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## **ENVIRONMENTAL MONITORING OF HALON AND CFC EMISSIONS FROM BANKED STOCKS.**

By

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### **ABSTRACT**

With the gradual phase out of the CFC's and HALONS and their storage in International Banks, the environmental concern for accidental releases of these highly ozone damaging substances is an oncoming issue.

The increase in the global awareness to the environment and the need to monitor toxic releases has prompted legislation like "Clean Air Act" and similar laws world-wide. This legislation will enforce a tight control on the various Toxics emissions, among which the CFC's and HALONS are certainly the most damaging to the environment now, and even more in the future. Development of reliable recycling systems, as well as substantive research for safe and environmentally friendly destruction methods, have enhanced and accelerated the need for accurate early warning and detection systems for these materials.

The present paper presents a novel approach for detecting these substances at very low concentrations in the atmosphere (at PPM level), by remote sensing using electro-optical means. This method, patented and implemented in the development of Flammable and Toxic gases monitoring (**SAFEYE** Systems) promises to be similarly effective in the monitoring and early warning of CFC's and HALONS accidental emissions.

## 1. INTRODUCTION

The increase in the global awareness to the changes in the environment is caused by two major trends observed in the atmosphere surrounding the earth. The first alarming change in the atmosphere observed in the late 80's was the hole in the ozone layer and it's continuing depletion in the various areas over the globe.

The major contributors to this ozone depletion process were found to be the Chloro-Fluoro-Carbons (CFC) and Halons and the following paragraph describes the problem and it's legislation status:

### A. Halocarbons Problem & Status

1. Stable Ozone Depleting Substances (ODS).
2. Toxic Decomposition Products.
3. International Legislation on:
  - Halocarbons Phaseout by 2000.
  - No Production by January 1994.
  - Strict recycling processes.
  - Prevent unwanted emissions.
  - Search for ODS destruction technologies.
  - Search for alternatives & replacements.

The second alarming change in the surrounding atmosphere is the Global warming effect that causes climate changes worldwide. The various pollutants released to the atmosphere create a "green house" effect whereby infrared radiation from the sun and the earth is trapped in the atmosphere and causes continuous warming of the environment.

The following paragraph describes this phenomena, it's causes and the Clean Air Act legislation and restrictions:

B. Pollutants Problem & Status

1. Clean Air Act - Ecological Awareness.
  - Limits the concentrations of toxic materials in the air.
  - Defines permissible conc. per industry per site and sets penalties.
2. Pollution Monitoring (Urban & Industrial).
3. Petrochemical unwanted emissions:
  - Storage "Fence Line" Protection.
  - Toxic Chemical Cloud Migration.
  - Prevention Monitoring.

In order to facilitate the enforcement of the international legislation and the Clean Air Act, accurate, real-time monitoring of the CFC, Halons and Toxic pollutants is required.

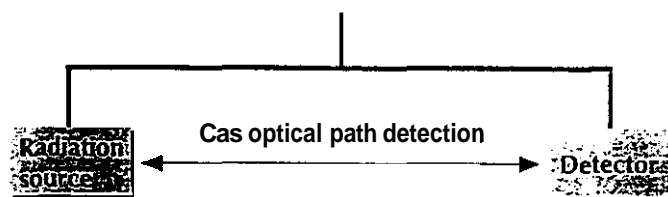
The present paper presents a novel approach for detecting these substances at very low concentrations by remote sensing using electro-optical means.

This method, patented (U.S. 5,281,816) and implemented in the development of Flammable and Toxic gases monitoring (SAFEYE system) promises to be similarly effective in the monitoring and early warning of CFC's, Halons and various Pollutants emissions.




## 2. TECHNICAL BACKGROUND

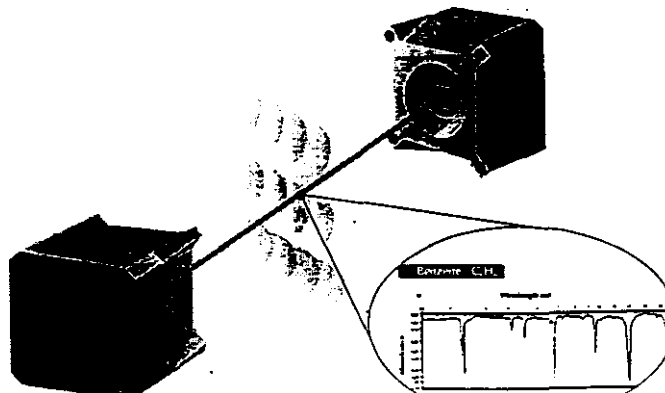
The entire technical background and scientific data for this technology is described in the U.S. patent 5,281,816 that is available either from the Commissioner of patents and trademarks or from Spectrex or Spectronix companies. The patent describes a method of detecting the presence of predetermined chemical vapours by their spectral signature ("finger print") in several spectral ranges from the U.V. VISIBLE and I.R. spectral bands. The use of a radiation source and a detector is described in the following schematic figure:

### **Basic unit**



### The detection process

-  The radiation source of the SAFEYE emits a wide spectral beam directed toward the detector
-  The detector continually monitors the intensity of the radiation emitted from the source at the two mentioned bands. The ratio between these two intensities is continually calculated by the S A F M
-  Intrusion of gas into the line of sight between the source and the detector, immediately influences the ratio between the two bands and thus the SAFEYE identifies the gas.



Similar spectral absorption data can be obtained for the various CFC, Halons and atmospheric pollutants. The following Figures (1 - 3) show the Halon 1301 spectral "finger prints" in the I.R. band, Figure 4 shows the I.R. absorbance spectrum of Freon 13 (C Cl F<sub>3</sub>), Figure 5 shows the mid - I.R. absorbance spectra of halocarbon 1-1-1 TCA.

Table I details the various spectral absorption parameters in the U.V. for Bromocarbon molecules, best known as Halons 1301, 1211, etc.

All the CFC and Halons exhibit absorption maxima between 200 and 230 nm, with long wavelength absorption decreasing beyond this maxima by a factor of 10 for every 12 - 15 nm.

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

| $\lambda$ , nm | $\sigma$ , <sup>a</sup> cm <sup>2</sup> molecule <sup>-1</sup> |                                 |                   |                                 |                     |                                 |   |
|----------------|--|---------------------------------|-------------------|---------------------------------|---------------------|---------------------------------|---|
|                | CH <sub>3</sub> Br   | CH <sub>2</sub> Br <sub>2</sub> | CBrF <sub>3</sub> | CBr <sub>2</sub> F <sub>2</sub> | CBrClF <sub>2</sub> | C <sub>2</sub> BrF <sub>5</sub> | C <sub>2</sub> Br <sub>2</sub> F <sub>4</sub> |
| 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)                         |                     |                                 |   |

<sup>a</sup> Exponent for base 10 in parentheses.

### 3. EXPERIMENTAL DATA

Extensive experimental research has been conducted in order to develop a detection system capable of differentiating between regular paraffins and aromatic or toxic substances. This research and development effort led to the development of the SAFEYE system, that has the following characteristics:

- a. The absorption bands of most aromatic, toxic and Halocarbon gases are in the U.V. spectral range 0.2 - 0.3 microns (200 - 300nm), while the absorption bands of the paraffins are in the near I.R. and halocarbons and CFC in the mid I.R. (8 - 12 $\mu$ ).
- b. In order to detect a gas, the SAFEYE utilizes one sensor for the absorption band and one sensor for the non absorption band. (several such pairs in the U.V and I.R are used in one system to detect several gases or chemical families).
- c. Smoke, fog and rain along the line of sight decrease the intensities of the two bands equally, without changing the ratio and SAFEYE continues its measurements.
- d. Solid objects obstructing the line of sight block the radiation. The SAFEYE identifies them as obscurant and provides warning signal for malfunction.
- e. The system can be calibrated to detect gases and vapors at ppm level or at LEL (lower explosive limit) percentage level.
- f. The system can incorporate a flame detection built-in module, that enables the detection of a fire event at it's very beginning.

Various experimental results obtained with this system are detailed in figures 6 to 9, while the system is detailed in the adjacent photographs.

#### 4. CONCLUSIONS

Optical detection of chemical substances in the vapors or gaseous form is a highly reliable technique for environmental monitoring purposes.

In order to prevent unwanted emissions from banked stocks of CFC, Halocarbons and various toxic substances, as well as monitor the pollutants occurrence in certain protected areas, the use of an electro-optical monitoring system can offer a large area coverage and perimeter (fence-line) continuous surveillance and alarm options at various substances concentrations in the atmosphere.

The present study and developed system have proved the feasibility of its implementation in the detection of flammable and toxic vapours at various concentrations (ranging from PPM to LEL level), however, additional R&D effort is required to adapt this type of system to detect CFC, Halocarbons and specific toxic pollutants.

The adaptation includes selection of additional filters, unique algorithm analysis and calibration versus several concentration levels, according to the permitted (or restricted) emissions from banked stocks.

#### BIBLIOGRAPHY

1. The Journal of Physical Chemistry, Vol. 86, No. 14, 1982.
2. U.S. patent 5, 281, 816.
3. Catalog of Infrared Spectra for qualitative analysis of gases, Analytical Chemistry, Vol. 28, 1956.
4. Experimental results - Spectronix R&D internal report 93/1.

# Principles of operation

## 1 Typical absorption spectrum

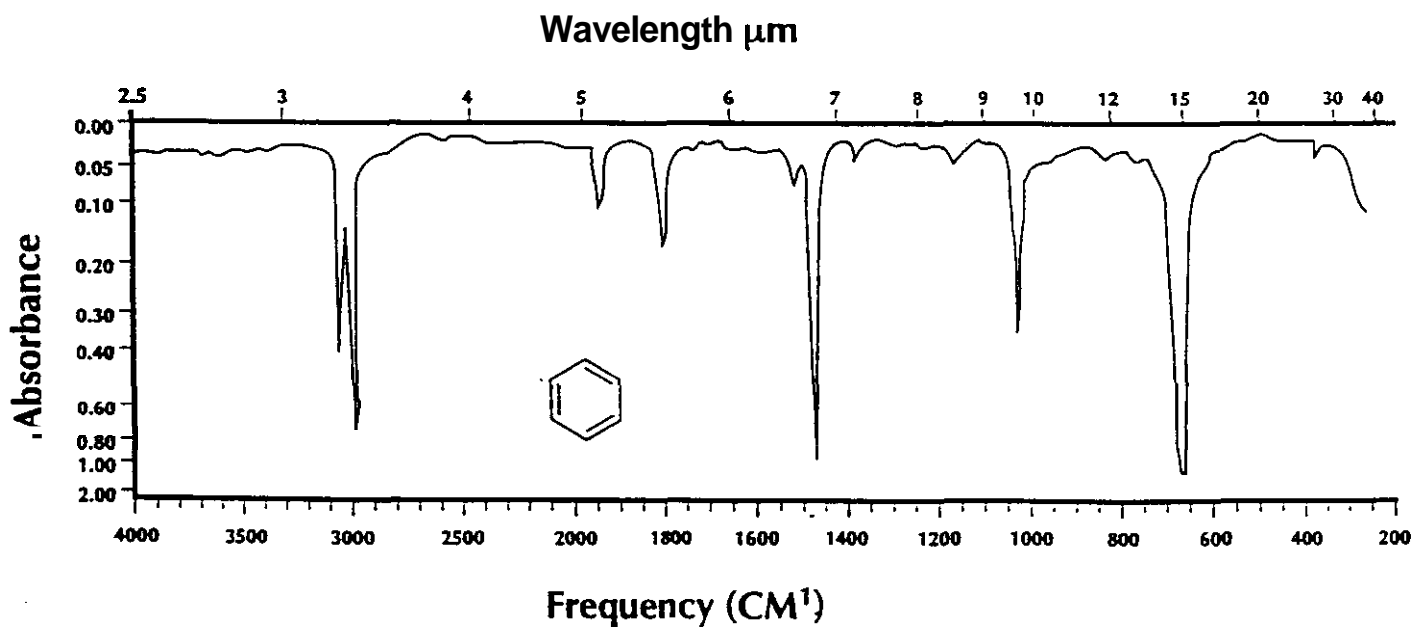


Each gas or group of gases has a typical absorption spectrum which can provide a key to identifying the gas



This typical spectrum consists of bands of wavelengths with high absorption (absorption band) and low absorption

## Benzene $C_6H_6$





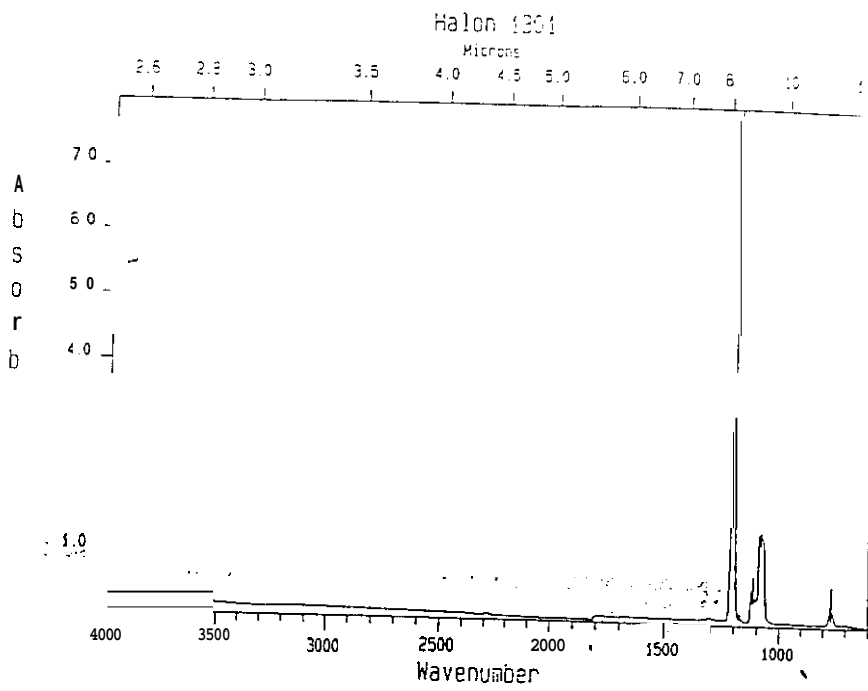


Figure 1. IR Spectrum of Halon 1301

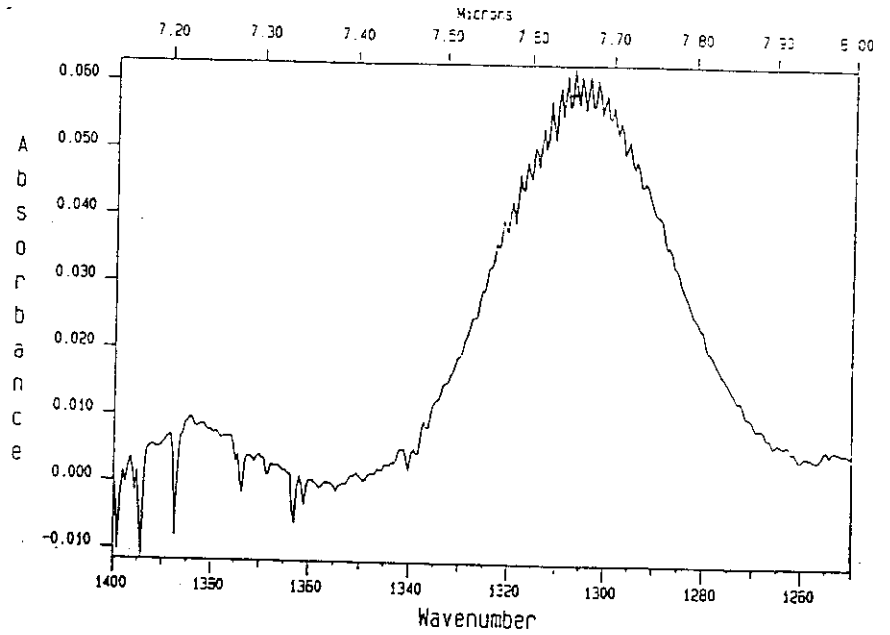


Figure 2. An Expanded View of the IR Spectrum of Halon 1301 from 1400 to 1250  $\text{cm}^{-1}$ .

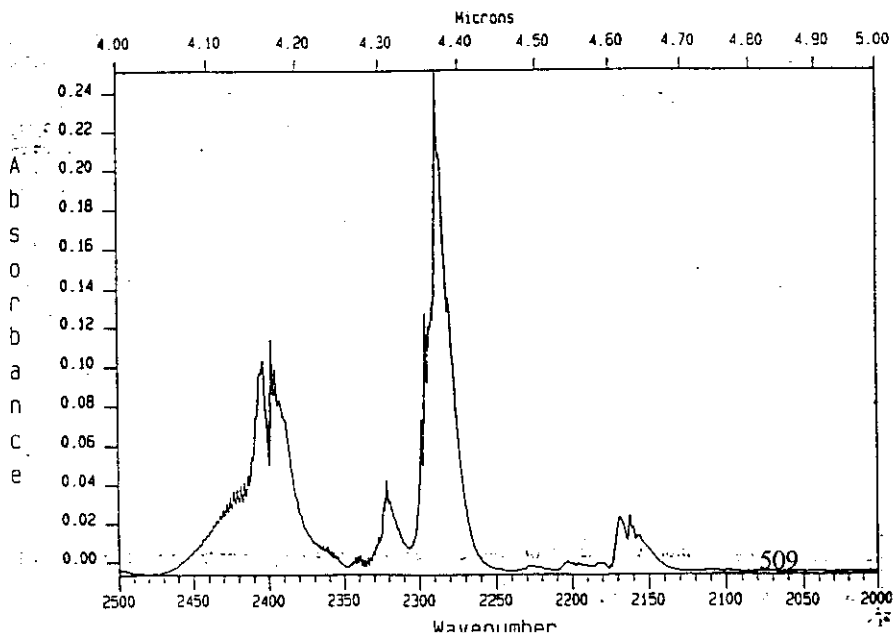


Figure 3. An Expanded View of the IR Spectrum of Halon 1301 from 2500 to 2000  $\text{cm}^{-1}$ .

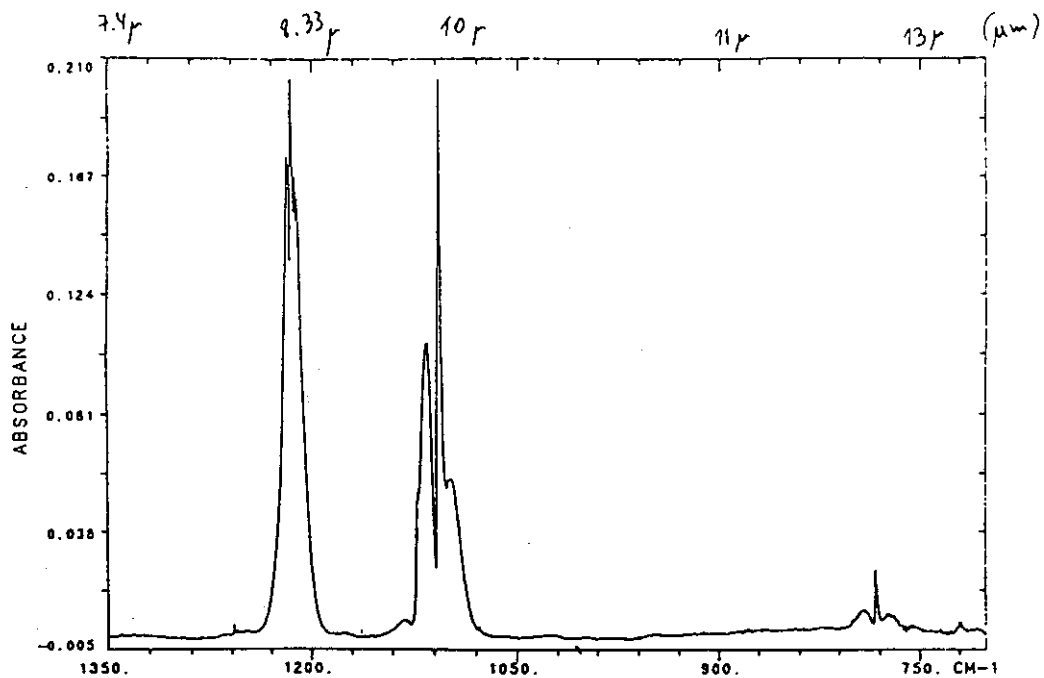


Figure 4. Calibration of spectrometer for Freon 13 (CCl<sub>3</sub>F) at .1225 torr ? Lect. bot. Source 25 cm from aperture and 16 cm cell mirror 35 cm 740.0 torr.

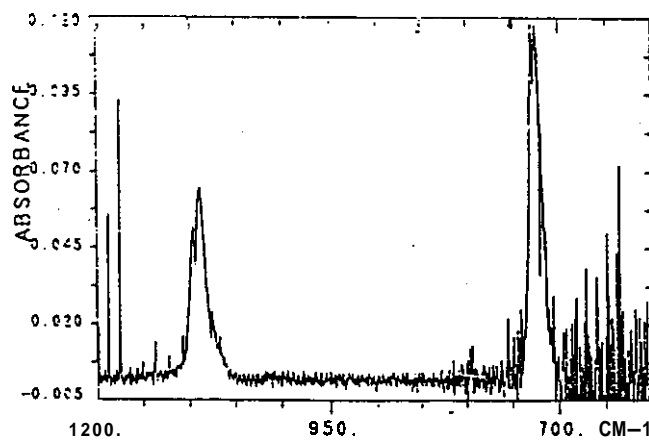
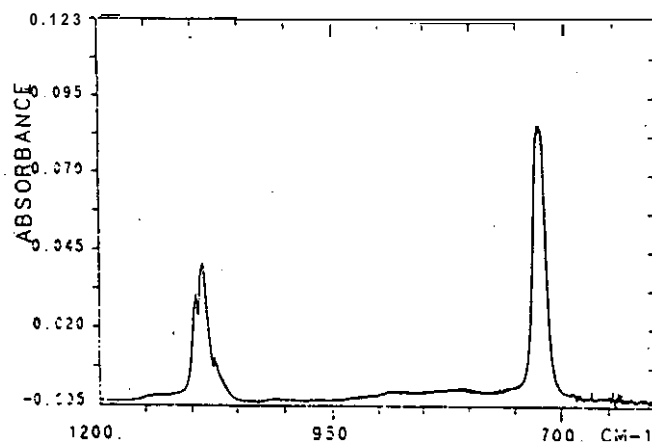
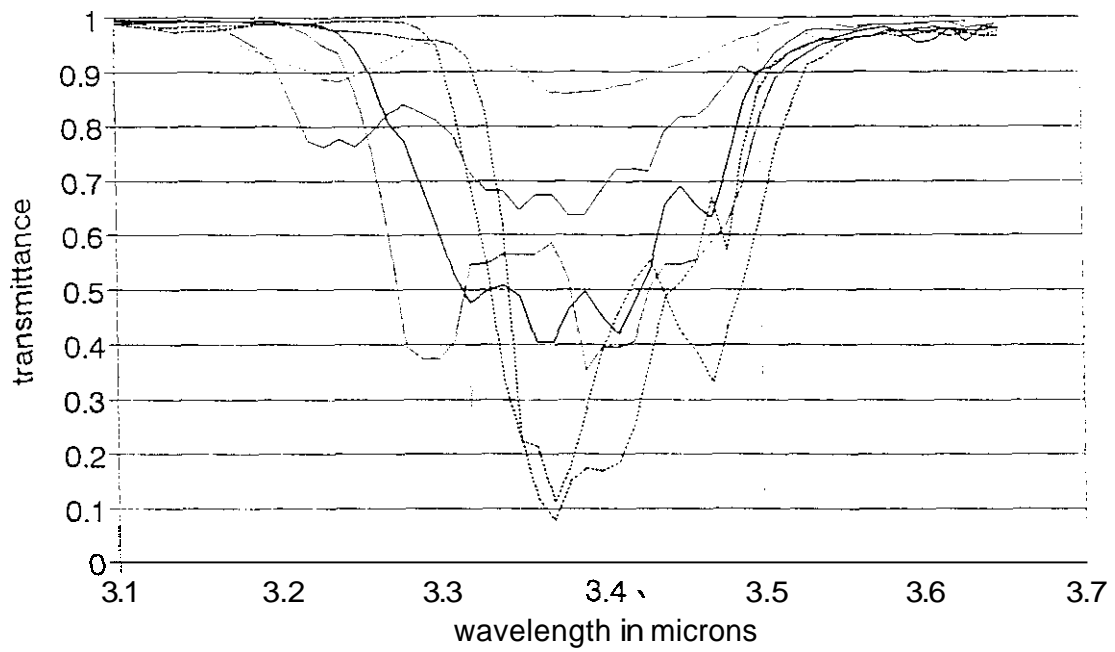


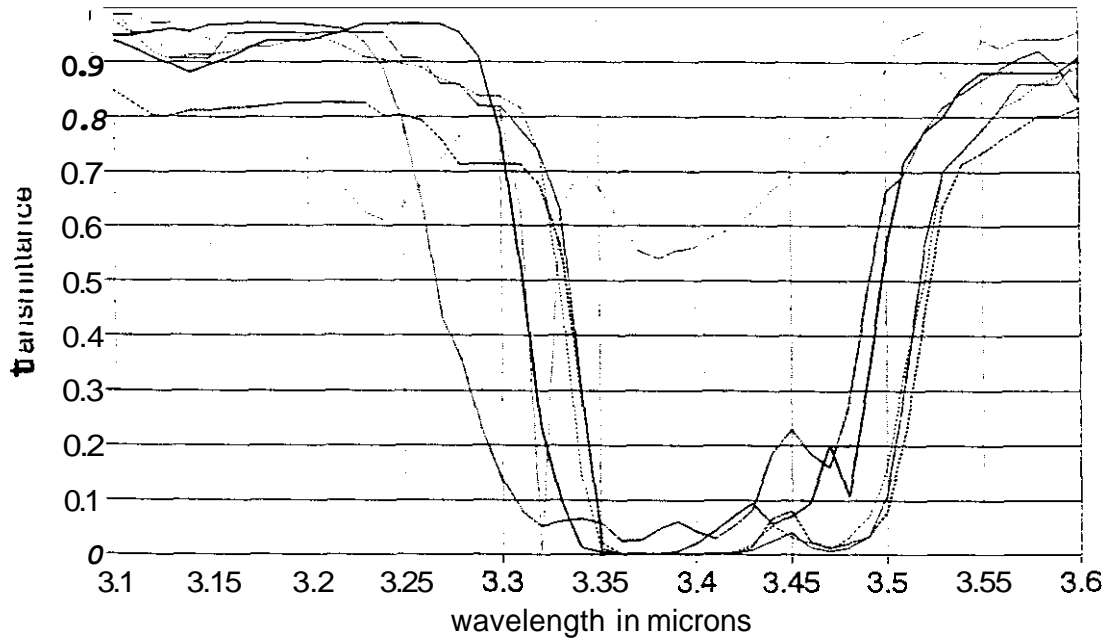
Figure 5. Mid-infrared absorbance spectra of 1,1,1-trichloroethane (1,1,1-TCA). (A) (top) Laboratory calibration spectrum in 16 cm cell at 0.5 cm<sup>-1</sup> resolution. (B) (bottom) Field spectrum for 117 meters at 0.5 cm<sup>-1</sup> resolution.

Fig 6 : 1m, pressure 0.1 LEL(experimental data)



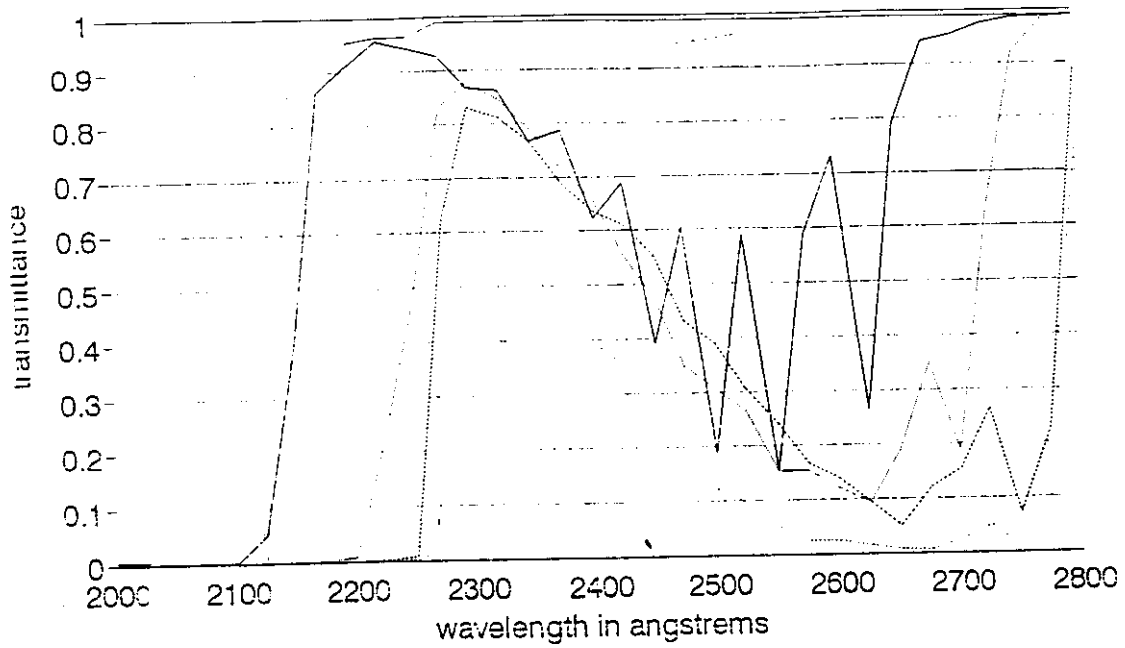
|         |          |          |
|---------|----------|----------|
| methane | ethane   | propane  |
| pentane | propylen | butylene |

Fig. 7 : 1m , pressure 0.4 LEL(experimental data)



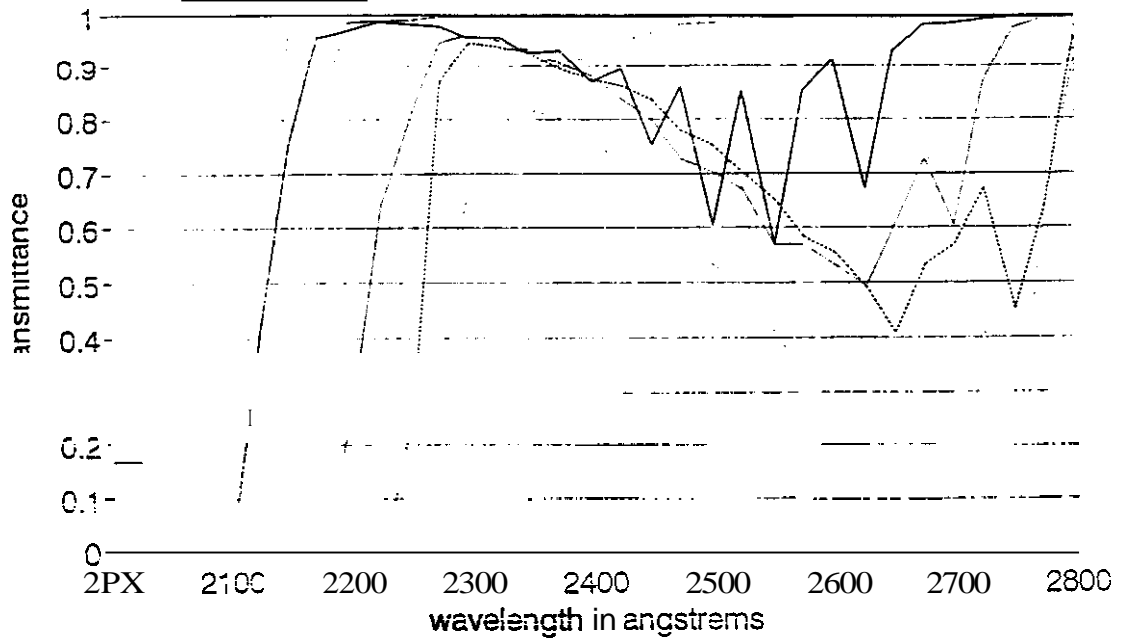
|              |               |               |
|--------------|---------------|---------------|
| C1H4 methane | C3H8 propane  | C5H12 pentane |
| C6H14 hexane | C7H16 heptane | C2H6 ethane   |

FIG. 8 : 1m, 1000ppm



|       |         |         |           |
|-------|---------|---------|-----------|
| —     | benzene | toluene | tetraline |
| ..... | xylene  | H2S     | amonia    |

FIG. 4 : 1m, 300ppm



|       |         |         |           |
|-------|---------|---------|-----------|
| ..... | benzene | toluene | tetraline |
| ..... | xylene  | H2S     | amonia    |

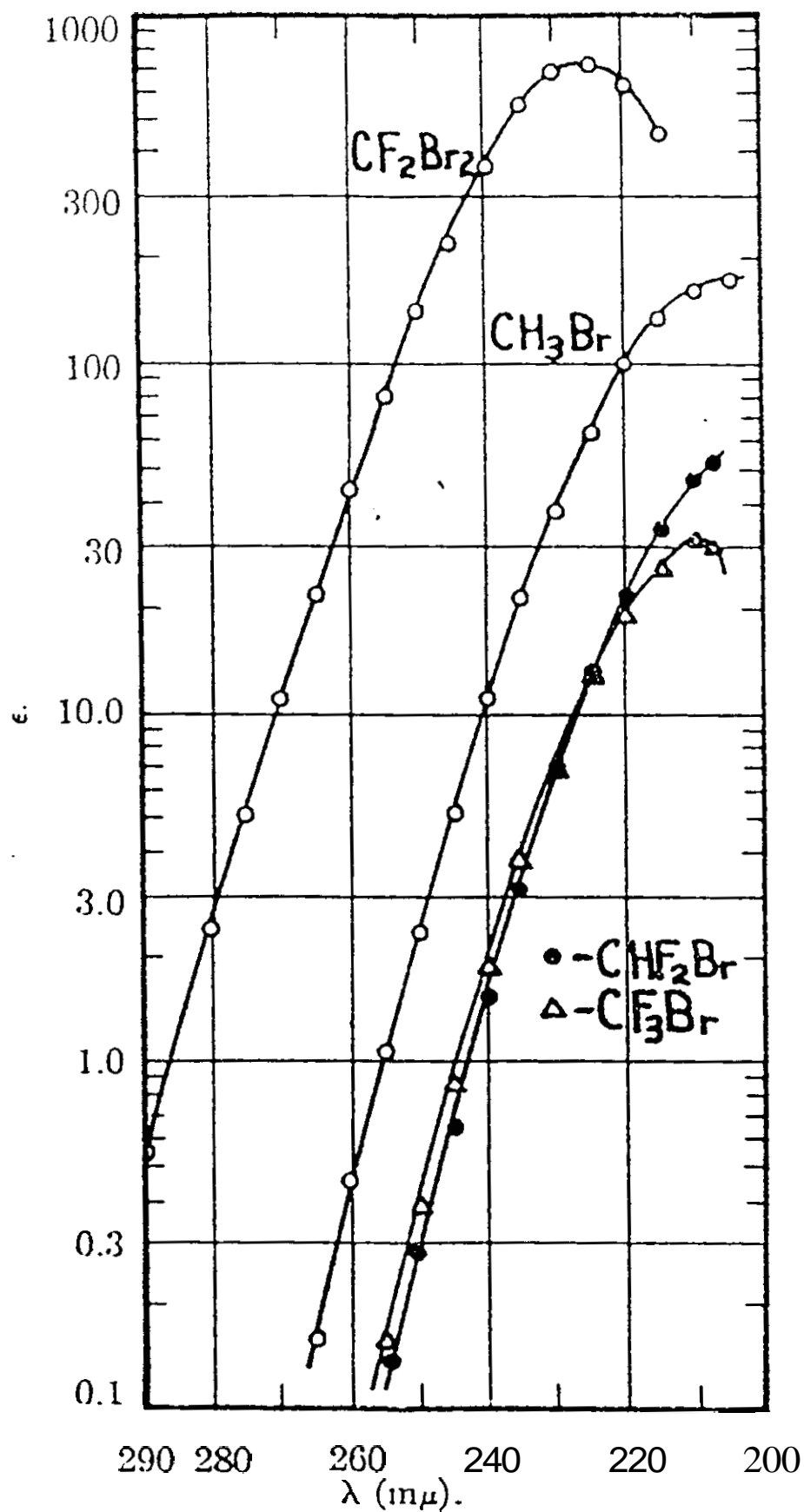


Fig. 10. Absorption spectra of  $\text{CF}_2\text{Br}_2$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CHF}_2\text{Br}$  and  $\text{CF}_3\text{Br}$  ( $\epsilon = (1/lc) \log_{10}(I_0/I)$  liters/mole cm.).

