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QUANTITATIVE DETERMINATION OF VOLATILES IN NON-VOLATILE MATRICES

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SUMMARY

An integrated vacuum distillation-gas chromatographic method has been developed for measuring total volatiles content and absolute levels of specific volatiles in polymers and other relatively non-volatile matrices. The method is very versatile and is used for the simultaneous determination of moisture and organic volatiles over the range 0.0005% to 40% by weight with a precision of $\pm 4\%$ relative. The lower limit of detection for hydrocarbon volatiles is 1 ppb* with flame ionization detection. Specific applications to the quantitative determination of hydrocarbon volatiles in high-density polyethylene (HDPE), moisture and hexane in atactic polypropylene, and a trace odorant in HDPE are presented.

INTRODUCTION

Synthetic polymers often contain small amounts of residual volatile material such as monomers, processing solvents, additives, moisture, or other impurities. When polymers are heated, they may also release material as a result of volatilization or thermal degradation of either the polymer or additives. All of these volatiles can have an important effect on a polymer's processability, thermal stability, odor, color, and general acceptability.

The separation and quantitation of volatile mixtures is best accomplished by gas chromatography (GC). If the volatile material is contained in a relatively non-volatile matrix, however, some prior method of separation is necessary before the GC analysis can be initiated. Various methods for accomplishing this have been discussed by Teranishi *et al.*¹ and Mlejnek². The most simple approach is direct sampling of headspace volatiles; however, this technique is limited to relatively low boiling hydrocarbon volatiles. It may also be difficult to relate the gas-phase concentration to that in the solid phase³. Solvent extraction is sometimes useful if selective extractions are minimal and solvent impurities and/or extractable non-volatiles do not interfere in the GC analysis.

Dissolving the polymer is useful for polymers that are totally soluble at room temperature; however, some of the volatiles (*e.g.*, moisture or CO₂) may not be soluble in the solvent. For polymers that will not go into solution except at elevated temperatures, there is the additional problem of volatiles loss. Dissolution and extraction also

* Throughout this article the American billion (10⁹) is meant.

require large amounts of solvent which may dilute the volatiles to a level that is difficult to detect by GC, and the large solvent peak in the gas chromatogram may obscure peaks of interest or create extraneous peaks. Also, none of these methods gives a total volatiles weight loss.

Desorption of volatiles into the GC carrier gas stream is widely used and many methods of accomplishing this are currently in use². This technique is very useful for hydrocarbon volatiles; however, it is very difficult to use for low-level moisture analysis due to problems in minimizing background moisture level. Also, isolation of the total volatile content for analysis by ancillary techniques or odor appraisal is not easily accomplished.

Distillation is a simple and useful technique for removing volatiles from relatively non-volatile matrices. Teranishi *et al.*¹ point out, however, that quantitative results are imprecise owing to loss of low-boiling components during subsequent handling of the distillate or because of inefficient condensation in the cold traps. Representative sampling of heterogeneous distillates is also a problem.

To obviate many of the above problems, an integrated vacuum distillation-gas chromatography method has been developed. High vacuum represents the ideal "solvent" for a volatiles-in-polymer analysis since it removes only volatile materials from the sample, gives no large solvent peak in the gas chromatogram, introduces no artifact peaks, is non-selective, and allows very small amounts of distillate to be easily handled without sample loss. The latter is accomplished by cryogenic distillation from point to point under vacuum.

In our method an accurately weighed amount of polymer is placed in a tared sample container and distilled under vacuum at elevated temperatures for varying lengths of time. The evolved material is isolated in a cold trap and then transferred to a novel sample loop apparatus which interfaces the vacuum system to a gas chromatograph. The sample loop apparatus is constructed from a Rotoflo PTFE stopcock and is rugged, has a low dead volume, can be heated to 150°, and is very simple to use. The method is versatile and can be applied to a variety of volatile materials which are present in polymers or other relatively non-volatile materials such as waxes and oils.

A similar approach, used for determining ethylene oxide in polymers, has been developed by Mogenhan *et al.*⁵ Their system, however, would not be suitable for moisture analysis and the sample loop/valve arrangement has a relatively large volume which leads to low column efficiency.

Specific applications to the quantitative determination of hydrocarbon volatiles in high-density polyethylene (HDPE), moisture and hydrocarbon volatiles in polypropylene (PP), and trace odorants in HDPE are presented.

EXPERIMENTAL

The simple high-vacuum apparatus used for distillation and cryogenic trapping of the distillate is shown in Fig. 1. It consists of a small manifold line, a spiral cold trap (B), and a sample holder (A) along with associated stopcocks. The system is kept relatively "grease free" by using Rotoflo PTFE stopcocks. At point (1) a 2-mm Rotoflo stopcock is used to admit ultra-dry nitrogen or air to the system.

Stainless-steel bellows joints were also put in the system to give it flexibility and less susceptibility to breakage due to sudden jarring or movement of the system.

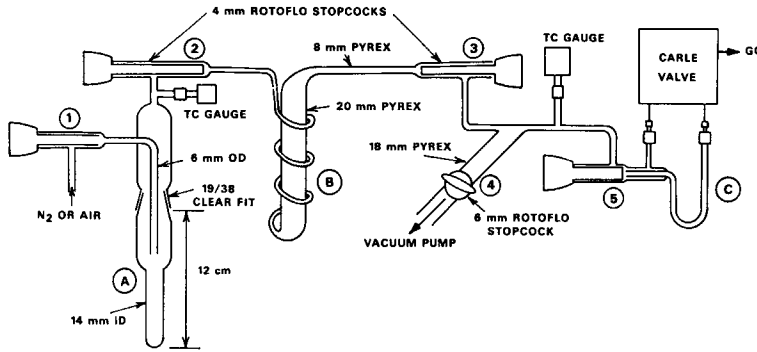


Fig. 1. Vacuum system used for collecting and handling volatiles from non-volatile matrices.

The pumping system consists of a Sargent-Welch Duo Seal vacuum pump (Model 1400) equipped with a Consolidated Vacuum Corporation oil diffusion pump (Type VMF-10). Pressure is monitored in the 1- to 1000-mtorr range with a GT-340A thermistor gauge available from the Bendix Corporation.

The specially designed apparatus to interface the vacuum system with a gas chromatograph is shown in Fig. 2a. It consists of two major parts: a pyrex U-tube attached via a ring seal to a 4-mm RotoFlo stopcock with the PTFE barrel pointing toward the loop, and a 4-port Carle valve. The Carle valve is of the microvolume type (Carle catalog No. 2017) which has been factory conditioned for high-vacuum operation. It has two modes, as shown in Fig. 2b. In one, carrier gas is bypassed through the valve and back to the gas chromatograph; in the other, the carrier gas is diverted through the sample loop before returning to the gas chromatograph. The Carle valve is attached to the sample loop with 1/8-in. Swagelock fittings on 1/8-in. Kovar metal which has been fused to the glass tubing.

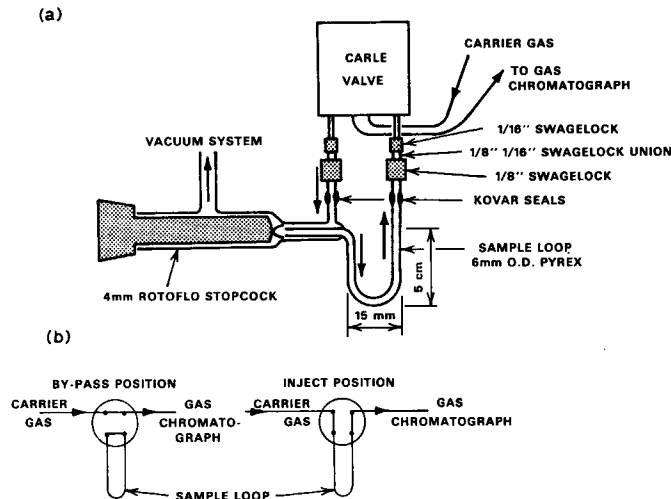


Fig. 2. (a) Device for interfacing vacuum system with gas chromatograph. (b) Carrier gas flow diagram for Carle valve attached to interface device in Fig. 2a.

The Carle valve body and a portion of the connecting tubing are placed inside an insulated box which is heated to 150° and the temperature is continuously monitored with an iron-constantan thermocouple attached to the valve body. The entire stopcock body (except for the PTFE barrel) is wrapped with insulated nichrome wire and heated to 150°.

The Carle valve-glass loop interface apparatus is then attached to the gas chromatograph. A schematic flow diagram is shown in Fig. 3. A two-way valve is placed downstream from the carrier gas flow controller so that carrier gas may be diverted either to the injection port or to the Carle valve simply by rotating the valve stem. A pressure gauge is located between the two-way valve and Carle valve to measure the pressure in the sample loop.

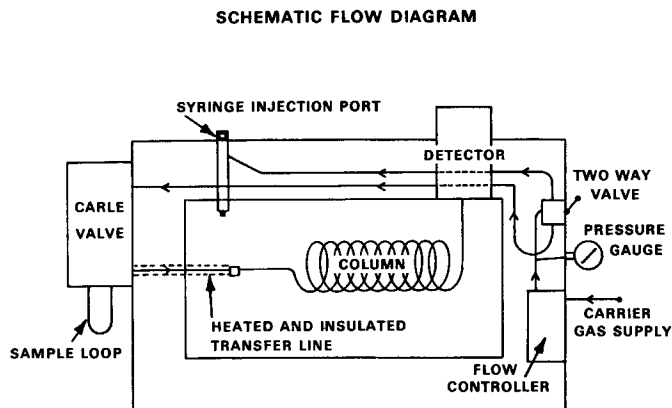


Fig. 3. Schematic flow diagram for operation of gas chromatograph with syringe injection or with interface device shown in Fig. 2.

A Varian 1400 gas chromatograph equipped with a hydrogen flame ionization detector and a programmed temperature oven was used for hydrocarbon volatile levels of 1% or less. The gas chromatography column is a 16-ft. \times 1/8-in. stainless-steel tube packed with 10% SE-30 silicone on 60–80 mesh acid-washed Chromosorb W.

The GC analysis of distillates containing moisture was done on a Hewlett-Packard Model 5700 gas chromatograph equipped with thermal conductivity detection. The GC column was a 4-ft. \times 3/17-in. stainless-steel tube packed with 80–100 mesh Porapak Q (ref. 4).

Specific volatiles are quantitated in the GC analysis by direct calibration of the detector. This is accomplished by injecting absolute weights of each volatile into the gas chromatograph and constructing a calibration plot. For hydrocarbon volatiles the preferred method is to prepare standard solutions of the volatiles in question and to inject accurately measured volumes of each by syringe. In this technique it is mandatory that the solutions are quantitatively and reproducibly injected by backing the sample in the syringe barrel with air and a pure solvent flush of sufficient size to completely sweep the needle. Fig. 4 shows a calibration plot constructed for hexane and a C_{10} – C_{12} paraffinic material over the weight range 2–180 μ g. Relative standard

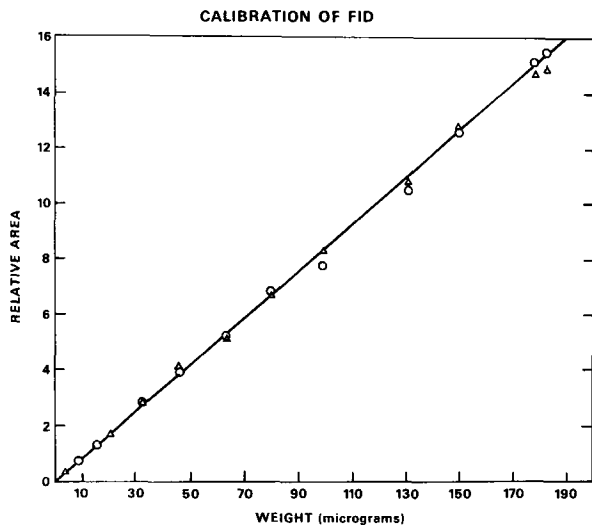


Fig. 4. Direct calibration of flame ionization detector with hexane (Δ) and RAF-B (\circ).

deviations of 2–3% were calculated for data over a two-week period. Frequent calibration is necessary when using absolute responses from flame ionization detectors because of collector surface changes with time. Flame response is, however, relatively stable and reproducible over short periods of time.

The thermal conductivity detector is calibrated in a different manner owing to the difficulty of obtaining precise results by syringe injection. In this case accurately known weights of water are generated by heating sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) to 200° in the vacuum distillation apparatus. At this temperature it gives off a stoichiometric amount of water within 10 min. Accuracy can be checked by reweighing the sample container after heating. The water generated is then cryogenically transferred under vacuum to the sample loop from which it is flushed into the gas chromatograph. The direct calibration procedure for thermal conductivity detectors requires that all experimental parameters such as flow-rate, detector current, and detector temperature be rigorously controlled.

Fig. 5 is a calibration plot constructed from data taken over a one-year period, and shows a linearity of response over the weight range 0.0010–2.0 mg of water. The standard deviation calculated from over 200 calibration points during this period was 3.0% relative.

13×100 mm test tubes are used as sample containers for samples in which only hydrocarbon volatiles are evolved. Test tubes were chosen for several reasons: (1) They fit snugly into the sample container holder (A) in Fig. 1. (2) While the lower one third of the sample container is being heated, the upper portion can be kept cool with a stream of cooling air, and any high-boiling volatiles such as additives or oligomers can be condensed on the top of the test tube while the lower-boiling ones transfer to the cold trap. (3) The test tubes can easily be removed from the sample container holder and reweighed for a gravimetric volatiles determination.

For cases in which a moisture determination is required, the sample containers are 13×13 mm cups fashioned from aluminum foil. Glass test tubes are unsatisfac-

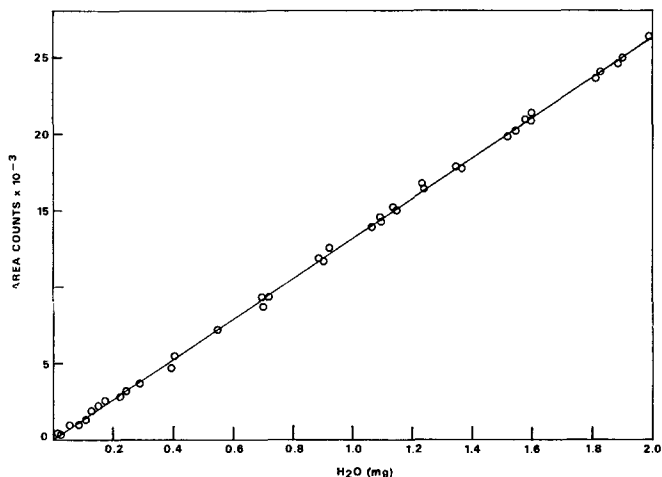


Fig. 5. Direct calibration of Hewlett-Packard Model 5700 thermal conductivity detector with water.

tory because water adsorbed on the surface causes large background effects. At 50% relative humidity, for example, the surfaces of the 13×100 mm test tubes held approximately $700 \mu\text{g}$ of water, whereas the aluminum cup surfaces held less than $10 \mu\text{g}$ of water. This small amount can easily be corrected for.

PROCEDURE

The general procedure for quantitative determination of specific volatiles and total volatiles in relatively non-volatile matrices involves vacuum distillation of an accurately measured weight of sample followed by GC analysis of the distillate. The distillation conditions such as sample size, distillation temperature, and time of distillation are determined empirically for each particular type of sample. For example, the distillation temperature is usually set at the melting point for synthetic polymers and the sample size set at a level where the quantity of volatiles fall within the calibration range of the detector. The distillation time is then determined simply by sampling the distillate at fixed time intervals until 99+ % of the volatile material has been recovered.

A specified weight of polymer is loaded into the appropriate sample container and dropped into the sample container holder (A) (Fig. 1) which is then attached to the vacuum system at the 19/38 clear fit joint. In samples where a moisture determination is required, the sample container holder is continuously flushed with dry nitrogen during sample loading.

The sample container holder is then immersed in a liquid nitrogen-filled dewar for approximately 5 min. This has the effect of freezing the volatiles in the polymer so the nitrogen and air in the system can be pumped out before the distillation step begins. If this step is omitted, there is the danger of volatiles loss during initial cold trapping due to the formation of micro-fogs which can be swept through the trap by nitrogen or air¹.

When all the air has been pumped from the system, stopcock (3) is closed and

the spiral trap (B) is immersed in a liquid nitrogen-filled dewar. The sample container (A) is then immersed in a heat bath set at a predetermined temperature. For most hydrocarbon polymers, such as polyethylene or polypropylene, the temperature is 230°. The length of time needed for complete removal (99+%) of specified volatiles is determined empirically simply by sampling the distillate at increasing time intervals and by closing stopcock (2) and observing the pressure increase inside the sample container via the TC gauge. The sample size should be held constant within $\pm 10\%$ since the distillation time needed to quantitatively remove specified volatiles increases with increasing sample size.

The specified volatiles in the distillate are then quantitated by GC. This is accomplished by transferring the distillate in trap (B) to sample loop (C) by trap-to-trap distillation under vacuum. The extent of transfer is monitored by the thermocouple gauge installed between (B) and (C). Stopcocks (2) and (4) are closed with (3) and (5) open during the transfer step. When the transfer step is completed, stopcock (5) is closed and the entire distillate is isolated in sample loop (C).

The distillate in sample loop (C) is chromatographed by heating the loop with a heat gun and switching the Carle valve from the "bypass" to the "inject" position which sweeps the distillate with helium carrier gas through heated transfer lines to the GC column. The column selected for the GC analysis depends on the chemical nature of the volatiles and their number. After separation by GC, the specific volatiles are quantitated by comparing peak areas with those generated by injecting known weights of each compound. The concentration of each volatile in the original polymer sample is then calculated by dividing the weight of the specific volatile determined from GC by the sample weight.

The gravimetric determination of total volatiles is done by reweighing the cooled polymer sample and dividing the difference in weight by the original polymer sample weight.

RESULTS AND DISCUSSION

High-density polyethylene

Fig. 6 shows a typical gas chromatogram of the separation of a vacuum distillate from HDPE. The hexane peak is usually accompanied by three smaller peaks, which are impurities in most commercial-grade hexane. They elute in the following order: 2-methylpentane, 3-methylpentane, *n*-hexane, and methylcyclopentane and, since most commercial hexane includes these isomers in the purity assay for hexane, they are included in the hexane area calculation. RAF-B is a mixture of hydrocarbons which elutes in a broad array of peaks over the C₁₀ to C₁₂ boiling range. The small peaks eluting after RAF-B are probably HDPE oligomers.

Precision of the combined vacuum distillation-gas chromatographic procedure for hexane and RAF-B was checked by repeated sampling of several batches of HDPE pellets. Table I lists data for three samples of pellets and illustrates the excellent precision of the analysis.

The recovery of volatiles by this method was demonstrated in several ways. In the first, several samples were vacuum distilled at 230° for periods up to 2 h and the trapped distillates were gas chromatographed every 30 min. The data in Table II show that 98+ % of the RAF-B and 99+ % of the hexanes that can be removed

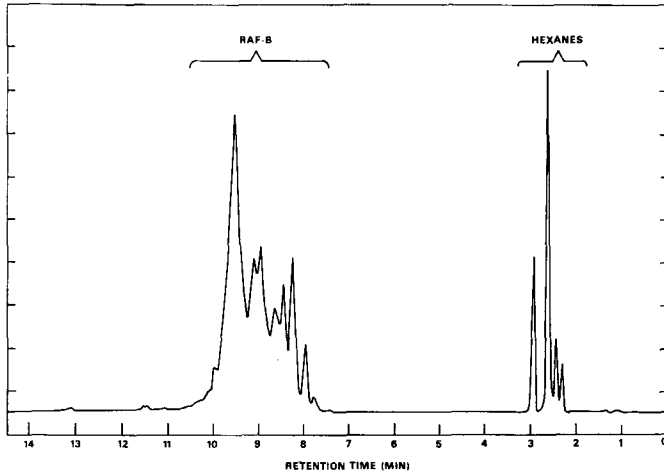


Fig. 6. Gas chromatogram of a vacuum distillate from high-density polyethylene. Column was a 16-ft. \times 1/8-in. stainless-steel tube packed with 10% SE-30 on 60-80 mesh acid-washed Chromosorb W, temperature programmed from 40° to 300° at 15°/min. Helium flow-rate, 40 ml/min; hydrogen flow-rate, 40 ml/min.

from the polymer under the conditions of the experiment are removed in the first 30 min. Similar results were also obtained over the distillation temperature range 180°-250° with the required heating time decreasing as temperature increased.

In another check on recovery, hexane and RAF-B were determined in HDPE by completely dissolving the polymer in hexadecane, reprecipitating the polymer, filtering off the hexadecane solution, and analyzing it by GC. An accurately known weight of HDPE was dissolved in *n*-hexadecane at 130° in a loosely capped vial equipped with a small magnetic stirring bar. Accurately weighed amounts of *n*-nonane and

TABLE I
PRECISION STUDY OF VOLATILES RECOVERY

Sample	Sample weight (mg)	GC area counts		Weight (mg)		Wt. %	
		Hexane	RAF-B	Hexane	RAF-B	Hexane	RAF-B
A	144	15,189	57,353	0.183	0.691	0.127	0.481
	168	16,102	72,625	0.194	0.875	0.118	0.520
	152	16,434	59,262	0.198	0.714	0.130	0.472
	158	15,106	66,898	0.182	0.806	0.116	0.511
	140	13,944	59,262	0.168	0.714	0.120	0.510
	142	14,608	61,005	0.176	0.735	0.124	0.517
						$\bar{X} = 0.122\%$	$\bar{X} = 0.501\%$
						$\sigma = 0.006$	$\sigma = 0.018\%$
B	551	19,981	53,773	0.241	0.648	0.0437	0.118
	223	8,419	23,011	0.101	0.277	0.0453	0.124
	168	6,437	15,745	0.0776	0.190	0.0462	0.112
						$\bar{X} = 0.0450\%$	$\bar{X} = 0.118\%$
						$\sigma = 0.030$	$\sigma = 0.005$

TABLE II

VOLATILES RECOVERY *versus* DISTILLATION TIME

Distillation temperature: 230°.

Sample	Time (min)	Hexane area	RAF-B area	Hexane	RAF-B
C	30	19,981	53,773	0.046%	0.120%
	60	215	850	0.0005%	0.0019%
	90	40	162	<1 ppm	0.0004%
	120	26	73	<1 ppm	~1 ppm
D	30	4,625	11,084	0.018%	0.042%
	60	45	319	0.0002%	0.0012%
	90	~0	100	~0	0.0004%

n-tridecane were added as internal standards. The mixture was heated and continuously stirred for approximately 30 min or until the polymer had dissolved and then allowed to cool to room temperature, where it formed a solid slush. A portion of the cooled slush of polymer and solvent was then pressure filtered through a 0.8- μ m Millipore filter. Hexane and RAF-B were then quantitated by GC analysis of the filtrate. A representative chromatogram of the filtrate is shown in Fig. 7. Table III lists data for a sample of HDPE pellets which were analyzed both by the solution technique and by the vacuum distillation-gas chromatographic technique. The solution values for hexane were consistently lower by approximately a factor two than those obtained in the combined vacuum distillation-gas chromatographic technique. This was not unexpected and was due to its relatively high volatility and subsequent loss during the polymer dissolution process at elevated temperature. In sample I, the

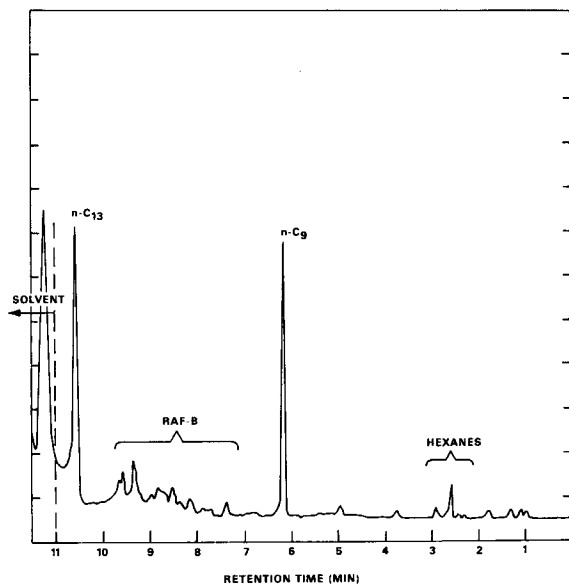


Fig. 7. Gas chromatogram of material extracted from high-density polyethylene with *n*-hexadecane and *n*-C₉ and *n*-C₁₃ as internal standards.

TABLE III
COMPARISON OF VOLATILES RECOVERY METHODS

Sample	Hexane		RAF-B		Gravimetric (%)
	Vac-GC (%)	Solution (%)	Vac-GC (%)	Solution (%)	
I	0.13	0.069	0.49	0.49	0.74
	0.12	0.071	0.54	0.45	0.88
	0.13	0.054	0.47	0.49	0.82
	0.12	0.047	0.50	0.42	0.65
	0.12	0.071	0.48	0.48	0.86
	0.13	0.065	0.51	0.48	0.81
	$\bar{X} = 0.12\%$ $\sigma = 0.005$	$\bar{X} = 0.063\%$ $\sigma = 0.009$	$\bar{X} = 0.50\%$ $\sigma = 0.02$	$\bar{X} = 0.47\%$ $\sigma = 0.03$	$\bar{X} = 0.79\%$ $\sigma = 0.08$
II	0.048	0.025	0.13	0.14	0.24
	0.048	0.032	0.12	0.13	0.26
	0.046	0.030	0.12	0.13	0.28
	$\bar{X} = 0.047\%$	$\bar{X} = 0.029\%$	$\bar{X} = 0.12\%$	$\bar{X} = 0.13\%$	$\bar{X} = 0.26\%$

average value of RAF-B from the vacuum distillation-gas chromatographic technique (0.50%) is in excellent agreement with the RAF-B level from the solution technique (0.47%). The slightly lower value for the solution technique may be due to difficulty in locating the proper baseline since, as shown in Fig. 6, the RAF-B elutes on a slightly rising baseline. The gravimetric values are consistently high since they also include volatiles such as additives and oligomers not detected in the GC analysis.

Polypropylene

Fig. 8 shows the gas chromatogram of a vacuum distillate from atactic PP in

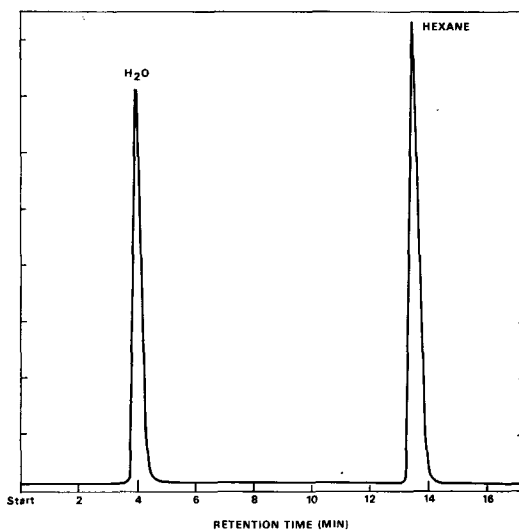


Fig. 8. Gas chromatogram of vacuum distillate from atactic polypropylene. The column was a 4-ft. \times 3/16-in. stainless-steel tube packed with 80-100 mesh Porapak Q temperature programmed from 60° to 250° at 16°/min.

TABLE IV
VOLATILES RECOVERY FROM ATACTIC PP

Run No.	Recovery (wt. %)	
	Water	Hexane
1	0.187	0.301
2	0.180	0.300
3	0.192	0.295
4	0.190	0.303
5	0.186	0.307
6	0.187	0.307
7	0.189	0.300
8	0.181	0.294
9	0.190	0.295
10	0.185	0.299
	$\bar{X} = 0.187\%$ $\sigma = 0.004$	$\bar{X} = 0.300\%$ $\sigma = 0.005$

which it was necessary to monitor the concentrations of water and hexane. In this case, the distillation time for quantitatively removing hexane and water was 20 min at 230°. Table IV lists data for hexane and water taken on an atactic PP sample over a three-week period and again indicates excellent precision. The procedure was used routinely for water and hexane levels over the range 0.0005% to 5% by weight.

High-density polyethylene odor

In another sample of HDPE synthesized by a different route, it was necessary to identify and quantitate odorant(s) present in the polymer. Vacuum distillation of the polymer followed by isolation of the distillate for a "sniff test" showed that the odorant(s) were being removed from the polymer and concentrated in the distillate. Fig. 9 shows the gas chromatogram of a vacuum distillate from the odorous HDPE in which the peak mainly responsible for the odor was identified by combined gas

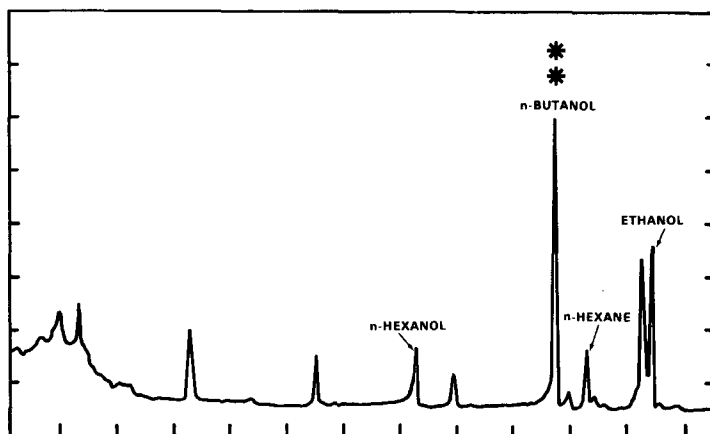


Fig. 9. Gas chromatogram of vacuum distillate from odorous high-density polyethylene. Same column and conditions as in Fig. 6.

chromatography-mass spectrometry as *n*-butanol. The concentration in the polymer sample was 300 ± 10 ppm. In subsequent analyses it was shown that the odor threshold for *n*-butanol was 1 ppm in HDPE. The integrated vacuum distillation-gas chromatographic procedure allowed the concentration to be accurately monitored down to 0.1 ppm during the testing of deodorization procedures. At *n*-butanol concentrations of <1.0 ppm a Porapak P column was used because of tailing problems on the SE-30 column.

CONCLUSIONS

The integrated vacuum distillation-gas chromatographic procedure is the first general method for quantitatively sampling all types of volatiles in non-volatile matrices. One of its main virtues is the ability to simultaneously determine water and organic volatiles in polymers. Also, the vacuum distillation approach allows volatiles in thermally unstable matrices to be conveniently removed. Besides the applications mentioned in the paper, it has also been used to accurately determine inorganic volatiles such as CO₂ and NH₃ and decomposition volatiles from polymers as a function of temperature. The technique has an obvious application to determination of trace odorants in non-volatile matrices such as waxes, oils, and natural products.

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