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NEUTRALIZING HALOGENATED HYDROCARBONS (CFC and HALONS)

by

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1. BACKGROUND

Chlorofluorocarbons (CFC and Halons) belong to the family of chemical compounds known as halogenated hydrocarbons or halocarbons. They are hydrocarbons in which some or all of the hydrogen atoms have been replaced by atoms of halogens such as fluorine, chlorine, bromine and Iodine. CFC's are those in which all hydrogen atoms have been replaced i.e.CFC-12 ($CF_2 Cl_2$). Partially halogenated CFC's are compounds that have hydrogen atoms as well as halogens, such as HCFC-22 (CHF_2Cl). Halons (employed especially as extinguishing agents) are compounds that comprise fluorine, chlorine, as well as bromine, such as Halon 1211 (CF_2ClBr) and Halon 1301 (CF_3Br).

The usefulness of these chemicals lies in their relative inertness and their volatility. These chemical substances (liquids and gases) have been found in the last 40 years to have a vast range of industrial applications in areas such as:

- Air conditioning and refrigeration
- Cleaning and degreasing processes
- Organic extracting solvents
- Fire retardant additives
- Fire extinguishing agents
- Aerosol propellants and foam blowing agents
- Various intermediate and precursors in organic syntheses.

Since the worrying discovery of the "HOLE" in the Ozone layer in the atmosphere over the antractic pole in 1986, the world wide community of environmental scientists has accumulated much data on the ozone depleating substances found in that region.

Various materials possess the capability to reach the stratosphere, react with the ozone and dissociate it to oxygen molecules and atoms. These materials have been classified according to their ability to destroy the ozone in the atmosphere. A mathematical parameter called the ozone depletion potential (ODP) was devised to measure and compare the ozone destruction capability of materials. The higher the ODP the more potentially dangerous the substance. Among the materials with high ODP are the halocarbons, especially the CFC(chlorofluorocarbons) and the halons, due to their high content of active halogen atoms that act on the ozone molecule and cause its dissociation. These materials, being stable for many years (their life-time is well over 20 years), pose a continuous threat to the ozone layer since their release into the atmosphere is inevitable. Even close circuit systems (such as air conditioning and refrigeration systems) and certainly open systems, release into the atmosphere these materials, when tested, calibrated, repaired or regularly maintained, or during malfunction.

However, these halocarbon materials are of outmost importance in military and civilian applications and for industrial and domestic purposes. So far no alternative substances have been approved and the development process is complicated because of the unique chemical and physical characteristics of these substances.

CFC's and halons are released at the earth's surface and then transported to the upper atmosphere (stratosphere), where they can remain for long periods of time due to their inertness. However, in this region, the halocarbons react with the ozone in a series of chemical reactions, causing the ozone's decomposition.

Ozone (O_3) is a trace gas in the earth's atmosphere. It predominates in the stratosphere where it shields the earth's surface from damaging U.V radiation from the sun. Ozone itself undergoes photodissociation when exposed to UV radiation in some of the following processes:

O_3 + UV radiation ------------- O_2 + O
O_3 + O ------------------------ O_2 + O_2
O + O + E --------------------- O_2 + E (E - excess energy)

The amount of ozone in the stratosphere is determined by the balance between the physical and the chemical processes responsible for both its production and destruction.

Compounds like CFC's are likely to undergo photodissociation in the stratosphere, hence generating halogen atoms that then react with the ozone to cause it's destruction in reactions like:

$CFCl_3$ + UV radiation ------------- $CFCl_2$ +Cl
Cl + O_3 -------------------------- ClO + O_2
ClO + O -------------------------- Cl + O_2 (The Cl can attack another O)

The process is similar for halon, but this time bromine is also produced, which is far more effective at destroying the ozone.

The following table demonstrates the damage that can occur to the ozone layer if these materials were released directly to the atmosphere.

COMPOUND	IFETIME EARS)	ZONE DEPLETION OTENTIAL (ODP)	OBAL WARMING TENTIAL (GWP)	PRIMARY USES
HCFC-22	15	0.5	0.34	ir conditioning, efrigeration, foam packaging.
HCFC-123	2	0.02	0.02	efrigeration, insulating Foams solvents.
HCFC-124	7	0.02	0.1	ir conditioning, insulating Foams.
HCFC-141b	8	0.1	0.09	Insulating foams, solvents.
HCFC-142b	19	0.06	0.36	Insulating foams, solvents.
WC-125	28	0	0.58	Refrigeration
HFC-134a	16	0	0.26	Refrigeration, air conditioning.
HFC-152a	2	0	0.03	Insulating foams, aerosols
m-11	60	1	1	Insulating foams, refrigeration, air conditioning.
m-12	120	1	3	Refrigeration, air conditioning, insulating foams.
CFC-113	90	0.8	1.4	Solvents.
CFC-114	200	0.7	3.9	Foam packaging, aerosols
CFC-115	400	0.4	7.5	Refrigeration
HALON 121	25	3.0		Fire extinguishing
HALON 130	110	10.0 - 15.0		Fire extinguishing
HALON 240 586	NOT teporte	6.0		Fire extinguishing

The manufacturers as well as the users of the halocarbons are fully aware of the serious damage that could be caused by the release of these materials to the atmosphere, and are taking all reasonable steps to reduce unnecessary emissions and seek environmentally safe alternatives. Legislation and international agreements will enforce penalties on unnecessary releases, and since alternative materials are not yet available it seems essential to find a method to destroy these materials once they are likely to be released into the atmosphere. (whether the release is on purpose or accidental).

Various methods (chemical and physical) could be applied for the halocarbon's destruction such as: heat decomposition [incineration), photolysis, absorbance, chemical decomposition with catalysts, metals scrubbing, pyrolysis, wet air oxidation and supercritical water oxidation, corona discharge (energized electrons).

To summarize the status of the CFC's destruction, the only demonstrated technology which is currently being used is incineration. However, all these methods, are not specifically destroying the active site of the material, i.e. the halogen atom, and allow many potential hazardous by-products to be released into the atmosphere. These by-products may still contain damaging amounts of halogenated hydrocarbons with high ODP and long life-time.

The present project introduces a new concept of selective dissociation of the halocarbons, i.e, the cleavage of the halogen atom from the halocarbon molecule, by applying concentrated energy (laser or other irradiating means) to the material. The products of such a reaction can be controlled (by the amount of energy applied to the material) and absorbed or reacted according to preselected processes.

This concept is the basis of the apparatus described herein, that can be designed either for portable or fixed location uses, working manually or automatically, in areas where halocarbons are likely to be employed andlor released.

2. TECHNICAL DESCRIPTION

The proposed method combines photolysis of the CFC compounds with neutralization of the products to convert them to harmless materials.

The photolysis process has been selected according to the absorption spectra of the CFC materials, which has. a maximum in the W spectral band.

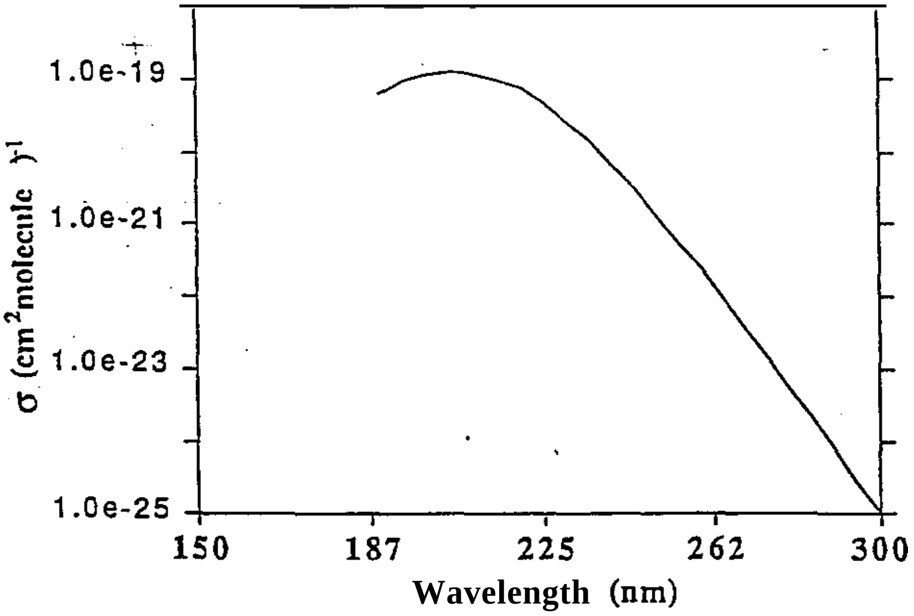

Fig. 1 Absorption Spectrum of CF_3Br
(Molina et. al. J. Phys. Chem. 86,2672(1982))

Excitation of the CFC molecule by W radiation at the specific spectral band of the absorption causes cleavage of the c-x chemical bond (1). For the HALON 1301, with the chemical formula CF_3Br, the maximum absorption wavelength is 205 nm, with an absorption cross section of
$6 = 1.29 \times 10^{-19}$ cm^2 $molecule^{-1}$ . .

The chemical reactions taking place:

$$1)\quad CF_3Br + h\nu \dashrightarrow CF_3Br^*$$

$$\begin{array}{lll} 2)\quad CF_3Br^* \longrightarrow & CF_3 + Br & \\ & \quad\big\downarrow & \\ \text{(main products)} & C_2F_6 + Br_2 & \end{array}$$

For any halocarbon molecule, the weak chemical bond of C-X (where X is a halogen atom) will be the first to decompose, thus providing halogen atoms and radicals for neutralization or scrubbing. The neutralization process can be carried out in the decomposition (dissociation) chamber, where group IV chemical elements can act as scavengers for the halogen dissociated species and further on scrubbed by basic compounds. An alternative method is pumping the dissociation products in a reaction chamber where they can be scrubbed, absorbed or treated with alkali materials, or reacted on active metal catalyst beds to produce harmless compounds.

The proposed system includes:

- A halocarbon detection unit capable of detecting small amounts of halon in the pumped air drawn from any enclosure (after the halon has been released during an extinguishing process, following a non-fire event where halon is accidentally released or from any other process where halocarbons are released.)

- Radiation means (preferably a laser source) generating high energy pulses at a predetermined level of intensity and duration.

- A pumping device drawing the air containing halocarbons into a cyclone separator where the heavy halocarbons are separated from the air. Afterwards the air is released back .to the surrounding area while the halocarbons are pumped into the dissociation chamber.

- A dissociation chamber where the high energy pulses delivered by the radiation means cause selective dissociation of the halocarbons, causing complete cleavage of the halogen atom from the molecule. The products of the dissociation are pumped into the reaction chamber.

- A reaction chamber where the halogen products of the selective dissociation are scrubbed, absorbed or treated with alkali materials to produce harmless salts (like NaCl, KBr, NH_4Cl etc.).

This component of the system could be disposable (like a scrubber) or for continuous use if it is cleaned periodically.

The apparatus has an independent energy source (battery) which is activated manually (by the human operator when a halocarbon release is detected) or automatically by the triggering signal from the halocarbon detection unit. This activates the pump drawing air contaminated by halocarbons into the separator where the halocarbons are separated from the air (either by cyclone centrifuge, molecular sieve separation or gas chromatography).

The halocarbons are pumped into the dissociation chamber where the radiation source (laser or/and UV means of radiation) is activated on the gaseous stream enabling its selective dissociation.

The gaseous products of the selective dissociation are pumped into the reaction chamber where they are scrubbed, absorbed or treated with

produce harmless compounds (mostly solid salts).

This apparatus can be attached to the various systems supplying or using halocarbons, so as to ensure that once the halocarbon is released into the surrounding area (whether following a malfunction or a controlled release such as an extinguishing process) it is drawn into the invented apparatus and selectively dissociated to the predetermined products.

References:

1) H. Okabe, Photochemistry of Small Molecules, Wiley, New York, 1978, P. 298.

2 T. Molina, M.J. Molina and F.S. Rowland, J. Phys. Chem. 86, 2672 (1982).

3. R. Wurzberg, L.J. Kovalenko and P.L. Houston, Chem. Phys. 35, 317 (1978).

4. V.N.Bagratashvili, M.V. Kuzmim and V.S. Letokhov, J. Phys. Chem. 88, 5780 (1984).

5. A. Cornu and R. Massot "Compilation of Mass Spectral Data", second edition, Heyden and Son, London (1979).

3. EXPERIMENTAL RESULTS

Several laser systems can be employed for the halocarbon dissociation:

- ArF excimer laser with a wavelength of 193nm (near the max.absorption of the halocarbon CF_3Br).

- Nd:YAG laser with a wavelength of 266nm (fourth harmonic) or multi photon process at 1064 nm.

- CO_2 laser with a wavelength of approx. 10µ (multiphoton process)[3,4].

Photo flash lamps, with a high UV yield at 200-280 nm are also suitable for dissociation process.

In the experimental set-up described herein, the dissociation means was an ArF excimer (Lambda Physik, EMG MSC101) with a wavelength of 193nm, pulses of 16 nanoseconds at a rate of 7.7 - 10Hz.

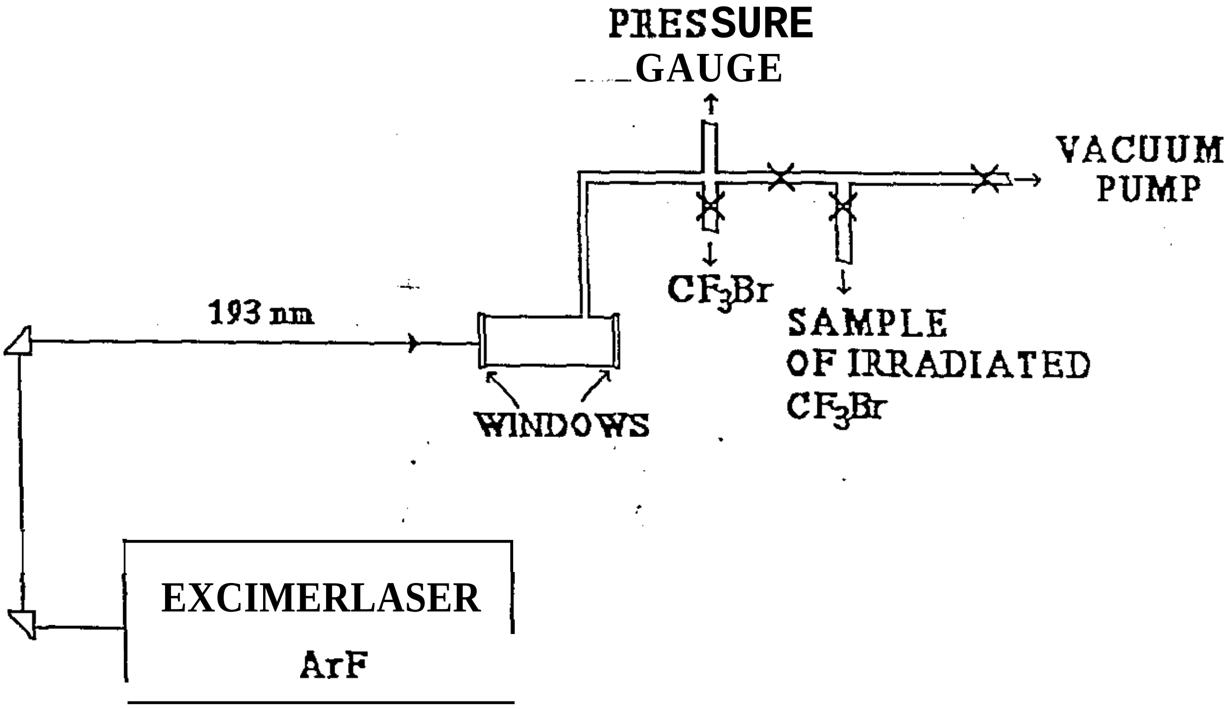

Fig. 1. Experimental set up

The test chamber was made of brass with quartz (Sl-WA) windows, dimensions: $\phi=5cm$, length 10cm. The chamber was connected trough a pressure gauge to a rotary pump that enabled various gas pressures in the test chamber. The test chamber was vacuumed down to 10^{-3} torr, and various gas pressures were tested form 1-760 torr. At the test chamber's entrance the excimer energy was 50 mJ and the beam area 2.5 x 10 mm. Once the dissociation process is completed, the products are tested by a quadrupole mass spectrometer (Balzers mass spectrometer, QMG 511).

The expected mass spectrum of CF_3Br and it's major dissociation product C_2F_6 can be seen in fig. 2.

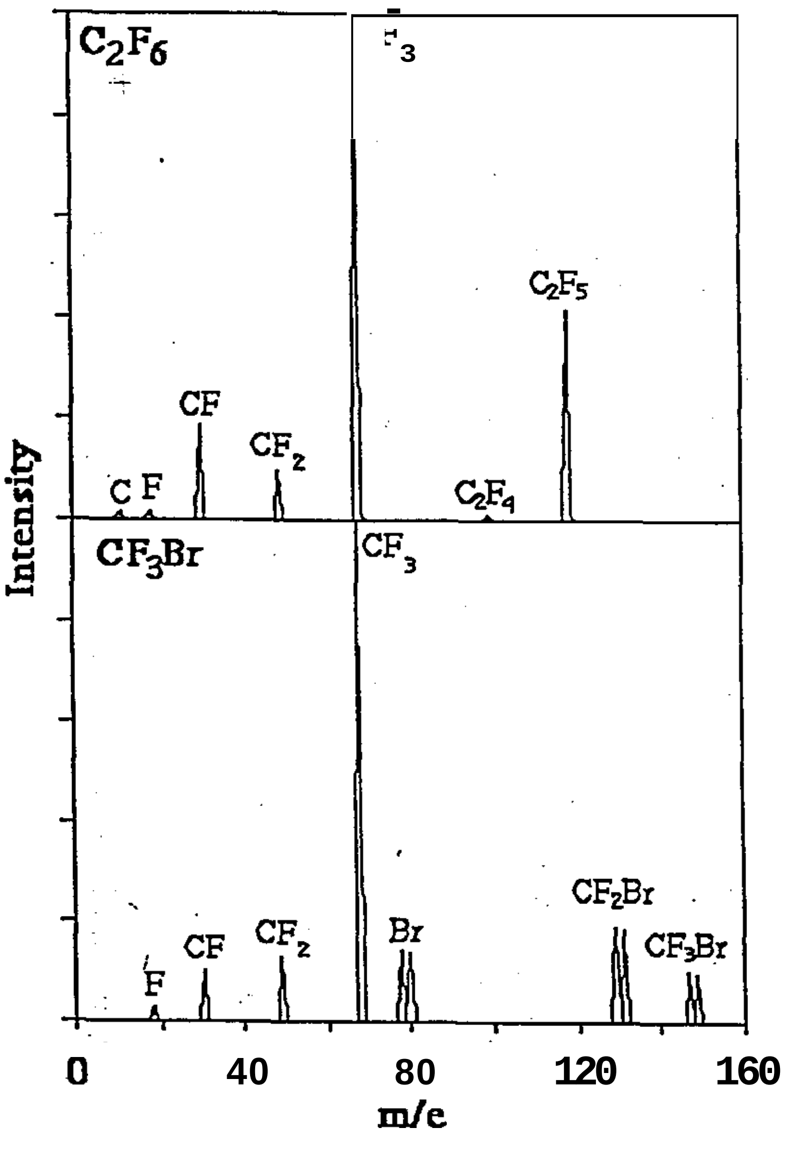

Fig. 2 Mass Spectra of CF_3Br and C_2F_6
(from "Compilation of Mass Spectral Data" A. Cornu et. al, Heyden & Son, London 79).

The actual dissociation products were tested by the mass spectrometer and compared to similar analytical grade compounds (C_2F_6 Aldrich). The similarity can be seen in fig. 3.

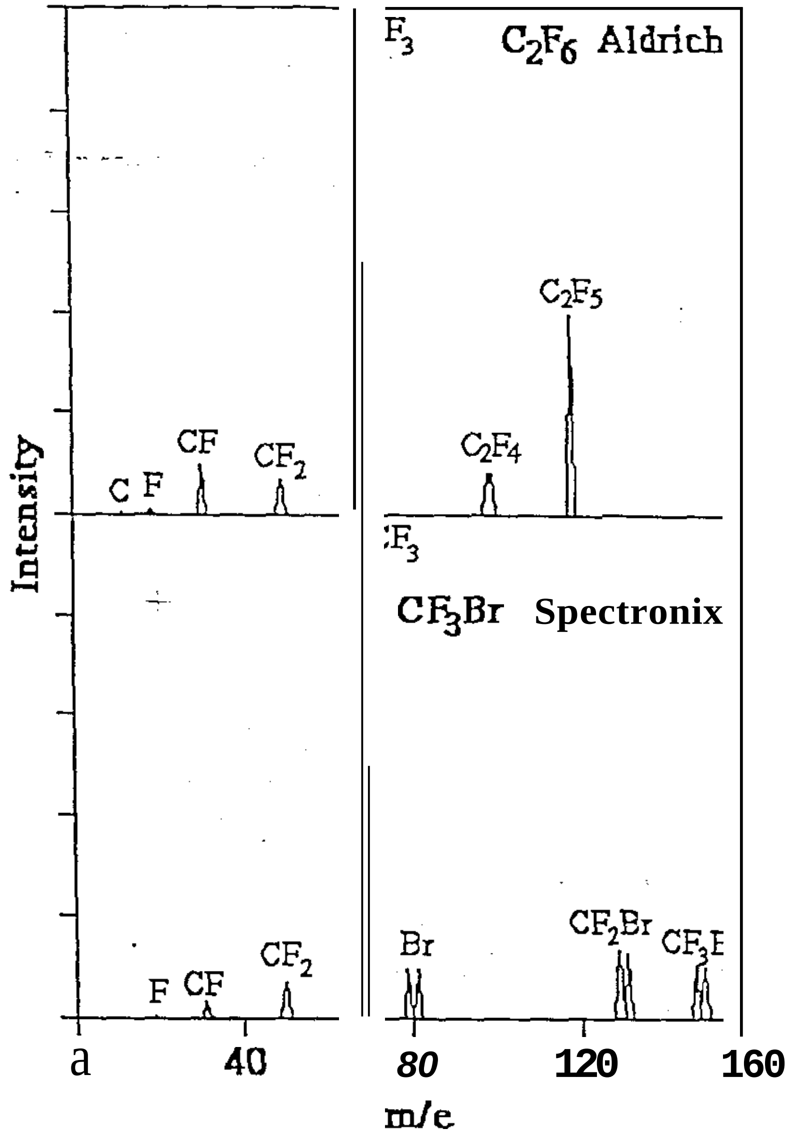

Fig. 3. Mass Spectra of a sample of CF_3Br dissociation products and of C_2F_6

At a halon gas pressure of 60 torr only 10% of the excimer radiation was transmitted trough the chamber, while 90% was absorbed by the halon in the optical path. The absorption of this radiation cause the specific halon dissociation. The mass spectra analysis of the dissociation products shows distinctly the appearance of mass 119 (C_2F_6) and lower yield of masses 131, 129, 148, 150 that are typical to CF_3Br and CF_2Br (that are destroyed in the process). Additional masses such as 260, 258, 200, 198, 210, 208 that are typical to $C_2F_4Br_2$, C_2H_5Br, CF_2Br_2 did not appear in the dissociation products, thus confirming the assumption that this dissociation process is specific. The dissociation products obtained at a gas pressure of 1 torr that was irradiated by 27,000 pulses of ArF with an energy of 50mJ and a frequency of $10H_z$ are detailed in fig.4.

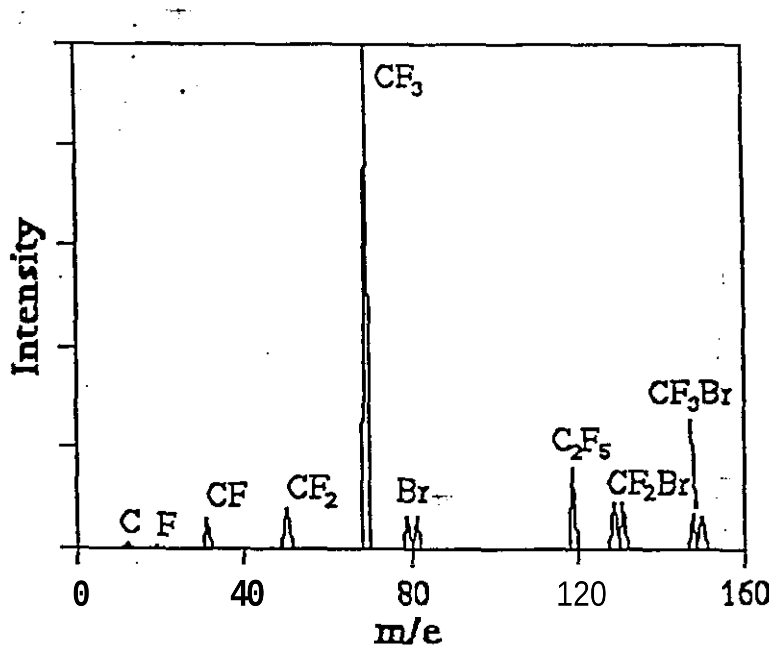

Fig. 4. Mass Spectra of 1 torr of CF3Br irradiated by 27000 pulses of 50 mJ.

Testing the dissociation products mass spectra after severa d fferent periods of irradiation, we found the relation between the C_2F_5 intensity (occurence) and the number of excimer pulses. Fig 5. shows this relation, where the C_2F_5 intensity grows with the increase in the number of excimer pulses, up to a plato - where the increase in the pulses number (over 100,000 pulses) did not influence anymore.

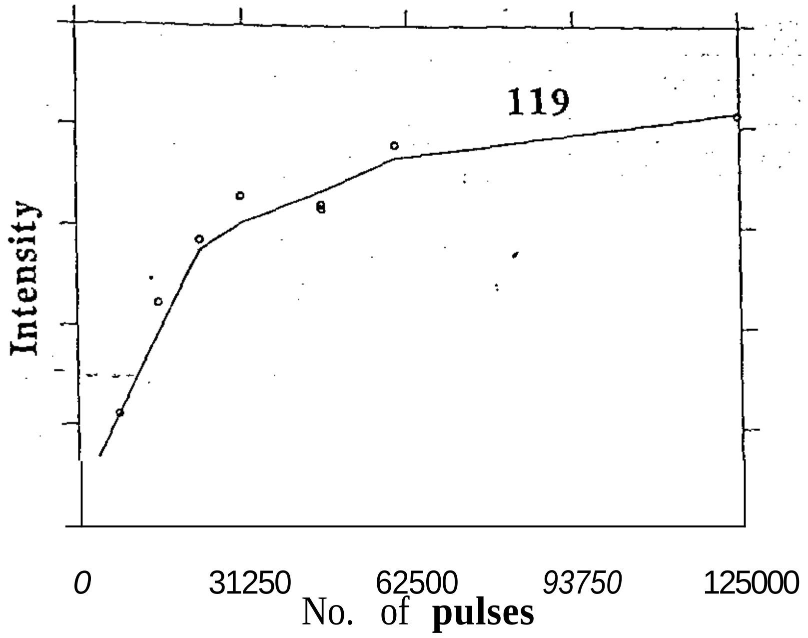

Fig.5. At 60 torr CF_3Br, the occurrence intensity of C_2F_5 as a function of excimer number of pulses.

The relation between the CF_3Br declining intensity following the C_2F_5 growing intensity as a function of excimer irradiation is detailed in fig. 6.

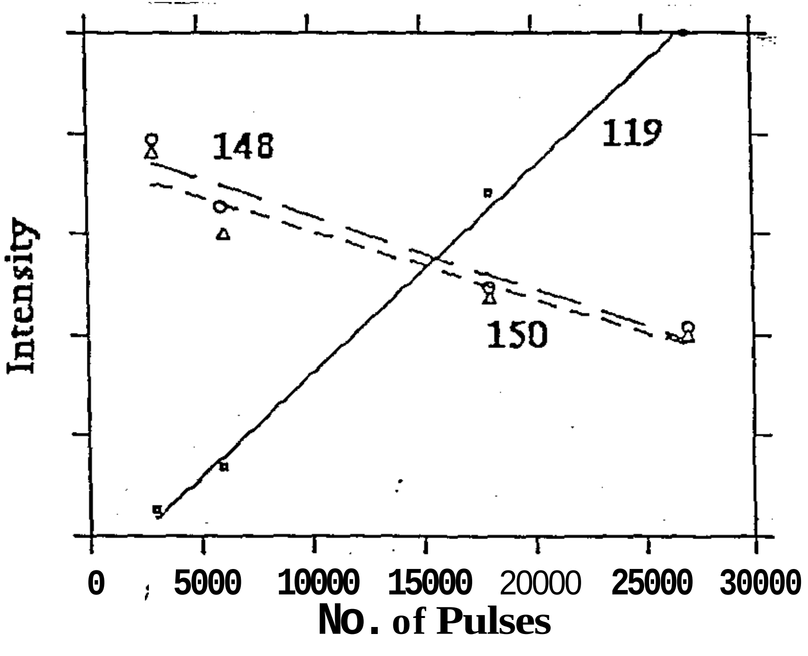

Fig.6. C_2F_5 (119) and CF_3Br (148,150) Intensities as a function of excimer no. of pulses.

According to these results, the dissociation process of halocarbons using excimer energy, gave specific dissociation products such as C_2F_6 and Br_2. These products can further on be scrubbed or neutralized to harmless materials.

NEUTRALIZATION SYSTEM DESCRIPTION

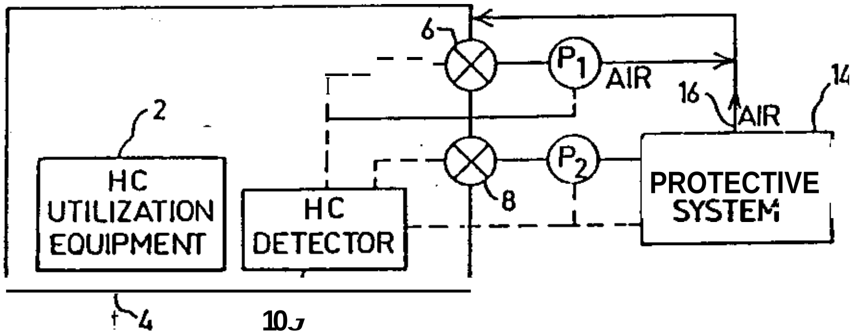

FIG 1

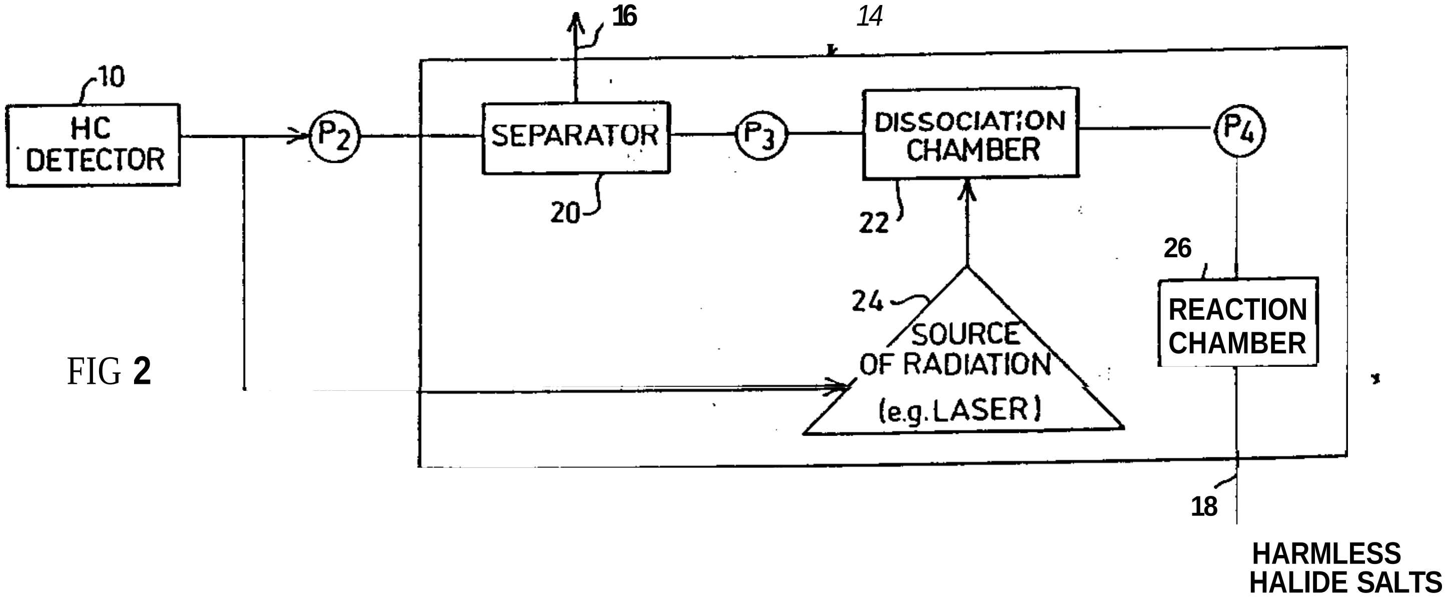

FIG 2