



SUBJECT Forensic Analysis of Animal and Vegetable Oil and Fat Residues
RELEASE DATE 30 March 2016
ISSUED BY Alexander Visotin, Laboratory Manager

Introduction

Recently, our laboratory was appointed to perform some sample analyses relating to a residential house fire. Our client had performed a fire examination of a dwelling that was under renovation. A painter had been working at the dwelling on the day before the fire. The painter had been treating a timber wall surface with a finishing oil and a hardener. The fire occurred at the dwelling on the night after this work was undertaken. That night was, ostensibly, one of the hottest the area had experienced for some time. Our client determined that an area around where the painter had been working was the area of origin for the fire. The remains of some rags were recovered from this area, allegedly used by the painter to apply the oil. The probable cause of the fire, therefore, was determined to be self-heating of the oils within the rags. Our laboratory was asked to perform analyses to confirm or deny this hypothesis.

This Technical Bulletin is designed to be a primer for forensic animal and vegetable oil residue analysis as it relates to fire examination. This is a type of analysis that we can perform on residues of most organic oils to determine their propensity for self-heating. Consider these analytical techniques next time you examine a fire scene where the ignition of organic oils may have been involved.

What are animal and vegetable oils?

NOTE: The term *vegetable oil* is used throughout this document purely out of convenience as vegetable oils are more commonly encountered than animal oils. However, the term refers to both vegetable and animal oils and fats.

Vegetable oils are extracted from plant matter. Most oils are extracted from the fruits, seeds or nuts generated by a parent plant. Linseed oil, for example, is derived from ripened flax seeds, while palm oil is extracted from palm oil fruit pulp. Vegetable oils are typically extracted by crushing the source plant matter, rinsing it with a solvent, and filtering the liquid extract. Animal oils and fats are most commonly extracted from the rendered tissue fats of livestock such as pigs and cows. The extracted oils are refined to remove undesirable natural contaminants. Additives are also added to modify the physical properties of the oil.

The primary components of vegetable oils are lipids in the form of triglycerides. Triglycerides consist of a glycerol ester backbone with three fatty acids attached to it. The fatty acids are straight chains, generally 16 or 18 carbons in length, though shorter and longer chains also occur in some oils. Most fatty acid chains contain an even number of carbons. Fatty acids can be saturated, or

unsaturated, based on the number of double bonds present in the carbon chain. Saturated fatty acids contain only single carbon-carbon bonds, while unsaturated acids contain one (monounsaturated), or more double bonds (polyunsaturated). In a similar way to how ignitable liquids can be characterised by their aromatic, alkane, or cycloalkane content, vegetable oils can be characterised by their fatty acid content.

The degree of saturation affects the physical properties of the oil. The various *cis*- and *trans*-double bond configurations in unsaturated fatty acids will bend the acid chains, preventing cohesion of the mass as a solid. Therefore, oils with mostly saturated fatty acids will be more solid at room temperature, while polyunsaturated oils are generally liquids. This is the primary difference between a fat and oil.

Vegetable oil behaviour during combustion

Before a vegetable oil can burn, oxidation inhibitors that are naturally present in the oil must be removed. These antioxidants prevent auto-oxidation of oil, as they do not generate free radicals upon reaction with oxygen. This is why it often takes some time for a self-heating event to reach a point where thermal runaway occurs: the 'incubation' time is the period in which the antioxidants are depleted. After they are removed, the fatty acids themselves begin to auto-oxidise, creating heat and leading to thermal runaway. The addition of driers and hardeners to oils will also impact their auto-oxidation ability.

Different oils have different propensities toward self-heating based on their fatty acid content. Generally, only polyunsaturated fatty acids will undergo self-heating to the point of autoignition. This is because the auto-oxidation reaction at the heart of a self-heating event is favoured as the number of double bonds in a fatty acid chain increases (i.e. the degree of unsaturation). The more double bonds that are present in the chain, the faster heat will be generated. This is because the double bonds in the fatty acid chain weaken the adjacent carbon's bond to hydrogen, reducing the energy required for oxidation or removal of the atom. The more double bonds that are present, the "weaker" the acid will be to oxidation. Linseed oil, for example, contains many polyunsaturated fatty acids and will self-heat readily. By comparison, olive oil is unlikely to self-heat as it contains mostly monounsaturated fatty acids. The table below lists a number of vegetable and animal oils, as well as their tendencies to self-heat. This is not an exhaustive list as essential oils can be extracted from an endless number of plant and animal products. However, effort has been made to include common oils that may be encountered at a fire scene, in addition to less common oils that have a high tendency for self-heating.

Oil	Self-heating Tendency	Source Material	Common Uses
Alfalfa	Moderate	Alfalfa seeds	Medicinal
Almond	Low	Almond kernels	Cooking oil; cosmetics
Amaranthus	Moderate	Amaranth seeds	Cooking oil
Argemone	Moderate	Mexican poppy seeds	Biodiesel feedstock
Arnebia	High	Arnebia seeds	Medicinal
Avocado	Low	Avocado fruit pulp	Cosmetics; cooking oil
Basil	High	Basil seeds	Cooking oil
Blackcurrant	Moderate	Blackcurrant seeds	Medicinal
Borage	Moderate to high	Starflower seeds	Medicinal
Buffalo gourd	Moderate	Buffalo gourd seeds	Soap; biodiesel
Calendula	High	Pot marigold seeds	Medicinal; drying oil
Candlenut	Moderate to high	Candlenuts	Cosmetics; medicinal
Cashew	Low	Cashew nuts	Cosmetics; cooking oil
Castor	Low	Castor beans	Medicinal; coatings; precursor
Chia	High	Chia seeds	Medicinal
Coconut	Very slight	Kernel or meat of coconuts	Biodiesel feedstock
Corn	Moderate	Maise germ	Biodiesel feedstock
Cottonseed	Moderate	Cottonseeds	Cooking oil
Echium	High	Paterson's curse seeds	Medicinal
Evening primrose	Moderate	Evening primrose seeds	Medicinal
Fish	High	Tissues of oily fish	Medicinal
Gold of Pleasure	Moderate to high	Gold of pleasure seeds	Drying oil; biodiesel

Hemp	Moderate to high	Cannabis sativa seeds	Cosmetics
Hyptis	High	Hyptis seeds	Medicinal
Kiwi	High	Kiwifruit seeds	Cosmetics
Macadamia	Low	Macadamia nuts	Cooking oil; cosmetics
Linseed	High	Flaxseeds	Drying oil
Oiticica	High	Oiticica kernels	Drying oil
Olive	Low to moderate	Olives	Cooking oil
Palm	Low	Mesocarp of palm oil fruit	Cooking oil
Peanut	Low	Peanuts	Cooking oil
Perilla	High	Perilla seeds	Drying oil
Purslane	Moderate to high	Purslane seeds	Medicinal; culinary
Rapeseed	Moderate	Rapeseeds	Cooking oil; biodiesel
Raspberry	High	Raspberry seeds	Cosmetics
Rice bran	Low to moderate	Rice husks	Cooking oil
Rose hip	High	Rosehip seeds	Cosmetics
Safflower	Moderate	Safflower seeds	Cooking oil; drying oil
Sacha Inchi	High	Sacha inchi plants	Culinary
Sea buckthorn	Moderate to high	Sea buckthorn seeds	Culinary; medicinal
Sesame	Low to moderate	Sesame seeds	Cooking oil
<i>Sisymbrium irio</i>	Moderate	<i>Sisymbrium irio</i> seeds	Cosmetic
Soybean	Moderate	Soybean seeds	Cooking oil; drying oil
Stillingia	Moderate to high	Chinese tallow tree kernels	Drying oil
Sunflower	Moderate	Sunflower seeds	Cooking oil
Tobacco	Moderate	Tobacco seeds	Drying oil
Tung	High	Tung tree nuts	Drying oil
Walnut	Moderate to high	Walnuts	Culinary

Extraction of vegetable oils from fire debris

As oils are far less volatile than ignitable liquid residues, they are not captured as readily by the same adsorbents used to extract ILR. As a result, headspace-based extraction techniques are not effective for oil extraction. Oil residues are more efficiently extracted from debris via washing with a solvent, followed by filtration. This creates a liquid extract, which can potentially be analysed via gas chromatography-mass spectrometry (GC-MS).

Unfortunately, the triglycerides that make up vegetable oils are not readily detected by GC-MS. This is because they do not elute from a typical GC column within a reasonable timeframe as a result of their high molecular weights. Instead, the extracted sample must undergo additional preparatory steps whereby the triglycerides are converted into free fatty acids (FFAs). These FFAs are then derivatised, in the presence of a catalyst, to form fatty acid methyl esters (FAMES). FAMES are more stable and volatile than triglyceride molecules, thus they can be detected via GC-MS more reliably.

Analysis of vegetable oil residues

The fatty acid composition of oil will change as it oxidises. Storage conditions and modes of ignition will have the largest impact. To reduce the potential for degradation, debris containing as little water as possible should be collected. Samples should be delivered to the laboratory as soon as possible and should be refrigerated wherever possible. Even after a fire, any remaining vegetable oil residues will continue to auto-oxidise until cooled, further changing the composition of the sample and making classification more difficult. Prompt analysis is always desirable.

The amounts of fatty acids recovered from a sample of fire debris depend on the nature of the source oil, how significantly that oil has been degraded, as well as the nature of the receiving substrate. If vegetable oil is detected, conclusions can generally be drawn about the propensity of the oil to self-heat based on the number of polyunsaturated fatty acids detected. However, note that these conclusions are based on the condition of the oil *after involvement in a fire*, where significant thermal degradation may have occurred. As the fatty acids oxidise, the ratios between

saturated and unsaturated acids will change. These ratios can change to a point that the original oil is no longer identifiable.

Unfortunately, the decomposition patterns of specific oils are not well known and determining the identity of the original oil from residues in debris is difficult without performing test burns with control samples. However, it is known that degradation of oils generally favours polyunsaturated fatty acids before saturated ones. This means that oils with a very high propensity to self-heat (containing polyunsaturated acids) can degrade into oil residues that look like they have a low propensity to self-heat (containing monounsaturated and saturated acids).

A finding of a vegetable or animal oil residue in a sample therefore comes with the disclaimer that oil with a higher propensity to self-heat may have originally been present before the fire. As a result, analysis of the original, neat oil is always desirable, and samples of the neat oil product should be collected (if possible). If it can be proven – via methods other than chemical analysis – that a specific oil was present at the point of origin, the results of the neat oil analysis may be helpful in establishing the cause of the fire, even if debris samples are negative.

Bibliography

Ackland, P. (2012). *A Guide for Commercial Kitchen Fires: Prevention and Investigation*. Summerland, British Columbia, Canada: Phillip Ackland Holdings Ltd.

Gambrel, A. K., & Reardon, M. (2008). Extraction, Derivatization, and Analysis of Vegetable Oils from Fire Debris. *J Forensic Sci*, 53 (6), 1372-1380.

Schwenk, L. A., & Reardon, M. (2009). Practical Aspects of Analyzing Vegetable Oils in Fire Debris. *J Forensic Sci*, 54 (4), 874-880.

Shahidi, F. (2006). *Nutraceutical and Specialty Lipids and their Co-Products*. Boca Raton: CRC Press.

Stauffer, E. (2006). A review of the analysis of vegetable oil residues from fire debris samples: analytical scheme, interpretation of the results, and future needs. *J Forensic Sci*, 51 (5), 1016-1032.

Stauffer, E. (2005). A review of the analysis of vegetable oil residues from fire debris samples: spontaneous ignition, vegetable oils, and the forensic approach. *J Forensic Sci*, 50 (5), 1091-1100.

Stauffer, E., Dolan, J. A., & Newman, R. (2008). *Fire Debris Analysis*. Burlington: Academic Press.