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Characterization of ageing products of ester-based synthetic lubricants by liquid chromatography with electrospray ionization mass spectrometry and by electrospray ionization (tandem) mass spectrometry

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Abstract

Ageing products of a commercial jet engine oil based on pentaerythritol tetraesters which were formed upon operation in an aviation turbine were detected by electrospray ionization mass spectrometry (ESI-MS) and characterized by LC-ESI-MS. The fatty acid composition of these ageing products was investigated by ESI-MS-MS analysis. The ammonium adducts of the newly formed pentaerythritol tetraester degradation products were found to be suitable parent ions for further structure elucidation work. ESI-MS, LC-ESI-MS and ESI-MS-MS proved to be versatile tools to study the chemical composition (distribution of homologues) as well as the mechanism of ageing of ester based lubricants on a molecular level. Due to its high sensitivity, ESI-MS can also be used to characterize and identify trace levels of ester-based lubricants. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ester-based synthetic lubricants such as phthalates, adipates, sebacates, neopentyl polyol esters and pentaerythritol tetraesters are widely used due to their excellent tribological properties and high thermal stability. A typical application of these products are jet engine oils. For this highly demanding application, durability at operation temperatures above 200°C is required. The thermal stability of these compounds is improved through additives such as *N*-phenylnaphthylamine, dioctyldiphenylamine,

and tricresyl phosphate. The key to improve the long-term stability of such lubricants is to understand the chemical and physical processes induced by tribological stress (friction, wear, heat, water and oxygen). The investigation of chemical modifications provides direct information on the nature and the kinetics of degradation processes being responsible for the ageing of a lubricant. Compared to standard methods for the characterization of lubricant ageing processes, such as monitoring changes of viscosity and total acid number [1], as well as determination of thermal stability by differential scanning calorimetry (DSC) and related methods [2–5], structure elucidation goes one step further towards the understanding of the ageing processes involved.

A variety of analytical methods are available for

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the chemical characterization of ester-based synthetic lubricants and their ageing products, the standard technique being gas chromatography–mass spectrometry (GC–MS) [6,7]. Other techniques include liquid chromatography (LC) [8], infrared spectroscopy (IR) [4], as well as chemical ionization mass spectrometry (CI–MS) [9,10]. Recently, Bartl and Völkl [11] reported the successful application of matrix-assisted laser desorption/ionization mass spectrometry (MALDI–MS) for the characterization of polyol ester-based jet engine oils. Based on the molecular mass and polarity of ester-based synthetic lubricants, we found liquid chromatography–electrospray ionization mass spectrometry (LC–ESI–MS) to be a powerful technique to study the chemical composition and the molecular distribution of homologues, as well as the mechanisms of ageing processes such as oxidation and hydrolysis [12] of synthetic lubricants on a molecular level. In this paper, we show how chemical modifications of a commercial jet engine oil after operation in an aviation turbine can be detected unambiguously by ESI–MS, LC–ESI–MS and ESI–MS–MS.

2. Experimental

2.1. Sample preparation

A commercial jet engine oil (pentaerythritol tetraester) was analyzed before and after its application as a lubricant in a jet engine of an aircraft. Samples were diluted in methanol (100 ng/ μ l) prior to analysis. Ammonium acetate buffer (5 mM) was added (2%) to the samples for ESI–MS–MS experiments to induce NH_4^+ adduct formation.

2.2. Liquid chromatography

LC was performed on a C_8 column (125 \times 4 mm, Nucleosil 100-5, C_8 , Marchery–Nagel, Switzerland) using a water–methanol gradient (80% methanol to 98% methanol in 15 min with a constant amount of 2% ammonium acetate buffer, prepared as a 5 mM solution of ammonium acetate in water), followed by isocratic elution for 30 min. The LC flow-rate was 200 μ l/min (same conditions for both examples shown in this manuscript). The LC system was a

SpectraSystem P4000 (ThermoQuest, USA), the injector was a Rheodyne 7125NS (USA).

2.3. Mass spectrometry

ESI–MS, ESI–MS–MS and LC–ESI–MS were carried out on a TSQ 7000 triple stage quadrupole mass spectrometer (ThermoQuest) in positive ion mode at sample flow-rates of 3 μ l/min (direct inlet ESI–MS and ESI–MS–MS) or 200 μ l/min (LC–ESI–MS). Spectra were acquired at a tube lens voltage of 10 V [in-source collision-induced dissociation (CID)], a spray voltage of 3.8 kV, a capillary temperature of 200°C, a sheath gas pressure of 480 kPa (N_2), a scan rate of 500 u/s, a scan time of 2 s and a detector voltage of 1.2 kV. Acquisition times were 2 min (direct inlet ESI–MS and ESI–MS–MS) or 45 min (LC–ESI–MS). ESI–MS–MS spectra were acquired at a collision energy of 25 eV using argon as a collision gas at a pressure of 0.16 Pa.

3. Results and discussion

An example of a direct inlet ESI mass spectrum of a new jet engine oil is given in Fig. 1, showing sodium adducts $[\text{M}+\text{Na}]^+$ of homologous pentaerythritol tetraesters between m/z 495 and m/z 663, and dipentaerythritol hexaesters between m/z 781

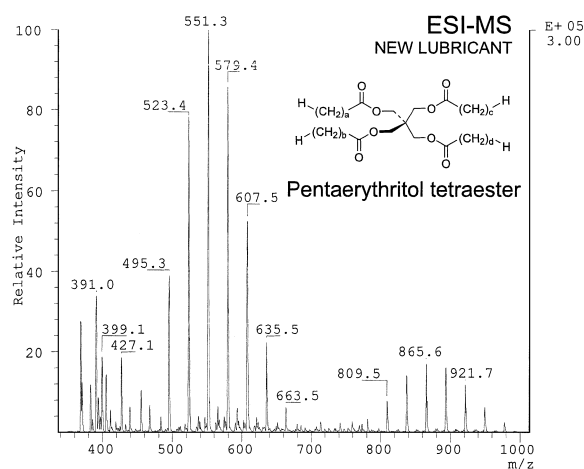


Fig. 1. Direct inlet positive ion ESI–MS of the new pentaerythritol tetraester jet engine oil (100 ng/ μ l, sample consumption 600 ng).

and m/z 977. For the new lubricant, seven homologues tetraester and eight hexaester signals being 28 m/z units apart were observed, corresponding to mixed esters of C_5 , C_7 and C_9 carboxylic acids and pentaerythritol (see Table 1). These data demonstrate that ESI-MS is a versatile technique to characterize and identify complex mixtures of ester based lubricants. A reasonable spectrum can be obtained based on a sample consumption of 600 ng of a mixture of 15 pentaerythritol esters, as shown in Fig. 1. The signals at m/z 369 and m/z 391 correspond to the protonated $[M+H]^+$ and the sodiated $[M+Na]^+$ forms of tricresyl phosphate, which is one of the additives used in this lubricant. The ESI mass spectrum of a sample of the same lubricant, taken after operation in a jet engine is given in Fig. 2. This spectrum shows, in addition to the esters described before, a series of new compounds which were formed upon jet engine operation. Two series of 13 homologues pentaerythritol tetraesters (see Table 1) and 16 homologues dipentaerythritol hexaesters differing by 14 m/z units were detected. LC-ESI-MS experiments confirm the formation of these new species (see Fig. 3). The new compounds and the

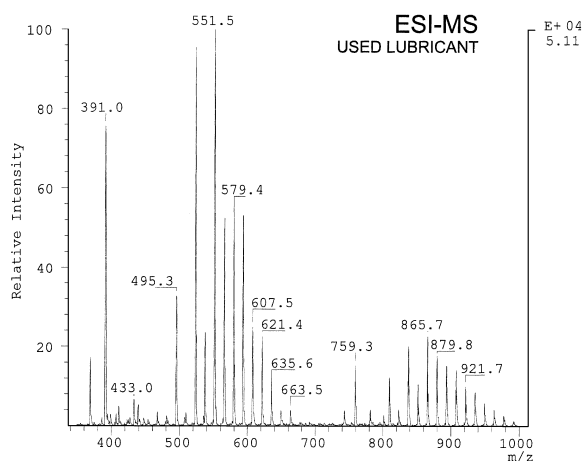


Fig. 2. Direct inlet positive ion ESI-MS of the used pentaerythritol tetraester jet engine oil (100 ng/ μ l, sample consumption 600 ng).

homologues of the pentaerythritol esters are interleaved. Each signal in the LC-ESI-MS chromatogram corresponds to a series of pentaerythritol tetraesters or dipentaerythritol hexaesters, demonstrating that we observe indeed the formation of new

Table 1

Pentaerythritol tetraesters, their adduct ions and their chromatographic retention times

No.	C_n^a	$(CH_2)_m^b$	m/z		t_R (min:s)
			$[M+Na]^+$	$[M+NH_4]^+$	
1	25	16	495	490	16:06
2 ^c	26	17	509	504	18:02
3	27	18	523	518	19:42
4 ^c	28	19	537	532	21:13
5	29	20	551	546	22:29
6 ^c	30	21	565	560	23:45
7	31	22	579	574	24:47
8 ^c	32	23	593	588	25:41
9	33	24	607	602	26:37
10 ^c	34	25	621	616	27:21
11	35	26	635	630	28:00
12 ^c	36	27	649	644	28:36
13	37	28	663	658	29:08

^a Total carbon number of the pentaerythritol tetraester ($n=a+b+c+d+9$).

^b Number of methylene groups of the four fatty acid chains ($m=a+b+c+d$).

^c These pentaerythritol tetraesters are predominantly found in the used lubricant.

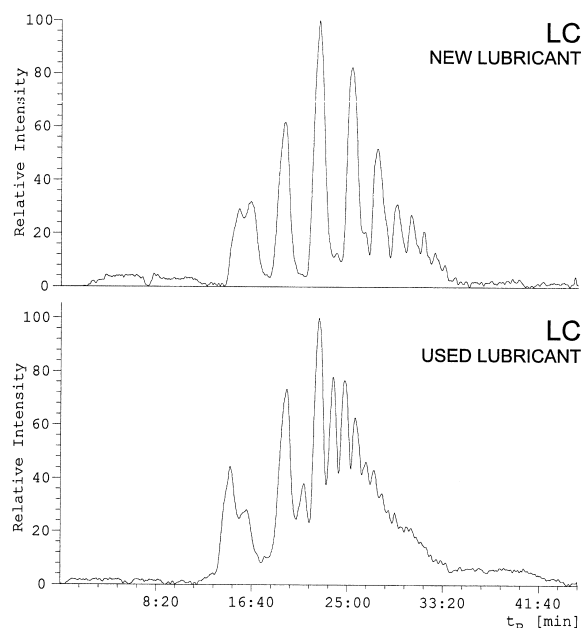


Fig. 3. LC-ESI-MS of new (top) and used (bottom) pentaerythritol tetraester jet engine oil (sample consumption 2 μ g).

species upon ageing of the lubricant. In addition, the increased chromatographic retention time indicates the presence of new, less polar compounds (reversed-phase chromatography).

In order to further elucidate the chemical structure of these new homologous species, ESI-MS–MS experiments (product ion spectra) of their ammonium adducts $[M+NH_4]^+$ were carried out. As expected, ammonium ion induced fragmentation reactions were found to result in much higher daughter ion intensity than fragmentation of the corresponding sodium adducts $[M+Na]^+$. Collisions of selected tetraester ions $[M+NH_4]^+$ (such as m/z 546, m/z 560, m/z 574, and m/z 588) with argon resulted in daughter ions which are interpreted as the corresponding pentaerythritol triester carbonium ions. Fig. 4 displays a selection of neutral loss spectra (neutral loss of ammonium carboxylates). From the parent ions at m/z 546, which correspond to a mixture of isobaric ammonium salts of different C_{29} tetraesters, about equal amounts of the C_5 and C_7 carboxylic acids are cleaved as ammonium carboxylates and therefore lost as neutrals, resulting in two prominent daughter ions at m/z 427 and 399. These species are also formed by in-source CID, as demonstrated by their

presence in the ESI-MS (Figs. 1 and 2). The loss of C_5 and C_7 carboxylic acid ammonium salts is apparent in all examined MS–MS spectra. However, the loss of C_8 or C_{10} carboxylic acid salts can only be detected in case of the newly formed compounds. Therefore, the corresponding tetraesters formed during tribological stress upon jet engine operation must have a different fatty acid composition containing, in parts, longer fatty acid chains. These findings are consistent with increased chromatographic retention times of these newly formed compounds. Further work is underway to gain a more complete understanding of these ageing processes through the use of various standardized methods for inducing tribological stress and through structural elucidation of the new, unknown products formed upon these processes. The analytical methods described in this paper can easily be applied to other ester based synthetic lubricants such as phthalic acid esters, sebacic acid esters, adipic acid esters or triglycerides. Fig. 5 shows a LC–ESI-MS analysis of a typical mixture of homologous phthalic acid esters (C_{26} to C_{29}). Other examples in this field include LC–ESI-MS analysis of partially hydrolyzed phthalic and sebacic acid esters (formation of these species was induced by tribological stress) as well as oxidation processes of linoleic acid esters induced by exposure to air and moisture on a steel surface at elevated temperature [12].

4. Conclusions

ESI-MS in combination with LC is a versatile method to verify the chemical composition of ester oils. Molecular mass and distribution of homologous species, as well as degradation products such as partially hydrolyzed or oxidized esters can be determined by ESI-MS. Ammonium adducts of the pentaerythritol tetraesters or the dipentaerythritol hexaesters are suitable MS–MS parent ions to investigate the fatty acid composition of such esters. In addition, additives such as tricresyl phosphate can be determined simultaneously. Due to its high sensitivity, ESI-MS can also be used to characterize and identify trace levels of ester based lubricants in other matrices such as mineral oils.

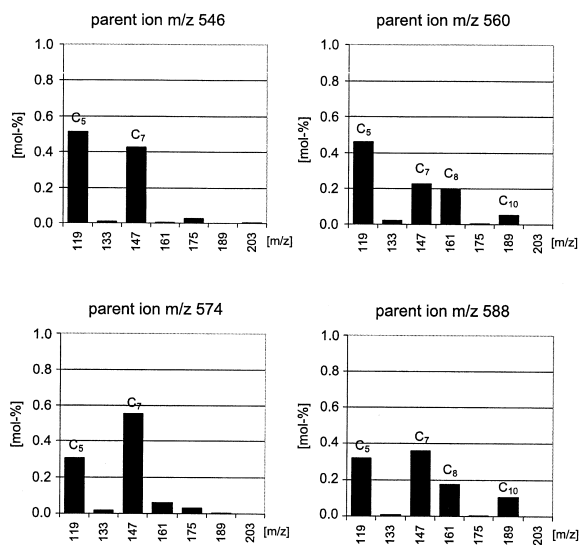


Fig. 4. ESI-MS–MS neutral loss spectra of pentaerythritol tetraesters (neutral loss of carboxylic acid ammonium salts).

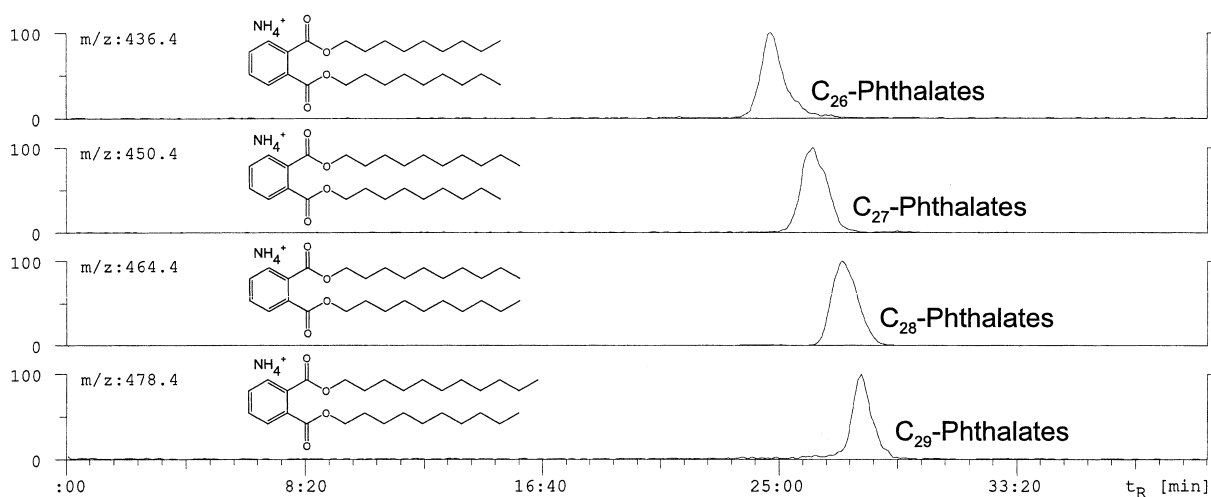


Fig. 5. LC-ESI-MS of a typical phthalate ester base oil mixture (sample consumption 2.3 μg).

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