

Determination of Hydrocarbons in Water and Wastewater Samples

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INTRODUCTION

Growing concerns about the natural environment and new regulations introduced to address them, have produced an increased demand for quick and accurate analysis of air, water, and soil samples. In many instances, older and well proven methods are used to determine levels of pollution in the environment. Modern instrumentation and new technologies offer excellent opportunities for greater speed, consistency, and often a high degree of automation for many of these procedures. The EPA methods 418.1, 413.2 and the ASTM method D3921 originally developed on dispersive IR instrumentation, clearly benefit from the advantages of the FT-IR spectrometry. These methods cover determination of hydrocarbons in surface and saline waters, industrial and domestic wastes and are based on the extraction of hydrocarbons with 1,1,2-trichloro-1,2,2-trifluoroethane.

EQUIPMENT AND SUPPLIES

- FT-IR Spectrometer
- 10, 50, and 100 mm IR quartz cells
- 2000 ml separatory funnel with teflon stopcock
- Glass funnel
- Filter paper, Whatman No. 40, 11 cm
- Magnetic stirrer with stirring bars
- One 50 ml, one 200 ml and six 100 ml volumetric flasks
- Sample collection bottles - 1000 ml

REAGENTS

- 1,1,2-trichloro-1,2,2-trifluoroethane, b.p. 48 deg. Celsius
- n-hexadecane
- Isooctane
- Chlorobenzene
- 1:1 hydrochloric acid
- Sodium sulfate anhydrous crystal
- Silica gel, 60-200 mesh, Davidson grade 950, 1-2 % water content

PROCEDURE

1. Standards

The standard reference oil solution is typically prepared by mixing 15.0 ml of n-hexadecane, 15 ml of isooctane and 10 ml of chlorobenzene in a 50 ml volumetric flask. A 1.0 ml aliquot of the reference oil is pipetted into a 200 ml volumetric flask, weighed and diluted to volume with 1,1,2-trichloro-1,2,2-trifluoroethane. Up to five standard solutions are prepared by subsequent dilution of this standard (the working ranges are listed below).

Pathlength	10 mm	50 mm	100 mm
Range	2-40 mg	0.5-8 mg	0.1-4 mg

2. Sample preparation

The sample is acidified to pH 2 or lower with 1:1 hydrochloric acid and poured into a separatory funnel. The sample bottle is rinsed with 30 ml of 1,1,2-trichloro-1,2,2-trifluoroethane and the solvent is also added to the funnel. The content is shaken vigorously for two minutes. After the layers separate, the solvent is filtered into a 100 ml volumetric flask (draining the solvent through 1 gram of sodium sulfate placed in a paper cone dissipates emulsions, if formed during the process). The extraction is repeated two more times with fresh portions of 1,1,2-trichloro-1,2,2-trifluoroethane. The glassware and the filter paper used in the process are rinsed with 5-10 ml of the solvent which is also added to the volumetric flask. The flask is filled to volume with 1,1,2-trichloro-1,2,2-trifluoroethane. (The extract is diluted if it contains more than 100 mg of non-hydrocarbon organic material). 5 to 10 ml of the solution is removed, and 3 g of silica gel* is added to the flask. The content is stoppered and stirred on a magnetic stirrer for 5 minutes. After the silica gel settles down, the extract is analyzed.

*This step is used only in determination of petroleum based hydrocarbons.

3. Instrument calibration

Although the procedure described below was designed on the Nicolet's Model 205 system, it can be used on any other type of the FT-IR spectrometer with slight modifications.

a. Collection of standard spectra

Before the actual determination of hydrocarbons can be carried-out, background and standard spectra must be collected and stored (typically, the instrument is set to run 32 scans at 4 cm^{-1} resolution and automatic gain). In the first step, a cell containing 1,1,2-trichloro-1,2,2-trifluoroethane is placed in the sample compartment and background collection is performed (the background is automatically stored in the instrument's memory). The solvent is then replaced with the first standard and scanned. The resulting spectrum is labeled and saved in a spectral library designated for the development of quantitative methods. The entire process is repeated until spectra of all the standards are collected and saved under their unique names. Standard preparation and collection of standard spectra are the most critical steps in a development of the method. Any errors committed in this process will effect the accuracy of final results.

b. Generation of the quantitative method

The quantitative calculations are based on the set of standard spectra collected in the previous section. The method is developed by following a series of instructions displayed on the screen. Parameters needed in method development are listed below:

Type of analysis: peak height

Component name: Total Hydrocarbons

Units: mg/l

Conversion factor: D/V (dilution factor/sample volume)

Leading baseline: 3200

Peak location: 2930

Trailing Baseline: 2700

Calibration standards: list of standard filenames and concentrations

The calibration is performed automatically after all the parameters are entered.

Collection of standard spectra and generation of the quantitative program do not have to be repeated until a new variable is introduced to the process (e.g. new, different pathlength cell). The calibration, however, should be frequently verified by running samples of known concentration.

4. Sample analysis

Upon completion of the above steps, a new background spectrum of 1,1,2-trichloro-1,2,2-trifluoroethane is collected (background collection should be performed on the regular basis—typically every 60 minutes). Afterwards, the sample is placed in the sample compartment and scanned. Sample concentration is determined through a quantitative method selected by the operator.

Simplified routine analysis

For a single push-button operation, all of the above steps can be assembled in one method (macro) which is automatically created by the instrument in the LEARN mode. Once the method is recorded, the entire process of sample analysis is simplified to inserting of the sample cell in the instrument and pressing the METHOD key.

5. Results

Calibration spectra of five standard solutions are shown in Figure 1. Typical spectrum of the water sample analyzed in the process described above is shown in Figure 2. Results of analysis and printout format are displayed in Table 1.

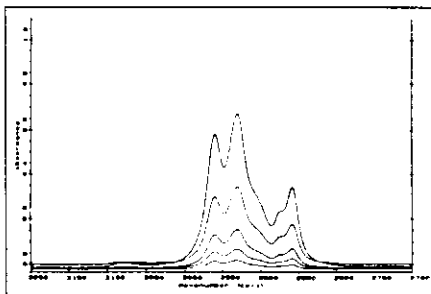


Figure 1

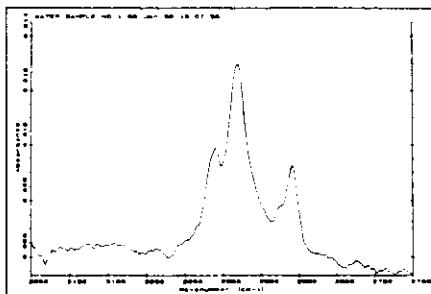


Figure 2

SAMPLE spectrum
Title: WATER SAMPLE NO. 1
Method: EPA 418.1

Date: 09/01/06 18:07:00

TOTAL HYDROCARBONS 2.530 mg/l

Table 1

REFERENCE

Reference: Petroleum Hydrocarbons, Total Recoverable. EPA Method 418.1, Storet No. 45501; Oil and Grease, Total Recoverable. EPA Method 413.2, Storet No. 00560. Standard Test Method for Oil and Grease and Petroleum Hydrocarbons in Water, ASTM Designation: D 3921 - 85

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INSTRUMENTS OF DISCOVERY

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