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Analysis of Diphenyl-Terphenyl Mixtures by Gas Chromatography

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A gas chromatographic method has been developed for the quantitative determination of diphenyl, ortho-, meta-, and para-terphenyl in various organic coolant mixtures. The technique involves relating the component peak heights to the peak height of an added internal standard after determination of the appropriate calibration factors. The method has been successfully used in the analysis of both unirradiated and irradiated coolant containing up to 40 per cent HBR (High Boiler Residue).

Instrument Description

The instrument used for the development of this method was an especially modified design based on the Loe Engineering[1] Chromat-O-Flex and is now available as the Model 1X from the company. Any gas chromatograph capable of stable operation at 300°C with comparable sensitivity and equipped with a back-flush attachment could be used for the analysis described. The Model 1X instrument is illustrated in Figure 1. This instrument uses a filament-type four element detector placed in the column oven. The column oven is a forced circulation air bath type with a door opening out of the front panel. Strip-type base load heaters (300 watt) controlled by a variable autotransformer are located on either side of the oven lining. A trim load coil-type heater (250 watt) is placed in the air bath just downstream from the circulating fan. The detector and column are enclosed by vertical baffles which serve the dual functions of directing air bath circulation and of shielding the detector and column from trim heater irradiation. The front baffle is removable and gives access to the space occupied by the detector and column. A resistance-bulb electronic temperature controller having proportional-band plus reset responses is used for oven temperature control. Figure 2 is a sectional view of the oven showing the location of major components and circulation paths.

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(1) 237 North Fairoaks, Pasadena, California

The detector circuitry is conventional. Bridge balance is established by the use of coarse- and fine-zero potentiometers. The applied voltage is varied by means of a rheostat in series with the detector bridge circuit and the batteries which are used for the detector supply. A step-type attenuator (ternary from 1 to 243) adjusts the signal input to a 1 millivolt recorder.

The carrier gas flow path splits just downstream from the pressure regulator. Each stream then passes through a sintered metal flow restrictor. One stream flows through the reference side of the detector to the atmosphere. The other stream flows in series through the hypodermic sample vaporization block, the column, the sample side of the detector, and to the atmosphere through a sample outlet-fitting located on the front panel. Sample injection is accomplished by the use of a hypodermic syringe (Beckman Liquid Sampler)(2) through an 1/8-inch thick silastic seal(3). When necessary, the column is back-flushed by connecting the reference stream outlet to the sample stream outlet and removing the silastic injection seal from the sample vaporization block. A flow diagram of the instrument is shown in Figure 3.

Column Preparation

Weigh the proper amounts of Apiezon L(4) and 30 - 60 mesh chromasorb(5)(weight ratio 1 : 4 for 20 per cent immobile phase). Dissolve Apiezon L in ethyl ether, add chromasorb, and evaporate the ether with mixing. (Vacuum evaporation using a Rinco evaporator(6) is convenient.) Sieve dry material to 30 - 60 mesh and load into a 2 meter stainless steel column (1/4-inch O.D.) using an air-operated vibrator to insure absence of voids. (2 meter column requires about 20 gm. of packing.) Plug ends of column with glass wool, bend, and mount column in chromatograph. Flush column with helium (ca 100 ml/min) for about thirty minutes and bring chromatograph to operating temperature. (If column is left at 300°C continually, tailing will start to develop in about two to three weeks which will necessitate a column change).

Operation Conditions

Column Temperature	300°C
Immobile Phase	20% Apiezon L on 30-60 Mesh Chromasorb
Helium Flow Rate	87 ml/min (30 psig)
Detector Filament Voltage	10 volts
Column Length	2 meters

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(2) Beckman Instruments, Fullerton, California

(3) Dow Corning No. 50 Silicone Rubber

(4) James G. Biddle Co., 1316 Arch St., Philadelphia, Pennsylvania

(5) Johns-Manville Co., Manville, New Jersey

(6) A. S. Aloe Co., St. Louis, Missouri

Determination of Calibration Factors

Accurately weigh about 75 mg diphenyl, 200 mg ortho-terphenyl, 250 mg triphenylmethane (as internal standard), 150 mg meta-terphenyl, and 50 mg para-terphenyl into a 10 ml volumetric flask, add tetrahydrofuran, swirl until solution is complete, and dilute to mark. Stopper flask with rubber serum cap, mix thoroughly, and chromatograph at least 3 - 0.02 ml aliquots of this solution. The compounds elute in the order given above. The first three peaks should be recorded at 3 mu full scale while the later two are recorded at 1 mu full scale. Draw the base line under each peak and measure the height of each peak from its base line to the nearest 0.01 inch. Calculate the calibration factor for each component using the following formula:

$$F_C = \frac{H_T \times W_C}{H_C \times W_T}$$

where: F_C = component calibration factor
W_C = weight of component (mg)
W_T = weight of triphenylmethane (mg)
H_C = component peak height
H_T = triphenylmethane peak height

Average the factors thus obtained for each component. The deviation from the average should be within ±2 per cent relative.

Analysis of Organic Coolant Mixtures

Accurately weigh about 300 mg of Santowax R or 500 mg of Santowax OM and 250 mg of triphenylmethane into a 10 ml volumetric flask, add tetrahydrofuran, swirl until solution is complete, and dilute to mark. Stopper with rubber serum cap, mix, and chromatograph a 0.02 ml aliquot. If components less volatile than p-terphenyl are present, it will be necessary to back-flush the column for ca thirty minutes after each run. Measure peak heights as described under "Determination of Calibration Factors" and calculate the amount of each component using the following forumula:

$$\%C = \frac{\frac{H_C}{H_T} \times F_C \times W_T \times 100}{W_S}$$

where: %C = weight per cent of component
H_C = component peak height
H_T = triphenylmethane peak height
F_C = component calibration factor
W_T = weight of triphenylmethane (mg)
W_S = weight of sample (mg)

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Accuracy and Precision

The accuracy of the method was checked by analysing four known synthetic mixtures, with and without added high boiler residue. The average relative error obtained from fifty-four determinations was ±1.7 per cent with a range of +4.6 to -6.4 per cent. To obtain this accuracy, it is necessary that component peaks in the analysis of a sample be recorded at the same attenuation as was used in the determination of the calibration factors. If the composition of the sample is such that any of the component peaks go off scale at the prescribed attenuations, the sample size should be reduced and the analysis repeated. Recalibration may be necessary after two or three days if there has been sufficient boil off of immobile phase to significantly change the retention time of the components, particularly meta- and para-terphenyl.

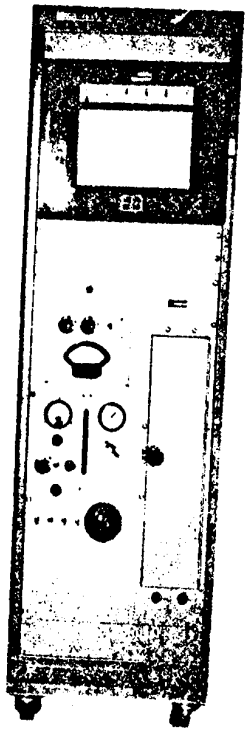

FIG. 1

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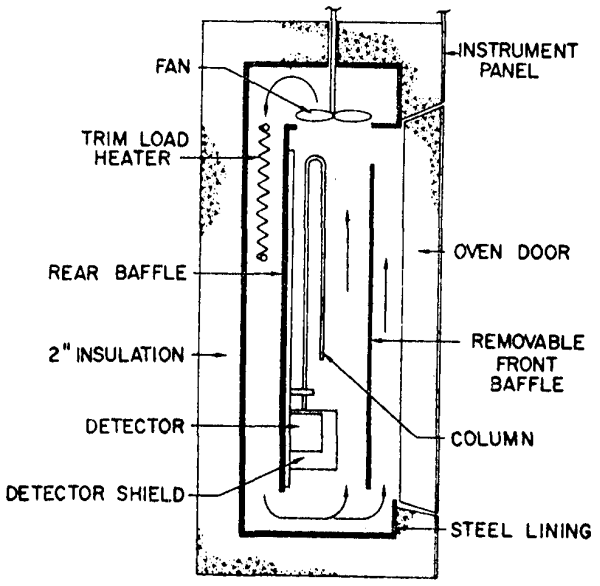

FIG. 2

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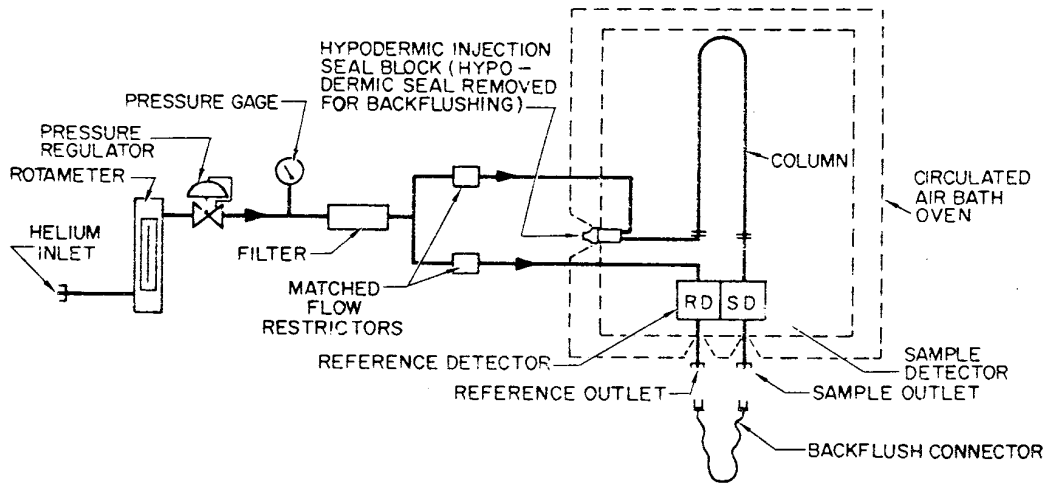

FIG. 3

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