Titration of Aldehydes Present in Poly(Ethylene Terephthalate)

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SYNOPSIS

Aldehydes are known to be present in PET preforms and PET bottles. However, the analysis of these aldehydes is difficult because of the high crystallinity of PET and because of its insolubility in common solvents. Titration of acetaldehyde was investigated comparatively by four different methods: by the solid/gas headspace technique (s/g HS), accepted industrially as the standard method, by colorimetry, based on complexation with pararosaniline dye, by colorimetry, based on derivatization as 2,4-dinitrophenyhydrazones, and by headspace liquid/gas chromatography (l/g HS). Similar results were achieved by the last three methods. In contrast, the standard solid/gas headspace chromatography yielded data that was one order of magnitude smaller. The presence of formaldehyde in PET preforms was detected by liquid/gas headspace chromatography only. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In 1954, the U.S. Food and Drug Administration approved poly(ethylene terephthalate), also known as PET, for applications in the food industries. In 1973, this approval was extended to food packaging,[1] and PET is now used worldwide for the bottling of many drinks. However, various volatile compounds are formed during the molding of PET bottles by the injection-blowing technique;[2] acetaldehyde amounts for 80%. The presence of residual acetaldehyde appears as a critical shortcoming and restrains the use of PET bottles to flavored carbonated drinks. The unpleasant taste produced by the released acetaldehyde affects dramatically the organoleptic quality of unflavored mineral water and precludes the use of PET bottles, despite their attractive appearance. Regulations limit at 5 ppm the acceptable AA content in PET-injected preforms that are used to blow bottles. An assay of AA, present in PET preforms, is standardized. The approved method is based on the use of solid/gas headspace chromatography (s/g HSGC), applied to fragments of preforms obtained by grinding at low temperature, in order to reduce the evaporation of volatile compounds and to avoid secondary reactions, such as oxidation. Typically, the resulting powdered PET is sieved and heated in a closed vial, equipped with a rubber septum. The entrapped gas above the solid phase is finally injected in the gas chromatograph via a headspace accessory.[3,4] Calibration is done with AA aqueous solutions of known concentrations. Suppression of preliminary thermal treatment has been proposed to improve the procedure[5] and to prevent extra degradation during the preliminary thermal treatment. Despite this improvement, data produced by the standard procedure are still viewed suspiciously, because of the absence of control of the evaporation of AA at the grinding and sieving stages and because of the possibility of uncomplete desorption of AA.

From a general viewpoint, aqueous solutions of acetaldehyde can be titrated by using different methods, including spectrophotometric ones. Procedures have been proposed, which were based on the use of thiourea,[6] 2-hydrazino triazole,[7] oximes,[8] 3-methyl 2-benzo thiazole,[9,10] pararosaniline hydrochloride,[11] and 2,4-dinitro phenylhydrazone.[12] The last two dyes allowed titration of AA at concentrations as low as 0.08 ppm in aqueous media.[11] How-

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ever, since PET is not soluble in water, spectrophotometric techniques cannot be used without the transfer of AA from the polymeric matrix to an aqueous medium. Therefore, it appeared that AA titration was at a critical stage to be controlled prior to any research work aimed at decreasing the acetaldehyde present in PET preforms and bottles.

In this article are reported the results of our attempts to quantitatively assay the residual AA present in injection-molded PET preforms. For the sake of comparison with the standard s/g HSGC method, AA was tentatively assayed by colorimetry, based on pararosaniline dye (pRA), by colorimetry based on derivatization with 2,4-dinitro phenylhydrazine (DNPH), and by headspace gas chromatography, based on liquid/gas exchanges (l/g HSGC). The presence and abundance of by-products arising from polymerization and from melt processing of PET is highly dependent on processing conditions and on thermal and thermo-oxidative degradation processes. For the sake of consistency, analytical data reported in this article were collected from the same defined batches of industrially processed preforms.

EXPERIMENTAL

PET Preforms

PET (from AKZO Co) preforms were supplied by SIDEL Co., Le Havre, France.

Pararosaniline-Based spectrophotometry

Reagents ($Na_2[HgCl_2SO_3]$)

$HgCl_2$ (27.2 g) and NaCl (11.7 g) were introduced in a 1 dm^3 calibrated flask, which was then filled up with distilled water, to yield a 0.1 M $Na_2[HgCl_4]$ aqueous solution. Na_2SO_3 (452.53 g) was then introduced into a 100 cm^3 calibrated flask, which was filled up with the previously prepared $Na_2[HgCl_4]$ solution to form a standard solution of the $Na_2[HgCl_2SO_3]$ complex, which was used later for all pararosanilide-based titrations.

Pararosaniline Solutions

Pararosaniline hydrochloride (0.3 g) was dissolved in a mixture of 7.5 cm^3 methanol and 7.5 cm^3 distilled water under stirring. The resulting 2% stock solution was allowed to stand for 2 days and was finally filtrated. For each series of titrations and standardizations, 1.2 cm^3 of concentrated HCl were added to 2 cm^3 of the stock solution in a 100 cm^3 calibrated flask, filled with distilled water.

0.08% Acetaldehyde Solution

Acetaldehyde (0.05 cm^3) was injected in a vial containing water (0.05 cm^3) and closed by a rubber septum. The exact amount of acetaldehyde that was introduced was determined by weighting.

Method

PET (1 g of a preform) was dissolved in 10 cm^3 trifluoroacetic acid (TFA). 40 cm^3 of water were added to the resulting solution and the precipitated polymeric mass was dispersed before filtration through a sintered glass filter that was equipped for pressure filtration. Ten cm^3 of the $Na_2[HgCl_2SO_3]$ solution were added to 10 cm^3 of the collected filtrate and 2 N NaOH was used to adjust the pH of the mixture at 3. Five cm^3 of the pararosaniline hydrochloride solution were then added and the volume was extended to 50 cm^3 by adding distilled water in a suitable calibrated flask. The resulting solution was allowed to stand for 20 min before measuring absorbance at 560 nm. Data were compared with absorbance values at 560 nm of acetaldehyde solutions, obtained by introducing known amounts of the 0.08% standard acetaldehyde solution to a mixture of 10 cm^3 of a solution of TFA (20 cm^3 TFA in 80 cm^3 of water) and 10 cm^3 of the $Na_2[HgCl_2SO_3]$ solution, adjusted to pH = 3, the resulting solution being then treated as above. Absorption measurements were carried out with a UV-visible Shimadzu 240 or Perkin–Elmer Lambda 15 spectrophotometers.

2,4-DNPH-Based Colorimetry

Reagents

–*p*–chlorophenol was distilled before use.

–2,4-dinitrophenylhydrazine was obtained from Aldrich and was used without further purification.

Method

A sample of PET preform (1.6 g) was first mixed with *p*-chlorophenol (10 g) in a extraction device, which was placed in a water bath thermostated at 50°C. Volatile compounds were displaced by a flow of nitrogen gas, which was allowed to bubble gently into the acetaldehyde-containing solutions (standards or to be titrated) for 15 min. The extracted compounds were condensed in a trap that was placed in liquid nitrogen, which was followed by another

trap that was loaded with distilled water. Water was added to the first trap and the contents of the two traps were mixed with 2,4-dinitrophenylhydrazine (10 cm^3 of the stock solution). Absorbance measurements were carried out at 380 nm, using a Perkin–Elmer Lambda 15 spectrometer.

Liquid/Gas Headspace Chromatography

Method

0.8 g of PET preform and 2.5 g of distilled *p*-chlorophenol were introduced in a headspace vial, which was purged with argon before sealing. The vial was allowed to stand at 100°C for 8 h, that is, up to complete dissolution. After cooling, the vial was introduced in the headspace furnace and was allowed to stand for 20 min at 90°C before injection into the gas chromatograph (Perkin–Elmer, equipped with headspace HS6 accessory; stationary phase: Carbowax 1540 0.8% chromosorb W, $\frac{1}{8}$" diameter × 2 m long; oven temperature 70°C; mobile phase: helium; detector: FID supplied in hydrogene and a 20/80 oxygene/nitrogen mixture). Standards were prepared by mixing 3.3 g of *p*-chlorophenol with known amounts of a 0.03% acetaldehyde aqueous solution, the procedure described for the PET analysis being then applied to the resulting solutions.

Solid/Gas Headspace Chromatography

Solid/gas headspace chromatography (s/g HSGC) titration was performed by SIDEL (France), according to the standard procedure. Typically, a sample of PET preform was ground at low temperature, the grinder being cooled by liquid nitrogen to prevent AA evaporation and oxidation. The ground product was sieved and was then placed in a sealed flask, which was heated at 150°C for 1.5 h, and was then cooled. Part of the gas was sampled with a syringe and was injected in the gas chromatograph. Standards were prepared with known amounts of AA in aqueous solution.

RESULTS AND DISCUSSION

In order to compare the analytical techniques, which have been selected to assay the acetaldehyde present in injection-molded PET preforms, several industrially prepared preforms were first analyzed according to the standard solid/gas headspace chromatography (s/g HS) and averaged data were taker as references to form two homogeneous groups (preforms A and preforms B) for the sake of comparison. The average content in acetaldehyde of each group was in the range of 2–4 ppm and 7–8 ppm (Table I), as determined by the standard method. Samples, derived from the same group of preforms, were then analyzed by spectrophotometry on the basis of the formation of a colored complex between acetaldehyde and pararosaniline (pRA), in the presence of sulfurous anhydride SO_2.

Acetaldehyde Assay Based on Pararosaniline

This technique consists of measuring UV absorption of the SO_2/AA/pRA complex. It was proposed by Stankova and Jaremova[11] for the assay of acetaldehyde in aqueous solution. Under these conditions, the absorption of the solution is proportional to the content in acetaldehyde.[11,13] PET being insoluble in all the common solvents, the first stage of this investigation was to find a way to extract acetadehyde quantitatively from the preforms and to have this acetaldehyde conditioned in an aqueous medium. Solubilization in solvents such as hexafluoroacetone (HFA), parachlorophenol (PCP), and trifluoroacetic acid (TFA), was first attempted. HFA was discarded because of possible interferences, due to the carbonyl form of the sesquihydrate and because of cost. PCP was also discarded because it is in a solid state at room temperature (M_p = 45°C) and it must be melted to dissolve PET. The melting stage increases the risk of acetaldehyde evaporation, the boiling temperature of AA being 21°C at normal pressure. TFA appeared acceptable, provided that

Table I Contents in Acetaldehyde of Injection-Molded PET Preforms as Determined by Various Analytical Techniques

Batch	s/g HSGC (ppm)	Pararosaniline (ppm)	DNPH (ppm)	l/g HSGC (ppm)
A	2–4	56[a]	49	35[c]
B	7–8	108[b]	—	—

[a] 33 ppm after standing one week.
[b] 65 ppm after standing one week.
[c] Not included the 20 ppm formaldehyde.

the pH of the aqueous solution, resulting from the precipitation of PET from a TFA solution by the addition of water, was first set between 2 and 5, by the addition of suitable amounts of sodium hydroxide, as recommended for correct SO_2/acetaldehyde/pararosaniline complex formation.[14] Standard acetaldehyde solutions and PET-derived solutions were prepared under similar conditions, including amounts of TFA, sodium hydroxide, and water. Three parameters were critical, namely the pH of the aqueous solution, the postmixing time, and the temperature at which UV absorption measurements were performed. The absorption of the complex was maximum at pH = 1.85[11] and a precipitate appeared at pH = 5. Finally, pH = 3 was selected as a usuable standard pH for AA titration in TFA-containing acetaldehyde solutions. As for the postmixing measurement time, 20 min was selected, because absorption leveled off at this time, provided that temperature was fixed at 25°C and calibration was repeated at each measurement campaign, the standard solutions being unstable with time.[15] It is of value to note that changing the temperature from 19 to 29°C increased the absorbance by 50% for a 7.64×10^{-6} M solution of acetaldehyde (Fig. 1).

As shown in Table I, the contents in acetaldehyde, obtained by the pararosaniline complex assay, appeared at least one order of magnitude larger than those given by the standard s/g HSGC technique. The difference could be due to polymer degradation in TFA with the formation of extra aldehydes. However, the difference could be also assigned to the fact that the s/g HSGC technique did not titrate all the acetaldehyde that was initially present in preforms or to the fact that the presence of other aldehydes, which are known to complex pararosaniline as does acetaldehyde.[11] Each of these possibilities can be the source of inconsistent data. According to literature, PET degradation can generate several by-products, namely, polyenealdehydes,[2] formaldehyde, as suggested by Kovarskaya et al.,[16] or even aldehyde-terminated short PET chains.[17] It is of interest to note that measurements carried out with a neutralized TFA solution, which was allowed to age for one week prior to titration, led to significantly lower contents in acetaldehyde. However, the ratio of batch A/batch B data remained the same. This feature suggested that part of the acetaldehyde extracted from PET was evaporated during the aging time, or reacted with other components present in the solutions. Control experiments were performed, which consisted in titrating benzaldehyde and acetone in aqueous solutions of known concentrations by the pararosaniline technique. Both carbonyl

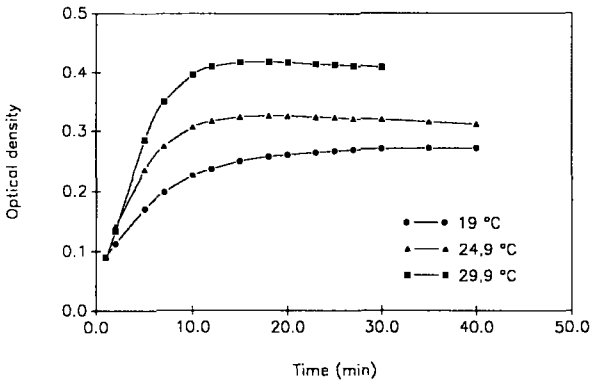

Figure 1 Variations of optical density of the pararosaniline/aldehyde complex with time and temperature (λ = 560 nm).

compounds formed complexes. It was found that these two complexes and the acetaldehyde one, absorbed at the same wavelength. However, molar absorption coefficients, produced by the benzaldehyde and acetone complexes, were 1/2 and 1/100 smaller than for AA, respectively. The reliability of the pararosaniline-based acetaldehyde assay was also checked by adding extra acetaldehyde or benzaldehyde to PET aliquots at the dissolution stage. The extra acetaldehyde was not detected because of volatility, in contrast to the extra benzaldehyde, which has a higher boiling point. These findings argued in favor of acetaldehyde leakage as the actual source of the lower amount of acetaldehyde, detected by s/g HSGC chromatography (Table I). In the pRA assay, a loss of acetaldehyde might occur because of warming when water is mixed to the TFA solution prior to analysis. A comparison with data obtained by other assays appeared of great interest to clear up this point.

2,4-DNP-Based Colorimetry

2,4-dinitro phenylhydrazine and carbonyl compounds are known to react and to yield 2,4-dinitro phenylhydrazones, which absorb in UV. In order to overcome the possible shortcomings of pRA-colorimetric assay previously mentioned, and especially to minimize the risk of acetaldehyde loss by evaporation, attempts were made to extract AA from a PET solution and to collect it directly in a 2,4-DNPH aqueous solution. AA was extracted by a flow of nitrogen and was collected in a liquid nitrogen trap before dissolution in a 2,4-DNPH solution. From preliminary experiments, performed to validate the method, it was shown that more than 90%

of AA could be extracted from standard solutions, provided that nitrogen was allowed to flow for at least 15 min. The selected procedure was applied to the determination of the AA content present in PET preforms of batch A. The average result was 49 ppm, a value comparable to that given by the *p*-RA-based assay (56 ppm) and much higher that that given by the s/g HSGC technique (5 ppm).

Liquid/gas Headspace Chromatography (l/g HS)

As compared with the solid/gas exchanges used in the s/g HSGC procedure, the liquid/gas exchanges, occurring in l/g HSGC chromatography, minimize the risk of AA evaporation, at least basically. The polymeric sample was dissolved in a sealed vial with no previous grinding. Furthermore, liquid/gas exchanges are basically easier than solid/gas exchanges. The main problem was the dissolution of PET in a solvent compatible with l/g HSGC gas chromatography. PCP, whose boiling temperature is 220°C at normal pressure, appeared suitable, provided that the equilibrium temperature was below 100°C. A standard curve was built up from AA solutions of known concentrations, which provided a well-defined GC peak, whose area was proportional to the AA content. Surprisingly, extracts from PET preforms led to GC chromatograms composed of two peaks (Fig. 2). The peak at 2.4 min corresponded to the well-identified GC peak of acetaldehyde. The extra peak at 1.25 min was assigned to formaldehyde on the basis of a comparison with the peak obtained after injection of the formaldehyde that was issued from depolymerized paraformaldehyde. This source of formaldehyde was preferred, because aqueous formaldehyde is generally polymerized. According to l/g HSGC, the AA content of the preforms of batch A (Table I) was 35 ppm. This value was slightly lower than those given by the *p*-RA-based and the 2,4-DNPH-based colorimetric assays (56 and 49 ppm, respectively), and almost one order of magnitude higher than that given by s/g HSGC chromatography (5 ppm). It is of interest to note that adding the FA content to the AA content (20 ppm) leads to an acetaldehyde equivalent content of 55 ppm, a value close to those produced by the colorimetric assays. It is also of interest to note that the presence of traces of water and dissolution times, greater than 8 h affected the results, probably because of PET degradation and subsequent AA formation, which is a point that will be discussed in another article.[18]

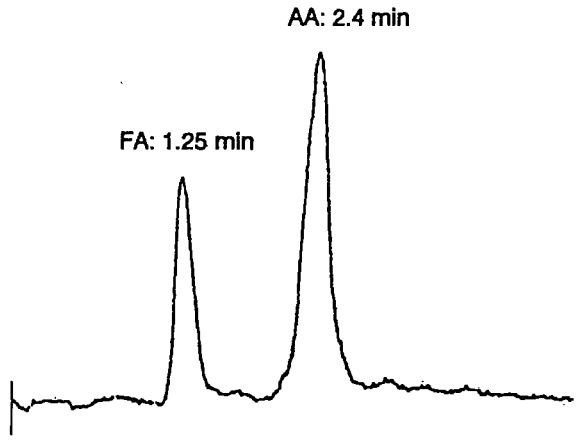

Figure 2 Liquid/gas Headspace chromatogram of PET preforms.

CONCLUSIONS

The content in AA of industrially injection-molded PET preforms was determined comparatively by three different techniques, namely pararosaniline-based colorimetry, 2,4-dinitrophenylhydrazine-based colorimetry, and liquid/gas headspace gas chromatography. The three methods agreed to show that data, obtained by the standard solid/gas headspace gas chromatography, were one order of magnitude lower than reality. Furthermore, l/g HSGC appeared to be able to detect the presence of formaldehyde, besides acetaldehyde, in PET preforms and to quantify both aldehydes. The formation of aldehydes depends on many factors, including origin, formulation, and processing of industrial PET preforms and PET bottles. The effects of some of these factors have been investigated in detail on the basis of the results of the present evaluation of available analytical techniques. Data will be reported in a following article.[18]

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REFERENCES

1. D. B. G. Jacquiss, W. F. H. Borman, and R. W. Campbell, in: *Encyclopedia of Chemical technology*, H. F.

Mark, D. F. Othmer, C. G. Overberger, and G. T. Seaborg, Wiley, New York, Vol. 18, 1982, pp. 549–574.
2. E. P. Goodings, *Soc. Chem. Ind. Monograph no. 13,* 211–228 (1961).
3. M. W. Dong, A. H. DiEdwardo, and F. Zitomer, *J. Chromatogr. Sci.,* **18,** 242–246 (1980).
4. M. W. Dong, *Chromatogr.,* **14,** 447–451 (1981).
5. D. M. Wyatt, *J. Chromatogr. Sci.,* **21,** 508–511 (1983).
6. H. L. Iversen and S. E. Damgaard, *Clin. Chim. Acta,* **135,** 151–158 (1983).
7. E. Sawicki and T. R. Hauser, *Anal. Chem.,* **32,** 1434–1436 (1960).
8. J. W. Vogh, *Anal. Chem.,* **43,** 1618–1623 (1971).
9. E. Sawicki, T. R. Hauser, T. W. Stanley, and W. Elbert, *Anal. Chem.,* **33,** 93–96 (1961).
10. T. R. Hauser and R. L. Cummins, *Anal. Chem.,* **36,** 679–681 (1964).
11. O. Stankova and M. Jaremova, *Acta Universitatis Palackianae Olomuc. Facultas Rerum Natur.,* **41,** 87–95 (1973).
12. E. Puputti and P. Lehtonen, *J. Chromatogr.,* **353,** 163–168 (1986).
13. J. H. Robins, G. D. Abrams, and J. A. Pincock, *Can. J. Chem.,* **58,** 339–347 (1980).
14. O. Stankova, *Acta Universitatis Palackianae Olomuc. Facultas Rerum. Natur.,* **61–65,** 199–205 (1979/1980).
15. M. Mauzac, F. Guérard, J. Mathieu, and J. Laroche, *Analusis,* **4,** 236–245 (1976).
16. B. M. Kovarskaya, I. I. Levantovskaya, A. B. Blumenfel'd, and G. V. Draluk, *Plast. Massy.,* **5,** 42–46 (1968).
17. L. H. Buxbaum, *Angew. Chem. Internat. Ed.,* **7,** 182 (1968).
18. F. Villain, J. Coudane, and M. Vert, *Polymer Degradation and Stability,* to appear.

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