

**HALOCARBONS EMISSIONS MONITORING BY U.V SPECTRAL ANALYSIS
USING SAFEYETM GAS DETECTION SYSTEM**

by

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ABSTRACT

The increase in the global awareness to the environment and the need to monitor ozone depleting substances emissions into the atmosphere have prompted world-wide legislation (Clean Air Act) and restrictions as well as advanced electro-optical monitoring techniques.

The world-wide ban and phaseout of CFC's and Halons has initiated their decomisioning from the systems and storage in international banks, development of various recycling methods and systems as well as an ever growing list of halocarbons replacement and alternative substances like: HCFC, PFC, HFC, FIC, etc.

These have accelerated the need for accurate early warning and detection systems, capable of detecting and monitoring very low concentrations in the atmosphere (at ppm level).

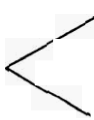
The present paper describes the application of U.V spectral analysis to the detection of these substances by a remote sensing, open path gas monitoring system. The SAFEYETM monitoring system identifies halocarbon molecules at very low concentrations in air, over an optical path of 100m and more without the need to draw samples or chemically analyze the air. The spectral "finger print" of the halocarbon gas is identified optically by the system, compared by microprocessor means to a predetermined detection algorithm and quantified insitu to give concentration of gas per integrated distance.

Thus fugitive emissions that migrate in the form of plumes (clouds) of very low concentration can be detected immediately upon their release by perimeter monitoring.

GAS DETECTION METHODS

I. Point - Detection

All methods require **gas** to be drawn from monitored area, sampled over a period of time, introduced into the detection system via a probe/pump/permeable filter and analyzed according to one or several of the following methods:

- RTD (Resistance Temperature Detector)
- Catalytic (Combustion Methods)
- TOC (Total Organic Carbon Analysis)
- FID (Flame Ionization Detector)
- G.C (Gas Chromatographic Methods)
- M.S (Mass-Spectrometry)
- IMS (Ion Mobility Spectrometry)
- Chemical Adsorption 
 - SAW (Surface Acoustic Waveguide)
 - SOW (Surface Optical Waveguide)

Optical spectrometry (U.V, I.R, VIS)

11. Remote (Open-Path) Optical Detection

All methods rely on “spectral finger print” absorption pattern of substance/vapour in air to be determined over the optical line of sight open-path in front of the detector, or between a radiation source and a detector.

A. Passive Methods

A detector is calibrated to detect background radiation (from the sun and earth) and identify the spectral absorption of a gas against this background.

- FTIR spectrometry (Fourier tranform infrared)

B. Active Methods

A radiation source (artificial) and a detector are communicating so that a gas passing the line of sight between them would be detected at the specific selected spectral band.

- DOAS (Dual Optical Absorption Spectra)
- U.V/I.R
- I.R
- U.V

OPTICAL GAS DETECTION

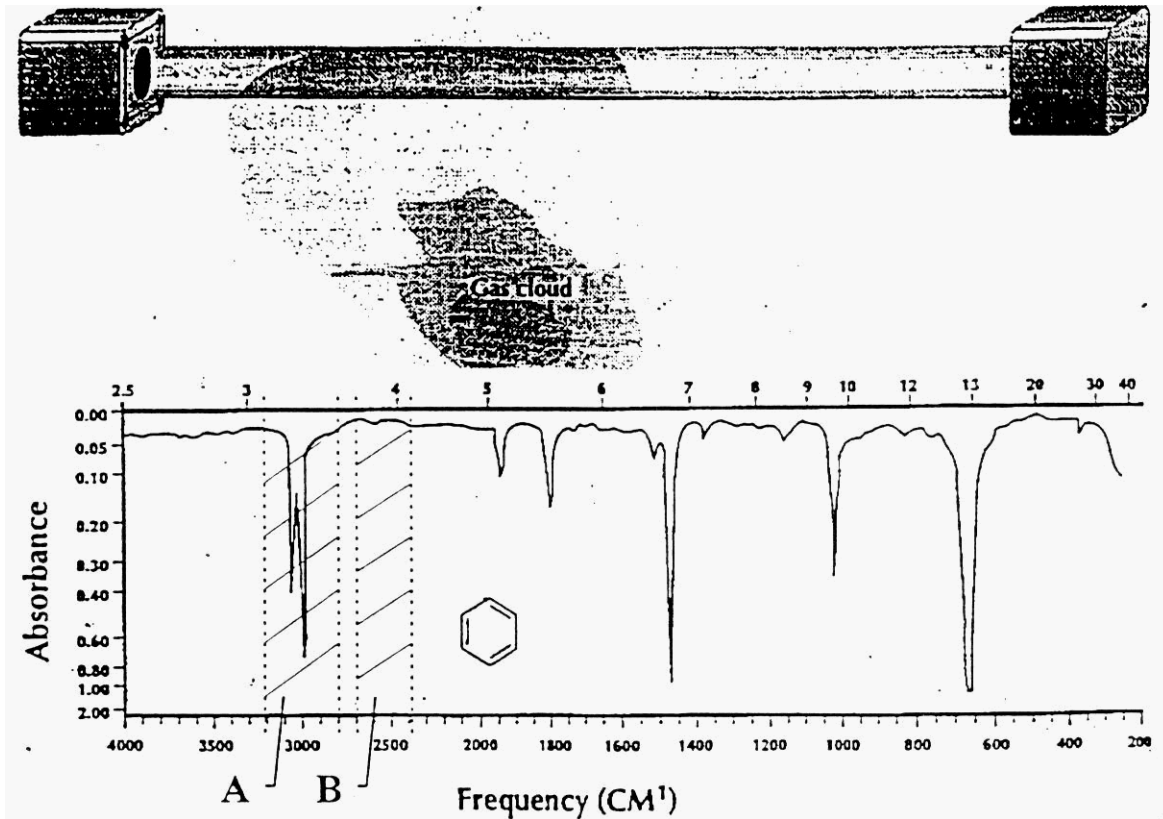
Each chemical substance has an unique “spectral finger print” absorption in the U.V, VIS, I.R portions of the spectrum.

The absorption intensity is related to the concentration of the chemical substance. In the gaseous form the absorption of a gas is according to Beer-Lambert law:

$$I_t = I_0 e^{-E \times C \times L}$$

- Where:
- I_t - Intensity of radiation passing through the gas at a given time (t) and received by the detector.
 - I_0 - Intensity of radiation passing through clean atmosphere (no gas) or calibrated as background.
 - e - Exponent
 - E - Molar extinction co-efficient (e/mole/cm) for the detected gas.
 - C - Gas concentration (mole/l)
 - L - Optical path length (cm)

TYPICAL OPEN PATH DETECTOR LAYOUT



A - Absorption channel

B - Reference channel

Detection signal = A/B ratio

Optional - Several absorption channels
or reference channels
to enhance detection reliability.

HALOCARBON OPTICAL DETECTION

All the CFC and Halons exhibit optical absorption spectra in the U.V band, with a maximum absorption peak between 200 and 230 nm. At longer wavelengths the absorption decreases by a factor of 10 for every 12-15 nm.

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TABLE I: Ultraviolet Absorption Cross Sections for Seven Bromocarbon Molecules at 298 K

λ , nm	σ , ^a cm ² molecule ⁻¹						
	CH ₃ Br	CH ₂ Br ₂	CBrF ₃	CBr ₂ F ₂	CBrClF ₂	C ₂ BrF ₅	C ₂ Br ₂ F ₄
190	4.41 (-19)		6.71 (-20)	1.16 (-18)	4.24 (-19)	1.81 (-19)	1.09 (-18)
195	6.75 (-19)		9.61 (-20)	9.77 (-19)	7.11 (-19)	1.84 (-19)	1.19 (-18)
200	7.85 (-19)	2.31 (-18)	1.18 (-19)	7.68 (-19)	9.62 (-19)	1.81 (-19)	1.22 (-18)
205	7.63 (-19)	2.20 (-18)	1.29 (-19)	7.86 (-19)	1.09 (-18)	1.69 (-19)	1.16 (-18)
210	6.49 (-19)	2.42 (-18)	1.23 (-19)	1.10 (-18)	1.05 (-18)	1.48 (-19)	1.01 (-18)
215	5.06 (-19)	2.74 (-18)	1.03 (-19)	1.63 (-18)	8.96 (-19)	1.20 (-19)	8.31 (-19)
220	3.60 (-19)	2.83 (-18)	7.50 (-20)	2.16 (-18)	7.00 (-19)	8.94 (-20)	6.48 (-19)
225	2.38 (-19)	2.58 (-18)	4.83 (-20)	2.44 (-18)	5.13 (-19)	6.13 (-20)	4.78 (-19)
230	1.45 (-19)	1.98 (-18)	2.70 (-20)	2.31 (-18)	3.42 (-19)	3.83 (-20)	3.28 (-19)
235	8.05 (-20)	1.37 (-18)	1.48 (-20)	1.86 (-18)	2.33 (-19)	2.22 (-20)	2.11 (-19)
240	4.11 (-20)	8.65 (-19)	6.95 (-21)	1.33 (-18)	1.44 (-19)	1.20 (-20)	1.27 (-19)
245	2.04 (-20)	5.08 (-19)	3.25 (-21)	8.65 (-19)	8.87 (-20)	6.20 (-21)	7.30 (-20)
250	9.49 (-21)	2.76 (-19)	1.39 (-21)	5.32 (-19)	5.29 (-20)	3.05 (-21)	3.98 (-20)
255	4.05 (-21)	1.37 (-19)	5.89 (-22)	2.96 (-19)	2.97 (-20)	1.35 (-21)	2.02 (-20)
260	1.63 (-21)	6.31 (-20)	2.34 (-22)	1.55 (-19)	1.56 (-20)	5.90 (-22)	9.57 (-21)
265	6.22 (-22)	2.82 (-20)	9.05 (-23)	7.81 (-20)	7.91 (-21)	2.60 (-22)	4.40 (-21)
270	2.36 (-22)	1.21 (-20)	3.48 (-23)	3.84 (-20)	3.92 (-21)	1.12 (-22)	2.06 (-21)
275	9.0 (-23)	5.11 (-21)	1.38 (-23)	1.85 (-20)	1.90 (-21)	5.05 (-23)	9.28 (-22)
280	3.3 (-23)	2.16 (-21)	5.5 (-24)	8.45 (-21)	8.83 (-22)	2.18 (-23)	4.07 (-22)
285	1.1 (-23)	9.1 (-22)	2.2 (-24)	3.81 (-21)	3.98 (-22)	1.00 (-23)	1.75 (-22)
290	3 (-24)	3.5 (-22)	8 (-25)	1.69 (-21)	1.82 (-22)	4.5 (-24)	7.4 (-23)
295		1.2 (-22)	3 (-25)	7.73 (-22)	8.21 (-23)	2.0 (-24)	3.3 (-23)
300		3 (-23)	1 (-25)	3.56 (-22)	3.61 (-23)	9 (-25)	1.6 (-23)
305				1.74 (-22)	1.65 (-23)		8 (-24)
310				9.2 (-23)	6.6 (-24)		4 (-24)
315				5.5 (-23)	2.6 (-24)		2 (-24)
320				2.9 (-23)	9.8 (-25)		1 (-24)
325				1.3 (-23)	3.7 (-25)		
330				7 (-24)	1.5 (-25)		
335				4 (-24)			
340				2 (-24)			

^a Exponent for base 10 in parentheses.

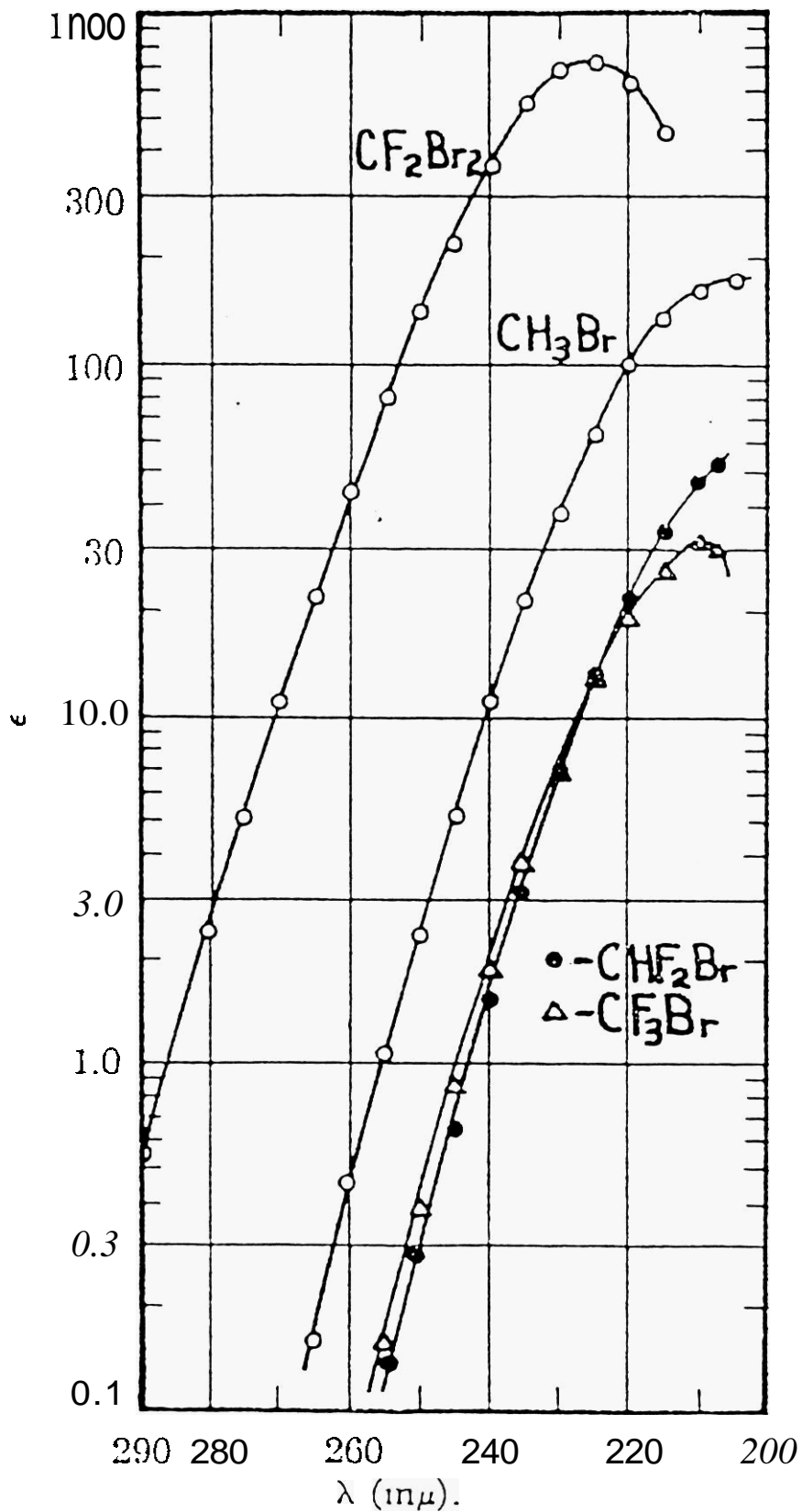


Fig. 1 Absorption spectra of CF_2Br_2 , CH_3Br , CHF_2Br and CF_3Br ($\epsilon = (1/lc) \log_{10}(I_0/I)$ liters/mole cm.).

SYSTEM DESCRIPTION

The SAFEYE™ U.V Halon monitoring system consists of a radiation source and a detector located along a line of sight at a distance from several meters **up** to 100 m.

The detector contains two or three U.V sensors with narrow filters that detect the radiation from the radiation source. The selected narrow bands are 205-225 (absorbance band) and 250-270 (reference band).

CONCLUSIONS

Employing a remote open path monitoring system based on U.V spectral analysis of Halocarbons in the U.V narrow band of 200-230 nm, enables their emissions monitoring at low concentrations in air, over long distances.

The unique design of the monitoring system ignores false alarm stimulus such as various atmospheric conditions, direct sunlight, heaters and light radiators, snow, rain, etc.