Bull. Environ. Contam. Toxicol. (1986) 37:207–212

Environmental
Contamination
and Toxicology

# Residual Styrene Monomer in Chilean Foods by Headspace Gas Chromatography

I. Santa María, J. D. Carmi, and A. G. Ober*

Departamento de Quimica, Facultad de Ciencia, Universidad Federico Santa Maria, Casilla 110-V, Valparaiso, Chile

The harmful effects of residual monomers in polymers used in contact with foodstuffs have prompted legislative authorities in many countries to take action to set limits to their levels in plastic articles and in foods (Council Directive EEC 1978; HM Stationary Office 1978). In Chile unfortunately, there are no regulations in this respect, and concerned about the possible health effects on the population, we are studying the residual monomer content of foods packaged in polymeric materials.

Styrene is a widely used monomer in the food-contact packaging polymers in the world, especially in packaging for fresh meat and poultry, fresh fruits and vegetables, cottage cheese and many other dairy products. Styrene has a toxic effect on the liver, acts as a depressant on the nervous system, and causes neurological impairment (Harkonen et al. 1978; Veretinskaya et al. 1978).

Residual styrene in foods has been determined by several methods which include hexane and methanol extraction-distillation (Brun et al. 1977), azeotropic distillation followed by reverse phase liquid chromatography (Gawell and Larson 1980), and headspace gas chromatography (Steichen 1976; Whithey and Collins 1978; Varner et al. 1983). This last method has been specified by a EEC Directive to be the official method for residual monomer determination in plastics and foodstuffs (Council Directive EEC 1978).

This paper deals with the headspace gas chromatographic determination of residual styrene in Chilean foods packaged in polystyrene and that are normally consumed by the population.

## MATERIALS AND METHODS

All the solvents and reagents used were analytical grade or equivalent. Styrene monomer, 99%, was obtained from BASF-Chile, and N,N-Dimethylacetamide (DMA), 99%, from Merck.

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*Correspondence and reprint requests.

Table 1. Food packaging polymers used in Chile.

| | Polymer types | | | | | | |
|---|---|---|---|---|---|---|---|
| Food | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Chili sauce | | X | | | | | |
| Cottage cheese | X | | X | | | | |
| Dairy cream | | X | | | | | |
| Fresh meat | X | | X | | | | |
| Honey | | X | | | | | |
| Jam | | X | | | | | |
| Jelly | | | X | | | | |
| Margarine | | X | | X | | | |
| Mousse | | | X | | | | |
| Oil and vinegar | | X | | X | | | |
| Pickles | | | X | | | | |
| Pudding | | | X | | | | |
| Sausage | | | X | | | X | X |
| Soft drinks | | X | | X | X | | |
| Sweet milk dessert | | X | X | | | | |
| Yoghurt | | | X | | | | |

(1) Polypropylene; (2) Polyethylene; (3)Polystyrene; (4) Polyvinyl chloride; (5) Polyethylene terephtalate; (6) Cellulose; (7) Polytetrafluoroethylene.

The food samples were purchased from local area stores. The range of samples included in this study were a new type of yoghurt with strawberry jam, recently appeared in our market, vanilla pudding with caramel, strawberry mousse, and raspberry jelly. Six samples of each type of food were purchased and stored refrigerated till their analysis, which were performed before the manufacturers recommended durable lifetime for the foodstuffs. The residual styrene level was determined both in the food and in the polystyrene packaging.

The gas chromatograph used in this work was a Perkin-Elmer F-33 equipped with a flame ionization detector(FID). A 6' x 1/8" s.s. column packed with 5% Hallcomid M-18 on Chromosorb W AW (80-100 m) was used for the chromatographic analysis. A second column, 6' x 1/8" s.s. tubing packed with Chromosorb 101 was used to confirm the styrene peak identity on the chromatograms.

Glass vials (30 ml) equipped with septa and aluminum sealing caps were used to contain the samples and calibration solutions. These vials, septa, and caps were purchased from Supelco Inc. (U.S.A.).

The styrene calibration standards were prepared by dissolving a weighted portion of styrene in septum-sealed vials containing measured aliquots of DMA. The vials were heated to 40 C to assist the dissolution of the standard sample and then cool down to room temperature. Aliquots of the standard monomer solution (10,30, 50, and 80 ul) were injected into the sample solutions using a 100 ul syringe (Hamilton Co.). A 0.02 ug/ul standard solution was used

Table 2. Residual styrene monomer content in pudding, yoghurt, and their packagings (ppm).

| | Pudding | | | Yoghurt | | |
|---|---|---|---|---|---|---|
| Sample | Days | Food | Pack. | Days | Food | Pack. |
| 1 | 1 | 0.11 | 238 | 3 | 0.04 | 262 |
| 2 | 2 | 0.02 | 235 | 3 | 0.10 | 212 |
| 3 | 4 | 0.08 | 256 | 8 | 0.05 | 250 |
| 4 | 4 | 0.06 | 245 | 12 | 0.07 | 260 |
| 5 | 6 | 0.04 | 244 | 17 | 0.06 | 278 |
| 6 | 7 | 0.12 | 250 | 17 | 0.03 | 252 |
| Average | | 0.07 | 245 | | 0.06 | 252 |

for the food samples and a 0.2 ug/ul solution for the packaging samples.

Preparation of the samples: 0.2 g of the polystyrene packaging material were dissolved with DMA (4 ml) in a septum-sealed vial, and the dissolution assisted by heating the vial to 40 C. A measured volume (3 ml) of deionized water was injected into the sample vial (Steichen 1976) and the vial shaken. The solution were equilibrated at 70 C for 60 min prior to headspace sampling. The food samples were prepared in a similar way as the packagings, except that 1.0 g of sample was placed into the septum-sealed vial, and no solvent or water was added.

The food samples and containers were analyzed according to the general procedure described by Crosby (1982) ; the gas chromatographic conditions are shown in Figure 1.

## RESULTS AND DISCUSSION

A summary of our investigation about the polymer types used in Chile as food packaging materials is shown in Table 1. The different polymers were characterized by classical methods (behaviour on heating, combustion properties, solubility, fusion and softening temperatures), as well as by comparison of their IR spectra with the ones of known standards. As it can be seen from Table 1, polystyrene packaging in Chile is limited to fresh meats, honey, desserts, and some dairy products. Because fresh meats are mostly sold in butcheries without any plastic wrapping, and because only one brand of honey, from the many available had polystyrene packaging, we centered our study on desserts and dairy products.

Tables 2 and 3 show the residual styrene monomer levels found in the analyzed food samples and their containers. The six samples in each one of the four chosen foods were all of the same brand and flavor, but purchased in different stores. The figures listed in Tables 2 and 3 are expressed in ppm and represent the average values of a sample run in duplicate.

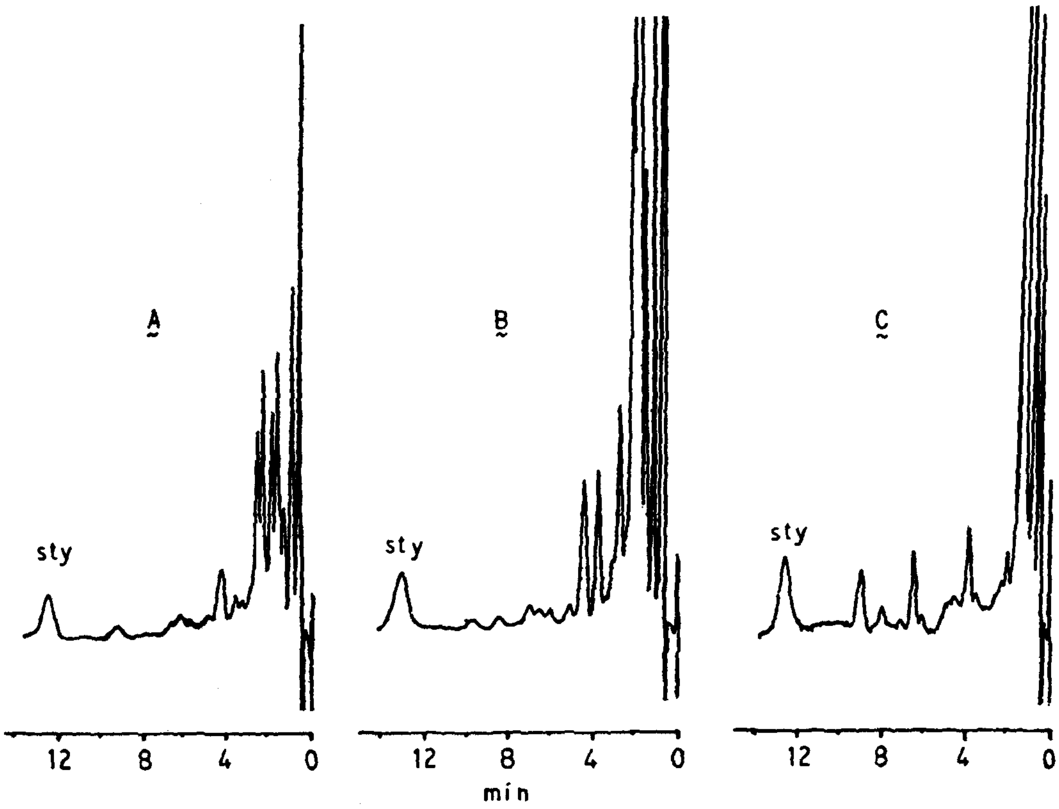

Figure 1. Gas chromatograms of 1 ml headspace injections from A, jelly; B, mousse; and C, pudding. 6'x 1/8" S.S. column packed with 5% Hallcomid M-18 on Chromosorb W AW(80-100m). Carrier gas: $N_2$, 40 ml/min. Column temperature: 90°C. FID at 175° C.

Table 3. Residual styrene monomer content in mousse, jelly and their packagings (ppm).

| | Mousse | | | Jelly | | |
|---|---|---|---|---|---|---|
| Sample | Days | Food | Pack. | Days | Food | Pack. |
| 1 | 4 | 0.39 | 263 | 10 | 0.74 | 4.7 |
| 2 | 5 | 3.59 | 263 | 10 | 0.79 | 3.6 |
| 3 | 5 | 1.44 | 276 | 14 | <0.01 | 3.2 |
| 4 | 5 | 3.72 | 298 | 14 | <0.01 | 3.2 |
| 5 | 5 | 1.45 | 231 | 19 | 0.06 | 3.8 |
| 6 | 13 | 0.46 | 271 | 21 | 0.04 | 3.7 |
| Average | | 1.84 | 270 | | 0.27 | 3.7 |

Figure 1 shows the headspace gas chromatograms of a jelly, a pudding, and a mousse sample. Although there are some spurius peaks arising from the flavoring and other volatile materials, these do not interfere with the styrene peak which elutes cleanly at 12.9 min. The styrene peak was confirmed by coinjection of pure styrene monomer on a second chromatographic column packed with Chromosorb 101.

Three of the four packaging materials were relatively homogeneous as far as their styrene monomer content was concerned, with average values within the 10% variation. The fourth packaging material, which was a transparent polymer without any pigment or filler, was significantly different to the other three and as it can be seen from Table 3, it had a very low styrene monomer content.

From the data in Tables 2 and 3 , it can be concluded that there is no clear relationship between the styrene monomer content of the containers and the amount found in the foodstuff samples. The higher extent of styrene migration of the mousse samples however, also correspond to a relatively higher content of the mousse packaging polymer, but another explanation could be the higher fat content of this foodstuff (Varner et al. 1983).

Surprisingly, no progressive increase in the amount of the styrene monomer in the foods was observed with increasing packaging time. This could be an indication that most of the monomer migrates into the foodstuff during a short period immediately after the the food is placed into the polystyrene container. Moreover, there are too many variables which may affect the amount of styrene which passes into the food; besides the original styrene content of the polymer, the container wall thickness, the time elapsed between the manufacture of the package and its filling, the physical treatments of the package, etc., are all factors that will affect the amount of styrene that is leached.

The styrene monomer content of all the polystyrene containers examined in this work fell far below the standards set in the U.S. and other countries, but the styrene content of the analyzed foods seems to be higher (Whithey and Collins 1978).

Acknowledgments. The authors thank Mirta Rodriguez and Victor Cifuentes for technical assistance. This work was supported by the Dirección de Investigaciones y Postgrado, Universidad Federico Santa María.

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Received October 8, 1985; accepted October 20, 1985.