CHAPTER 1

INTRODUCTION

1.1 Background of the problem

Fully halogenated chlorofluorocarbons (CFCs) are suspected of depleting the Earth's ozone layer (1,2) and will be regulated through an international agreemant signed in Montreal in September 1987. One of these compounds is trichloro-fluoromethane (CCl_3F, CFC-11) which is used as a blowing agent in the manufacture of polyurethane, polyisocyanurate and phenolic foams. CFCs are also used in refrigeration and air conditioning.

In January 1988, fourteen worldwide producers of CFCs joined together to study the toxicity profiles of 1,1,1,2-tetrafluoroethane (CF_3-CH_2F,HFC-134a) and 1,1-dichloro-2,2,2-trifluoroethane ($CHCl_2$-CF_3, HCFC-123), as potential substitutes for the CFCs. That study is known as the Program for Alternative Fluorocarbon Toxicity Testing (PAFT I). In that study, 1,1-dichloro-1-fluoroethane (CCl_2F-CH_3, HCFC-141b) was not added and in August 1988, ten chlorofluorocarbon producers established a second program to accelerate toxicity testing on HCFC-141b being considered as an alternative to CFC-11. The participants in that second program, PAFT II, were Akzo (Netherlands), Allied-Signal (US), Atochem (France), Daikin (Japan), Du Pont (US), ISC Chemicals (England), Penwalt (US) and Solvay & Co. (Belgium). Showa Denko and Asahi Glass joined in September 1988. The testing program, a requirement to commercialize alternative products, should shorten the time required for toxicity testing from an average of six or seven years to about five years. It should also avoid replication of tests by the participating companies. The study involved the toxicity, potential mutagenicity and tumorigenic potential of HCFC-141b.

At the end of 1988, fourteen worldwide producers of CFCs, five of them US and nine of them European companies, joined together to study the environmental acceptabilty of alternatives to fully halogenated CFCs (3). This study is known as the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS) and will evaluate the potential effect of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) alternatives on stratospheric ozone, tropospheric ozone, global warming and acid deposition.

In June 1989, a fourth program PAFT III, was established to evaluate the toxicity of 1-chloro-1,2,2,2-tetrafluoroethane($CHClF-CF_3$, HCFC-124) and pentafluoroethane (CHF_2-CF_3, HFC-125).

These different programmes have stressed the need for improving both analytical techniques and basic knowledge on the physico-chemical properties of the involved molecules and their degradation products. The Central Laboratory of the Belgian chemical company Solvay, has started to study the behavior of chlorofluorocarbons and their partly hydrogenated substitutes in linear-temperature programmed gas chromatography.

1.2 Scope of this work

For the work concerning this thesis,the correlations that can predict the retention indices of CFCs, HFCs and HCFCs with one and two carbon atoms will be performed. For this, the retention times of these compounds available from the Solvay Laboratory Centre will be examined with linear programmed-temperature gas chromatography (GC) on three columns of different nature and polarity. All these pure compounds are divided into families, according to the number of carbon and hydrogen atoms in the molecule. The retention parameters will then be converted into linear-programmed retention indices as described by Van den Dool and Kratz (4) and based on the Kovats

retention index (5).

In the theoretical part , these retention indices will be correlated with parameters that describe the structure and physico-chemical properties of the molecule (such as boiling point, molecular weight, topological descriptors, number of carbon, chlorine, fluorine hydrogen atoms and quantum chemical parameters, etc.). Three methods of analysis will be used to obtain the correlations. They are the principal component analysis (PCA),the partial-least squares analysis (PLS) and the multiparameter regression analysis.

PCA is a method used to analyze a set of data in matrix form. Each row of the data matrix concerns particular compounds and each column of the data matrix concerns particular parameters. Using the mathematical method of "eigenanalysis", the raw data matrix will be decomposed into "score" matrix, which depends solely on the nature of the compounds, and "loading" matrix, which depends solely on the nature of the parameters. This can help us gain insight into the true nature of the problem. The model can be obtained from linear combinations of score and loading factors.

PLS is a method which operates under a principle which is the same as PCA but which works on two matrices of independent variables (parameters) and dependent variables (retention indices). PLS will fit the model with these two matrices, to make use of the independent variables matrix to predict the dependent variables matrix.

A stepwise regression analysis is used to find the parameters that account for the largest dependent variables and find the relationship between them.

Each model obtained for the individual families and for the individual columns will be used in order to gain insight in the

physical background. At the end, all the information will be combined into one model that describes the retention indices of all the families on the three columns. Once this relationship is known,it can be used to predict the retention index of non-available products and/or to calculate missing physical properties in the data matrix. The retention index of non-available products can be predicted with a defined percentage of certainty (or uncertainty). Furthermore, based on the models obtained from regression analysis, unknown peaks in the GC chromatogram can also be recognized (if they are CFCs).