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GAS CHROMATOGRAPHIC DETERMINATION OF TETRAMETHYLSUCCINONITRILE IN POLY(VINYL CHLORIDE) PRODUCTS IN CONTACT WITH FOOD

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SUMMARY

A method is described for the determination of tetramethylsuccinonitrile (TMSN) in poly(vinyl chloride) (PVC) products in contact with food. TMSN was extracted from PVC with dichloromethane, steam distilled, extracted from the distillate with dichloromethane, then determined with a gas chromatograph equipped with a nitrogen–phosphorus detector and a 6-ft. glass column packed with Chromosorb W coated with 5% Thermon 1000 plus 0.5% phosphoric acid. Recoveries between 98.3 and 100.6% were obtained in the range of 0.5–12.5 ppm of TMSN by the use of nitrobenzene as an internal standard. The detection limit was 0.05 ppm of TMSN in 1 g of PVC products. The highest residue to TMSN found in PVC products in contact with food was 13.9 ppm.

INTRODUCTION

Tetramethylsuccinonitrile (TMSN, tetramethylbutanedinitrile) is the major decomposition product of 2,2′-azobisisobutyronitrile[1,2] which is used as a forming agent in the production of plastics or as a catalyst for the polymerization of vinyl compounds such as vinyl chloride[3,4]. It is known to have acute toxicity; LD_{50} is 18 mg intraperitoneal (i.p.) per kg body weght in mice[5], and the lethal function in hamsters is considered to be the central neurotoxicity[6].

Nevertheless, few analytical studies of residual TMSN in plastics have been reported. Mandik and Culkova[7] reported an analytical method for TMSN in polystyrene using gas chromatography (GC) and flame ionization detection (FID). The sample was dissolved in carbon disulphide and the detection limit was 5 ppm. This method, however, could not be applied to poly(vinyl chloride) (PVC) products because of its low sensitivity and the presence of many interfering peaks near the retention time of TMSN.

The present paper describes a clean-up method for extracts obtained from PVC and a sensitive GC method for the determination of TMSN. The method was used to determine residual TMSN in PVC products in contact with food.

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EXPERIMENTAL

Apparatus

An Hewlett-Packard Model 5711OA gas chromatograph, equipped with a nitrogen–phosphorus detector, was used with a Shimadzu Chromatopac C-R1A integrator. The coiled glass column (6 ft. × 2 mm I.D.) was packed with Chromosorb W AW DMCS (80–100 mesh) coated with 5% Thermon 1000 plus 0.5% phosphoric acid.

The steam distillation apparatus with ground-glass joints was almost the same type as that described in ref. 8. The distillation flask had a volume of 100 ml. Biotron BT10 20 3500 was used to homogenize the samples.

An high-performance liquid chromatograph Model L-2000 (Yanagimoto) equipped with an ODS-A column (250 mm × 4.6 mm I.D.) and a gas chromatograph–mass spectrometer Model JMS-DX300 (Jeol) equipped with a Carbowax 20M column (10 m × 0.530 mm I.D.) were used for clean-up and confirmation of TMSN, respectively.

Reagents

All solvents and reagents were reagent grade. TMSN (98% pure) was obtained from Tokyo Chemical Industry (Tokyo, Japan).

Samples

Food packages and a wrapping film made of PVC were obtained from markets in Tokyo.

Standard and internal standard solutions

TMSN and nitrobenzene (99.5% pure) (each 100 mg) were weighed into separate 100-ml volumetric flasks, dissolved with methanol and made up to 100 ml. Both solutions (1000 μg of TMSN or nitrobenzene per ml) were used as stock solutions, and were stable for at least 1 month in a refrigerator. These solutions were diluted in methanol to definite concentrations before use. The diluted solutions of TMSN were used as standard solutions and those of nitrobenzene were used as internal standard solutions. For the recovery test, the stock solution of TMSN was diluted in dichloromethane to definite concentrations.

Preparation of test solutions

Samples were cut into small pieces. A 1-g amount of the pieces was put into a 50-ml centrifuge-tube and 20 ml of dichloromethane were added. After 10 min, the mixture was homogenized with the homogenizer for 30 s and then left to stand for 10 min. Methanol (20 ml) was added to the homogenate and the mixture was centrifuged at 2000 rpm (700 *g*) for 5 min. The supernatant was transferred to a round-bottom flask. The pellet in the centrifuge-tube was suspended with 20 ml of dichloromethane and the suspension was left to stand for 10 min. Methanol (20 ml) was added to the suspension and the mixture was centrifuged for 5 min. The supernatant was added to the former extract. The solvent was evaporated to 5–7 ml under reduced pressure at 30–35°C. The concentrate was transferred to a distillation flask with 2 ml of dichloromethane, and 10 ml of water and 3 g of sodium chloride were added. The mixture was steam distilled till 70 ml of distillate including organic solvents were obtained. A definite amount of nitrobenzene, usually 1 ml of the 25 ppm solution, was added to the distillate as the internal standard. The mixture was shaken with 50 ml of dichloromethane. The extraction was repeated two more times with 30 ml of dichloromethane. The solvent layers were pooled, dried with 2 g of anhydrous sodium sulphate and concentrated to 5–7 ml under reduced pressure at 30–35°C. The extract was further concentrated to a definite volume, usually 1 ml, under a stream of nitrogen gas. This solution was used for GC. In the recovery test, a definite amount of TMSN in dichloromethane was added after the sample had been weighed and placed into a centrifuge-tube.

Determination

TMSN was determined by GC under the following conditions: nitrogen carrier gas, 45 ml/min; hydrogen, 3 ml/min; air 100 ml/min; injection port, 150°C; column, 125°C; detector, 250°C; injection volume, 2 μl. TMSN and nitrobenzene appeared at retention times of 3.5 and 4.5 min, respectively. All results were calculated as the mean ± S.D. of three experiments.

Confirmation

To confirm TMSN, the solution for GC was obtained by the method described with 10 g of sample, and was concentrated to 0.2 ml. The concentrate was subjected to high-performance liquid chromatography (HPLC), eluting with 50% methanol at the flow-rate of 0.78 ml/min. The fraction eluted between 5.5 and 6.5 ml which corresponded to the retention volume of TMSN was shaken with 10 ml of dichloromethane. The dichloromethane layer was dried with a small amount of anhydrous sodium sulphate and concentrated to 0.1 ml under a stream of nitrogen gas. A 5-μl portion of the concentrate was injected for gas chromatography–mass spectrometry. The conditions were as follows: ionization voltage, 70 eV; carrier gas (helium), 15 ml/min; column temperture, 70°C for 4 min, then raised to 130°C at 4°C/min.

RESULTS AND DISCUSSION

Using 5% Thermon 1000 plus 0.5% phosphoric acid as the liquid phase in GC, sharp peaks of TMSN and nitrobenzene were obtained. A similar chromatogram was observed with 5% polyethylene glycol 20M, but on Amipack 124, 3% OV-17, 5% polyethylene glycol plus 1% potassium hydroxide, Chromosorb 101 or 5% Thermon 1000 the peaks were not as sharp. A linear response on the column packed with 5% Thermon 1000 plus 0.5% phosphoric acid was observed between 0.1 and 5 ppm of TMSN: $y = 0.2598x - 0.0003$, $r = 0.9999$, where y = peak area of TMSN relative to that of 25 ppm of nitrobenzene as an internal standard, x = ppm of TMSN and r = correlation coefficient. The detection limit of TMSN was 0.05 ppm in GC.

The method recommended[4] for the determination of TMSN in work-place air is GC with FID. Biber and Fales[9] developed an analytical method for TMSN in heptane using capillary column GC; the detection limit was 0.05 ppm using nitrogen–phosphorus detection (NPD), although application to plastic products was not reported. Mandik and Culkova[7] used GC–FID for the determination of TMSN

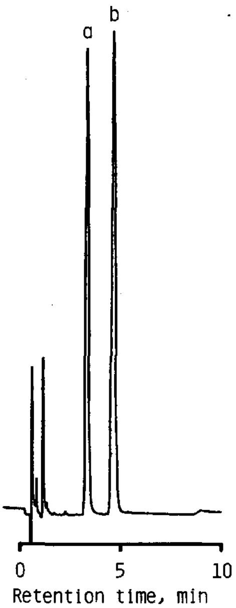

Fig. 1. A typical gas chromatogram of the extract obtained from a PVC product. Peaks: a = tetramethylsuccinonitrile; b = nitrobenzene (internal standard).

in impact-resistant polystyrene, and reported that the detection limit was 5 ppm. These two methods are direct injection methods, *i.e.*, the heptane solution of TMSN or carbon disulphide solution of PVC was used for GC, and were not subjected to extraction or any other pretreatment for purification.

With PVC products, TMSN in dichloromethane extracts could not be determined by direct injection because of the presence of many interfering substances on

TABLE I

CONTENTS OF TETRAMETHYLSUCCINONITRILE IN PVC PRODUCTS IN CONTACT WITH FOOD, AND RECOVERY TESTS

Sample	*TMSN content** *(μg/g)*	*TMSN spiked (μg)*	*Found (μg)*	*Recovery** *(%)*
Case 1	1.27 ± 0.05	1.0	2.27 ± 0.05	100.0 ± 4.7
2	9.79 ± 0.92			
3**	13.94 ± 0.07	12.5	26.27 ± 0.39	98.6 ± 3.2
Film 1	n.d.***			
Cup 1	0.06 ± 0.05	0.5	0.55 ± 0.02	98.0 ± 3.5
2	7.25 ± 0.05	5.0	12.28 ± 0.19	100.6 ± 3.9

* Mean ± S.D. ($n=3$).
** Confirmed by GC–MS.
*** Less than 0.05 ppm.

the chromatograms, despite the use of NPD. Most of these substances were removed by steam distillation of the dichloromethane extract, and no peak was observed at the retention time of the internal standard. A typical gas chromatogram is shown in Fig. 1.

Recoveries of TMSN by the proposed method were between 98.3 and 100.6% (Table I). Recoveries were reduced by dryness of the extracts when the solvent of dichloromethane extracts obtained from PVC and from steam distillate was evaporated; then the concentration of the extracts was stopped at about 5 ml. The amounts of TMSN spiked in the recovery tests were roughly the same as the TMSN content in the samples, except for sample Cup 1 where the content of TMSN was almost the same as the detection limit. The recoveries and standard deviations were not affected by the amount of TMSN.

The residual concentrations of TMSN in food packages made of PVC are shown in Table I. The concentrations of TMSN ranged from n.d. (less than 0.05 ppm) to 13.9 ppm. In general, the concentrations were lower than those in polystyrene, between n.d. (less than 5 ppm) and 85 ppm[7].

TMSN in PVC product Case 3 was confirmed by the coincidence of the GC and HPLC retention times with that of authentic TMSN and by the mass spectrum.

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