Determination of CFC and HCFC in Polyurethane Rigid Foams Using Neutron Activation Analysis

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ABSTRACT

Several works have developed methods to analyze the content of CFC/HCFC inside polyurethane rigid foams. In any case there is a lack and necessity of a quick, precise and reliable methodology for absolute and effective CFC/HCFC determination.

Actually gas chromatography has been the principal technique used for cell gas analysis in plastic foams. However, this method has some limitations. We cannot get all information at the same time about the real CFC/ HCFC content inside the foams, whether it's in the gas phase or dissolved in the polymer matrix. Moreover, the experimental setup and sampling have some limitations.

The proposal of this work is to present a new, simple, precise and highly sensitive analytical methodology for CFC/HCFC determination inside polyurethane rigid foams, using neutron activation analysis.

In this method, the sample and a standard are irradiated together in a nuclear research reactor using a thermal neutron flux around 10^{11} to 10^{12} neutrons $cm^{-2} \cdot s^{-1}$, and measuring the radioactivity of ^{20}F and ^{38}Cl produced.

The accuracy and precision of the method for the analysis of F and Cl were tested by analyzing certified reference materials.

The main advantages of this method are:

1. The organic compounds constituted by atoms of carbon, hydrogen, nitrogen, oxygen and sulfur do not produce radioactive isotopes. Since the polyurethane foams are basically an organic polymer, the chlorine and fluorine atoms from CFC/HCFC molecules are the only target which will be radioactive in the foam.
2. The radioisotopes produced are ^{38}Cl ($t_{1/2}$ = 37.2 min) and ^{20}F ($t_{1/2}$ = 11.4 sec). Hence the time for analyzing CFC/HCFC in the foam is very short due to the short half-life time of both radioisotopes.
3. This technique is very precise and accurate.

Using this method it has been possible to quantify the content of CFC/HCFC in all parts of the foam as the quantity dissolved in the polymeric matrix, the quantity in the gas phase and the quantity lost during the foam preparation.

INTRODUCTION

In the decade of twenty, when CFCs were first synthesized, these compounds were considered as having ideal properties, being odorless, colourless, flameless, non-reactive and of low cost. They have since then had multiple industrial applications, being used in air conditioners, refrigerators, aerosols and in the fabrication of plastic foams. As a result, thousands of tons of CFCs began to be thrown in the atmosphere, without any kind of control.

Only in 1974, the first scientific paper was published [1] about the risks of damage that could be caused to the ozone layer by CFCs. In 1985, the effective destruction of the ozone layer, which became known as the "ozone hole," was measured over the South Pole during the Antarctic spring.

After many experimental evidences appeared, the problem became a worldwide concern due to the severe damage that can be caused to the environment by this phenomenon. In 1987, the countries belonging to the European Community and 26 others countries met in Canada and signed the Montreal Protocol [2], in which they agreed to reduce drastically the production and use of certain kinds of CFCs that can cause damage to the ozone layer. The Protocol is valid from the 1st of January of 1989.

Through many observations made by satellites, it became evident that the situation of the ozone depletion and global warming problems is much more critical than first imagined, and according to many scientists, its tendency is to become worse in the coming years. Another problem arises from the fact that these CFC compounds have average lives in the atmosphere of tens of years, which means that, even if the production of CFCs was immediately interrupted, their deleterious potential would be maintained for many years.

In recent years the situation has become so critical that several countries, mainly from the European Community, are planning to advance the proposed dates of the Montreal Protocol. Sweden and Norway, for instance, have not allowed the use of CFC-11 since the beginning of 1991.

Of all the CFCs produced regularly, CFC-11 is one of the most aggressive to the ozone layer and as a consequence is one of the first compounds of this kind whose production will be interrupted. Specifically in the case of the polyurethane foams used for insulation, where CFC-11 is the most important component, the simple substitution or lowering of the concentration is not so easy as in other areas of application of the CFCs.

Although the substituting products must contain hydrogens atoms in their molecular structure in order to reduce the GWP (Global Warming Potential) and they must not contain chlorine atoms due to the Ozone Depletion Potential (ODP), actually the alternatives for substitution of the CFCs are basically the compounds HCFC-123 and HCFC-141b.

In the cases where the foams are to be employed as thermal insulations in refrigerators or freezers, the reduction in CFC-11 or the use of substituting products causes a decrease in the insulation power of these materials and consequently provokes an increase in the energy consumption so as to maintain the same original insulation rate.

The evident importance of CFC-11 in the foam insulation coupled to its destructive potential for the ozone layer has made the industry and research institutes more concerned about the problem, which has led to more detailed studies of the structure of this compound and to a search for substituting compounds, such as HCFC-123 and HCFC-141b.

Also the need for determination of the concentration of CFC-11 as well as of the substituting compounds inside the foam has motivated the development of some instrumental analytical techniques specifically for this purpose. This development is growing increasingly important due to the fact that the use of the CFCs is under regulation and there are definite dates for the reduction of their use. From December 31, 1989, users are being charged for the use of these compounds, with real increases each year.

Many studies are being made in the field of insulation, because the reduction or substitution of the CFCs in the foams would bring not only losses in the insulation power, but also a deterioration in the physical properties of the foam. Due to these facts, the development of a methodology that is fast, accurate and precise for the determination of CFC-11 as well as for possible substituting compounds is of the greatest importance.

In the literature some methods are described for the analysis of CFCs inside the cellular foams [3–5]. Generally this determination is made by gas chromatography [3], which is limited by the step of gas sampling and by the need to guarantee that all the gaseous CFC contained in the foam is really being analyzed. For the determination of the CFC dissolved in the solid phase, other complementary techniques are being employed.

The proposal of the present work is to apply the method of neutron activation analysis for the determination of CFC, HCFC or HFC, based on the analysis of chlorine and fluorine inside the foams.

PRINCIPLE OF THE METHOD

Neutron activation analysis is a nuclear method, based on the occurrence of nuclear reactions, on submitting a sample to a neutron flux, generally in a nuclear research reactor. In the case of fluorine and chlorine, the nuclear reactions involved are:

$$^{37}Cl + {}^{1}n \longrightarrow {}^{38}Cl + \gamma$$

$$^{19}F + {}^{1}n \longrightarrow {}^{20}F + \gamma$$

The isotopes formed are radioactive, emitting gamma radiation, and can be measured in a gamma-ray spectrometer, constituted mainly of a solid state Ge(Li) or Ge detector and associated electronics.

The radioisotopes produced can be identified by their half-life and by the energy of the gamma rays emmited. In the case of ^{38}Cl, the half-life is 37.3 minutes and the main gamma-ray energy is 1642.4 keV. For ^{20}F, these parameters are 11.41 seconds and 1633.1 keV, respectively. Data reduction of the gamma-ray spectra obtained can be performed by means of one of the many softwares that have been developed for gamma-ray spectroscopy.

Neutron activation analysis is a very sensitive and multielemental technique and can be applied to the determination of most of the elements of the periodic table in many different kinds of matrixes, such as geological samples (ores, rocks, soils, coal), environmental samples (aerosols, water), biological samples (hair, tissues, medicinal plants, snake venoms, blood, etc.) and many others.

The polyurethane rigid foams, or organic polymers in general, show a great advantage with this technique. The organic compounds, formed by carbon, hydrogen, nitrogen, oxygen and sulphur, generates stable radioisotopes when irradiated with a neutron flux. Hence, these radioisotopes do not generate competitor radiations and, then, do not interfere in the analysis of the other radioisotopes.

In the polyurethane foams the additives added in the resin (catalyst, polyols and surfactants) and isocyanate are all based on organic compounds. Then, the chlorine and fluorine atoms from the CFC, HCFC and HFC molecules are, basically, the only targets of the neutron flux so the spectrum of their radioisotopes will be practically without interference.

The quantity of CFC, HCFC and HFC in the foam can be evaluated by the chlorine and fluorine radioisotope independent of the CFC present and as chlorine and fluorine atoms are from the same molecule, the quantity of CFC, HCFC and HFC can be evaluated analysing either chlorine or fluorine, or both simultaneously.

EXPERIMENTAL

Two basic formulations, formulation A and formulation B, were prepared for polyurethane rigid foams using as blowing agent the CFC-11 and HCFC-141b, respectively. Five samples of the foams were obtained for each formulation and the only variable was the blowing agent concentration (Table 1). The foam without the blowing agent was used as a blank.

The blank used in this procedure was used to avoid any kind of interference deriving from the foam and to guarantee that the analysis is exclusively of CFC-11 and HCFC-141b. However, later on a simplified method will be proposed where we can obtain the same results without the blank.

Figure 1 presents schematically the main steps involved in the analysis procedure either for CFC-11 formulation or HCFC-141b formulation. The analysis AN 4 and AN 8 are done with the intention of evaluating the quantity of CFCs dissolved in the solid phase of the foams. The foam powders

Table 1. Densities and quantity of CFC-11 and HCFC-141b for each foam.

	Foams	CFC-11 (pbw)	% of CFC-11 in the Resin	Density of the Foam (kg/m^3)
Formulation A	A0	0	0	47.4
	A1	9	3.0	41.0
	A2	18	5.9	34.9
	A3	34	10.8	30.0
	A4	50	14.8	33.3
		HCFC-141b (pbw)	% of HCFC-141b in the Resin	Density of the Foam (kg/m^3)
Formulation B	B0	0	0	68.7
	B1	7	2.9	41.3
	B2	15	6.1	34.0
	B3	28	10.8	31.7
	B4	40	14.8	28.6

were obtained by carefully grinding samples of the foams, to guarantee that all the cells in the foams are broken. The analysis AN 5 and AN 8 refer to the powder of the foam after 1 hour at 180°C, respectively.

Preparation of the Samples and Irradiation

The samples of the foams were cut from the centres of approximately 25 × 25 × 3.5 cm boardstock insulation prepared at the laboratory, using a band saw. Each sample was carefully encapsulated in polyethylene envelopes and placed, together with fluorine and chlorine standards prepared at the laboratory, in a special container for irradiation with neutrons (Figure 2). During the sample manipulation the use of gloves and tweezers are recommended to avoid contact with the hands because of contamination.

The fluorine standards were accurately weighed masses of LiF encapsulated in polyethylene envelopes. The chlorine standards were prepared by pipetting aliquots of NaCl solution on sheets of Whatman No. 40 filter paper of about 1 cm^2 area. These sheets were also encapsulated in polyethylene envelopes.

The irradiations were carried out for a period of 15 seconds at a pneumatic station (Figure 3) where the thermal

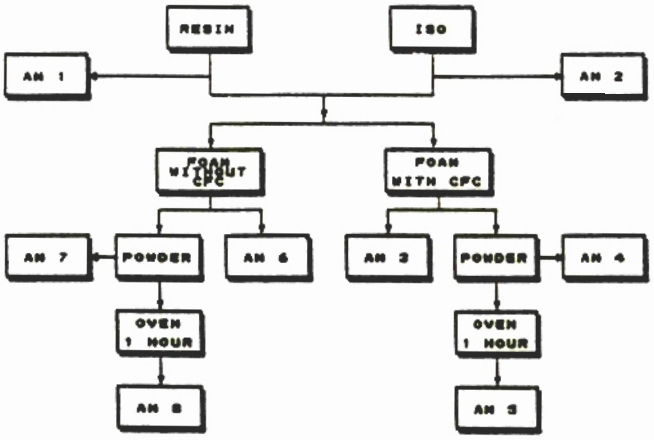

Figure 1. Scheme of the main steps involved for analysis of CFC-11 and HCFC-141b in the foams.

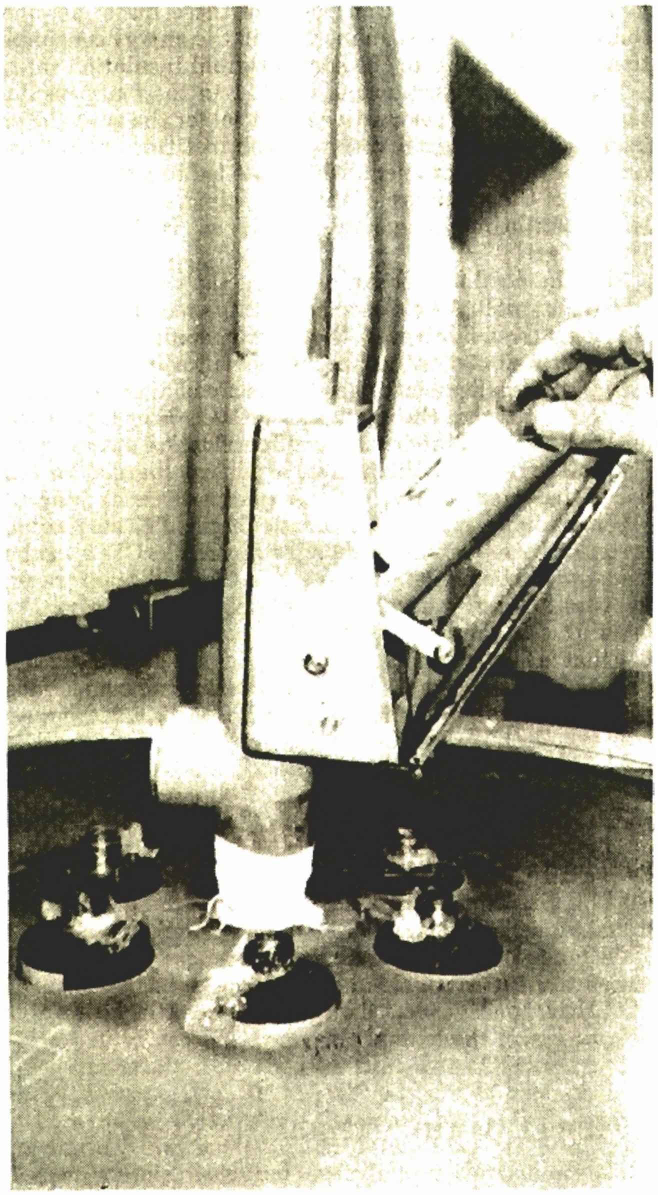

Figure 2. Container used for irradiation.

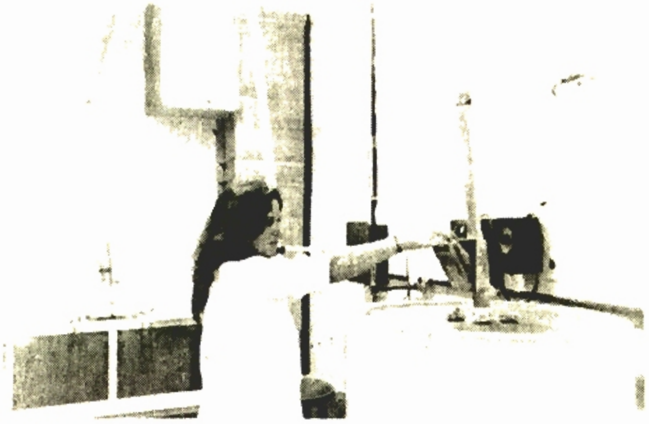

Figure 3. Pneumatic system used for irradiation.

neutron flux is about 4 × 10^{11} $n \cdot cm^{-2} \cdot s^{-1}$. Measurements were started after a decay time of about 30 seconds.

Measurements

Measurements were carried out using a gamma ray spectrometer constituted of a GMX 20195 ORTEC Ge detector, with a resolution of 1.9 keV in the 1332 peak keV of ^{60}Co. The detector is coupled to an ADCAM 918A Multichannel Buffer and associated electronics (Figure 4).

A first series of measurements was started after about 30 seconds following the end of the irradiation, for the determination of fluorine, by means of the radioisotope ^{20}F ($t_{1/2}$ = 11.41 s). The measurement time was 30 seconds. In a second series of measurements, started about 5 minutes after the end of irradiation, the determination of chlorine was carried out, by means of ^{38}Cl ($t_{1/2}$ = 37.3 minutes). The measurement time was in this case of 20 seconds.

Calculation

Spectrum analysis was performed by means of the VISPECT2 software, developed by D. Piccot, from Saclay, France.

This software performs mathematical fitting of the data obtained, locates the gamma-ray peaks in the spectrum and calculates peaks' areas, together with their standard deviations and resolution.

In the case of the present work, the comparative mode of neutron activation analysis was employed, which means that the areas obtained for the peaks, for instance of ^{38}Cl and ^{20}F, have to be compared to the respective areas corresponding to standards containing known amounts of these elements. These standards, or comparators, are prepared at the laboratory and irradiated at the nuclear reactor simultaneously with the samples.

The following expression allows the calculation of the elemental concentration desired:

$$C_s = A_s C_c M_c e^{\lambda(t_s - t_c)} / A_c M_s \qquad (1)$$

where *s* and *c* refer to sample and comparator, respectively and:

C = concentration of the element
A = peak area (counting rate obtained at time t)
t = cooling (decay) time
M = mass of sample or comparator
λ = decay constant ($\lambda = 0.693/t_{1/2}$; $t_{1/2}$ = half-life)

The concentrations of fluorine and chlorine are calculated according to expression (1), using the software PAKI, specially developed at the Radiochemistry Division of IPEN for determination based on short-lived isotopes.

RESULTS AND DISCUSSION

Following the scheme shown in Figure 1, Table 2 shows the results obtained for the resin without CFC-11 and HCFC-141b (AN 1), the isocyanate (AN 2) and the samples of the foams (AN 3). Table 2 shows that the isocyanate has a significant quantity of chlorine (0.3%) deriving basically from the phosgene $COCl_2$) used during its synthetic route. In the resin the quantity of chlorine and fluorine were practically negligible. The 0.3% of chlorine derived from the isocyanate can cause differences on the final calculations in the determination of CFC-11 and HCFC-141b. Hence, the mass of isocyanate used during the foams and blank preparation cannot be very different.

The other factor refers to the amount of CFC-11 and

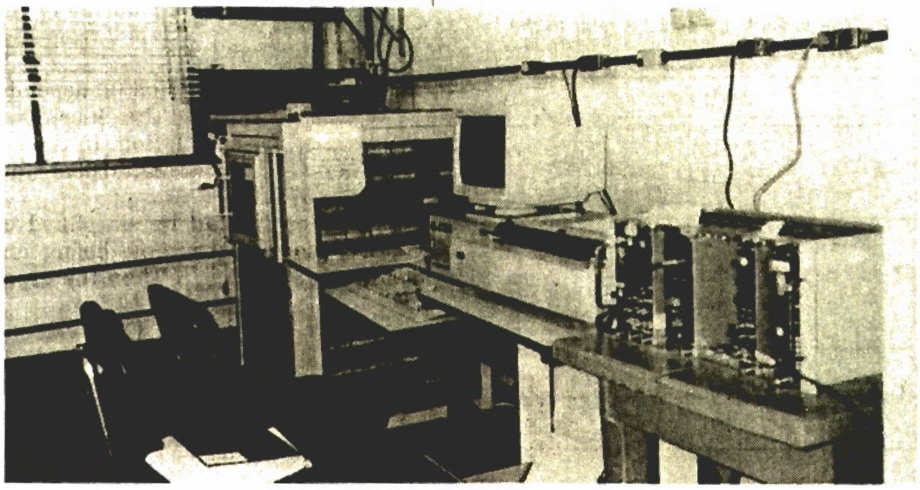

Figure 4. Gamma-ray spectrometer used for radioactivity measurements.

Table 2. Results from the analysis of the foams, resins and isocyanate.

Foams	%Cl	%F
A0	0.254	—
A1	1.73	0.278
A2	3.09	0.518
A3	5.88	0.990
A4	7.52	1.29
B0	0.090	—
B1	1.42	0.311
B2	2.74	0.691
B3	4.61	1.35
B4	7.04	1.84
Formulation A without CFC-11	—	—
Formulation B without HCFC-141b	—	—
Isocyanate[1]	0.3	—

[1] MDI Desmodur 44V20 BRA.

Table 3. Results from the analysis of the powders of the foams prepared with CFC-11. The indices 4,5 and 7,8 refer to the respective analysis in Figure 1.

	Samples	%Cl	%F
A0	A0$_7$	0.247	—
	A0$_8$	0.173	—
A1	A1$_4$	0.251	—
	A1$_5$	0.0684	—
A2	A2$_4$	0.249	—
	A2$_5$	0.100	—
A3	A3$_4$	0.759	0.0865
	A3$_5$	0.140	—
A4	A4$_4$	0.540	—
	A4$_5$	0.118	—

Table 4. Results from the analysis of the powders of the foams prepared with HCFC-141b. The indices 4,5 and 7,8 refer to the respective analysis in Figure 1.

	Samples	%Cl	%F
B0	B0$_7$	0.118	—
	B0$_8$	0.051	—
B1	B1$_4$	0.257	—
	B1$_5$	0.102	—
B2	B2$_4$	0.280	—
	B2$_5$	—	—
B3	B3$_4$	0.797	0.285
	B3$_5$	—	—
B4	B4$_4$	1.35	0.259
	B4$_5$	0.101	—

HCFC-141b dissolved in the polymeric matrix of the foam. Tables 3 and 4 show the results obtained from the foam powders for CFC-11 and HCFC-141b, respectively. In the table, the indices 4, 5 and 7, 8 refer to the respective analysis in Figure 1. It should be pointed out that the first powder (AN 4), even after the correction of the blank still has a significant quantity of chlorine but, after 1 hour in an oven at 180°C, the quantity of chlorine (AN 5) reduced drastically. The chlorine might be derived from the CFC-11 and HCFC-141b dissolved in the solid phase of the foam.

In Tables 3 and 4 the quantity of fluorine in some powders was below the detection limit of the analytical method due to the low concentration. Moreover, the radioisotope ^{20}F has a very short half-life (11.4 seconds) which makes the analysis very much dependent on the decay time for the measurement. But, even considering one fluorine atom to one blowing agent molecule, the usual CFCs, HCFCs and HFCs concentration in the polyurethane rigid foams are more than enough to be detected by this method. In the case of chlorine, the half-life of its radioisotope ^{38}Cl (37.3 minutes) allow a longer time of analysis. So, the quantity of CFC, HCFC and HFC in the polyurethane rigid foams can be evaluated analysing either the chlorine atom or fluorine atom because both atoms belong to the same molecule.

Calculation of CFC-11 and HCFC-141d in the Solid Phase of the Foam

The amount of CFC-11 and HCFC-141b dissolved in the solid phase of the foam was calculated by the following expression:

$$\%_{sd} = \frac{M_{\text{powder}}(\%_{ps} - \%_{pb})}{M_{\text{foam}}} \times P \qquad (2)$$

where

$\%_{sd}$ = percentage of CFC-11 or HCFC-141b in solid phase of the foam
M_{powder} = mass of the sample powder irradiated (g)
M_{foam} = mass of the foam before grinding (g)
$\%_{ps}$ = percentage of chlorine or fluorine in the powder of the sample (AN 4 from Figure 1)
$\%_{pb}$ = percentage of chlorine or fluorine in the powder of the blank (AN 7 from Figure 1)

The P value in expression (2) depends on the agent, CFC-11 or HCFC-141b, and the chlorine or fluorine atom that will be used for calculation. In the case of chlorine, the P value for CFC-11 is 137.5/106.5 and for fluorine the P value is 137.5/19.

Expression (2) can be simplified considering that the mass of foam is the same before and after grinding; it means $M_{\text{foam}} = M_{\text{powder}}$. Then the expression (2) is reduced to:

$$\%_{sd} = (\%_{ps} - \%_{pb}) \times P \qquad (3)$$

Calculation of Gaseous Amounts of CFC-11 and HCFC-141b in the Foam

The gaseous mass of CFC-11 and HCFC-141b in the closed cells of the foams can be calculated by the expression as follows:

$$M_{gas} = \frac{M_{foam} \times [\%_{s} - (\%_{b} + \%_{sp})]}{100} \times P \qquad (4)$$

where

M_{foam} = mass of the foam irradiated (g)
$\%_{s}$ = percentage of chlorine or fluorine in the sample of the foam (AN 3 from Figure 1).
$\%_{b}$ = percentage of chlorine or fluorine in the blank of the foam (AN 7 from Figure 1)
$\%_{sp}$ = percentage of chlorine or fluorine in the solid phase of the foam [$\%_{ps} - \%_{pb}$ from expression (3)]
P = depends on the blowing agent used [see expression (2)]

The results for the quantity of CFC-11 and HCFC-141b in the gaseous phase was expressed as gaseous percentage and gaseous concentration. The concentration unit adopted was: mass of CFC-11 or HCFC-141b/liter of cured foam. The volume was calculated from the sample weight and the density of the foam irradiated. For the gaseous percentage the following expression was used:

$$\%_{gas} = \frac{M_{gas}}{M_{foam}} \times 100 \qquad (5)$$

Substituting expression (4) into (5) leads to the simplified expression:

$$\%_{gas} = [\%_{s} - (\%_{b} - \%_{sp})] \times P \qquad (6)$$

The mass of CFC-11 or HCFC-141b in the gaseous phase by liter of the cured foam was calculated by the following expression:

$$C_{gas} = \frac{M_{gas}}{(M_{foam}/D_{foam})} \qquad (7)$$

where

C_{gas} = gaseous concentration of the blowing agent (g/liter of cured foam
D_{foam} = density of the foam irradiated (g/L)

Substituting expression (4) into (7) leads to the following expression:

$$C_{gas} = \frac{[\%_{s} - (\%_{b} - \%_{sp})] \times P}{100} \times D_{foam} \qquad (8)$$

or

$$C_{gas} = \frac{\%_{gas}}{100} \times D_{foam} \qquad (9)$$

Results

The results are shown in Table 5. The amount of CFC-11 and HCFC-11 dissolved in the solid phase was calculated using expression (3) and the gaseous percentage and gaseous concentration in the foam were obtained using expressions (6) and (9), respectively. The percentage of gas dissolved in the solid phase was calculated using only the chlorine experimental data due to the low concentration of the gases in these samples. Notice that the results for gas percentages calculated from the fluorine experimental data have good agreement with the results from chlorine. The results in Table 5 show that HCFC-141b is more absorbed in the polymeric matrix than CFC-11 and the gaseous loss during the reaction is lower.

The gaseous loss of CFC-11 and HCFC-141b was calculated by subtracting the quantity of CFC-11 and HCFC-141b added in the resin (Table 1) from the quantity of the gas in the cells and dissolved in solid phase (Table 5).

The values of the gas concentration of CFC-11 and HCFC-141b in the foam was compared with the theoretical values calculated from the experimental data as total gaseous loss, quantity of CFC-11 and HCFC-141b added and ratio and density of the foams.

Comparing the density values of the foams in Table 1 with the gaseous concentration of CFC-11 and HCFC-141b in Tables 6 and 7, the foams with higher densities have concentrations higher than the theoretical values and foams with lower densities have concentrations lower than the theoretical values. This probably happened because of the differences in the permeability of the blowing agents through the foams, as higher the density the lower is the permeation. In the theoretical values, calculations for CFC-11 and HCFC-141b did not consider the diffusion coefficient of these gases through the foam.

Table 5. Percentage of CFC-11 and HCFC-141b in the foams.

	Gaseous Phase (%)		Dissolved in the Solid Phase (%)	Gaseous Loss (%)
	from Cl	from F	from Cl	
CFC-11				
A1	1.9	2.0	0.010	1.0
A2	3.6	3.7	0.026	2.2
A3	6.6	6.7	0.66	3.5
A4	9.0	9.3	0.38	5.3
HCFC-141b				
B1	1.9	2.0	0.23	0.72
B2	4.1	4.3	0.27	1.6
B3	6.3	6.5	1.1	3.3
B4	9.4	9.7	2.0	3.5

Table 6. Gaseous concentrations of the CFC-11 in the foams.

Foams	Concentration (g of CFC-11/L of cured foam)		
	from Cl	from F	Theoretical
A1	0.78	0.82	0.54
A2	1.26	1.29	1.09
A3	1.98	2.01	1.93
A4	3.00	3.1	3.07

Table 7. Gaseous concentrations of the HCFC-141b in the foams.

Foams	Concentration (g of HCFC-141b/L of cured foam)		
	from Cl	from F	Theoretical
B1	0.78	0.83	0.54
B2	1.40	1.44	1.22
B3	2.00	2.06	2.26
B4	2.69	2.77	2.92

Table 8. Gaseous concentrations of the CFC-11 calculated by the simplified method.

Foams	Concentration (g of CFC-11/L of cured foam)	
	from Cl	from F
A1	0.78	0.82
A2	1.28	1.31
A3	1.98	1.96
A4	3.00	3.11

Table 9. Gaseous concentrations of the HCFC-141b calculated by the simplified method.

Foams	Concentration (g of HCFC-141b/L of cured foam)	
	from Cl	from F
B1	0.79	0.79
B2	1.38	1.45
B3	2.00	2.08
B4	2.68	2.78

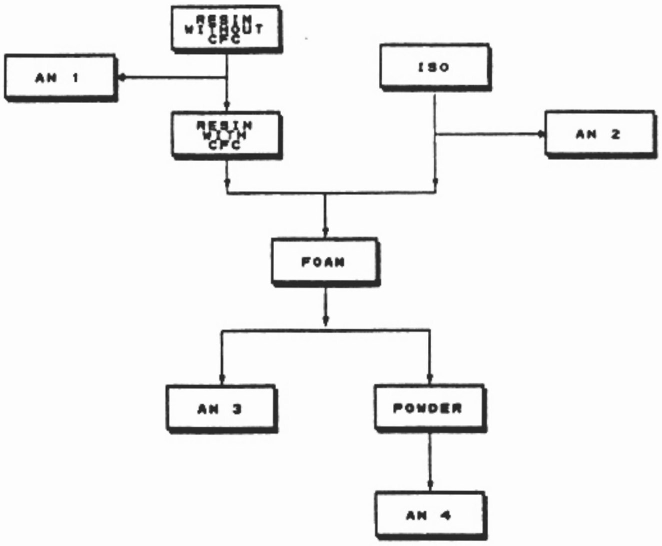

Figure 5. Scheme of the simplified method.

Simplified Method

The previous method was carried out following the general standard procedure for analysis where a blank is used to remove all kind of interference and simplifies the analysis of the desired compound. However, due the high sensitivity of the neutron activation analysis method and the advantage of few interferences, the method proposed in Figure 1 can be simplified by eliminating the blank use. Figure 5 shows the simplified method proposed.

From the scheme shown, the following data can be obtained: the gaseous quantity of CFC in the cells of the foam, AN 3–AN 4, and the quantity of CFC dissolved in the solid phase of the foam, AN 4–(An 1–AN 2). The results obtained are shown in Tables 8 and 9. The values found by this simplified method have a good agreement with the values obtained from the first method (Tables 6 and 7). The experimental data used for calculation were obtained from Tables 2 and 3.

The gaseous concentration of CFC-11 and HCFC-141b in the foam was calculated using the following simplified expression:

$$C_{gas} = \frac{D_{foam} \times (\%_s - \%_{ps})}{100} \times P \qquad (10)$$

where

C_{gas} = gaseous concentration of the blowing agent (g/liter of cured foam)
D_{foam} = density of the foam irradiated (g/L)
$\%_s$ = percentage of chlorine or fluorine in the sample of the foam (AN 3 from Figure 5)
$\%_{ps}$ = percentage of chlorine or fluorine in the powder of the foam (AN 4 from Figure 5)
P = depends on the blowing agent used [see expression (2)].

The percentage of CFC-11 and HCFC-141b dissolved in the solid phase was calculated by the simplified expression.

$$\%_{sd} = [\%_{ps} - (\%r + \%_i)] \times P \qquad (11)$$

where

$\%_{sd}$ = percentage of chlorine or fluorine dissolved in solid phase of the foam
$\%_{ps}$ = percentage of chlorine or fluorine in the powder of the foam (AN 4 from Figure 5)
$\%_{r}$ = percentage of chlorine or fluorine in the resin (AN 1 from Figure 5)
$\%_{i}$ = percentage of chlorine or fluorine in the isocyanate (AN 2 from Figure 5)
P = depends on the blowing agent used [see expression (2)]

The main advantage of this method for determination of CFCs in the gas phase is the necessity of using only a sample of the foam and two irradiations in the neutron activation analysis procedure: the foam and the powder of the foam. The determination of the gas dissolved in the solid phase can be simplified if the gas dissolved would be completely removed, i.e., by controlled thermal treatment not affecting the polymeric matrix. Hence, this method will be very helpful when the analysis AN 1 and AN 2 are not accessible. These studies have been done using the TGA instrument.

CONCLUSIONS

The neutron activation analysis technique has been showing to be an excellent method for determination of CFCs/HCFCs and HFCs in the polyurethane rigid foams either in the gaseous phase or dissolved in the solid phase of the foam. As the polyurethane and its additives are organic compounds, the chlorine and fluorine atoms from the blowing agents are, basically, the only targets of the neutron flux. Therefore, the analysis is very clear without interferences and safety due the short half-life of the radioisotopes.

In the proposed method the time of analysis is very quick, the method is not destructive, so the gas sampling is not a problem, and the procedure of analysis and calculation is very simple. In addition, the results have shown that the concentration of CFC-11 and HCFC-141b can be evaluated analysing either chlorine or fluorine, or both simultaneously.

Using the simplified method, the analysis of CFC, HCFC and HFC in the foam becomes very simple and practical. This method is very helpful for analysis of unknown samples. In the evaluation of the quantity of the gas dissolved in the solid phase, the chlorine from isocyanate should be considered.

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