GC Determination of Halogenated Olefins by Photoionization and Hall Electrolytic Conductivity Detectors in Series in Matrices of Hydrofluorocarbons and Hydrochlorofluorocarbons

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Summary
Gas chromatography (GC) with photoionization (PI) and Hall electrolytic conductivity (EIC) detectors connected in series, has been used for the determination of chlorofluorinated olefins. The separation of different standard solutions containing eight chlorofluorinated ethenes in nitrogen and in halogenated matrices has been performed in wide bore capillaries, 0.53 mm i.d., and normal capillaries, 0.32 mm i.d.. The quality of separation is obviously influenced by their limited load capacity and by the response time of the Hall detector.

At concentrations 1–150 µL L⁻¹ halogenated olefins, both PI and EIC detectors have linear response and can detect minimum levels of 0.2–0.5 ng and 0.4–1.2 ng, respectively. The PID is particularly selective toward halogenated olefins and is extremely useful for the determination of traces of unsaturated halogenated hydrocarbons in a matrix of saturated homologues.

The results of this work are of great interest for the detection of chlorofluorinated olefins, highly toxic compounds usually formed as by-products in the industrial production of hydrofluorocarbons and hydrochlorofluorocarbons.

Introduction
Generally, the term fluorocarbons is used to indicate partially or completely halogenated alkanes containing fluorine. The general formula is as follows:

\[ C_nH_{2n+2} - x - yCl_xF_y \quad \text{with} \quad x + y < 2n + 2 \]

Chlorofluorocarbons (CFCs) have been used for more than fifty years as industrial solvents, refrigerants, expanding agents and quenching fluids. Applications of CFCs result from their particular physico-chemical properties; they consist of inert and harmless molecules which are chemically and thermally very stable. Presently, these compounds are recognized as serious hazards for the deterioration of the ozone layer in Antarctica [1]. Their use is subject to progressive elimination according to the 1987 convention in Montreal [2, 3].

The hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) are fluorinated ethanes and propanes which possess minor numbers of chlorine atoms; they are called “CFCs of the second generation”. These substances are special owing to their reduced impact on the ozone layer, while retaining all the useful properties of traditional CFCs [4].

One of the principal difficulties regarding the synthesis of these HFCs and HCFCs is the formation of variously chlorofluorinated olefins as by-products which are highly toxic, difficult to isolate from the main products and favour deactivation of the catalyst. Furthermore, the concentration of impurities affects the final product quality as well as its designated use. The threshold limit values (TLV), which define the toxicity and the harmfulness of these unsaturated molecules, are given for dichloroethene:

time-weighted-average for an eight-hour workday (TLV TWA) 5 ppm (20 mg M⁻³)
short time exposure limit (TLV STEL) 20 ppm (79 mg M⁻³).

The analysis of these complex matrices used to be by gas chromatography coupled with mass spectrometry (GC-MS), this technique no longer satisfies quantitation of traces of unsaturated impurities due to its limited sensitivity, to the matrix effect and to the coelution of similar mass spectra compounds. These limitations will be demonstrated below.
The gas chromatographic photoionization detector (PID) owes its wide usage to high sensitivity (in the ng L\(^{-1}\) range) and selectivity toward aromatics and alkenes and especially to its non-destructive nature. Depending on the compounds considered, there exist various lamps characterized by different photon energies, for example, the 11.7 eV lamp enables detection of hydrocarbons (except methane) with a higher sensitivity than a flame ionization detector (FID), while the 10.2 eV lamp is used for selective analysis of unsaturated compounds. The latter UV source is the most commonly used due to its large photon flow and hence its high sensitivity and is used in the present work.

The electrolytic conductivity detector (E1CD) is principally used to reveal compounds containing halogen or sulphur or nitrogen, depending on the operation mode. It has been applied in the determination of volatile halogenated hydrocarbons in potable and exhaust water (EPA 502.2 method); low picogram quantities of common chlorinated hydrocarbon pesticides and PCBs can also be easily detected using E1CD.

In the present work, GC coupled with PID and E1CD is demonstrated as particularly efficient in quantifying all trace impurities present in HFC and HCFC matrices. When using the PID it is especially suitable for the determination of halogenated olefins contained in halogenated saturated hydrocarbon matrices.

### Experimental

#### Reagents

Concentrated standard solutions of chlorofluoroethenes were kindly supplied in resistant stainless steel containers by a research centre that produces HFCs and HCFCs with the following concentrations in nitrogen:

- 1-chloro-2,2-difluoroethene and cis 1-chloro-1,2-difluoroethene 500 µL L\(^{-1}\)
- 1-chloro-1-fluoroethene, trans 1-chloro-1,2-difluoroethene and 1,1-dichloroethene 1000 µL L\(^{-1}\)
- cis-trans 1,2-dichloro-1,2-difluoroethene 2000 µL L\(^{-1}\).

These solutions were furtherly diluted with nitrogen and with pure 1,1,1,2-tetrafluoroethane to the concentration calibration range 1 to 150 µL L\(^{-1}\).

Samples of gas with different concentrations were prepared in a gas sampling bag previously flushed by applying alternatively vacuum and nitrogen. High purity nitrogen was used for eventual dilution. Sampling of the prepared gas sample was effected by syringe through a septum in the windbox. Two kinds of bag were used for gas sampling: 7 x 10 Teflon gas sampling bag with Teflon valve and Teflon lined silicone septum, from Alltech, 1 L Tedlar gas sampling bag with polypropylene valve and Teflon lined silicone septum, from Supelco.

The same procedure is used to prepare the standard mixtures in 1,1,1,2-tetrafluoroethane.

### Instruments

Analyses were carried out with a HP 5890 II gas chromatograph equipped with a split-splitless injector, a PID (4430 O.I. Corporation) and an E1CD (4420 O.I. Corporation) connected in series.

GC analyses were performed using wide bore capillaries

\[
30 \, \text{m} \times 0.53 \, \text{mm i.d.} \times 2 \, \mu \text{m GS-Q (J&W Scientific)} \quad \text{and normal capillaries} \quad 30 \, \text{m} \times 0.32 \, \text{mm i.d.} \times 1.5 \, \mu \text{m Poraplot Q (Chrompack)}.
\]

A 5 m postcolumn with HP1 phase was placed after both columns to prevent stationary phase particles reaching the detector and causing possible spikes.

Another GC, model HP5890 series II, connected to a mass spectrometer (GC-MS) HP5970 and equipped with a 0.32 mm i.d. capillary, has been used to identify compounds.

For GC injections, a 1 mL gas syringe was used (Dynatech type Pressure-lok A2).

### Results and Discussion

The influence of the make-up gas flow on the response factor (RF) of the PID was controlled by using three different rates of the make-up gas: 27 mL min\(^{-1}\), 10 mL min\(^{-1}\), 1 mL min\(^{-1}\). The calibration curve was obtained from six concentrations ranging from 1 to 150 µL L\(^{-1}\). It can be seen that the response factor increases from 30 to 50 times for all compounds on reducing the make-up gas flow. This behaviour should be a consequence of the fact that the PID has a proportional response to the concentration of the compound in the measurement cell, like all non-destructive detectors. The trend of PID and E1CD response factors as a function of the helium flow gas (carrier + make-up) for 1,1-dichloroethene is illustrated in Figure 1; the result is consistent with that reviewed above concerning the PID [5] and the E1CD [6].

For all GC analyses in this work, a make-up flow rate of 10 mL min\(^{-1}\) has been chosen which gives optimum compromise between PID and E1CD performance. The GC operating conditions are reported in Table I.

![Figure 1](image-url)

Trend of PID and E1CD response factors as function of He flow for 1,1-dichloroethene.