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NOVEL CHEMILUMINESCENCE DETECTOR FOR DETERMINATION OF VOLATILE POLYHALOGENATED HYDROCARBONS BY GAS CHROMATOGRAPHY

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SUMMARY

Based on the chemiluminescence reaction with atomic sodium vapour under reduced pressure, a novel gas-chromatographic chemiluminescence detector (CLD) for the determination of volatile polyhalogenated hydrocarbons (VPHHCs) has been developed; the characteristics of the CLD are compared with those of the electron-capture detector (ECD). The CLD constructed is simple and unique in that it exhibits high sensitivity and good selectivity towards VPHHCs; CCl_4 , $\text{ClCH}_2\text{CH}_2\text{Cl}$, $\text{ClCH}_2\text{CHCl}_2$, $\text{ClCH}=\text{CCl}_2$, and $\text{Cl}_2\text{C}=\text{CCl}_2$ have low detection limits of the order of 10^{-13} g/sec (in the picogram range) and their molar response ratios to compounds other than VPHHCs exceed 10^4 . The CLD can compete in terms of sensitivity with the ECD and also surpasses the ECD with regard to linear dynamic range and selectivity. In addition, it is free from the drawbacks associated with the ECD. These detector characteristics allow us to expect that the CLD will be used in place of the ECD, depending on the kinds of VPHHCs which are to be determined.

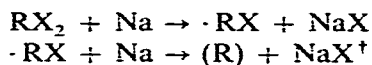
INTRODUCTION

To date many classes of compounds associated with human activities have been discharged into the environment in varying amounts. Strong emphasis has been placed on the environmental and health aspects of anthropogenic organic compounds, one class of which, volatile polyhalogenated hydrocarbons (VPHHCs), have a wide variety of industrial applications, notably as refrigerants, aerosol propellants, solvents, chemical intermediates and fire extinguishers. Since the original work of Molina and Rowland¹, a large number of investigators have studied the interaction of VPHHCs (the so-called halocarbons, fluorocarbons or chlorofluorocarbons) with stratospheric ozone. In another field of research, the presence of VPHHCs such as trihalomethanes was recently identified in water samples obtained from several sources²: for instance, the average levels of CHCl_3 , CHCl_2Br and CHClBr_2 in samples of drinking water from 80 cities in the United States were found to be 21, 6 and 1.2 $\mu\text{g/l}$,

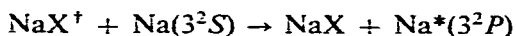
respectively³. The main interest in these types of compounds is focused on their possible toxic effects, particularly with regard to carcinogenicity.

Most of the VPHHCs in environmental samples in general involve a mixture of chlorinated hydrocarbons with both other halogenated and non-halogenated compounds. Suitable methods of detection and quantification are therefore essential, and the electron-capture detector (ECD) in gas chromatography (GC) has been commonly used for VPHHC analysis because of its exceedingly high sensitivity, despite a number of drawbacks *viz.* (1) the linear dynamic range is short, in the d.c. and pulsed mode being typically less than two orders of magnitude, although being extended to about four or five orders in the pulse-modulated constant-current mode; (2) the sensitivity towards individual halogenated hydrocarbons differs and varies over several orders of magnitude, *e.g.*, the response for CH₂Cl₂ is 10⁴–10⁵ times less than that for CCl₄ (see Table IV); (3) the ECD has poor specificity, *i.e.* it is highly sensitive to electronegative compounds other than halogenated hydrocarbons (such as those containing –NO₂, –N, –COCO–, and –COCH=CHCO– groups) and consequently, particular attention must be paid during analysis to avoid contamination of samples; and (4) the radiative sources used are controlled by government regulations.

This work reports attempts to develop a novel chemiluminescence detector (CLD) for GC which is free of the above drawbacks and is capable of selectively detecting VPHHCs in nanogram to picogram amounts, together with a comparison with the ECD. The high CLD response arises from the chemiluminescence reaction between atomic sodium vapour and volatile aliphatic hydrocarbons containing more than two halogen atoms in the molecule^{4,5}. The chemiluminescence reaction involves two primary steps, corresponding to successive removals of the halogen atoms X,



followed by a vibrational-to-electronic energy transfer reaction,



where † denotes a minimum vibrational excitation of 48.5 kcal/mole, the energy required to excite the *D*-lines. Here R is an aliphatic hydrocarbon group and (R) corresponds to a stable alkene or cyclic hydrocarbon formed by exothermic rearrangement of the biradical during the collision, the stabilization energy being deposited as vibrational excitation in the nascent NaX molecules. The resultant chemiluminescence intensity in the emission of the sodium *D*-lines is monitored.

On the basis of the chemiluminescence reaction, whose reaction mechanism is somewhat different with that above, we had previously reported a new CLD permitting determination of atmospheric N₂O at sub-ppm levels without the need for pre-concentration processes⁶. Accordingly, the present work was initially undertaken for preliminary experiments, employing the same type of detector as that used for the N₂O determination; improvements in the construction of the detector were then made.

PRELIMINARY INVESTIGATIONS

The same type of detector as used in the previous work⁶ (a CLD made of Pyrex glass tubes) was newly constructed for the preliminary experiments (Fig. 1). As the chemiluminescence reaction described above suggests, the amount of atomic sodium vapour and the detector pressure play important roles in the chemiluminescence intensity. The former, which depends mainly on both the cell temperature and the flow-rate of the atomic sodium vapour carrier gas, must be much greater than the amount of VPHHC admitted into the reaction cell, in order to ensure that the chemiluminescence intensity is proportional to the VPHHC concentration. The latter is correlated with collisional deactivations of vibrationally excited NaX molecules which are thus lost for the subsequent excitation of sodium atoms. The effects of these parameters on the chemiluminescence intensity were examined, and preliminary results, *viz.* lower detection limits (LDLs), linear dynamic ranges (LDRs) and relative molar responses (RMRs), were obtained (Table I). All calibration graphs (log-log plots) gave straight lines; slopes were not always equal to unity, that for the LDRs being more than three orders of magnitude. It is found from the RMRs that the sensitivity exhibits a pronounced dependence on the type of compounds and the number of chlorine atoms in the molecule. In the chloromethane homologous series, for instance, the response increases with an increase in the number of chlorine atoms, while for chloroethanes there is no such tendency. In analogous series, the response cannot be explained in terms of the number of chlorine atoms. This response behaviour will be discussed later. At any rate, the preliminary investigations indicate that the CLD will be capable of completing with the ECD if improved.

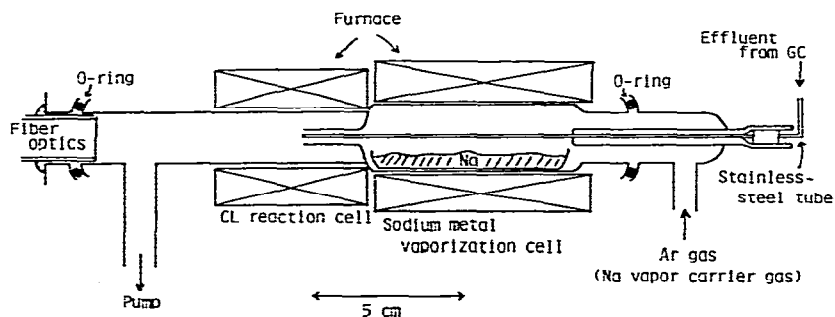


Fig. 1. Pyrex chemiluminescence detector.

However the preliminary experiments reveal that the Pyrex detector suffers the following intrinsic defects derived from both the material and the geometry: many parameters affecting response behaviour, gradual corrosion of the Pyrex glass, contamination of the fibre optics surface owing to deposition of sodium atoms and reaction products, a troublesome procedure for loading the sodium metal, and the inevitable seepage of stray light into the apparatus. Thus, a metallic detector was designed to remove the above defects and to improve the detector characteristics, resulting in a simplified detector construction and easier operation.

TABLE I
PRELIMINARY RESULTS

Operating conditions: sodium vaporization cell temperature, 280°C; chemiluminescence reaction cell temperature, 300°C; sodium vapour carrier gas flow-rate, 17 ml/m; detector pressure, 5 Torr. Background current: $3 \cdot 10^{-10}$ A. Noise current: $1 \cdot 10^{-11}$ A.

VPHHC	LDL (g/sec)	LDR	RMR**
CH ₂ Cl ₂	$7.1 \cdot 10^{-10}$	10 ³	1
CHCl ₃	$1.5 \cdot 10^{-10}$	10 ⁴	6
CCl ₄	$5.3 \cdot 10^{-12}$	10 ⁵	63
CFCl ₃	$1.2 \cdot 10^{-11}$	10 ⁴	95
CF ₂ Cl ₂	$2.4 \cdot 10^{-11}$	10 ⁴	69
CF ₃ Cl	$1.4 \cdot 10^{-9}$	10 ³	1
ClCH ₂ CH ₂ Cl	$4.3 \cdot 10^{-12}$	10 ⁵	112
CH ₃ CHCl ₂	$1.3 \cdot 10^{-9}$	10 ³	0.1
ClCH ₂ CHCl ₂	$2.0 \cdot 10^{-11}$	10 ⁴	126
CH ₃ CCl ₃	$3.6 \cdot 10^{-10}$	10 ³	0.6
ClCH=CCl ₂	$6.7 \cdot 10^{-12}$	10 ⁴	19
Cl ₂ C=CCl ₂	$1.1 \cdot 10^{-11}$	10 ⁴	56

* For a signal-to-noise ratio of 3.

** Normalized with respect to the value for CH₂Cl₂.

EXPERIMENTAL

Apparatus

A Shimadzu Model GC-3A gas chromatograph, equipped with a 10% DC550 column (3 m × 3 mm I.D.) and a thermal conductivity detector (TCD) was used. Pure argon gas from a cylinder was supplied to the chromatograph after having been dried with activated alumina and then with magnesium perchlorate. A three-way micro needle valve (MNVTU-100, Scientific Glass Engineering, North Melbourne, Australia) was installed between the chromatograph and the CLD for controlling the stream of argon gas to the CLD. The remaining exit of the micro needle valve opened into the atmosphere, resulting in a constant flow-rate of argon into the CLD. Consequently, part of the sample eluted from the GC column has to be discarded along with the argon carrier gas. The flow-rate of the argon stream was indirectly determined by calculating the difference between the flow-rate of the vented gas stream before and during the experiment. The CLD was evacuated by a rotary vacuum pump (Model C-150, Tokyo Vacuum Machinery, Tokyo, Japan) and the pressure was measured with a Mcleord gauge. The CL produced was detected by a photomultiplier tube (Hamamatsu TV-R453) through an interference filter (max. 590 nm, Toshiba-KL59). The photomultiplier tube was cooled to *ca.* -20°C in an electronic cooler (Hamamatsu TV-C659B) and operated at -700 V from a high-voltage d.c. stabilizer (Hamamatsu TV-C448A). The signal from the photomultiplier tube passed into an electrometer (tr-8651, Takeda Riken) and was then recorded by a dual pen recorder along with the signal from the TCD, via a laboratory-built low-pass active filter⁷ (frequency cut-off *ca.* 0.1 Hz) between the electrometer and the recorder.

Stainless-steel CLD

A metallic CLD (illustrated in Fig. 2) was constructed in order to improve detector performance. It is composed of stainless steel tubes with Swagelok fittings, *viz.* a "Union Tee", a "Reducer" welded to the Union Tee, and a "Plug". The tube fittings are heated by an aluminium block in which are buried two firerod cartridge heaters (120 V/200 W, Watlow, St. Louis, MO, U.S.A.). The temperature can be regulated up to 400°C by an electronic controller. The inside pressure of the detector is maintained at a few torr. Sodium metal is loaded into the Plug fitting which can be easily detached from the Union Tee, resulting in ease of loading of the sodium metal. No atomic sodium vapour carrier gas is admitted to the detector, unlike the Pyrex detector. As a result of the chemiluminescence reaction, a small diffusion flame due to the chemiluminescence is formed on the nozzle (0.8 mm I.D.) and the chemiluminescence intensity is measured through a quartz window, with no use of fibre optics. In contrast to the Pyrex detector, no stray-light shield was needed.

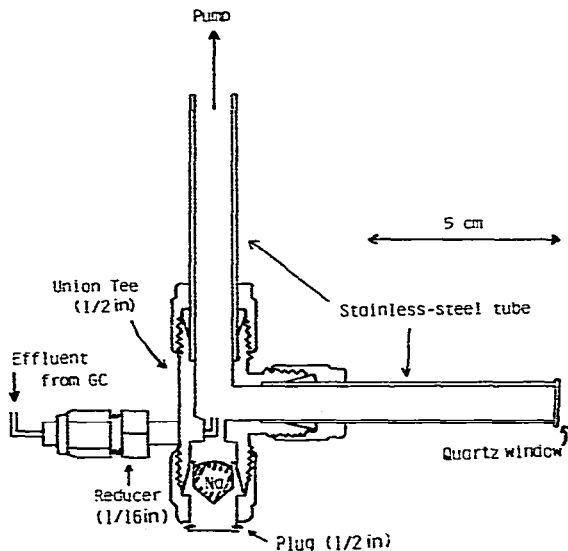


Fig. 2. Stainless-steel chemiluminescence detector (improved detector).

Since the lower detection limit ultimately depends on the noise level, great care was taken over lowering the background signal. This signal involves chemiluminescence based on trace amounts of oxygen in the argon gas stream and the stray light. Some of the oxygen comes from impurities in the argon gas used but the majority comes from air diffusing into the argon gas stream through the analytical lines. The oxygen molecules then react with atomic sodium vapour to give a weak chemiluminescence. This stainless-steel detector gives a lower background noise signal because there is no use of an extra argon carrier gas and because there is complete shielding of stray light because of the material of the detector. Employment of the low-pass active filter further lowers the noise signal.

ECD

A 10-mCi ^{63}Ni ECD in the fixed-frequency pulsed mode (frequency 12 kHz,

pulse width 8 μsec , voltage 50 V), in conjunction with a Shimadzu GC-3AE gas chromatograph, was used for comparison with the CLD. The chromatographic column was the same as that for the CLD study and the carrier gas was pure nitrogen (99.999%).

Reagents

All chemicals were of analytical-reagent grade. Each standard solution of VPHCs, except for the chlorofluoromethanes, was prepared by successive dilution with toluene or *n*-hexane. Low concentrations of chlorofluoromethanes were provided by passing nitrogen gas containing *ca.* 100 ppm of chlorofluoromethanes (Nippon Sanso) and pure nitrogen gas through a standard gas generator (Model SGGU-72, Standard Technology). A 1-ml sample of each prepared gas was introduced into the GC column by means of a gas sampler. Argon gas used had a purity of 99.999%. Sodium metal was boiled enough in toluene before use and *ca.* 1 g was used in each experiment.

RESULTS AND DISCUSSION

As a result of the simplified detector, only two variables, the temperature and pressure of the detector, were examined for detector optimization. Instead of the chemiluminescence intensity, the chemiluminescence intensity-to-noise ratio was plotted for the dependence on the detector temperature (Fig. 3), since the background and noise signals also varied. It can be seen from this figure that the curve for CCl_4 shows a trend opposite to the other two. This trend is also seen in the relation between the detector pressure and the chemiluminescence intensity (Fig. 4). Among the VPHHCs studied (including other halomethanes), only CCl_4 exhibits such behaviour, which was always observed in the preliminary experiments. This behaviour seems unreasonable because a higher detector temperature increases both the amount of atomic sodium vapour and the reaction rate and also because a higher detector

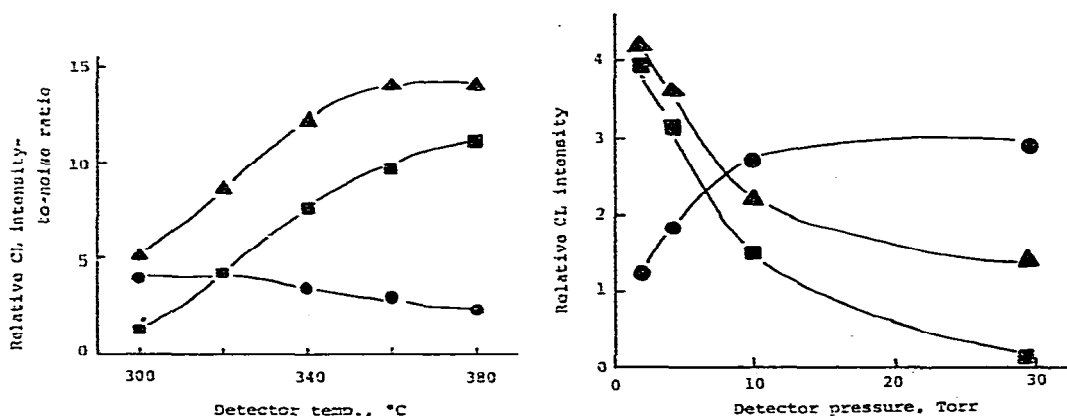


Fig. 3. Detector response as a function of detector temperature. Detector pressure: 2 Torr, ●: CCl_4 ($1.8 \cdot 10^{-10}$ mole), ▲: $\text{ClCH}=\text{CCl}_2$ ($1.9 \cdot 10^{-10}$ mole), ■: $\text{ClCH}_2\text{CHCl}_2$ ($1.9 \cdot 10^{-10}$ mole).

Fig. 4. Detector response as a function of detector pressure. Detector temperature: 350°C. Symbols as in Fig. 3.

pressure causes deactivation of the vibrationally excited NaCl molecules. One of the possible reasons is that CCl_4 is reduced to carbon atoms through the chemiluminescence reaction while other VPHHCs provide hydrocarbon molecules. However, further discussion of this topic is beyond the scope of this article.

Although optimum conditions for most of the VPHHCs studied could not be easily obtained, the detector temperature and pressure were determined, as shown in Table II, for subsequent experiments, taking into account the consumption of sodium metal during the experiment and the ease of operation. The results obtained under these conditions are also summarized in the table. The calibration graphs plotted logarithmically for the VPHHCs exhibited straight lines with slopes of unity. The table shows that the detector characteristics are significantly better than those of the Pyrex detector, *i.e.* the background and noise signals decrease by a factor of 100, and the LDLs and LDRs are 10–100 times lower and longer, respectively; in addition the detector response is arithmetically proportional to the amount of the VPHHCs. Under the optimum conditions, the relative standard deviation was less than 2% for ten successive measurements of a $1 \cdot 10^{-11}$ -mole amount of $\text{ClCH}_2\text{CH}_2\text{Cl}$. Although the RMRs show similar tendencies to those for the Pyrex detector, the following favourable trends imply that this type of detector will not suffer geometrical constraint. The sensitivities to chloromethanes, chlorofluorocarbons, and chloroethylenes increase with increasing chlorine numbers. Halomethanes containing equal numbers of chlorine atoms show approximately comparable sensitivities; even replacement of the bromine atoms in bromomethanes by chlorine gives little change. Com-

TABLE II

CHARACTERISTICS OF IMPROVED CLD

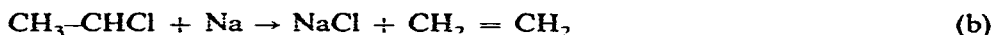
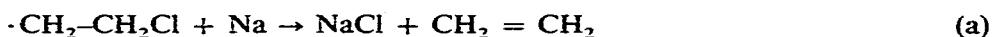
Operating conditions: detector temperature, 360°C ; detector pressure, 4 Torr. Background current: $5 \cdot 10^{-12}$ A. Noise current: $1 \cdot 10^{-13}$ A.

VPHHC	LDL (g/sec)*	LDR	RMR**
CH_2Cl_2	$7.3 \cdot 10^{-12}$		1
CHCl_3	$2.3 \cdot 10^{-12}$		3
CCl_4	$3.1 \cdot 10^{-13}$		230
CF_3Cl	$1.3 \cdot 10^{-10}$		0.04
CF_2Cl_2	$5.4 \cdot 10^{-12}$		1
CFCl_3	$1.4 \cdot 10^{-12}$		5
CHBr_3	$4.6 \cdot 10^{-11}$		4
CHBr_2Cl	$2.0 \cdot 10^{-11}$		3
$\text{ClCH}_2\text{CH}_2\text{Cl}$	$9.1 \cdot 10^{-14}$		430
$\text{ClCH}_2\text{CHCl}_2$	$1.0 \cdot 10^{-13}$		540
$\text{Cl}_2\text{CHCHCl}_2$	$8.0 \cdot 10^{-13}$	$10^4\text{--}10^6$	25
$\text{ClCH}_2\text{CCl}_3$	$3.7 \cdot 10^{-13}$		26
CH_3CHCl_2	$1.9 \cdot 10^{-10}$		0.4
CH_3CCl_3	$8.6 \cdot 10^{-11}$		0.7
$\text{Cl}_2\text{CFCF}_2\text{Cl}$	$7.3 \cdot 10^{-12}$		4
<i>cis</i> - $\text{ClCH}=\text{CHCl}$	$7.2 \cdot 10^{-12}$		2
<i>trans</i> - $\text{ClCH}=\text{CHCl}$	$2.8 \cdot 10^{-11}$		2
$\text{ClCH}=\text{CCl}_2$	$1.7 \cdot 10^{-13}$		230
$\text{Cl}_2\text{C}=\text{CCl}_2$	$7.9 \cdot 10^{-14}$		590

* For a signal-to-noise ratio of 3.

** Normalized with respect to the value for CH_2Cl_2 .

parison of the sensitivities to chloromethanes and chlorofluorocarbons makes the fluorine atoms appear inactive in the chemiluminescence reaction. This idea is supported by the experimental result that introduction of 1 ml of a gas containing 100 ppm of CF_4 , corresponding to *ca.* 10^{-9} mole of CF_4 , gives no response. This may be ascribed to the higher energies of the C–F compared to the C–Cl bonds. On the other hand, the sensitivity to chloroethanes varies with the positions of the chlorine atoms in the molecule rather than with the actual numbers of chlorine atoms. This can be interpreted by the following reaction mechanism⁵:



(R) in the chemiluminescence reaction described previously is an unsaturated molecule formed either by the closure of a double bond (a) or by the migration of a hydrogen atom (b). Reaction (b), which requires hydrogen atom migration, *e.g.*, for CH_3CHCl_2 and CH_3CCl_3 , has a much smaller light yield than that of reaction (a), *e.g.*, for $\text{ClCH}_2\text{CH}_2\text{Cl}$ and $\text{ClCH}_2\text{CHCl}_2$. Other chloroethanes listed show moderate sensitivity, with both reactions (a) and (b) being responsible for the chemiluminescence reaction. It is found from these detector characteristics that chemiluminescence will occur more smoothly and efficiently in this type of detector rather than in the Pyrex apparatus.

Atomic sodium vapour also reacts with monohalogenated compounds and with some types of nitrogen- or oxygen-containing compounds to produce chemiluminescence, the reaction mechanisms being unknown and light yields low. Thus various kinds of compounds were tested in order to estimate the selectivity of the detector. Table III expresses the results as the RMRs compared with the value for CH_2Cl_2 . Zero values mean that compounds concerned show no response at amounts of *ca.* 10^{-7} – 10^{-8} moles; *i.e.* the CLD is practically insensitive to them. On the other hand, some compounds show sensitivities of the order of 10^{-2} times that for CH_2Cl_2 . The lowest detectable amounts of these compounds are calculated as *ca.* 10^{-9} – 10^{-10} moles since that of CH_2Cl_2 is in the order of 10^{-11} – 10^{-12} moles. The amount corresponds to a 1- μl intake of solution at a concentration of *ca.* 10–100 $\mu\text{g}/\text{ml}$ or a 1-ml intake of gas at a concentration of *ca.* 1–10 ppm. It seems unlikely that these compounds are normally present in the environment in this concentration range or higher. Therefore, it can be said that the CLD is highly selective to the VPHHCs.

Comparison with the ECD

For the purpose of evaluating the CLD characteristics, the CLD was compared with the ECD with regard to LDL, LDR, RMR and selectivity. The LDLs for signal-to-noise ratios noted in Table IV are shown in nanogram units, obtained by measurements of the peak heights. The values listed may vary slightly with the elution times and in the case of the ECD they may also depend on the operating conditions. Although there is therefore no consistency in the experimental conditions in the table, it may be seen that a complementarity is found between the LDLs. For several VPHHCs especially those containing two chlorine atoms in the molecule, the CLD has a comparable or superior LDL to the ECD. For the VPHHCs containing fluorine, bromine, or localized chlorine atoms in the molecule, however, the CLD is markedly

TABLE III
RELATIVE MOLAR RESPONSE OF OTHER COMPOUNDS TO CH₂Cl₂ (= 1)

Compound*	CLD	ECD**
n-C ₃ H ₇ I	0.02	1000
C ₂ H ₅ NO ₂	0.009	1
CH ₃ COCOCH ₃	0.007	10000
(CH ₃ O) ₃ P	0.007	0.06
n-C ₃ H ₇ Br	0.007	2
CH ₃ CN	0.001	0.04
n-C ₃ H ₇ Cl	0.0009	0.03
C ₂ H ₅ OH	0.0002	0.08
CH ₃ COCH ₃	0	0.03
C ₂ H ₅ CHO	0	0.2
(C ₂ H ₅) ₂ NH	0	
C ₂ H ₅ OC ₂ H ₅	0	0.04
(C ₂ H ₅) ₂ S	0	0
C ₆ H ₅ Cl	0	0.06
C ₆ H ₆	0	0.0001

* Elution from GC column was confirmed by TCD signal.

** At 70°C.

TABLE IV
COMPARISON OF CLD AND ECD

S/N = Signal-to-noise ratio.

VPHHC	LDL (ng)				RMR**			
	CLD		ECD*		CLD		ECD*	
	S/N = 3	(A) ⁸ S/N = 2	(B) ⁹ S/N = 2 or 3	(C) S/N = 3	(B) ⁹	(D) ¹⁰	(C)	
CH ₂ Cl ₂	0.3		8.6	20	1	1	1	1
CHCl ₃	0.2	0.003	0.08	0.01	3	150	120	2000
CCl ₄	0.003	0.0003	0.002	0.0001	230	7700	2400	280000
CF ₃ Cl	10				0.04		2	
CF ₂ Cl ₂	0.5	0.002			1		46	
CFCl ₃	0.1	0.0002			5		1200	
CHBr ₃	0.2			0.0004	4			140000
CHBr ₂ Cl	0.3			0.0009	3			54000
ClCH ₂ CH ₂ Cl	0.0009		13	10	430	0.8		2
ClCH ₂ CHCl ₂	0.0009		0.07	0.002	540	190	1	18000
Cl ₂ CHCHCl ₂	0.03		0.008	0.01	25	2100		2700
ClCH ₂ CCl ₃	0.02			0.0005	26			80000
CH ₃ CHCl ₂	0.9			80	0.4			0.3
CH ₂ CCl ₃	0.8	0.002	0.03	0.003	0.7	430		10000
ClCF ₂ CFCl ₂	0.2			0.008	4			5800
cis-ClCH=CHCl	0.2		13	30	2	0.8	0.3	0.9
trans-ClCH=CHCl	0.2		8.4		2	1	0.4	
ClCH=CCl ₂	0.002		0.02	0.02	230	670	130	1800
Cl ₂ C=CCl ₂	0.001		0.003	0.001	590	5600	1100	29000

* ⁶³Ni; (A) = d.c. mode, 300°C; (B) = not specified; (C) = pulsed mode, 70°C; (D) = pulse-modulated constant-current mode, 250°C.

** Normalized with respect to the value for CH₂Cl₂.

less sensitive, as speculated from the chemiluminescence reaction mechanism. Needless to say, the LDR for the CLD is much longer than that for the ECD operated in the d.c. of pulsed mode. The RMRs in the table indicate that the CLD sensitivity to individual VPHHCs in homologous series does not differ as much as that for the ECD. The selectivities, upon which along with sensitivity great emphasis should be laid, are expressed in terms of the RMRs of various other compounds to CH_2Cl_2 (Table III). It is obvious from the table that the CLD is much more selective than the ECD; in contrast to the ECD, no compounds are more sensitive than the VPHHCs. This means that the basic problem of the ECD, the practical impossibility of predicting which compound is giving a particular response, is not present in the CLD. Consequently, the CLD possesses the advantage of permitting a more elegant detection of the VPHHCs in complex mixtures of polar compounds. On the other hand, the CLD suffers difficulties which arise from operation of the detector under reduced pressure and from consumption of sodium metal. However, these difficulties seem trivial when compared with the marked advantages described above: a load of 1 g of sodium metal can allow *ca.* 40 h of operation without any pronounced change in sensitivity, and loading of the sodium metal is easily accomplished by preparing another Plug fitting, in which sodium metal is already loaded, in advance. Thus the CLD with these favourable features succeeds in overcoming the drawbacks of the ECD. This promises to lead to its wide usage as a detector for the determination of VPHHCs by GC.

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