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Freons and Hydrocarbons in Aerosol Spray Cans

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Chlorofluorocarbons (CFCs) are non-flammable, non-explosive and non-toxic. They are thought to be inert chemically in general. CFCs have found wide spread use in industry as coolants used in refrigeration and air-conditioning which account for almost 40% of the total use in Canada. Its lesser use as blowing agents for foamed food plastics in packaging industry accounts for another 33% of the total. In the 1970s, use of CFCs by the aerosol spray industry accounted for nearly 50% of the total volume produced. Major products using CFCs as propellants are personal care products such as hair sprays, antiperspirants and deodorants (Glandon 1980).

In the early 1970s (Molina and Rowland 1974), it was postulated that CFCs can undergo photo-dissociation in the stratosphere and produce significant amount of free chlorine which can then react with ozone in this layer causing the depletion of ozone. The use of CFCs and the depletion of ozone layer has been since connected and this connection has been strengthened due to the observation of a substantial drop of ozone levels over Antarctica (EPA 1988).

Trichlorofluoromethane (Fll), dichlorofluoromethane (Fl2) and dichlorotetrafluoroethane (Fll4) are the three CFCs primarily used as propellants in aerosol cans. A program to monitor the compliance of manufacturers and importers for not using or importing aerosol spray cans containing CFCs has been in effect since the promulgation in March 1, 1980 of the legislation banning the making and importation of CFCs containing spray cans in Canada.

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In this study we purchased random samples in Montreal area of Canada to investigate the trend of reducing use of CFCs in aerosol cans and the trend of increasing use of CFCs substitutes such as propane, butane and isobutane in aerosol spray cans.

MATERIALS AND METHODS

A total of 45 aerosol spray cans; 34 domestic and 11 imported were purchased randomly from pharmacies, grocery stores, chain stores and beauty salons in Montreal. These aerosol cans were classified as shown in Table 1, as hair spray, deodorant, deodorant/antiperspirant and antiperspirant respectively.

Table 1. Type of aerosol spray cans

Product type	Domestic	Imported	Total
hair spray	17	0	17
deodorant	11	9	20
deodorant/antiperspirant	3	0	3
antiperspirant	3	2	5
Total	34	11	45

Freons; F11, F12, F13, F14, F114, F13B1, F22 and hydrocarbons; propane, butane and isobutane were purchased from Liquid Carbonic Ltd. All standard CFCs were 99% pure except for F114 which was 95.0% pure. Hydrocarbons were 99.0% pure.

Two samples of 30 ul from each aerosol can were taken at the same time with one for analysis over the column Carbopak B and the other for analysis over the column n-Octane on Porasil C with a gas chromatograph equipped with FID detector. In Table 2, the experimental conditions were given for these two set-ups.

Table 2. Gas chromatographic conditions

Model:	Hewlett-Packard 5711	Hewlett-Packard 5880A
Column:	Carbopak B 2m x 2mm i.d.	n-Octane on Porasil C 2m x 2mm i.d.
Carrier gas:	helium	helium
Gas flow:	20 ml/min	20 ml/min
Inlet temperature:	ambient	ambient
Detector temperature:	250°C	250°C
Column temperature:	from 70°C (hold for 4 min), 30°C/min to 200°C (hold for 5 min).	from 35°C (hold for 2 min), 32°C/min to 130°C (hold for 5 min).

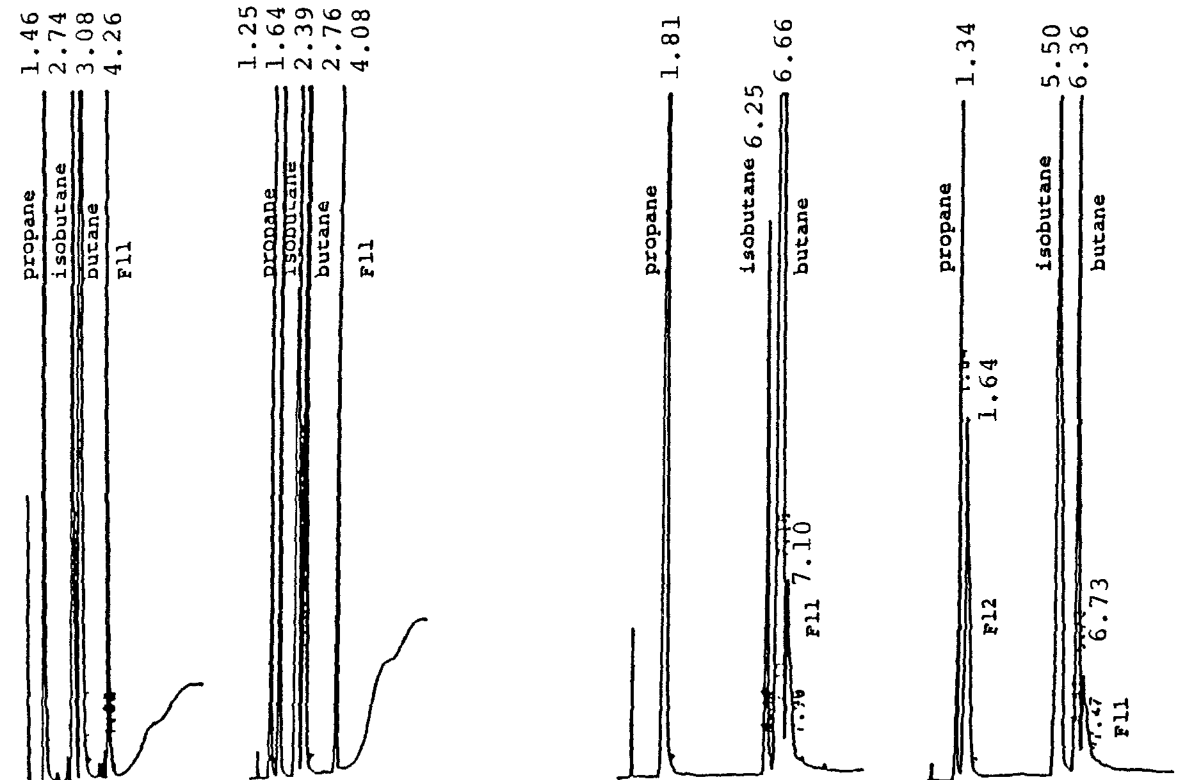

Figure 1: GC chromatograms of aerosol spray formulations.

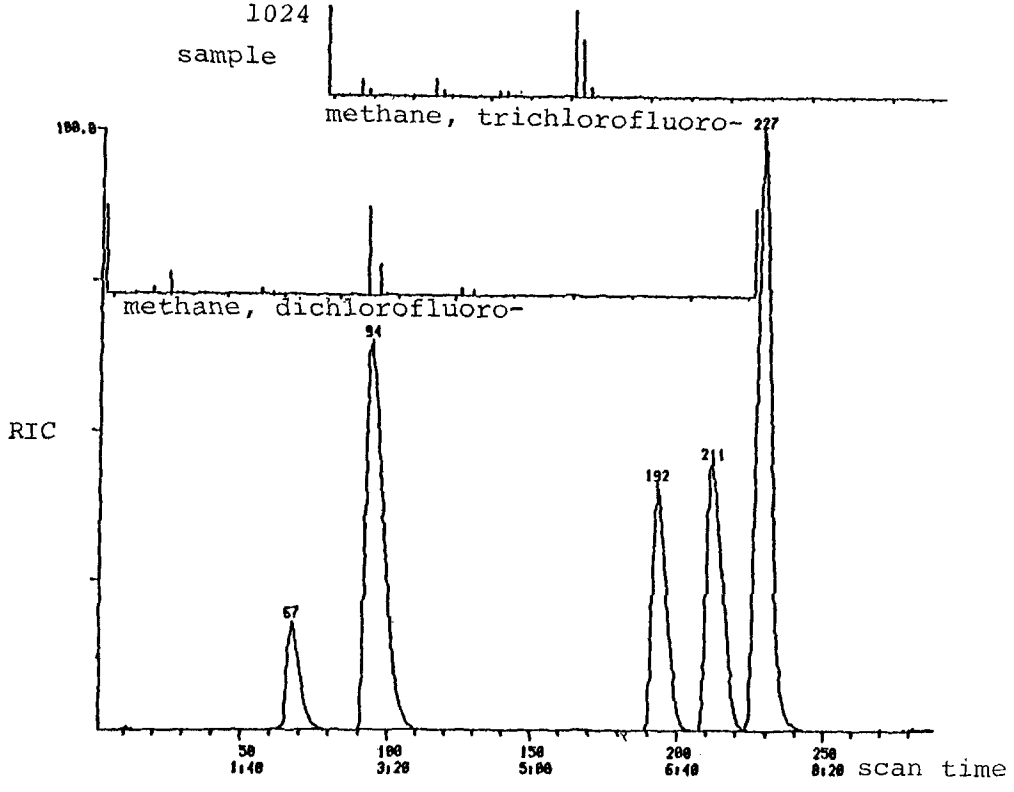

Figure 2: GC/MS confirmation of F11 and F12.

CFCs were further confirmed using a Finnigan 4500 GC/MS with a column Carbopak B, 5ft x 2mm i.d. and temperature was programmed from 70°C to 200°C at 20°C per minute. The INCOS computer was used for analysis. Further details of the analytical method have been described elsewhere (Matheson and Wrench 1982).

RESULTS AND DISCUSSION

Figure 1 shows chromatograms of analysis using the column n-Octane on Porasil C and the column Carbopak B. Freons in aerosol formulations were confirmed by GC/MS and are shown in Figure 2. GC chromatograms of these 45 aerosol formulations fall into three general groups. These formulations are either a straight blend of Freons and a straight blend of hydrocarbons or a mixed blend of Freons and hydrocarbons.

Among 45 aerosol cans, 10 were found containing either F12 alone or both F12 and F11. Their maximal levels of concentration are a few milli-grams per milli-liter. Except for 3 cans using a straight blend of F12 or the blend of F12 and F11, the other 7 cans were found to be using a blend of F11, F12, propane, butane and isobutane as aerosol propellants. These 10 aerosol cans were either deodorants or antiperspirants. Those 35 cans found not using CFCs in their formulations used either a blend of butane and isobutane or a blend of propane, butane and isobutane. Aerosol propellant concentrations in mg/ml are given in Table 3 for those 10 spray cans found using CFCs.

Table 3. Aerosol propellant concentrations in mg/ml

Product	F11	F12	Hydrocarbons
deodorant 1,	---	5.9	---
deodorant 2,	1.8	3.7	---
deodorant 3,	2.2	2.2	---
deodorant 4,	2.9	---	presence
deodorant 5,	2.0	2.4	presence
deodorant/antiperspirant 6,	0.3	---	presence
antiperspirant 7,	0.4	---	presence
antiperspirant 8,	0.5	0.2	presence
antiperspirant 9,	0.9	0.8	presence
antiperspirant 10,	1.1	0.7	presence

Among 34 domestic products analyzed, only 3 cans were found containing CFCs; one was deodorant/antiperspirant and the other two were antiperspirants. From this result it appears that CFCs are no longer being used in domestic hair spray and deodorant aerosol cans. Among 11 imported cans analyzed, 7 were found containing CFCs and 5 were deodorants and 2 were antiperspirants. It appears that CFCs are no longer being used in imported hair spray aerosol cans.

Out of 45 aerosol spray cans, 3 cans had straight F12 or both F12 and F11; 7 cans had a mixed blend of Freons and hydrocarbons; and 35 cans had substitutes of Freons such as propane, butane and isobutane. This study tends to indicate a drastic reduction of CFCs use and a significant increase of hydrocarbons use in the aerosol spray industry in Canada.

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