Electron-Capturing Compounds and Selected Elements in Paper

by

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Many novel solutions to the nationwide problem of solid waste disposal have been proposed. A recent one which has been studied is the feeding of paper products to farm animals such as dairy cattle as a source of cellulose (MERTENS et al. 1971a). Cattle will consume rations containing up to 20 weight % paper and assimilate up to 90% of the dry matter of certain of them such as brown cardboard (MERTENS et al. 1971b). Office paper has also been advantageously incorporated in sheep rations (NISHIMOTA et al. 1969).

It is known that compounds such as the polychlorinated biphenyls (PCB's) are used as dye carriers in specialty printing inks. High concentrations of PCB's have been reported as present in carbonless copying paper (MASUDA et al. 1972). It is possible that these compounds may survive when specialty paper products are regenerated for use in other paper products such as cardboard. Paperboard has been reported to contain PCB-type compounds (ANONYMOUS 1972). These compounds could be transferred to cows' milk or meat as residues. Contamination of food by contact is possible if the paper material becomes part of a food container. Electron capturing peaks in extracts of cereal grains have been traced to the presence of corresponding compounds in cloth bags (LEVI and NOWICKI 1972). Certain metals may also be present in paper as constituents of the ink or as a result of the printing process. Furthermore deep rooted trees may absorb unusual elements from lower soil horizons (ROBINSON et al. 1958) which may then be present in paper. In the work reported a survey of about 300 papers and paper products has been made for the presence of chlorinated organic compounds using gas chromatography with electron affinity and electrolytic conductivity detectors and the combination gas chromatography-mass spectrometry. Metals and other elements in paper were also determined by spark source mass spectrometry.

Experimental

Paper samples were obtained and milled to a fine powder and mixed. The newspapers analyzed issued between December, 1970 and April, 1971. In sampling newspapers and magazines prior to grinding, only the center portions of pages were taken to minimize contamination from human handling near page edges. Twenty five grams of the powdered paper was blended with 200 ml of hexane in an ice bath and the solution was decanted and filtered. The paper was blended twice more with 50 ml portions of hexane and the solutions were filtered, combined, concentrated by rotary evaporation to about 10 ml and made to a final volume of 25 ml. The

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TABLE 1

Electron capturing compounds in various papers

Paper Newspapers (black and white)	No. of peaks
Afro-American (Baltimore, Md.)	4
The Atlanta Journal & Constitution	12
The Atlanta Journal & Constitution - Magazine	14
The Baltimore Sun	13
Boston Globe - Magazine	7
Buffalo Evening News	10
Chicago Tribune	9
Chicago Tribune - Magazine	10
Christian Science Monitor	12
The Clarion-Ledger (Jackson, Miss.)	12
Commercial Appeal (Memphis, Tenn.)	19
Courier Journal (L'ville, Ky.)	14
Courier Journal & Times - Magazine (L'ville, Ky.)	17
The Dallas Morning News	>25
Delta Democrat-Times (Greenville, Miss.)	9
The Denver Post	5
The Denver Post - Sunday Empire	5
The Detroit News	18
The Detroit News - Magazine	21
Discover - Sunday Bulletin (Philadelphia, Pa.)	17
The Evening Bulletin "	>23
Family Weekly - Magazine	33
Greenfield Recorder (Mass.)	15
Herald-American - Empire (Syracuse, N.Y.)	17
Ithaca Journal	15
Journal & Guide (Norfolk, Virginia)	13
Los Angeles Sentinel	13
Los Angeles Times	12
Los Angeles Times - Magazine	10
Manchester Guardian (England)	>23
The Miami News	22
Mid-South - Magazine (Memphis, Tenn.)	23
The Minneapolis Tribune	8
The Minneapolis Tribune - Magazine	10
The Montreal Star - Weekend Magazine	>25
New Brunswick Daily (N.J.)	21
New York Post	7
New York Times	9
New York Times - Magazine	7
The Oregonian (Portland, Oregon)	20
Parade - Magazine (Albany, N.Y.)	10
The Plain Dealer (Cleveland, Ohio)	17
The Plain Dealer - Magazine	16
The Post Standard (Syracuse, N.Y.)	30
Rochester Democrat & Chronicle - Upstate Magazine	21
San Francisco Examiner - Magazine	8

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St. Louis Post Dispatch	7
St. Louis Post Dispatch - Magazine	9
Seattle Post-Intelligence	34
The Sun - Magazine (Washington)	10
Sunday News (New York, N.Y.)	25
Sunday Telegram (Elmira, N.Y.)	>29
The Times Picayune (New Orleans)	10
The Times Picayune - Magazine (New Orleans)	10
The Times Union (Albany, N.Y.)	11
The Washington Evening Star	20
The Washington Evening Star - Magazine	7
The Washington Post	9
The Washington Post - Magazine	11
The Washington Post - Potomac Magazine	15

Newspapers (colored)

The Atlanta Journal & Constitution	21
Boston Sunday Globe	10
Buffalo Evening News	29
Chicago Tribune	30
The Courier Journal & Times (L'ville, Ky.)	20
The Delta Democrat Times (Greenville, Miss.)	23
The Denver Post	>11
The Detroit Sunday News	18
Herald American (Syracuse, N.Y.)	16
The Minneapolis Tribune	14
The Plain Dealer (Cleveland, Ohio)	10
Rochester Democrat & Chronicle	19
St. Louis Post Dispatch	26
San Francisco Examiner & Chronicle	14
The Sun (Baltimore, Md.)	20
The Sunday Bulletine (Philadelphia, Pa.)	21
Sunday Telegram (Elmira, N.Y.)	20
The Times Picayune (New Orleans)	8
The Times Union (Albany, N.Y.)	25
Washington Post	12

Magazines

American Home	28
Feedstuff	>20
Hoard's Dairyman	23
Life	20
Newsweek	23
Playboy	25
Saturday Review	23
Science	18
Successful Farming	17
Sunset	25
U.S. News & World Report	17

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Miscellaneous products

Brown cardboard	26
Brown paper towels	16
Brown paper bags (miscellaneous sources) - 7	>6 - >20
Columbia-Missourian, Newsprint	
black ink	25
without ink	>20
colored ink	18
Computer Paper	>22
Gray cardboard	19
Solka Floc (purified wood cellulose)	23
Wash. State Univ. Hilltopics	>21

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resulting solution was analyzed by gas chromatography using an electron affinity and an electrolytic conductivity detector in the chlorine mode. The column was 6 feet long, packed with 10% DC-200 on Gas-Chrom Q and operated at 200°C. Selected papers were also specifically analyzed for the presence of polychlorinated biphenyl compounds (see Figure 1) using adaptations of the published procedures (GRANT et al. 1971; SNYDER and REINERT 1971) involving sulfuric acid partitioning and column chromatography on silica gel followed by electron affinity gas chromatography. A Perkin-Elmer Model 270 and a Finnigan Model 1015 quadrapole gas chromatograph-mass spectrometer were also used in analysis for these compounds. Following dry ashing of the paper at 400°C certain of the papers were also analyzed for metal content by spark source mass spectrometry using a Model MS-7 (Associated Electrical Industries) instrument with silver as an internal standard.

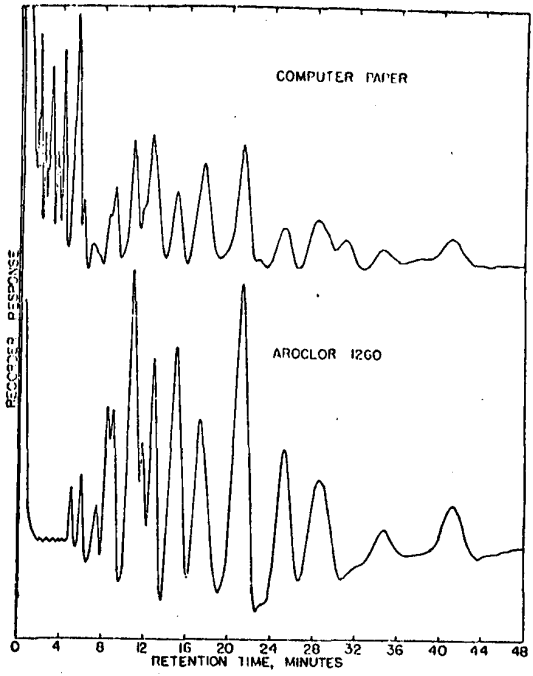
Results and Discussion

Table 1 lists the number of peaks observed in the various paper samples by electron affinity gas chromatographic analysis. "Greater than" a certain number of peaks are indicated when a cluster of them could not be separated. Response by electrolytic conductivity detection indicated the presence of chlorine-containing compounds in these same paper samples. Since these compounds were extracted with hexane, it would indicate that they are fat soluble and therefore would be of concern if they entered animal or human foods. The peaks eluted had retention times up to about 25 minutes. The specific retention times of many of the peaks were identical from one paper sample to another and also identical with various of the isomers found in the polychlorinated biphenyls (1242, 1248, 1254 and 1260) which were concurrently chromatographed. Based on the comparative detector responses of the compounds in the papers surveyed to those of known quantities of PCB standards the papers contained from about 2 to 40 ppm (as equivalent PCB's) of these contaminants.

Table 2 lists analysis of several papers for various elements. The precision of the method is about ±30%. The samples of Ithaca Journal and Buffalo Evening News were black and white while Parade magazine was both black and white and colored. The high levels of certain elements such as antimony, lead and barium in the Parade Magazine paper is noteworthy from a toxicologic standpoint. The presence of lead in the cardboards in substantial concentrations would indicate that it survives the process of regeneration of paper into cardboard. The concentrations of boron and gallium shown may be low owing to possible vaporization losses during sample ashing. Although not listed in Table 2, silicon and sodium were also found as major elements in the papers.

Figure 1 shows chromatograms of computer paper (the injected volume of extract represented 48 milligrams of paper) and 3 nanograms of the PCB, Aroclor 1260. The paper sample was analyzed by electron affinity gas chromatography following preliminary separation procedures (GRANT et al. 1971; SNYDER and REINERT 1971)

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COMPUTER PAPER
AROCLOR 1260
RECORDER RESPONSE
0
4
8
12
16
20
24
28
32
36
40
44
48
RETENTION TIME, MINUTES

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TABLE 2

Selected elements in various papers
(ppm by weight)

	Ithaca Journal	Buffalo Evening News	Parade Magazine	Gray Cardboard	Brown Cardboard	Computer Paper
B	260	3.6	31	550	900	25
Mg	960	600	920	4800	940	400
Al	83,000	500	530	27,000	2000	75,000
K	76	760	1800	330	40	1100
Ca	4400	1000	3900	4300	1900	890
Ti	1000	36	250	620	300	3700
V	3.7	0.58	2.7	5.2	0.15	29
Cr	19	6.0	25	60	3.2	50
Mn	110	190	220	98	120	8.3
Fe	250	200	100	45	70	1100
Co	0.7	0.16	0.52	1.2	3.2	2.5
Ni	3.3	1.7	0.45	4.5	130	14
Cu	15	8.6	9.0	25	5.2	2.1
Zn	110	150	86	690	8.0	9.5
Ga	3.1	0.3	1.8	3.2	1.5	31
Ge	0.18	0.02	0.27	0.12	0.11	0.05
As	0.10	0.02	0.11	0.22	0.04	0.1
Rb	0.41	2.4	1.5	0.30	0.64	3.3
Sr	1.4	0.78	4.3	19	9.6	11
Zr	0.56	0.05	0.68	0.57	0.92	13
Y	0.11	0.01	0.12	0.06	0.006	0.089
Sb	0.1	0.29	6.5	0.01	0.24	0.2
Ba	15	4.6	2.3	0.18	6.6	1.5
Ce	0.21	0.03	0.45	15	0.01	0.21
La	0.26	0.04	0.23	0.01	0.01	0.12
Pb	10	5.0	180	8.3	3.3	0.02

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mentioned earlier specifically designed to isolate PCB's. It is obvious that several of the peaks in the sample of computer paper are similar in retention time to those of Aroclor 1260. Other earlier eluting peaks in the computer paper sample correspond in retention time to those in gas chromatograms of Aroclor 1254. Extracts of grey cardboard were subjected to thin layer chromatography on alumina and eluted with heptane. The Rf value of the spot developed with silver nitrate also corresponded to Aroclor 1254.

Gray cardboard is a composite of regenerated papers from many sources. Logically, then, it is more apt to contain PCB's and other foreign compounds. It was decided to use gas chromatography and mass spectrometry for verification of the presence of PCB's in gray cardboard and computer paper. Both a Perkin Elmer Model 270 and a Finnigan Model 1015 quadrapole gas chromatograph-mass spectrometer and computer system were employed. Samples were extracted and possible PCB's were isolated by adaptations of published procedures (PESTICIDE ANALYTICAL MANUAL 1971). Complete mass spectra were obtained at approximately 3 second intervals on gas chromatographic effluents. Evidence for the presence of PCB's was indicated by the appearance of isotopic chlorine clusters at the appropriate masses for PCB-type compounds. To further enhance sensitivity selective monitoring of the specific PCB chlorine mass clusters was performed and the presence of PCB's was again indicated. The existence of other chlorinated components was evidenced by the appearance of chlorine clusters at masses not corresponding to PCB's. It is possible that other chlorinated aromatic compounds such as the chlorinated naphthalenes (ARMOUR and BURKE 1971) would also be isolated by the procedure (PESTICIDE ANALYTICAL MANUAL 1971). From the preliminary analysis of paper presented here it is obvious that there is a need for caution and further investigation when paper is regenerated for use in food containers or as proposed for use as a cellulose substitute in animal feeds.

Acknowledgements

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