

## A - 7. 1. 4 Behaviors of CFC Alternatives in the Atmosphere

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### Abstract

Production and use of ozone-destroying CFCs have been controlled with a goal of the complete phaseout and several alternative compounds (HCFCs and HFCs) have been proposed. Analytical systems and procedures were developed to achieve highly sensitive and precise determination of CFC alternatives in the atmosphere. Background air samples collected in Hokkaido were analyzed to obtain their atmospheric concentrations. The following results were obtained in this work:

1. Since HCFC-22 (  $\text{CHClF}_2$  ) and HFC-134a (  $\text{CH}_2\text{FCF}_3$  ) ( typical CFC alternatives ) are hardly detectable in ECD gas chromatography, we attempted to enhance the HCFC-22 sensitivity in ECD by adding oxygen into the carrier gas, and preconcentration of the components in the air samples at low temperatures was also examined. Trend in average atmospheric concentration of HCFC-22 was roughly estimated in these preliminary measurements.

2. While GC/FID and GC/MS methods were examined for the detection of HFC-134a, neither method was sensitive enough to detect the extremely low concentration level of HFC-134a currently anticipated.

**Key Words** CFC Alternatives, HCFC-22, HFC-134a,  
Atmospheric Concentration, Ultratrace Analysis

### 1. Background

Production and use of ozone-destroying chemicals such as CFCs have been controlled since 1989 according to the Montreal Protocol towards a goal of the complete phaseout by the end of this century. In view of the rapid progress of stratospheric ozone depletion observed very recently, the time limit for the complete phaseout has been further moved up to 1996. However, behaviors of CFC alternatives such as HCFCs and HFCs are not well understood, while their clarification is vitally important for the assessment of environmental effects of CFC alternatives.

## 2. Objective

Analytical system and procedures should be improved to achieve highly accurate / precise analysis of CFC alternatives ( HCFCs ) ; background air samples collected in Hokkaido are analyzed to obtain their average atmospheric concentrations.

## 3. Results

### (1) HCFC-22

Unlike chlorofluorocarbons such as CFC-11 and CFC-12, HCFC-22 ( a typical CFC alternative ) is hardly detectable in an ordinary ECD gas chromatograph. Hence, accurate / precise determination of HCFC-22 requires some extremely sensitive detector and fractional condensation of HCFC-22 from larger amounts of atmospheric samples. We have attempted to increase the HCFC-22 sensitivity in ECD by adding small amounts of oxygen into the carrier gas ( nitrogen ). Preconcentration of trace components in the air samples at low temperatures has also been examined.

In this work, HCFC-22 and methyl chloride ( a major natural chlorine source ) were found to become detectable in ECD gas chromatography in the presence of 0.3 % oxygen in the carrier gas ( Fig. 1 ). Over the analytical range of interest, the HCFC-22 response shows good linearity and reproducibility : thus determination of HCFC-22 are attained at a highest precision level in the world.

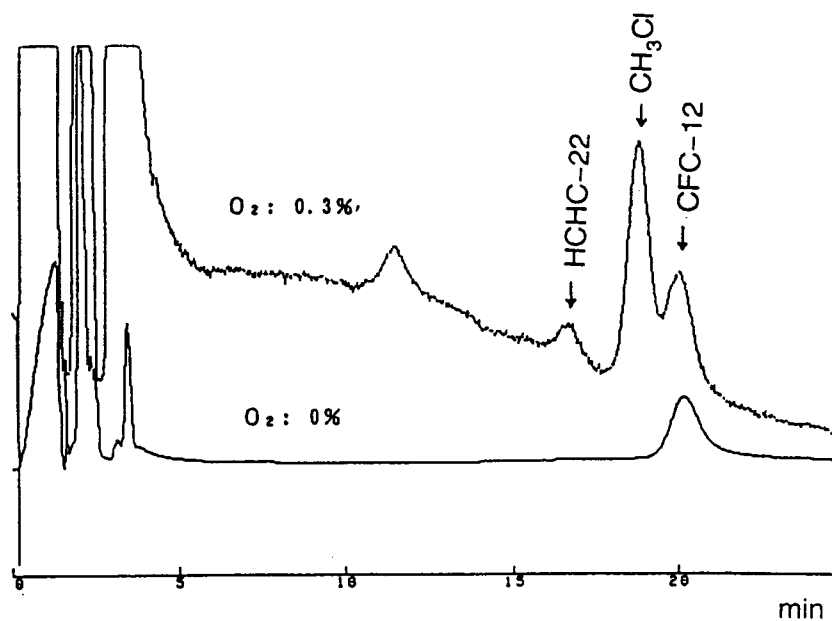


Fig. 1

The atmospheric concentration of HCFC-22 was found to be about 140 pptv in air samples collected at remote locations in Hokkaido. This may well represent the average HCFC-22 concentration in the mid-latitude Northern Hemisphere. Based on these preliminary measurements, the average HCFC-22 concentration has been increasing by 10-15% a year over the past decade ; the growth rate has jumped up in late 1980s in accordance with the enhanced regulation on CFCs.

## (2) HFC-134a

While GC / FID and GC / MS methods were examined for detection of HFC-134a, neither method was sensitive enough to detect the extremely low concentration level ( below 0.1 pptv ) of HFC/134a, currently anticipated on the basis of its world production / emission : the limit of detection of atmospheric HFC-134a ( in a 500 ml sample ) was about 200 pptv by GC / FID and more by GC / MS. Further study is needed for improvement of analytical means to detect HFC-134a in the atmosphere.