SHIMADZU
Excellence in Science

Application News

Gas Chromatography

No. SCA_180_021

Fast and efficient analysis of mineral oil in environmental samples according to H53

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 split/ splitless 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. Disadvantages of on-column injection, however, are the high matrix load of the column and the use of a retention gap. A more column- and maintenance-friendly alternative is to use a split/splitless injector (SPL) provided it meets the above requirement.

Repeated measurements of an alkane standard using Nexis GC-2030 achieved an area ratio C40/C20 > 0.96 proving the SPL injector of GC-2030 to be sufficiently discrimination free (Fig. 1). For this, a SH-Mxt-1 column (15 m, 0.25 mm ID, 0.1 µm film thickness) and an Uniliner (#980-01051) were used. The method was optimized for both baseline separation of alkanes and chromatogram runtime. Retention time of C40 was 7.8 min, i.e. analysis up to C40 finishes in less than 9 min.

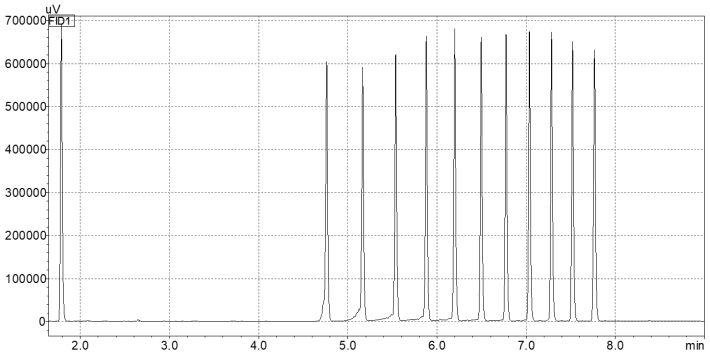

Figure 1: Chromatogram of an alkane standard (C10, C20 to C40) using a split/splitless injector, area ratio C40/C20 > 0.98

- **Faster analysis with hydrogen as carrier gas**

The use of hydrogen as carrier gas makes higher linear velocities at still optimum chromatographic resolution possible. 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 6 min. This leads to injection cycles of 10 min including cooling and equilibration time. Sample introduction was still free of discrimination with a ratio of C40/C20 > 0.90.

SPL temperature	320 °C
Injection volume	1 µL, splitless
Linear velocity	80 cm/s
Column oven program	50 °C, 0.7 min, 95 °C/min, 115 °C, 65 °C/min, 200 °C, 55 °C/min, 370 °C, 0.22 min
FID temperature	370 °C

Table 1: Method parameters fast GC on SH-Mxt-1 column

Based on the above method (Table 1), real samples were measured (Fig. 2). 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. 3).

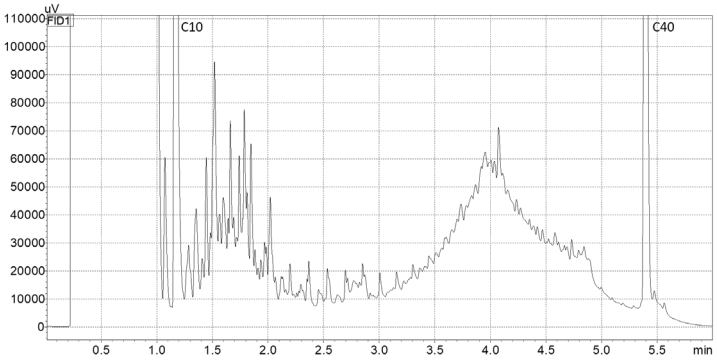

Figure 2: Chromatogram of a real sample

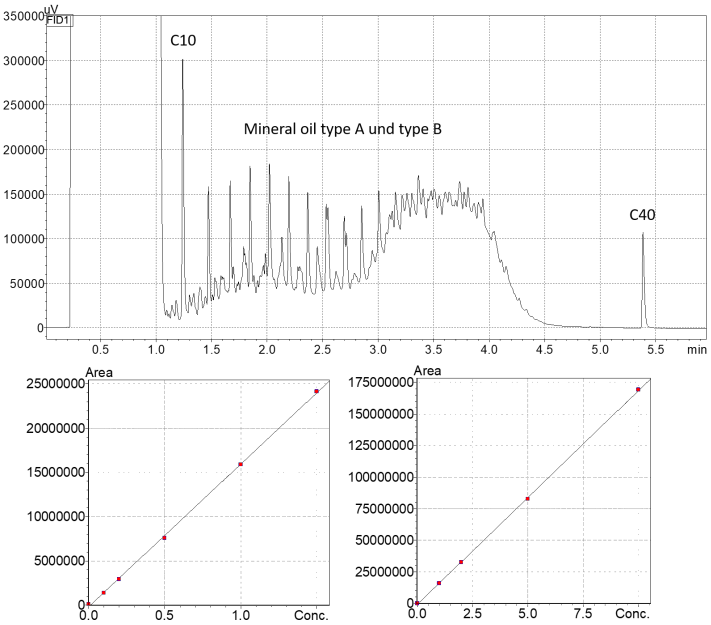

Figure 3: Chromatogram of a mineral oil standard and calibration curves (0 to 1.5 mg/mL, 0 to 10 mg/mL)

Since the expected concentration of the real samples was not known, two calibrations were performed: a 6-point calibration in a range of 0 to 1.5 mg/mL and a 5-point calibration in a larger range of 0 to 10 mg/mL. For both calibrations regression coefficients greater than 0.9998 were obtained (Fig. 3).

The tested real samples showed different mineral oil impurities, most of them being within the smaller calibration range.

- **Conclusion**

GC-2030 with SPL-2030 injector simplifies and accelerates H53 measurements as it meets the requirements of the ISO 9377-2 standard with a ratio greater than 0.9. With the help of hydrogen as carrier gas chromatogram runtimes can be significantly reduced, down to 6 minutes, while maintaining the same reliability of the results.

Shimadzu Europa GmbH

www.shimadzu.eu

Related Products Some products may be updated to newer models.

› Nexis™ GC-2030
Gas Chromatograph

Related Solutions

› Environment

› Price Inquiry

› Product Inquiry

› Technical Service / Support Inquiry

› Other Inquiry