

Note

Determination of 2H-hexafluoropropanol-2 in air

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2H-Hexafluoropropanol-2 (HFIP) is a chemical intermediate and a powerful solvent, used especially for polymers in commercial and analytical applications¹. HFIP is also used to analyze blends of fibers and to determine dyes in synthetic fibers²⁻⁵.

While HFIP can be handled safely in a laboratory hood, exposure to HFIP vapor in air may cause lacrimation, hyperemia and other breathing problems¹. The HFIP content of air has to be monitored where large amounts of HFIP are used or produced. A method for the determination of HFIP in air is therefore needed.

The chemical properties of HFIP differ from those of typical aliphatic alcohols. The acidity of HFIP (pK_a 9.3) is comparable with that of phenol⁶. The relatively high acidity and strong hydrogen bonding complicate chromatography of HFIP.

Adsorption on a solid adsorbent and thermal desorption is not a satisfactory procedure for collection of HFIP in air. As much as 1 mg of HFIP can be essentially quantitatively adsorbed on 200 mg of charcoal, but desorption of HFIP from charcoal is incomplete. Although Tenax GC is a less efficient HFIP adsorbent than charcoal, flash desorption of HFIP from Tenax GC is incomplete even at temperatures sufficiently high (300°C) to cause decomposition of HFIP. We decided therefore to collect HFIP in a liquid absorbent, using a series of impingers.

EXPERIMENTAL

Apparatus

The apparatus used for collecting HFIP in air, consisting of two to four midget impingers in series and a pump, has been described in detail previously⁷. The cell for determining recovery of HFIP in air also has been described⁷. A Varian Model 3700 gas chromatograph equipped with a flame ionization detector and an electron-capture detector was used throughout the study. A Hewlett-Packard computer, Model 3354, was used to calculate peak areas.

Reagents

HFIP, 99.7% pure (Du Pont), N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) (Pierce), and methanol, absolute, certified A.C.S. grade (Fisher), were used as received.

Procedure

Unless stated otherwise HFIP was collected by drawing air through two or three midjet impingers, each impinger containing 20 ml of water. The impingers were placed into a Styrofoam box, cooled with ice and connected to a pump (Model 222-3, SKC) via a tube containing charcoal. The pumping rate was 120–140 ml/min. The contents of the impingers were weighed and analyzed by gas chromatography (GC) for HFIP, after combining the contents of the first two impingers.

Gas chromatography

A 5- μ l volume of water containing HFIP was injected on a 12-ft. column, 1/4" O.D., 2 mm I.D., packed with 10% Silar 10-C on 80–100 Chromosorb W HP. The flow-rate of helium was 30 ml/min. The chromatograph was programmed from 40 to 210°C at 12°C/min. The flame ionization detector was heated at 300°C. The injection of a sample was alternated with an injection of 5 μ l of BSTFA. The injection of BSTFA was essential for the proper functioning of the column.

RESULTS AND DISCUSSION

Difficulties with the determination of HFIP in air by absorption in a solvent followed by GC increase with decreasing amounts of HFIP to be determined. One

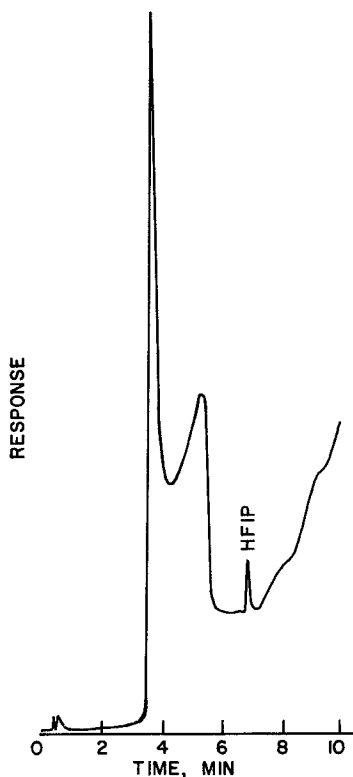


Fig. 1. A gas chromatogram of 17.58 μ g/ml of HFIP in water injected onto a column packed with 10% Silar 10-C on 80–100 Chromosorb W HP.

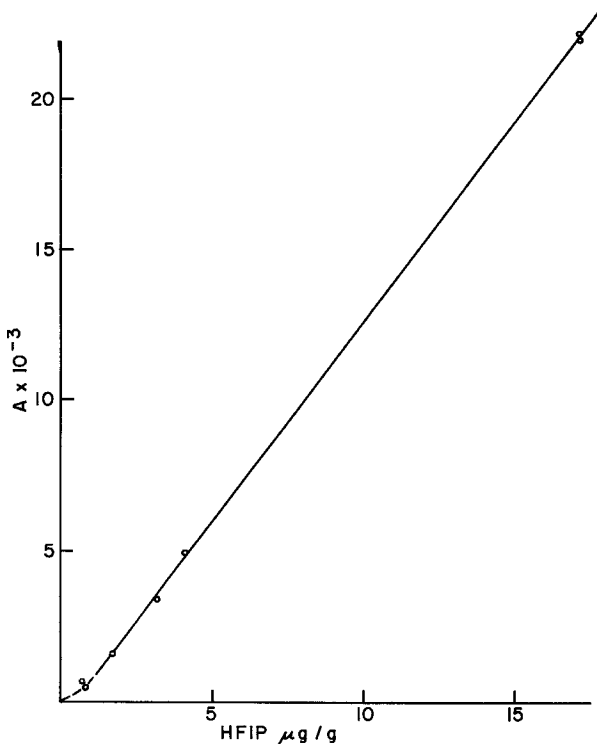


Fig. 2. The HFIP peak area as a function of the HFIP concentration in the aqueous sample injected.

of the major problems is the limited purity of solvents suitable for collecting HFIP in air and GC of HFIP.

Methanol of A.C.S. grade is a sufficiently pure solvent for chromatography of HFIP in trace amounts. Separation of HFIP (retention time 10.7 min) from methanol (retention time 8.2 min) was accomplished using a 24-ft. column packed with 20%

TABLE I

ABSORPTION OF HFIP IN A SERIES OF IMPINGERS CONTAINING WATER

Total amount of HFIP absorbed (μg)	HFIP absorbed in impingers* (percentage of total amount absorbed)			
	1	2	3	4
86.8	77	17	6	0
652	84	12	4	0
13,660	81	17	2	0.3
Average	81	15	4	0
Calculated for 81% absorption	81	15	3	0.6

* HFIP in concentrations below $1 \mu\text{g}/\text{ml}$ was determined as fluorine by combustion in an oxyhydrogen torch.

TABLE II
RECOVERY OF HFIP VAPORIZED IN AIR

Sampling conditions		HFIP vaporized		HFIP found (mg)	Recovery (%)
Time (h)	Air sample volume (l)	Average conc. in air (ppm)	Weight of HFIP (mg)		
2.8	32.6	0.05	0.011	0	
3.6	42.1	0.31	0.0896	0.087	97
3.0	35.0	4.02	0.9546	0.93	97
4.0	21.3	82.4	14.40	13.4	93

SE-30 on 80-100 Chromosorb W HP. However, the determination of HFIP in air gave occasionally spurious results which were traced to absorption of water in methanol during air sampling.

Both problems, interferences by impurities in the solvent and water vapor in air, were solved by using water to collect HFIP vapor. A highly polar column (10% Silar 10-C on 80-100 Chromosorb W HP) was used for chromatography (Fig. 1). Sample injections were alternated with BSTFA injections to preserve the column and to suppress the background. This unorthodox procedure proved to be quite reliable and sensitive with a detection limit of *ca.* 0.5 $\mu\text{g/g}$ of HFIP in water (Fig. 2). This corresponds to *ca.* 0.1 ppm of HFIP in air, assuming a 30-l air sample and 40 ml of water (the contents of first two impingers combined for chromatography). The precision of GC, determined by six analyses of 17.58 $\mu\text{g/g}$ of HFIP in water, is 0.15 $\mu\text{g/g}$ or 0.82% relative.

The sorption of HFIP in a series of four impingers, the first three impingers containing 20 ml of water and the fourth impinger 10 ml of water, is shown in Table I. The average values of the percentage of HFIP absorbed in each impinger are in agreement with values calculated for 81% absorption in each impinger in series. The sorption of HFIP is seemingly independent of the total amount of HFIP collected, at least in the concentration range of interest. Since the amounts of HFIP found in the fourth impinger are relatively insignificant, a fourth impinger is not needed for HFIP collection. For practical purposes the third impinger also may be deleted.

The recovery of HFIP in air was determined by vaporizing known amounts of HFIP in a septum vial through which air was drawn into a series of three impingers containing water⁷. HFIP was dissolved in a small volume of methanol to increase the weight of the sample gradually injected with a syringe into the septum vial. The recovery of HFIP was quite good (Table II).

The sensitivity of the method is adequate for monitoring air in the plant where HFIP is produced. By increasing the air sample to 120 l, as little as 0.03 ppm of HFIP was detected.

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