uop

Heavy Polynuclear Aromatics (HPNA) in Petroleum Fractions by Fluorescence Spectroscopy

UOP Method 860-07

Scope

This method is for estimating total aromatic hydrocarbons having 11 or more (11+) aromatic rings (heavy polynuclear aromatics, or HPNA) in petroleum fractions using fluorescence spectrophotometry. It is often used in support of commercial HPNA removal (HPNA RM) units. The method has been applied to petroleum products; e.g., hydrocracking fractionator bottoms (recycle oil). This method is not applicable to heavy feedstocks; e.g., vacuum gas oils, because of suspected interference from aromatic nitrogen compounds (see *Note 1*). This method may also be applicable to extracts from catalysts and plant deposits (see *Note 2*). The estimated value, in µg/mL, is reported for total HPNA and for distributed HPNA at specific wavelengths that are attributable to HPNA. The lower limit of detection for total HPNA is approximately 2.5 µg/mL. The upper limit is 1000 to 2000 µg/mL depending on the solubility of the HPNA and possible interferences (see *Note 1*).

Reference

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Outline of Method

The sample is diluted in chlorobenzene. The synchronous fluorescence spectrum of the sample is obtained and quantitatively compared to the spectrum of an appropriate reference standard of Rhodamine B. A correlation has been established between the response of Rhodamine B and the response of known concentrations of HPNA. The reference standard can be either a primary standard solution of Rhodamine B dissolved in tetraethylene glycol and diluted in 1-pentanol, or a Fluorescence Intensity Sample (FIS). An FIS is a commercially available polymethylmethacrylate (PMMA) block containing Rhodamine B, sized to fit into the spectrofluorometer in place of the sample cell. Analysis of the spectra is achieved by using non-linear curve fitting to compare the emission intensity of the sample spectrum to that of the reference solution at five wavelengths attributed to HPNA (see *Note 3*).

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used unless otherwise indicated.

Balance, readability 0.1-mg

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

Previous editions 1985, 1987, 1989, 1993, 1998, 2005

Beakers, borosilicate glass, 50-, 150- and 250-mL, Fisher Scientific, Cat. Nos. 02-539G, J and K, respectively

Bottletop dispenser, 5- to 25-mL, 2 required (3 are required if serial dilutions of samples are required, see *Note 4*), Fisher Scientific, Cat. No. 13-688-134

Constant temperature bath (circulator), optional (see *Note 5*), 0.01°C temperature control, Fisher Scientific, Cat. No. 13-873-301; with Bead Bath Accessory, Fisher Scientific, Cat. No. 11-715-45BB

Dry bath incubator, Fisher Scientific, Cat. No. 11-715-145D

Flask, volumetric, Class A, 1000-mL, Fisher Scientific, Cat. No. 10-210-5G

Fluorescence cell, 10-mm path length, polished quartz all sides, Wilmad/Lab-Glass, Cat. No. WG-3-Q-10

Funnel, long stem, Fisher Scientific, Cat. No. 10-326A

Micro spatula, Fisher Scientific, Cat. No. 21-401-15

Mixing cylinder, 10-mL, Fisher Scientific, Cat. No. 08-531A

Pipetter, digital microdispenser, adjustable dispensing volume, 50-µL capacity, Drummond, Fisher Scientific, Cat. No. 21-169-20C

Pipetter, digital microdispenser, adjustable dispensing volume, 1000-µL capacity, Drummond, Fisher Scientific, Cat. No. 21-169-10A (see *Note 4*)

Regulator, air, two-stage, high purity, Matheson Tri-Gas, Model 3122-590

Rhodamine B in PMMA (polymethylmethacrylate) Block, Fluorescence Intensity Sample (FIS), a minimum of 3 are required, Varian, Cat. No. 6610021900

Software, OriginPro™ with Peak Fitting Module, non-linear curve fitting software available from OriginLab, no substitution

Spectrofluorometer, having dual monochromators, equipped with individual and dual scan control, PerkinElmer, Model LS-55

Ultrasonic bath, 3.2-L capacity, Fisher Scientific, Cat. No. 15-335-30

Weighing funnel, Fisher Scientific, Cat. No. 14-353B

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Air, compressed, oil-free

Bottles, amber wide-mouth, Teflon™-lined closure, 5 required, Fisher Scientific, Cat. No. 03-320-8D

Chlorobenzene, 99.9% minimum purity, Aldrich, Cat. No. 270644-1L

Gloves, N-DEX, Fisher Scientific, Cat. Nos. 11-395-19A to D, depending on size

Pasteur pipette bulbs, 2-mL, Fisher Scientific, Cat. No. 14-065B

Pasteur pipette, glass, Fisher Scientific, Cat. No. 13-678-20B

1-Pentanol, 99+% purity, Aldrich Chemical, Cat. No. 398268-1L

Pipetter, disposable glass bores, Fisher Scientific, Cat. No. 21-169D, for use with digital microdispenser, Cat. No. 21-169-20C

Pipetter, disposable plastic bores, Fisher Scientific, Cat. No. 21-169-10G, for use with digital microdispenser, Cat. No. 21-169-10A

Rhodamine B, 99+% purity, suitable for dye laser, Acros Organics, Cat. No. 41900-0010, Fisher Scientific

Tetraethylene glycol, 99% minimum purity, Aldrich Chemical, Cat. No. 11017-5

Vials and caps, 22-mL, glass, molded screw cap with polyvinyl liner, Fisher Scientific, Cat. No. 03-338H

Wiper, Kimwipes™, 110- x 220-mm, Fisher Scientific, Cat. No. 06-666A

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of fluorescence spectroscopy, and the equipment being used.

Preparation of Apparatus

The instrument settings shown in Table 1 have been found to be satisfactory for the spectrofluorometer listed in *Apparatus*. Other settings may be used if equivalent performance is obtained.

Table 1

Instrument Settings for Synchronous Fluorescence

Δλ	**6 nm**
Monochromator bandpass	**2.5 nm**
Photomultiplier voltage	**600 V**
Scan rate	**1 nm/sec**
Step	**1.0 nm**
Wavelength range	
Excitation	**294 to 594 nm**
Emission	**300 to 600 nm**

Preparation of Primary HPNA Calibration Standard (PCS)

The HPNAs are quantitated by comparing the HPNA synchronous fluorescence peak areas of the sample to the synchronous fluorescence peak area of a standard solution of Rhodamine B. The solution of Rhodamine B in tetraethylene glycol is considered to be the Primary HPNA Calibration Standard, and is not intended to be analyzed each time the analysis is performed.

1. Weigh 0.16 ± 0.02 g, to the nearest 0.1 mg, of Rhodamine B into the weighing funnel.
   - Rhodamine B is a very strong dye, do not let it contact any stainable materials. Use appropriate personal protective equipment.
2. Using the long stemmed funnel, transfer the Rhodamine B to the dry 1000-mL volumetric flask directly from the weighing funnel.
   - Do not let any Rhodamine B contact the neck of the volumetric flask.

3. Wash the residual Rhodamine B that may stick to the weighing funnel through the long stemmed funnel into the volumetric flask by dropwise addition of tetraethylene glycol (TTEG).
4. Using the long stemmed funnel, finish filling the volumetric flask with approximately 950 mL of TTEG.
   - Fill the volumetric flask to just below the base of the neck. When the solution is heated by sonication and expands, the top of the solution should always remain below the graduation line. For best quantitation, do not allow the TTEG to wet the neck of the volumetric flask near or above the graduation line. Do not shake the volumetric flask.
5. Place the volumetric flask into the ultrasonic bath and sonicate the solution for 15 to 30 minutes with the ultrasonic bath at ambient temperature. If the Rhodamine B is not fully dissolved after 30 minutes, remove the volumetric flask from the ultrasonic bath and let it cool for 15 to 30 minutes. After cooling, re-insert the volumetric flask into the ultrasonic bath for another 15 to 30 minute period. Repeat the ultrasonic treatment/cooling until particles of Rhodamine B are no longer visible.
   - The ultrasound treatment will typically warm the solution slightly; this aids the dissolution of the Rhodamine B and is acceptable.
7. Allow the TTEG solution in the volumetric flask to cool to ambient temperature while on the bench top.
   - This may take 2 to 4 hours depending on the laboratory conditions, or it may be left overnight to eliminate any concerns about whether is has reached equilibrium.
8. Use the long stemmed funnel to fill the volumetric flask to just below the graduation line with TTEG. Do not allow the TTEG to wet the neck of the volumetric flask above the graduation line. Use the Pasteur pipette to fill the flask to the graduation line.
9. Mix the TTEG solution of Rhodamine B by inverting the flask several times.
10. Transfer the standard solution of Rhodamine B in TTEG into five amber, wide-mouthed bottles. Cap the bottles tightly.
11. Calculate the concentration of Rhodamine B in the PCS using Equation 1:

Concentration of Rhodamine B (called "T" in subsequent equations), moles/L

$$= \frac{G}{(479.02)(1)} \qquad (1)$$

where:

G = number of grams of Rhodamine B weighed into the weighing funnel
1 = number of liters used to prepare primary standard solution, L
479.02 = molecular weight of Rhodamine B

12. Label the bottles with the concentration of Rhodamine B and all appropriate safety information, and store in a safe place. Under typical storage conditions, the PCS is stable for more then one year. After one year, prepare a new PCS.

Standardization of the Fluorescence Intensity Sample (FIS)

From the known concentration of Rhodamine B in the PCS, the equivalent concentration of the Rhodamine B in the PMMA (polymethylmethacrylate) block FIS is calculated. The FIS is analyzed and used to calculate the HPNA concentrations in the samples. It is also used to confirm correct instrument operation.

1. Obtain a background spectrum as described in *Sample Analysis*, Steps 4 through 6.