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**DETERMINATION OF TRACE QUANTITIES OF FREON BY LASER OPTOACOUSTIC DETECTION AND CLASSICAL INFRARED SPECTROSCOPY\***

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The sensitivity threshold was determined for a homebuilt apparatus with laser optoacoustic detection, enabling gases absorbing in the range of emission by the CO<sub>2</sub> laser used to be detected selectively in trace concentrations. Gravimetrically calibrated homemade permeation tubes containing Freon 11 (CCl<sub>3</sub>F) were used, and a sensitivity threshold of 20 ppb was established. The dependence of the optoacoustic signal on the concentration of Freon 11 was measured in the dynamic mode; this concentration is given by the permeation standard type, carrier gas flow rate, and temperature. Classical IR spectroscopic measurements in the static mode were also performed.

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Analytical methods for the detection of trace quantities of substances often call for the use of internal calibration standards. For the analysis of substances in the vapour form, permeation sources<sup>1,2</sup> delivering the substances in trace concentrations can be used. These sources are hermetically closed vessels fitted with a membrane enabling the substance contained to diffuse from the vessel more or less extensively. The substance in the vessel is in a liquid-vapour equilibrium, so that its vapour pressure inside the vessel remains constant over a long period of time, depending only on the substance and temperature. As long as the liquid phase is present, the weight loss of the substance over a time unit is constant and the amount diffused can be determined by repeated, periodical weighing. Permeation standards with a filling facility, enabling them to be filled repeatedly, have been developed<sup>3</sup>. The body of the vessel can be made of a polymer such as Teflon or polyethylene, serving as the membrane, and hermetically closed at one end and fitted with a filling facility at the other end.

Such permeation standards were used in this work for determining the detection threshold of our apparatus and obtaining calibration plots for the quantitation of trace amounts of Freon 11 by two independent analytical methods, viz. classical infrared spectroscopy and optoacoustic (OA) detection using a CO<sub>2</sub> laser. It is

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common knowledge that used in sprays and as industrial coolants, Freons can disturb the ozone layer in the atmosphere, and so their monitoring is gaining in importance.

### THEORETICAL

In the dynamic mode, where carrier gas is allowed to flow about the permeation tube, the concentration of the substance examined,  $x_s$  (in ppm (mol/mol) throughout this paper), is given by the relation

$$x_s = (10^3/86.4) (\Delta m_s/M_s) (V_c/Q_c), \quad (1)$$

where  $\Delta m_s$  is mass loss of the substance (permeation tube contents) in 24 h (mg per day),  $M_s$  is the molar mass of this substance ( $\text{g mol}^{-1}$ ),  $V_c$  is the molar volume of carrier gas ( $V_c = 22.413 \text{ l mol}^{-1}$  at 273.15 K and 101.325 kPa) and  $Q_c$  the flow rate of carrier gas ( $\text{ml s}^{-1}$ ). The  $\Delta m_s$  value can also be expressed by means of the rate of permeation of the gas through the wall of the permeation tube,  $I_s$  ( $\text{mol s}^{-1}$ ) as

$$\Delta m_s = 86.4 \cdot 10^6 I_s M_s \quad (2)$$

which inserted in Eq. (1) gives

$$x_s = 10^9 I_s V_c / Q_c. \quad (3)$$

The permeation rate  $I_s$  is strongly temperature dependent.

In the static mode, where the permeation standard is accommodated in an enclosed cell filled with air under atmospheric pressure, the concentration of the substance detected increases with time. Concentration in time  $\tau$  (s) in a cell with a volume  $V_{\text{cell}}$  (ml), arising from diffusion at a rate  $I_s$  from a permeation tube with a volume  $V_p$  (ml), will be

$$x_s = 10^9 I_s V_c \tau / (V_{\text{cell}} - V_p). \quad (4)$$

In this case,  $x_s$  is both temperature and time dependent. The time dependence will be linear as long as the volume of the substance analyzed can be neglected with respect to the volume of air, viz. up to concentrations about  $10^4$  ppm, and it can be distorted due to sorption of molecules of the substance on walls of the cell and temperature variations, associated with changes in the permeation rate. The total pressure in the cell will increase, being contributed to by the partial pressure of the gas followed outside the permeation tube. In case that leaks occur from the cell, the concentration can decrease due to the difference between the interior and exterior pressures.

## EXPERIMENTAL

A survey of the polymeric permeation tubes used, fitted with filling facilities or not, is given in Table I. These tubes were employed for the calibration of two detection systems, both of them based on the absorption of infrared radiation, using Freon 11 ( $\text{CCl}_3\text{F}$ , b.p.  $23.8^\circ\text{C}$ ,  $M_r = 137.4$ ) as analyte. The apparatus for the classical spectroscopic measurements comprised a Specord 75 IR spectrometer (Carl Zeiss, Jena, G.D.R.), on-line interfaced to a KSR 4 100 computer (Robotron, G.D.R.). Samples were measured in the liquid state in KBr cells 0.1 mm pathlength and in the gaseous state in a commercial 100 mm gas cell or in a 150 mm cell with NaCl windows sealed to the glass body with Lukopren N 1 522. The analytical bands are given in Table II. The well-known Lambert-Beer law,

$$A(\tilde{\nu}) = a(\tilde{\nu}) x_s d, \quad (5)$$

where  $A(\tilde{\nu})$  and  $a(\tilde{\nu})$  are the absorbance and absorptivity, respectively, at wavenumber  $\tilde{\nu}$  in a cell with an optical pathlength  $d$  (m), transforms into

$$A(\tilde{\nu}) = 10^{-9} x_s d \sigma N_A / V_c, \quad (6)$$

where  $x_s$  is the concentration expressed by Eq. (1) for the flow-through mode and by Eq. (4) for the static mode,  $\sigma$  is the collision cross section of the molecule ( $\text{m}^2$ ) and  $N_A$  is Avogadro's number.

TABLE I

Permeation tubes used and daily losses of Freon 11 through them at  $25^\circ\text{C}$

Label <sup>a</sup>	Material (manufacturer)	Length mm	Wall thickness mm	Inner diameter mm	Daily loss <sup>b</sup> mg	Standard deviation mg
PE Z <sub>1</sub>	polyethylene	40	1.6	5.8	81.7	2.2
PE Z <sub>2</sub>	polyethylene	79	1.6	5.8	247.4 <sup>c</sup>	23.4
TL Z	Teflon	73	1.0	6.0	5.2	0.5
TL	Teflon	86	1.0	6.0	7.1 <sup>c</sup>	0.3
TT Z	Teflon	108	0.3	3.3	25.0 <sup>c</sup>	3.0
OA <sub>1</sub>	Optimit Odry	95	1.2	4.2	8.8	0.4
OA <sub>2</sub>	Optimit Odry	100	1.2	4.2	12.6	1.5
OB	Optimit Odry	104	1.2	8.1	14.9	0.9
MB	Mecano Bundy	108	1.5	8.7	9.7	0.9
DT <sub>1</sub>	Deutsche Tecalemit	53	1.0	4.0	1.6	0.2
DT <sub>2</sub>	Deutsche Tecalemit	162	1.0	4.0	4.8	0.5
DT <sub>3</sub>	Deutsche Tecalemit	320	1.0	4.0	10.2	0.9
LH	Leybold-Heraeus <sup>d</sup>	—	—	—	1.0	0.1

<sup>a</sup> Z denotes permeation tubes fitted with filling facility; <sup>b</sup> arithmetic mean from 30 days; <sup>c</sup> ref. <sup>3</sup>; <sup>d</sup> commercial standard.

In the flow-through mode the carrier gas passes first at a constant flow rate about the permeation standard in a thermostated measuring apparatus and then enters the cell. In the static mode the permeation standard is encased in a cell filled with the carrier gas (air) under atmospheric pressure. The cell volume is 200 ml, the volume of the standard without the filling facility is calculated from Table I for the tube used.

For reproducibility testing, the measurements were repeated in 8–14 day periods, between which the cell was air purged until the base level of the maximum transmittance of the cell was attained; the tube was not removed from the cell for this procedure. In the static mode, only the TL, OA<sub>1</sub>, PE, DT<sub>1</sub>, TT Z and a Leybold-Heraeus commercial standard were used for spatial reasons (Table I).

TABLE II  
Analytical IR bands used for CCl<sub>3</sub>F and suitable concentration regions for the static mode

Wavenumber cm <sup>-1</sup>	Intensity	Vibrational mode	Concentration	
			ppm · 10 <sup>-3</sup>	mg/200 ml
843	very strong	$\nu_s(\text{C—Cl})$	0.04 – 1.6	<2
928	strong	$\nu_{as}(\text{C—Cl})$	0.04 – 163	<200
1 074	very strong	$\nu(\text{C—F})$	0.04 – 9.8	<12
1 374	weak	$\delta$	1.6 – 163	20 – 200
2 138	weak	$2\nu(\text{C—F})$	8.1 – 163	10 – 200

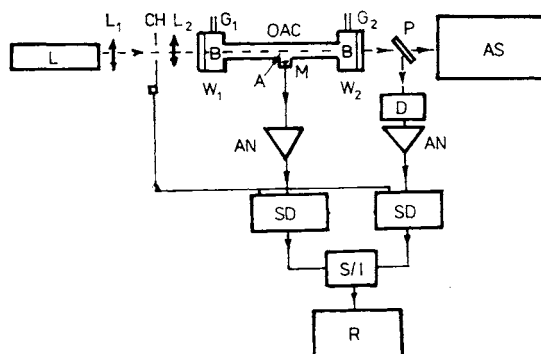


FIG. 1

Apparatus for laser optoacoustic detection. L CO<sub>2</sub> laser, L<sub>1</sub> germanium lens 25 cm focal length, L<sub>2</sub> germanium lens 10 cm focal length, CH chopper, OAC optoacoustic cell, W<sub>1</sub> entrance window, W<sub>2</sub> exit window, B damping compartments, A absorption compartment, M pressure sensor, G<sub>1</sub> gas inlet, G<sub>2</sub> gas outlet, P NaCl plate, AS laser spectrum analyzer, D radiation detector, AN amplifiers, SD synchronous detectors, S/I ratiometer, R recorder

Optoacoustic detection<sup>4</sup> was accomplished<sup>5</sup> in the flow-through mode as shown in Fig. 1. The optoacoustic cell 200 mm long, 6 mm i.d., was flushed continuously with air in the same arrangement as for the spectrometric measurements. The radiation from a laboratory CO<sub>2</sub> laser modulated with a chopper was absorbed by molecules of Freon, and the associated  $V$ - $T$  relaxation caused pressure changes, which were detected with a TESLA AMC 412 microphone with a gain of  $100 \mu\text{V Pa}^{-1}$  as the pressure transducer. Radiation that passed through the cell was measured with a simple homebuilt pyrodetector. The signals from the microphone and detector were amplified and processed in synchronous detectors and the outputs were ratioed in an analogue ratiometer whose output was interfaced to an Endim 62002 recorder (G.D.R.). The adjustment of the pertinent rotational-vibrational line was checked by using an Optical Engineering spectral analyzer.

## RESULTS AND DISCUSSION

The concentration generated by the permeation tube can be controlled by *a*) permeation standard used (tube material, length, and wall thickness); *b*) carrier gas flow rate; *c*) permeation standard temperature; and *d*) time of accommodation of the standard in the cell. The data in Table I indicate that the concentration can be adjusted over a span of more than two orders of magnitude by a suitable choice of the material (see also Fig. 2). In the flow-through mode the concentration can be varied over several ppm by flow rate control within limits given by the flowmeter used and the requirement of a laminary flow. The optoacoustic responses for the TT Z and TL Z standards and flow rates of  $14$ – $24 \text{ ml s}^{-1}$  are compared in Fig. 3.

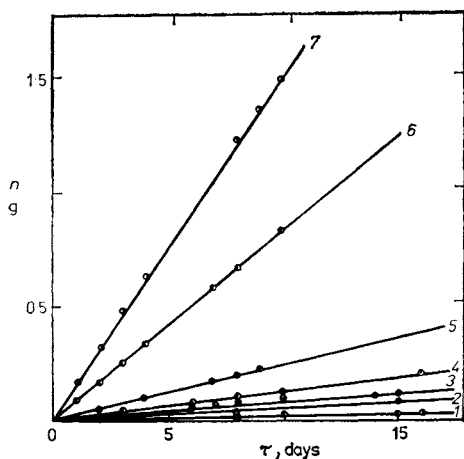


FIG. 2

Time dependence of weight loss  $n$  of Freon 11 from permeation tubes at  $25^\circ\text{C}$ . Tube: 1 DT<sub>1</sub>, 2 DT<sub>2</sub>, 3 TL Z, 4 OA<sub>2</sub>, 5 TT Z, 6 PE Z<sub>1</sub>, 7 PE Z<sub>2</sub>

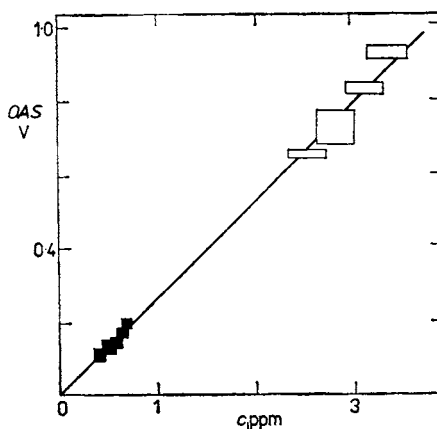


FIG. 3

Concentration dependence of optoacoustic signal for flow rate control. Tube: □ TT Z, ■ TL Z

A constant temperature is imperative for keeping the concentration constant; temperature control, on the other hand, can be employed for concentration adjustment.

The results of IR spectrometric measurements in the static mode are given in Table II. This mode can serve to monitor the time increase in the analytical band intensity.

The sensitivity of the analytical methods is of importance. An advantage of the optoacoustic method is the wide span of measurable concentrations, whereas an asset of IR spectrometry is the choice of several analytical bands suitable for different concentrations according to their intensity. Fig. 4, showing the concentration dependences of the optoacoustic response and IR absorbances, demonstrates that the optoacoustic signal is directly proportional to concentration over a wide region,

TABLE III

Comparison of daily losses of  $\text{CCl}_3\text{F}$  from permeation tubes determined by IR spectroscopy in the static mode and by gravimetric measurements

Permeation tube <sup>a</sup>	Daily loss, mg	
	IR spectroscopy	gravimetry
DT <sub>1</sub>	1.3 <sup>b</sup>	1.6
MB	10 <sup>b</sup>	9.7
OB	16 <sup>c</sup>	14.9
PE Z <sub>1</sub>	79 <sup>c</sup>	81.7

<sup>a</sup> Labelling conforming to Table I; <sup>b</sup> analytical band at  $843\text{ cm}^{-1}$ ; <sup>c</sup> analytical band at  $928\text{ cm}^{-1}$ .

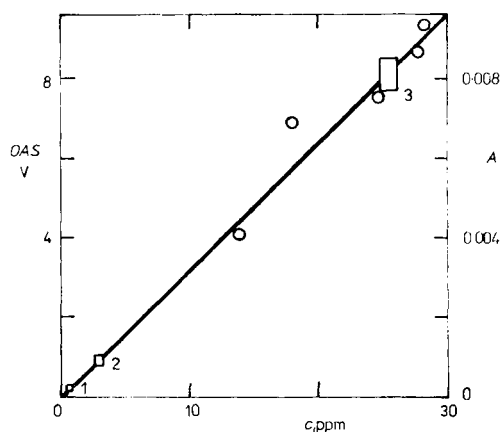


FIG. 4

Optoacoustic signals for Freon 11 generated by TL Z (1), TT Z (2), and PE Z<sub>2</sub> (3) tubes for three months at constant flow rate and temperature, and IR absorbances for PE Z<sub>2</sub> tube and flow rate control

starting from tenths or hundredths ppm, while IR spectrometry suits to higher concentrations (in excess of 15 ppm in our case). Concentrations generated by PE Z<sub>2</sub> tube could be monitored by both methods, which gave identical results (Fig. 4).

Calibration errors can be due to various factors. In the flow-through mode, the primary source of error is in the inaccurate carrier gas flow rate measurement, dependent on the atmospheric pressure and accuracy of data reading. The average error in our case was  $\pm 1 \text{ ml s}^{-1}$  over the region of 8–40  $\text{ml s}^{-1}$ , hence, the relative error was higher at lower flow rates. Other errors arise from leaks from the optoacoustic cell, subatmospheric pressure in the cell causing suction of air from the outside and thereby dilution of the analyte, and from temperature variations, amounting to  $\pm 0.5^\circ\text{C}$  in our arrangement. In the case of concentration adjustment by temperature control, the nonlinear shape of the temperature dependence of pressure inside the tube must be taken into account.

The IR spectroscopic method suits to the measurement in a closed system where the time increase in the analytical band intensity is monitored. The losses of Freon 11 from various sources, determined by the spectroscopic and gravimetric methods, are compared in Table III; the data are in a good mutual agreement. Errors in the static mode arise from temperature variations in the (unthermostatted) cell compartment, adsorption of Freon on the cell walls and Freon leaks from the cell during atmospheric pressure changes.

## CONCLUSIONS

A laser optoacoustic analyzer was set up and tested using homemade permeation standard sources of Freon 11. The sensitivity limit of this device under the conditions used was 20 ppb. Classical IR spectroscopy was employed as an independent method for a comparison, applicable to concentrations higher than 15 ppm. Using the permeation standard approach in the dynamic mode, the CO<sub>2</sub> laser optoacoustic analyzer can serve as a sensitive and selective tool for monitoring Freons or other gases in working or industrial air or for air pollution monitoring in general, in defectoscopy, etc.

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