

Automating the Analysis of Mineral Oils in Water as according to ISO/DIS 9377-4 Using the Focus Sample Processing Robot.

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Introduction

Current methods for the analysis of mineral oils in water employ a Freon extraction combined with infrared spectrophotometry. Freons and other suitable solvents (such as Tetrachloromethane) are damaging to the environment and covered by the terms of the Montreal Protocol. As a consequence, there is an urgent need for an alternative method of performing this analysis.

ISO/DIS 9377-4 describes a Gas Chromatographic method for the analysis of Total Petroleum Hydrocarbons (TPHs) in water by hexane extraction followed by Florisil clean-up of the extract, with a 1 µl injection into the GC. This note describes an adaptation of the method to permit the extraction, clean up and large volume injection of the sample to be performed automatically using the Focus Sample Processing Robot combined with the Optic 2-200 programmable injector.

Good quality results can be obtained using this approach, with the use of less environmentally damaging materials and at a much lower cost per analysis than is possible with manual sample preparation.

ISO/DIS 9377-4

Scope:

The determination of total hydrocarbons in water, between n-C₁₀ and n-C₄₀

Principle:

1. Extract water sample with a non polar solvent (petroleum ether, n-hexane or cyclohexane).
2. Dry the extract with sodium sulphate and adsorb polar compounds using Florisil
3. Separation of the extract by Gas Chromatography with summation of all of the peaks between n-C₁₀ and n-C₄₀

Instrumentation

- n ATAS Optic 2-200 Programmable Injector
- n Focus Sample Processing Robot
- n Finnigan GCQ

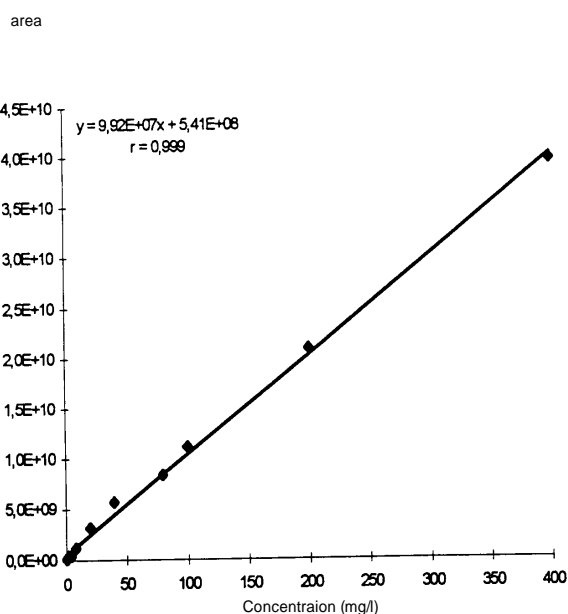
Comparison of Methods

| ISO/DIS 9377-4 | Focus Method |
|--|---|
| 900 ml of water sample is buffered to pH2, 80 g of MgSO ₄ is added plus 50 ml of the extraction solvent. The sample is then magnetically stirred. | The water sample is buffered to pH2 and 10 ml placed in a 20 ml auto sampler vial together with 0.9 g of MgSO ₄ . 1 ml of the extraction solvent is added by the auto sampler and the sample agitated. |
| The organic phase is separated using a micro-separator. | The organic phase is separated by the auto sampler. |
| The organic phase is dried and polar species removed using column chromatography with an anhydrous NaSO ₄ /Florosil column. | 500 µl of the organic layer is removed from the 20 ml vial and placed into a 1.5ml vial containing 0.03 g of NaSO ₄ . The sample is agitated by the auto sampler. |
| The organic phase is concentrated by evaporation down to 5 ml (a x10 concentration step). | 350 µl of the extract from this vial is transferred by the auto sampler to a second 1.5 ml vial containing 0.02 g of Florisil. The sample is agitated by the auto sampler. No concentration step is used. |
| 1 µl of the concentrated organic phase is injected into the GC. | 100 µl of the extract is injected into the GC. |

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Calibration Curve



2.5% Relative Standard Deviation for 6 injections of a 2 mg/l oil standard in water

Reproducibility of the extraction and injection combined:

2.7% Relative Standard Deviation for 6 extractions and injections of a hydrocarbon standard in water.

Relative Recovery:

102.5% for a 1.6mg/l oil standard in water.

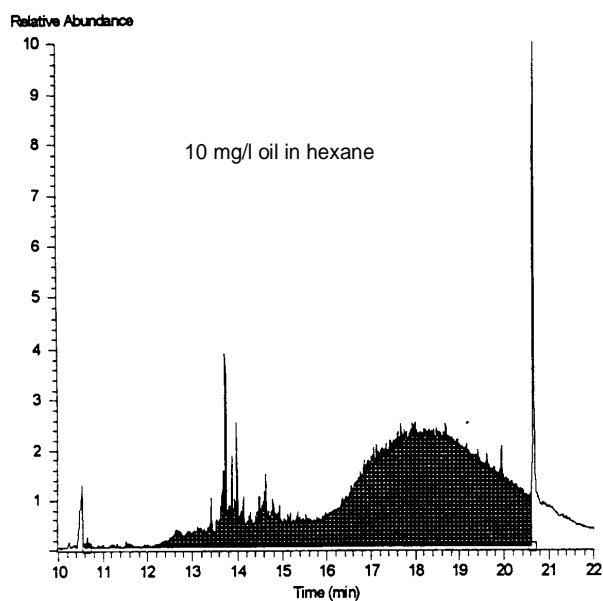
Test Samples:

Distilled water spiked with 1.6 mg/l oil, determined as 1.8 mg/l.
 Lake water from Kemnader See, NR Bochum (hydrocarbon content below the limit of detection) spiked with 1.6 mg/l oil, determined as 1.6 mg/l.

Cycle time:

60 minutes per sample.

Calibration Sample



Conclusions

ISO/DIS 9377-4 provides a valuable alternative to the older infrared method for the analysis of Total Petroleum Hydrocarbons in water. It delivers good quality results with the use of solvents that are less harmful to the environment. In addition, the GC separation provides for speciation of the sample and provides additional information as to the source of the oil in the sample.

Automation of this procedure using a sample processing

Reproducibility of the Injection:

robot in combination with large volume sampling has proved to be a practical proposition and is able to deliver results equivalent to those obtained by manual sample preparation, but at a lower cost in terms of the labor required. Human error is largely avoided and smaller quantities of reagents are required.

Performance of the Method

Linear range using GC-MS:

1-2 to 300-400 mg/l for the calibration standards (limited by the choice of detector).

0.1 to 0.2 to 30-40 mg/l for spiked lake water samples.

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