Bull. Environ. Contam. Toxicol. (1993) 50:787-793

Environmental
Contamination
and Toxicology

Volatile Organic Solvents in Correction Fluids: Identification and Potential Hazards

C. N. Ong,[1] D. Koh,[1] S. C. Foo,[1] P. W. Kok,[1] H. Y. Ong,[1] and T. C. Aw[2]

[1]Department of Community, Occupational and Family Medicine, National University of Singapore, Lower Kent Ridge Road, Singapore 0511 and [2]Institute of Occupational Health, Birmingham, United Kingdom

Exposure to organic solvents is widespread in today's environment. The extent of exposure differs, high concentration exposure is being often experienced by workers in uncontrolled factories. Exposure in schools, however, was not an area of concern until recently when glue sniffing was reported to be practiced by children of school going age. The common solvents encountered in schools include paint diluents, adhesives, nail polishers and correction fluids. The abuse of nail polishers and correction inks as substitute for recreational drugs have become popular as they are readily available at supermarkets and stationery shops (Lee, 1990). In the Asian developing countries, the use of correction inks have become popular as they are readily available at supermarkets and stationery shops.

Correction fluids are used to blank out typing error, and are commonly sold as 10 ml bottles of white opaque liquid with an application brush. A large number of school children also use such correction fluids for their school work. There are indications that some manufacturers are increasing the use of more volatile compounds in these fluids to enhance the drying process. As far as we know, there have been no comprehensive study conducted on the hazardous components in correction fluids. This paper reports on an investigation carried out on 20 brands of correction fluids widely used among school children in Indonesia, Malaysia and Singapore.

MATERIALS AND METHODS

All the reagents used in this study were of reagent grade from E. Merck (Germany).

A total of twenty different brands of correction ink commonly used by school children and office workers in Indonesia, Malaysia and Singapore were used for the study. All specimens investigated were brand new and analysis was carried out within one week after purchase. The twenty brands represented what was available in supermarkets and stationary shops in these countries.

Send reprint requests to Dr. C.N. Ong at the above address

Analysis was performed by using the head-space technique. This was carried out by transferring two drops of a well mixed correction fluid into a 2 ml glass gas chromatography vial and sealed with a Teflon faced septum by an open top aluminium seal. After 10 min of equilibrium at room temperature, 4 ul of the head-space air was injected into a gas chromatograph with flame ionization detector for analysis. The head-space technique has been used for several earlier studies on organic solvents such as methyl ethyl ketone (Sia et al, 1991), cyclohexanone (Ong et al 1991) and tetrahydrofuran (Ong, 1991). This technique has been found to yield satisfactory results in the laboratory.

A Hewlett Packard model 5890A gas chromatograph with a methyl silicone gum capillary column (30 m x 0.53 mm I.D., 2.65 um film thickness, model HP-1) was used for the identification and quantification of major volatile components in correction fluids. The carrier gas, N_2 was at 0.7 kg/cm^2, while those of H_2 and air were 1.4 kg/cm^2 and 2.1 kg/cm^2, respectively. The oven temperature was programmed as follows: 50°C for 3 min, followed by an increase at the rate of 50°C/min to 150°C for 3 min to clean the column. The injector and detector temperatures were 100°C and 200°C, respectively. Quantitation was determined with a Hewlett Packard integrator (model 3396A) for retention time and percentage of peak area measurement.

In the confirmation analysis, a HP gas chromatograph 5890 Series II equipped with a 5971A mass selective detector (MSD) and a PONA capillary column (crosslinked methyl silicone gum, 50m x 0.2 x 0.5 um film thickness) was used. Injector and detector temperatures were 150^{o}C and 280^{o}C, respectively. The initial oven temperature was 70^{o}C for 3 minutes followed by an increase of 13^{o}C/min to 220^{o}C. The carrier gas was helium with head pressure at 2.1 kg/cm^2. Splitless injection was used and injection volume was 2 ul of correction fluid head-space air. The ion source temperature for the mass detector was held at 280^{o} C. The column/oven temperature was held from 70-220^{o}C at the rate of 13^{o}C/min. The mass spectra were obtained at 70eV of electron energy, 1.6 kV of electron multiplier voltage. The scan speed was at 2.7 amu/sec.

RESULTS AND DISCUSSION

The major components of volatile organic compounds in the 20 brands of correction fluids were identified. Products from EEC countries usually stated the main component of the correction inks. Eight out of the 20 brands, however, did not provide ingredients nor did they indicate countries of manufacture on the label. Only two of the 20 correction fluids investigated gave brief warnings regarding use.

Figure 1 shows a typical chromatogram of a correction fluid. The appearance of a large number of peaks indicated that different types of organic solvents were used in the manufacturing of correction inks. Our results also indicate that organochloro compounds are the most commonly used solvent for the correction inks. Among the 20 brands analysed 14 were found to contain trichloro or tetrachloro compounds represented 70% of the correction fluid investigated.

Table 1 shows the major components of organic solvent's among the 20 types of correction fluid analysed. It was noted that 1,1,1-trichloroethane (TCE, methyl chloroform) was one of the major components for most of the commonly used fluids. Carbon tetrachloride, n-hexane, methylene chloride and methyl cyclohexane were also detected in significant amounts.

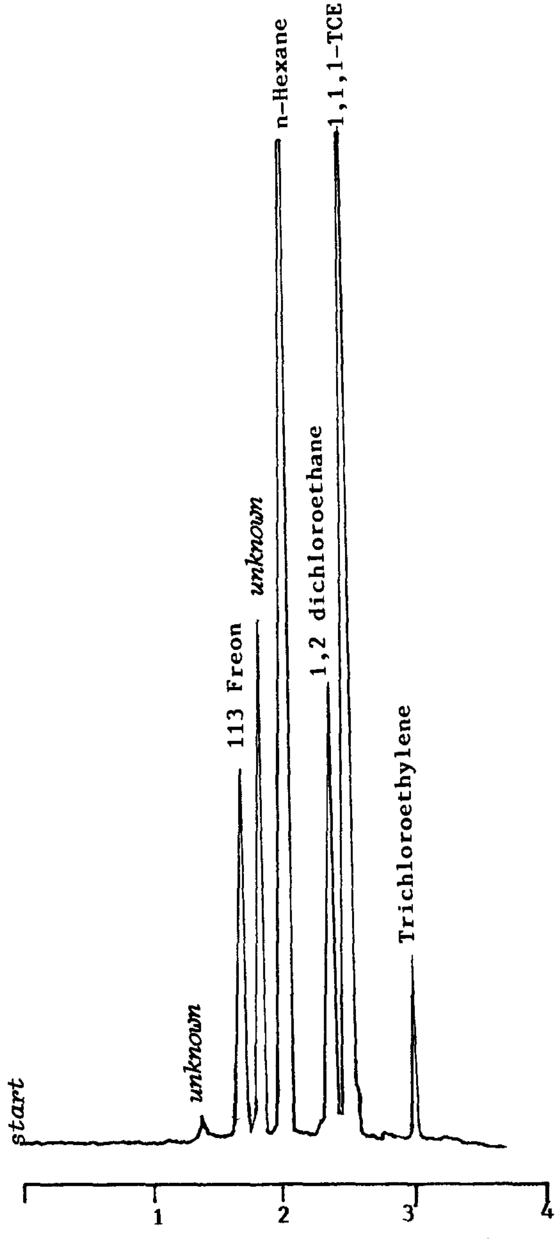

Fig 1. Chromatogam of a typical fluid analysed according to the conditions as described.

The principal effect of organochloro compounds is on the central nervous system (CNS) depression. The symptoms of addicts with over exposure are dizziness, nausea, tingling and drunkenness. Exposure to high concentrations leads to rapid unconsciousness (Torkelson and Rowe 1986).

Table 1. Organic compounds in different brands of correction fluid (percentages by volume of vapour)

Brand Name	Methylene chloride	n-Hexane	111-Trichloro-ethane	Trichloro-ethylene	CFC-113	Methyl-cyclohexane	Carbon tetra-Chloride	Unknown
Flomo (Japan)	50	15						35
Gangy (unknown)						97		3
H & O (Germany)			94	<2				4
Laser (unknown)		35	26	10				29
Nikko (Japan)			1	1		94		4
Nissay (Japan)	25		40			<10		25
Liquid Paper (Australia)	<8		90		<1			
Nikko (Japan)						94		
Pentel (Japan)				<2		98		
Prokil (unknown)			80		17			3
Red Star (unknown)	21				23		52	4
Robot (unknown)			85	2	1		1.5	10
Sakura (Japan)	25	1			25			45
Shadow (unknown)	27	36	<1			2	30	
Star I & II (unknown)	20				24		50	6
Sunny (unknown)	4	32	35		2			27
SW (UK)		16	51	2				21
Tipp Ex (UK)			95	2				3
UNI (Japan)				95		5		

Two of the 20 correction fluids analysed were found to contain high levels (about 50%) of carbon tetrachloride (tetrachloromethane). The spectrum of the specimen is shown in Fig 2. Carbon tetrachloride is a potential hepatotoxic agent in man. The development of fatty liver and centri lobular necrosis can occur after a single, acute high exposure (ACGIH, 1986). This effect is also seen among workers with chronic exposure at low levels. In man, kidney failure may also ensue (Torkelson and Rowe, 1986). In occupational situations, workers who had been acutely exposed to CCl_4 reported symptoms of nausea and abdominal discomfort. Liver cancer in animals and humans have also been reported (O'Donoghue, 1985). It has been classified by the National Cancer Institute and the American Conference of Governmental Industrial Hygienists (ACGIH) as a suspected carcinogen for humans (ACGIH, 1989). The International Agency for Research on Cancer classified carbon tetrachloride as a Group 2B agent, which is possibly carcinogenic to humans (IARC, 1992).

One of the specimens analysed was found to contain about 10% of trichloroethylene. Seven out of the twenty correction inks also contained trace amounts of this compound (Table 1). Depression of the central nervous system is the main effect seen in exposure to trichloroethylene. Commonly noted neurological effects of trichloroethylene exposure include sensory disturbances and anesthesia (Hartman, 1988). Another general property of this hydrocarbon is its ability to cause cardiac arrest when very high concentrations are inhaled. There have been cases reported in Singapore recently that exposure to high concentration of trichloroethylene leads to rapid unconsciousness and death (Tan et al, 1982). Owing to its environmental polluting property, its use in most industrialised countries has been gradually reduced. However, in many Asian developing countries it is still used as a cheap source for commercial solvent.

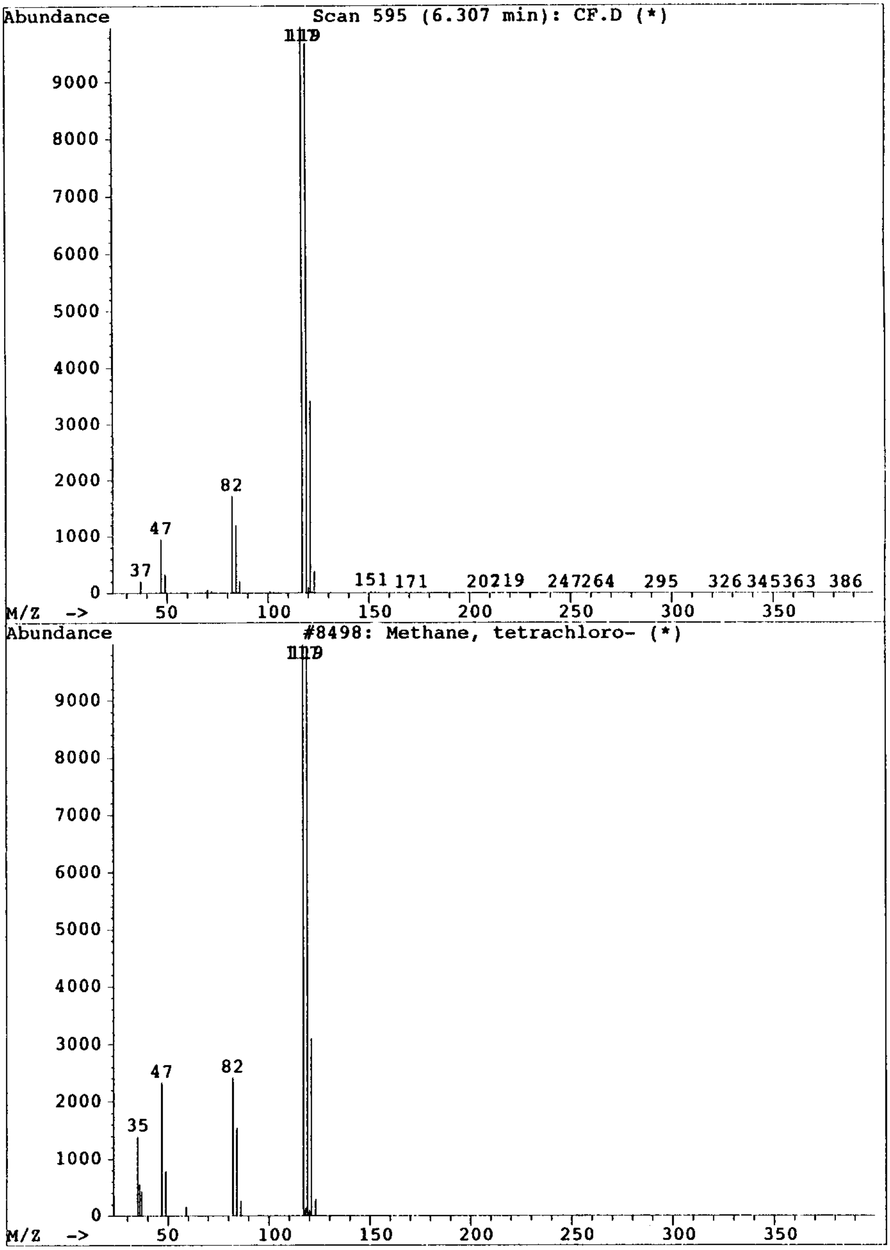

Figure 2 Mass spectra of peaks of the capillary gas chromatograms of a samples which was found to contain high concentration of carbon tetrachloride (tetrachloromethane).

Table 1 shows that 6 out of the 20 brands of the correction ink contained methylene chloride (dichloromethane). Four of them had concentrations over 20%. The main effect of exposure to methylene chloride is as a central nervous system depressant manifesting discoordination and a sensation of drunkenness. Psychomotor performance is decreased with narcosis occurring at high concentrations and irritation of mucous membrane at lower levels (Gamborale et al, 1974). Liver effects included increase in hepatocellular vacuolization with increased multinucleated hepatocytes (McKennen et al 1979). Methylene chloride undergoes metabolic transfer to carbon monoxide and this leads to elevation of carboxyhaemoglobin levels in circulating blood. Therefore, individuals with heart disease are especially at risk when exposed to methylene chloride, because of the hypoxic effect (WHO, 1982). This chemical is currently considered by International Agency for Research on Cancer as a potential human carcinogen (IARC, 1992) and the ACGIH has reduced the threshold limit value for methylene chloride exposure from 200 ppm in 1979 to 50 ppm in 1989 (ACGIH, 1989).

1,1,1-trichloroethane (TCE) appears to be relatively less toxic than the other solvents discussed. The main effect of exposure appeared to be anaesthesia. Occupational exposure to over 200 ppm for up to six months did not cause any significant change in liver function (ACGIH, 1986). However, cardiac effects can occur if exposure are excessive (Torkelson and Rown, 1986).

Normal-hexane was one of the major components for five types of correction fluid analysed. The concentration can be as high as 50% of the total volatile air (Table 1). N-hexane is one of the most toxic members of the alkanes and causes polyneuropathy (Pezzdi et al, 1989). This presents as muscular weakness and sensory impairment in the extremities.

The other components found in the correction fluids were CFC-113, methyl cyclohexane and 2-nitropropane. Recent literatures have shown that CFC-113 can generate vapour sufficient to cause death by cardiac arrhythmia or asphyxiation. NIOSH has requested that all users be brought to attention of its acuity (NIOSH, 1989). Uncontrolled use of the correction ink may therefore pose a significant hazard. Methylcyclohexane was the main component for three of the inks analysed. This compound is considered as the least toxic among those chemicals in the list (Table 1). However, recent publication has indicated that this chemical may potentiate the effects of other toxic agents (Clayton and Clayton, 1986).

Our data here show that several of the solvents present in correction fluids are highly toxic. Adequate control measures have to be considered in order to provide a safe work environment. As more and more chemicals are used in the manufacturing of consumable products, public as well as school children should be informed of the potential toxicity of the chemicals used in correction fluids and health promotion programs can focus on reducing its abuse. Intensive effort should be directed at substituting the use of highly toxic compounds for consumable products.

The wide variety of solvents in correction fluids could be reduced to a smaller number of safer ingredients. In a follow-up study, we noted that water-based correction fluids are now available. Ethanol was the main component found in the water-base correction fluid.

REFERENCES

ACGIH (1986) Documentation of the threshold limit values and biological exposure indices (5th Ed). American Conference of Governmental Industrial Hygienists. Ohio, USA.

ACGIH (1989) Threshold limit values and biological exposure indices for 989-1990. American Conf Govern Ind Hyg. Ohio, USA.

Gamborale F, Anwall BA, Hultgren M (1974) Exposure to methylene chloride. II. Psychological functions. Scan J Work Env Hlth 11: 95-103.

Grasso P (1988) Neurotoxic effects of organic solvents on the nervous system. State Art Rev Occup Med 3: 529-39.

Hartman DE (1988) Neuropsychological toxicology. Permagoon Press, Oxford.

International Agency for Research on Cancer (1992) IARC monographs on the evaluation of carcinogenic risks to humans, IARC, Lyon.

Lee ST (1990). Fear of hazard at school, Straits Times May 16, 1990.

McKennen MJ, Zempel JA and Braun WH (1979) The pharmacokinetics and metabolism of inhaled methylene chloride. Tox Applied Pharmacol 48: A10.

NIOSH (1989) Request for assistance in preventing death from excessive exposure to chloroflurocarbon 113. US Department of Health and Human Services.

O'Donoghue JL (1985) Neurotoxicology of industrial and commercial chemicals. CRC Press, New York.

Ong CN, Chia SE, Phoon WH, Tan KT (1991) Biological monitoring of occupational exposure to tetrahydrofuran. Br J Ind Med 48:616-621.

Ong CN, Chia SE, Phoon WH, Tan KT, Kwok PW (1991) Biological monitoring of exposure to cyclohexanone through the analysis of breath and urine. Scan J Work Environ Hlth 17: 231-236.

Pezzdi G, Barbieri, Ferrante C, Zecchivelli, Foa V (1989) Parkinsonism due to N-hexane exposure. Lancet, i: 874.

Sia GL, Ong HY, Chia SE, Phoon WH and Tan KT (1991) Environmental and Biological monitoring of methyl ethyl ketone. Environ Monitor Assess 16: 423-428.

Tan KJ, Phoon WH (1982) An episode of trichloroethylene poisoning. Ann Acad Med 9: 532-6.

Torkelson TR, Rown VK (1986) Halogenated aliphatic hydrocarbons. In, Patty's industrial hygiene and toxicology. Ed. Clayton GD and Clayton FE, Wiley & Sons, New York. p.3437-3556.

WHO (1982) Environmental Health Criteria 32. Methylene chloride. International Programme on Chemical Safety. World Health Organization.

Received May 23, 1992; accepted December 15, 1992.