

Scope

Lubricants include many different types of additives with versatile demands. Among them, zinc bis(O,O'-dialkyl dithiophosphates) (ZnDTPs) are used concerning their antiwear, antioxidant and anticorrosion attributes. Depending on the purpose of the lubricant, the employed concentration of this additives is located about 0.2 to 4%. The identification and quantification of these additives is required because the character of the used ZnDTPs and their concentration is an important parameter regarding the quality of the lubricant. The aim of this study [1] was to explore an analytical strategy for identification and quantification of lubricant additives combining HPTLC and infrared spectroscopy.

Results and discussion

Two chromatographic systems for separation of the lubricant additives were established (Fig. 1). The **reversed** phase system was performed on RP-2 F₂₅₄ plates using a 2-step development with acetonitrile – water 11:9 (v/v) for ZnDTPs and methanol – water – acetic acid 6:3:2 (v/v/v) for Anglamol 99®. The **normal** phase system using HPTLC or preparative plates silica gel 60 F₂₅₄ was based on an 14-step gradient containing methanol, toluene and *n*-hexane (AMD 2, CAMAG). The plates of both chromatographic systems were derivatized with 0.05% primuline in acetone – water 4:1 (v/v).

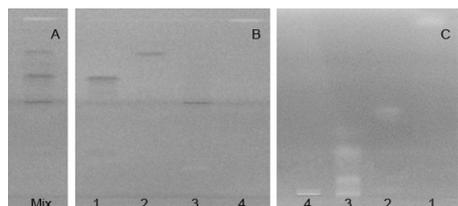


Fig. 1: Separation of the lubricant additives zinc bis(O,O'-disobutyl dithiophosphate) (track 1), zinc bis(O,O'-didodecyl dithiophosphate) (track 2) and Anglamol 99® (track 3) from the mineral oil matrix (track 4): A), B) normal phase system and C) reversed phase system.

For **infrared spectroscopy** three to five additive zones, depending on the layer thickness and the respective cutting edge of the plunger (0.2 mm or 0.5 mm), were online eluted via the Interface ChromeExtract [2] into a vial. After a concentration step the whole sample was dropped onto the diamond crystal of the ATR-IR.

The additives' spectra showed characteristically bonds (Fig. 2): stretching vibrations (CH₃, CH₂, CH) between 2957 and 2855 cm⁻¹, bending vibrations (CH₃) in the region of 1470 cm⁻¹, P-O-(C) bond at 997 or 991 cm⁻¹, and P-S bond at 680 or 679 cm⁻¹. The splitting of the bending vibration into two bands (1396 and 1359 cm⁻¹) was the most obvious difference between the two ZnDTPs. Identification of the additives by FTIR was performed analogously by concentrated drops on a NaCl carrier (not shown).

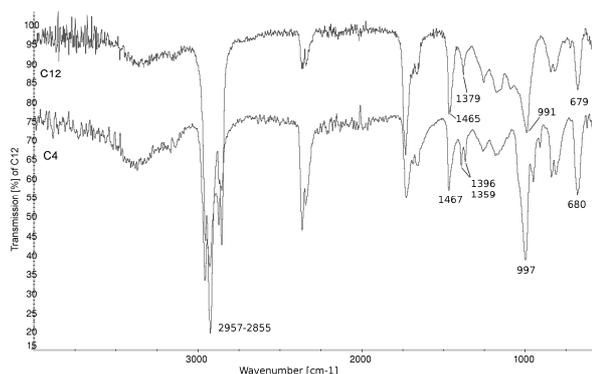


Fig. 2: HPTLC/ATR-IR spectra of zinc bis(O,O'-didodecyl dithiophosphate) (C12) and zinc bis(O,O'-disobutyl dithiophosphate) (C4) in the range of 4000 – 400 cm⁻¹.

Quantification of the additives was performed via absorbance measurement at UV 220 nm. The results showed a precision (%RSD, n = 6, 3-7 µg/band) between 2.2 and 5.5%. Using derivatization with the primuline reagent, the LOQs were improved by a factor of 2 down to 309 ng/band for ZnDTPs and 65 ng/band for Anglamol 99®. The correlation coefficients obtained in the working range of 0.5 - 5 µg/band for ZnDTPs and 0.7 - 7 µg/band for Anglamol 99® were highly satisfying (> 0.9973).

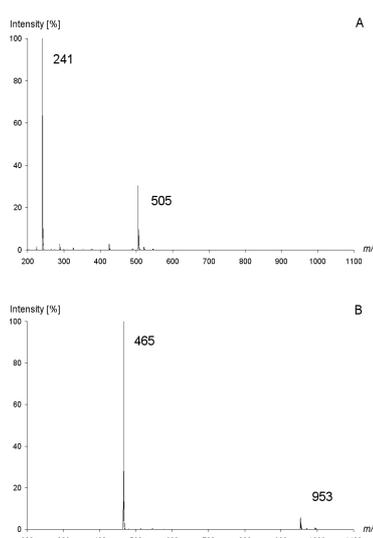


Fig. 3: HPTLC/ESI-MS spectra of zinc bis(O,O'-disobutyl dithiophosphate) (A) and zinc bis(O,O'-didodecyl dithiophosphate) (B).

For **HPTLC/ESI-MS** the additive zones were directly eluted into the ion source using the ChromeExtract interface (Fig. 3). In the negative ESI mode zinc bis(O,O'-diisobutyl dithiophosphate) showed its main fragment O,O'-diisobutyl dithiophosphate at *m/z* 241. The minor signal at *m/z* 505 was the sodium adduct of the dimer. Analogously zinc bis(O,O'-didodecyl dithiophosphate) showed the respective fragments at *m/z* 465 and *m/z* 953. After cutting the HPTLC plate into stripes the main fragments were additionally confirmed by **HPTLC/DART-MS** with which the mass spectra were recorded within seconds.

Conclusion

Using the ChromeExtract interface the coupling of HPTLC with infrared spectroscopy was shown for the first time. By separating the lubricant additives via the developed HPTLC methods from the oil matrix, their identification via infrared spectroscopy was rapidly enabled. In contrast to in situ HPTLC/DRIFT recording, the whole wave number range (4000 – 400 cm⁻¹) including the valuable fingerprint region was available. The HPTLC/IR techniques do not need an extensive sample preparation and can be integrated into a quality assurance system. The coupling of HPTLC with MS via ChromeExtract interface or DART confirmed the identification of the lubricant additives by IR.

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[1] Dytkiewitz, E., Morlock G. (2008) J. AOAC Int. in print
[2] Luftmann, H. (2004) Anal. Bioanal. Chem. 378, 964-968