

# Determination of Residual Acetaldehyde in Polyethylene Terephthalate Bottles, Preforms, and Resins by Automated Headspace Gas Chromatography

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## Abstract

**A rapid and sensitive method based on automated headspace gas chromatography for the determination of residual acetaldehyde in polyethylene terephthalate (PET) resins, preforms, and bottles is described. The analysis sequence entails sample grinding in a liquid nitrogen mill, storage in septum capped vials, thermal treatment to liberate acetaldehyde, and subsequent headspace analysis for acetaldehyde content. Quantification is based on comparison to acetaldehyde in a PET reference sample. The method offers significant advantages in sensitivity, precision, and sample through-put compared to solid injection gas chromatography. Acetaldehyde analysis of PET carbonated beverage bottles and resins is important because small amounts of acetaldehyde can affect beverage taste and hence consumer acceptance.**

The presence of acetaldehyde in polyethylene terephthalate (PET) is well documented (1,2). It is a thermal degradation product formed during the melt polycondensation reaction and melt processing of PET (3). Acetaldehyde possesses a distinctive odor and taste. Because of this, it is used as both a flavor and fragrance ingredient (4,5). Minute amounts of acetaldehyde have been shown to affect the taste of cola beverages (6), and therefore, the availability of PET resins with low acetaldehyde content is a key requirement for the PET carbonated beverage container industry. The ability to analyze trace levels of acetaldehyde is thus important for the development and production of PET bottle resins.

At Celanese Research Company a procedure for measuring residual acetaldehyde using solid injection gas chromatography (GC) was developed and used for a number of years (7). Briefly, the procedure involved weighing 10-30 mg of powdered PET into a glass sleeve, placing the filled sleeve in a GC injection port at 150°C for 20 minutes, trapping the off-gas on a cold column, and analyzing the acetaldehyde levels by GC. Aqueous standard solutions of acetaldehyde were injected for calibration. The method worked well and has been adopted as a quality control procedure. Reported here is

an improved method using an automated headspace analyzer. The new method exhibits superior performance in sensitivity, precision, and sample through-put.

Headspace gas chromatography (HSGC) is a useful technique for the analysis of volatiles in polymers and other solid materials. The principles and applications have been reviewed in a recent article by Kolb (8). Two approaches for the headspace analysis of residual volatiles in polymers have been used. One utilizes solid sampling, and the second requires a solutioning process.

The solid approach involves the equilibration of a solid polymer sample in a sealed system. The residual volatiles are partitioned between the headspace and the polymer phase, and an aliquot of the headspace is analyzed by GC. The original concentration of the residual volatile is obtained by comparison of the GC peak area to that derived from a standard polymer of a known concentration. Alternatively, if the vapor/solid system follows Henry's Law, the original concentration of volatile components in the polymer can be calculated by applying the appropriate equilibrium constants (9). According to Beren (9), the solid approach works best for finely powdered materials that are heated above their glass transition temperatures.

The solution approach involves equilibration of the sample solution in a sealed system followed by the analysis of the headspace. The polymer is first dissolved in a suitable solvent at a concentration of 10 to 20%. Equilibration is rapid and calibration is easily accomplished by internal or external standard techniques.

The advantages and disadvantages of these two approaches have been reviewed (8,10). The solid approach for acetaldehyde analysis was chosen because of higher sensitivity. Acetaldehyde levels in PET bottle resin range typically from 0.5-6 ppm. At these low levels, further sample dilution by solvents was found unacceptable. Using PET samples ground in a freezer mill, it was shown that vapor/solid equilibrium can be reached in 2 hours. Quantification is based on a PET reference with a known acetaldehyde concentration. In practice, these references are obtained by standard addition to acetaldehyde-free PET powders with known quantities of acetaldehyde. The accuracy of the above method was cross checked by using the discontinuous gas extraction technique (11) and solid-injection GC.

## Experimental

### Reagents

Acetaldehyde was obtained from Aldrich Chemical Company (Milwaukee, Wisconsin). Shortly before use it was distilled to remove any auto-oxidation products.

### Apparatus

For analysis, either a Perkin-Elmer, (Norwalk, Connecticut) Model F-42 or F-45 headspace analyzer was used. Detailed descriptions of the instruments are given elsewhere (12).

Each instrument consists of a thermostated sampling turntable which accommodates up to 30 samples, an electropneumatic dosing head for automatic injection and a F-22 gas chromatograph equipped with a flame ionization detector. The F-42 analyzer uses a Haake (Saddle Brook, New Jersey) circulating oil bath for temperature control of the turntable. The Model F-45 uses a self-contained temperature controlling unit which has a temperature limit of 150°C. These headspace analyzers were coupled to a Hewlett Packard (Avondale, Pennsylvania) HP3354 laboratory data system for data acquisition.

For grinding PET samples, a freezer mill by Spex Industries Inc. (Metuchen, New Jersey) was used. For weighing samples, a Mettler (Highstown, New Jersey) Model E200 top loading balance was used. Other accessories required included: headspace glass vials with silicone septums and aluminum caps (Perkin-Elmer #105-0118); crimper (Perkin-Elmer #038-143); 100  $\mu$ l gas-tight syringe (B-110 from Precision Sampling, Baton Rouge, Louisiana); 10  $\mu$ l Hamilton (Reno, Nevada) syringe. For cutting PET preforms and bottles a bandsaw, scissors, shears, and clippers were used.

### Procedure

The procedure is summarized as a flow chart in Figure 1. Details are described below.

**Preparation of standard acetaldehyde solution.** Aqueous standards were prepared by adding cold liquid acetaldehyde from a syringe to a septum-capped vial containing known volumes of water. The concentrations were determined by weighing.

Before use, the acetaldehyde was distilled to eliminate possible auto-oxidation products such as peroxyacetic acid or peroxides. Purified acetaldehyde was stored in an amber enclosed vial in the freezer. Twenty-three milliliters of distilled water were pipetted into a headspace vial. After being septum capped, the weight of the filled vial was determined to the nearest 0.1 mg on an analytical balance. It is important to fill these vials almost completely with water so that significant amounts of acetaldehyde cannot diffuse into the headspace. Due to the volatility of acetaldehyde (B.P. 20.8°C), both acetaldehyde and the gas-tight syringe must be chilled to near 0°C before transferring 100  $\mu$ l of liquid acetaldehyde into the filled headspace vial. The concentration of this resulting solution was determined by weighing. This value should be about 3.4  $\mu$ g/ $\mu$ l. Duplicate vials of this aqueous standard were made for cross checking acetaldehyde concentration by the bisulphite method (13). In this laboratory, the concentration

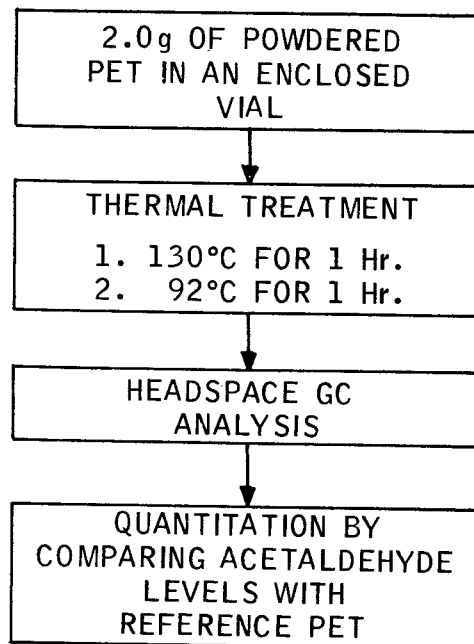


Figure 1. Procedure of residual acetaldehyde analysis by headspace GC.

derived from weighing agreed within 2-3% of that derived from a modified bisulphite method using potentiometric titration (14). Standards of different concentrations were prepared in a similar manner. Aqueous standards thus prepared can be stored in a refrigerator for 2-3 months without significant loss or decomposition of acetaldehyde.

**Preparation of PET samples.** Before grinding, bottle side-walls were cut into small pieces. Preforms were first sliced into rings 3-4 mm thick and then cut into small pieces. Resin pellets were ground as received. The acetaldehyde profile was found to be fairly uniform along the axis of bottles and preforms with the exception of the bottom region, which, under severe molding conditions, showed variation in acetaldehyde levels (15). Approximately 4-5 g of resin or preform pellets were ground for 10 min in a freezer mill under liquid nitrogen. Because PET bottles are more difficult to shatter, only 2-3 g of bottle pieces should be ground in one tube. The mesh sizes of the ground resins were 40/100 and preforms/bottles were 20/80. After grinding, the freezer mill tube containing the sample and the impactor was allowed to defrost for 5 to 10 min near to room temperature. With the aid of a small plastic powder funnel, 2.0 g of PET powdered sample was transferred into an empty headspace vial on a top loading balance. The filled vials were capped immediately to avoid any loss of acetaldehyde. The vials were sealed tightly such that rotation of cap by hand was not possible. To facilitate rapid migration of acetaldehyde into the vial headspace, sample vials were heated in an oven at 130°C for 1 hr. A GC oven with good temperature control was found to be adequate for this purpose. The vials were then transferred to the headspace turntable thermostated at 92°C. Samples were allowed to equilibrate for a least one hour before analysis.

**Calibration procedure.** Reference samples of PET resins with known acetaldehyde content were prepared by adding known quantities of acetaldehyde to acetaldehyde-free PET resins. The acetaldehyde-free resins were prepared by heating ground resins and/or preforms in a vacuum oven overnight at 150°C. Typically, PET reference standards of about 1.7 ppm acetaldehyde level were prepared by adding 1  $\mu$ l of 3.4  $\mu$ g/ $\mu$ g acetaldehyde standard solution to 2.0 g of acetaldehyde-free ground resin. After vigorously mixing the resin powder, these PET reference standards were allowed identical thermal treatments before analysis. Carrier gas was used for pressurizing vials during sample injection. In this laboratory, duplicate vials were prepared for each sample. Averages of 2 analyses were reported.

**Discontinuous gas extraction.** To cross check the accuracy of the headspace method, a discontinuous gas extraction apparatus (Perkin-Elmer accessory for F-22 GC) was installed. The procedure according to Kolb and Pospisil (11) was used to quantify acetaldehyde in PET samples. Approximately 1.0-1.5 g of sample were used at an injection temperature of 140°C. A 15 min equilibration period and a 15 sec injection time were found to give the most satisfactory results. Four extraction cycles were performed on each sample. Results are presented below.

#### Gas Chromatographic Conditions

GC conditions for headspace GC analysis were optimized as follows:

Column: 4 ft x 1/8 in SS Porapak Q 80/100 mesh.

Temperature: Oven, 175°C; injector, 150°C; sampling needle, 150°C; detector, 200°C; sample turntable, 92°C.

Time: Injection, 8 sec; analysis, 9.9 min to allow elution of high boilers; flush time, 15 sec to prevent sample cross contamination in the dosing head. Column back flushing was not necessary.

Detector: Flame ionization detector.

Flow Rate: 30 ml/min of nitrogen measured at ambient temperature.

Under these conditions, acetaldehyde emerged as a sharp peak at under 0.8 min. A typical headspace GC trace is shown in Figure 2.

**Calculations.** Both peak height or peak area analyses were found to be satisfactory and yielded essentially the same results. Peak areas were used in this study. The levels of residual acetaldehyde in the samples were calculated by comparing areas of the acetaldehyde peak to that of a reference PET of comparable level.

## Results and Discussion

#### Accuracy and Precision

Table I shows residual acetaldehyde values on several PET samples as determined by headspace, solid injection GC, and discontinuous gas extraction. Discontinuous gas extraction is a quantitative technique recently developed by Kolb and Pospisil (11). It is based on a stepwise extraction of a solid sample in a thermostated glass GC injection port. Good agreement between the head space and solid injection GC techni-

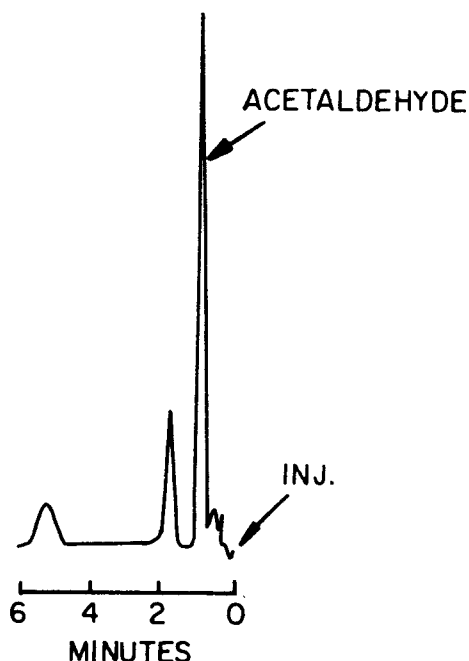


Figure 2. Typical headspace GC trace of PET bottle resin.

Table I. Comparison of Residual Acetaldehyde Values as Determined by Headspace, Discontinuous Gas Extraction, and Solid Injection GC Methods

Sample	Acetaldehyde, ppm		
	Solid GC	Gas Extraction	Headspace
Resin A	—	1.4	1.7
Resin B	2.4	2.4	2.2
Resin C	35.5	—	34.0
Resin D	0.6	—	0.6
Resin E	1.7	—	1.8
Bottle B	—	9.0	7.7
Bottle D	8.9	—	8.4

ques was obtained. Preliminary data from the gas extraction experiment also showed fairly good correlation.

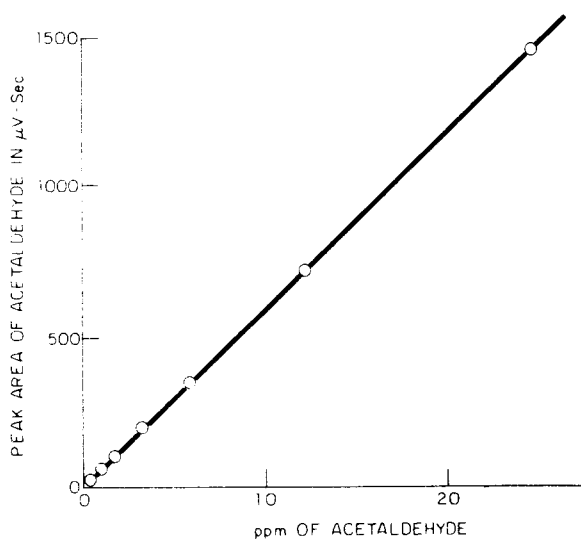
The precision of the headspace acetaldehyde analysis was determined by repeated analyses of the same batch of resin or bottles over a period of 10 days. Typical results are shown in Table II. The coefficient of variation is about  $\pm 6\%$  for duplicate analyses at acetaldehyde levels from 2-20 ppm.

#### Linearity and Sensitivity

Using spiked standards, the acetaldehyde peak areas were found to be linearly proportional to the quantities of acetaldehyde injected into the resin up to 30 ppm (Figure 3). The limit of detection is about 50 ppb based on the procedure previously described.

**Table II. Ten-Day Analysis of the Same Lot of PET Bottles**

Day	Acetaldehyde Value (ppm) <sup>a</sup>
1	10.5
2	12.1
3	10.0
4	10.9
5	12.6
6	12.0
7	11.3
8	12.0
9	11.2
10	11.0
Average	11.4 ± 0.7
Coefficient of Variation	6.1%

<sup>a</sup>Average of duplicate analyses.**Figure 3. Linearity of spiked PET standards.**

### Equilibration Temperature

Equilibration conditions, 1 hr at 130°C followed by 1 hr at 92°C, are designed to ensure complete vapor/solid equilibrium in the shortest time span. The 130°C temperature facilitates rapid diffusion of the acetaldehyde out of the polymer matrix. Prolonged treatment of PET at 130°C is not recommended due to the possibility of polymer degradation. Minimum equilibration time is established by following the peak areas of acetaldehyde during the time course of thermal treatment. A one step equilibration at approximately 90°C can be used; however, equilibration takes a significantly longer time.

### PET Reference

To avoid daily handling of acetaldehyde solutions in preparing PET standards, the feasibility of using a batch of previously calibrated PET resin as reference standard was examined. Results showed this approach to be feasible for short-term analysis. Periodic recalibration is necessary to detect any significant loss of acetaldehyde over a period of time. Room temperature storage of these reference PET pellets in a screw-cap jar is recommended. Storage in a refrigerator must be avoided due to the possibility of contamination from condensed organics.

### Acetaldehyde Levels in PET Resins, Preforms, and Bottles

Of the PET samples analyzed in this laboratory, acetaldehyde levels ranged from 0.5-6.0 ppm for commercial resin; from 30-60 ppm for amorphous resin; and from 6-24 ppm for preforms and bottles. The acetaldehyde level increases from resin to preform/bottle, because it is formed during melt processing (3). Typical levels of acetaldehyde in resins, preforms, and bottles from different resin manufacturers are shown in Table III. Preforms and bottles were molded at Celanese.

**Table III. Typical Acetaldehyde Levels of PET Resins, Preforms, and Bottles from Different Manufacturers**

PET Samples	Acetaldehyde, ppm
Resin from Manufacturer A	2.1
B	4.0
C	1.3
D	3.8
E	2.4
F	1.3
G	1.3
H	2.0
Preforms from Resin A	9.0
B	6.7
C	15
Bottles from Resin A	8.0
B	7.5
C	12

Because only a limited number of lots were examined, these data might not be representative of the actual acetaldehyde level in commercial PET bottle resins presently available.

### Acknowledgement

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