Styrene Monomer in Foods A Limited Canadian Survey

Jim R. Withey and Peter G. Collins

Health Protection Branch
Food Directorate
Bureau of Chemical Safety
Toxicology Division
Tunney's Pasture
Ottawa, K1A 0L2
Canada

INTRODUCTION

A preliminary report (WITHEY, 1976) of the styrene monomer content both of the package and foodstuff contained in polystyrene-related material indicated levels as high as 2,000 p.p.m. and 140 p.p.b. (wt/wt) respectively. No record of the history of these food samples or packages was available and it became clear that a wider variety of foodstuffs than those examined was available to Canadian consumers.

A letter of enquiry to food packagers across Canada yielded information on the variety of foods which were packaged in polystyrene containers and they agreed to provide samples for a limited survey. As a consequence the Field Operations Bureau, of the Health Protection Branch, Health and Welfare Canada, arranged to collect samples which had a known history of packaging and storage.

EXPERIMENTAL

Collection and Nature of Samples. Food processing plants, located in British Columbia, Saskatchewan, Ontario and Quebec, were asked to provide local Food Inspectors with fifteen samples packaged in the polystyrene containers usually used, fifteen samples of the empty container and a 200 ml. or 6 oz. sample of the food product taken prior to its contact with polystyrene. The latter was to be placed and shipped in a glass container and sealed with a metal foil lined cap. The date and time of sample pick-up were recorded and all samples were shipped in refrigerated containers by air express freight to the laboratories in Ottawa. The samples were then unpacked and stored according to the manufacturer's recommendations. The range of foods which were included in this study were yoghurt, milk, butter fat cream, cottage cheese, sour cream, yopi (gelified milk) and honey.

Each food sample, which had not been in contact with polystyrene or styrene monomer, was used to evaluate a suitable methodology for the quantitative analysis of styrene monomer and to obtain calibration

Bulletin of Environmental Contamination & Toxicology,
0007-4861/78/0019-0086 $1.80

curves from prepared mixtures containing different concentrations of the monomer. Minimum levels for the detection and estimation of styrene monomer content were also estimated from this procedure.

Ten units of food sample in its polystyrene container were then stored for a period which was one week longer than the manufacturer's recommended durable life time*. Sequential samples from each of the ten units of food were then taken, at convenient time intervals and analysed for their styrene monomer content.

Analytical Methods and Results

(a) Styrene Monomer in Polystyrene. The procedure and method for the analysis of styrene monomer in polystyrene have been described previously (WITHEY, 1976). Since the packages containing the food samples were required for the durable life time of the food, it was considered that an analysis of styrene monomer in ten similar unfilled packages collected from the same source immediately upon receipt would adequately represent the initial exposure potential which the food received. It was found that some solutions containing 2 g of the plastic dissolved in 10 ml of diethylbenzene were rather viscous and so only 1 g of the polymer was used in this study. The lower viscosity of the resultant solutions appeared to facilitate the rapid equilibration of styrene monomer in solution with head space. The results are presented in table 1.

(b) Styrene Monomer in Foods. The food specimens were sampled and analysed according to their physical state and the pertinent information is given in table 2. The head space method of analysis and the relevant Gas-chromatographic conditions were essentially the same as those described previously (Withey, 1976). Samples of Yoghurt (2-1, 3-4 and 4-3), Yopi (6-1), Homogenized Milk (5-1) and Butter Fat Cream (2-2) were all sufficiently fluid to allow sampling by means of hypodermic syringe through a size 19 G needle and behaved as liquids at the shaker bath temperature of 60°. The Sour Cream samples (3-3, 4-1 and 5-3) and Honey (7-1) were rapidly dispersed by

---

*"Durable life" means the period, commencing on the day on which a prepackaged product is packaged for retail sale, during which the product, when it is stored under conditions appropriate to that product, will retain, without any appreciable deterioration, its normal wholesomeness, palatability, nutritional value and any other qualites claimed for it by the manufacture. (Food and Drug Regulations, 1974).

TABLE 1

Styrene Monomer Content of Polystyrene Food Containers[(b)]

Styrene Monomer Concentration, p.p.m. by weight[(a)]

Code	1	2	3	4	5	6	7	8	9	10	Mean	S.D.[(c)]
1-1	2919	2964	3077	3056	3068	2635	2846	3084	3285	3254	3019	191
2-1	760	856	813	912	812	767	805	780	764	821	809	47
2-2	1308	1126	1288	1279	1179	1177	1225	1185	1209	1208	1219	57
2-3	1244	1425	1688	1398	1439	1483	995	1074	1153	1264	1316	210
3-3	977	890	884	912	984	744	820	763	763	849	859	87
3-4	1000	844	1013	877	776	881	917	813	865	883	887	75
4-1	1007	939	997	983	934	908	977	772	878	939	933	70
4-2	791	816	853	822	834	716	833	851	807	771	809	41
4-3	2345	2522	2508	2584	2691	2752	2577	2613	2889	2404	2589	161
5-1	801	858	804	854	854	861	823	826	803	730	821	40
5-2	1140	1148	-[(d)]	1148	1196	1142	1178	1095	1117	1126	1143	30
5-3	698	741	697	763	721	786	784	791	744	725	745	35
6-1	991	1090	973	1046	909	970	929	900	923	904	964	64
7-1	1419	1296	1329	1464	1574	1249	1170	1254	1101	1272	1313	140

(a) The lower limit of detection was 1 p.p.m.
(b) The food associated with each package code is given in table 2.
(c) S.D. is the standard deviation.
(d) Only nine units of this sample were available.

shaking with an equal volume of water to give a mixture of low viscosity. Cottage Cheese samples (2-3 and 4-2) were mixed with an equal volume of water and blended in a Waring blender for 1 min. A two ml sample of the fluid mixture was then analysed by the head space technique. The results are presented in table 3. The code numbers are the same as those used for table 1 and allow a comparison of the styrene monomer leached into the food with the original styrene monomer concentration in similar packages.

Our analytical techniques did not permit the analysis of styrene monomer in margarine below 1 p.p.m. (1,000 p.p.b.) so that, in spite of the relatively high monomer concentration in the package (Code 1-1), styrene monomer was not detected in the food contents even after 180 days of storage. It should also be mentioned that the margarine containers were unlike any of the other polystyrene packaging in that they did not dissolve in the diethylbenzene solvent but rather swelled in a manner similar to that observed with previous samples of authentic acrylonitrile-butadiene-styrene (ABS) copolymer.

TABLE 2

Physical Characteristics and Method of Sampling for each Food

Code	Food Type	Amount in Package	Physical State	Sampling Method	Durable Life (days)
1-1	Soft Margarine	8 oz.	Semi-Solid	1 g wall sample	180
2-1	Yoghurt (Blueberry)	4 oz	Semi-Solid	1 ml (by syringe) through foil seal	29
2-2	Butter-Fat Cream	½ oz.	Liquid	1 ml (by syringe) through foil seal	16
2-3	Cottage Cheese	5 lb.	Heterogeneous Solid-liquid	50 g wall sample blended with 50 ml water	20
3-3	Sour Cream	10 oz.	Semi-Solid	1 g weighed added to 1 ml water	20
3-4	Yoghurt (Plain)	16 oz.	Semi-Solid	1 ml (by syringe) through foil seal	30
4-1	Sour Cream	10 oz.	Semi-Solid	1 g wall sample dissolved in 1 ml water	25
4-2	Cottage Cheese	16 oz.	Heterogeneous Solid-liquid	50 g wall sample blended with 50 ml water	18
4-3	Yoghurt (Raspberry)	4 oz.	Semi-Solid	1 ml (by syringe) through foil seal	49
5-1	Homogenized Milk	8 oz.	Liquid	1 ml (by syringe) through foil seal	12
5-2	Fruit Juice (Orange)	4 oz.	Liquid	1 ml (by syringe) through foil seal	12
5-3	Sour Cream	10 oz.	Semi-Solid	1 g wall sample dissolved in 1 ml water	28
6-1	Yopi (Caramel)	4 oz.	Semi-Solid	1 ml (by syringe) through foil seal	21
7-1	Honey	12 oz.	Solid	1 g wall sample dissolved in 1 ml water	90

TABLE 3

Styrene Monomer Content of Foods

Food Type and Code	Mean Styrene Content (p.p.b.)[(a)(b)]												Lower Detection Limit (p.p.b.)
Butter-Fat Cream (2-2)	22.4 ±13.4 (5)	37.7 ±20.0 (11)	43.7 ±27.6 (17)	59.2 ±40.4 (24)									6.7
Cottage Cheese (2-3)	7.9 ±3.5 (18)	6.2 ±2.4 (22)	9.3 ±3.4 (27)										1.5
Sour-cream (3-3)	4.2 ±7.1 (6)	26.4 ±18.8 (16)	13.7 ±4.4 (20)	24.0 ±17.8 (27)									1.1
Yoghurt (Plain) (3-4)	-(c) - (7)	8.5 ±3.6 (15)	10.9 ±3.1 (22)	9.9 ±3.6 (29)	13.0 ±4.1 (36)								0.73
Yoghurt (Raspberry) (4-3)	20.4 ±8.3 (5)	22.9 ±10.8 (14)	25.8 ±9.5 (21)	39.5 ±19.5 (26)	56.7 ±17.0 (35)	59.7 ±14.8 (42)	70.7 ±12.0 (49)	77.6 ±20.2 (56)					0.91
Homogenized Milk (5-1)	- - (4)	- - (8)	14.3 ±9.3 (12)	17.2 ±9.8 (19)									1.6
Sour-cream (5-3)	143.3 ±34.1 (5)	245.9 ±90.5 (29)(d)	242.2 ±89.6 (35)										13.4
Yopi (6-1)	14.4 ±5.2 (9)	40.8 ±11.8 (15)	36.3 ±11.9 (21)	39.7 ±11.6 (28)									1.7
Honey (7-1)	12.6 ±4.6 (15)	13.2 ±4.1 (22)	15.5 ±2.9 (29)	16.2 ±4.2 (37)	14.9 ±4.5 (43)	15.9 ±5.9 (50)	17.5 ±5.3 (57)	20.1 ±6.7 (78)	21.2 ±2.8 (85)	16.6 ±3.7 (92)	17.5 ±3.3 (99)	22.7 ±5.1 (120)	0.33

(a) The mean value for ten samples is given together with ± the standard deviation and, in parentheses, the number of days which had elapsed between packaging and sampling. Individual sample data is available from the authors on request.

(b) The Styrene Content of the package, for the same Code Numbers, is given in Table 1.

(c) The entries designated with a dash indicate that only a few samples showed trace amounts of Stryene.

(d) Sample analysis between 5 and 29 days was considered to be unreliable due to the appearance of interfering peaks. The styrene monomer peak was resolved by using a freshly prepared column containing the same packing material.

Interfering peaks, arising from the flavorings used, in the samples of Blueberry Yoghurt (Code 2-1) and Orange Fruit Juice (Code 5-2) did not permit the resolution of the styrene peak in the derived gas chromatograms and were therefore not analysed. Two other food samples were not included in the tables. For one of these, which was Sour Cream (Code 4-1), no styrene was detected in any sample up to its durable life date (25 days). However, each of the ten units of this sample yielded relatively high levels of styrene monomer (with a mean 53±46.0 p.p.b.) when sampled at 34 days. The other set of samples, for which data was not included in the table, was of Cottage Cheese (Code 4-2), with a durable life time of 18 days, since only five units showed trace amounts (< 7 p.p.b) after 25 days of storage.

DISCUSSION

Three lots of food samples, from two different manufacturers, which consisted of ice cream, cottage cheese and honey were found to contain no trace of styrene monomer in either the food or packaging material. Spurious gas chromatographic peaks arising from material of low volatility were observed on the chromatograms derived from samples of their plastic packages dissolved in diethylbenzene. Since several hundred previous samples of polystyrene had already been examined by us and all of these were found to contain substantial amounts of the monomer, we requested the food processors to make enquiries of their package suppliers as to the precise nature of the plastic which was supplied for the sampled batch. In these instances it was found that containers fabricated from polyethylene plastic had been substituted. In the case of the supplier of the honey samples an additional batch, which was packaged in polystyrene, was supplied. It would appear that different types of plastic can be substituted by suppliers without the knowledge of the food packagers and that it is often impossible to distinguish between one kind of plastic and another by its appearance or texture.

Certain food flavorings interfered with our head space method of analysis for styrene monomer. Attempts to resolve the styrene monomer peak, from the peaks produced from the flavorings, by altering gas chromatographic parameters were either unsuccessful or resulted only in a sensitivity which proved unsuitable for the quantitative estimation of the levels expected in the food sample. Notable among those samples which gave difficulty in analysis was a sample of blueberry flavored yoghurt in that we had previously analysed the styrene monomer content of a similarly flavored yohurt from a different manufacturer and achieved a high sensitivity (< 0.5 p.p.b.).

It was disappointing to find that, with the head space technique, the lower limit of detection for margarine was only about 1 p.p.m. since the ABS material in which it was packaged had the highest monomer content of the packaging examined in this study. A probable explanation for this arises from the consequence that styrene monomer is miscible in all proportions with oils and fats and that the latter have very low vapor pressures. It is evident that the head space above a dilute solution of styrene monomer would have a relatively low partial vapor pressure of styrene monomer which would consequently result in a low g.l.c. response to the injected vapor sample. Very similar results were also obtained for solutions of styrene monomer in vegetable oils. Evidence of a low partial vapor pressure for styrene monomer in butter fat cream (code 2-2) and one sample of sour cream (code 5-3) probably arising from a similar consequence also gave rise to relatively less sensitive analytical data as is apparent from their respective lower limits of detection (table 3).

The majority of the food packaging material samples of a specific type were relatively homogeneous as far as their styrene monomer content was concerned since the coefficients of variation in table 1 are, for the most part, less than 10%. While it was difficult to distinguish the different types of polystyrene by appearance or physical properties, their styrene monomer content varied from a low of 745 p.p.m. (code 5-3) to a high (for the pure polystyrene type) of 2588 p.p.m. (code 4-3). The styrene monomer content of the various packages appeared to fall into one of three classes: a class with the highest content (codes 1-1 and 4-3) of about 2,500 p.p.m.; a class with a medium content of around 1300 p.p.m. (codes 2-2, 2-3 and 7-1) and a class with low content of between 750 to 960 p.p.m. (codes 3-3, 3-4, 5-1, 5-3 and 6-1).

No clear relationship between the styrene monomer content of the package and the amount leached into the foodstuff after comparable residence times emerged from an inspection of table 3. The highest extent of migration which was observed for any samples was for the sour cream (code 5-3) which, surprisingly, had the lowest monomer content in the package.

It was apparent from the data for the two samples of yoghurt (Codes 3-4 and 4-3) that for foodstuffs of approximately the same composition, the extent to which styrene monomer was leached was proportional to the original styrene monomer content of the package. This observation was also pertinent to the samples of homogenized milk and butter-fat cream (Codes 2-2 and 5-1). An exception was provided by the two samples of sour cream (Codes 3-3 and 5-3) where the mean values for styrene monomer content of the food after 27 and 29 days respectively differed by a factor of ten.

There was, in nearly every case, a progressive and regular increase in the amount of styrene monomer in the food with increasing time. It was also evident, particularly in the examples where many more samples could be analysed as a consequence of a longer durable life recommendation, that relatively large amounts of styrene monomer migrate during a short period immediately after the food is placed in the polystyrene container. A good example of this phenomenon was illustrated by a plot of the mean styrene monomer concentrations against time for the sample of honey (code 7-1). An extrapolation of the approximately linear relationship to the ordinate axis implied that a wall concentration of styrene monomer in the honey of about 11 p.p.b. was immediately generated. In separate leaching studies which we have conducted, it was noted that water, poured into a rigid polystyrene drinking cup and sampled immediately, gave a relatively high styrene monomer concentration which was followed by a low leaching rate process over the next few hours. These empirical observations suggested that there may be an adsorbed surface film of styrene monomer arising as a consequence of the physical interaction of the monomer and the plastic after styrene has either diffused from the body of the plastic or has been "squeezed" from the matrix by the mechanical processing of the plastic.

It must be emphasized that sampling for the solid food specimens for the determination of styrene monomer was of food which was immediately adjacent to the wall of the container. Samples which were taken simultaneously from locations adjacent to the container wall and from the centre of the food mass always indicated a concentration gradient for viscous or semi-solid foods. Samples from the centre were frequently found to have undetectable concentrations of the monomer. Although this method of sampling did not yield smooth linear or curved relationships for styrene monomer plotted against time it was considered to be a realistic approach for this comparative study.

Clearly, many complex variables affect both the leaching rate and the total amount of styrene monomer which passes into the foodstuff. Of those which affect the rate of leaching perhaps the most important are the viscosity of the plastic body from which the styrene originates, the viscosity and homogeneity of the foodstuff and physical interactions between styrene monomer, the plastic and constituents of the food. The amount of monomer which is leached will be related to the original styrene monomer in the plastic, the container wall thickness, the contact area between the container wall per unit mass of the food and the residual adsorbed styrene monomer on the surface of the container prior to filling (this parameter will be related to the time lapse between the manufacture of the package and its filling as well as physical treatments, like extrusion or blow moulding, which have been used in its fabrication). The residence time of the food in the container is likely to be influenced by the shelf-life or durable life time of the food which can vary from a few days to several months.

The monomer content of all food containers which were examined in this study fell well within the standards set by the U.S. Food and Drug Administration of 10,000 p.p.m. In fact all containers met the more stringent standard (less than 5,000 p.p.m.) required for fatty foods (Code of Federal Regulations, 1976). Whether or not the presence of styrene monomer in foods, at the levels reported in this communication represent a potential carcinogenic health hazard cannot be decided until the results of chronic studies now underway are known (I.A.R.C., 1976).

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the assistance of Mr. B.C. Williams, of the Bureau of Field Operations, Health and Welfare Canada, who arranged and coordinated the collection and delivery of the samples and to the Food Packaging Section of the Additives and Pesticides Division, who provided the information on foods packaged in polystryene.

REFERENCES

Code of Federal Regulations, U.S.A., 21, parts 10-199, paragraph 121.2510, Revised April 1st, 1976.

Food and Drug Regulations, Health and Welfare Canada, Section B.01.001. Revised March 12th, 1974.

International Agency for Research on Cancer, Information Bulletin on the Survey of Chemicals Being Tested for Carcinogenicity #6, pages 45, 194, 211, March, 1976.

WITHEY, J.R., 1976. The Quantitative Analysis of Styrene Monomer in Polystyrene and Foods Including Some Preliminary Studies of the Uptake and Pharmacodynamics of the Monomer in Rats. W.H.O.-N.I.E.H.S. Symposium on Potential Health Hazards from Technological Developments in the Plastics and Synthetic Rubber Industries, Research Triangle Park, North Carolina, March 1-3, 1976. (To be published in Environmental Health Perspectives).