

Comparison between off-line and on-line derivatisation methods in the characterisation of siccative oils in paint media

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Abstract

The characterisation of siccative oils (drying oils used in paint media) by gas-chromatography/mass-spectrometry using three derivatisation methods has been investigated and the differences in results discussed. The classic off-line derivatisation method with (trimethyl)silyldiazomethane has been compared with two alternative methods. The first involves on-line derivatisation using tetramethylammonium hydroxide; in this case the reaction is performed in a pyrolysis interface at 600 °C. The second uses (*m*-trifluoromethylphenyl)-trimethylammonium hydroxide as a derivatisation reagent (lower temperature required for methylation reaction without using the pyrolysis interface). The three methodologies have been found to give reproducible and comparable results for the different types of fresh and aged oils investigated.

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1. Introduction

The study of paint media has received particular attention because of increasing interest in the characterization and conservation of cultural heritage. For preservation and restoration, it is important not only to characterize the original substances used in the painting, but also to identify their degradation products. Gas chromatography-mass spectrometry (GC-MS) has proved to be a suitable technique for identification of pictorial organic material because of its specific response and the possibility of obtaining structural information from very small samples [1]. The aim of this technique is the identification of some compounds as markers of various natural and synthetic binders. To distinguish the drying oils from different kinds of media, the chromatographic peaks of saturated (palmitic and stearic acids) and unsaturated (oleic, linoleic, linolenic, azelaic and suberic acids) fatty acids and their ratios are used. For examination by GC-MS, an oil paint sample must be

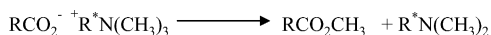
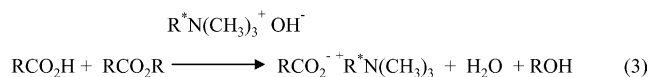
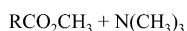
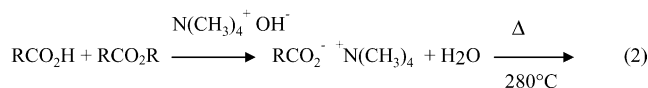
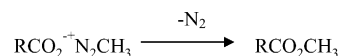
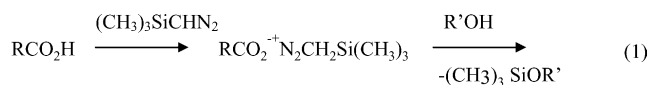
hydrolysed and methylated to obtain more volatile fatty acid methyl esters, which can be analysed by gas chromatography.

The traditional off-line method, proposed by Mills [1,2], uses an alkaline solution to saponify the sample, producing a solution of fatty acid salts, which is acidified to convert the salts into free fatty acids. These are extracted from aqueous solution into organic phase, and methylated using diazomethane or (trimethylsilyl)diazomethane (TMSDM).

Off-line methods are normally used in the characterisation of binding media in paintings and several analytical procedures have been developed for the identification of drying oils [3–5]. However, off-line methods can introduce artifacts due to sample losses or to introduction of external substances during the sample preparation.

In this work, the classic off-line characterisation method has been applied with some modifications and compared with two alternative procedures. One is the on-line derivatisation using tetramethylammonium hydroxide (TMAH), where quaternary ammonium salts of fatty acids are produced and immediately thermally decomposed into

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Scheme 1. Schemes of reactions involved into: (1), off-line derivatisation with TMSDM; (2), on-line thermally assisted derivatisation with TMAH; and (3), on-line derivatisation with TMTFTH. R represents the long chain and R* represents the *m*-trifluoromethylphenyl group.

the corresponding methyl esters in a pyrolysis interface, (thermally assisted hydrolysis and methylation THM [6–10]) (Scheme 1).

The second alternative approach is the on-line derivatisation using TMTFTH ((*m*-trifluoromethylphenyl)trimethylammonium hydroxide), originally introduced for biological applications, but also applied to art samples [8,11,12].

Thermally assisted derivatisation gas chromatography/mass spectrometry (GC/MS) has proved to be a suitable technique without the need of any preliminary treatment [6–10], even if with this method additional compounds are obtained in the GC profile [8,13]. The formation of polyunsaturated fatty acid isomers as conjugated *trans-trans* isomers in oils, for example, has been attributed to base catalysed and thermally induced isomerisation of unsaturated fatty acids [8]. The base catalysed isomerisation is believed to be caused by excess of TMAH and higher required temperature during the thermally assisted hydrolysis and methylation. This can be reduced by using acetic acid or methyl acetate that reacts with the excess of TMAH [8]. Reducing the pyrolysis temperature or using TMTFTH ((*m*-trifluoromethylphenyl)trimethylammonium hydroxide) as derivatisation reagent has been proposed as a solution [8,11].

In addition to methylation and transesterification of the fatty acid groups, TMAH can also react with acidic protons on the α -position, giving rise to different species of unwanted alkylated fatty acid methyl esters [13]. The reactivity of TMAH was demonstrated to be higher in methanolic systems than in concentrated aqueous solutions [13]. To avoid unwanted isomerisation reactions, it has been also proposed to use as methylation reagent a 1:50 TMAH:methanol solution [14].

In recent published work [15], the two tetra-alkyl ammonium salts, TMAH and TMTFTH, were compared to optimise the direct procedure for characterisation of lipid binders. The TMTFTH was used, in the same way as

TMAH, directly in the quartz probe of the pyrolyser interface, giving results in agreement with the standard methods.

The base catalysed isomerisation of polyunsaturated fatty acids was almost eliminated by using TMTFTH at temperatures (280 °C) lower than those generally applied with TMAH. Moreover, the low temperature required for methylation with this reagent makes it feasible to inject the analyte solution directly into the gas chromatograph [11].

This paper presents the results of a comparative evaluation of the two methods described above and the traditional off-line methylation, applied to common siccative oils, linseed oil, linseed stand oil, poppyseed and walnut oil. Fresh films of the different oils and films aged in the laboratory, either naturally or artificially, are studied.

Reproducibility and accuracy has been evaluated, as well as isomerisation phenomena and reagent interferences.

2. Experimental

2.1. Chemicals

Twenty-five percent aqueous tetramethylammonium hydroxide solution, (trimethylsilyl) diazomethane 2 M in hexane, diethyl ether and methanol from Aldrich (USA).

Meth-Prep II ((*m*-trifluoromethylphenyl)trimethylammonium hydroxide) 0.2N in methanol from Alltech (USA). Benzene was obtained from Carlo Erba (Italy).

2.2. Samples

Thin films were prepared on glass slides with linseed oil (025 Talens, The Netherlands), stand oil (031 Talens, The Netherlands), walnut oil (654 Maimeri, Italy) and poppyseed oil (Lefranc and Bourgeois, France).

Indoor laboratory exposure to air at room temperature was selected as natural ageing and a high-speed exposure unit Suntest CPS (Heraeus, Germany), equipped with a Xenon lamp and a UV filter that absorbs wavelengths lower than 295 nm, was used to simulate outdoor solar exposure. Irradiation was set at 765 W m⁻² and the maximum temperature on the sample was kept below 50 °C by forced air circulation.

2.3. Derivatisation reactions

Scheme 1 summarises the derivatisation reactions, which take place for the free fatty acids (or via transesterification), using the different derivitizing reagents.

2.4. TMSDM procedure (off-line)

One milligram of fresh or aged oil was mixed with 1 ml of 10% KOH (w/w), stirred 4 h at 80 °C and then stirred at

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