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# IDENTIFICATION OF CHLORINATED NAPHTHALENES IN HALOWAXES 1031, 1000, 1001 AND 1099

FREDERICK A. BELAND and RICHARD D. GEER
*Department of Chemistry, Montana State University, Bozeman, Mont. 59715 (U.S.A.)*
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## SUMMARY

The identities of the chlorinated naphthalenes in the commercial mixtures of Halowaxes 1031, 1000, 1001 and 1099 have been established. These preparations contain 22, 26, 50 and 52% of chlorine, respectively. Both monochloronaphthalenes were found to be present. All of the disubstituted isomers, with the exception of 2,6-dichloronaphthalene, together with several of the possible tri- and tetrachloronaphthalenes, were detected in the mixtures. At least three components did not seem to be chlorinated naphthalenes. Other commercial preparations of chlorinated naphthalenes appear to be of similar composition, *i.e.*, isomers that have been identified in Nibren D88 are also present in Halowax 1001.

## INTRODUCTION

Polychlorinated naphthalenes (PCNs) are industrial compounds manufactured in different countries under various trade-names such as Halowax (Koppers Company, Inc., Pittsburgh, Pa., U.S.A.), Seekay Wax (Imperial Chemical Industries, Manchester, Great Britain) and Nibren Wax (Bayer, Leverkusen, G.F.R.). These products vary in chlorine content from 22 to 70% and have properties and uses similar to those of polychlorinated biphenyls (PCBs)[1,2]. From reported production figures, it can be estimated that the PCNs are manufactured in at least 10% of the amount of the PCBs[1,3]. As PCBs and PCNs have similar chemical and physical properties, it has been suggested that chlorinated naphthalenes might interfere in organochlorine insecticide analysis in a manner analogous to the chlorobiphenyls[4].

PCNs have been implicated in causing various diseases, such as chloracne, liver damage, X-disease in cattle and chick edema[5]. In order to understand the metabolism, toxicity and environmental degradation of PCNs better, it would be advantageous to establish the identity of the individual components in the chlorinated naphthalene mixture.

The purpose of this paper is to report the individual components of Halowaxes 1031, 1000, 1001 and 1099. These mixtures contain 22, 26, 50 and 52% of chlorine, respectively, and represent the lower chlorine content end of the Halowax series.

## EXPERIMENTAL

### *Materials*

1,8-Dichloronaphthalene was synthesized from 1,8-naphthalenediamine (Aldrich, Milwaukee, Wisc., U.S.A.). The diamine (5 g) was added to 35 ml of concentrated sulfuric acid in 74 ml of water and tetrazodized with 4.8 g of sodium nitrite in 43 ml of water, keeping the temperature below 5°. The resultant solution was stirred for 1 h and added to 5 g of cuprous chloride in 25 ml of concentrated hydrochloric acid, stirred for 2.5 h and filtered. The solid product was washed with water, dried and recrystallized from aqueous ethanol. Further clean-up was afforded by passing the compound through a silica gel column by eluting with hexane (m.p. 87–88°, Fischer-Johns apparatus; literature[6], 88.5–90°.)

2,3-Dichloronaphthalene was prepared by adding 0.15 g of 2,3-dinitronaphthalene (obtained from Dr. Julius Hyman) to 1.5 g of phosphorus pentachloride and

TABLE I

RETENTION TIMES AND IDENTIFICATION OF COMPONENTS OF HALOWAXES AS ESTABLISHED FROM CARBOWAX 20M

Retention times in mm (5.08 mm = 1.0 min); + = component found in Halowaxes; $^{n}$ = component found in Nibren D88 [10]; u = components that appear not to be chlorinated naphthalenes.

| *Retention time (mm)* | *Chloronaphthalene* | *Halowax* | | | |
|---|---|---|---|---|---|
| | | *1031* | *1000* | *1001* | *1099* |
| 32.0 | 1-; 2- | + | + | + * | + * |
| 42.5 | u | + | + | | |
| 54.0 | u | + | + | | |
| 57.0 | 1,3- | + | + | | |
| 62.0 | 1,4-; 1,5- | + | + | + | + ** |
| 69.0 | 1,6-; 1,7- | + | + | | |
| 77.0 | 1,2-; 2,7- | + *** | + | | |
| 84.0 | 2,3- | + | + | + | + |
| 94.5 | 1,3,5- | + | + | + | + |
| 108.5 | 1,2,4-; 1,4,6-$^{n}$ | + | + | + | + |
| 127.0 | 1,8-; 1,3,5,7-$^{n}$ | + | + | + | + |
| 140.0 | | | + | + | |
| 154.5 | 1,2,6- | + | + | + | + |
| 165.0 | | | + | | |
| 177.0 | 1,2,4,6- | + | + | + | + |
| 199.0 | 1,4,5-$^{n}$ | + | + | + | + |
| 237.0 | | + | + | + | + |
| 254.0 | 1,3,5,8- | + | + | + | + |
| 272.0 | 1,2,3,4- | + | + | + | + |
| 294.0 | | + | + | + | + |
| 312.0 | | + | + | + | + |
| 336.0 | | + | + | + | + |
| 393.0 | | + | + | + | + |
| 420.0 | | | | | + |
| 526.0 | 1,4,5,8-$^{n}$ | + | + | + | + |
| 582.0 | | + | + | + | + |
| 634.0 | | + | + | + | + |
| 666.0 | | + | + | + | + |

* Peak that contains only 2-chloronaphthalene, as established from Bentone 34–OV-101.

** Peak that contains only 1,4-dichloronaphthalene, as established from Bentone 34–OV-101.

*** Peak that contains only 2,7-dichloronaphthalene, as established from Bentone 34–OV-101.

heating at 160–165° for 4.5 h. After cooling to room temperature, water was added. The dichloronaphthalene was extracted with benzene, evaporated to dryness, run through a silica gel column with hexane and recrystallized from ethanol (m.p. 118–119°; literature[7], 119.5–120.5°.)

1,2-Dichloronaphthalene was prepared by adding 1 g of 1-chloro-2-naphthylamine hydrochloride (Aldrich) to 5 ml of concentrated hydrochloric acid and diazotizing with 0.5 g of sodium nitrite in 20 ml of water at 5°. The resultant diazonium compound was treated with cuprous chloride–hydrochloric acid as above and the product was purified by passing it through a silica gel column with hexane (m.p. 34–35°; literature[6], 34–35°.)

The monochloronaphthalenes were purchased from J. T. Baker (Phillipsburgh, N.J., U.S.A.). The other possible di- and trichloronaphthalenes, as well as several of the tetrasubstituted isomers, were obtained from Dr. Dusan Hadži and Ludvik Cencelj (University Institute of Boris Kidric, Yugoslavia), Dr. Julius Hyman (Berkeley, Calif.)

TABLE II

RETENTION TIMES AND IDENTIFICATION OF COMPONENTS OF HALOWAXES AS ESTABLISHED FROM BENTONE 34–OV-101

Retention times in mm (5.08 mm = 1.0 min); + = components found in Halowaxes; $^{n}$ = components found in Nibren D88 [10]; u = components that appear not to be chlorinated naphthalenes.

| *Retention time (mm)* | *Chloronaphthalene* | *Halowax* | | | |
|---|---|---|---|---|---|
| | | *1031* | *1000* | *1001* | *1099* |
| 58.0 | 2- | + | + | + | + |
| 66.5 | 1- | + | + | | |
| 88.0 | u | + | + | | |
| 99.0 | 1,5- | + | + | + | |
| 110.0 | 1,3- | + | + | | |
| 112.0 | 1,6- | + | + | | |
| 118.0 | u | + | + | + | + |
| 131.0 | 2,7- | + | + | | |
| 163.5 | 2,3-; 1,4,6-$^{n}$ | + | + | + | + |
| 175.0 | 1,2- | | + | | |
| 181.0 | 1,7- | + | + | | |
| 186.5 | 1,3,5- | + | + | + | + |
| 215.0 | 1,2,4- | + | + | + | + |
| 226.0 | 1,3,5,7-$^{n}$ | + | + | + | + |
| 240.0 | 1,2,6- | + | + | + | + |
| 276.0 | 1,4,5-$^{n}$ | + | + | + | + |
| 299.0 | 1,2,4,6- | + | + | + | + |
| 316.0 | 1,8- | + | + | + | + |
| 390.0 | 1,3,5,8- | + | + | + | + |
| 407.0 | | + | | + | + |
| 482.0 | | + | + | + | + |
| 555.0 | 1,4,5,8-$^{n}$ | + | + | + | + |
| 572.0 | | | + | | |
| 606.0 | | + | | + | + |
| 642.0 | 1,2,3,4- | + | + | + | + |
| 657.0 | | + | + | + | + |

and I.C.I., to whom we are deeply indebted. Halowaxes 1031 (lot B-50), 1000 (B-91), 1001 (B-269) and 1099 (B-92) were generous gifts of Koppers.

*Procedure and apparatus*

Owing to the small amounts of material available for some of the isomers, the

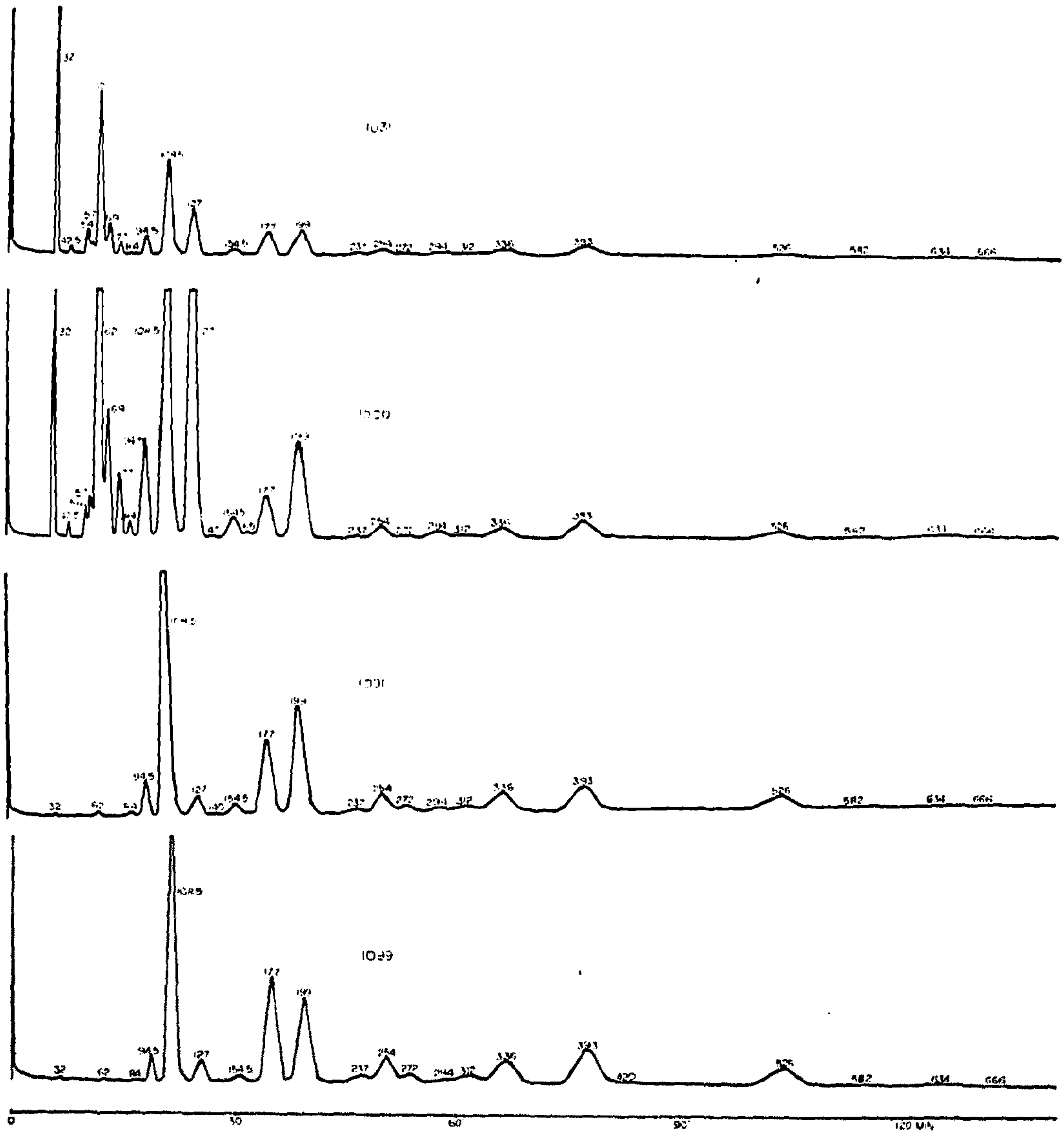

Fig. 1. Electron capture chromatograms of Halowaxes on Carbowax 20M packed column. Amounts: 3 $\mu$g of Halowax 1031, 3 $\mu$g of Halowax 1000, 30 ng of Halowax 1001 and 30 ng of Halowax 1099, with attenuation setting maintained at $16 \cdot 10^{-10}$.

identities of the components were established by electron capture gas–liquid chromatography (GLC). A Varian 1200 gas–liquid chromatograph equipped with a tritium detector was used. The operating temperatures were as follows: injector, 190°; oven, 180°; detector, 190°. Nitrogen was used as the carrier gas (30 ml/min). All runs

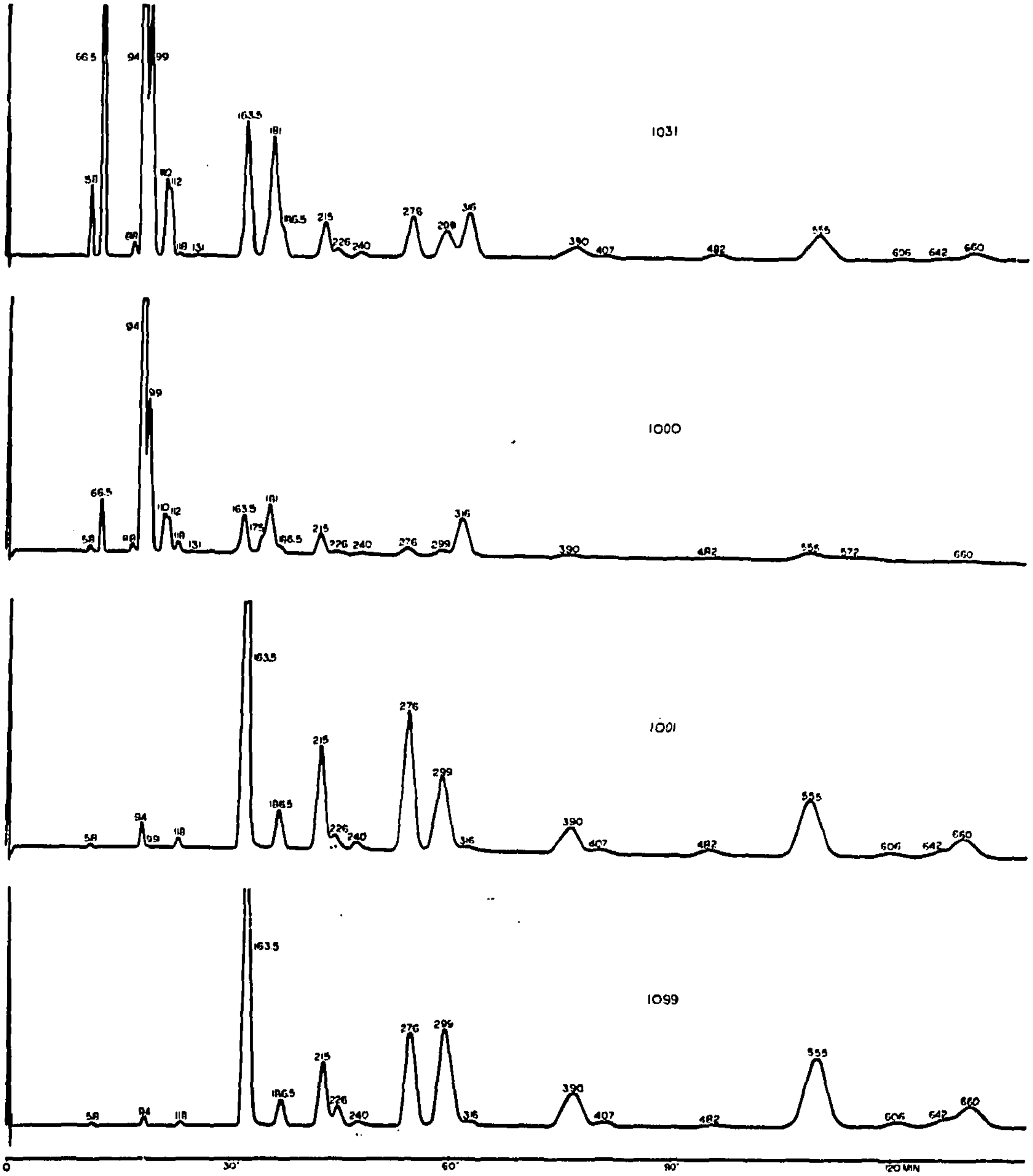

Fig. 2. Electron capture chromatograms of Halowaxes on Bentone 34–OV-101 packed column. Amounts: 3 µg of Halowax 1031, 0.3 µg of Halowax 1000, 30 ng of Halowax 1001 and 30 ng of Halowax 1099, with attenuation setting maintained at $16 \cdot 10^{-10}$.

were made isothermally with on-column injections into an all-glass system. Separations were made on two different columns: a 10% Carbowax 20M on 60–80 mesh Chromosorb W, 10 ft. × 1/8 in. column of silanized Pyrex glass; and a mixed 5% Bentone 34–10% OV-101 on 100–120 mesh Supelcoport, 10 ft. × 1/8 in. column of silanized Pyrex glass.

Individual isomers were injected into both columns to establish retention times. To confirm the presence of a particular component, a simultaneous injection was made with the individual isomer and the Halowax mixture.

## RESULTS AND DISCUSSION

Fig. 1 shows the chromatograms of the Halowaxes run on the Carbowax 20M column, and Fig. 2 shows the chromatograms on the Bentone 34–OV-101 column. The use of two different columns was necessary to confirm the results because there were some peaks that contained more than one compound on each column. Components that eluted as a single peak on one column were separated on the other column. The only exception was 1,4,6-trichloronaphthalene, which has a retention time identical with that of 1,2,4-trichloronaphthalene on Carbowax 20M and to 2,3-dichloronaphthalene on the Bentone 34–OV-101 column. In comparing the results, it can be seen that while 2-chloronaphthalene was found in all four mixtures, 1-chloronaphthalene was present only in Halowaxes 1031 and 1000. 1,2-Dichloronaphthalene was detected only in Halowax 1000, while the 1,5-isomer was not found in Halowax 1099. The only disubstituted isomer not found was 2,6-dichloronaphthalene.

There are two unidentified peaks at retention times of 42.5 and 54.0 on the Carbowax 20M column. These peaks are found only in Halowaxes 1031 and 1000. On the Bentone 34–OV-101 column, there are also two unidentified peaks at retention times of 88 and 118. The first unknown peak is present only in Halowaxes 1031 and 1000, while the latter is found in all four mixtures. Owing to their relatively short retention times and their failure to correspond with any possible di- or trichloronaphthalene, it is highly probable that these compounds are not chlorinated naphthalenes. At present, the identities of these compounds are unknown.

The remainder of the unidentified peaks are assumed to be chlorinated naphthalenes containing four or more chlorine atoms. None of these unknown peaks has a retention time identical with those of any of the possible trisubstituted isomers or with those of the tetrachloronaphthalenes that we have in our possession.

The electron capture chromatograms are misleading as to the amount of each isomer present. With PCBs it has been shown that there is a 500-fold increase in detector response between 4-chloro- and decachlorobiphenyl, most of this increase occurring in the mono- to trichloro-range[8]. We have observed a similar trend with the chlorinated naphthalenes but as yet we do not know the magnitude of this effect. For instance, Halowax 1031 contains a minimum of 96% of monochloronaphthalene, which is predominantly the 1-isomer[9]. Yet the chromatogram of this mixture (Figs. 1 and 2) shows a clear indication of tetrachloronaphthalenes being present even though this may be at very low concentrations.

One would expect to find the same components in similar commercial preparations of chlorinated naphthalenes supplied by other manufacturers, and this seems to be so. Cencelj and Hadži[10], using column chromatography and infrared spectrophotometry, identified 1,4,5- and 1,4,6-trichloro- and 1,3,5,7- and 1,4,5,8-tetrachloronaphthalenes as components of Nibren D88. These isomers are also found in Halowax 1001 and both of these mixtures contain 49–50% of chlorine[1,9].

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## REFERENCES

1 D. W. F. Hardie, in A. Standen (Editor), *Kirk–Othmer Encyclopedia of Chemical Technology*, Vol. 5, Interscience, New York, 2nd ed., 1964, p. 297.
2 H. L. Hubbard, in A. Standen (Editor), *Kirk–Othmer Encyclopedia of Chemical Technology*, Vol. 5, Interscience, New York, 2nd ed., 1964, p. 289.
3 Anonymous, *Chem. Eng. News*, Dec. 6 (1971) 15.
4 J. A. Armour and J. A. Burke, *J. Ass. Offic. Anal. Chem.*, 54 (1971) 175.
5 R. D. Kimbrough, *Arch. Environ. Health*, 25 (1972) 125.
6 A. Weissberger, R. Sängewald and G. C. Hampson, *Trans. Faraday Soc.*, 30 (1934) 884.
7 G. C. Hampson and A. Weissberger, *J. Chem. Soc.*, (1936) 393.
8 V. Zitko, O. Hutzinger and S. Safe, *Bull. Environ. Contam. Toxicol.*, 6 (1971) 160.
9 *Halowax® Chlorinated Naphthalene Oils and Waxlike Solids*, Technical Bulletin, Koppers Co.
10 L. Cencelj and D. Hadži, *Spectrochim. Acta*, 7 (1955) 274.