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Application News

Gas Chromatography

Analysis of mineral oil in environmental samples according to H53

No. SCA_180_022

Introduction

Every day, worldwide, large quantities of crude oil are processed into various mineral oil products such as petrol, kerosene, diesel, heating oil, and lubricating oil. Mineral oil products are generally composed of mostly saturated hydrocarbons, so-called mineral oil hydrocarbons (MOH). During the production as well as the commercial and private use of mineral oil products, water and soil are repeatedly contaminated.

Since mineral oil hydrocarbons are difficult to biodegrade, it is very important to control the contamination of environmental samples with MOHs. The analysis of mineral oil hydrocarbons in drinking water, surface water, and waste water is defined by the European standard EN ISO 9377-2, colloquially called H53.

A water sample is extracted and then purified with Florisil to remove polar substances. The purified extract is analyzed by gas chromatography with flame ionization detection (GC-FID). It is not required to assign individual substances due to the complexity of the hydrocarbon mixtures. Quantification is therefore performed by integrating the total peak area between the marker substances n-decane (C10) and n-tetracontane (C40). Thus, the examined boiling point range is between 175 and 525 ºC.

For determination of mineral oil concentration, a mineral oil mixture (diesel lubricating oil mixture, mineral oil type A and type B) is used as an external standard.

Soil and sludge samples can be determined analogous to H53, as defined by the European standard ISO 16703:2011.

Analysis using the on-column injector

Since determination of mineral oil hydrocarbons covers a wide boiling range, analysis is carried out conventionally using an on-column injector (OCI) to ensure non-discriminatory sample introduction. ISO 9377-2 specifies an area ratio of the alkanes n-tetracontane (C40) to n-eicosane (C20) of at least 0.8. In case of a fully non-discriminatory injector, the result is expected to be 1.0.

Using an OCI-injector, the injection is performed directly into the column. This requires either an analytical column with 0.53 mm ID or the combination of a smaller diameter column with a retention gap (0.53 mm ID). The latter setup makes shorter analysis times possible. Therefore, a SH-Mxt-1 column (15 m, 0.25 mm ID, 0.1 µm film thickness) was combined with a deactivated retention gap (0.5 m, 0.53 mm ID, Restek, #10081).

Repeated measurements of an alkane standard using Nexis GC-2030 achieved an area ratio C40/C20 > 0.98 (Fig. 1). Retention time of C40 was 7.4 min, i.e. analysis up to C40 finishes in less than 8 min.

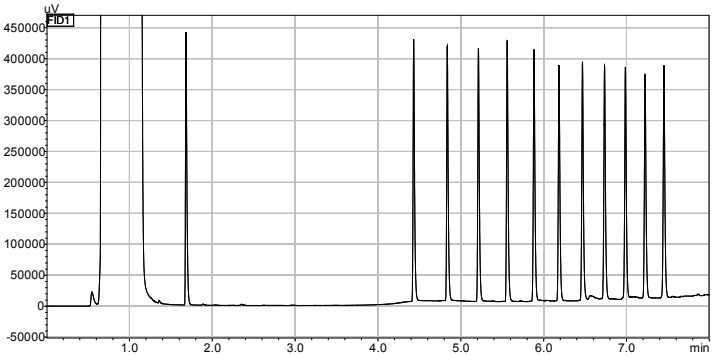

Figure 1: Chromatogram of an alkane standard (C10, C20 to C40) using an on-column injector, area ratio C40/C20 > 0.98

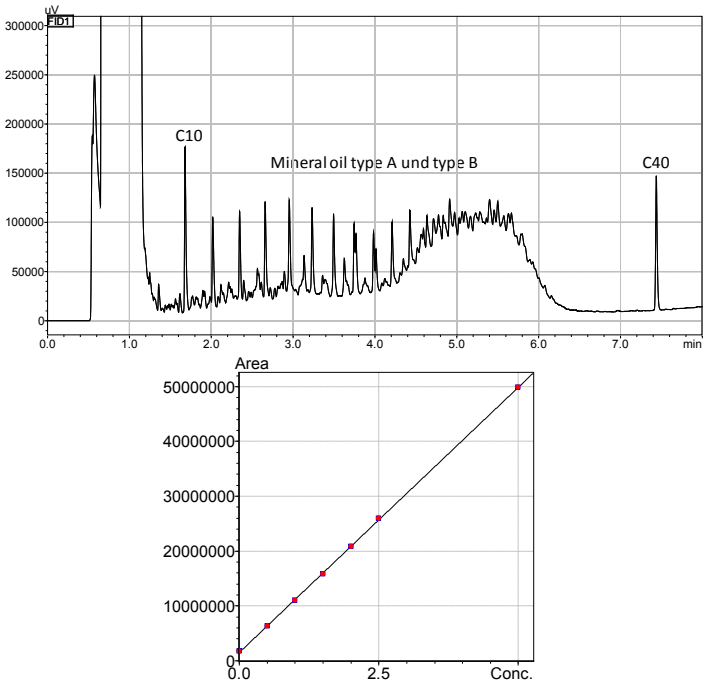

Figure 2: Chromatogram of a mineral oil standard and calibration curve (0 to 5 mg/mL)

To create a calibration series, a mineral oil standard type A and type B as well as an extraction solution already mixed with C10 and C40 were used, both commercially available (Sigma Aldrich, #18602, #49574, Fig. 2). A 7-point calibration in the range of 0 to 5 mg/mL showing a regression coefficient bigger than 0.9999 was obtained (Fig. 2).

Real samples (example in Fig. 3) were measured and showed different mineral oil impurities within the chosen calibration range.

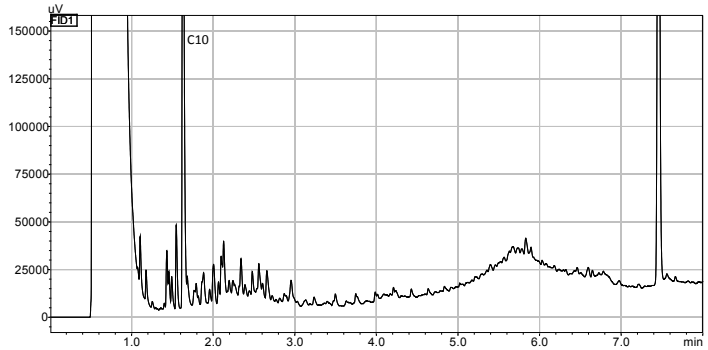

Figure 3: Chromatogram of a real sample

▪ Optional usage of hydrogen as carrier gas

The use of hydrogen as carrier gas gains importance as an alternative due to helium shortage. Moreover, it allows higher linear velocities at still optimum chromatographic resolution. Thus, analysis times can be significantly decreased. The combination of the SH-Mxt-1 column with hydrogen as carrier gas enabled a chromatogram runtime of less than 7 min.

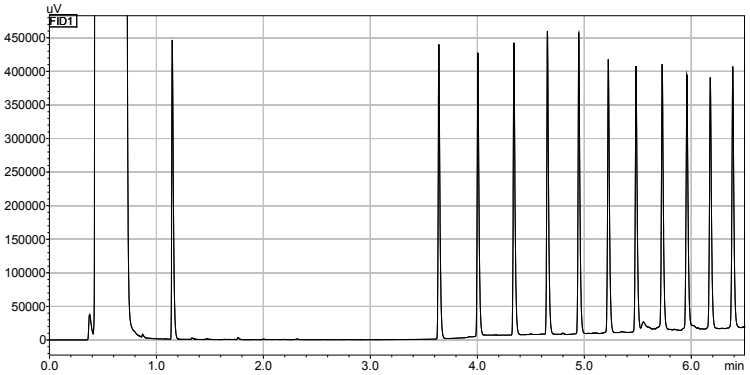

Figure 4: Chromatogram of an alkane standard (C10, C20 to C40), area ratio C40/C20 > 0.99

▪ Optional usage of a simple-on-column liner

An alternative to the retention gap solution is the simple on-column liner (#980-00371) which allows the user to directly connect the analytical column (in this case a Restek Rxi-1HT, 15 m, 0.25 mm, 0.1 µm) to the OCI-injector. Both solutions result in similar analysis times as in both setups C40 elutes at 7.4 min using helium as carrier gas and 6.4 min in case of hydrogen.

▪ Conclusion

GC-2030 with OCI-2030 injector enables efficient H53 measurements as short narrow-bore columns can be combined with a retention gap or a simple on-column liner. With the help of hydrogen as carrier gas chromatogram runtimes can be further reduced, while maintaining the reliability of the results.

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