U. S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1596

Dinitropyrene Isomers and 1-Nitropyrene in Methylene Chloride

This Standard Reference Material (SRM) consists of five vials, each containing approximately 1.3 mL of a methylene chloride solution of four nitrated polycyclic aromatic hydrocarbons (N-PAH): 1-nitropyrene, 1,3-dinitropyrene, 1,6-dinitropyrene, and 1,8-dinitropyrene. SRM 1596 is intended primarily for use in calibrating chromatographic instrumentation used for the determination of N-PAH.

Certified Concentrations of Nitro-PAH:
Certified concentrations of the four N-PAH in SRM 1596 are given in Table 1. The concentration values are certified in μg/g units but are also reported in μg/mL for user convenience. The certified values in Table 1 are derived from the concordant results obtained from high-performance liquid chromatography (HPLC) and gas chromatography/mass spectrometry (GC/MS). The N-PAH used in the preparation and certification of this SRM were obtained from Midwest Research Institute, Kansas City, MO. Compound purities were determined at Midwest Research Institute. Each compound was at least 99 percent pure and, therefore, no correction was made for purity.

NOTICE AND WARNINGS TO USERS

Expiration of Certification: This certification is valid, within the limits certified, for one year from the date of shipment from NBS. In the event that the certification should become invalid before then, purchasers will be notified by NBS.

Storage: Sealed ampoules, as received, must be stored in the dark at temperatures between -25 and 0 °C.

Use: Prior to use, samples for analysis should be brought to room temperature and equilibrated for one hour. Certified values are not applicable for ampoules stored after opening, even if resealed. Aliquots should be withdrawn from the ampoules immediately after opening and processed without delay for the certified values in Table 1 to be valid within the stated uncertainty. However, if this is impossible or impractical, we recommend that after aliquots are removed from the ampoules, the solution should be transferred to amber containers and sealed with Teflon-lined septa.

CAUTION: The toxicity or carcinogenicity/mutagenicity of the N-PAH in this SRM has not been defined precisely; however, this material should be treated as a potential health hazard.

Preparation and analytical determinations for this standard were performed in the Organic Analytical Research Division, Center for Analytical Chemistry, by L. C. Sander and L. R. Hilpert.

Consultation on the statistical design of the experimental work was provided by R. C. Paule of the National Measurement Laboratory.

The coordination of the technical measurements leading to certification were performed under the direction of S. A. Wise and W. E. May.

July 17, 1987
Gaithersburg, MD 20899

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

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The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R. Alvarez.

Preparation and Analysis

The solution of four N-PAH in methylene chloride was prepared and ampouled in the NBS Toxic Chemicals Handling Facility. SRM 1596 was prepared from a mixture of three dinitropyrene isomers; 1-nitropyrene was added as an individual component. An electrobalance was used for the determination of the mass of dinitropyrene isomer mixture and 1-nitropyrene. Each of the solids was weighed into gold foil weighing boats, and transferred into a 4000-mL volumetric flask previously filled with argon and methylene chloride was added and the solution weighed. Aliquots (1.3 mL) of dinitropyrene solution were placed in 2-mL amber ampoules. The ampoules were filled with argon just prior to flame sealing.

A stratified random sampling scheme was used to obtain a representative cross section of the ampouled solution for analyses. A total of eighteen ampoules were analyzed by HPLC and GC/MS. Sample homogeneity was determined based on the HPLC measurements. No evidence of sample heterogeneity was observed.

HPLC Analysis

In total, ten ampoules were analyzed in duplicate by HPLC. Propylbenzene was used as an internal standard for the determinations. Aliquots (500 μL) of the N-PAH SRM solution were mixed with 500 μL of a methylene chloride solution containing propylbenzene. Aliquots (20 μL) of the internal standard fortified N-PAH SRM solution were chromatographed using a monomeric C_{18} (25 cm x 4.6 mm, 5 μm particle size) column with ultraviolet detection at 235 nm. The separation was accomplished using isocratic elution (75:25 methanol:water) at a flow rate of 20 μL/min, at ambient temperature. Analyte concentrations were determined from peak areas of the analyte and internal standard, based on response factors determined from analyses of a gravimetrically prepared solution of the analytes. A chromatogram demonstrating the separation of the compounds in this SRM is shown in Figure 1.

GC/MS Analysis

GC/MS measurements were made using selected ion monitoring detection (SIM) under methane negative ion chemical ionization (NICI) conditions. Deuterated dinitropyrenes were used as internal standards for quantitation. One (1) mL aliquots of the N-PAH SRM solution were mixed with 1.0 mL of a solution containing 1-nitropyrene-d_9, 1,3-dinitropyrene-d_8, 1,6-dinitropyrene-d_8, and 1,8-dinitropyrene-d_8. Aliquots (2.0 μL) of the internal standard fortified SRM solutions were injected onto a 30 m x 0.25 mm i.d. fused silica capillary column coated with a 0.25 μm film of a non-polar methyl silicone bonded liquid phase. The molecular ions for the analytes and deuterated internal standards were monitored with a dwell time of 200 ms for each ion. Figure 2 shows a representative GC/MS SIM analysis of the N-PAH SRM solution. Concentrations of the analytes were determined from the analyte peak areas, the internal standard peak areas, and response factors determined from analyses of gravimetrically prepared solutions of the analytes and internal standards.

Table 1
Certified Values for SRM 1596[a]

Compound	(μg/g)	(μg/mL)[b]
1-nitropyrene	4.38 ± 0.08[c]	5.81 ± 0.11
1,3-dinitropyrene	2.10 ± 0.03	2.79 ± 0.04
1,6-dinitropyrene	4.82 ± 0.17	6.39 ± 0.23
1,8-dinitropyrene	7.90 ± 0.15	10.48 ± 0.20

a The certified values and associated uncertainties were derived from the weighted combination of HPLC and GC/MS data as described by Paule and Mandel in "Consensus Values and Weighting Factors," Journal of Research of the National Bureau of Standards, Vol 87, No. 5, Sept-Oct (1982), pp 377-385.

b These values are provided for user convenience and were obtained by applying a density conversion to the certified concentrations in μg/g. The uncertainties apply only at 20 °C (density 1.326 g/mL). A concentration change of less than 1% will occur for a 5 °C temperature change.

c The listed uncertainties are ± two standard deviations of the certified values and include both within- and between- analytical method differences.

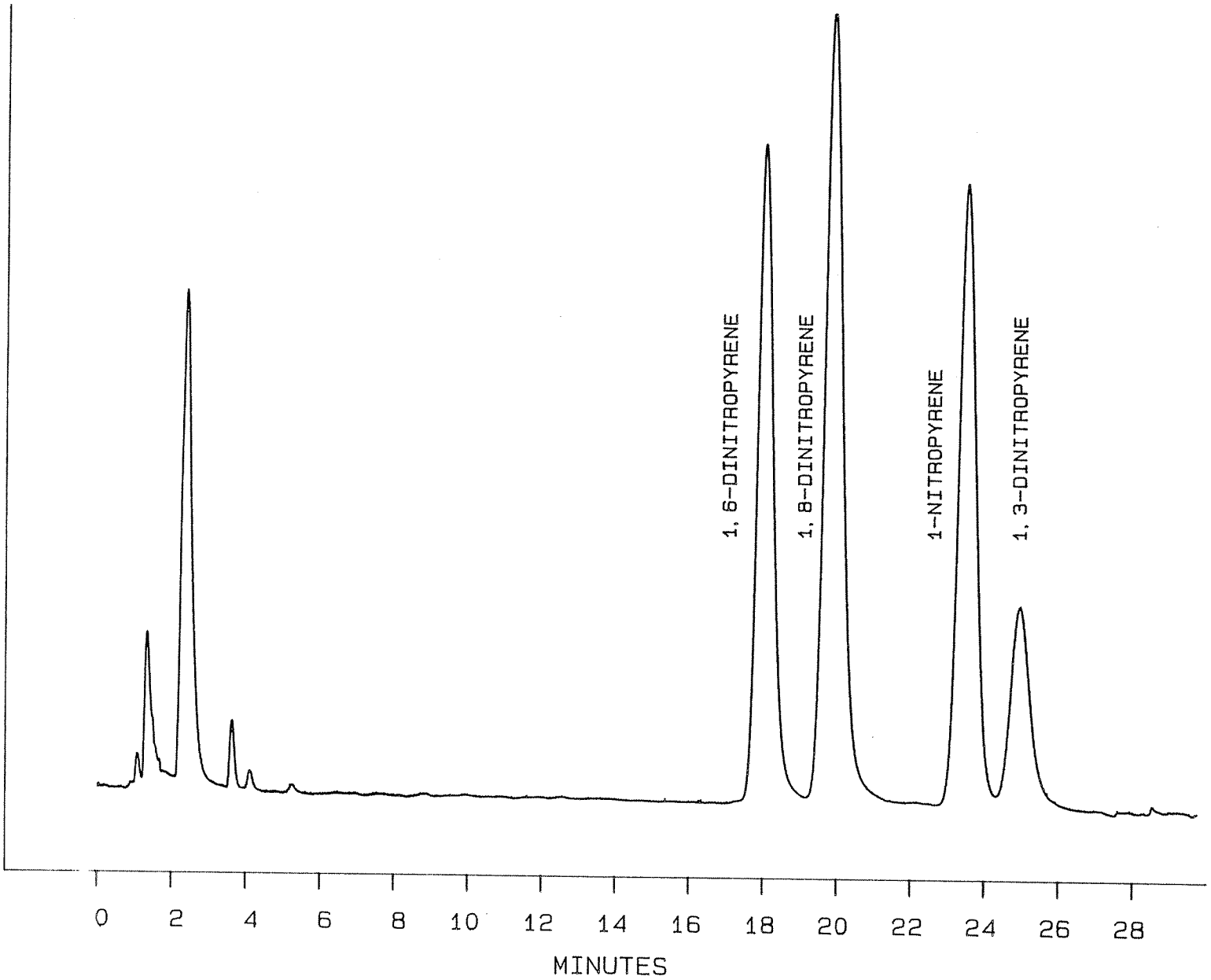

Figure 1. Chromatogram showing separation of N-PAH compounds in SRM 1596 by HPLC

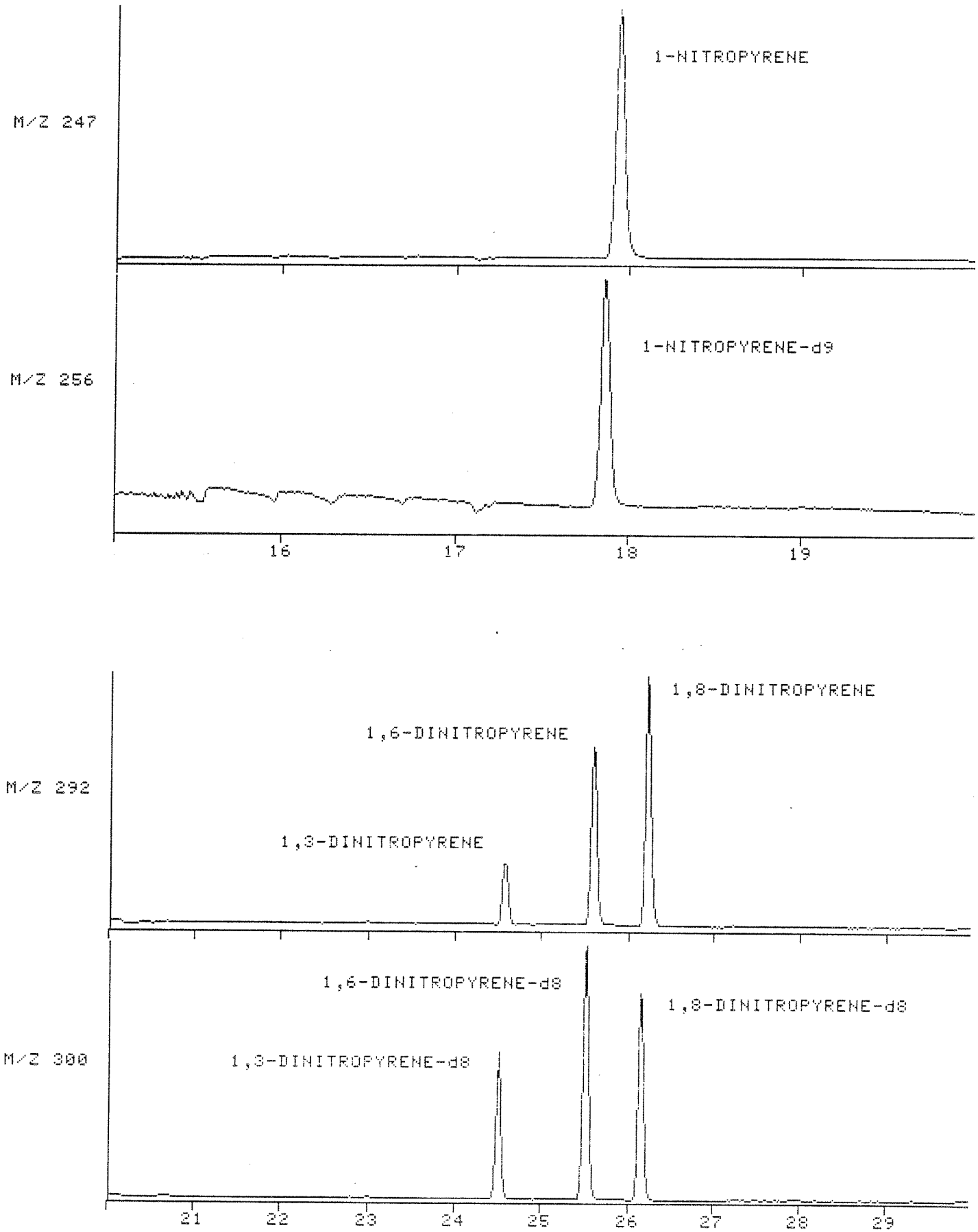

Figure 2. Representative GC/MS SIM analysis of N-PAH SRM solution