J Occup Health 1998; 40: 348–349

Short Communication

Environmental and Biological Monitoring of 2,2-Dichloro-1,1,1-trifluoroethane (HCFC-123)

Shigeru TANAKA[1], Isamu KABE[2], Toru TAKEBAYASHI[2], Yu'ichi ENDO[2], Hiroyuki MIYAUCHI[3], Kazuko NOZI[2], Ken TAKAHASHI[2], Yukio SEKI[1] and Kazuyuki OMAE[2]

[1]Faculty of Hygienic Technology, School of Allied Health Sciences, Kitasato University, [2]Department of Preventive Medicine and Public Health, School of Medicine, Keio University and [3]The Association of Industrial Health

Key words: 2,2-dichloro-1,1,1-trifluoroethane, Chlorofluorocarbon substitute, Environmental monitoring, Biological monitoring, Trifluoroacetic acid

2,2-Dichloro-1,1,1-trifluoroethane (HCFC-123, CAS No. 306-83-2), a colorless liquid with a light ether odor and boiling point of 27.6°C is a substitute for the strong ozone-depleting chlorofluorocarbon, trichlorofluoromethane. Recent case reports clearly indicate that repeated exposure to a high concentration of HCFC-123 causes severe liver damage[1, 2]. This report describes a method of determining HCFC-123 in the environment and the usefulness of trifluoroacetic acid in urine (TFA-U) as a biological monitoring parameter of HCFC-123.

Materials and Methods

HCFC-123 measurement was investigated with a sampling tube containing 400 mg activated charcoal adsorbent (Jumbo Type; Shibata Scientific Technology, Ltd.), Tedlar® bag, (1L, film thickness 50 μm; GL Sciences Inc.), an air sampling pump (PMD-05D; Shibata Scientific Technology, Ltd.), HCFC-123 compressed gas in cylinders calibrated at 101 and 1,114 ppm (Taiyo Toyo Sanso Co., Ltd.) reagents (dichloromethane, sulfuric acid and dimethyl sulfide; Wako Pure Chemical Industries, Ltd.) and gas chromatography (GC, Table 1). The flow rate of the air sampling pump was set at 0.1 liter/min.

To measure the breakthrough time of the sampling tube, 1,114 ppm, 487 ppm or 101 ppm HCFC-123 was continuously passed through the sampling tube until the HCFC-123 concentration in the downstream of the sampling tube exceeded 5 ppm. The desorption efficiency was assessed after 101 or 12 ppm HCFC-123 was sampled for 10 min and desorbed with 2 m*l* dichloromethane for more than 1 h. To determine the storage stability conditions for HCFC-123 samples, the sampling tubes were exposed to 10 ppm HCFC-123 for 10 min, tightly sealed, kept at room temperature (20°C) or in a refrigerator (5°C), and monitored for the HCFC-123 concentration for up to 25 days. Similarly, 12 or 101 ppm HCFC-123 was collected in the Tedlar® bags and kept at room temperature, and the concentration of HCFC-123 was traced for 84 h.

Analysis of TFA-U was performed by the method of Maiorino *et al.*[3] Briefly, urine, sulfuric acid and dimethyl sulfide were mixed in a cooled, tightly capped vial. After the bottle was heated in boiling water for 20 min to form methyl TFA, it was kept at 30°C for 20 min, and then 1 m*l* of the head space gas was injected into GC (Table 1).

As volunteers, four of the authors joined a 6-h field experimental survey executed in a plant to clarify the causal relationship between HCFC-123 exposure and acute liver damage observed in several workers[2, 4]. The HCFC-123 exposure concentration and TFA-U in the four volunteers were measured. Urine was collected before starting the survey, during the survey, 0 and 3–96 h after finishing the survey. The 50-m*l* urine samples were kept in a freezer (− 20°C) until analysis.

Results and Discussion

The HCFC-123 concentration on the GC chart linearly increased to 1,114 ppm with a detection limit of 0.1 ppm. TFA also linearly increased within the range of 1 to 100 mg/L with a detection limit of 1 mg/L. The breakthrough times for the sampling tube were 185 min for the 1,114 ppm HCFC-123 sampling, 280 min for the 487 ppm sampling, and 1,410 min for the 101 ppm sampling. The average weight of HCFC-123 adsorbed on the activated charcoal was 99 mg (n=6, range: 86–119). Generally the breakthrough time of an organic solvent vapor with a low boiling point is short[5], but in the case of HCFC-123

Table 1. Analytical condition of gas chromatograph

	HCFC-123	TFA-U
Apparatus Detector	5890SEIES II FID	G1800A MSD
	Hewlett Packard Co.	
Column	DB-WAXETR (50 m × 0.25 mm film thickness; 1 μm, J&W)	
Temp. Inlet, Detector Oven	 150°C 40°C	 120°C 25°C
Carrier gas Gas flow	Helium 1.0 ml/min	
Mass Range Retention time	– 2.3 min	SIM (59 m/z) 1.3 min

Received Sept 16, 1998; Accepted Sept 28, 1998
Correspondence to: S. Tanaka, Faculty of Hygienic Technology, School of Allied Health Sciences, Kitasato University, 1–15–1 Kitasato, Sagamihara, Kanagawa 228-8555, Japan

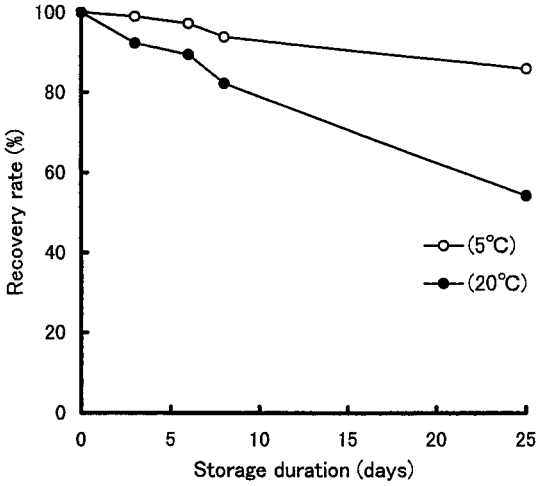

Fig. 1. Effect of the storage stability condition of the sampling tube at room temperature (20°C) and in a refrigerator (5°C).

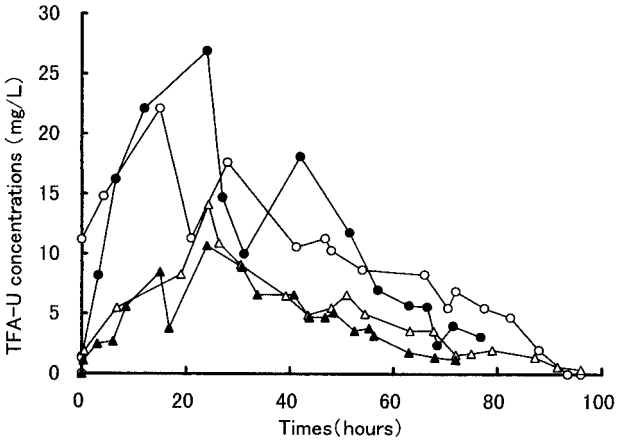

Fig. 2. Changes in TFA-U concentrations in four volunteers. HCFC-123 exposure concentrations for the four subjects were 73.3 ppm, 60.2 ppm, 62.3 ppm, and 66.4 ppm, indicated by a black circle, white circle, white triangle, and black triangle, respectively.

it is long enough for a sampling tube containing activated charcoal to be useful in environmental monitoring. The average desorption efficiencies were 98.5% (n=5, range 95–103) in the 101 ppm experiment and 100.2% (n=5, range 92–105) in the 12 ppm experiment. This indicates that dichloromethane is an appropriate desorption solvent for HCFC-123. The concentration of HCFC-123 adsorbed in the sampling tubes stored at room temperature noticeably decreased, but that of those stored in a refrigerator remained >90% on day 8 and 86% on day 25 (Fig. 1). Therefore, refrigerated storage can be recommended for HCFC-123 adsorbed sampling tubes. The Tedlar bag is also useful for environmental monitoring, in view of the present finding that >95% of HCFC-123 of 12 or 101 ppm remained in the Tedlar® bag 84 h after filling.

The exposure concentrations of HCFC-123 in the four volunteers were 73.3 ppm, 60.2 ppm, 62.3 ppm and 66.4 ppm. Chronologic changes in the TFA-U of the volunteers are illustrated in Fig. 2. Excretion of TFA-U gradually increased after finishing the exposure and reached peak levels about 20–30 h later. The biological half life was estimated to be 25 h (range 23–28), indicating that HCFC-123 is likely to be accumulated in the body day-by-day in workers repeatedly exposed to HCFC-123, and that the optimal time for urine sampling is at the end of the shift. The relationship between the HCFC-123 exposure level and TFA-U was unclear due to the narrow range of exposure levels and the small number of samples. Further observation will be needed to confirm the quantitative validity of TFA-U as a biological monitoring parameter.

References

1) Hoet P, Graf ML, Bourdi M, et al. Epidemic of liver disease caused by hydrochlorofluoro-carbons used as ozone-sparing substitutes of chlorofluorocarbons. Lancet 1997; 350: 556–559.
2) Takebayashi T, Kabe I, Tanaka S, et al. Acute liver dysfunction among workers exposed to 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123): A case report. J Occup Health 1998; 40: 169–170.
3) Maiorino RM, Gandolfi AJ, Sippes IG. Gas-chromatographic method for the halothane metabolites, trifluoroacetic acid and bromide, in biological fluids. J Anal Toxicol 1980; 4: 250–254.
4) Takebayashi T, Kabe I, Tanaka S, et al. Exposure to 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123) and acute liver dysfunction: a causal inference. J Occup Health 1998; 40: 334–338.
5) Tanaka S, Kido S, Seki Y, Imamiya S. Service lives of respiratory cartridges for 46 organic solvent vapors. Jpn J Ind Health 1993; 35: 290–291 (in Japanese).