LETTERS TO THE EDITOR

Analysis of Trace Impurities in Reagent and Technical Grade Trichloroethylene

Key words: Trichloroethylene—Epichlorohydrin—1,2-Epoxybutane—GC-MS

Trichloroethylene (TCE) is one of the most commonly used solvents in industry. Henschler *et al.*¹⁾ have reported that technical grade TCE contained considerable amounts of epichlorohydrin and 1,2-epoxybutane as stabilizers, and these epoxides were highly mutagenic in the Ames test.

Therefore, it is important to reveal trace impurities in TCE used in studies on the toxicity and carcinogenicity of TCE. In this study, we analyzed the trace impurities in reagent and technical grades of TCE commercially available in Japan. Samples of reagent grade TCE were purchased from Wako Pure Chemical Industries Ltd., Kanto Chemical Co. Inc., and Kokusan Chemical Co. Inc. Samples of technical grade TCE were obtained from Asahi Glass, Ltd. Trace impurities in TCE were analyzed and determined by gas chromatography and identified by gas chromatography-mass spectrometry. Analysis and determination of trace impurities in TCE were carried with a Hewlett-Packard Model 5880A gas chromatograph equipped with a flame ionization detector. The column was 4 ft × 2 mm ID glass packed with 20% PEG-20M on gaschrom Z, 80–100 mesh. For the column temperature, a multi-level temperature program was used. The initial oven temperature was 80°C. Upon injection, this temperature was maintained for three minutes and then increased to 200°C at 20°C/min. After four minutes at 200°C, the temperature program was stopped. Injector and detector temperatures were 220°C and 270°C, respectively.

One μ l of TCE sample was directly injected into the gas chromatograph. Concentrations of trace impurities in TCE were calculated by using the response factors of each impurity, which had been determined previously using a known amount of authentic compounds. For identification of trace impurities in TCE, a Finnigan Model 1015D gas chromatograph quadrupole mass spectrometer was used and operated in a chemical ionization mode using methane as a reagent gas. The gas chromatograph conditions were the same as described above. The mass spectrometer conditions were held constant throughout: methane reagent gas at a flow rate of 30 ml/min; temperature of the ion source, 50°C; the ionization energy, 100 eV; the emission current, 350 μ A; electron multiplier voltage, 1400 V. Mass spectra were recorded exponentially over the m/e range of 70 to 300 at a scan rate of 0.1 sec/mass range. One μ l of TCE sample was injected directly into the GC-MS. Mass spectra of each GC peak were recorded. The chemical

Fig. 1. Gas chromatograms of typical TCE samples [Reagent grade (B. Co.-G.R.) and technical grade (vapor agent) in Table 1].

Table 1. Impurities in reagent and technical grade compounds

Compound	Proportion of impurities in trichloroethylene (% , W/W)							
	Reagent grade						Technical grade	
	A. Co.		B. Co.		C. Co.		Liquid agent	Vapor agent
	G.R.	E.P.	G.R.	E.P.	G.R.	E.P.		
Triethylamine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.009
1,1,1-Trichloroethane	0.013	0.019	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Carbon tetrachloride	0.015	0.010	0.077	0.113	0.016	0.060	0.055	0.042
Benzene	n.d.	n.d.	0.014	0.016	0.004	0.002	0.009	0.004
Trichloroethylene	99.920	99.850	99.803	99.711	99.937	99.874	99.775	99.599
1,2-Dichloroethane	0.020	0.045	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Epichlorohydrin	0.047	0.050	0.052	0.094	0.013	0.011	0.099	0.301
1,1,2-Trichloroethane	0.009	0.023	0.042	0.045	0.025	0.047	0.042	0.032
1,1,2,2-Tetrachloroethane	n.d.	n.d.	0.003	n.d.	0.001	n.d.	nd.	n.d.
Unknown substance	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.011
Phenol	0.004	0.003	0.009	0.021	0.004	0.006	0.021	0.002

A Co., B. Co. and C. Co. are the fictitious names of companies producing TCE.

G.R.: Guaranteed reagent. E.P.: Extra pure. n.d.: not detected (less than 1 $\mu\text{g/ml}$).

Liquid agent: TCE used for liquid degreasing. Vapor agent: TCE used for vapor degreasing

ionization mass spectra of trace impurities were determined and compared with the mass spectra from approximately 0.2 mg samples of the authentic compounds. The substances were identified from their mass spectra, and the identifications were confirmed by comparison with the spectra of authentic compounds.

Fig. 1 shows the gas chromatogram of typical TCE samples. Six to eight impurities were found for the reagent grade TCE and the technical grade TCE. Each impurity was identified by GC-MS. The proportion of each impurity was calculated by using the response factor. The results are listed in Table 1. The following impurities have been identified: triethylamine, 1,1,1-trichloroethane, carbon tetrachloride, benzene, 1,2-dichloroethane, epichlorohydrin, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, and phenol. Triethylamine, epichlorohydrin and phenol are used as stabilizers.²⁾ The other impurities have been reported as components in the manufacturing processes of TCE.²⁾ Benzene may be an impurity in TCE produced by the acetylene-based process,³⁾ while 1,1,1-trichloroethane and 1,2-dichloroethane may arise from the ethylene-based process.²⁾

The proportion of all identified impurities was in the range of 0.1–0.3% for the reagent grade and 0.3–0.4% for the technical grade TCE. 1,2-Epoxybutane was not detected in any of these samples. Epichlorohydrin was contained at the level of 0.3% in the vapor agent of technical grade TCE, although it was less than 0.1% for the reagent grade TCE.

Thus, TCE used in Japan also contained considerable amounts of epichlorohydrin, and the amounts differed according to the manufactures and grades of TCE. Therefore, it is necessary to pay sufficient attention to the impurities in TCE used in studies⁴⁾ on the carcinogenicity and toxicity of TCE.

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