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METHODS OF ANALYSIS FOR
TRACE AMOUNTS OF CFC IN
POLYMERIC FOAMS

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ABSTRACT

Methods of analysis for trace amounts of CFC in polymeric foams

As a complement to restrictions on the use of CFC:s in the manufacture of polymeric foams various type import and/or trading restrictions are being introduced with regard to these foams. The objective of this project was to devise methods of screening and laboratory confirmative analysis in order to verify when CFC has in fact been used in the production of imported foams.

Gas chromatographic laboratory methods utilizing an electron capture and a mass selective detector, respectively, were designed and tested. On-column injection as well as a cryo trap technique were employed. Possible interference from a number of HCFC:s and HFC:s was investigated.

A sample preparation technique was devised for releasing trapped CFC in polymeric foams with open cells where the CFC is merely a production aid and not an intended component of the finished product. In foams with closed cells gas samples for analysis are simply withdrawn from the foam as such.

Alternative methods of screening for CFC-containing foams were looked into, in most cases involving a separation step. A gas chromatographic method utilizing a flame ionization detector was defined and tested. It was demonstrated that a leak detector instrument can be used as a detector in a gas chromatographic system for screening purposes. - So far, no acceptable screening method with regard to specificity has been found for foams with open cells.

The possibility that non-CFC produced foams may become contaminated by the presence of CFC foams was examined. The results show that contamination is not a likely problem. Judging from the results of the investigation aging of the foam does not deplete the content of CFC in foams with open cells to such an extent that it can not be found and identified.

Key words: chlorofluorocarbons, polymeric foams, trace analysis, screening, laboratory method, sample preparation, identification
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SUMMARY

As a complement to restrictions on the use of CFC:s in the manufacture of polymeric foams various type import and/or trading restrictions are being introduced with regard to these foams. The objective of this project has been to devise methods of screening and laboratory confirmative analysis in order to verify when CFC has in fact been used in the production of imported foams.

Gas chromatographic laboratory methods utilizing an electron capture and a mass selective detector, respectively, have been designed and tested. On-column injection as well as a cryo trap technique have been employed. Possible interference from a number of HCFC:s and HFC:s has been investigated.

A sample preparation technique has been devised for releasing trapped CFC in polymeric foams with open cells where the CFC is merely a production aid and not an intended component of the finished product. In foams with closed cells gas samples for analysis are simply withdrawn from the foam as such.

Alternative methods of screening for CFC-containing foams have been looked into, in most cases involving a separation step. A gas chromatographic method utilizing a flame ionization detector has been defined and tested. It has been demonstrated that a leak detector instrument can be used as a detector in the gas chromatographic system for screening purposes. - So far, no acceptable screening method with regard to specificity has been found for foams with open cells.

The possibility that non-CFC produced foams may become contaminated by the presence of CFC foams has been examined. The results show that contamination is not a likely problem.

Also, judging from the results of the investigation aging of the foam does not deplete the content of CFC in foams with open cells to such an extent that it can not be found and identified.
INTRODUCTION

To become effective, restrictions on the use of CFC within a country must be complemented by other types of regulations, e.g. import regulations. Otherwise domestic CFC-based production may simply turn out to be replaced by import of CFC-manufactured products.

The ban on using CFC in the manufacture of polymeric foams is now being supplemented by import restrictions in most of the Nordic countries (1, 2). However, unless it is possible to ascertain unambiguously when CFC has in fact been used import restrictions are of limited value.

When CFC is a component of the finished product, as in foams with closed cells, the CFC is usually present in large amounts and there is no real problem in sampling and identifying the blowing agent used. In a previous project SP (Swedish National Testing and Research Institute), as an assignment from the Nordic Council of Ministers, among other things explored the possibilities for tracing residues of CFC in foams with open cells where CFC is not an intended component of the final product. The verdict was that enough CFC remains in the polymeric material as such to allow confirmation by experiment when CFC has been used in the manufacturing process (3, 4). However, there was no time then for a more systematic investigation of possible interferences or limitations and a number of questions had to be left unanswered.

A follow-up project regarding CFC in polymeric foams was assigned to SP by the Nordic Council of Ministers. In this new project the task has been

- to design and/or test methods of screening in order to single out products likely to contain or to have been produced using CFC;

- to design laboratory methods of analysis adequate for establishing the presence of even minute quantities of CFC and to confirm unambiguously the identity of the CFC used;

- to investigate whether foams that are produced without CFC might get significantly contaminated by foams produced with CFC during storage or transport;

- to examine the effects of aging of the foam upon the CFC content in the material.

Furthermore, sampling strategy and procedures were to be explored.
CFC - HCFC - HFC

The five CFC compounds listed in table 1 are the ones taken into account by the restrictions. The designation CFC in this report refers to fully halogenated chlorofluorocarbons.

Table 1. CFC compounds affected by the present regulations.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>Synonym or trade name</th>
<th>Boiling point/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trichlorofluoromethane</td>
<td>CCl$_3$F</td>
<td>CFC 11, R 11</td>
<td>24</td>
</tr>
<tr>
<td>Dichlorodifluoromethane</td>
<td>CCl$_2$F$_2$</td>
<td>CFC 12, R 12</td>
<td>-30</td>
</tr>
<tr>
<td>Trichlorotrifluoroethane</td>
<td>C$_2$Cl$_3$F$_3$</td>
<td>CFC 113, R 113</td>
<td>48</td>
</tr>
<tr>
<td>Dichlorotetrafluoroethane</td>
<td>C$_2$Cl$_2$F$_4$</td>
<td>CFC 114, R 114</td>
<td>4</td>
</tr>
<tr>
<td>Chloropentafluoroethane</td>
<td>C$_2$ClF$_5$</td>
<td>CFC 115, R 115</td>
<td>-38</td>
</tr>
</tbody>
</table>

HCFC designates partially halogenated chlorofluoro hydrocarbons (alkanes), such as e.g. chlorodifluoromethane, whereas the notation HFC is used for partially fluorinated alkanes (without chlorine), e.g. tetrafluoroethane. Neither HCFC:s nor HFC:s are yet affected by the CFC regulations in the Nordic countries. In some applications they are, or may become, alternatives to the banned CFC:s. At present the alternatives are in general considered too expensive for the manufacture of e.g. flexible foams.

Table 2. Some "alternative" HCFC and HFC compounds.

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Chemical formula</th>
<th>Synonym or trade name</th>
<th>Boiling point/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorodifluoromethane</td>
<td>CHClF$_2$</td>
<td>HCFC 22, R 22</td>
<td>-41</td>
</tr>
<tr>
<td>Dichlorotrifluoroethane</td>
<td>C$_2$HCl$_2$F$_3$</td>
<td>HCFC 123</td>
<td>29</td>
</tr>
<tr>
<td>Dichlorofluoroethane</td>
<td>C$_2$H$_3$Cl$_2$F</td>
<td>HCFC 141b</td>
<td>32</td>
</tr>
<tr>
<td>Chlorodifluoroethane</td>
<td>C$_2$H$_3$ClF$_2$</td>
<td>HCFC 142b</td>
<td>10</td>
</tr>
<tr>
<td>Tetrafluoroethane</td>
<td>C$_2$H$_2$F$_4$</td>
<td>HFC 134a</td>
<td>-26</td>
</tr>
<tr>
<td>Difluoroethane</td>
<td>C$_2$F$_2$</td>
<td>HFC 152a</td>
<td>-2</td>
</tr>
</tbody>
</table>
POLYMERIC FOAMS

In the previous project four characteristic types of polymeric foams were studied: extruded polystyrene foam (XPS), rigid polyurethane foam (rigid PUR), flexible foams, more specifically flexible polyurethane foam (flexible PUR), and polyethylene foam (PE).

The CFC:s mostly used in the production of polymeric foams are CFC 11 and 12. For rigid as well as flexible PUR CFC 11 has been used and for XPS CFC 12 has dominated. Alternatives discussed at the present time for the production of polymeric foams, other than CO₂ from the reaction between water and isocyanate, seem to be HCFC 22, 123 and 141b and HFC 134 (5).

Rigid PUR and the greater part of XPS basically belong to the category of foams with closed cells. In these materials the content of CFC is relatively high and neither screening nor confirmative laboratory analysis present any particular problems.

Flexible PUR acquires open cells in the manufacturing process, i.e. the blowing agent is vented into the air and the foam contains "CFC" only as a residue and as such at low levels. The CFC one may expect to find in these foams is that remaining in micro cavities and/or dissolved in the polymer itself.

THE CURRENT PROJECT

The main objective of this project has been to define methods that with a high degree of accuracy (certainty) can be used to identify CFC-produced polymeric foams. The attention has largely been focused on designing ways and methods to release and confirm the identity of traces of CFC in flexible foams, i.e. foams with open cells. Methods adequate for that can then easily be adapted to the simpler tests for CFC in foams with closed cells.

An absolute requirement for a CFC laboratory analysis method is that it must discriminate between CFC:s on the one hand and HCFC:s and HFC:s on the other, the latter being legitimate (alternative) blowing agents. For screening methods the requirement is that they must be reasonably selective. To be of value they must single out foams containing fair amounts of CFC. It may, however, be difficult to rule out "alternatives" in the screening process unless a separation step is involved.

A number of possible methods for screening have been considered. Three procedures have been looked into in more detail.

Two gas chromatographic methods for laboratory confirmative analysis have been developed and tested. The method most extensively used in the systematic studies of CFC concentration levels, of sample preparation techniques and of the effects of aging and possible contamination utilized an electron capture detector (ECD)
- a specifically halogen-sensitive detector. In the second method a mass selective detector (MSD) was used and, also, a cryo trap technique employed.

Various sample preparation techniques have been tested and considered in relation to what appears realistic in terms of sampling in real cases. Memory effects in the analytical equipment and various kinds of contamination risks have been looked into.

Most of the systematic studies have been performed on flexible PUR. Foams produced both with and without CFC have been available for study. For two of the CFC-produced type foams significantly different concentrations of CFC (ratio 3:1) had been used in the manufacturing process. Samples with a difference "in age" of about 5 months have been available for both of these CFC-blown foams. The time for the manufacturing was identified for all of these foams.

The investigation and the results obtained are reported on in the following. Defined methods for screening and for laboratory analysis are detailed in annex A and B, respectively.

5 SAMPLING STRATEGIES AND PROCEDURES

Where and how frequently polymeric foams are to be identified as suspect and taken for examination is, of course, for the appropriate authorities to decide. A system where foam products have to be certified as "non-CFC produced" actually implies that suspect products can be singled out at any time, i.e. also after a foam product has entered a particular country. Taking samples for analysis may well be organized as "CFC campaigns" as a supplement to picking out foams for analysis at the border. To some extent the quality of available screening methods will influence upon sampling strategies; cf. paragraphs 6 and 10.

5.1 Foams with closed cells

There is not much of a problem in taking samples from foams with closed cells. When a small piece of foam can be removed this is a convenient way. A gas phase sample can then be withdrawn for analysis at any time later on. Foam samples are best stored in closed containers until the analyses are to be performed.

Another way of taking a sample is to use a single-use syringe (to avoid contamination risks) to take a 2 to 5 mL gas sample from inside the foam and then inject that into a septum-sealed glass bottle, from 10 to 100 mL in volume. The needle used should be one with a small outer diameter to avoid creating leaks in the septum. From the septum sealed vials used in the sample preparations described later on (7.1), samples have been taken repeatedly over a period of several days after the first sample was withdrawn. The technique of injecting gas phase CFC, HCFC and HFC samples into
100 mL septum-sealed bottles with subsequent repeated withdrawal of samples has been used on several occasions in this project.

In cases where it is necessary to pierce for instance a metal coating to get at the foam it may be required to drill a tiny hole through that covering.

All sample containers used must be clean. Lids should be used only once unless it has been ascertained that they do not retain traces of CFC or other volatile materials from previous samples. Septa are to be considered single-use items.

The samples taken are analysed either directly, if a suitable (portable) instrument is available, or sent to the laboratory for analysis.

5.2 Foams with open cells

In the case of foams with open cells a small piece of the foam has to be removed for analysis (cf. 7.1). One should avoid taking samples close to the outer surface. This means that it may not be possible to avoid entirely causing minor damage to the sampled product. If possible, a few grams should be taken.

The foam samples should be stored in closed bottles. The volume of the bottle should be in accord with the size of the sample. The bottles must be perfectly clean, preferably conditioned at 100 °C for an hour or more. Special care should be taken to use lids that are not contaminated from previous use.

Foams with open cells and hence low amounts of possible CFC should be analysed using one of the methods outlined in this report or an equivalent one in terms of sensitivity and accuracy in discriminating between CFC:s and legitimate blowing agents or other components present. As the storage and/or transportation contamination risks are considered small (cf. 8.3) there is generally no reason for intentional venting of the foam sample before preparing it for analysis.

6 SCREENING METHODS

The most promising alternative for a screening method depicted in the earlier project was one based on a good leak detector. It was, however, generally concluded that screening would normally have to be supplemented with confirmatory laboratory analysis.

In this project various possibilities for utilizing a leak detector for screening have been explored. The possibilities for using portable gas chromatographs have been looked into. A more sophisticated instrument for screening based on an MSD has also been considered.
6.1 Leak test instruments

The Inficon HLD 3000 Halogen Leak Detector (Leybold-Heraeus) has been tried as a screening instrument. This leak detector certainly has sufficient sensitivity to detect even the low levels of CFC in the gaseous phase above samples of many flexible foams. Unfortunately, it is not as specific in its response as is required. It would not rule out this leak detector as a screening instrument if it in addition to detecting CFC:s just singled out similar compounds such as HCFC:s and/or HFC:s. But depending on the gas phase concentration the detector does respond to e.g. pentane.

One way of increasing the specificity is to include a separation step into the screening process. Experiments have been performed where the "sniffer" of the leak detector was connected to the exit of a packed column (ordinarily connected to a FID; see below). Samples in this case have to be introduced into the system via some injection device with e.g. a syringe.

To check out the feasibility of such a system a piece of 4 mm i.d. glass tubing was connected to the column in question. The length of the glass tubing was chosen such that the end of a wide bore needle came close to the outlet from the column itself. The sniffer was connected to the other end of the needle. The CFC:s 12 and 115, and HCFC:s 22 and 142b were used as trial samples at various concentration levels. For CFC 12 the instrument indicated the presence of a CFC 12 peak for 0.1 mL of an 80 ppm by volume gas sample.

Much larger samples can be used in order to cover lower concentrations. Peak broadening is of little or no consequence here. For foams with closed cells it may be possible to design a system that would allow positive identification of a particular CFC (e.g. with more than one column).

The leak detector is attractive in combination with a gas chromatograph because it is an easy-to-operate, self-contained unit. To make the instrument convenient to use as a gas chromatographic detector it would have to be modified such that the detector signal can be registered on a recorder. This would also be required for documentation purposes. - The cost for the standard version of this leak detector today is around 28 000 SEK. The additional cost for getting it equipped with a recorder port is estimated at somewhere around 3 000 SEK. For the price of a portable gas chromatograph, see below.

6.2 Gas chromatographs

Portable gas chromatographs are available e.g. with flame ionization detectors (FID) and even with electron capture (EC) detectors. These instruments are generally easy to operate. Designing a screening method based on the use of a packed, or a so-called megabore column is relatively easy. For screening, isothermal operation of column temperature is desirable and should suffice.
A 2 m packed, stainless steel column with a packing of Porapak Q was tested as an alternative for screening of CFC:s. The system utilized a FID and was tested for CFC:s 11, 12, 113, 114 and 115, for HCFC:s 22, 123 and 142b and for HFC:s 134a and 152a. In addition, possible interference from vinyl chloride, dichloromethane, trichloromethane and 1,1-dichloroethane was investigated. - The method as such is defined in appendix A.

The conclusion is that a portable gas chromatograph for isothermal operation could be used as a screening instrument. Again, methods may be designed that allow positive identification of a particular CFC for samples from foams with closed cells.

Modern instruments are reasonably easy to operate. It is, however, recommended that an analytical chemist is called upon to set the experimental parameters and to confirm that the system works as is expected. The initial instructions on the proper use of the instrument and on how to interpret the results also have to be given by a qualified person.

CFC reference samples of good quality should be available for the rather frequent checks on retention times that are called for. The CFC concentrations are not critical in this case and thus do not have to be accurately known but should be chosen to give peaks of moderate size in the chromatograms. If necessary, samples can easily be diluted in the syringe for the present purposes.

If the instrument is to be used for positive identification special care in the choice of column(s) and analysis parameters are required. The availability of reference samples of good quality is then an absolute requirement.

Portable gas chromatographs with EC detectors are available in the price range from about 75 000 to 135 000 SEK. For a chromatograph without a detector system the price may be expected to be reduced by some 25 000 SEK. A recorder may, or may not, be included in the price for a portable instrument.

6.3 Mass spectrometer for screening

A mass spectrometer with a sniffer may, at least in principle, be an alternative as a screening instrument. Instruments are available that allow operation at different locations. The operation of that type of instrument as well as interpretation of the results requires specially trained, skilled personnel. - The cost for a complete, operable MSD instrument is of the order of 275 000 to 350 000 SEK.

Samples of flexible polyurethane foams have been submitted for screening tests but at the present time no results are available.
LABORATORY ANALYSIS METHODS

For the laboratory analyses only gas chromatography has been considered. It is a well established technique for advanced as well as routine type analyses and gas chromatographic equipment is available in most analytical laboratories.

7.1 Sample preparation

From a CFC-analysis point of view, a considerable disadvantage with polyurethane is that it is neither soluble in common solvents, nor does it melt without undergoing pyrolysis at the same time. For other polymeric-foam materials any CFC present may be efficiently released simply by dissolving the polymer in a suitable solvent or by melting it, thus transferring the main part of the CFC into the gaseous phase. For polyurethane other ways of liberating the CFC must be devised.

By application of high pressure to the foam a large part of any CFC present is released from the polymer. The problem is that the tools used become contaminated (with CFC) to such an extent that this technique must be regarded as too cumbersome unless there is no other alternative.

Heat treatment of foam samples to liberate the CFC was used with some success in the exploratory GC-ECD measurements carried out for the previous project (3, 4). In this project various types of glass containers with volumes from about 100 mL down to 1.8 mL have been tested in the heat treatments of the foams, in all cases with reasonably good results. Most of the quantitative measurements on flexible PUR have been carried out on foams stored in 10 mL glass jars with heavy screw caps and in 1.8 mL glass vials sealed with Teflon-coated septa (autosampler vials), respectively. To allow gas phase samples to be withdrawn from the screw-cap closed jars, a 0.6 mm hole was drilled through the center of the cap. The hole was effectively sealed with a tight-fitting pin during heat treatment and equilibration periods.

It was found that keeping the foam samples at temperatures from 95 to 110 °C for one hour liberated enough "CFC" to give GC peaks safely above normal background, allowing positive identification of CFC:s present. A routine procedure was developed where samples (in sealed vials) were kept for 1 h at 95 °C and then stored at room temperature. Prior to taking a gas phase sample for analysis the container was kept at 50 °C for about 15 min, the idea being to free surface-adsorbed "CFC" before withdrawing a sample.

All sample containers were conditioned at 95 to 115 °C for an hour or more in a well ventilated oven prior to using them.

The ratio of sample mass to container volume does, of course, in some measure affect the concentration of "CFC" in the gas phase.
As the project progressed it became evident that a ratio as high as between 20 to 80 mg of foam sample per mL container volume is a suitable range for samples of flexible PUR; cf. 8.2.

However, it should be noted here that pretreatment of foams with closed cells prior to taking gas phase samples for analysis is normally not required. Gas phase samples are simply taken by inserting the needle of the syringe into the foam to withdraw an analysis sample.

7.2  The gas chromatograph

7.2.1  Detectors

Positive identification of CFC:s by gas chromatography calls for either a mass selective detector (MSD) or one that is in some measure halogen-specific, e.g. an electron capture detector (ECD).

Unless an MSD - a rather expensive detector - is already available in the laboratory, an ECD should be an acceptable alternative. As it is more straightforward to operate, an ECD may, in fact, be the best choice. As a result of the selectivity of the ECD, the majority of non-halogen compounds will not show in ECD-derived chromatograms, not even when present in high concentrations. Furthermore, by operating the ECD at moderate temperatures (150 °C in our case) the response for most of the possibly interfering polar substances (alcohols, nitro compounds etc.) is reduced to more or less insignificant levels (6). Altogether, this substantially reduces the number of substances that have to be taken into account in order to ensure correct conclusions as to the identity of possible CFC:s.

The sensitivity of a good ECD is more than adequate for the purpose of these CFC analyses; cf. 8.1. Working at maximum sensitivity is actually not worthwhile since background levels then tend to increase to a point where they start interfering.

An MSD, at least in principle, allows positive identification based on measurements of mass fragments of an individual peak, i.e. one does not have to rely entirely on reference compounds and established retention times for the CFC:s and possibly interfering compounds.

To arrive at analytical levels comparable to those of our ECD the MSD had to be operated in a "selected ion monitoring" mode (SIM), i.e. such that only selected mass numbers characteristic for the CFC in question are scanned. This way the scanning is concentrated on a few CFC-typical masses resulting in a much improved signal-to-noise level and an enhanced detector signal. - Another way of increasing the detector signal is, of course, to increase the amount of sample. When the MSD is operated in a system with a cryo trap this is easily done; see 7.2.3.
7.2.2 Columns

For the analysis of the highly volatile CFC:s a column is required with a stationary phase that provides a high retention, e.g. a thick film or a porous polymer.

Most of the ECD measurements have been performed using a CP-Sil 5 CB (methyl silicone) 50 m x 0.32 mm capillary column which has a film thickness of 5 μm. Some initial checks on concentration levels and relative retention times for the CFC:s and a number of other "halocarbons" were carried out with an HP-1 (cross-linked methyl silicone) 50 m x 0.32 mm x 1.05 μm capillary column. This column was used for the MSD measurements as well. A new column, CP-Sil 13 CB (phenyl methyl silicone; film thickness 2.0 μm), announced as being "specially developed for the separation of very volatile halogenated hydrocarbons" (according to EPA methods 624 and 601) was tried but considered too fast for the present work.

The order of elution of the banned CFC:s and the, in this context, most interesting HCFC:s, HFC:s and organochlorine solvents were checked on the methyl silicone capillary columns (CP-Sil 5 CB; HP-1) with helium as carrier gas. The observed order was

\[
\begin{array}{ll}
\text{Air} & \text{Air} \\
C_2\text{ClF}_5 & \text{or-} \\
C_2\text{H}_2\text{F}_4 & \text{CFC 115} \\
C_2\text{H}_4\text{F}_2 & \text{HFC 134a} & \text{elute close together} \\
\text{CHClF}_2 & \text{HFC 152a} \\
\text{CCl}_2\text{F}_2 & \text{HCFC 22} \\
\text{C}_2\text{H}_2\text{ClF}_2 & \text{CFC 12} \\
\text{CH} = \text{CHCl} & \text{HCFC 142b} \\
\text{C}_2\text{ClF}_2 & \text{Monochloroethene} \\
\text{C}_2\text{HCl}_2\text{F}_3 & \text{CFC 114} \\
\text{CCl}_3\text{F} & \text{HCFC 123} \\
\text{C}_2\text{Cl}_3\text{F}_3 & \text{CFC 11} \\
\text{CH}_3\text{CCl}_3 & \text{CFC 113} \\
\text{CCl}_2 = \text{CHCl} & \text{1,1,1-trichloroethane} \\
\text{CCl}_2 = \text{CCl}_2 & \text{1,1,2-trichloroethene} \\
\end{array}
\]

Caution is required with regard to the separation of HCFC 22 and CFC 12. With the temperature profile used in most of this work it has been possible to distinguish between the two, unless one or both of them are present in large amounts; cf. appendix B. Dilution of the gas phase sample under investigation is one way of confirming which of the two is present. "Standard addition" is
another strategy to be recommended. If necessary, the separation may be improved by operating at a lower initial temperature.

CFC 12 in combination with appreciably larger concentrations of HCFC 22 may be difficult to detect unless the separation of the two is improved. However, in such a case CFC 12 is likely to have its origin as an impurity in HCFC 22 and can then hardly be looked upon as being the blowing agent used.

In the above list CFC 113 is the last of the forbidden compounds to elute. If one wants to cover the whole group of banned CFC:s in analyses using the type of column specified above one must make sure to design a temperature-time program that includes the retention time for CFC 113.

The response of our ECD for HFC:s 134 and 152 is almost marginal compared to that for CFC 115. The HFC:s consequently must be present in very large amounts in order to interfere or be mistaken for CFC 115. Whenever there is any doubt, parallel measurements should be performed using a flame ionization detector (FID) where the relative response for these compounds is significantly different.

A word of caution is called for. Some of the CFC samples that were used as references were not very pure. From the ECD chromatogram only it is not always easy to judge which one is the main peak and hence what the correct retention time is. Supplementary measurements using a different type detector are then required.

7.2.3 Injection system

The original idea was to use a loop injection system connected either directly or via a cryo trap to the column. A cryo trap would, if necessary, allow a simple enrichment step to be included. The chromatograph was thus equipped with a 10-port valve. A fused-silica loop (ca 50 μL) and a stainless-steel loop (ca 70 μL) were mounted. Initial tests indicated, however, that the loops were easily contaminated by CFC from previous measurements.

In parallell to testing the loops, a simple injector system was built by connecting a 0.7 mm inner diameter stainless steel tubing to one of the valve ports. A Swagelok "union tee" tube fitting provided inlet for the carrier gas and a mounting port for a duck-bill "septum" lined up with the stainless steel tubing. Samples were injected with a gas tight syringe, of the type that has a gas sealing gland (GSG). With the syringe the contamination problem was easier to keep in check. This system, in fact, worked so well that it became the preferred procedure.

However, it must be emphasized that it is indeed very important to check up on the status of the syringe used, e.g. by running laboratory air samples frequently, preferably between each sample studied and certainly when the previous measurement showed a high content of any component other than air.
The size of the air peak is in most cases a good criterion of the amount of sample injected. Experience has shown that 15 μL can be injected quite reproducibly with a 25 or a 50 μL syringe. For standard samples based on dilution with nitrogen the "air" peak is substantially smaller. For some foams the air oxygen seems to be consumed to some extent during the sample preparation heating process.

For the MSD measurements a cryo trap was mounted, primarily to avoid disturbances from injected air. The trap was made of 0.32 mm diameter, coated (methyl silicone; thin film) fused silica tubing, about 25 cm in length connected to a vent. (Uncoated tubing did not seem to retain the sample efficiently enough under the conditions utilized.) The cryo trap was set to operate at -120 °C. In the MSD measurements carried out the total sample consisted of 3 x 100 μL gas phase samples injected into the cryo trap. The total amount can easily be increased at least tenfold.

7.3 Reference samples of CFC 11 and CFC 12

Working with samples at low levels of concentration presents special problems when it comes to determining the amounts quantitatively. In particular, preparation of well defined calibration samples is not simple in cases where the components of interest are suspected of being adsorbed on the walls of the container used. Calibration mixtures or reference samples should then be prepared and used within short periods of time. Furthermore, particular attention should be paid to the choice of container material. - CFC:s at low concentrations may be suspected of poor behaviour in terms of adsorption.

Even though the exact concentrations of the CFC:s are not of prime concern in this study it is desirable to have approximate values for the amounts of CFC liberated from different foams. It may also be of interest to track long-term changes in detector response. It is therefore advantageous to be able to prepare references and/or reference mixtures of reasonably well defined concentrations, e.g. within ± 10 to 15 per cent on a relative basis.

A method for the preparation of such reference samples, and mixtures, over a wide range of concentrations has been developed. Basically, the procedure builds on mixing a restricted flow of CFC with an adjustable, much larger flow of nitrogen. In this manner, a number of reference samples have been prepared for CFC 11 and CFC 12, respectively. CFC 12, gaseous at room temperature, is the easier one to handle in this case.

Pure CFC 12 (stored in a high-pressure bottle at room temperature) exiting at a reduced pressure of 2.0 bar above atmospheric and flowing through 0.5 m of an 8 to 10 μm i.d. fused silica capillary tubing gave a flow of 0.5, μL/min. Together with a defined flow of nitrogen, adjustable between 0 and 200 mL/min, the CFC flow was passed through an impinger bottle (ca 0.5 L) where the two components were mixed. The concentration of the mixture leaving the
bottle was considered constant after the flow had been left on for about half an hour. The mixture was then filled into an empty Tedlar bag (3 L). With this set-up reference mixtures of CFC 12 down to concentrations around 3 ppm by volume were easily, and reproducibly, prepared.

For CFC 11 a concentrated mixture was prepared by weighing accurately a small amount of the pure CFC compound into a previously evacuated gas bottle, subsequently filled to about 100 bar with nitrogen and weighed again. The resulting CFC 11 in nitrogen mixture (1.2 mass-%) was then, in a process similar to that described for CFC 12 (1.0 bar and 2.5 m 25 μm i.d. fused silica tubing gave 1.3 μL/min), dilute to concentrations around 30 ppb by volume.

References containing two or more of the compounds of interest are readily prepared using the same basic procedures. In figure 1 an example is given of a chromatogram for a three-component mixture.

<table>
<thead>
<tr>
<th>PKNO</th>
<th>TIME</th>
<th>AREA</th>
<th>NAME</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.138</td>
<td>26230</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.938</td>
<td>1460</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.117</td>
<td>14117</td>
<td>CFC 12</td>
<td>2.3 ppm</td>
</tr>
<tr>
<td>4</td>
<td>3.792</td>
<td>3473</td>
<td>CFC 114</td>
<td>0.6 ppm</td>
</tr>
<tr>
<td>5</td>
<td>6.3</td>
<td>118</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.816</td>
<td>2046</td>
<td>CFC 11</td>
<td>0.05 ppm</td>
</tr>
</tbody>
</table>

Figure 1. Reference mixture of CFC 11, CFC 12 and CFC 114. - The second chromatogram represents laboratory air; the peak at 2.9 min is a "system" peak.
In order to prove that CFC:s have been used in the manufacture of polymeric foams, it is necessary to establish that there is a distinct difference between background CFC concentrations (laboratory air, slightly "contaminated" equipment, impurities in non-CFC foams etc) and CFC concentration levels obtainable for samples of CFC-produced foams. A large number of measurements have been carried out on non-CFC and on CFC produced foams for the principal purpose of finding out whether there is enough of a margin in the results from measurements on the two types of foams to allow conclusions to be drawn about the manufacturing.

A fair number of these measurements were performed before a defined procedure had been established with regard to sample preparation and/or gas chromatographic conditions. Some of the results are therefore not directly comparable. The limited time available for completing the work has not allowed repetition of the earlier measurements to refer them to the same base as the later ones. However, there are groups of results that are consistent among themselves and some of those will be reported.

In the following the concentration levels involved in identifying CFC produced foams are indicated. A systematic study of CFC concentrations in the gas phase as a function of the ratio of the mass-of-foam to container-volume is accounted for. Moreover, attempts to contaminate non-CFC foams by storing them together with CFC produced foams are reported on.

3.1 Detector response and levels of detection - ECD

The sensitivity of an ECD to a specific compound is, in addition to being dependent on detector design, strongly influenced by factors such as the purity of the carrier gas, column bleed, leaking fittings and detector temperature (7). Care therefore must be exercised in comparisons of ECD response factors, and even relative response factors, from different sources for a given set of compounds (8).

Generally, for halogenated compounds the response should be in the order F < Cl < Br < I. The response per halogen atom in a molecule (for halogens of the same kind) is for one much smaller than it is for two, which is smaller than it is for three.

Quantitative measurements of the ECD response have been made on a number of occasions for CFC 11 (CCl₃F) and for CFC 12 (CCl₂F₂). One of the later sets of measurements on freshly prepared reference mixtures gave for 15 µL injected of 0.36 µg/L CFC 11 and 84 µg/L CFC 12, respectively, peak areas equal to 1640 and 16480 integrator area units (a.u.), respectively. For 15 µL of reference mixture injected this corresponds to
CFC 11: 4500 a.u. per μg CFC/L 26000 a.u. per ppm by volume
CFC 12: 196 a.u. per μg CFC/L 980 a.u. per ppm by volume

At the time the noise level was such that 50 area units (a.u.) gave a peak that could be reasonably well identified. This means that the level of detection (for 15 μL injected) was about 11 ng/L or 2.0 ppb(vol) for CFC 11 and 250 ng/L or 50 ppb(vol) for CFC 12. The total amount corresponding to 50 area units was for CFC 11 0.16 pg (pg = 10^{-12}g) and for CFC 12 3.8 pg.

Lately, with a different setting for the cell current, the response in general has increased as judged from the size of the air peak. But at the same time the noise level increased slightly leaving the level of detection about the same unless reintegration with noise reduction was utilized.

Should there be a need for a slight improvement in the level of detection, sample size in our case can be increased to 50 μL without noticeable peak broadening. One would then still have a quantifiable air peak.

While this report was in preparation, measurements were performed to examine the dilution linearity and the precision obtained for reference sample concentrations, for samples prepared using the system described in section 7.3. Response factors for CFC 11 and CFC 12 were determined. For CFC 11 samples were prepared with concentrations from 4 to about 120 ppb(vol). The response factor determined (for 15 μL) was 58 area units per ppb of CFC 11, with a standard deviation equal to 3 a.u./ppb. Similarly, for CFC 12 the reference samples yielded a response factor of 6 area units per ppb(vol) with a standard deviation of 0.6 a.u./ppb; the concentration of CFC 12 was from 0.2 to about 7 ppm(vol). No systematic trend as a function of concentration was observed.

8.2 The ratio of sample mass to sample container volume

The earliest experiments were carried out with rather low ratios of foam sample mass to sample-preparation container volume. At the time, an enrichment procedure was assumed to be required anyhow. As the work progressed it became clear that it was sufficient, and indeed more convenient, to increase the amount of foam per mL of container volume and take gas phase samples for direct injection.

For the systematic studies of CFC gas phase concentration as a function of the mass-to-volume ratio, a flexible polyurethane foam with the higher manufacturing ratio of CFC 11 was chosen, cf. section 4. The bulk density of this foam was 20 kg/m³. (It had been produced week 31, 1990.) The results from two sets of measurements are shown in figure 2. For this foam a mass-to-volume ratio above 30 g/L tends to give gas phase concentrations of CFC that are more or less constant. Other foams appear to behave similarly. It is therefore recommended that a ratio of at least 30 g/L should be used in this type of measurement. For unknown or older
foams it is recommended to make measurements at more than one ratio, if possible at ratios higher than 30 g/L.

8.3 Foam contamination risks

An important question is whether foams that have not been produced with CFC may become contaminated by CFC-produced foams during storage or transportation.

For the contamination studies two different non-CFC foams were chosen with a density of 25 and 30 kg/m³, respectively. Small samples were stored in 1 L metal containers with tight fitting
Table 3. Results from CFC 11 measurements after attempts to contaminate non-CFC foams by storing them with CFC-produced foams. Area unit values refer to normalized areas (see text).

<table>
<thead>
<tr>
<th>Foams stored</th>
<th>Storage container Gas phase CFC 11- area*</th>
<th>Foam samples after storage CFC foam CFC 11- area (g/L)</th>
<th>Non-CFC foam CFC 11- area (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-CFC foam 9025 25 kg/m³ stored with:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High CFC 9031 185</td>
<td>500 33</td>
<td>6 29</td>
<td></td>
</tr>
<tr>
<td>High CFC 9012 6</td>
<td>300 34</td>
<td>6 34</td>
<td></td>
</tr>
<tr>
<td>Low CFC 9032 11</td>
<td>53 34</td>
<td>5 33</td>
<td></td>
</tr>
<tr>
<td>Low CFC 9013 &lt;6</td>
<td>86 29</td>
<td>3 30</td>
<td></td>
</tr>
<tr>
<td>Non-CFC foam 9031 30 kg/m³ stored with:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>High CFC 9031 250</td>
<td>520 26</td>
<td>9 32</td>
<td></td>
</tr>
<tr>
<td>High CFC 9012 45</td>
<td>370 29</td>
<td>5 34</td>
<td></td>
</tr>
<tr>
<td>Low CFC 9032 55</td>
<td>42 35</td>
<td>5 31</td>
<td></td>
</tr>
<tr>
<td>Low CFC 9013 45</td>
<td>70 36</td>
<td>5 31</td>
<td></td>
</tr>
</tbody>
</table>

* Contamination storage-container gas phase values normalized to an m/V value of 4 g/L.

Lids together with a high CFC and a low CFC produced foam, respectively. After about 3 months samples were taken for analysis. Immediately upon first opening the lid of the storage container a gas phase sample was withdrawn and analysed. Samples for heat treatment and subsequent GC analysis were then prepared from each of the stored foams, from the CFC as well as from the non-CFC foams, with mass-to-volume ratios around 30 and 60 g/L, respectively.

The results are shown in table 3. The CFC 11 concentrations are expressed in terms of normalized areas, i.e. the actual peak area
in integrator units, for 15 μL of sample injected, divided by
the mass-to-volume ratio (m/V) in g/L. The storage-container gas
phase values were normalized to an m/V value of 4, close to the
actual value for the 1 L containers used. - In the table the
number 9031, for instance, is to be interpreted as week 31 1990
and denotes the time of manufacture for the particular foam sample.

The CFC 11 concentrations found for the non-CFC foams are about
the same as normal blank values or the results from measurements
on "untreated" non-CFC foams, i.e. from 50 to about 400 area
units. Converted to normalized areas this roughly corresponds to
values from 1 to about 8. - An area of 1000 integrator units cor-
responds to a gas phase CFC 11 concentration of about 30 ppb(vol).

The results indicate that there is, in fact, little risk that
foams get contaminated by other foams. The non-CFC foam samples
were weighed into sample vials as soon as they were removed from
the container where they had been stored with the CFC foams. If
there was "initially" any contamination the non-CFC foams were
indeed very rapidly decontaminated.

The risk is probably much larger that a foam gets contaminated in
changes from CFC- to non-CFC-containing reagents in the manufac-
turing or, for that matter, from using "contaminated" reagents.
This is a risk the producer should be aware of.

The simple linear model applied to convert measured response areas
to so-called normalized areas is not really appropriate for mass-
of-foam to container-volume ratios exceeding 30 to 40 g/L. As
shown in figure 2, peak areas, i.e. CFC concentrations, tend to
level off around m/V values of 50 g/L for the foam studied in that
case. A non-linear normalization would therefore be more appropri-
ate. But for the present purposes the simpler linear "normalization"
should suffice. - When m/V values in excess of about 40 are
utilized consistently there is no real need for normalizing the
measured areas for comparison purposes.

8.4  CFC in aged foams

It is not yet clear how fast the CFC levels decrease in CFC pro-
duced foams. The results for the CFC produced foams in table 3
indicate that after 20 weeks the levels are almost the same as
they were originally. In fact, for the low CFC foam the results
indicate a slightly higher CFC level for the foam produced week 13
than for that from week 32. As the foams for the contamination
studies were "sealed" week 33 they have not been subject to normal
venting conditions after that.

A safe conclusion appears to be that CFC adsorbed on the surface
of the foam and the foam cells disappears rather rapidly but that
CFC trapped in micro cavities and dissolved in the polymer mate-
rial remains for quite some time unless the foam is heated for an
extended period or subjected to tough compressions.
MEASUREMENTS ON SOME CONSUMERS FOAM PRODUCTS

Measurements have been performed on some consumers foam products. One of the reasons was to confirm that it is indeed possible to detect CFC in polymeric foams with open cells found in the ordinary store. The "history" of such foams is, of course, not known but they have been subjected to the customary venting and squeezing during transport and handling.

Another, equally important, motive was to see whether one would find such a distinct difference between groups of CFC levels measured on "real" products that it would allow classifying the foams as CFC and non-CFC produced, respectively.

The results from a number of measurements on products from polymeric foams with open cells are listed in Table 4. As is evident from the table it is certainly possible to trace CFC in such foams. In some cases CFC was present in appreciable amounts. The chromatogram obtained for one of the products investigated is shown in figure 3.

Table 4. Results from measurements on some consumers products made from polymeric foams with open cells.

<table>
<thead>
<tr>
<th>Foam product</th>
<th>CFC 11 areas*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kitchen accessories -</td>
<td></td>
</tr>
<tr>
<td>Artificial sponge, yellow**</td>
<td>9</td>
</tr>
<tr>
<td>Red and white sponge, red part</td>
<td>2</td>
</tr>
<tr>
<td>Sink mat**</td>
<td>4</td>
</tr>
<tr>
<td>Grill cleaner, yellow part</td>
<td>1320</td>
</tr>
<tr>
<td>, green part</td>
<td>2</td>
</tr>
<tr>
<td>Sport (jogging) shoe -</td>
<td></td>
</tr>
<tr>
<td>Tongue</td>
<td>10</td>
</tr>
<tr>
<td>Arch support</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Layer on top of sole</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Inside material of sole</td>
<td>3</td>
</tr>
<tr>
<td>Insulating seat cushion</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Insulating seat pad</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Upholstery items -</td>
<td></td>
</tr>
<tr>
<td>Cushion, patterned fabric***</td>
<td>204, 22</td>
</tr>
<tr>
<td>Seat cushion, &quot;thick&quot;</td>
<td>55, 52</td>
</tr>
<tr>
<td>Seat cushion, &quot;thin&quot;</td>
<td>3, 10, 12</td>
</tr>
<tr>
<td>Yellow wadding material</td>
<td>106</td>
</tr>
<tr>
<td>Green wadding material</td>
<td>144, 203, 267</td>
</tr>
</tbody>
</table>

* Normalized areas; for m/V ratios >50, the value 50 was used.
** Labelled "Manufactured without CFC".
*** Stuffed with wadding material of more than one type.
Figure 3. Chromatogram for a sample from a consumers foam product.

Some of the foams purchased were labelled "Manufactured without CFC". The CFC levels found in these foams were not significant (cf. table 3) and they could hence be classified as non-CFC produced; see table 4.

In addition to the measurements accounted for in table 4, a number of polyurethane foam products used as safety devices in cars were investigated, e.g. dashboards, head- and armrests etc. Most of these products are produced in some type of mould and obtain a tight skin in the manufacturing process. Even though the foams as such have open cells the skin tends to prevent gases trapped during the foaming process from leaving.
Besides using CFC:s as blowing agents, the mould release agent used may contain CFC. In fact, at the present time a considerable part of the mould release agents used in the manufacture of these products do contain CFC.

Most of the measurements performed on the moulded components were made early in the project on samples with m/V ratios from 4 to 7 g/L and the results can therefore not be directly compared with the results presented in table 4. However, some general conclusions may be drawn.

The measurements disclosed that foams produced with CO₂ as the blowing agent and a CFC containing mould release agent may give rise to significant CFC 11 peaks - "normalized" peak areas as large as 200 - for the foam itself. The skin may, or may not, have retained significant amounts of the CFC. It is therefore to be recommended that when large amounts of CFC are found in moulded components of the open cell type with a skin, analyses should also be performed on "aired" material.

The results from measurements on the foam products listed in table 4 indicate that non-CFC products can, with care taken, in most cases be distinguished from CFC products. A normalized area less than 20 - with the enhanced detector response corresponding to gas phase concentrations around 25 ppb by volume - should be a reasonably clear indication of a non-CFC produced product. Areas between 20 and 50 should lead to measurements on at least another sample before a verdict is given, whereas areas in excess of 50 may be judged as indicative of a CFC-produced foam. - The normalized areas referred to must, of course, be translated into the appropriate equivalent units for the instrumentation used under other conditions or circumstances.

It should be pointed out that, for obvious reasons, the range of products that have been studied is limited. The criteria given in the previous paragraph are not to be regarded as absolute values. Different types of foams may call for slightly different values for the limits set for "non-CFC".

10 CONCLUSIONS AND RECOMMENDATIONS

In this investigation it has been demonstrated that enough CFC remains trapped also in polymeric foams with open cells to allow unambiguous identification of CFC:s when used as blowing agents in the manufacturing process. For foams with closed cells CFC identification is easy.

The CFC trapped in foams with open cells must, however, be forced out of the material either by heating to temperatures at or above 100 °C or by application of high pressures in order to make e.g. micro cavities release their share of the CFC.
Designing methods of laboratory analysis that are sensitive enough in terms of levels of detection with respect to the CFCs in question is not a problem. Enhancement techniques or procedures other than heating flexible polyurethane samples in a closed vessel are in most cases not required. If necessary, a cryo trap technique may be employed.

Background levels from sampling devices and laboratory air generally determine how far attempts to increase the "response" in the measurements is still beneficial. Great care must be taken to avoid contaminating any of the equipment used. Blanks should be run regularly on sample preparation containers with no sample but otherwise treated in the same way as containers with foam samples.

Reference gas mixtures of known concentrations should be available for at least one or two of the most likely CFCs even though the exact amounts measured are not the principal concern. Safe discrimination between CFC and non-CFC produced foams, respectively, is facilitated by knowledge of the levels of CFC measured.

Sampling can normally be effectuated without noticable damage to foams with closed cells. For flexible foams it is necessary to remove a small piece of material for analysis. Furthermore, this should not be taken close to the outer surface. Minor damage may therefore be caused by sampling. Samples taken should be stored in small, closed containers until preparations for analysis commence in the laboratory.

Methods for screening of foams with closed cells present no serious problems. The less expensive alternatives, with regard to instrumentation and instruction of personnel, include a separation step to facilitate the identification. In some cases special care must be taken in order to differentiate between illegal and legitimate "halocarbons". Normally, screening should be complemented with a confirmative laboratory analysis.

Since the CFCs need to be forced out of most foams with open cells before an analysis can be performed, screening is not really feasible for these foams. Good leak detector instruments are believed to have enough sensitivity for screening of many of the flexible foams but are not specific enough to give conclusive information. Instead of screening, CFC-hunting campaigns could be employed.

Contamination of non-CFC foams by CFC-produced ones does not appear to be a problem. Deliberate attempts in the laboratory to contaminate non-CFC foam samples by CFC-containing foams were all without success.

Flexible foams seem to retain CFC for a considerable period of time and there ought to be no problem of detection of CFC in foams of interest for import control.
REFERENCES

1 "Förordning om CFC och halon", Svensk författningssamling SFS 1988:716.


5 "CFC – Åtgärder och alternativ", Sveriges Tekniska Attachéer, Utlandsrapport STAT 8907.


APPENDIX A

SCREENING METHOD - GAS CHROMATOGRAPHIC METHOD UTILIZING A FLAME IONIZATION DETECTOR (FID)

The basic requirement with regard to the gas chromatograph is that it has a temperature controlled oven for packed columns and means for controlling the flow of carrier gas. It must also be equipped with a standard injector system for packed columns.

The detector may be an ordinary FID. A more specific detector such as an ECD is in some ways a better choice also for screening (cf section 7.2.1), but may require more maintenance to keep in good working conditions. As outlined in section 6.1 it should be possible to adapt a leak detector instrument as a detector for screening.

The parameters for the GC-FID method tested were

Detector: Flame ionization detector operated at 250 °C

Injector temperature: 250°C

Column: Porapak Q, 2 m 1/8" packed stainless steel

Carrier gas: Nitrogen, 30 mL/min

Oven temperature: 120 °C, isothermal

Sample volume: 0.1 to 0.5 mL

Reference samples: Gas phase reference samples of CFC:s 11, 12, 114 and possibly also 113 and 115 in concentrations around 0.1 to 1 % by volume

Samples were injected using a 1 mL gas-tight syringe. For screening purposes single-use syringes are recommended.

Detector range and attenuation depend on the concentration of the component of interest. For about 1 vol-% gas phase samples range 10 to range 100 and attenuations from 4 to 32 were used.

Retention times for the samples tested are listed below. In addition to the gas phase and headspace samples, respectively, from pure compounds a gas phase sample was also withdrawn from and analysed for a foam with closed cells. The foam contained HCFC 142b.

Under the conditions chosen CFC 115 and HFC:s 134a and 152a elute rapidly and close together. HCFC 22 follows quite closely. As CFC
115 is not a likely blowing agent for polymeric foams and as the time for the project was limited no attempt was made here to separate it from the legitimate HCFC and HFC compounds. If the presence of CFC 115 is suspected samples can, of course, be taken for identifying laboratory analysis. If required it is certainly possible to separate all four by operating at some lower temperature.

CFC 11, CFC 12 and CFC 114 are well separated from the other compounds investigated and should hence be easy to pick out for further analyses. CFC 113 elutes at approximately the same time as 1,1-dichloroethane. Should it be necessary to separate the two, the analysis temperature must be changed.

Reference samples of the CFC:s to be identified must be available and used frequently to determine and check the constancy of the retention times. Care must be exercised not to use contaminated syringes. Blanks, i.e. air samples, should be analysed at regular intervals.

When required, gas phase samples are easily diluted with air up to a factor of about ten directly in the syringe.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFC 115</td>
<td>1.49</td>
</tr>
<tr>
<td>HFC 134a</td>
<td>1.49</td>
</tr>
<tr>
<td>HFC 152a</td>
<td>1.56</td>
</tr>
<tr>
<td>HCFC 22</td>
<td>1.70</td>
</tr>
<tr>
<td>CFC 12</td>
<td>2.4</td>
</tr>
<tr>
<td>HCFC 142b</td>
<td>3.38</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>3.49</td>
</tr>
<tr>
<td>CFC 114</td>
<td>5.05</td>
</tr>
<tr>
<td>CFC 11</td>
<td>10.4</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>10.8</td>
</tr>
<tr>
<td>HCFC 123</td>
<td>12.4</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>15.3</td>
</tr>
<tr>
<td>CFC 113</td>
<td>21.1</td>
</tr>
<tr>
<td>1,1-Dichloroethane</td>
<td>21.9</td>
</tr>
<tr>
<td>Trichloromethane</td>
<td>29</td>
</tr>
</tbody>
</table>
APPENDIX B

GAS CHROMATOGRAPHIC METHOD - ELECTRON CAPTURE DETECTOR

Instrument: Varian 3300
Detector: Varian Electron Capture, at 150 °C
Make-up gas N₂ at 55 mL/min
Injector: Split/splitless or On-column
Injector temperature: 100 °C
Column: CP-Sil 5 CB, 50 m x 0.32 mm,
film thickness 5 μm
Carrier gas: Helium, 1.5 bar, corresponding to 40 cm/s
linear speed
Temperature program - column:
40 °C - 2 min
40 °C to 100 °C at 5 K/min
Column about 100 mm into the ECD

Retention time/min

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>2.20</td>
</tr>
<tr>
<td>CFC 115</td>
<td>2.50</td>
</tr>
<tr>
<td>HCFC 22</td>
<td>3.07</td>
</tr>
<tr>
<td>CFC 12</td>
<td>3.17</td>
</tr>
<tr>
<td>HCFC 142b</td>
<td>3.55</td>
</tr>
<tr>
<td>CFC 114</td>
<td>3.85</td>
</tr>
<tr>
<td>HCFC 123</td>
<td>6.22</td>
</tr>
<tr>
<td>CFC 11</td>
<td>6.83</td>
</tr>
<tr>
<td>1,1-Dichloroethene</td>
<td>8.10</td>
</tr>
<tr>
<td>CFC 113</td>
<td>8.54</td>
</tr>
<tr>
<td>Trichloroethene</td>
<td>16.2</td>
</tr>
</tbody>
</table>

COMMENTS

With this temperature program, peaks from CFC 12 and HCFC 22 are close in their retention times and caution is called for in identifying a component as being CFC 12 or HCFC 22 (see figure B2).
Preferably, the initial temperature should be changed to 30 °C, or lower. A 3 min period of isothermal operation may also facilitate increased separation of the CFC and the HCFC. Another approach is to dilute the sample to pinpoint the retention time and/or work with a standard addition technique.

Other choices of column temperature profile may, in fact, be more of an optimum than the one presented here. But the order of elution and the closeness of the different components to each other should be a good guide in designing more optimal temperature programs.

A sample preparation technique is defined in section 7.1 of the main text. The mass of foam sample should be at least 30 mg per mL of sample container volume, cf. section 8.2. The range of gas phase sample volume for injection used in this project was from 15 to 50 μL.

The sample containers should be conditioned at high temperature before use, e.g. by keeping them at 100 to 110 °C for a period of at least one hour in an oven with forced air circulation. It is recommended that "blanks" are run regularly on containers with no sample but treated in the same manner as those with foam samples.

For day-to-day checks on detector response one may simply use headspace samples taken over a suitably diluted chloroorganic solvent. For instance, in a 1.0 mass-% solution of 1,2-dichloroethane in n-heptane or methylhexane the mole fraction of dichloroethane is 0.010 and hence its partial pressure above such a solution is reduced by a factor of 100 from the vapour pressure of the pure compound, i.e. from 10.7 to 0.11 kPa (0.80 Torr). Taking 100 μL of this solution plus 100 mL of the pure hydrocarbon reduces the partial pressure of dichloroethane further and the equilibrium concentration of dichloroethane in the gaseous phase should now be around 1 ppm by volume at room temperature. A suitable amount of this further diluted solution is best kept in a septum-closed bottle for withdrawal of headspace GC samples.

As the original 1 % solution was prepared from compounds with vapour pressures that are approximately equal at room temperature it can be used as a stock solution over an extended period of time, provided it is kept in a reasonably well closed bottle.

Chromatograms obtained for mixtures of CFC 11 and CFC 12 at two different levels of concentration are shown in figure B1. Figure B2 illustrates the close separation of HCFC 22 and CFC 12.
Figure B1. CFC 11 and CFC 12 at different levels of concentration.
Figure B2. Example of the close separation of HCFC 22 and CFC 12.