

Olefin Isomerization in Adsorptive Sampling on Activated Carbon

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► Bimethallyl, biallyl, and 1-hexene were selected for study of olefin isomerization in adsorption and desorption with activated carbon. Bimethallyl, which is particularly labile to isomerization to conjugated dienes, produces 5 to 15% rearranged products. Biallyl, which is generally more resistant to change, yields 1 to 2% rearrangement. The mono-olefin, 1-hexene, gives no detectable change. It is concluded that most gasoline-range hydrocarbons can be sampled on carbon and recovered for analysis without serious double bond migration or skeletal rearrangement. New designs for desorption apparatus are described.

TO ASSESS the validity of adsorptive sampling (1, 2, 6-8) of atmospheres for gases and vapors, it is necessary to determine the degree to which the

sample is altered prior to analysis. Such alteration may occur during adsorption, retention on the adsorbent, or desorption, and may conceivably entail reaction with normal components of air (oxidation, hydrolysis), interaction among sample molecules (polymerization, condensation), decomposition, or isomerization. In sampling atmospheres for olefinic vapors, the known proclivity of some structures to undergo double bond migration or skeletal rearrangement (4), and the importance of the molecular location of the double bond in determining the degree to which the olefin may act as a smog precursor, make the study of isomerization especially important.

Three unsaturated hydrocarbons were selected for this study: 2,5-dimethyl-1,5-hexadiene (bimethallyl), 1,5-hexadiene (biallyl), and 1-hexene. Bimethallyl, upon allylic-type shift of each of its double bonds, produces the more stable, conjugated, 2,5-dimethyl-2,4-hexadiene

(biisocrotyl); the methyl side chains facilitate the accommodation of charge on the transition intermediate and promote the isomerization. Using an alumina-chromia catalyst, Henne and Turk (4) obtained an 81% yield of the conjugated diene. Biallyl also isomerizes to a stable conjugated diene (2,4-hexadiene, bipropenyl), but the facilitating methyl groups are absent and the change is more sluggish; under the catalytic conditions described above, a 39% yield was obtained. The driving force for isomerization of 1-hexene is the greater stability of more highly substituted double bonds or more highly branched carbon skeletons; the energy profit is not so great as that produced by conjugation, and the change is more difficult to effect.

EQUIPMENT AND METHODS

Adsorptive Sampling. The method whose validity is under study uses a

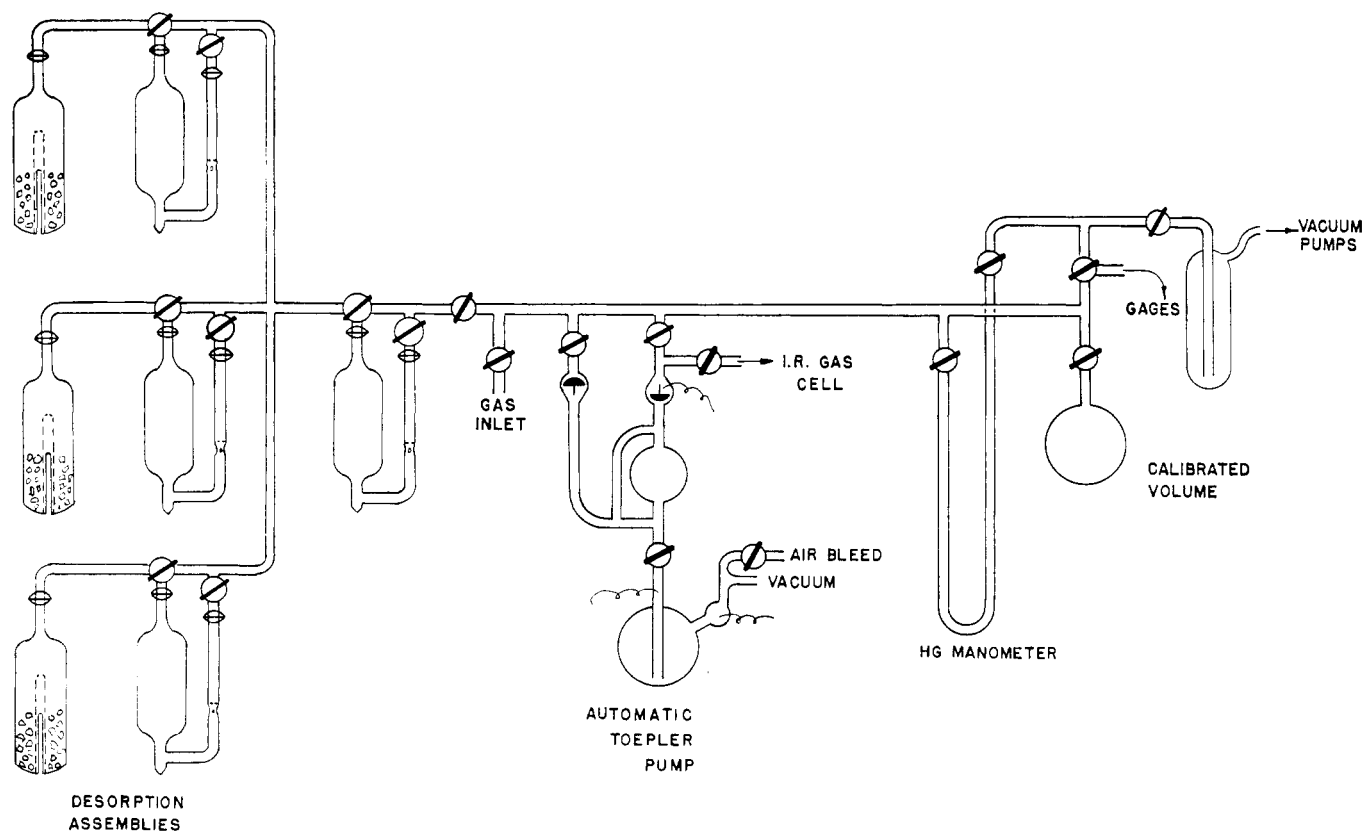


Figure 1. Vacuum desorption system

bed of 6 to 14 mesh (Tyler sieve series) granular activated carbon, of uniform 1.9 ± 0.1 cm. depth in the direction of air flow. The carbon is of the small pore variety made from a nut or coal source and used commercially for air purification. The bed is retained between rigid layers of perforated metal sheeting. To achieve high sampling efficiency for organic vapors of boiling points exceeding about 0°C ., a bed detention time of about 0.3 seconds is needed. Details of the method are described in an ASTM Tentative Recommended Practice (2).

For outdoor sampling under ambient conditions, these requirements are conveniently embodied in a canister-blower assembly which has been illustrated previously (2, 6, 7). In this study, the sampling conditions were simulated in glass equipment (7), and hydrocarbon vapor was introduced by evaporation into the dry air to which the carbon was exposed. Concentrations were kept sufficiently low (~ 100 p.p.m.) so that no sensible temperature rise due to adsorption was produced. The carbon was allowed to adsorb about 2% of its weight of vapor. The desorption of 25-gram samples thus yielded about 0.5 gram of desorbate for analysis.

Adsorption could also be carried out more simply by introducing the vapor into the gas inlet of Figure 1 and allowing it to diffuse toward the carbon in one of the sample tubes shown on the left. For the purposes of the isomerization study, the method of introduction of the adsorbate was not critical.

Desorption. Arrangement of components for desorption is shown in Figure 1. Ovens and cold traps are on the left and are manifolded for three simultaneous desorptions. A second in-line trap may be used in series with any of the manifolded

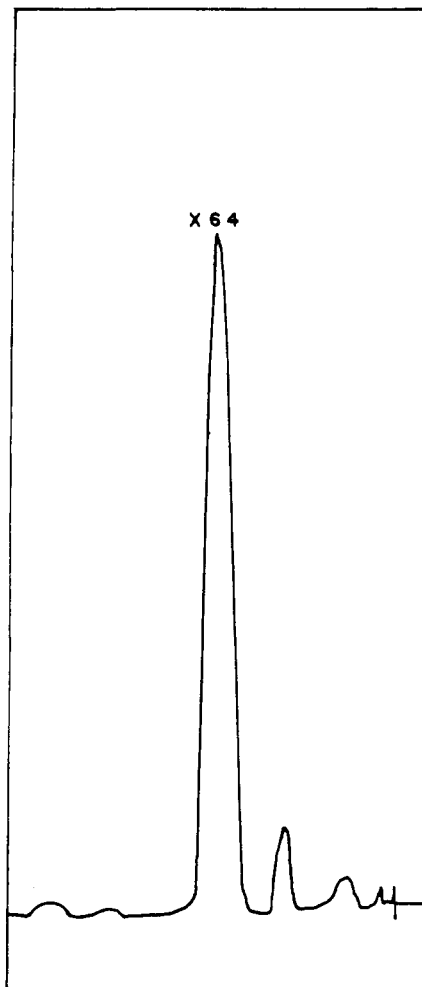


Figure 2. Chromatogram of pure bimethallyl

traps, if desired. The gas inlet is provided for access for adsorption of gases onto the carbon in the fixed-bed tube, for studies of displacement, reactions on the carbon surface, etc. A relay-activated Toepler pump compresses gaseous material into a cell for infrared or other studies. The system also includes the usual vacuum line components for pressure measurement and pumping.

The desorption ovens, new in design, hold the granular carbon in the annular space between the outer wall and an inner perforated tube. The bed depth for desorption is small (about 1 cm.) and independent of the quantity of carbon used. An inner well accommodates a thermometer or thermocouple. The assembly is linked to the vacuum manifold by a greaseless O-ring joint. A cylindrical heater, not shown in the diagram, is fixed around the desorption oven for uniform heating. The carbon to be desorbed is simply poured into the tube and settled by gentle tapping. During the time that the vapor traverses the granular adsorbent bed, it is subject to repeated adsorptions and desorptions. This trap holds such detention time to a small and constant value and is therefore a distinct advance over U-tubes and flasks in which the bed depth depends on the quantity of adsorbent.

The cold traps shown are also new in design. The expanded section accommodates a large quantity of ice without clogging and avoids the requirement for pre-drying the desorbate stream. The O-ring joints are staggered to accommodate joint clamps compactly and allow the entire trap to fit into a 1-liter laboratory Dewar flask. The perforated shelf in the short arm supports a glass wool plug for filtration of condensation particles that may be produced inside the tube. The organic matter is removed by rinsing the plug with solvent and tamping it against the shelf so that the liquor runs down to the bottom of the tube. The shelf also supports other material which may be used to react with trapped vapors—e.g., Ascariite for neutralization of HBr from brominated carbon. The side-arm design allows all liquid to be removed from the trap by sucking it out with a long pipet or syringe from the small tip at the bottom of the longer tube. When the organic matter is rinsed down with a heavy solvent (CCl_4), its direct separation from water is very conveniently accomplished.

Desorption is carried out by heating the carbon and passing the desorbate through the adjoining trap which is refrigerated in liquid nitrogen. At the end of the run, the trap is isolated from the carbon, and its contents are allowed to warm to the temperature of a warmer refrigerant or of the room. Any significant gaseous material produced may be measured and pumped into a cell for infrared or other examination. After the contents of the trap have melted, the walls may be rinsed carefully with solvent (CCl_4 is the solvent of choice). The glass wool plug in the short arm may also be wetted with solvent and tamped down, so that any sample recovered from it joins the main batch. For quantitative study, the organic content may be made up to a standard volume by addition of solvent, and may be removed from supernatant water by pipet or syringe. This solution may be used directly for gas chromatographic examination, or dried and used for infrared study.

The retention of biallyl (the most volatile liquid studied) in the liquid-nitrogen cooled traps at about 10^{-6} mm. pressure was found to be complete over a period of 3 hours.

ISOMERIZATION STUDIES

Bimethallyl. The material used was a fractionated commercial product. Chromatographic examination (Figure 2) showed only traces of impurities comprising, in aggregate, about 0.1%. A Perkin-Elmer Model 154-C Vapor Fractometer, with a 1-meter column of di-2-ethylhexyl sebacate on diatomaceous earth, was used. The expected conjugated isomer (biisocrotyl) was prepared by isomerization over alumina (4) for use as a reference compound. Table I shows degrees of isomerization obtained under various conditions of desorption. For

Table I. Desorptive Recovery of Dienes

Time to Reach Temperature, Hours	Maximum Temperature, $^\circ\text{C}$.	Per Cent of Maximum Yield	Percent of Yield Isomerized
BIMETHALLYL			
$\frac{1}{2}$	250	75	4.2
	300	90	7.5
	350	100	15.5
1	250	95	7.4
	300	96	7.3
	350	100	12.2
2	250	100	3.0
	300	100	13.2
	350	100	14.2
4	250	65	2.4
	300	95	5.5
	350	100	12.2
BIALLYL			
$\frac{1}{2}$	250	95	1.2
	300	93	0.7
	350	100	1.2
1	250	100	0.6
	300	100	1.3
	350	100	0.8
2	250	95	2.2
	350	100	1.5

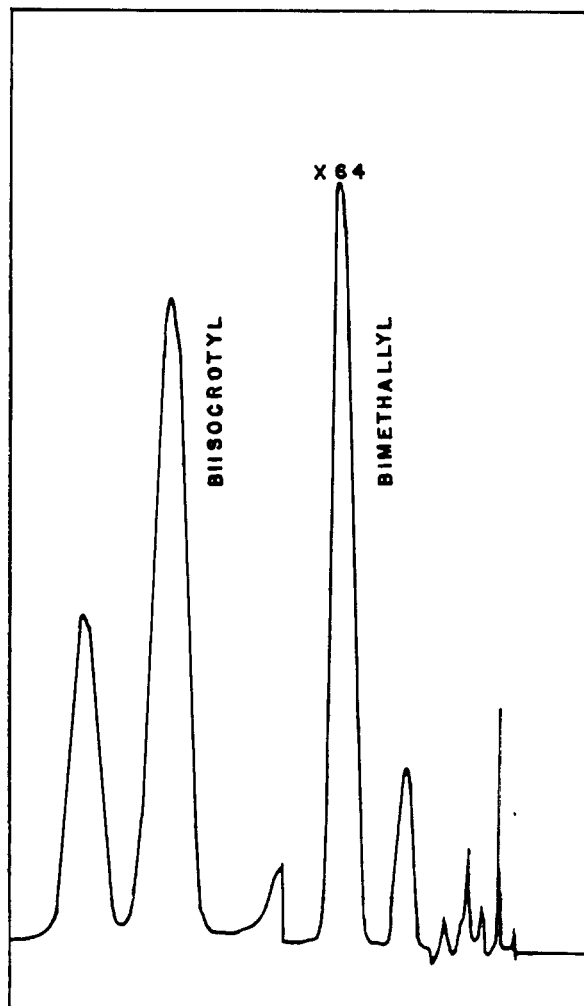


Figure 3. Chromatogram illustrating the desorptive isomerization of bimethallyl

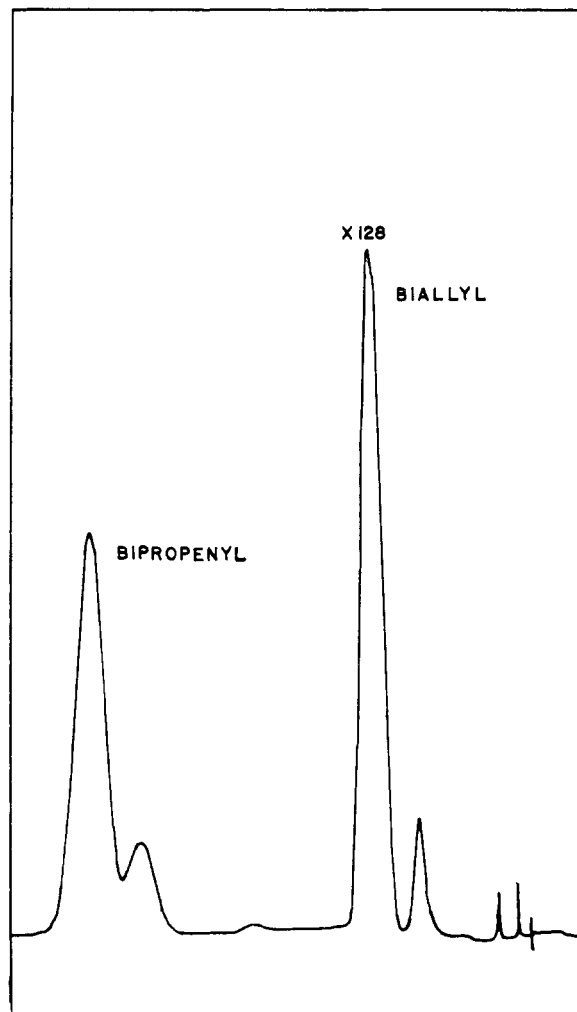


Figure 4. Chromatogram illustrating the desorptive isomerization of biallyl

uniformity in comparison, each of the samples was heated and pumped for 5 hours. Heating schedules and maximum temperatures varied as shown. Over-all maximum yields were 85 to 90%. Some of the loss is accounted for by production of polymerized product. The study of the distribution of this loss between polymerization on the carbon surface, alteration after recovery, or other fates will be undertaken. The isomerized product consisted of two major components, one of which was identified as biisocrotyl by matching it with the authentic material. A typical chromatogram (CCl_4 peak omitted) taken from a run at 350°C . is shown in Figure 3.

Biallyl was prepared by condensation of allyl chloride over magnesium (3, 5) and was fractionated to a purity about the same as that of the bimethallyl. Isomerization data also appear in Table I. A typical chromatogram (CCl_4 peak omitted) taken from a run at 350°C . appears in Figure 4. The method was the same as that used for bimethallyl.

A mixture of 1-hexene (b. p. 63.49°C .)

and its higher-boiling isomers *cis*-3-hexene (66.44°C .), *trans*-3-hexene (67.08°C .), *trans*-2-hexene (67.87°C .) and *cis*-2-hexene (68.84°C .) was found to be resolvable into components by a 150-foot Golay column using a flame ionization detector. When 1-hexene was adsorbed and desorbed under the conditions described here (300°C . and 350°C .), and the desorption products were examined, only 1-hexene was recovered. No isomerization products resulted.

DISCUSSION

The data show that the more isomerizable diene (bimethallyl) undergoes significantly less change at the lower temperatures used, but that this recovery is achieved at the expense of diminished over-all yield. Attempts to desorb quickly by rapid heating do not forestall isomerization. Such effects are not noted for biallyl, the lower boiling, more stable diene.

The general conclusion is that, under the experimental conditions described in this study, the contamination of

sampled olefins by their rearrangement products does not present itself as a significant invalidation of the sampling method. Molecular structures which are particularly susceptible to change will isomerize when desorption conditions become stringent, but most of the gasoline-range hydrocarbons would be expected to fall outside this class. Nonetheless, efforts to increase sampling validity by reducing the required rigor of desorption conditions are considered worthwhile and are under investigation. These efforts comprise, in major part, the use of adsorption-desorption cycles in the presence of a foreign displacing gas or vapor.

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LITERATURE CITED

- (1) Adams, D. F., Koppe, R. K., Jungroth, D. M., *Tappi* **43**, 602 (1960).

- (2) Am. Soc. Testing Materials, Philadelphia, Pa., Tentative Recommended Practice for Sampling Atmospheres for Analysis of Gases and Vapors, D-1605-58 T, 1958.
- (3) Henne, A. L., Chanan, H., Turk, A., *J. Am. Chem. Soc.* **63**, 3474 (1941).
- (4) Henne, A. L., Turk, A., *Ibid.*, **64**, 826 (1942).
- (5) Turk, A., Chanan, H., *Org. Syntheses* **27**, 7 (1947).
- (6) Turk, A., Sleik, H., Messer, P. J., *Am. Ind. Hyg. Assn. Quart.* **13**, 23 (1952).
- (7) Turk, A., Morrow, J., Levy, P. F., Weissman, P., *Intl. J. Air and Water Pollution*, **5**, 14 (1961).
- (8) West, P. W., Sen, B., Gibson, N. A.,

ANAL. CHEM. **30**, 1390 (1958).

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Analysis of 4,4'-Isopropylidenediphenol by Isotope Dilution

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► An isotope dilution procedure is described for the direct assay of the *p,p'*-isomer of bisphenol A. The method is accurate to approximately $\pm 0.5\%$ *p,p'*-BPA and is applicable over a wide concentration range.

THE importance of 4,4'-isopropylidenediphenol (bisphenol A) as a raw material in the manufacture of epoxide resins and other polymers has accentuated the need for a more direct and comprehensive method of analysis, free from the limitations of existing procedures. Paper chromatographic analysis, described by workers of this laboratory, involves determining individual known impurities and then obtaining the major *p,p'*-BPA isomer by difference (1). ASTM precision freezing and melting point determinations are not generally applicable to low purity samples, are tedious to apply, and require considerable amounts of sample material for analysis. Isotope dilution techniques afford quantitative analysis without quantitative separation, provided that qualitative isolation of the component of interest in high purity is possible. Accordingly, an isotope dilution method applicable over a wide concentration range has been developed for direct assay of *p,p'*-BPA. The method applies not only for technical and high purity grades of bisphenol A, but for crude in-process materials as well, and requires only a fraction of a gram of sample for analysis.

OUTLINE OF METHOD

A known amount of high purity, carbon-14-labeled *p,p'*-BPA of known specific activity is intimately blended with a known amount of sample by dissolution in hot chlorobenzene; then a high purity fraction of *p,p'*-BPA containing a representative mixture of labeled and unlabeled molecules is

recovered by recrystallization. Comparative specific activities of the recovered sample fraction and of the labeled reference material are determined by liquid scintillation counting for calculation of the final result.

APPARATUS AND REAGENTS

Apparatus. A manually operated Tri-Carb liquid scintillation spectrometer (Packard Instrument Co., La-Grange, Ill.) is used for counting. Counting vials are of low potassium glass, with a 20-ml. capacity.

Reagents. The liquid scintillation counting solution has the following composition: 500 ml. of reagent grade toluene; 500 ml. of 1,4-dioxane treated with activated alumina and activated charcoal and then filtered; 0.3 gram of 2,5-diphenyloxazole; 0.05 gram of 1,4 bis[2-(5-phenyloxazolyl)]-benzene (POPOP); and 50 grams of naphthalene recrystallized from ethyl alcohol. The carbon-14-labeled *p,p'*-BPA was synthesized by the catalytic condensation of phenol with 0.5 mc. of carbon-14-labeled acetone at a phenol-to-acetone molar ratio of 10 to 1. Unconverted reactants were distilled from the crude product, then high purity *p,p'*-BPA was recovered by three successive recrystallizations from chlorobenzene at a 5 to 1 weight ratio of solvent to bisphenol A. The final recovered crystalline fraction was 99.9% wt. pure *p,p'*-BPA with a specific activity of approximately 2 μ c. per gram. Purity of the labeled reference material was checked by paper chromatography and by ASTM freezing point methods.

PROCEDURE

Tagging and Blending. Accurately weigh into a 25-ml. glass-stoppered Erlenmeyer flask approximately 0.2 gram of sample and approximately 0.05 gram of carbon-14-labeled reference *p,p'*-BPA. Add approximately 15 ml. of reagent grade chlorobenzene and dissolve the mixture on a hot plate set at low heat. During the solution and subsequent crystallization

steps, stopper the flask lightly to avoid solvent evaporation. Remove the flask from the hot plate and stir the solution gently with a narrow spatula to ensure thorough mixing of the labeled and unlabeled *p,p'*-BPA molecules. Avoid getting liquid on the sides of the flask.

Crystallization. Allow the solution to cool slowly to room temperature; then add a single *p,p'*-BPA crystal to initiate crystallization. Crystallization is normally rapid, requiring less than 45 minutes for recovery of approximately 50% wt. of the available *p,p'*-BPA. The resulting crystals should separate from the mother liquor into clear, long, needle-like structures. An amorphous, gel-like mass enveloping the entire volume of sample may form during the crystallization step, particularly during analysis of high purity bisphenol A samples. If this happens, redissolve the mixture and repeat the crystallization step until satisfactory crystals are obtained. Formation of the gel-like material is objectionable because of possible coprecipitation of impurities and because of difficulty in removing the solvent during the filtration and drying steps.

Filtration and Drying. As soon as a recoverable amount of crystals is available for counting, collect the crystals on a medium pore fritted-glass filter attached to a vacuum system. Rinse the crystals once with several milliliters of fresh chlorobenzene to remove occluded mother liquor, then follow this initial rinse with several milliliters of benzene to remove chlorobenzene, thus expediting crystal drying. Dry the crystals by air flow under vacuum for about a half hour before weighing and counting.

Counting. Accurately weigh 0.1 gram or less of the dry recovered crystals into a 20-ml. glass counting vial. Add scintillation counting solution, keeping the level of liquid just below the shoulder of the vial. In a similar manner, prepare a standard counting solution containing approximately the same amount of accurately weighed carbon-14-labeled reference *p,p'*-BPA tracer dissolved in liquid scintillator. Prepare a third vial con-