

Detection of Tetramethylsuccinonitrile in Food Packaging Containers of Plastics

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Tetramethylsuccinonitrile (TMSN) was determined in plastic products in contact with food. TMSN was extracted from plastic products with dichloromethane, steam distilled, extracted from the distillate with dichloromethane and determined with G.L.C. using nitrogen-phosphorus detector. TMSN was detected positive in 14 samples out of 35 samples. The resins in which TMSN was detected were polyacrylo nitrile (PAN), polyvinyl chloride (PVC) and polymethyl methacrylate (PMMA). The highest frequency of detection of TMSN was observed in PMMA (158 µg/g).

INTRODUCTION

Aromatic and aliphatic nitriles are widely used in manufacturing of plastics. 2,2'-Azo bis-isobutyronitrile (AIBN) is used as a catalyst in production processes of various kinds of resins, such as polyvinyl chloride (PVC), polystyrene and acrylonitrile copolymer. During the processing AIBN is decomposed into tetramethyl succinonitrile (TMSN) at 90–100°C. The potent acute toxicity of TMSN has been well established²⁻⁴. The use of packed food items in India and abroad is increasing rapidly and plastic food containers and other plastic packaging materials for packed food is being extensively used these days. A few analytical studies of residual TMSN in plastic in contact with food have been reported⁵. The present paper describes the results of determination of residual concentration of TMSN in plastic products made of various kinds of resins used for making the food containers and other food packaging material and to assess the present market status.

EXPERIMENTAL

Food containers and packaging materials made of plastics were obtained from market. The plastic products material taken in the present study are polycarbonates (PC), styrene-acrylonitrile resin (SA), poly-methylmethacrylate (PMMA), polyacrylonitrile (PAN), polyethylene (PE), polyvinyl chloride (PVC) and polyethylene terephthalate (PET).

Preparation of test solution

The method described by Ishiwata *et al.*⁶ was followed with some modifications. For dichloromethane in soluble plastics 20 mL of methanol was added to homogenate mixture. This was centrifuged at 2000 rpm for 10 min. Supernatant was evaporated to 5–7 mL under reduced pressure at 30–35°C. The concentrate was transferred to a distillation flask with a small portion of dichloromethane and 10 mL of water and 10 g of sodium chloride was added.



For making the solution of dichloromethane soluble plastics, 1 g of sample was added to a steam distillation flask with 10 mL of dichloromethane after dissolution of 10 mL of water and 10 g of sodium chloride.

The mixture was steam distilled until 100 mL of distillate had been collected. A known amount of nitrobenzene was added to distillate as an internal standard and mixture was shaken with 50 mL of dichloromethane. The extraction was repeated twice with 30 mL of dichloromethane and solvent layers were combined, dried with 5 g anhydrous sodium sulphate and concentrated to 1 mL.

The TMSN was determined by GC-NPD under the following condition. Nitrogen carrier gas 50 mL/minute; hydrogen 3 mL/min; air 100 mL/min; injection port temperature 250°C; column temperature 125°C, detector temperature 250°C. Experiments were carried out in triplicate and the results are presented as mean \pm S.D.

Recovery test

TMSN in known amount was added to dichloromethane suspension of sample and recovery of TMSN was estimated.

RESULTS AND DISCUSSION

The method for determination of TMSN was applicable to all kinds of samples in the study at the level of 0.1 μ g/g of plastic.

The recoveries of TMSN were between 96–98.2% from PC. The recovery of TMSN was between 95.2–99.1% from PE, which was one of the dichloromethane insoluble samples. The recoveries were between 93–97% from PMMA, which was soluble in dichloromethane and contained TMSN. In all other samples the recoveries were comparatively low. These results are slightly different from the studies of Ishiwata *et al.*⁵. Analytical gas chromatogram of the test solution obtained from PMMA is shown in Fig. 1. During steam distillation dichloromethane was distilled first and then polymer dissolved in dichloromethane get precipitated in distillation flask. However, recoveries of TMSN for dichloromethane soluble plastic were not affected by precipitation of polymers, which is also clear from the result that TMSN was not retained in precipitated polymer.

No peak was observed, at the time corresponding to the retention time of nitrobenzene used as an internal standard substance, in the chromatogram of test solution of samples without nitrobenzene. In case of PET products many peaks appear within 5 minutes after the injection of test solution. So it was not possible to identify the peaks of TMSN and nitrobenzene.

TMSN was detected in 14 samples of plastic products among the 35 samples studied. Out of 14, in 3 samples of PET, concentration could not be ascertained. The highest frequency of detection of TMSN was observed in PAN *i.e.*, 4 out of 5 samples were TMSN positive.

The highest concentration of TMSN was observed in PMMA and lowest concentration was detected in PC. The highest concentration of TMSN in the present study was higher than those in previous study of Ishiwata *et al.*⁶ (523 ± 0.30 μ g/g). TMSN was not detected in any sample of PET. Migration of

TMSN from PVC into olive oil has been reported to occur in accordance with the formula

$$Y = 0.08786t - 5.696$$

where Y is the concentration ($\mu\text{g/mL}$) of TMSN in olive oil and t is temperature between 80 and 140°C when PVC product containing 523 $\mu\text{g/g}$ of TMSN is used; Ishiwata *et al.*⁶. However, as the temperature 80°C is higher than the softening point of PVC product, no migration of TMSN has been reported into water, 4% acetic acid, 29% ethanol or olive oil when the PVC product is treated at 60°C for 30 min.

Although in another case the possibility of migration of TMSN into food in contact of plastic cannot be ignored. It was estimated in the present study that in food stimulating solvent under the condition of 60°C for 1 h, concentration of TMSN migrated was approx. 4.6 $\mu\text{g/mL}$. This was observed in case of TMMA showing highest concentration.

Result presented here clarified the carrying over of TMSN, a decomposition product of 2-2'-azo-bis-isobutyronitrile into final product of plastic products. However the migration of TMSN in food and food simulating solvents in contact of these plastic products demands further study.

TABLE-1
TMSN IN FOOD PACKAGING CONTAINER MADE OF PLASTICS

Material	Concentration of TMSN $\mu\text{g/g}$				
	1	2	3	4	5
PC	0.2	nd	nd	nd	nd
PMMA	18	658	nd	nd	nd
PAN	12.6 \pm 6	nd	18	6.3	11.2
PE	nd	nd	0.8	7.1	nd
PVC	21.2 \pm 0.4	nd	nd	0.8	nd
PET	nd*	nd*	nd*	nd	nd
SA	nd	nd	nd	nd	nd

Results are shown as mean \pm S.D. of triplicate experiment.

*Detected but concentration could not be determined by this method.

TABLE-2
RECOVERY TEST OF TMSN

Material	Spiked μg	Content $\mu\text{g/g}$	Rec. %
PC	0.2	10.0	98.2
PMMA	650.0	658.0	97.0
PAM	18.0	20.0	89.9
PE	7.1	10.0	99.1
PVC	21.2	20.00	88.9
PET	nd	10.0	89.0
SA	nd	10.0	85.8

Results given are maximum values of recovery percentage.

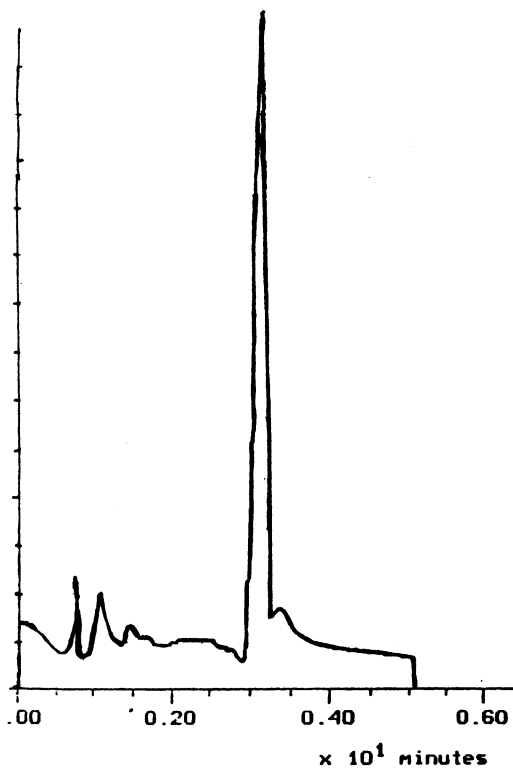


Fig. 1. Gas chromatogram of TMSN

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