Journal of Agricultural and Food Chemistry

AUGUST 1995
VOLUME 43, NUMBER 8

SHORT COMMUNICATIONS

Analytical Method for Quantifying Butyric Acid, Malathion, and Diazinon in Recycled Poly(ethylene terephthalate)

Keywords: *Analytical method; contaminant(s); recycled poly(ethylene terephthalate); PETE*

INTRODUCTION

Butyric acid, malathion, and diazinon are polar surrogate contaminants chosen in accordance with the guidelines of the U.S. Food and Drug Administration (FDA, 1992) for testing levels of potential contaminants that may be retained through plastic recycling processes. Butyric acid is a volatile, polar contaminant that may result from milk residues in high-density polyethylene (HDPE) milk bottles. It is a persistent residue in this matrix and may also be difficult to remove from poly(ethylene terephthalate) (PETE). Malathion and diazinon are nonvolatile, polar contaminants that are components of household pesticides which could potentially have been stored in such 2-L bottles. These pesticide contaminants are toxic and could be a risk to public health if present in recycled plastics intended for use in food packaging; analytical methods are needed to quantify residues of concern in PETE.

Because no analytical method is available specifically for these surrogates in PETE, the existing methods for determining these compounds in other matrices were investigated. Analytical procedure 232.4, taken from the *Pesticide Analytical Manual* (PAM) (FDA, 1989), had been previously used for malathion determination in PETE, but recoveries were inconsistent and below 70% and had a large variation. The dissolution procedure developed by Pierce and co-workers (D. Pierce, A. Lawson, G. Sadler, Illinois Institute of Technology, Chicago, IL, personal communication, 1993) was also tested. In their procedure, trifluoroacetic acid (TFA) was used to dissolve PETE to free the nonpolar contaminants that had been added to the polymer matrix. These contaminants were then removed by liquid–liquid extraction using isooctane or heptane. The nonpolar contaminants were extracted into the heptane, resulting in high recoveries. When this method was applied to the above polar contaminants, the recoveries were found to be low because the partitioning of the polar contaminants favors the TFA phase rather than the heptane.

The dissolution method developed by Begley and Hollifield (1989) was also evaluated. Their method was initially developed to extract and quantify monomers and small oligomers in PETE materials. In the method, PETE was dissolved in a large volume of a mixture of hexafluoro-2-propanol (HFIP) and methylene chloride (MC). Large oligomers were then removed from the solution by polymer precipitation using acetone. The mixture was then filtered and the solution was concentrated prior to analysis by high-pressure liquid chromatography (HPLC). The dissolution coupled with polymer precipitation does not depend on the partition coefficient of the analyte. However, the method does depend on compatibility between the analyte and the solvents used. The solvents must neither interact with nor decompose the analyte.

This paper describes a dissolution procedure that is a modification of the procedure developed by Begley and Hollifield (1989).

MATERIALS AND METHODS

Reagents. All chemicals were of reagent grade.

Standard Spike Solutions. Standard spike solutions were 2–1000 ppm (w/v) of butyric acid in methylene chloride, 2–1000 ppm of malathion in ethyl acetate, and 2–1000 ppm of diazinon in ethyl acetate.

PETE Material. Clean blow-molded 2-L clear PETE bottles without caps and base cups were supplied by Eastman Chemical Co. (Kingsport, TN). They were prechipped by Eastman Chemical before they were shipped to the test laboratory.

Butyric Acid-Spiked PETE. Clean PETE chips were cryogenically ground with dry ice in an ultracentrifugal mill (GlenMills Inc., Clifton, NJ) equipped with a 1-mm sieve and operated at 20 000 rpm for 1 min. The ground PETE was placed in a mechanical convection oven (Precision Model STM 40, Scientific Inc., Chicago, IL) maintained at 90 °C until a

Table 1. Gas Chromatography Conditions for Determining Butyric Acid, Malathion, and Diazinon

	butyric acid	malathion	diazinon
injector[a]	SPI, 220 °C	SPI, 220 °C	SPI, 110 °C for 2 min, 200 °C/min to 220 °C, hold 9 min
column	Nukol, 30 m × 0.32 mm i.d. × 0.25 μm (Supelco, Bellefonte, PA)	SPB-5, 30 m × 0.53 mm i.d. × 0.5 μm (Supelco)	SPB-5, 30 m × 0.53 mm i.d. × 0.5 μm (Supelco)
column temp, °C	40 °C for 2 min, 6 °C/min to 190 °C, hold 8 min	60 °C for 2 min, 15 °C/min to 210 °C, hold 8 min	same as for malathion
carrier gas, mL/min	nitrogen, 2.5	helium, 10	helium, 10
makeup gas, mL/min	nitrogen, 27	helium, 20	helium, 20
detector[b]	FID, 250 °C	FPD, 250 °C	FPD, 250 °C
hydrogen flow rate, mL/min	30	140	140
air flow rate, mL/min	300	air 1, 80 air 2, 170	air 1, 80 air 2, 170

[a] SPI, septum programmable injector. [b] FID, flame ionization detection; FPD, flame photometric detection.

constant weight was obtained. This PETE was stored in a desiccator before it was spiked with butyric acid. The spiked PETE was prepared by placing approximately 2 g of the ground PETE in a chamber containing butyric acid at room temperature. The chamber consisted of a 950-mL glass jar containing a glass dish (9 cm o.d. × 5 cm high) filled with 30 mL of butyric acid. Weight gain of the PETE was measured periodically on an analytical balance until the adsorbed butyric acid reached a concentration of 0.7% relative to the weight of PETE. The loss of butyric acid from the spiked PETE while weighing was not measured, but it was minimized by rapidly weighing within 10 s. The spiked PETE was transferred to another desiccator before use. During storage, there was some loss of butyric acid but the concentration became stable at approximately 0.3%. The spiked PETE was diluted with uncontaminated chips for preparation of the lower concentrations of spiked PETE.

Butyric Acid Extraction. In this method, 2 g of uncontaminated (control) or spiked PETE chips was placed in a 250-mL Erlenmeyer flask and dissolved in a mixture of 5 mL of HFIP and 10 mL of MC. The dissolved PETE was diluted with an additional 60 mL of MC to freely disperse the butyric acid in the solution. MC was used to facilitate dissolution of PETE through swelling, as observed by Haga (1981). The PETE was then removed by precipitation induced by adding another solvent to modify the polarity of the mixture, as observed by several researchers (Jameel et al., 1981; Makarewicz and Wilkes, 1978; Moore and Sheldon, 1961). The rate of PETE precipitation depends on the type of solvent used. In this study, PETE was precipitated more rapidly by acetone and methanol than by hexane. For recovery of butyric acid, 100 mL of acetone was used to precipitate the polymer. The mixture was then vacuum-filtered in a 500-mL filtering flask. The precipitate was rinsed twice with an additional 20 mL of acetone. The filtrate and rinsings were combined, transferred to a 500-mL round, flat-bottom flask, and concentrated to a final volume of 2–3 mL with a rotary evaporator (Rotavapor RE120, Brinkmann Instruments Inc., Westbury, NY) operated at 30–35 °C and 50–60 rpm. This step is critical for satisfactory recovery of butyric acid. If the filtrate is concentrated almost to dryness (<1 mL), more than 30% of the butyric acid can be lost. In the final step the concentrate was diluted with acetone to 10 mL and filtered again using a 0.2-μm pore filter unit (Millipore Inc., Milford, MA) to remove any remaining polymer residue.

Malathion and Diazinon Extraction. Malathion and diazinon were separately extracted from the spiked PETE by using a procedure similar to that used for butyric acid. The polymer solution was diluted with MC as before, but the polymer was precipitated by using methanol instead of acetone. The mixture was filtered, and the filtrate was concentrated almost to dryness (<1 mL) by using a rotary evaporator to remove the HFIP residue. Because the HFIP appeared to decompose malathion and diazinon, any remaining HFIP was removed by using a C_{18} cartridge. For diazinon, the concentrate was diluted with 20 mL of a 0.1 M disodium phosphate buffer solution adjusted to pH 7.6. This solution was applied (5 mL/min) to the C_{18} cartridge (Sep-Pak, Waters Associates, Inc., Milford, MA), which had been previously wetted with 5 mL of methanol and rinsed with 5 mL of the buffer solution. The loaded cartridge was washed with another 5 mL of buffer solution and vacuum-dried before the cartridge was eluted with 5 mL of methanol. The eluate was filtered through a 0.2-μm pore membrane filter unit to remove any remaining polymer residue and was diluted to 5 or 10 mL with methanol.

For malathion, the concentrate was diluted with 20 mL of a 0.1 M potassium acetate buffer solution that was adjusted to pH 5.2. The mixture was applied to the C_{18} cartridge and eluted with 5 mL of methanol. The eluate was filtered to remove any remaining polymer residue and finally diluted to 5 or 10 mL with methanol.

Gas Chromatography Analysis. A gas chromatography system (Varian Analytical Instruments, Sugar Land, TX), operated and controlled with a 486 microcomputer using STAR workstation software (Varian Analytical Instruments), was used to separate and quantify butyric acid, malathion, and diazinon in PETE extracts. One milliliter of extract was transferred to a 2-mL vial and placed on the carousel tray of the autosampler. Four microliters of the extract was injected into the GC system for analysis. The GC conditions used to determine each contaminant are described in Table 1. The SPB-5 column was preceded by a guard column (1 m × 0.53 mm i.d., deactivated fused silica capillary column) to trap nonvolatile impurities present in the extract.

Limit of Detection. The limit of detection (LOD) of standard solutions of butyric acid, malathion, and diazinon was determined at a signal-to-noise (S/N) ratio of 3. With this criterion it was found that the minimum concentration measurable was 50 ppb. The LOD of these compounds in the polymer extract was also 50 ppb; however, the limit of quantitation (LOQ) in the actual PETE matrix, determined from the amount of each compound spiked in dissolved PETE during extraction, was approximately 1 ppm. Lower concentrations were not investigated because of decreasing S/N ratio.

Recovery Studies. For these studies, 2 g of uncontaminated chips was placed in a 250-mL Erlenmeyer flask, followed by 1 mL of each standard spike solution, 9 mL of MC, and 5 mL of HFIP. The flask was closed with a stopper, and the polymer, the spiking solution, and the solvents were mixed. With a mechanical shaker, the PETE was dissolved within 0.5 h. The polymer solution was then diluted with MC and subjected to the extraction procedure as described previously. Three replicates were used at each spiking concentration.

Additional studies were performed using ground PETE that had been spiked with a known amount of butyric acid quantitated gravimetrically. In this study, approximately 0.1 g of the ground spiked PETE was diluted with uncontaminated PETE chips to a total weight of 2 g. The PETE mixture was dissolved, extracted, and quantitated using the procedure previously described. Four replicates were analyzed. Because malathion and diazinon are nonvolatile, it was not possible to spike PETE with these compounds in this manner.

Table 2. Recoveries from PETE Extract Spiked with Butyric Acid, Malathion, and Diazinon

spike concn in PETE, ppm	av % recovery ± CV			
	no. of replicates	butyric acid	malathion	diazinon
1	3	87 ± 5	84 ± 5	95 ± 5
5	3	88 ± 4	84 ± 3	98 ± 3
20	3	90 ± 4	ND[a]	ND
100	3	89 ± 5	89 ± 6	98 ± 2
500	3	89 ± 4	80 ± 8	81 ± 1
PETE spiked gravimetrically 150	4	86 ± 4		

[a] Not determined.

RESULTS AND DISCUSSION

Recoveries of butyric acid, malathion, and diazinon added to PETE polymer/HFIP/MC solutions at the dissolution step were determined, and the results are shown in Table 2. The recoveries of butyric acid were in the range of 85–95% with a coefficient of variation (CV) of 5%. The percent recovery of butyric acid from gravimetrically spiked PETE powder at a concentration of 150 ppm is also shown in Table 2. The average recovery for four replicate determinations was 86% with a CV of 4%. This value is in the same range as those obtained for PETE solution spiked with butyric acid.

In Table 2, recoveries for malathion are in the range of 72–93% with a CV of 8%, and for diazinon they are 80–100% with a CV of 5%. Recoveries for malathion and diazinon were higher than 80% at spiking concentrations of 1–100 ppm but about 80% at a spiking concentration of 500 ppm. The high recovery at low concentrations could be contributed by an increase in the analyte's peak area from detector, electronic noise, and any coeluting materials. However, the lower recovery at the higher concentrations is possibly due to greater decomposition of the compounds in the presence of HFIP during extraction.

The solvent choice of HFIP or TFA is a key to this method. TFA was not chosen because it is corrosive and incompatible with the GC column. Because HFIP is much more expensive than TFA, this method uses only 5 mL of HFIP to dissolve the polymer. In the analysis, it was observed that HFIP decomposed diazinon and malathion upon concentration of the extract to <1 mL.

This total dissolution method can simultaneously extract butyric acid, malathion, and diazinon from PETE spiked at concentrations of 1–500 ppm of each contaminant and may be applicable to the determination of other contaminants in recycled PETE.

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Received for review April 5, 1995. Accepted June 1, 1995. This research was supported by Cooperative Agreement FD-000431 from the U.S. Food and Drug Administration and by the National Center for Food Safety and Technology.

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JF9502008

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