serum over a 2-week period gave $(0.59 \pm 0.03) \times 10^{-3} \text{ M Mg}^{2+}$ and $(1.62 \pm 0.07) \times 10^{-3}$ M Ca²⁺. Errors given are ± 1 standard deviation. The relative standard deviations, 5% and 4%, respectively, are characteristic of ion chromatographic measurements made by direct injection.

Peak heights are linear with concentration in the range measured, from 0 to 1.7×10^{-3} M Ca²⁺, with a relative standard deviation of 3%. Eight measurements were made at three different Ca²⁺ concentrations.

An earlier dialysis chamber was constructed with a 55 mm length. The hollow fiber was surrounded by a 0.038 in. i.d. (in place of the 0.022 in. i.d.) TFE tubing for most of its length and by Lexan at each end. The hollow fiber volume represented 6% of the total volume in this device and peak heights obtained were proportionately smaller than those with the dialysis chamber described above and shown in Figure 1. A dialysis time of 40 s (60 pump strokes) was required for dialysis of 0.154 M NaCl into water at 37 °C to be 90% of equilibration. In all other respects this earlier dialysis chamber gave results of the same quality as those reported above.

CONCLUSIONS

The dialyzing injection system described is a substantial improvement over previous methods of sample preparation by dialysis or filtration. The dialyzing time is not lengthy (about 1 min) and can be overlapped with the elution of the previous sample. There is little loss of precision introduced by the dialysis manipulation. Buffers or background compounds can be added to the material to be injected into the chromatograph simultaneously with the dialysis, if desired, by adding them to the water of the dialysis chamber rinse solution. Analysis of low volume samples is facilitated because a minimum volume of sample is required by this method. The system will also lend itself to fully automated sample handling.

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Generation of Perfluorolsobutylene Reference Sample and Determination by Gas Chromatography with Electron Capture and Flame Ionization Detection

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Perfluoroisobutylene (PFIB) is reported to be a byproduct obtained during heating of tetrafluoroethylene at temperatures in excess of 750 $^{\circ}$ C (1) and from the synthesis of tetrafluoroethylene from chlorodifluoromethane, bromodifluoromethane, or tetrafluoromethane (1). Small amounts of PFIB may also be formed during condensation reflow soldering which utilizes various fluorinated organic compounds as high-temperature nonflammable primary fluids (2, 3). The most common synthetic routes to PFIB utilize reactions of perfluorocyclobutane (4) or perfluoropropylene (5) at high temperatures. These routes are only feasible for generating large quantities of this highly toxic material.

Studies on the thermal decomposition of polytetrafluoroethylene (PTFE) have been reported as early as 1947 when C_2F_4 , C_3F_6 , and C_4F_8 (perfluorocyclobutane) were identified as pyrolysis products (6). Perfluoroisobutylene was first reported as a decomposition product in 1953 (7). Work by Atkinson et al. (8) indicated that PFIB is formed from perfluoropropene, tetrafluoroethylene, or perfluorocyclobutane at temperatures in excess of 600 °C. They also report that at 725 °C, PFIB pyrolyzes to form perfluoromethane. The catalytic effect of oxygen (and other gases) on the pyrolysis of PTFE was noted by Michaelson et al. (9). More recently, PTFE and polyfluoroethylenepropylene (PFEP) were pyrolyzed in both nitrogen and air under both dry and humid conditions in a flowing system by Arito et al. (10). They reported that oxygen suppressed the formation of PFIB and postulated its formation from radical recombination. They also suggest that PFIB may be more readily produced in a static system.

The analyses of highly volatile fluorocarbons have long presented a challenge to chromatographers. Fluorocarbons are not retained or well-separated by most stationary phases because of their high vapor pressure and poor solubility. Gas chromatography of fluorocarbons has been reported on fluorocarbon (11, 12) or chlorofluorocarbon (11) stationary phases, on *n*-hexadecane on Chromosorb P (13), on silica gel (14, 15), on Porapak (16), and on SP1000 on Carbopack C (17).

The utilization of electron capture detection in chromatography has recently benefited from an excellent monograph (18) as well as a comprehensive review (19). One can conclude from these references that the change in response of various compounds with respect to detector temperature can vary from no change to over 1000-fold over the normal range of detector temperatures. Therefore, detector temperature control is critical; the operating temperature should be maintained at ± 0.2 °C (20). To further complicate the situation, Hattori et al. (21) reported response vs. temperature



Figure 1. Apparatus used in PFIB generation from Teflon: generation tube (a), extension tube (b), female 10/30 taper adaptor (c), gas bulb with 10/30 male taper (d), and silicone septum adaptor (e).

results for a dc system which differed from those obtained with a pulsed system for several substituted benzenes. In fact, the same electron capturing derivative of different functional groups can result in species which show different temperature behavior and therefore capture electrons by different mechanisms, although the electron capturing portion of the molecules is essentially the same (22). One can conclude that the temperature dependence can vary widely even with minor changes in structure. An increased response with increasing detector temperature is indicative of a dissociative electron capture mechanism; a decreased response with increasing temperature indicates that electron capture occurs through a nondissociative mechanism. Owing to the large C-F bond energy, fluorinated compounds in general do not dissociate and capture electrons via a nondissociative mechanism (23).

The objectives of this study were (1) to provide a method for the in-house generation of a perfluoroisobutylene reference which can be standardized against a commercially available fluorocarbon (PFIB is not readily available commercially and is shipped with great difficulty), (2) to provide a reliable gas chromatographic procedure for the analysis of trace amounts of PFIB in the presence of other volatile fluorocarbons, and (3) to examine the electron capture temperature dependence of PFIB response on several commercial electron capture detectors.

EXPERIMENTAL SECTION

Generation of Perfluoroisobutylene. Approximately 500 mg of Teflon 6C powder (Du Pont Co., Wilmington, DE) was placed in the center 4-in. section of a 1/4 in. o.d. \times 12 in. stainless steel tube fitted with a 1/4 in. to 1/16 in. stainless steel Swagelock reducing union and a 1/4 in. to 1/8 in. reducing union (Figure 1). The Teflon powder was held in place with glass wool plugs. One end of the tube was capped with a $1/_{16}$ in. stainless steel plug. The 1/8 in. end was mated to a 1/8 in. o.d. \times 6 in. stainless steel extension tube fitted with 1/8 in. stainless steel nuts. The open end was capped with a 1/8 in. stainless steel cap. A hinged tube furnace (Hevi Duty, Type 70, 750 W, 115 V ac, Hevi Duty Furnace Co., Milwaukee, WI) was modified by drilling a 5/8 in. hole through two 1.5 in.² firebrick squares which were machined to fit in the 1 in. tube in the center of the tube furnace. The furnace was preheated to 500 °C and the $^{1}/_{4}$ in. portion of the generation tube was inserted through the holes in the firebrick squares so that the extension tube was external to the furnace. The temperature was monitored with a thermocouple probe placed in the middle region of the furance. (The probe was not in contact with the wall of the generation tube.) Temperature was adjusted by varying the voltage input to the furnace with a variable transformer (General Radio Corp., Cambridge, MA). After 1 h at 500 °C, the hot tube was removed from the tube furnace and cooled to approximately room temperature with cold water. The generation tube was then further cooled in a Dewar flask containing liquid nitrogen for 15-20 min to ensure condensation or solidification of the more volatile fluorocarbons. After this cooling period, the generation tube was kept in liquid nitrogen. The 1/8 in stainless steel cap was removed and quickly replaced (to avoid condensation of oxygen, water, etc.) with a 10/30 female taper 1/4 in. adaptor reduced to 1/8 in. with a stainless steel reducing union. An evacuated (approximately 250 mL) glass gas sampling bulb equipped with a stopcock leading to a $^{10}/_{30}$ male taper was mated to the female taper. The stopcock of the evacuated gas bulb was then opened and the generation tube was removed from the Dewar flask and allowed to warm to room temperature. The generation tube was then lowered into an ice water bath for 5 min to recondense the higher boiling products of the Teflon decomposition. The generation tube was then removed from the ice bath, the $1/_{16}$ in. plug was removed to allow air to help flush the volatile products from the generation tube into the gas bulb. The stopcock was then closed and the gas bulb was detached from the tapered joint. This sample is to become the PFIB reference. The peak corresponding in retention time to PFIB was verified by GC/MS identification. Our PFIB standard was synthesized according to Pearlson (4) and analyzed by gas chromatography with flame ionization detection and by infrared spectrometry.

Gas Chromatographic Conditions. A Hewlett-Packard (Avondale, PA) 5840A gas chromatograph equipped with a six-port gas sampling valve (V-6-HPa, Valco Instruments, Houston, TX) and a 4-mL $^{1}/_{8}$ in. stainless steel sample loop was used for the analysis. The following conditions were utilized in the analysis of high PFIB levels and for standardization of the PFIB reference: a 1/8 in. \times 12 ft stainless steel column packed with a 100/120 mesh Carbowax 400 on Porasil C (Waters Associates, Milford, MA) was held isothermal at 60 °C for 10 min and then programmed to 150 $\,$ °C at 15 °C/min and held at 150 °C for 10 min. The gas sample valve was not heated. The flame ionization detector temperature was 300 °C. Helium carrier gas was used at 25 mL/min. For low-level (less than 500 ppb) and analysis, the same column and temperature programs were used with a 95% argon 5% methane carrier at 25 mL/min. The electron capture detector temperature was 250 °C

Preparation and Dilution of Standards. Perfluorocyclopentene, PFCP, was obtained from PCR Research Chemicals (Gainesville, FL) in liquid form. An "external standard" of PFCP was prepared by syringe-injecting several microliters of PFCP into a tared septum-capped vial, and the weight of PFCP was recorded. A glass gas bulb of known volume with a stopcock and 10/30 taper was evacuated and the stopcock closed. A female 10/30 glass taper was fused to a 2 mm capillary glass tubing whose end was modified to hold a cylindrical 6 mm o.d. \times 9 mm Thermogreen LB silicone rubber septum (Supelco, Bellefonte, PA) (Figure 1e). This modified silicone septum adaptor was placed over the 10/30 taper of the gas bulb to be sampled. The evacuated bulb was then used to sample the PFCP-containing vial by inserting one end of a double-ended needle into the evacuated bulb septum and then inserting the opposite end into the PFCP vial. The vial was then heated with a heat gun to ensure complete vaporization of the fluorocarbon. Finally, a second needle was inserted through the septum of the PFCP vial allowing air to sweep through the vial into the glass bulb until atmospheric pressure was attained. The concentration of PFCP in the gas bulb was calculated from the weight of PFCP in milligrams and the gas bulb volume in liters

$$ppm \text{ of } PFCP = \frac{\text{mg of } PFCP}{\text{bulb vol (L)}} \times \frac{24450 \ \mu\text{L}}{\text{mmol at } 25 \ ^\circ\text{C}, 760 \ \text{mm}} \times \frac{1 \ \text{mmol}}{212 \ \text{mg of } PFCP}$$

The concentration of PFIB generated from Teflon can be calculated from the relative areas obtained from the analysis of the PFIB sample and the PFCP reference using a relative sensitivity of 0.61 ± 0.02 (2.6% relative standard deviation (RSD) for eight determinations):

ppm of PFIB = [area count PFIB × 0.61 × concn of PFCP (ppm)]/(area of PFCP)

Subsequent dilutions of the PFIB/PFCP samples were made

utilizing additional evacuated gas bulbs and PressureLok gas syringes (Precision Sampling Corp., Baton Rouge, LA). We have noted adsorption of PFIB on natural rubber; as a result, we have modified our dilution procedure to allow us to work with all-glass bulbs and silicone rubber septa. The previously described silicone septum adaptor was placed over a 10/30 taper of the gas bulb to be sampled. The space from the stopcock of the bulb to the silicone septum was evacuated through a needle attached to a vacuum line. The stopcock was then opened and the bulb contents were allowed to equilibrate into the adaptor fitting volume. After a 30-s equilibration time, this volume was sampled via a gastight syringe, whose contents were then transferred to a new gas bulb of known volume, thus achieving a dilution. Both PFIB and PFCP can be introduced in the same manner into a single bulb, thus creating a diluted PFIB reference with an internal reference of PFCP. We have been able to replicate dilutions of PFIB with a relative standard deviation of 6% utilizing this procedure. Repeatability of successive gas chromatographic injections of a single gas sample was approximately 2-3% RSD.

Conditions for Electron Capture Detector Temperature Study. A single standard of PFIB (265 ppb) (prepared by dilution of a synthesized standard of PFIB) and PFCP (230 ppb) was utilized to compare the response of various detector types with temperature. The gas chromatographic conditions are identical with those listed above with the exception of the variable detector temperatures and types and the flow rate of the carrier/purge gases:

detector	carrier flow	purge flow
H-P 5880 ⁶³ Ni ECD P-E Sigma One ⁶³ Ni ECD	He, 25 mL/min Ar:CH	N_2 , 50 mL/min Ar:CH
ATC ³ H ECD	$\begin{array}{c} 30 \text{ mL/min} \\ \text{Ar:CH}_4, \\ 30 \text{ mL/min} \end{array}$	30 mL/min Ar:CH ₄ , 30 mL/min

Disposal of Perfluoroisobutylene. PFIB has the highest reported toxicity of any fluorocarbon with an LC_{50} of 0.5 ppm. PFIB can be safely disposed of by reaction with HF or HCl in methanol (1). Alternatively, PFIB can be reacted with sodium hydroxide in methanol.

RESULTS AND DISCUSSION

Optimization of Perfluoroisobutylene Generation. Teflon powder samples varying in size from 100 mg to 1 g were heated at 500 °C for 1 h. The amount of PFIB generated increased steadily with sample sizes up to 500 mg. The 1 g sample appeared to physically block the generation tube. As a result, a 500 mg sample was chosen as optimal, resulting in approximately 250 ppm PFIB in a volume of 250 mL.

PFIB was not detected in appreciable amounts from Teflon samples heated for 1 h at 400 °C and 450 °C. This is consistent with literature reports of minimal PFIB generation at temperatures below 475 °C (24). Temperatures higher than 500 °C were not studied due to literature reports of PFIB decomposition at elevated temperature (8). If an ice water bath is not used to remove high-boilers, numberous additional components appear in the chromatogram, extending the analysis time and necessitating additional column cleanup at higher temperatures.

Chromatography. The gas chromatograms of PFIB generated from Teflon with flame ionization and electron capture detection are shown in Figure 2. The response of the flame ionization detector presents a more realistic representation of the distribution of the components from the thermal decomposition of Teflon. The low-boiling material consists chiefly of C_2 to C_4 perfluoroalkanes and perfluorocycloalkanes as identified via retention time matches with known standards and by GC/MS. No appreciable dependence of PFIB or PFCP response on flame ionization detector temperature was noted over the range of 200–350 °C. The FID response was linear in the range of 10–1000 ppm with an approximate detection limit of 1 ppm (S/N = 3).

The electron capture detector has a linear dynamic range of 25–1000 ppb with an approximate detection limit of 0.5 ppb



Figure 2. Flame ionization and electron capture gas chromatograms of PFIB (a) generated from Teflon.



Figure 3. Flame ionization gas chromatogram of PFIB (a) and PFCP (b).

(S/N = 3) at a detector temperature of 250 °C. Under the conditions of the analysis, PFCP (peak b in Figure 3) elutes at approximately 6.2 min with a relative retention time of 1.0. PFIB (peak a in Figure 3) elutes at 5.2 min with a relative retention time of 0.84 (Figure 3). Some passivation of the column is required; this is accomplished by injecting the most concentrated standard several times prior to attempting analytical determinations.

Variation of Response with Electron Capture Detector Temperature. According to the literature (18, 19), a plot of $\ln (KT^{3/2})$ or $\ln (AT^{3/2})$ vs. 1/T is an accurate representation of the temperature dependence of electron capture response for a given component where K is the electron capture coefficient, T is the detector temperature in Kelvin, and A represents the peak area for a constant mass of component. Plots of this type for the four electron capture detectors studied are shown in Figure 4. In all cases, PFCP response exhibits a significantly greater detector temperature dependence than PFIB. The slope of the dependence is consistent with a nondissociative electron capture mechanism. The temperature dependence of the response of both compounds varied significantly from one detector to another with minimal



Figure 4. Electron capture detector response variation with temperature for PFIB and PFCP on (a) H-P 5840, (b) P-E Sigma One, (c) H-P 5880, and (d) ATC tritium detectors.

temperature dependence exhibited by the Hewlett-Packard 5840 and Perkin-Elmer Sigma One detectors and maximum temperature dependence shown by the H-P 5880 and Applied Technology Corp. detectors. An alternate data presentation is shown in Figure 5 where the response of each detector is normalized to 200 °C. These graphs effectively illustrate the differences in concavity of response over the four detectors studied. There are no obvious reasons for the apparent grouping of the detectors into two different types; the two Hewlett-Packard detectors and the Perkin-Elmer detectors all have the basic pin and cup concentric geometry, whereas the ATC tritium detector is a parallel plate detector with the largest cell volume. All detectors are constant-current, pulsed-frequency types. The only possible similarity between the ATC and H-P 5880 detectors may be due to the fact that an analyte entering either detector may more readily attain true detector temperature at the time of electron capture for two different reasons: the large cell and tubing volume of the ATC may allow for more efficient thermal equilibrium whereas the H-P 5880 detector has a minimum amount of connecting tubing present in the relatively cool gas chromatograph oven, hence the analyte suddenly finds itself at temperature in the detector cell. There should be no real dependence of temperature response with the total flow (carrier plus purge flow)



Figure 5. Variation of relative response of (a) PFIB and (b) PFCP with electron capture detector temperature for four commercial detectors.

or with carrier type as long as the detector can accommodate various flows and carriers. Any variations of this type are expected to be normalized since total flow and carrier type remain constant for a given detector. The temperature dependence data indicate the necessity of doing a study of this type for any electron capture analysis on a given detector. This is the principal reason why standardization of the PFIB is done on the flame ionization detector. After dilution, relative response factors can be calculated for a given electron capture detector. Absolute response will vary depending on the cleanliness and type of the particular detector. However, despite these pitfalls, a precise analysis for PFIB is possible on a given detector at a specified temperature.

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