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Retention behaviour of volatile C_1–C_3 fluoroalkanes upon selected preconcentration adsorbents

I. Carbon molecular sieves and activated charcoals

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Abstract

The retention behaviour of several gaseous fluorinated greenhouse gases on carbon-based adsorbents is presented. Retention, calculated on the basis of compound breakthrough volume (BTV), is dependent on the molecular composition of the adsorbate, with compounds possessing chlorine or polarisable hydrogens being better retained than those possessing higher fluorine content. Of the adsorbents tested the carbon molecular sieves (CMSs) of highest surface area show greater retention than those with lower area. Retention of fluorocarbons is generally higher on activated charcoals but this adsorbent type can cause irreversible retention, possible degradation and is more difficult to use practically due to its heterogeneous composition. These breakthrough volume results can be used to determine the best combination and quantities of each adsorbent that can be used within a preconcentration device with a view to developing an analytical system for the determination of fluorocarbon gases in low concentration air samples.

Keywords: Carbon molecular sieve; Adsorbents; Carboxen; Activated charcoal; Preconcentration; Perfluorocarbons; Hydrofluorocarbons; Air analysis; Breakthrough volume

1. Introduction

Atmospherically important fluoroalkanes are generally man-made and can be classified as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) or perfluorocarbons (PFCs). The major CFCs (CF_2Cl_2, $CFCl_3$, $CF_2ClCFCl_2$) have been used as refrigerants, foam-blowing agents and industrial solvents for many years until their production, use and emission were banned under the Montreal Protocol and subsequent amendments to the protocol. Chlorine radicals, the photochemical breakdown product of CFC degradation in the atmosphere, have been cited as the principle cause of stratospheric ozone depletion [1]. The HCFCs also contain a proportion of chlorine and can also participate in catalytic ozone depletion, their production and use has been as intermediate replacement compounds for CFCs in their major use applications. The hydrofluorocarbons are chlorine-free and do not cause ozone depletion so are viewed as long-term replacements for CFCs and HCFCs. However hydrofluorocarbons, in common with the CFCs, HCFCs and PFCs are greenhouse gases, possessing active infrared adsorption bands in the 8–12 μm range and so can cause enhanced radiative forcing [2]. Perfluorocarbons (principally CF_4 and C_2F_6) have been emitted as by-products from aluminium electrolysis and from their use in production of semiconductors [3]. CF_4 also has a low emission from natural source which, coupled to the extremely long atmospheric lifetime (50 000 years) accounts for approximately half of the accumulated CF_4 emitted to the atmosphere [4,5]. In light of the ozone depletion and radiative forcing effect of fluorocarbons, numerous researchers have reported mixing ratios of the most abundant fluorocarbons using both adsorbent-based and cryogenic trapping methods (e.g. [6–13]).

Analysis of air samples for environmentally important fluoroalkanes will be governed principally on the detector technique employed. With the exception of the major chlorofluorocarbons (CF_2Cl_2, $CFCl_3$, $C_2F_3Cl_3$), whose responses are remarkably sensitive by electron-capture detection (ECD), most fluoroalkanes which are present in air samples require preconcentration

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prior to gas chromatographic analysis in order to present sufficient analyte to the chosen detector for reliable quantitation. The gases under investigation in this study exist or are anticipated to exist in the atmosphere in the low parts-per-trillion (ppt, $10^{-12}\,1\,1^{-1}$) concentration range, a detection limit which cannot be achieved by non compound-specific GC detectors.

Many procedures used for the preconcentration of volatile organic compounds (VOCs) in air samples rely on sampling tubes filled with solid adsorbents. Frequently employed adsorbents include Tenax TA [14], Tenax GR [15], Carbotrap C [16] and Carbopak [17], which are extremely helpful for the extraction of C_6–C_{10} hydrocarbons and the less volatile halocarbons (e.g. trichloromethane, tetrachloromethane and mixed halogen species) from air samples. They do not however have the adsorbent capacity to trap the more volatile hydrochlorofluorocarbons, hydrofluorocarbons and perfluorocarbons. These fluorocarbons require the use of high surface area and high capacity adsorbents such as carbon molecular sieves [18,19] as preconcentration devices. The capacity of an adsorbent filled trap is significantly increased when cooled to sub-ambient temperatures which can be achieved via cryogenic [20] or thermoelectric cooling devices [21,22]. Sub-ambient cooling minimises the quantity of adsorbent required and ensures that following thermal desorption the preconcentrated analytes enter the GC column as a sharp plug injection with little bandwidth spreading and minimal deterioration of chromatographic resolution. The desorption bandwidth is optimised via rapid heating of the preconcentration tube and using a sufficiently high flow of carrier gas to sweep the desorbed analytes into a chromatographic column [23]. Carbon-based adsorbent materials all rely on non-specific (Van der Waal) interaction between the adsorbed gases and the adsorbent surface [24]. The Van der Waal interactions (dispersion and induced dipoles) are surface dependant hence higher surface area adsorbents tend to have a higher capacity (breakthrough volume). Carbon molecular sieves possess a large size range of microporous structure and hence can act as size inclusion adsorbents (akin to inorganic Molecular Sieves), the diverse and extensive range of porosity is also responsible for their overall high surface area. Activated charcoals contain polar functional groups on their surface, so adsorbate molecules which possess large electronegative atoms or polarisible hydrogens can be retained also via hydrogen bridging [24].

An assessment of the retention capacity of an adsorbent prior to its use in air sampling is essential to ensure that the analytes are quantitatively and reproducibly trapped at the preconcentration stage. The most common method used is to test an adsorbent for its breakthrough volume towards a particular analyte [18,25–27]. The breakthrough volume for an adsorbent can be defined as the volume of gas containing the dilute analyte which can be passed through a stated adsorbent bed mass (or volume) at a set temperature before the analyte begins to break through the adsorbent bed. Quantitative trapping is achieved where the volume of gas sampled is smaller than the breakthrough volume of the adsorbent bed. Assessment of compound breakthrough volumes is generally undertaken using one or more of three methods, each method involving challenging a prepared adsorbent bed with a dilution of the analyte to be investigated until the analyte breaks through the end of the adsorbent bed. Indirect breakthrough volume determination involve injection of a single slug of diluted analyte through the bed and results in a chromatographic peak eluting (breaking through) the end of the adsorbent bed [27]. The indirect method is the simplest and quickest to perform. Direct breakthrough testing involves continual loading of the test adsorbent bed until all adsorption sites are saturated and hence breakthrough occurs. The method is akin to frontal chromatography and is more complicated and slower to perform than the indirect breakthrough volume method. Direct breakthrough volume test data generally present a more accurate measure of breakthrough volume in practical adsorbent tube sampling use. The discrete breakthrough volume method is an extension of the direct breakthrough volume method whereby the eluent from the exit of a continually-challenged adsorbent bed is discretely sampled using a gas sampling loop. The eluent stream samples are directed into a sensitive detector (e.g. a mass spectrometer) to essentially yield discrete sampled points from the frontal chromatogram resulting from adsorption site saturation. An excellent review of adsorbent properties including breakthrough volume techniques has been published [24].

The aim of the present work is to assess the breakthrough volumes of atmospherically important methane and ethane based fluorocarbons on various types of carbon-based adsorbent materials using both indirect and direct breakthrough volume methods. The breakthrough volume experiments described will demonstrate the efficiency of the selected adsorbents for retaining very volatile fluorocarbons.

2. Experimental

2.1. Preparation of adsorbent bed tubes for assessing breakthrough volumes

A list of the adsorbents assessed for retention of analytes is shown in Table 1. A 30 cm length of stainless steel tubing (1.6 mm O.D., 1.1 mm I.D.) was cut and cleaned. Swagelok gas tight fittings were attached to either end of the tube. One end was fitted with 2.5 cm fibrous glass wool and the end tightly packed using fibrous and silanized glass wool. This end of the tubing was attached to an in-house vacuum line. Approximately 200 mg of the adsorbent to be tested was accurately weighed in a glass vial. The adsorbent in the vial was sucked into the adsorbent bed tube

Table 1
Properties of adsorbent material assessed for retention capacity towards fluorocarbons

Adsorbent	Type[a]	Surface area (m^2/g)	Mesh size	Supplier
Carboxen 1000	CMS	>1200	60/80	Supelco
Spherocarb	CMS	880	60/80	PhaseSep
Carbosphere	CMS	1000	80/100	Altech
Carboxen 1004	CMS	1100	80/100	Supelco
Activated charcoal	AC (coconut)	1070	20–100	Supelco
SK-4 Carbon	AC (nut)	n/a	60/80	Altech

n/a: not available.
[a] CMS: carbon molecular sieve, AC: activated charcoal.