

94-374



Mine Safety Appliances Company • P.O. Box 426 • Pittsburgh, PA 15230

Telephone: (412) 967-3000

November 30, 1994

Writers Direct Dial No.  
412 967-3194

Mr. Richard Metzler  
Chief, Certification and Quality Assurance Branch  
NIOSH Division of Safety Research  
944 Chestnut Ridge Road  
Morgantown, WV 26505-2888

Dear Mr. Metzler,

Concern was aired by MSA and others in both the informal public meeting and in written public comments (to the NPRM on Respiratory Protective Devices, 42 CFR Part 84) that testing with cold-nebulized DOP resulted in lower filter penetration values than did testing with thermally-generated DOP. This result is only noticed when testing electrostatic filter media. Consequently, electrostatic filter efficiency values can be overstated, or understated, depending on how the DOP test aerosol is generated. At the public meeting and in written comments, MSA and other respirator manufacturers urged NIOSH to investigate this apparent disparity in the test protocol.

It's been reported that NIOSH's preliminary investigation into this matter showed that DOP breakdown occurs when DOP is exposed to heat (as it would be in the thermal generator) and it was speculated that these compounds (i.e., impurities) were adversely affecting electrostatic filter media. Testing conducted by WVU for NIOSH showed that new DOP, having an initial purity of 99.95%, was shown to decrease in purity to 94.36% after exposure to heat and light (copy of that report attached).

MSA has done much work in this area and unlike the results from WVU, our testing showed that DOP experienced **insignificant decomposition** after prolonged conditioning at elevated temperatures. MSA conducted X-ray fluorescence, gas chromatography-mass spectrometry, fourier transform infrared analysis, UV-visible spectrometry and light scattering techniques to analyze the degradation of DOP after exposure to 336 hours (42 eight hour cycles) at 167 °C. MSA respectfully submits the attached report for your consideration.

MSA would very much appreciate the opportunity to discuss this report with you and your staff as we feel it relates directly to NIOSH's position regarding the final rule of 42 CFR Part 84. Please contact me at your earliest convenience to discuss this further and hopefully set up a meeting .

Sincerely,

William M. Lambert  
Product Line Manager,  
Air Purifying Respirators

94-374  
12/5/94



INTER-OFFICE CORRESPONDENCE

GM94-2,101

November 2, 1994

TO: Wm. M. Lambert

CC: R. A. Erth  
W. B. Miller, Jr.  
C. LaRosa  
J. F. Kuhn

FROM: Z. N. Frund, Jr. *Z. N. Frund, Jr.*

SUBJECT: Decomposition of Dioctyl Phthalate (DOP)

INTRODUCTION

Recently, concern has arisen that dioctyl phthalate (DOP) decomposes after prolonged use in the "hot smoke" DOP generator. MSA's Chemical R&D Group conducted a controlled study to quantify the changes in the purity, structure and (aerosol) particle size distribution of DOP after prolonged heating in a "hot smoke" DOP penetrometer. The details of this investigation and analysis of the results are presented in this report.

MATERIALS AND SAMPLE PREPARATION

Dioctyl phthalate (di[2-ethylhexyl] phthalate) is produced by the reaction of 2-ethyl hexanol and phthalic anhydride. See Equation 1. Although the reaction is usually catalyzed by tetrabutyl titanate; toluene sulfonic acid and dibutyl tin oxides have also been used. Dioctyl phthalate is commercially available in purities of at least 96%. Several important properties of DOP are presented in Table I.

Equation 1

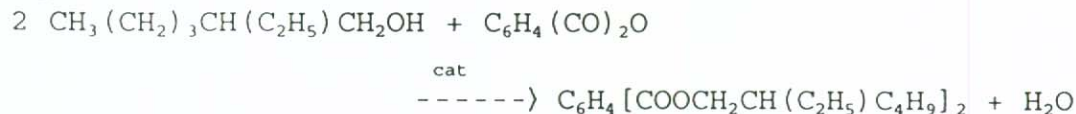




TABLE I  
PROPERTIES OF DIOCTYL PHTHALATE

Available purity	96+%
Molecular Weight	390 grams/mole
Flash Point	218°C
Boiling Point	231°C
Vapor Pressure	1.32mm Hg @ 200°C
Specific Gravity	0.986
Glass Transition Temperature	( -20°C
Refractive Index	1.4836

Dioctyl phthalate (DOP) has the unique properties of a high boiling and flash point, and a low glass transition temperature. These properties have made it a popular plasticizer for vinyl resins where thermal stability (for extrusion or molding of resins at temperatures exceeding 200°C) and low temperature flexibility (glass transition temperature ( -20°C) are necessary.

The DOP used in this investigation was produced by the Celanese Corporation. Celanese stated that this grade of DOP has a purity of approximately 99%. The material was received and stored, until use, in a sealed 5 gallon metal drum at 25°C. The fresh DOP sample was taken directly from this drum. To prepare the exposed sample, 500ml of DOP was taken from the drum and placed in an ATI Q127 DOP Penetrometer where it was heated for 42-eight hour cycles (336 hours in total) at 167+/-2°C.

#### EQUIPMENT

All testing was performed at the MSA J. T. Ryan Research and Engineering Laboratory. Several instrumental techniques were employed to determine the purity, structure, absorption of visible light and particle size distribution of the fresh and exposed DOP samples. These techniques included X-ray fluorescence, gas chromatography-mass spectrometry, Fourier Transform infrared analysis, UV-visible spectrometry and light scattering techniques. All of the instruments were calibrated before use, and testing was performed in duplicate or triplicate.

A Spectrace Model 6000 X-ray fluorescence spectrometer was employed to determine the presence of trace quantities of unreacted catalyst in the fresh DOP. A Hewlett Packard Model 5995 gas chromatograph-mass spectrometer equipped with a Supelco SP5, 15 meter, 530 micron column was used to quantify the purity, and identify organic impurities within the fresh and exposed DOP samples. One microliter samples of the fresh and exposed DOP were injected into the gas chromatograph operating at the following conditions:

Helium carrier gas flow rate = 20cc/minute

Injector temperature = 280°C

Oven temperature = 50°C to 320°C at a heating rate of 10°C/minute

Duration at 320°C = 23 minutes

The peak areas within the gas chromatograms were quantified (integrated) by Janel's Sigma Scan/Image Software-Version 1.2.

A Nicolet Magna 550 Fourier Transform Infrared Spectrophotometer equipped with an attenuated total reflectance accessory and zinc selenide crystal was employed to determine the differences between the chemical structures of the fresh and exposed DOP samples. A Spectronic Model 1000 UV-Visible spectrometer was used to determine the wavelengths of light absorbed by 10 ml samples of the fresh and exposed DOP.

Finally, an ATI Q127 DOP Penetrometer interfaced to an ATEC Model 303 dilution unit and a Particle Measuring Systems Model LAS-X laser/aerosol spectrometer was used to count the aerosol particles generated from the fresh and exposed DOP samples. A 500ml sample of each of the fresh and the exposed DOP were placed into the ATI reservoir and heated for at least 30 minutes until a sample steady state temperature of 167+/-2°C and a concentration of 100 micrograms of DOP per liter of smoke were attained. The DOP aerosol was diluted with the ATEC dilution unit (operating at a flow rate of 5cc/second) and subsequently introduced into the LAS-X spectrometer where the number of particles of specified sizes were counted. Three consecutive 20 second samplings were taken and averaged. Five minutes passed between each measurement.



## RESULTS

X-ray fluorescence revealed that little (below the detection limit of the spectrometer) or no inorganic-based catalyst impurities are present in the fresh DOP. The gas chromatograms for the fresh and exposed DOP samples are presented in Figures 1 and 2, respectively. The purity of each sample was determined by ratioing the integrated area of the "parent" DOP peak (between retention times of approximately 16.75 and 45 minutes) to the total area of all of the peaks. The calculated purity of the fresh and exposed DOP samples are comparable to one another (99.11% for fresh vs 98.49% for exposed). See Table II. In addition to the "parent" DOP (di[2-ethylhexyl] phthalate) peak, the fresh sample has peaks at retention times of 7.78 and 9.92 minutes, while the exposed sample has a peak at 5.31 minutes and a "shoulder" near 16 minutes.

TABLE II  
GAS CHROMATOGRAPHY PEAKS OF FRESH AND EXPOSED DOP

<u>SAMPLE</u>	<u>PEAK RETENTION TIME, MINUTES</u>	<u>COUNT OF INTEGRATED AREA</u>	<u>% OF TOTAL AREA</u>
Fresh DOP	16.75-45	356303	99.11
	7.78	614	0.17
	9.92	1259	0.35
	total of all other peaks	1325	0.37
Exposed DOP	16.75-45	416985	98.49
	5.31	133	0.03
	16.00	6262	1.48

Mass spectrometry revealed that the peaks in the fresh DOP at 9.92 and 7.78 minutes are associated with a 2-ethyl hexyl benzoic acid ester and 2-ethyl hexanol, respectively. The very small impurity peak in the exposed sample at 5.31 minutes is associated with phthalic anhydride. The "shoulder" near 16 minutes is associated with a long chain hydrocarbon.

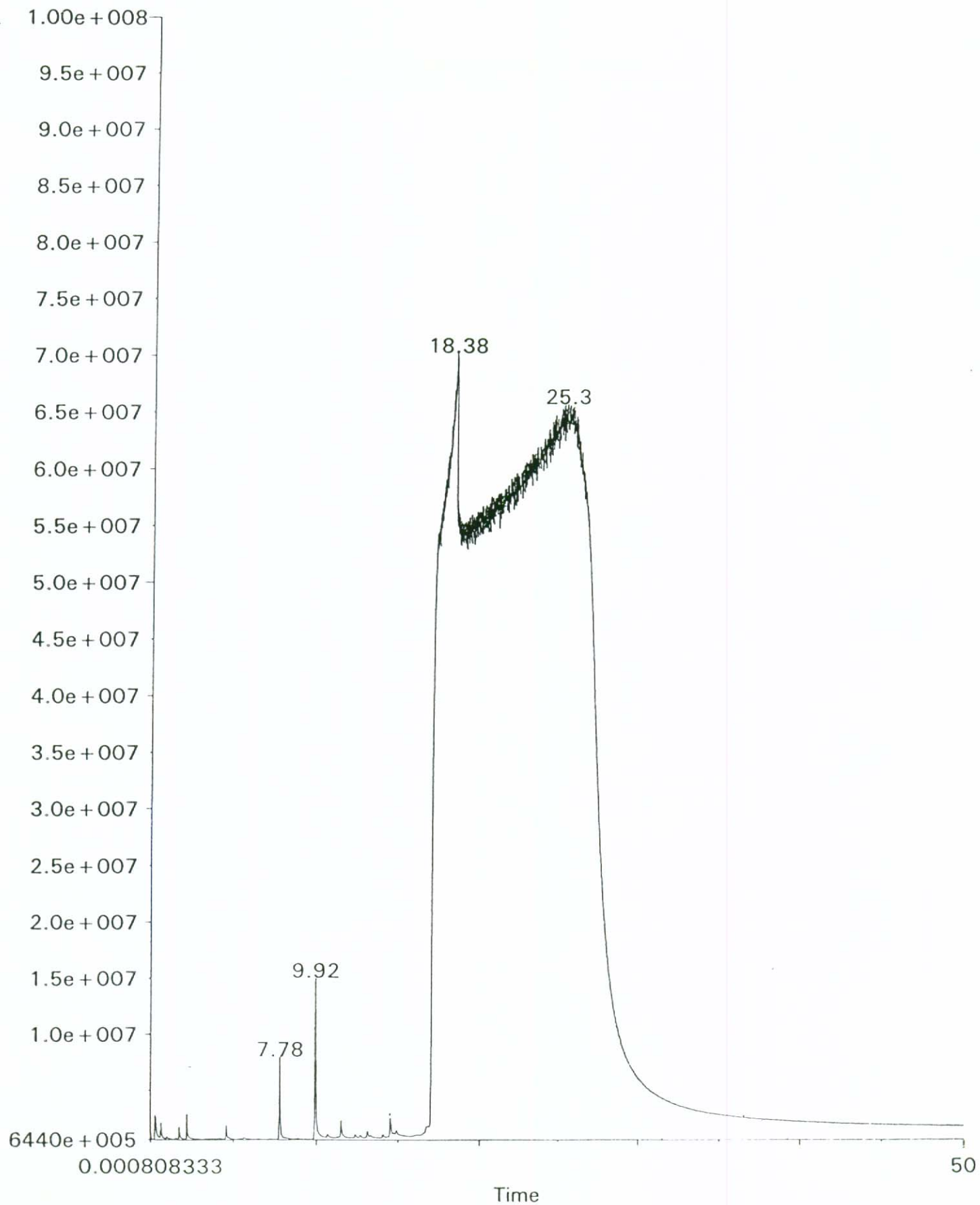


Figure 1. Gas-chromatograph of fresh DOP sample.

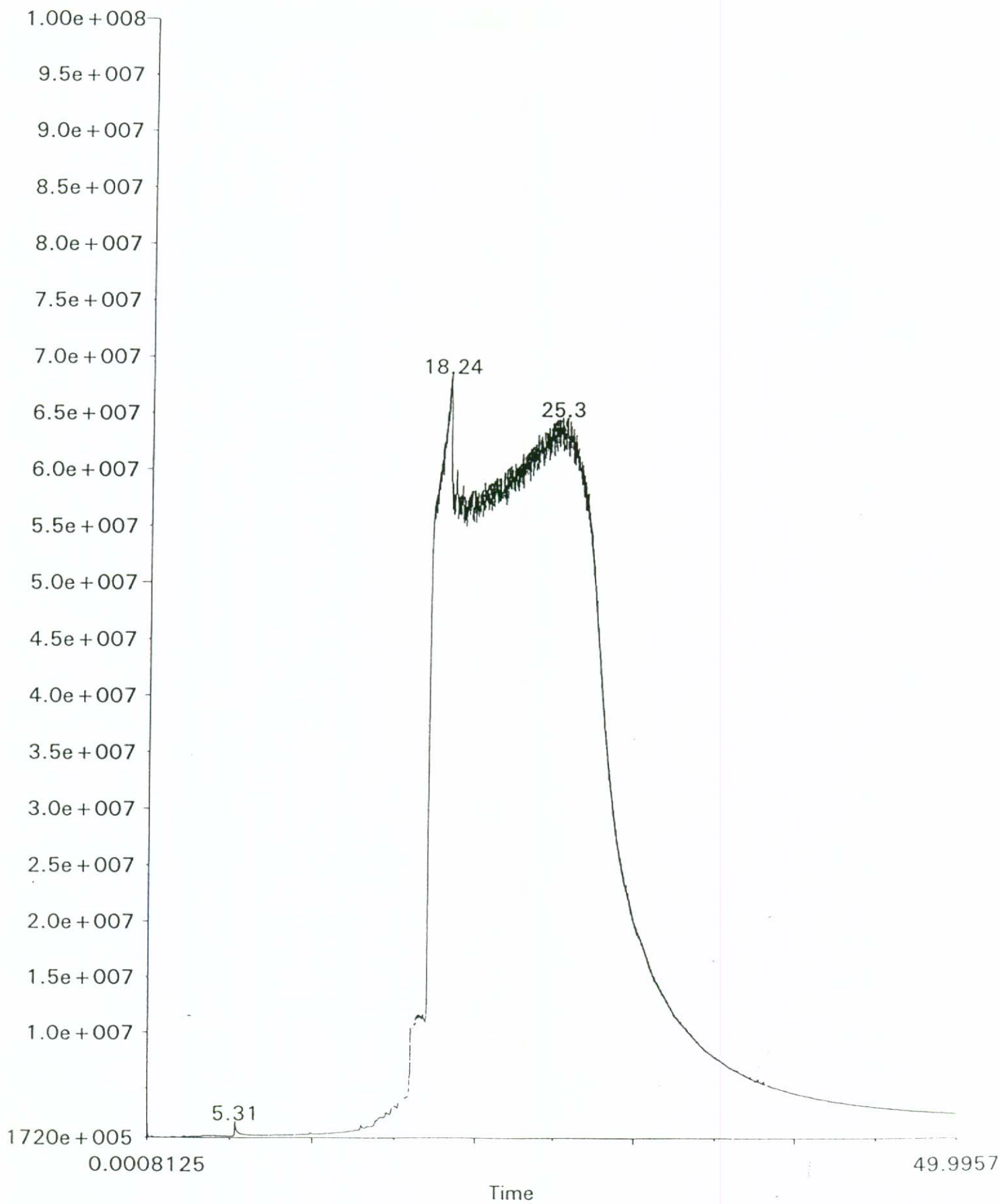


Figure 2. Gas-chromatograph of exposed DOP sample.

The infrared analysis spectra for the fresh and exposed samples are presented in Figures 3 and 4. Overall, the spectra revealed that the fresh and exposed DOP samples contain the same functional groups. After normalization of the spectra off of the prominent carbonyl (C-O) stretch at  $1271\text{ cm}^{-1}$ , most of the C-H and C-C stretches for the exposed sample are of greater intensity than those for the fresh sample. However, the C-O stretching for the exposed sample is slightly less intense than that for the fresh DOP. See Table III.

TABLE III  
NORMALIZED INFRARED ADSORPTION PEAKS OF DOP SAMPLES

FREQUENCY <u>CM<sup>-1</sup></u>	FRESH DOP <u>ABSORBANCE</u>	EXPOSED DOP <u>ABSORBANCE</u>	TYPE OF <u>STRETCH</u>
652	0.114	0.109	C-H
705	0.708	0.693	C-H
742	0.924	0.893	C-H
769	0.683	0.711	C-H
868	0.222	0.331	C-H
908	0.337	0.489	C-H
958	0.622	0.717	C-H
978	0.467	0.602	C-H
1040	0.843	0.819	C-O
1071	0.940	0.928	C-O
1118	0.949	0.940	C-O
1271	1.000	1.000	C-O
1338	0.317	0.344	C-O
1380	0.603	0.693	C-H
1462	0.756	0.807	C-H
1488	0.276	0.343	C-H
1580	0.343	0.398	C-C
1600	0.292	0.349	C-C
1719	0.949	0.916	C-O
2860	0.610	0.645	C-H
2873	0.603	0.651	C-H
2930	0.705	0.747	C-H
2958	0.740	0.783	C-H



Figure 3. Infrared spectrum of fresh DOP sample.

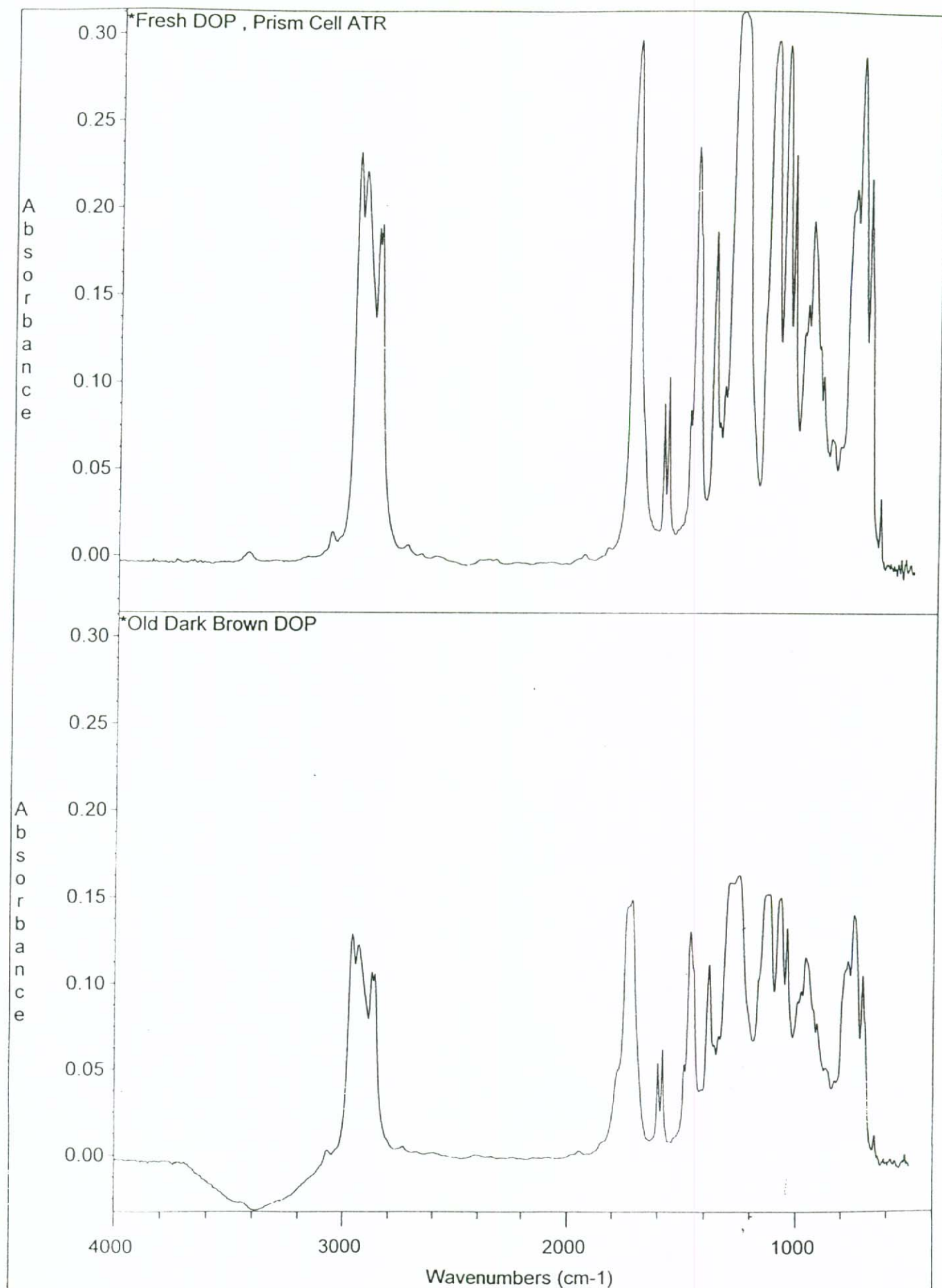


Figure 4. Infrared spectrum of exposed DOP sample.

The UV-visible scans in the wavelength range of 200 to 900 nm are presented in Figure 5. The fresh sample which is clear (refractive index of 1.4836 vs 1.33 for water) absorbs little or no radiation in the visible region (380 to 780 nm). Conversely, the exposed sample which is amber to dark brown in color absorbs radiation in the UV (< 380 nm) and visible regions up to wavelengths as great as 800 nm.

Finally, the distribution of particle sizes in the aerosols generated from the ATI DOP penetrometer are presented in tabular and graphic forms in Tables IV and V, and Figure 6. The data revealed that the geometric mean diameters of the particles generated from the fresh and exposed DOP samples were 0.224 and 0.244 microns, respectively. The particle size histograms are similar to one another, with forty-four percent of the aerosol particles generated from the fresh sample and fifty-three percent of the aerosol particles generated from the exposed sample ranging in size from 0.26 to 0.34 microns.

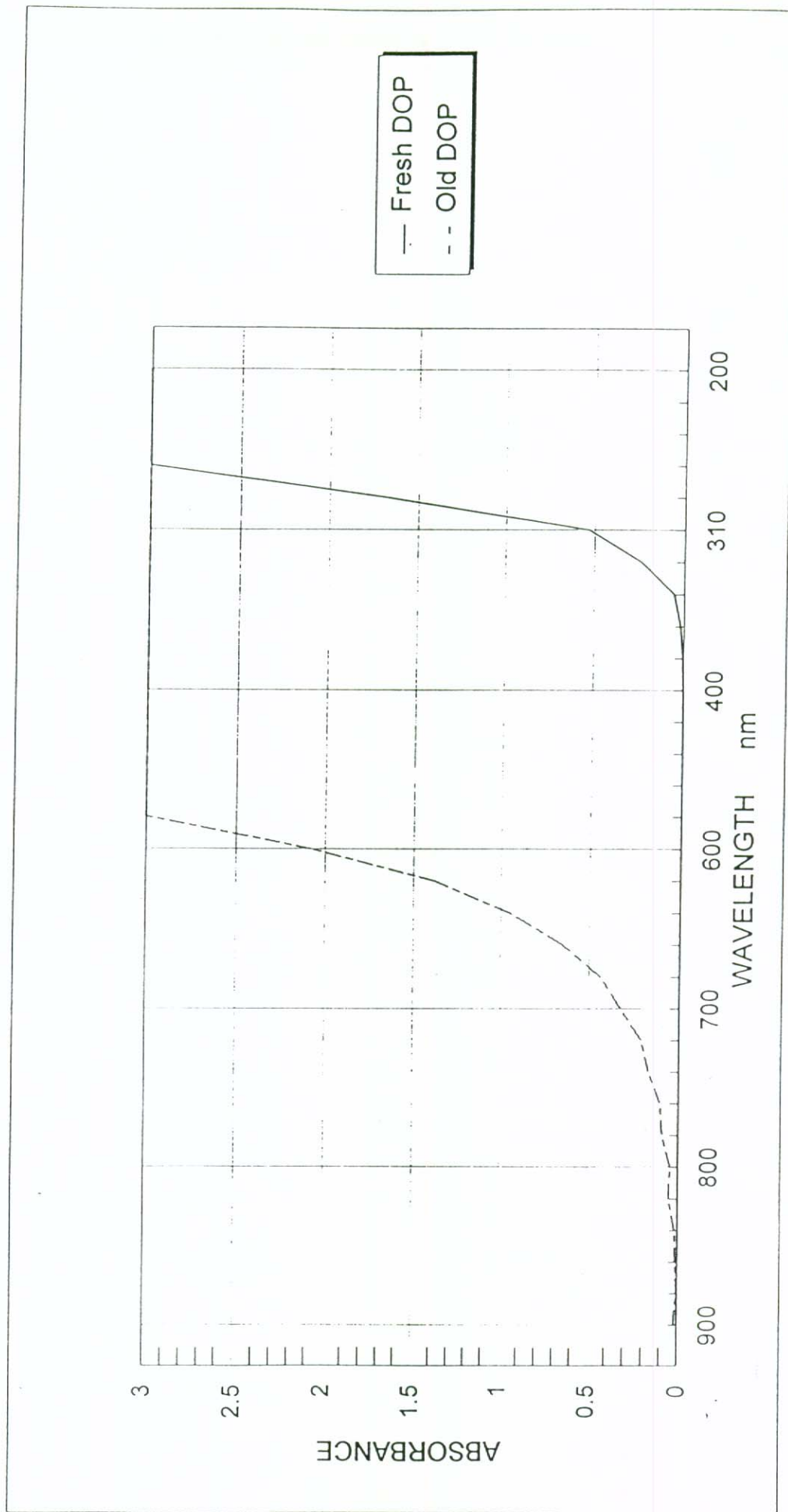


Figure 5. UV-Visible absorption spectrum of fresh and exposed DOP.



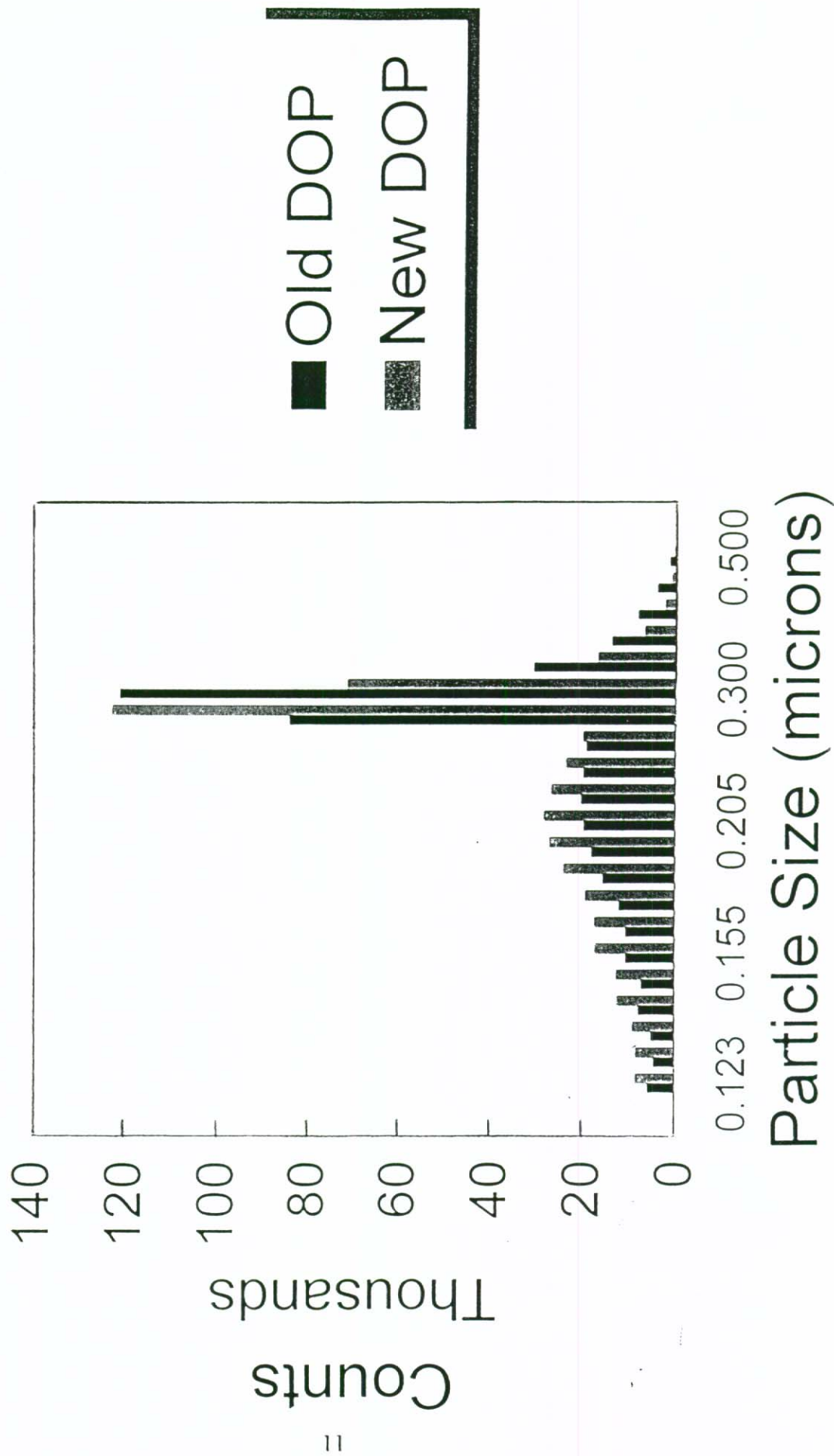


Figure 6. Distribution of particle sizes of aerosols generated from fresh and exposed DOP samples.

TABLE IV  
DISTRIBUTION OF PARTICLE SIZES WITHIN DOP AEROSOL

PARTICLE SIZE MICRONS	FRESH DOP COUNT VALUE # PARTICLES/CC OF <u>MEASURED SMOKE</u>	EXPOSED DOP COUNT VALUE # PARTICLES/CC OF <u>MEASURED SMOKE</u>
0.123	8558	5908
0.129	8443	4541
0.135	9080	5064
0.141	12363	7905
0.147	12577	7230
0.155	17138	10636
0.165	17210	10660
0.175	19208	12052
0.185	23996	15565
0.195	27062	17952
0.205	28258	19760
0.215	26728	20341
0.225	23573	19770
0.235	19810	19131
0.260	122745	84149
0.300	71252	121102
0.340	16704	30621
0.380	6734	13878
0.420	2345	8211
0.460	848	4092
0.500	371	1456
0.540	237	406
0.580	184	103
0.680	534	52
0.840	92	5
1.000	11	0
1.160	2	1

Note. The listed values are the average of three measurements.

TABLE V  
 GEOMETRIC MEAN DIAMETER AND STANDARD DEVIATION OF AEROSOLS

<u>SAMPLE</u>	<u>MEASUREMENT RUN</u>	<u>GEOMETRIC MEAN DIAMETER MICRONS</u>	<u>GEOMETRIC STANDARD DEVIATION</u>
Fresh DOP	1	0.223	1.297
	2	0.224	1.299
	3	0.226	1.298
Exposed DOP	1	0.244	1.323
	2	0.244	1.326
	3	0.244	1.324

#### DISCUSSION OF RESULTS

The aforementioned observations and analyses revealed that although DOP becomes brown in color after prolonged exposure to the conditions in the ATI DOP Penetrometer (336 hours at 167+/-2°C), very little decomposition occurs (< 1%). The fresh DOP has a calculated purity of 99.11%, while the exposed sample has a purity of 98.49%. These findings are not surprising. According to Farrer (1) and Nass (2), DOP is considered to be stable at temperatures greater than 200°C for extended periods of time. This is the primary reason that it is used as a plasticizer for polymers which are extruded and molded at temperatures exceeding 200°C. Farrer (1) and Nass (2) have stated that DOP should not decompose by more than 1% at 167+/-2°C. Unfortunately, neither could specify a time period.

DOP is a Newtonian fluid with a zero-shear rate viscosity approaching 8.14 Pascal-seconds. Although it was not quantified, the fresh and exposed DOP samples have comparable flow characteristics. This also suggests that little decomposition had occurred in the exposed sample.



Analysis of the data strongly suggests that the trace impurities within the fresh DOP react to a higher molecular weight hydrocarbon to produce a brown color (found within the exposed sample). More specifically, gas chromatography-mass spectrometry revealed that the lower molecular weight impurities within the fresh DOP are unreacted 2-ethyl hexanol and an ethyl hexyl benzoic acid ester, a "partially reacted phthalic anhydride". The trace impurities found within the exposed DOP are phthalic anhydride, and a high molecular weight hydrocarbon. The less intense carbonyl stretching found within the infrared spectrum of the exposed sample suggests some cleavage of the C-O bonds of the ethyl hexyl benzoic acid ester or DOP itself to produce phthalic anhydride. Also, the less intense C-O stretching and more intense C-H and C-C stretching found in the infrared scan of the exposed sample are probably associated the cleavage of the C-O bond of the 2-ethyl hexanol which is subsequently polymerized to a higher molecular weight hydrocarbon. This hydrocarbon is manifested by the "shoulder" (near 16 minutes) in the gas chromatogram for the exposed sample. According to Farrer (1), only a few tenths of one percent of a high molecular weight organic compound will produce a brown DOP solution which absorbs radiation in the visible region.

Only small differences were noted in the distribution of sizes for the aerosol particles generated from the fresh and exposed DOP samples. The geometric mean diameter of the particles from the exposed sample was 8.9% greater than that from the fresh sample, and its geometric standard deviation was only 2% greater than that for the fresh sample. Under the non-adiabatic conditions found within the ATI DOP Penetrometer, classical nucleation theory (3, 4) indicates that the number and size of the aerosol or vapor particles (DOP in this case) depends primarily upon the rate of homogenous nucleation and growth of the particles. Nucleation and growth are inversely proportional to the temperature of the airstream and proportional the activation energy barrier. See Equations 2 and 3. Consequently, small differences which exist between the particle size distributions, geometric mean diameters and standard deviations for the fresh and exposed DOP samples are due to slight differences in the aerosol temperatures, rather than differences in the purity or chemical structure of the samples.

Equation 2    Nucleation Rate  $\propto A \exp(-E_{a1}/RT)$

Equation 3    Growth Rate  $\propto B \exp(-E_{a2}/R\Delta T)$

where A and B are empirically derived constants,  $E_{a1}$  and  $E_{a2}$  are the activation energies for nucleation and growth, respectively, R is the Universal gas constant, T is the absolute temperature of the airstream and  $\Delta T$  is the degree of undercooling (difference between the airstream and DOP temperatures).

### CONCLUSIONS

In conclusion, testing and analysis by several analytical techniques revealed that dioctyl phthalate (di[2-ethylhexyl] phthalate) experiences very little decomposition (99.11% for fresh vs 98.49% for exposed) after prolonged conditioning (336 hours at 167+/-2°C) in the ATI DOP "Smoke" Penetrometer. Analysis also indicated that the brown color is due to the presence of a trace quantity (a few tenths of a percent) of a high molecular weight hydrocarbon produced primarily by the reaction (probably polymerization) of the 2-ethyl hexanol impurity within the fresh DOP.

Finally, light scattering measurements revealed that although the purity of the exposed DOP was slightly less than that of the fresh DOP, insignificant differences exist between the character (distribution of particle sizes, geometric mean diameter and standard deviation) of the aerosol particles generated from the fresh and exposed DOP samples. As further confirmation of their strong similarity, aerosol particles generated from the fresh and exposed samples will be collected and analyzed by gas chromatography-mass spectrometry and infrared spectroscopy.

#### REFERENCES

1. Martin Farrer, PhD, Former Director of (Plasticizer) R&D, Monsanto Corporation, personal communication.
2. Leonard Nass, PhD, President-Technical Information Exchange, personal communication.
3. M. Volmer and W. Doering, Phys. Chemie, Vol 119, page 277, 1926.
4. R. Becker and W. Doering, Ann. Phys., Vol 24, page 719, 1935.





Mr. Gary Fletcher  
NIOSH  
944 Chestnut Ridge Road  
Morgantown, WV 26505

March 29, 1994

RE: GC/Mass Spectrometer Analysis of D.O.P. Samples.

Four samples of D.O.P. were analyzed, they were as follows:

1. New D.O.P. (no light, no heat)
2. New D.O.P. (exposed to light only)
3. New D.O.P. (heated to 170 deg. C., no light) (Light tan liquid)
4. Old D.O.P. (Brown liquid)

All samples were analyzed under the same instrument conditions.  
(GC) 50-325deg. at 15deg/min. Post 10min.  
(Mass Spec) EI 70EV.

Figure 1. shows the ion curve of sample #1, the New D.O.P.

Figure 2. shows the ion curve of Sample #2, exposed to light.

Figure 3. shows the ion curve of sample #3, exposed to heat.

Figure 4. shows the ion curve of sample #4, old D.O.P.

Figure 5. shows a comparison of sample 1 to sample 2.

Figure 6. shows a comparison of the mass spectra of D.O.P. in  
sample 1 to sample 4.

Tables 2 through 4 show a difference in the amount of D.O.P when  
compared to that of Table 1. (New D.O.P.)

The NIST/EPA Library search of the peaks observed indicated the  
formation of other phthalic compounds and their esters among them  
the possibility of isomers from the D.O.P.

Breakdown transitional compounds were unidentifiable, although they  
gave the characteristic of a base peak(149amu) and a peak at 167amu  
that are good indicators of plasticizers.

From the results of the analyses it should be noted that the D.O.P.  
does breakdown when exposed to light and heat. The samples analyzed  
showed sample 1 was 99.95% pure and each sample decreased in purity  
to only 94.36% for sample 4.



Quantitation Report File B1QUANLIST

Date: NIOSH1.TI  
 04/20/94 13 08 00  
 Sample: DOP NEW NO LIGHT NO HEAT  
 Conds: 30-323 AT 15DEG/MIN POST 10MIN DB-5 CAP CCL 25ML  
 Formula: Instrument: 4500 Weight: 0.300  
 Submitted by: GF Analyst: BS Acct No:

TABLE 1.

New D.O.P.

AMOUNT=AREA \* REF AMNT/(REF AREA \* RESP FACT)  
 Resp. fac. from Library Entry

No	n/i	Scan	Time	Ref	RRT	Meth	Area(Hght)	Amount	XTot
1	RIC	570	9:30	3	0.615	A 88	8408.	0.023	0.02
2	RIC	835	13:39	3	0.901	A 88	484	0.001	0.00
3	RIC	839	13:39	3	0.905	A 88	92	0.000	0.00
4	RIC	845	14:25	3	0.933	A 88	3404.	0.010	0.01
5	RIC	927	15:27	3	1.000	A 88	34902700.	100.000	99.95
6	RIC	962	16:02	3	1.038	A 88	4880.	0.014	0.01

TABLE 2.

Exposed to Light

Data: NIOSH2.TI  
 04/20/94 14 41 00  
 Sample: FRESH DOP NOT HEATED EXPOSED TO LIGHT  
 Conds:  
 Formula: Instrument: 4500 Weight: 0.000  
 Submitted by: Analyst: Acct No:

AMOUNT=AREA \* REF AMNT/(REF AREA \* RESP FACT)  
 Resp. fac. from Library Entry

No	n/i	Scan	Time	Ref	RRT	Meth	Area(Hght)	Amount	XTot
1	RIC	554	9:16	3	0.542	A 88	2384.	0.004	0.00
2	RIC	659	10:39	3	0.643	A 88	2700.	0.003	0.00
3	RIC	1023	17:03	3	1.000	A 88	36484900.	100.000	99.94
4	RIC	1049	17:29	3	1.023	A 88	27216.	0.048	0.03

TABLE 3.

Exposed to Heat 170 Deg.

Data: NIOSH3.TI  
 04/20/94 15 34 00  
 Sample: NEW DOP HEATED 170DEG. CENT  
 Conds:  
 Formula: Instrument: 4500 Weight: 0.000  
 Submitted by: Analyst: Acct No:

AMOUNT=AREA \* REF AMNT/(REF AREA \* RESP FACT)  
 Resp. fac. from Library Entry

No	n/i	Scan	Time	Ref	RRT	Meth	Area(Hght)	Amount	XTot
1	RIC	478	7:58	3	0.516	A 88	4968.	0.015	0.02
2	RIC	487	8:07	3	0.526	A 88	2607.	0.008	0.01
3	RIC	570	9:30	3	0.616	A 88	14670.	0.045	0.04
4	RIC	848	14:28	3	0.937	A 88	3394.	0.010	0.01
5	RIC	926	15:26	3	1.000	A 88	32588900.	100.000	99.88
6	RIC	939	15:39	3	1.014	A 88	3184.	0.010	0.01
7	RIC	944	15:44	3	1.019	A 88	2752.	0.008	0.01
8	RIC	951	15:51	3	1.027	A 88	3466.	0.011	0.01
9	RIC	963	16:03	3	1.040	A 88	2848.	0.009	0.01

TABLE 4.

Old D.O.P.

Data: NIOSH4.TI  
 04/20/94 17 04 00  
 Sample: OLD DOP  
 Conds:  
 Formula: Instrument: 4500 Weight: 0.000  
 Submitted by: Analyst: Acct No:

AMOUNT=AREA \* REF AMNT/(REF AREA \* RESP FACT)  
 Resp. fac. from Library Entry

No	n/i	Scan	Time	Ref	RRT	Meth	Area(Hght)	Amount	XTot
1	RIC	464	7:44	14	0.465	A 88	15378.	0.074	0.07
2	RIC	690	11:30	14	0.691	A 8V	3478.	0.017	0.02
3	RIC	699	11:39	14	0.700	A 8V	6184.	0.030	0.03
4	RIC	714	11:54	14	0.715	A 88	904.	0.004	0.00
5	RIC	786	13:04	14	0.788	A 88	1852.	0.009	0.01
6	RIC	840	14:00	14	0.842	A 88	896.	0.004	0.00
7	RIC	844	14:24	14	0.844	A 88	2744.	0.013	0.01
8	RIC	847	14:27	14	0.849	A 88	3428.	0.018	0.02
9	RIC	874	14:34	14	0.876	A 88	2104.	0.010	0.01
10	RIC	888	14:48	14	0.890	A 88	24734.	0.120	0.11
11	RIC	913	15:13	14	0.915	A 88	3400.	0.017	0.02
12	RIC	922	15:22	14	0.924	A 88	34592.	0.167	0.16
13	RIC	947	15:47	14	0.949	A 88	8284.	0.040	0.04
14	RIC	998	16:38	14	1.000	A 88	20483100.	100.000	94.36
15	RIC	1004	16:44	14	1.006	A 88	137120.	0.663	0.63
16	RIC	1011	16:51	14	1.013	A 8V	173680.	0.840	0.79
17	RIC	1016	16:56	14	1.018	A 8V	104688.	0.506	0.48
18	RIC	1021	17:01	14	1.023	A 8V	278400.	1.346	1.27
19	RIC	1031	17:11	14	1.033	A 8V	399792.	1.933	1.82
20	RIC	1042	17:22	14	1.044	A 8V	6288.	0.030	0.03
21	RIC	1046	17:26	14	1.048	A 88	4504.	0.022	0.02
22	RIC	1051	17:31	14	1.053	A 88	1512.	0.007	0.01
23	RIC	1059	17:39	14	1.061	A 88	13064.	0.063	0.06
24	RIC	1067	17:47	14	1.069	A 88	7978.	0.039	0.04

I have enclosed the hard data collected from the analyses.

If there are questions concerning the analyses, please give me a call at 293-5970.

Robert R. Smith



Mgr/Mass Spectrometry Center



Quantitation Report File 31QUANLIST

Date: NIOSH1.TI

04/20/94 13 08:00

Sample COP NEW NO LIGHT NO HEAT

Conds 50-225 AT 15DEG/MIN POST 10MIN DB-5 CAP COL 25ML

Formula: Instrument: 4500

Submitted by GF

Analyst: BS

Weight 0.000

Acct No

AMOUNT=AREA \* REF AMNT/(REF AREA \* RESP FACT)

Resp. fac from Library Entry

No	m/z	Scan	Time	Ref	RRT	Meth	Area(Hght)	Amount	%Tot
1	RIC	570	9:30	5	0.515	A BB	8608.	0.025	0.02
2	RIC	535	13:55	5	0.701	A BB	484.	0.001	0.00
3	RIC	539	13:59	5	0.705	A BB	92.	0.000	0.00
4	RIC	565	14:25	5	0.933	A BB	3606.	0.010	0.01
5	RIC	527	15:27	5	1.000	A BB	34902700.	100.000	99.95
6	RIC	562	16:02	5	1.038	A BB	4880.	0.014	0.01

Quantitation Report File: 21QUANLIST

Data NIOSH2.TI

04/20/94 14:41:00

Sample: FRESH DOP NOT HEATED EXPOSED TO LIGHT  
Conds.:

Formula:

Instrument: 4500

Weight: 0.000

Submitted by:

Analyst:

Acct. No:

AMOUNT=AREA \* REF AMNT/(REF AREA \* RESP FACT)

Resp. fac. from Library Entry

No	n/z	Scan	Time	Ref	RRT	Meth	Area(Hght)	Amount	%Tot
1	RIC	555	9:16	3	0.542	A BB	2384.	0.004	0.00
2	RIC	559	10:59	3	0.643	A BB	2700.	0.005	0.00
3	RIC	1025	17:05	3	1.000	A BB	56484900.	100.000	99.94
4	RIC	1049	17:29	3	1.023	A BB	27216.	0.048	0.05

Quantitation Report File B1QUANLIST

Data: NIDH3.TI

04/20/94 15:54:00

Sample: NEW DOP HEATED 170DEG CENT.

Conds:

Formula:

Instrument 4500

Weight 0.000

Submitted by

Analyst

Acct. No

AMOUNT=AREA \* REF AMNT/(REF AREA \* RESP FACT)

Resp fac. from Library Entry

No	m/z	Scan	Time	Ref	RRT	Meth	Area(Hght)	Amount	%Tot
1	RIC	478	7:58	5	0.516	A BB	4968.	0.015	0.02
2	RIC	487	8:07	5	0.526	A BB	2607.	0.008	0.01
3	RIC	570	9:30	5	0.616	A BB	14670.	0.045	0.04
4	RIC	868	14:28	5	0.937	A BB	3394.	0.010	0.01
5	RIC	926	15:26	5	1.000	A BB	32588900.	100.000	79.88
6	RIC	939	15:39	5	1.014	A BB	3184.	0.010	0.01
7	RIC	944	15:44	5	1.019	A BB	2752.	0.008	0.01
8	RIC	951	15:51	5	1.027	A BB	3666.	0.011	0.01
9	RIC	963	16:03	5	1.040	A BB	2848.	0.009	0.01



Quantitation Report File 31GUANLIST

Data: NIOSH4.TI  
 04/20/94 17:04:00  
 Sample: OLD DOP

Conds: \_\_\_\_\_  
 Formula: \_\_\_\_\_ Instrument: 4500 Weight: 0.000  
 Submitted by: \_\_\_\_\_ Analyst: \_\_\_\_\_ Acct. No: \_\_\_\_\_

AMOUNT=AREA \* REF AMNT/(REF AREA \* RESP FACT)  
 Resp. fac. from Library Entry

No	m/z	Scan	Time	Ref	RRT	Meth	Area(Hght)	Amount	%Tot
1	RIC	464	7.44	14	0.465	A BB	15378.	0.074	0.07
2	RIC	690	11:30	14	0.691	A BV	3478.	0.017	0.02
3	RIC	699	11:39	14	0.700	A VB	6184.	0.030	0.03
4	RIC	714	11:54	14	0.715	A BB	904.	0.004	0.00
5	RIC	786	13:06	14	0.788	A BB	1852.	0.009	0.01
6	RIC	840	14:00	14	0.842	A BB	896.	0.004	0.00
7	RIC	864	14:24	14	0.866	A BB	2744.	0.013	0.01
8	RIC	867	14:27	14	0.869	A BB	3628.	0.018	0.02
9	RIC	874	14:34	14	0.876	A BB	2104.	0.010	0.01
10	RIC	888	14:48	14	0.890	A BB	24734.	0.120	0.11
11	RIC	913	15:13	14	0.915	A BB	3600.	0.017	0.02
12	RIC	922	15:22	14	0.924	A BB	34592.	0.167	0.16
13	RIC	947	15:47	14	0.949	A BB	8284.	0.040	0.04
14	RIC	998	16:38	14	1.000	A BB	20683100.	100.000	100.00
15	RIC	1004	16:44	14	1.006	A BB	137120.	0.663	0.63
16	RIC	1011	16:51	14	1.013	A BV	173680.	0.840	0.79
17	RIC	1016	16:56	14	1.018	A VV	104688.	0.506	0.48
18	RIC	1021	17:01	14	1.023	A VV	278400.	1.346	1.27
19	RIC	1031	17:11	14	1.033	A VV	399792.	1.933	1.82
20	RIC	1042	17:22	14	1.044	A VB	6288.	0.030	0.03
21	RIC	1046	17:26	14	1.048	A BB	4504.	0.022	0.02
22	RIC	1051	17:31	14	1.053	A BB	1512.	0.007	0.01
23	RIC	1059	17:39	14	1.061	A BB	13064.	0.063	0.06
24	RIC	1067	17:47	14	1.069	A BB	7978.	0.039	0.04