Pyrolysis-Gas Chromatographic Method for Polybutene Residues on Navel Oranges

by LYLE K. GASTON and F. A. GUNTHER
Department of Entomology
University of California, Riverside, California

Viscous polybutenes have been used to control mites on several greenhouse plants (1) and on lima beans and apples (2). The previous residue method (2) was based on the difference in the weight of a hexane wash between treated and control material. Quite frequently this resulted in untreated control values which were five times larger than the residue level. In order to explore the utility of pyrolytic gas-liquid chromatography in the field of residue analysis, navel oranges were treated with an olefin polymer (polybutene H-100, AMOCO Chemicals Corp.). The polymer residue was determined by its pyrolytic decomposition to isobutene which was separated from other material by gas-liquid chromatography and determined with a hydrogen flame ionization detector.

Materials and Methods

Immature navel oranges were sprayed on August 21, 1964, with 2 qts. H-100/100 gals. as previously described for oranges (3). Samples were taken on August

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27, 1964, (6 days) and on September 25, 1964, (35 days) (3) and processed with hexane, with 0.5 g. rind/ml. of solvent, as previously described (4).

Analyses were carried out using a gas chromatograph equipped with a hydrogen flame detector, a pyrolysis unit, and a 0.1 mV./in. recorder operated at 1 in./min. The gas chromatograph column was 3.05 m. x 2.16 mm. I.D. stainless steel filled with 3.971 g. of 10% Apiezon L on 60-80 mesh Chromosorb-W acid washed and silanized with hexamethyldisilazine. Isobutene had a retention time of 5.0 min. at 28° and a flow rate of 3.84 ml./min. at 727 mm. mercury and corrected to 0°. The pyrolysis unit used was a Wilkins Instrument and Research, Inc., Model A-425 with the platinum pyrolysis coil modified to three turns, 0.5 mm. I.D. This necessitated drilling the pyrolysis block to make room for the extra length of the pyrolysis coil. The pyrolysis was carried out for 6 sec. with a current such that a final temperature of ca 550° was reached (5.1 amp. final). The area of the isobutene peak was measured with a disc integrator.

A 5-µl. aliquot, equivalent to 2.5 mg. of orange rind, of hexane stripping solution was applied slowly to the middle coil while the coil was heated at 2 amp. For reproducible results all of the sample should be in

the hot zone of the coil. This zone is best observed in a black cavity with a dark-adapted eye using the pyrolysis conditions. After all the solvent evaporated, the coil was inserted into the pyrolytic chamber. Triplicated samples were decomposed at ca 550°. Between samples, the coil was cleaned by heating it to ca 1000° in air. A second coil was cleaned and loaded while the isobutene was being eluded. The column was purged every night at 200°. Occasionally the pyrolytic chamber had to be washed with benzene to remove nonvolatile materials.

Results

A standard curve for H-120 was linear between 0.1 μg. and 0.5 μg. with a slope of 48.4 $cm.^2/\mu g.$ (0.75 mV. min./μg.) and an intercept of zero. Control samples of 2.5 mg. each gave 0.71 $cm.^2$ (15 ng.) of apparent isobutene. A standard curve for H-120 fortified controls gave, after substraction of the above blank, a straight line between 0.1 μg. and 0.3 μg. with a slope of 46.0 $cm.^2/\mu g.$ (0.72 mV. min./μg.) and an intercept of zero, corresponding to a 95% recovery. Results from four field-treated samples are given in Table I; they were calculated from a control fortified with H-120 and then corrected to the corresponding amount of H-100. Relative yields of isobutene from H-120 and H-100 were

determined: H-120 gave an area of 20.2 ± 0.6 $cm.^2$ for 428 ng. whereas H-100 gave 17.9 ± 0.4 $cm.^2$ for 430 ng.

TABLE I

Polybutene Residues on Navel Oranges

Field Replicate	Days After Field Treatment	p.p.m. in Rind	
		From H-120	Corrected to H-100
A	6	68 ± 8	77 ± 9
B	6	67 ± 4	76 ± 5
C	6	89 ± 12	100 ± 13
D	6	80 ± 3	90 ± 3
E	35	72 ± 15	81 ± 17
F	35	33 ± 4	37 ± 4
G	35	73 ± 7	82 ± 8
H	35	87 ± 6	98 ± 7

Discussion

The composition and thermal decomposition of ionically polymerized mixed butenes has been studied by Barrall et al. (5). They found that their polybutene decomposed thermally by random cleavage to give mainly isobutene. For all their polymers the yield of isobutene was relatively constant between 500° and 530°.

Initial work was started with Indopol polybutene H-100. After the field treatment was completed, monomer composition and process variables were more closely controlled so that a new polymer, H-120, was produced. The primary differences between the two polymers are a higher viscosity for H-120 and a 13% increase in isobutene yield upon pyrolysis.

The precision of the method in the submicrogram region is very poor even with triplicate analyses: ± 10% at best with a standard, with ± 15% being a realistic working range. In order to achieve even a ± 15% deviation, meticulous care must be taken in the application of the sample to the coil. Oily samples tend to "creep" on the wire and carry material out of the hot zone. Lower pyrolysis temperatures, unmeasured but probably in the 400° region, gave no isobutene whereas higher pyrolysis temperatures, 700°-800°, of orange rind extractives gave quite a large peak in the isobutene region. Because of the low precision, the lower limit of determination would probably have to be a peak with 3 times the area of the control or 12 p.p.m. Peak area gave better precision than peak height because of the comparatively long "injection time" relative to the retention time of isobutene.

The Apiezon L column used probably would not separate isobutene from other C_4 hydrocarbons, but Ebner (private communication) has shown that isobutene comprises ca 90% of the volatile material from methane through C_5 hydrocarbons released by this polymer.

This analytical method could be applied to other polymers that might be found in foodstuffs such as polyethylene, polypropylene, waxes from paper wrappings, mineral oil, and others.

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