TEST METHOD

Effective: 24 March, 1986 DOWM 100011
Supersedes: (New)

Refined Diphenyl Oxide

1. Scope

This method is applicable to the analysis of refined diphenyl oxide (DPO). Procedures for the DPO assay and for the determination of certain impurities for the following concentration ranges are given:

Component	Validation Range
DPO	>99.9%
Naphthalene (Naph)	5-67 ppm.
2-Methylnaphthalene(2-Me-Naph	8-64 ppm.
1-Methylnaphthalene(1-Me-Naph)	4-91 ppm
Biphenyl (BP)	4-55 ppm,
o-Phenylphenol (OPP)	5-70 ppm.
Dibenzofuran (DBF)	5-46 ppm
Dibenzo-p-dioxin (DD)	4-11 ppm

Other impurities are analyzed as group of "high boilers". Diphenyl oxide is calculated by difference.

2. Principle

The components are separated by means of capillary gas chromatography. Concentration of the known impurities are determined by comparing the area counts of each impurity to the area count obtained from a standard of known concentration. The concentration of high boilers is determined by comparing the sum of their area counts to the area count of 1-hexadecene present in a standard solution. The diphenyl oxide assay is calculated by difference.

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3. Safety

3.1 Each analyst should be acquainted with the potential hazards of the equipment, reagents, products, solvents, and procedures before beginning laboratory work. SOURCES OF INFORMATION INCLUDE: OPERATION MANUALS, MATERIAL SAFETY DATA SHEETS, LITERATURE AND OTHER RELATED DATA. Safety information for products should be requested from the supplier. Disposal of waste materials, reagents, reactants, and solvents must be in compliance with laws and regulations from all applicable governmental agencies.

3.2 Prolonged or repeated contact with diphenyl oxide may cause irritation of skin and/or respiratory system. In case of contact, wash with plenty of water and contact appropriate personnel.

3.3 Toluene is a flammable solvent. Work in a well-ventilated area away from any sources of ignition.

3.4 Dibenzo-p-dioxin is considered a toxic material. Handle the solid and solutions with care to avoid contact.

4. Interferences

No direct interferences have been observed in the use of this method. If results are suspect based on the analytical history of the product, the data should be confirmed by an alternate method.

5. Reagents

5.1 Diphenyl oxide (99.9%), and biphenyl (99.5%) available from The Sample Coordinator, 779 Building, The Dow Chemical Company, Midland, MI, 48667. Diphenyl oxide may be refined by further crystallization to increase purity.

5.2 Dibenzo-p-dioxin (Standard Grade), available from Chem Service, P.O. Box 3108, Westchester, PA 19381.

5.3 Naphthalene (99.9%), available from Matheson Coleman and Bell, Norwood, OH.

5.4 1-Methylnaphthalene (99%), 2-methylnaphthalene (>99%), dibenzofuran (>99%) and o-phenylphenol (>99%), available from Aldrich Chemical Company, Milwaukee, WI 53233.

5.5 1-Hexadecene (97%), available from Alltech Associates, Deerfield, IL 49442.

5.6 Toluene (99.9%), available from Burdick and Jackson Laboratories Inc., Muskegon, MI.

6. Apparatus

6.1 Gas Chromatograph: Hewlett-Packard Model 5890, or equivalent, equipped with a flame ionization detector. The 5890A is available from Hewlett-Packard, 39550 Orchard Hill Drive, Novi, MI 48050.

6.2 Autosampler: HP 7673 or equivalent, available from Hewlett-Packard, 39550 Orchard Hill Drive, Novi, MI, 48050.

6.3 Capillary Column: 50 m x 0.32 mm ID fused silica coated with SE-54 (5% Phenyl methyl silicone) liquid phase, 1 micron film thickness, available from Quadrex Corporation, New Haven, CT.

6.4 Syringes, 10 and 100 microliter: Hamilton 701N, and 710N, or equivalent, available from Fisher Scientific Company, Midland, MI 48640.

6.5 Computing Integrator: HP 3392, or equivalent available from Hewlett-Packard, 39550 Orchard Hill Drive, Novi, MI 48050.

6.6 Analytical Balance, capable of measuring 0.1 mg: Mettler AE163 or equivalent, available from Mettler Instrument Corp., Princeton-Hightstown Road, Hightstown, NJ 08520.

6.7 Go-Getter (General Electric Co.) or Oxiclear Gas Purifier (Lab Clear, Inc.), or equivalent, available from The Anspec Company, Inc., 122 Enterprise Drive, Ann Arbor, MI 48107.

7. Chromatographic Conditions

Instrument:	HP 5890A
Detector:	Flame ionization
Column:	50 M x 0.32 mm ID x 1 micron film thick SE-54.
Initial temperature:	180° hold for 3 min
Program rate:	3 /Ein
Final temperature:	225 hold 2 min.
Injection port temperature:	280^0C
Detector temperature	300^oC
Carrier gas:	Helium at 2 cc/min.
Air flow rate:	250 cc/min
Hydrogen flow rate:	25 cc/min
Make-up flow:	Helium at 22 cc/min
Split ratio:	75:1
Injection volume:	1 microliter
Range:	2
Attenuation:	2 0

An efficient oxygen scavenging system such as the “Go-Getter” or “Oxiclear Gas Purifier” should be used with the helium supply.

See Figure 1 for a typical chromatogram of a standard sample and computing integrator parameters. See Figure 2 for a typical chromatogram of a production sample.

8. Preparation of Standard Solution

8.1 Warm the diphenyl oxide (refined 4 times) and melt it completely (see Note 15.2) and inject 1 microliter using the conditions mentioned in section 7. There should be no interferences. If there are any, repurify the DPO and reanalyze.

8.2 Standard stock solutions Al-A8: using an analytical balance and weighing to nearest 0.1 mg, prepare the stock solutions given below in toluene (10.0 mL).

	Component	Approx.Grams	Approx. Conc.%
A-1	Naph	0.025	0.25
A-2	1-Me-naph	0.025	0.25
A-3	2-Me-naph	0.025	0.25
A-4	BP	0.025	0.25
A-5	OPP	0.025	0.25
A-6	DBF	0.025	0.25
A-7	DD	0.025	0.25
A-8	1-Hexadecene	0.025	0.25

8.3 Standard Stock solution B: Inject various amounts (see table below) of the above stock solutions into a single vial and balance the total weight to 10.0 g with DPO.

Solution No.	Aliquot, Microliters	Approx. Conc. in Final Stock Soln. ppm
Al	40	10
A2	40	10
A3	40	10
A4	20	5
A5	40	10

9. Calibration

9.1 Warm solution (B) to melt it completely (See Note 15.2) and then inject 1 microliter into the chromatograph under the conditions described in section 7.

9.2 Repeat step 9.1 at least twice, and determine the average area counts of all peaks.

9.3 Calculate response factor for naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, biphenyl, o-phenylphenol, dibenzo-p-dioxin and n-hexadecene as given below:

$$R_f = \frac{(\text{Area A})(\text{Conc. B})}{(\text{Area B})(\text{Conc. A})}$$

R_f = response factor for component A
Area A = Average area of component A
Area B = Average area of diphenyl oxide
Conc A = Concentration of component A in cwt
Conc B = Concentration of diphenyl oxide in cwt
Weight % = ppm divided by 10,000

High boilers are assigned the same response factor as 1-hexadecene.

10. Procedure

10.1 Warm the diphenyl oxide sample and melt it completely (see Note 15.2) inject 1 microliter according to conditions in section 7.

10.2 Repeat step 10.1 and determine the average area counts of all peaks.

11. Calculations

Concentration in PPM by weight is calculated according to the following equation:

$$\text{ppm} = \frac{(\text{AreafA})(10^6)}{(R_f)(\text{Area B})}$$

For high boilers:

$$\text{ppm} = \frac{(\Sigma\text{Area i})(10^6)}{(R_i)(\text{Area DPO})}$$

Σ Area i = sum of all peaks eluting after DPO, but excluding those mentioned in section 8.
R_i = Correction factor of 1-hexadecene.

Report all results to the nearest ppm.

DPO Assay is calculated as (100% - %T) where %T is sum of all impurities. (% T = ppm T X 10^{-4})

12. Accuracy

Analysis of a series of synthetic mixtures gave the recoveries shown below.

Compound	Range (ppm)	Average Recovery	s, %
Naph	5-67	100%	3.7
2-Me-naph	8-64	99	4.5
1-Me-naph	4-91	105	14.8
BP	4-55	103	4.8
OPP	5-69	100	4.9
DBF	5-46	110	4.1
DD	4-11	91	3.5

13. Precision

Precision data for the compounds determined by this procedure are given below for a sample of production grade refined DPO. The values obtained may be expected to vary from the average, by not more than the values listed (relative precision) at the 95% confidence limit.

Component	Conc., ppm	Std. Dev. ppm	% Relative Precision(2s)
Naph*	15	0.28	3.7
1-Me-naph	7	0.31	8.5
2-Me-naph*	14	0.56	8.0
BP	6	0.48	14.
OPP	22	0.86	7.8
DBF	4	0.74	38.
DD*	4	0.80	40.5
High boilers	120	0.52	8.5

*Since these components were not present in production refined DPO precision results were obtained on a synthetic sample.

14. Linearity

Analysis of synthetic solutions for the following impurities exhibited a linear response over the range tested:

Compound	Range (ppm)
Naph	5-67
2-Me-naph	8-64
1-Me-naph	4-91
BP	4-55
OPP	5-69
DBF	5-46
DD	4-11

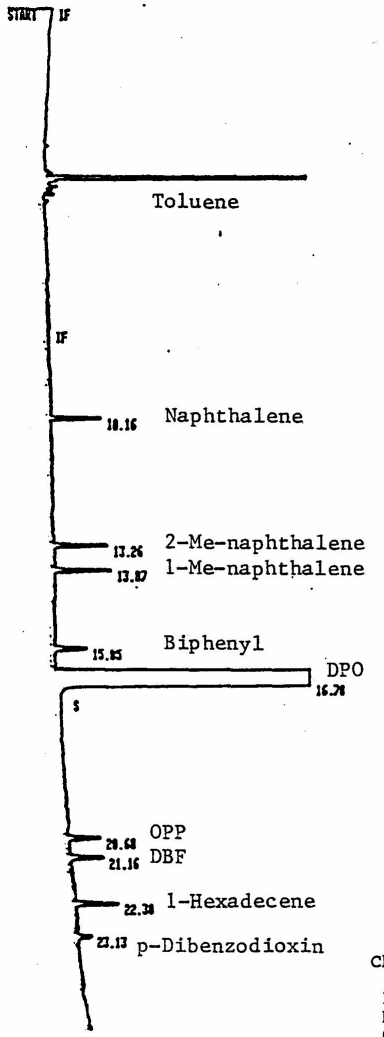
15. Notes

15.1 Standards should be stored in the refrigerator while not in use.

15.2 Diphenyl oxide samples must be melted completely in warm water or on a steam bath before injection. The syringe must be kept warm so that the diphenyl oxide does not solidify inside the syringe.

15.3 If injection volumes greater than one microliter or split ratios less than 75:1 are bred, the column and/or the detector can be overloaded and inaccurate results will be obtained.

Figure 1. Typical Chromatogram for Standard of Refined Diphenyl Oxide



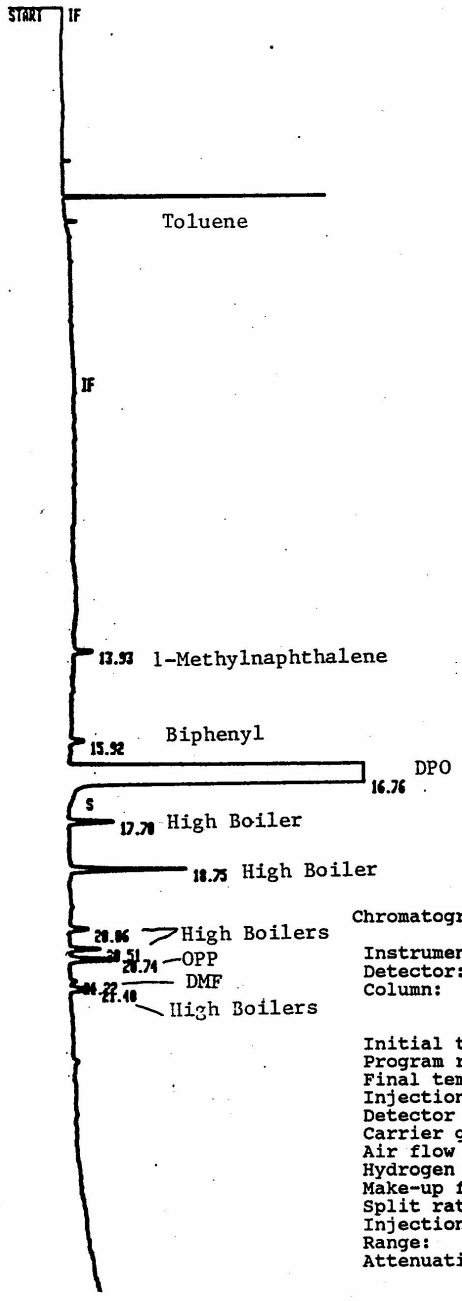
Integrator Conditions

```
RUN PRMTRS
ZERO   =  10
ATT 2↑ =  0
CHT SP =  1.0
PK WD  =  0.04
THRSH  =  0
AR REJ =  0

RPRT OPTNS
  2. RF UNC PKS=      0.0000E+00
  3. MUL FACTOR=
  4. PK HEIGHT MODE      NO
 .5. EXTEND RT           NO
  6. RPRT UNC PKS        NO

TIME TBL
   0.00 INTG 0 =  9
   0.00 INTG 0 =  8
   8.00 INTG 0 =  -9
  30.00 STOP

  7. SUPPRESS RPRT       NO
  8. TRANSMIT RPRT       NO
  9. HOW ROY DELAY       NO
 10. AUTOMATE RUNS      YES
 11. SAMPLER PRMTRS
 12. TRANSMIT PEAKS      NO
 13. TRANSMIT POINTS     NO
 14. SLICE WIDTH=     0.0000E+00
 15. ID:
 16. ISTD AMT=
     SAMPLE AMT=
 17. INSTR NETWORK CONFIG TBL
 18. NEXT WORKFILE:
     RUNS/SUBSEQ:
 19. TIME SCALE          NO
 20. SAMPLE TBL
     EMPTY

SIGNAL 1 = B
 INET RANGED DATA ON
 RANGE = 2
 ZERO  = 0.0
 ATTN  = 0

SIGNAL 2 = B
 RANGE = 2
 ZERO  = 0.0
 ATTN  = 0

DETECTOR A = TCD  (OFF)   POLARITY = +
DETECTOR B = FID  (ON)

PURGE A  = ON
PURGE B  = ON
```

Chromatographic Conditions

Instrument:	HP 5890A
Detector:	Flame ionization
Column:	50 M x 0.32 mm ID x 1 micron film thick SE-54.
Initial temperature:	150° hold for 3 min
Program rate:	3°/min
Final temperature:	225° hold 2 min.
Injection port temperature:	280°C
Detector temperature	300°C
Carrier gas:	Helium at 2 cc/min.
Air flow rate:	250 cc/min
Hydrogen flow rate:	25 cc/min
Make-up flow:	Helium at 22 cc/min
Split ratio:	75:1
Injection volume:	1 microliter
Range:	2
Attenuation:	2↑0

Figure 2. Typical Chromatogram for Sample of Refined Diphenyl Oxide



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Range:	2
Attenuation:	2 ↑ 0