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CHARACTERIZATION OF POLYCHLORINATED BIPHENYLS

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CHARACTERIZATION OF POLYCHLORINATED BIPHENYLS

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CHEMICAL STRUCTURE

Polychlorinated biphenyls (PCBs) are made by direct chlorination of biphenyl. The biphenyl molecule has ten possible sites at which chlorine atoms can be substituted. The numbering system for the biphenyl structure is shown in Figure 1. By convention, the two rings are numbered identically except the ring with the fewest chlorine substituents or substituted in the highest numerical positions is designated as primed. Examples of nomenclature for a tri- and a tetrachlorobiphenyl are included in Figure 1. An excellent discussion of PCB nomenclature can be found in a recent text by Hutzinger, Safe and Zitko (1).

There are 209 possible chlorobiphenyl isomers distributed as indicated in Table I. However, many of these isomers are not likely to occur at significant levels in commercial PCB mixtures. For example, isomers with four or five chlorine atoms on one ring but none on the other ring are not detectable in PCB products.

TABLE I

209 POSSIBLE PCB ISOMERS

Degree of Substitution	Number of Isomers
Mono	3
Di	12
Tri	24
Tetra	42
Penta	46
Hexa	42
Hepta	24
Octa	12
Nona	3
Deca	1
	209

AROCLOR PRODUCTS

The major producer of PCBs in the United States is Monsanto Company, which markets mixtures for closed electrical system applications under the Aroclor® trademark. Aroclor products are identified by a four digit numbering code in which the first two digits, 12, indicate the parent molecule is biphenyl and the last two digits specify the weight percent of chlorine. The exception is Monsanto's newest product, Aroclor 1016 (41% chlorine), which retained the 1016 designation by which it was known during development. Aroclor products manufactured in the United States are listed in Table II. Production of the materials listed as discontinued was terminated in or prior to 1971.

TABLE II

AROCLOR PRODUCTS MANUFACTURED IN THE U.S.

Current	Discontinued	Percent Chlorine
1221		21
	1232	32
1016		41
1242		42
	1248	48
1254		54
	1260	60
	1262	62
	1268	68

AROCLOR COMPOSITION

The composition of the four Aroclor products currently marketed in the United States is given in Table III. Aroclor 1221 is primarily monochlorobiphenyl while Aroclor 1016 and Aroclor 1242 are primarily trichlorobiphenyls. The major difference between these two products is the lower penta- and hexachlorobiphenyl content of Aroclor 1016. Aroclor 1254 is primarily pentachlorobiphenyl. The values in Table III were calculated from measurements by gas chromatography with flame ionization detection after component identification by gas chromatography/mass spectrometry. All gas chromatographic separations were made with a high resolution capillary column. Average response factors determined for each degree of chlorine substitution were applied to all components.

TABLE III

TYPICAL PERCENT COMPOSITION OF AROCLOR PRODUCTS

HOMOLOG # Cl/BIPHENYL	AROCLOR 1221	AROCLOR 1016	AROCLOR 1242	AROCLOR 1254
0	11	<0.1	<0.1	<0.1
1	51	1	1	<0.1
2	32	20	16	<0.5
3	4	57	49	1
4	2	21	25	21
5	<0.5	1	8	48
6	ND	<0.1	1	23
7	ND	ND	<0.1	6
8	ND	ND	ND	ND

ND = NONE DETECTED, <0.01%

Detailed chromatograms of these four products are illustrated in Figures 2-5. Specific isomer identifications determined by Webb and McCall (2) and Sissons and Welti (3) are listed for the major Aroclor 1242 components in Figure 4. The complexity of these mixtures was emphasized by amplifying the first and last portions of the Aroclor 1254 chromatogram in Figure 5. Eighty-five components were detected in Aroclor 1254. A .32 mm id X 50 m glass capillary column coated with OV-101 was used for these separations. The flow rate was 2 ml/min helium and the column temperature was programmed from 150° to 230°C at 2°C/min.

High resolution chromatographic conditions are very useful for characterizing PCB products. However, for routine monitoring of environmental materials, it is more appropriate to use gas chromatography with packed columns and electron capture detection. Typical chromatograms of this type for Aroclor 1016 and Aroclor 1242 are compared in Figure 6. The chromatograms are essentially identical for retention times less than 70 relative to p,p'-DDE. However, the higher chlorinated components with relative retention times 70 and greater represent a significantly smaller contribution in the Aroclor 1016 chromatogram. These chromatograms illustrate the feasibility of distinguishing these unaltered products. However, in environmental materials the characteristic features of Aroclor 1242 are frequently obscured by interfering compounds or by component alteration so the distinction is less clear or sometimes entirely lacking. These separations were carried out on a 6 ft. X 4 mm id glass column packed with 3% SE-30 on 80/100 mesh Chromosorb W - HP at 190°C.

PHYSICO-CHEMICAL DIFFERENCES

The physical and chemical properties of PCB isomers and commercial mixtures vary greatly depending on the degree and position of chlorine substitution. The effect of chlorine content on several physico-chemical properties is summarized in Table IV. Three of these properties, volatility, water solubility, and biodegradability, are very relevant to the environmental occurrence of PCBs. Volatility and water solubility represent potential mechanisms for introduction into and transport within the ecosystem. Biodegradation represents a mechanism for removing PCBs from the environment. Illustrations of the relative significance of these properties for different PCB isomers are evident from the following three examples.

TABLE IV

PHYSICO-CHEMICAL PROPERTIES FOR PCB PRODUCTS

Property	Percent Chlorine 21	42	54
Density (g/ml)	1.19	1.39	1.50
Distillation Range (°C)	275-320	325-366	365-390
Fire Point (°C)	176	None	None
Vaporization Rate (mg/cm²/hr @100°C)	1.74	.338	.053
Water Solubility (ppm)	>.2	.2	.04
Biodegradability*	81	26	15

*Percent degradation/48 hr cycle with semi-continuous activated sludge

Relative volatilities for the PCB components in Aroclor 1016 are indicated in Figure 7 by comparing chromatograms of liquid and vapor composition. The higher numbered components make successively less contribution to the total vapor composition.

Water solubility of Aroclor 1016 components is illustrated in similar fashion in Figure 8. Water saturated with Aroclor 1016 was extracted with hexane and the extract compared chromatographically to an Aroclor 1016 standard. The numbers above significant peaks express the percentage contribution of that peak area to the total area. Earlier eluting, lower chlorinated components are more soluble and contribute more to the water saturated composition. A related study has shown that PCBs leaching from Aroclor 1016 impregnated soils after the equivalent of forty years annual rainfall consist of lower chlorinated biphenyls (4) (Figure 9).

Microbial degradation also affects PCB isomers to different degrees. For example, Figure 10 shows chromatograms depicting Aroclor 1016 composition after exposure to a naturally occuring mixed microbial population for 1/2 hour (above) and 14 days (below). The number above each GC peak indicates the percent biodegradation for that component. These percentages range from 17 to >98 and in general are higher for lower chlorobiphenyls. The exposure was carried out with activated sludge from a domestic sewage treatment facility. The sludge was previously acclimated to a mixture of industrial organic compounds before addition of 3 ppm Aroclor 1016. PCB composition was determined by extracting a representative aliquot of mixed liquor with hexane followed by analysis by gas chromatography using a glass capillary column and electron capture detection.

It is apparent from these examples that introduction of PCBs into the ecosystem by volatility or water solubility would enhance the ratio of lower to higher chlorinated biphenyls in the environment. PCB removal from the environment by either of these mechanisms or by microbial degradation would reduce this ratio. These and related factors combine to make assessment of PCB environmental impact a very complex problem.

In view of the recognized complexity in studying commercial PCB mixtures, it would seem expedient to substitute for the mixture a single isomer product having the desired electrical and physical properties. The environmental properties of this isomer would be much simpler to

characterize and control. However, no such PCB isomer exists. Most PCB isomers are solid crystalline materials when isolated at 25°C. Commercial products are liquids only because of the mutual melting point depression exerted by the PCB components of the mixture.

CONCLUSIONS

Commercial PCB products are mixtures of many different isomers with varying chlorine content. The properties of these isomers, and hence the products, are vastly different and are complex to study. The environmental impact for each product must be accurately assessed and compared to the functional benefit.

REFERENCES

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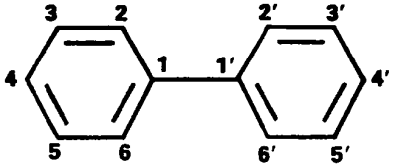
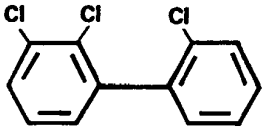
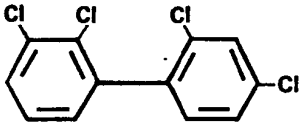
2. R. G. Webb and A. C. McCall, J. Assoc. Offic. Anal. Chem., 55, 746(1972).
3. D. Sissons and D. Welti, J. Chromatog., 60, 15(1971).
4. E. S. Tucker, W. J. Litschgi and W. M. Mees, Bull. Environ. Contam. Toxicol., 13, 86(1975).



BIPHENYL



2,2',3-TRICHLOROBIPHENYL



2,2',3,4'-TETRACHLOROBIPHENYL

Figure 1

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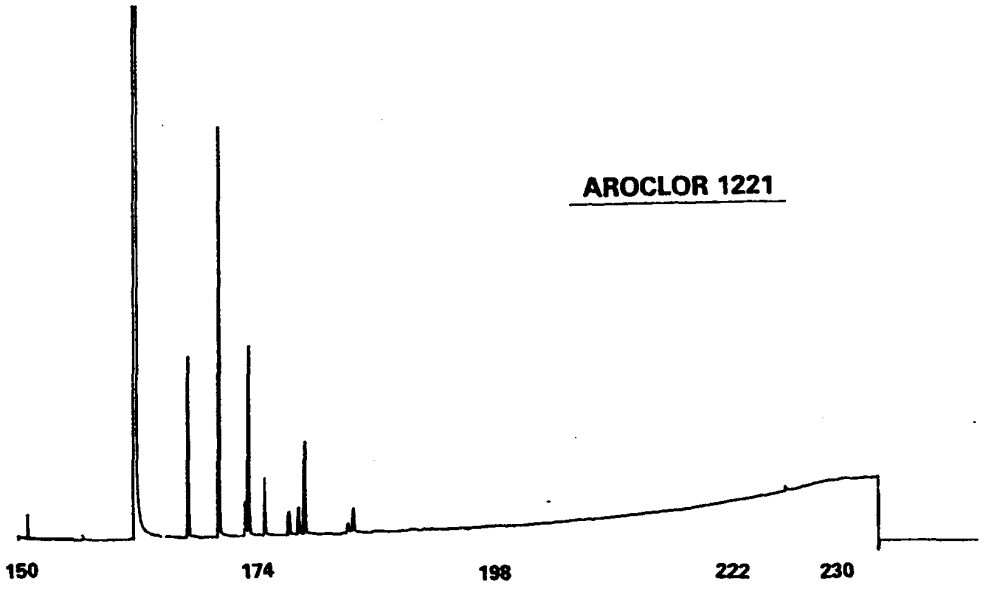

Figure 2

MONS 045160

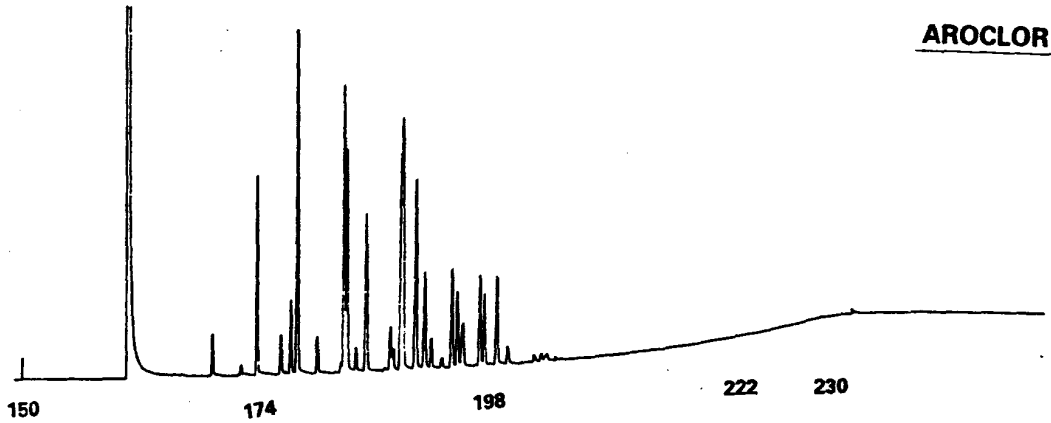

Figure 3

MONS 045161

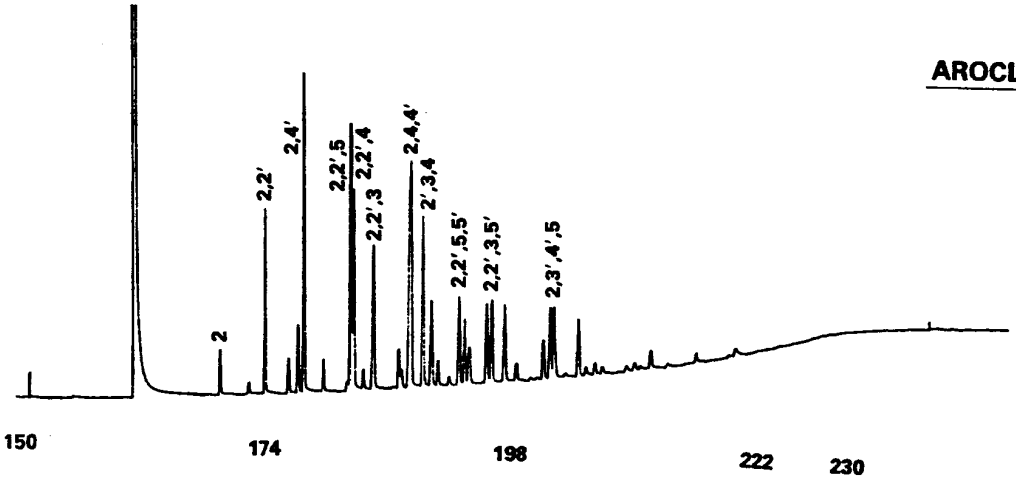

Figure 4

MONS 043162

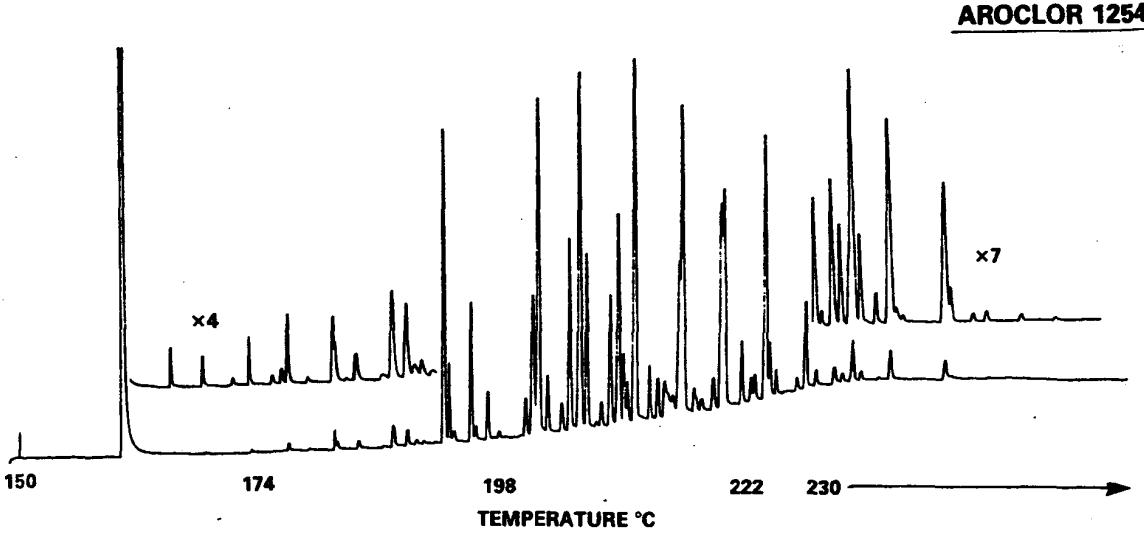

Figure 5

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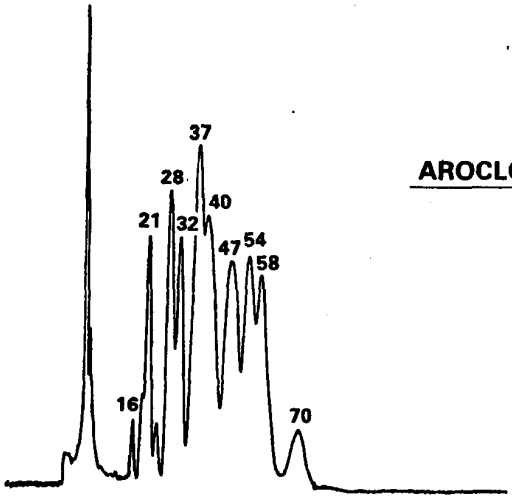

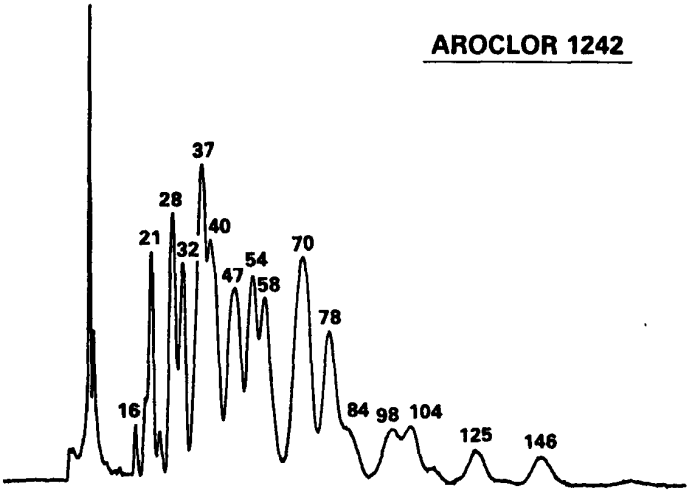

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Figure 6

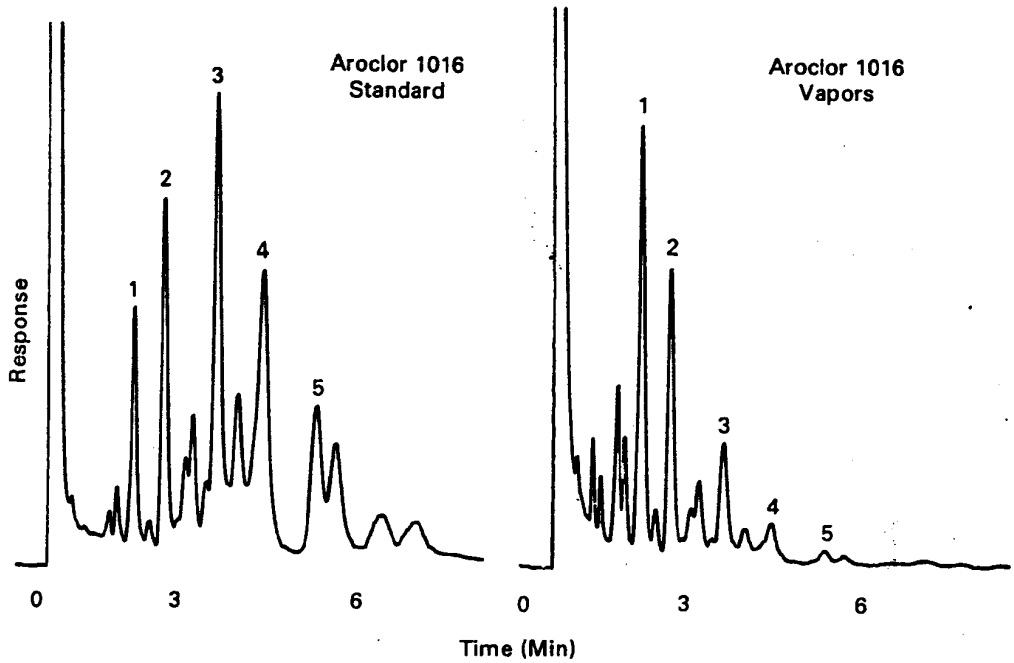

Figure 7

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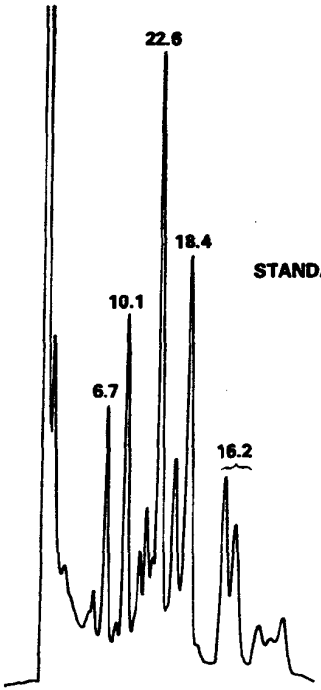
AROCLOR 1016



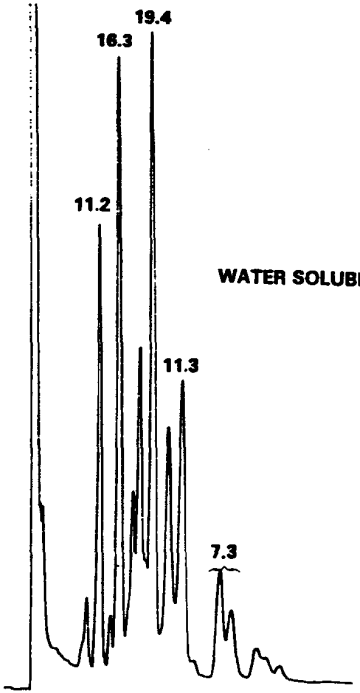


Figure 8

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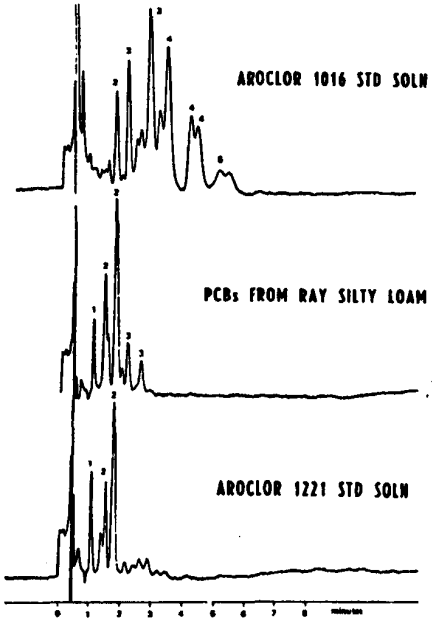
AROCLOR 1016 STD SOLN
PCBs FROM RAY SILTY LOAM
AROCLOR 1221 STD SOLN

Figure 9

AROCLOR 1016 BIODEGRADATION

SEMI-CONTINUOUS ACTIVATED SLUDGE

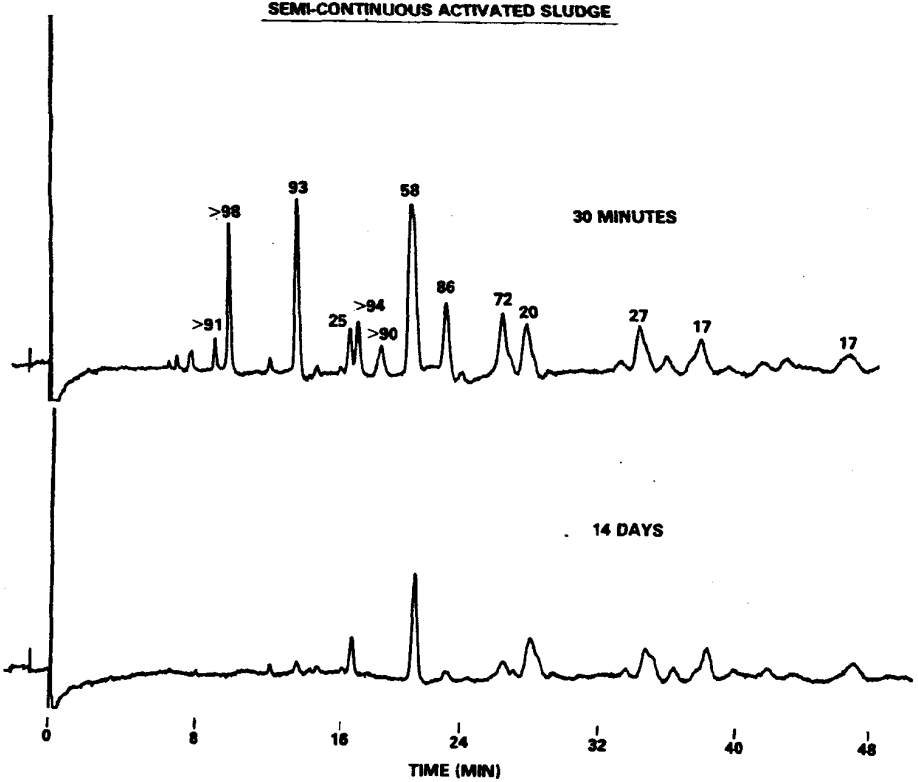

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Figure 10