



Criminal removal of fuel markers by distillation



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ABSTRACT

Samples of locally sourced UK Diesel fuel spiked with the two organic compounds 2-(butan-2-yl)-1-(decyloxy)-4-(triphenylmethyl)benzene (TPMB) and 1,3-dibromotetrafluorobenzene (BFB) were subjected to laboratory-scale distillations to assess the suitability of TPMB and BFB as effective markers of Diesel fuel. Industrial-scale distillations of these spiked Diesel samples were performed to establish whether TPMB and BFB could be successfully and cost-effectively separated from Diesel on a significantly larger scale. Diesel distillate does not contain any TPMB; newly formulated performance criteria of an ideal, distillation resistant fuel marker clearly reject TPMB as a marker suitable for the tagging of Diesel. In contrast, BFB is retained in all fractions of distilled Diesel and largely satisfies the performance criteria of a distillation resistant fuel marker. BFB consequently functions as a significantly better fuel marker than TPMB for the tagging of Diesel. It is demonstrated that distillation is also a highly effective means of removing current overt dye markers. Conservative estimates suggest that an appropriately equipped laundering facility for the distillative removal of fuel markers or vice versa fuel from marked Diesel offers the potential of generating a vastly lucrative, multi-million pound annual profit.

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1. Introduction

It is a common practice in many countries to tax fuel for use in industrial sectors such as the agricultural, marine or mining industries at a lower rate or to subsidise it compared to fuel employed for road transport. To ensure that such lower taxed or subsidised fuel is exclusively utilized for its intended purpose, it is frequently the case that a marker is added to distinguish it from the more expensive, higher taxed road fuel. Clearly there is every incentive for criminals to remove such a marker and subsequently sell the laundered fuel at the higher road transport price. The potential profits to the criminal and the consequent losses of tax revenue to governments are exceedingly high, running into many tens of millions of pounds per annum.

The typical methods for the removal of commonly employed markers are well known, through reporting by the media, and generally do not entail much sophistication or cost to the criminal. Should the identity of the marker be known, and in many instances such information is published as part of relevant legislation, it is a relatively trivial exercise for someone with only a basic knowledge of chemistry to identify a suitably effective laundering method. In the case of more sophisticated markers, it is usually not too onerous a task for a

professional chemist to identify weaknesses and vulnerabilities in a marker. However, for a removal method to be workable it must be cost-effective and not materially affect the physical properties of the fuel (such as colour, viscosity, and homogeneity). Such a laundering method will be judged to have been effective if it completely removes a marker, incompletely removes it but reduces it to a level for which quantification or prosecution cannot be assured, or degrades it to an extent that subsequent analysis will prove to be problematic and yield inconclusive results. There have been few systematic studies related to fuel laundering but several authors have either cited launder tests as part of their recommendations on the usefulness of materials as markers [1,2], or have looked to determine measurable compositional change in marked fluids to determine the occurrence of laundering once markers have been removed [3,4,5]. Most cite the use of typical chemical reagents such as acids and alkalis, or a physical adsorbant such as charcoal.

The mechanisms, by which certain laundering agents achieve marker removal, can be readily explained. For example, uses of acid or base washing may lead to protonation or deprotonation of the marker, permitting simple extraction of the now more polar marker into an aqueous phase. Physical adsorbants, such as charcoal and clays are also commonly employed for marker removal. Charcoal, exhibiting a very high surface area per weight, may be a particularly effective adsorbant.

The most commonly used overt markers are dyes. Most, if not all, overt markers and many covert markers are relatively easily laundered

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out by the simple removal methods identified above or by any other, more uncommon methods, such as the use of redox reagents. Degradation is also frequently achieved by subjecting marked fuel to (strong) ultraviolet radiation, which is usually provided by an appropriate spectral lamp. As a consequence of the ready removal of dye markers, more emphasis is being placed on harder-to-laundry covert markers.

Distillation is a commonly employed separation method both in the laboratory and, of course, in an industrial environment. We will examine the potential for use of distillation as a relatively simple and cost-effective method of separating a marker from fuel by effectively removing either the fuel from the marker or vice versa the marker from the fuel. It affords a key advantage in comparison to many of the other methods of marker removal mentioned above, since it does not require the large-scale procurement of laundry agents and does not leave any such spent agent for the criminal to dispose of. Distillation also offers the benefit of not leaving any residue in the fuel which may negatively impact upon engine performance and consequently affect the viability of the criminal operation. In view of the simplicity of a distillation it is apparent that an authority would be foolhardy to employ a marker whose boiling point fell just within, or entirely outside, the boiling range of the fuel to be protected.

Diesel is the name given to any fuel that can be used in a diesel engine. Most commonly it refers to the middle distillate obtained by the fractional distillation of petroleum (crude oil), within a typical boiling range of 160 to 360 °C and is often referred as petrodiesel. Petrodiesel is therefore a complex variable mixture of hydrocarbons composed of about 75% saturated hydrocarbons (paraffins and cycloparaffins) and 25% aromatic hydrocarbons (including naphthalene's and alkylbenzenes) [6,7]. It consists of hydrocarbons ranging in carbon numbers predominantly from C₉–C₂₀ [8]. The quantity and composition of the streams drawn off from distillation (“straight run”) are dependent upon the chemical composition of the crude oil feedstock which will vary from region to region. It should also be noted that crude oil yields of other distillate materials such as gasoline, kerosene, diesel, and residual fuel oils can be different from the product demand patterns in certain markets. The only way to balance production with market demand is to further process the straight run materials. This generally uses some form of “cracking” where large hydrocarbon molecules are broken into smaller ones. These “cracked” products are then blended with the “straight run” products to produce the final product. For this reason fuel standards tend not to mandate the chemical composition of the fuel, other than some unwanted impurities such as sulphur, but limit it to a number of performance and physical properties that must be met.

One such important specification for diesel fuels is the cetane number which is a measure of the ignition quality of the fuel and its cold flow properties. These can be typically altered by changing the composition of the fuel. For instance, the higher the content of paraffinic hydrocarbons the higher the cetane number, and thus lowers the autoignition temperature, but this may pose problems in meeting low-temperature specifications with high wax content. Accordingly more kerosene, or hydrocarbons from cracking processes, are blended into straight run diesels to produce ‘winter grades’ with improved flow properties [8]. Thus it can be seen that there can also be seasonal variations in diesel fuel specifications and thus differences in chemical and physical properties seasonally.

As previously stated the boiling range of Diesel typically spans the temperature interval from approximately 160 to 360 °C. Most authorities consequently request information on the boiling point of a marker as part of their evaluation process. However, the sole knowledge of the pure marker's boiling point does not provide sufficient information about the marker's physical properties to establish its effectiveness in actual use.

Although computational methods exist that may be used to estimate the behaviour of a mixture of an arbitrary number of components, they are not sufficiently reliable in predicting which distillation fractions a

marker might appear. Accurate vapour–liquid equilibrium data may only be obtained by measurement. Experiments were consequently performed that quantitatively measure marker distributions in Diesel distillation fractions and attempts are made to interpret and rationalise these findings. Based upon their distillation results the suitability of potential marker molecules to act as effective fuel markers is assessed. The utility and practicality of distillation as a cost-effective means for criminals to remove a fuel marker and its earning potential are also discussed. Legislators have publically stated that they consider scale-up of distillation from laboratory to larger, commercially viable scales to be problematic for criminals to achieve [9]. Bearing this statement in mind, the ease and cost-effectiveness of using distillation as a method of marker laundering are examined.

Specifically, the distillation behaviour of two known organic compounds is investigated in this study. Both are classed as non-launderable markers by conventional methods (*vide supra*), leaving only distillation as the primary means of separating these markers from fuel. Distillation would constitute an effective laundering method when the distillation process delivers a distilled product containing marker levels that are either insufficient for quantification to enable prosecution, small but could arguably originate in cross contamination, or undetectable because they are below the limit of detection (LOD) so that the distilled product merely indicates the absence of marker. In all cases the resulting distillate must still have suitable physical properties to render it usable as a fuel and, in order to be economically viable, the distillation must proceed with sufficiently high recovery levels of distillate. We also include a thorough economic analysis of the use of distillation techniques in the illicit removal of markers in Section 4.5.

2. Materials

For obvious reasons, the nature of covert fuel markers is generally not publically disclosed. However, in certain countries and regions the marker is identified as a requirement to enact appropriate legislation. In this study the resistance to distillation of two known organic compounds is examined that are classed as non-launderable markers by conventional methods.

The first is 2-(butan-2-yl)-1-(decyloxy)-4-(triphenylmethyl)benzene (TPMB), a tritylated alkylaryl ether also known as ((3-(sec-butyl)-4-(decyloxy)phenyl)methanetriyl)tribenzenes (CAS RN 1404190-37-9); its structural formula is depicted in Fig. 1. TPMB is commercially marketed as Accutrace™ S10 and has been identified [10,11] as being adopted as a fuel marker. It has a predicted boiling point of 606.5 ± 44.0 °C, calculated using the ACD/Boiling Point & Vapour Pressure Calculator algorithms [12].

Due to the lack of a commercial standard or suitably small sample size at the time of testing, TPMB was synthesised following a published synthetic route [13]. Confirmation of the structure was undertaken by the Analytical Services of the Department of Chemistry at Durham University who performed a series of one- and two-dimensional ¹H and ¹³C nuclear magnetic resonance (NMR) and mass spectrometry (MS) experiments where a mass ion consistent with the molecular ion was observed. The data from these experiments are fully consistent with the proposed structure (plus minor solvent impurities); alternative structures have not been postulated that could satisfactorily explain these data (*vide Supplementary material*).

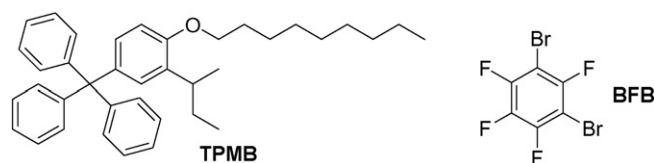


Fig. 1. Structural formulae of the two covert fuel markers 2-(butan-2-yl)-1-(decyloxy)-4-(triphenylmethyl)benzene (TPMB) and 1,3-dibromotetrafluorobenzene (BFB).

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