S., and Spotswood, T. 1967a. The formation of aromatic hydrocarbons at high temperatures. XXIX. Pyrolysis of 2-methylstyrene and 2-[1-14C] methylstyrene. *Aust. J. Chem.*, **20**, 1439–1450.

Badger, G., Jolad, S., and Spotswood, T. 1967b. The formation of aromatic hydrocarbons at high temperatures. XXVIII. Pyrolysis of n-[α-14C] propylbenzene. *Aust. J. Chem.*, **20**, 1429–1438.

Badger, G., and Kimber, R. 1961. The formation of aromatic hydrocarbons at high temperatures. Part XIV. The pyrolysis of [α-14 C] ethylbenzene. *J. Chem. Soc.*, **663**, 3407–3414.

Badger, G., Kimber, R., and Novotny, J. 1962. The formation of aromatic hydrocarbons at high temperatures. XVI. The pyrolysis of [1-14C] tetralin. *Aust. J. Chem.*, **15**, 616–625.

Badger, G., and Novotny, J. 1963. The formation of aromatic hydrocarbons at high temperatures. XIX. The pyrolysis of [δ-14C] butylbenzene. *Aust. J. Chem.*, **16**, 623–635.

Badger, G.M., Jolad, S.D., and Spotswood, T.M. 1964. The formation of aromatic hydrocarbons at high temperatures. XX. The pyrolysis of [1-14C] naphthalene. *Aust. J. Chem.*, **17**, 771–777.

Barrientos, E.J., Lapuerta, M., and Boehman, A.L. 2013. Group additivity in soot formation for the example of C-5 oxygenated hydrocarbon fuels. *Combust. Flame*, **160**, 1484–1498.

Bennett, P., Gregory, D., and Jackson, R. 1996. Mechanistic studies on the combustion of isotopically labelled cyclohexanes within a single cylinder internal combustion engine. *Combust. Sci. Technol.*, **115**, 83–103.

Benson, S.W., and Buss, J.H. 1958. Additivity rules for the estimation of molecular properties: Thermodynamic properties. *J. Chem. Phys.*, **29**, 546–572.

Berry, T., and Cullis, C. 1970. Quantitative studies of the role of alkenes during the combustion of alkanes. *Aust. J. Chem.*, **23**, 2309–2314.

Berry, T., Cullis, C., and Trimm, D. 1970. Isotopic tracer studies of the role of butenes in the combustion of *n*-butane. *Proc. R. Soc. London, Ser. A*, **316**(1526), 377–389.

Blake, M.E., Bartlett, K.L., and Jones, M. 2003. A m-benzyne to o-benzyne conversion through a 1, 2-shift of a phenyl group. *J. Am. Chem. Soc.*, **125**, 6485–6490.

Buchholz, B.A., Cheng, A., and Dibble, R. 2002. Isotopic tracing of bio-derived carbon from ethanol-in-diesel blends in the emissions of a diesel engine. SAE Technical Paper 2002-01-1704. DOI: 10.4271/2002-01-1704.

Buchholz, B.A., Dibble, R.W., Rich, D., and Cheng, A. 2003. Quantifying the contribution of lubrication oil carbon to particulate emissions from a diesel engine. SAE Technical Paper 2003-01-1987. DOI: 10.4271/2003-01-1987.

Buchholz, B.A., Mueller, C.J., Upatnieks, A., Martin, G.C., Pitz, W.J., and Westbrook, C.K. 2004. Using carbon-14 isotope tracing to investigate molecular structure effects of the oxygenate dibutyl maleate on soot emissions from a DI diesel engine. SAE Technical Paper 2004-01-1849. DOI: 10.4271/2004-01-1849.

Buczyńska, A.J., Geypens, B., Van Grieken, R., and De Wael, K. 2013. Stable carbon isotopic ratio measurement of polycyclic aromatic hydrocarbons as a tool for source identification and apportionment—A review of analytical methodologies. *Talanta*, **105**, 435–450.

Burley, H.A., and Rosebrock, T.L. 1979. Automotive diesel engines-fuel composition vs particulates. SAE Technical Paper 790923. DOI: 10.4271/790923.

Burri, J., Crockett, R., Hany, R., and Rentsch, D. 2004. Gasoline composition determined by 1 H NMR spectroscopy. *Fuel*, **83**, 187–193.

Buttini, P., and Manni, M. 2001. Emissions of deuterated tracers from oil in light and heavy duty diesel engine. SAE Technical Paper 2001-01-3531. DOI: 10.4271/2001-01-3531.

Chen, K., Khodakov, A., Yang, J., Bell, A.T., and Iglesia, E. 1999. Isotopic tracer and kinetic studies of oxidative dehydrogenation pathways on vanadium oxide catalysts. *J. Catal.*, **186**, 325–333.

Ciuparu, D., Altman, E., and Pfefferle, L. 2001. Contributions of lattice oxygen in methane combustion over PdO-based catalysts. *J. Catal.*, **203**, 64–74.

Criss, R.E. 1999. *Principles of Stable Isotope Distribution*, Oxford University Press, New York.

Cullis, C., Dominguez, J.G., Kiraly, D., and Trimm, D. 1966. Isotopic tracer studies of the thermal decomposition of tert.-butyl hydroperoxide. *Proc. R. Soc. London, Ser. A*, **291**(1425), 235–243.

Cullis, C., Fish, A., and Trimm, D. 1963a. Alkylperoxy radical rearrangements during the gaseous oxidation of isobutane. *Proc. R. Soc. London, Ser. A*, **273**(1354), 427–434.

Cullis, C., Fish, A., and Turner, D. 1962. The gaseous oxidation of 2-Methyl-but-2-ene. II. carbon-14 tracer studies. *Proc. R. Soc. London, Ser. A*, **267**(1330), 433–442.

Cullis, C., Hardy, F., and Turner, D. 1958. The point of oxygen attack in the combustion of hydrocarbons. I. The origin of carbon monoxide. *Proc. R. Soc. London, Ser. A*, **244**(1239), 573–580.

Cullis, C., Hardy, F., and Turner, D. 1959. The point of oxygen attack in the combustion of hydrocarbons. II. The formation and origin of ketones. *Proc. R. Soc. London, Ser. A*, **251**(1265), 265–273.

Cullis, C., and Hirschler, M. 1978. Isotopic tracer studies of the further reactions of pentenes in the combustion of pentane. *Proc. R. Soc. London, Ser. A*, **364**(1718), 309–329.

Cullis, C.F., Fish, A., and Trimm, D.L. 1963b. Isotopic carbon as a tracer in combustion research. *Symp. (Int.) Combust.*, **9**, 167–176.

Cypres, R., and Bettens, B. 1986. Study of the cracking mechanism of phenanthrene and perhydrophenanthrene, labelled in specific positions by 14C and 3H. *Fuel*, **65**, 507–514.

Diehl, B., and Randel, G. 2007. Analysis of biodiesel, diesel and gasoline by NMR spectroscopy—A quick and robust alternative to NIR and GC. *Lipid Technol.*, **19**, 258–260.

Eveleigh, A. 2015. The influence of fuel molecular structure on particulate emission investigated with isotope tracing. Doctoral thesis. University College London, UK.

Eveleigh, A., Ladommatos, N., Balachandran, R., and Marca, A. 2014. Conversion of oxygenated and hydrocarbon molecules to particulate matter using stable isotopes as tracers. *Combust. Flame*, **161**, 2966–2974.

Eveleigh, A., Ladommatos, N., Hellier, P., and Jourdan, A.-L. 2015. An investigation into the conversion of specific carbon atoms in oleic acid and methyl oleate to particulate matter in a diesel engine and tube reactor. *Fuel*, **153**, 604–611.

Eveleigh, A., Ladommatos, N., Hellier, P., and Jourdan, A.-L. 2016. Quantification of the fraction of particulate matter derived from a range of 13C-labeled fuels blended into heptane, studied in a diesel engine and tube reactor. *Energy Fuels*, **30**, 7678–7690.

Ferguson, R. 1955. On the origin of the electronically excited C2* radical in hydrocarbon flames. *J. Chem. Phys.*, **23**, 2085–2089.

Ferguson, R., and Yokley, C. 1958. Products of cool flame oxidation of propane-2-13C. *Symp. (Int.) Combust.*, **7**, 113–117.

Ferguson, R.E. 1957. An isotopic tracer study of carbon formation in hydrocarbon flames. *Combust. Flame*, **1**, 431–437.

Gray, P., Holland, S., and Smith, D. 1970. The effect of isotopic substitution on the flame speeds of hydrogen-oxygen and hydrogen-nitrous oxide flames. *Combust. Flame*, **14**, 361–374.

Gregory, D., Jackson, R.A., and Bennett, P.J. 1999. Mechanisms for the formation of exhaust hydrocarbons in a single cylinder spark-ignition engine, fueled with deuterium-labeled ortho-, meta- and para-xylene. *Combust. Flame*, **118**, 459–468.

Hanson, R.K., and Davidson, D.F. 2014. Recent advances in laser absorption and shock tube methods for studies of combustion chemistry. *Prog. Energy Combust. Sci.*, **44**, 103–114.

Hellier, P., Ladommatos, N., Allan, R., and Rogerson, J. 2012. The influence of fatty acid ester alcohol moiety molecular structure on diesel combustion and emission. *Energy Fuels*, **26**, 1912–1927.

Hilden, D.L., and Mayer, W.J. 1984. The contribution of engine oil to particulate exhaust emissions from light-duty, diesel-powered vehicles. SAE Technical Paper 841395. DOI: 10.4271/841395.

Homan, H.S., and Robbins, W.K. 1986. A carbon-14 tracer study of the relative fractions of various fuel carbons in soot. *Combust. Flame*, **63**, 177–190.

Jones, H., Mctaggart-Cowan, G., Rogak, S., Bushe, W., Munshi, S., and Buchholz, B. 2005. Source apportionment of particulate matter from a diesel pilot-ignited natural gas fuelled heavy duty DI engine. SAE Technical Paper 2005-01-2149. DOI: 10.4271/2005-01-2149.

Kajimoto, T., Yamada, E., Shinoda, M., Desmira, N., Kitagawa, K., and Gupta, A.K. 2013. Analysis of flame structure by isotope shift-planar laser induced fluorescence spectrometry of trace OH and OD radicals. *Microchem. J.*, **106**, 334–339.

Katoh, A., Kitagawa, K., and Gupta, A.K. 2006a. Examination of methane-hydrogen mixture flame using isotope shift/PLIF spectroscopy. In *Collection of Technical Papers—44th AIAA Aerospace Sciences Meeting*, American Institute of Aeronautics and Astronautics, Reston, VA, pp. 4407–4413.

Katoh, A., Oyama, H., Kitagawa, K., and Gupta, A.K. 2006b. Visualization of OH radical distribution in a methane-hydrogen mixture flame by isotope shift/planar laser induced fluorescence spectroscopy. *Combust. Sci. Technol.*, **178**, 2061–2074.

Katoh, A., Shinoda, M., Kitagawa, K., and Gupta, A.K. 2006c. Visualization of steam addition effect on OH distribution in a flame by isotope shift/planar laser-induced fluorescence (IS/PLIF) spectroscopy. *J. Eng. Gas Turbines Power*, **128**, 8–12.

Koroll, G., and Kumar, R. 1991. Isotope effects on the combustion properties of deuterium and hydrogen. *Combust. Flame*, **84**, 154–159.

Laurent, C., Frewin, C., and Pepiot, P. 2016. A novel atom tracking algorithm for the analysis of complex chemical kinetic networks. *Combust. Flame*, **173**, 387–401.

Lea-Langton, A., Andrews, G., Bartle, K., Jones, J., and Williams, A. 2015. Combustion and pyrolysis reactions of alkylated polycyclic aromatic compounds: The decomposition of 13 C methylarenes in relation to diesel engine emissions. *Fuel*, **158**, 719–724.

Lea-Langton, A.R., Ross, A.B., Bartle, K.D., Andrews, G.E., Jones, J.M., Li, H., Pourkashanian, M., and Williams, A. 2013. Low temperature PAH formation in diesel combustion. *J. Anal. Appl. Pyrolysis*, **103**, 119–125.

Lieb, D.F., and Roblee Jr., L.H.S. 1970. A radioisotopic tracer study of carbon formation in ethanol-air diffusion flames. *Combust. Flame*, **14**, 285–296.

Lima, A.L.C., Farrington, J.W., and Reddy, C.M. 2005. Combustion-derived polycyclic aromatic hydrocarbons in the environment—A review. *Environ. Forensics*, **6**, 109–131.

Lombaert, K., Le Moyne, L., De Maleissye, J.T., and Amouroux, J. 2006. Experimental study of PAH in engine soot by isotopic tracing. *Combust. Sci. Technol.*, **178**, 707–728.

Mack, J.H., Dibble, R.W., Buchholz, B.A., and Flowers, D.L. 2005a. The effect of the di-tertiary butyl peroxide (DTBP) additive on HCCI combustion of fuel blends of ethanol and diethyl ether. SAE Technical Paper 2005-01-2135. DOI: 10.4271/2005-01-2135.

Mack, J.H., Flowers, D.L., Buchholz, B.A., and Dibble, R.W. 2005b. Investigation of HCCI combustion of diethyl ether and ethanol mixtures using carbon 14 tracing and numerical simulations. *Proc. Combust. Inst.*, **30**(2), 2693–2700.

Mayer, W.J., Lechman, D.C., and Hilden, D.L. 1980. The contribution of engine oil to diesel exhaust particulate emissions. SAE Technical Paper 800256. DOI: 10.4271/800256.

Mcrae, C., Love, G.D., Murray, I.P., Snape, C.E., and Fallick, A.E. 1996. Potential of gas chromatography isotope ratio mass spectrometry to source polycyclic aromatic hydrocarbon emissions. *Anal. Commun.*, **33**, 331–333.

Mcrae, C., Snape, C.E., Sun, C.-G., Fabbri, D., Tartari, D., Trombini, C., and Fallick, A.E. 2000. Use of compound-specific stable isotope analysis to source anthropogenic natural gas-derived polycyclic aromatic hydrocarbons in a lagoon sediment. *Environ. Sci. Technol.*, **34**, 4684–4686.

Mueller, C.J., Pitz, W.J., Pickett, L.M., Martin, G.C., Siebers, D.L., and Westbrook, C.K. 2003. Effects of oxygenates on soot processes in Dl diesel engines: Experiments and numerical simulations. SAE Technical Paper 2003-01-1791.

Nisbet, I.C.T., and Lagoy, P.K. 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul. Toxicol. Pharm.*, **16**, 290–300.

Pang, G.A., Hanson, R.K., Golden, D.M., and Bowman, C.T. 2011. High-temperature measurements of the rate constants for reactions of OH with a series of large normal alkanes: *n*-Pentane, *n*-heptane, and n-nonane. *Phys. Chem. Chem. Phys.*, **225**, 1157–1178.

Pepiot-Desjardins, P., Pitsch, H., Malhotra, R., Kirby, S.R., and Boehman, A.L. 2008. Structural group analysis for soot reduction tendency of oxygenated fuels. *Combust. Flame*, **154**, 191–205.

Petch, G., Rhead, M., and Fussey, D. 1990. The use of radiolabelled polycyclic aromatic hydrocarbon fuel components to investigate diesel engine emissions. In *Fuels for Automotive and Industrial Diesel Engines*, London, November 19–20. Paper C65/88, 127–133.

Radiocarbon. 2016. List of known 14C laboratories. http://www.radiocarbon.org/Info/Labs.pdf (accessed Dec. 13, 2016).

Reddy, G.M., and Caldarelli, S. 2012. Identification and quantification of EPA 16 priority polycyclic aromatic hydrocarbon pollutants by maximum-quantum NMR. *Analyst*, **137**, 741–746.

Rhead, M.M., Fussey, D.E., Trier, C.J., Petch, G.S., and Wood, D. 1990. Investigation of the fate of specific hydrocarbon fuel components in diesel engine combustion. *Sci. Total Environ.*, **93**, 207–214.

Rhead, M.M., and Hardy, S.A. 2003. The sources of polycyclic aromatic compounds in diesel engine emissions. *Fuel*, **82**, 385–393.

Rhead, M.M., and Pemberton, R.D. 1996. Sources of naphthalene in diesel exhaust emissions. *Energy Fuels*, **10**, 837–843.

Rhead, M.M., and Trier, C.J. 1992. Fuel residues and organic combustion products in diesel exhaust emissions: Sources, sampling and analysis. *TrAC, Trends Anal. Chem.*, **11**, 255–259.

Schmieder, R.W. 1985. Radiotracer studies of soot formation in diffusion flames. *Symp. (Int.) Combust.*, **20**, 1025–1033.

Schönborn, A., Ladommatos, N., Williams, J., Allan, R., and Rogerson, J. 2009. The influence of molecular structure of fatty acid monoalkyl esters on diesel combustion. *Combust. Flame*, **156**, 1396–1412.

Sechrist, C., and Hammen, H. 1958. Radiotracer studies of engine deposit formation. *Ind. Eng. Chem.*, **50**, 341–342.

Shen, H., Huang, Y., Wang, R., Zhu, D., Li, W., Shen, G., Wang, B., Zhang, Y., Chen, Y., and Lu, Y. 2013. Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. *Environ. Sci. Technol.*, **47**, 6415–6424.

Shore, L., and Ockert, K. 1958. Combustion-chamber deposits—A radiotracer study. SAE Technical Paper 580030. DOI: 10.4271/580030.

Snape, C.E., Ray, G.J., and Price, C.T. 1986. Two-dimensional NMR analysis of aromatic fractions from a coal liquefaction solvent. *Fuel*, **65**, 877–880.

Sorek, H., and Anderson, J.E. 1985. Short communication: Radioisotopic study of relative fuel-to-soot conversion in diffusion flames of binary mixtures. *Combust. Sci. Technol.*, **43**, 321–328.

Sorek, H., and Anderson, J.E. 1986. C14 study of relative fuel-to-soot carbon conversion in premixed flames. *Combust. Sci. Technol.*, **49**, 201–204.

Sorek, H., Anderson, J.E., Siegl, W.O., and Otto, K. 1984. Radioisotopic study of methanol-to-soot conversion in methanol-hydrocarbon diffusion flames. *Combust. Sci. Technol.*, **41**, 203–209.

Stranic, I., Pang, G.A., Hanson, R.K., Golden, D.M., and Bowman, C.T. 2013. Shock tube measurements of the tert-butanol + OH reaction rate and the tert-C4H8OH radical β-scission branching ratio using isotopic labeling. *J. Phys. Chem. A*, **117**, 4777–4784.

Stranic, I., Pang, G.A., Hanson, R.K., Golden, D.M., and Bowman, C.T. 2014. Shock tube measurements of the rate constant for the reaction ethanol + OH. *J. Phys. Chem. A*, **118**, 822–828.

Sun, C., Cooper, M., and Snape, C.E. 2003a. Use of compound-specific δ13C and δD stable isotope measurements as an aid in the source apportionment of polyaromatic hydrocarbons. *Rapid Commun. Mass Spectrom.*, **17**, 2611–2613.

Sun, C., Snape, C.E., McRae, C., and Fallick, A.E. 2003b. Resolving coal and petroleum-derived polycyclic aromatic hydrocarbons (PAHs) in some contaminated land samples using compound-specific stable carbon isotope ratio measurements in conjunction with molecular fingerprints. *Fuel*, **82**, 2017–2023.

Tancell, P., and Rhead, M. 1996. Application of radio-chromatographic techniques to diesel emissions research. *J. Chromatogr. A*, **737**, 181–192.

Tancell, P.J. 1995. The origin of polycyclic aromatic hydrocarbons in diesel exhaust emissions. Thesis. University of Plymouth, UK.

Tancell, P.J., Rhead, M.M., Pemberton, R.D., and Braven, J. 1995a. Survival of polycyclic aromatic hydrocarbons during diesel combustion. *Environ. Sci. Technol.*, **29**, 2871–2876.

Tancell, P.J., Rhead, M.M., Trier, C.J., Bell, M.A., and Fussey, D.E. 1995b. The sources of benzo[a]pyrene in diesel exhaust emissions. *Sci. Total Environ.*, **162**, 179–186.

Trier, C.J., Rhead, M.M., Fussey, D.E., Ryder, D., and Graham, M.A. 1991. Development of radiotracer techniques for diesel fuel and exhaust emission research. In *IMechE, Internal Combustion Engine Research in Universities, Polytechnics and Colleges*, Conference, London, January 30–31. Paper C433/010, 159–164.

Zielinska, B., Campbell, D., Lawson, D.R., Ireson, R.G., Weaver, C.S., Hesterberg, T.W., Larson, T., Davey, M., and Liu, L.-J.S. 2008. Detailed characterization and profiles of crankcase and diesel particulate matter exhaust emissions using speciated organics. *Environ. Sci. Technol.*, **42**, 5661–5666.