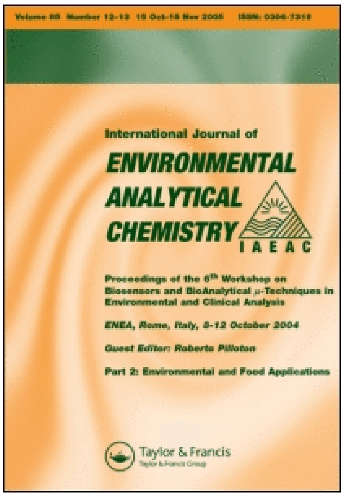


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Tracing Organic Gaseous Pollutants in the Atmosphere: The Gas Chromatographic Survey of Vinyl Chloride-and Paint industry

T. A. A. Rymen[a]
[a] Chemistry Department, S.C.K./C.E.N., Mol, Belgium

To cite this Article Rymen, T. A. A.(1979) 'Tracing Organic Gaseous Pollutants in the Atmosphere: The Gas Chromatographic Survey of Vinyl Chloride-and Paint industry', International Journal of Environmental Analytical Chemistry, 6: 1, 1 — 23
To link to this Article: DOI: 10.1080/03067317908071156
URL: http://dx.doi.org/10.1080/03067317908071156

Intern. J. Environ. Anal. Chem., 1979, Vol. 6, pp. 1–23

Printed in Great Britain

Tracing Organic Gaseous Pollutants in the Atmosphere:

The Gas Chromatographic Survey of Vinyl Chloride- and Paint Industry

T. A. A. RYMEN

Chemistry Department, S.C.K./C.E.N., Mol, Belgium

(*Received February 7, 1978; in final form May 22, 1978*)

Low molecular weight hydrocarbons, chlorinated hydrocarbons and aromatics are three groups of volatile organic chemicals that are widely used in industry and constitute a potential danger for the environment. Selective tracing of these pollutants in ambient air was performed with the aid of gas chromatography and flame ionization or electron capture detection, whichever yielded highest sensitivity. Methods of analysis, calibration procedures and sampling techniques are discussed, covering automatic operation in the field as well as discontinuous control by analyses performed in the laboratory. The efficiency of the overall procedure is illustrated by the results obtained during two pollution measuring campaigns, one performed in the neighbourhood of a vinyl chloride plant and the other in an area with an intensive paint industry.

KEY WORDS: air, pollution, organics, gas chromatography

INTRODUCTION

Organic chemicals accumulate in the air mainly as the result of either incomplete combustion or evaporation processes. The need for tracing these compounds became evident when it was realized that they are important reactants in the formation of photochemical smog and therefore, indirectly, can be deleterious to health.[1,2] This effect is strongly dependent on the type of organics present: it is generally accepted that olefinic and most aromatic hydrocarbons are more reactive than paraffinic and saturated compounds.[3]

Up to now, only a minor number of these substances have been proved to cause adverse effects directly. Well-known examples are ethylene, which even at the ppb level affects vegetation,[4,5] vinyl chlorides, a cancer provoking agent, and the cancerogenic polynuclear aromatic hydrocarbons.[6-10]

These differences among products with regard to their action, either direct or indirect, obviously raise the necessity of selective tracing. Moreover, because of the very low permissible levels, measuring techniques have to be extremely sensitive and reliable over long periods of time.

The combination of gas-solid or gas-liquid chromatography with one of the nowadays available highly sensitive detectors, meets both requirements. Provided some special care is taken regarding sampling and calibration, detailed quantitative analysis of a wide variety of pollutants can be performed at even ppb levels. The techniques described below were extensively tested during pollution monitoring campaigns performed since 1973 up to now by the Belgian Nuclear Research Center S.C.K./C.E.N., on account of the Belgian Government.

EXPERIMENTAL

Sampling

In air pollution studies the sampling method largely depends upon the ratio maximum permissible level to minimum detectable quantity. Since in the present study maximum permissible levels significantly exceeded the detection limits, direct sampling was generally preferred.

Field sampling

The technique used to take samples for laboratory analysis consists in collecting air in plastic bags. Only multi-wall bags were used, either from Carl Roth (West Germany) or from Calibrated Instr. (New York). The former consist of an aluminum foil sandwiched between polythene on the inside and polyester on the outside, the latter are made of aluminum foils embedded in polyester on both sides. After cleaning by repeatedly flushing with nitrogen and a gas chromatographic blank control, the empty bags are placed in cylinders that can be closed hermetically.

The sampling bags themselves are kept accessible for the surrounding air via a pipe, fed through the cylinder wall (Figure 1). Using a pumping system calibrated for this purpose, 5 litres of air are evacuated from the cylinder. They are compensated for by an equal volume of ambient air entering the sampling bag. As pumping time is set to take 30 minutes, the results obtained are 30 minutes' averages. This system is easily transportable and therefore permits selection of sampling areas according to

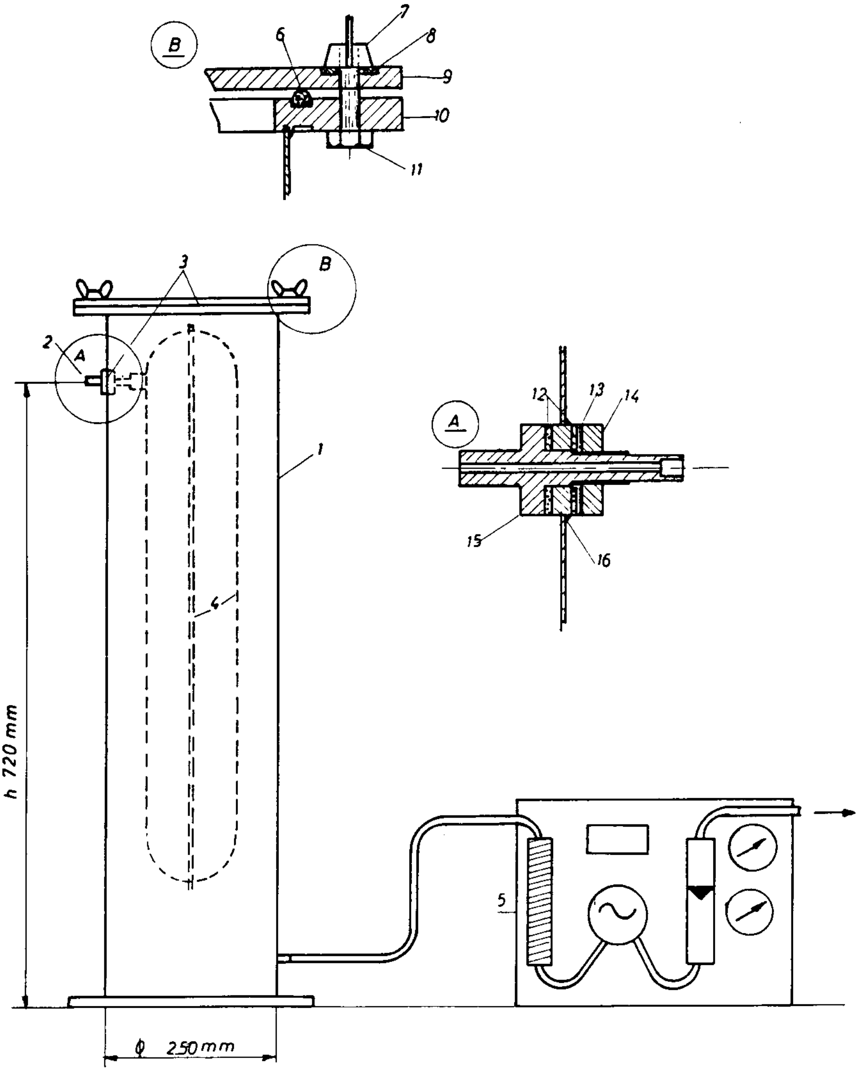


FIGURE 1 Set-up used for direct sampling. 1. Aluminum cylinder; 2. Sampling pipe; 3. Hermetical seals; 4. Sampling bag; 5. Automated pumping system with clock and timer; 6. O-ring seal; 7. Screw; 8. Rondel; 9. Plexiglass cover; 10. Aluminum flange; 11. Inox screw thread; 12. Rubber seals; 13. Rondel; 14. Brass nut; 15. Aluminium coupling; 16. Aluminium flange.

meterological conditions. Furthermore, as the air directly enters the bag, no contamination from any part of the sampling line must be feared. However, especially with the higher boiling compounds, some problems might arise from adsorption of the pollutants on the inner wall of the sampling bags. In the present application and provided the analyses were performed within three days after sampling, no troubles originating from this effect were observed. This conclusion was drawn from a preliminary investigation during which calibration mixtures prepared in sampling bags were compared with "reference standards" which were prepared by dissolving appropriate amounts of pollutants in a suitable liquid solvent, followed by dilution in this solvent. An investigation of g.c. calibration curves obtained for "bag standards" against curves found for "reference standards", never revealed significant differences (Table I). Moreover, bag standards analysed immediately or after three days storage always yielded the same results and heavily contaminated sampling bags could be cleaned rather easily by repeated flushing with nitrogen. Nevertheless, although evidently suitable for our present purpose, the sampling procedure described here may certainly not be considered as universally applicable to any organic pollutant. The possible gas adsorption on the inner walls of the sampling bags imposes a careful evaluation of the technique each time a new type of pollutant has to be traced.

TABLE I
Comparison of sensitivities resulting from "bag standards" and "reference standards"

Pollutant	Sensitivity† from "reference standard"	Sensitivity† from "bag standard"
Benzene	341 ± 5	339 ± 4
Toluene	193 ± 3	192 ± 5
Ethyl benzene	94 ± 3	93 ± 3
$(m+p)$ xylene	75 ± 2	73 ± 2
Dichloromethane	71 ± 0,6	70 ± 1
1,1,1-trichloroethane	2340 ± 70	2320 ± 37
Trichloroethylene	548 ± 3,6	545 ± 8,8
Tetrachloroethylene	9240 ± 162	9150 ± 367

†Sensitivities for different pollutants are expressed in units of area per ng of pollutant. They were calculated from 6 or more experimental measurements (covering the range from ppbv to ppmv) by the method of least squares.

Monitoring station's equipment

Permanent survey in the field was performed in a fixed monitoring station equipped to perform analyses continuously. Sample injection was either instantaneously, or was carried out from an integrated air mixture collected during 30 minutes with the aid of an Automatic Sequential Air Sampler (ASAS H 148, IG-TNO, The Netherlands). This device contains two sampling lines with a sampling bag in each of them (Figure 2).

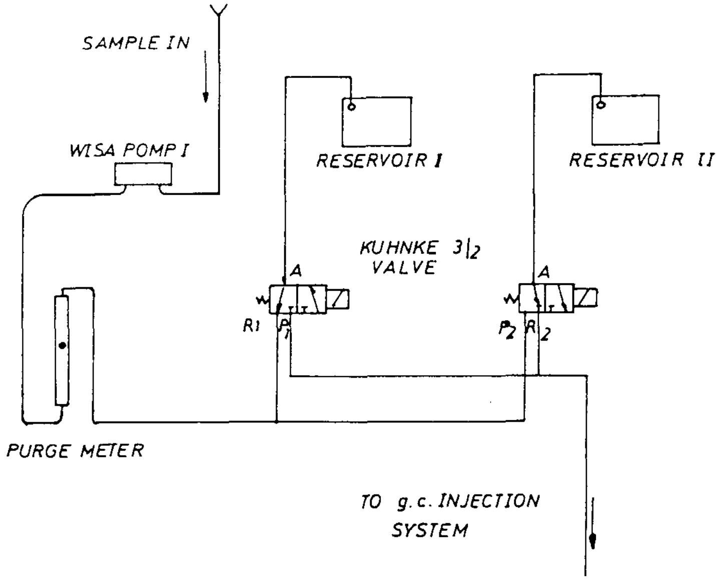


FIGURE 2 Schematic representation of the automatic sequential air sampler

Alternatively one of these bags is filled during 30 minutes, while the other is emptied through the 5 ml sample loop of the gas chromatographic injection system.

As can be seen from the set of results shown in Table II, the monitoring system quickly responds to pollution events and, afterwards, easily recovers. Therefore adsorption effects in the membrane pump, placed in front of the collecting and detecting device, must be negligible with respect to the pollutants traced and the concentration range studied ($>100\,\mu\mathrm{m}\cdot\mathrm{m}^{-3}$). This is most obvious from the large and fast variations observed for 1,2-dichloroethane.

Preconcentration on a suitable adsorbent was used a few times during the preliminary campaigns, to establish the order of priority among the pollutants present. Based upon the results obtained by Grob and Grob,[11] and Burghardt and Jeltes,[12] activated charcoal, 80–100 mesh, was chosen as the adsorbent. The material was activated by heating it for three hours at 300°C; 25 mg were then packed as shown in Figure 3, thoroughly washed with CS_2 and dried. The sampling flowrate through the carbon

TABLE II

An example of the results obtained from the monitoring station

		μg pollutant $\cdot m^{-3}$			
Date	Time	C_2H_4	Vinyl chloride	1,1-dichloroethane	1,2-dichloroethane
27.10.74	24.00	<100	<100	<100	<100
	0.30	<100	<100	<100	820
	1.00	<100	170	<100	2760
	1.30	220	<100	<100	2120
	2.00	<100	<100	<100	1440
	2.30	<100	<100	<100	810
	3.00	<100	<100	<100	<100
	3.30	<100	<100	<100	<100
	4.00	<100	<100	<100	330
	4.30	<100	<100	<100	970
	5.00	470	<100	<100	1990
	5.30	280	<100	<100	1130
	6.00	≈ 100	<100	<100	960
	6.30	<100	<100	<100	<100
	7.00	<100	<100	<100	<100
	7.30	<100	<100	<100	<100
	8.00	<100	<100	<100	<100
	8.30	<100	<100	<100	<100
	9.00	<100	<100	<100	<100
	9.30	<100	<100	<100	<100
	10.00	<100	<100	<100	<100
	10.30	620	170	<100	3250
	11.00	680	140	<100	5360
	11.30	640	180	<100	5690
	12.00	470	190	<100	4060
	12.30	500	190	<100	3580
	13.00	230	<100	<100	1480
	13.30	<100	<100	<100	330
	14.00	<100	<100	<100	<100
	14.30	<100	<100	<100	270
	15.00	140	<100	<100	1150
	15.30	≈ 100	120	<100	1190
	16.00	<100	170	<100	1650
	16.30	<100	<100	<100	340
	17.00	<100	≈ 100	<100	<100
	17.30	<100	<100	<100	1090
	18.00	<100	<100	<100	820

tube amounted to $1\,l \cdot min^{-1}$ for one hour. Desorption of the pollutants was performed by elution with 1 ml of CS_2, 1 or 2 μl being analysed gas chromatographically.

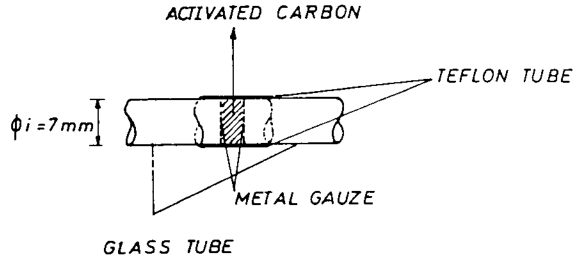


FIGURE 3 Carbon used for preconcentration purposes

Gas chromatography equipment

In the laboratory two gas chromatographic set-ups were used. The first was formed by the combination of a Pye Unicam GCV gas chromatograph with an Autolab System IV B computing integrator. Detection was performed by either FID or ECD (pulse modulated ^{63}Ni). Injection proceeded manually with the aid of 1 ml gas sampling valves. The second apparatus was a Hewlett Packard 5831-A gas chromatograph equipped with FID and a micro-processor-integrator unit as standard equipment. A special injection system permitted 16 consecutive analyses in a completely automatic way. It consists of a processor controlled 1 ml gas sampling valve in a combination with a 16 port valve and a pump. The combined equipment is processor controlled.

The field control station was set up with the aid of Techmation (Brussels) using a Tracor MF 150 G gas chromatograph (dual column, dual detector and electrometer) in combination with two Infotronics-CRS 204 integrators, a timer and a printer.

Optimum conditions for gas chromatographic analyses largely depend upon the number and types of pollutants present and, as a consequence, are more or less specific for the areas under investigation. Therefore each measuring campaign was preceded by a preliminary campaign.

Initially, g.c. columns and operating conditions were selected according to the main suspected pollutants. While information on pollutants really present in detectable amounts was accumulating, g.c. operating conditions were carefully adjusted for optimum quantitative analyses. The final operating conditions applicable to the vinyl-chloride- and paint production plants under investigation are summarized in Table III. Corresponding g.c. patterns are shown in Figures 4, 5, 6 and 7. It is obvious that different g.c. working conditions, used to trace different types of pollutants in the same area, were checked for possible interferences but none were found.

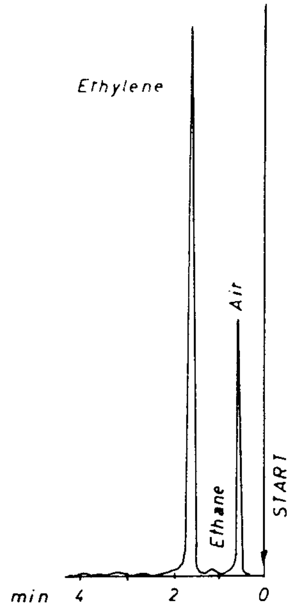


FIGURE 4 Separation of ethylene from other components in conditions described in Table I.

Calibration

Calibration was performed by the "external standard" method. Routinely standard mixtures were prepared by a two-stage procedure starting from the pure standard gases or liquids. At first an appropriate volume of liquid or gas is injected into an evacuated and previously calibrated 1-l flask. After evaporation of the liquid, the glass flask is filled with nitrogen up to atmospheric pressure. In the second step a suitable volume of this primary mixture is blended with a proper volume of nitrogen which is flowing through a line and entering a sampling bag as described previously. The total volume of nitrogen used is measured by a wet precision gas meter. Calibration mixtures prepared in this way (18 preparations over 6 months) showed a precision always better than 5% (Table IV). During the measuring campaigns detector sensitivities were checked each day with these mixtures. The detection limits reached for the different pollutants are summarized in Table V.

RESULTS AND DISCUSSION

After a preliminary research, two intensive measuring campaigns were performed in the areas to be controlled, each of them covering a six months' period. All together 980 samples were collected and analysed in

TABLE III

Gas chromatographic conditions used for quantitation of several pollutants in air samples

Area	Pollutants		g.c.-Conditions
Vinyl chloride plant	Ethylene		Alumina F column, 5′ × 1/4″, operating at 110°C Carrier gas: N_2, 60 ml·min^{-1} Detector: FID, 150°C, H_2 66 ml·min^{-1}, air 660 ml·min^{-1}
	Vinyl chloride		Tricresyl phosphate 5% on Chromsorb W, AW, 80–100 mesh, 7′ × 1/4″, operating at 60°C
	1,1,-dichloroethane		Carrier gas: N_2, 15 ml·min^{-1}
	1,2-dichloroethane		Detector: FID, 150°C, H_2 17 ml·min^{-1}, air 300 ml·min^{-1}
Paint industry	Dichloromethane	(○)	Tricresyl phosphate 5% Chromosorb W, AW, 80–100 mesh, 7′ × 1/4″, operating at 65°C
	1,1,1-trichloroethane	(×)	Carrier gas: N_2, 30 ml·min^{-1}
	Trichloroethylene	(×)	Detector: (○) FID: 150°C, H_2 33 ml·min^{-1}, air 330 ml·min^{-1}
	Tetrachloroethylene	(×)	(×) ECD: 150°C, no purge or quench gas, standing current 9.10^{-10} A
	Benzene		1,2,3-tris (2 cyanoethoxy) propane 15% on chromosorb W, AW,
	Toluene		8′ × 1/4″, operating at 65°C
	Ethyl benzene		Carrier gas: 60 ml·min^{-1}
	($m+p$) xylene		Detector: FID, 150°C, H_2 66 ml·min^{-1}, air 660 ml·min^{-1}

TABLE IV

Precision of calibration mixture preparation tested over a six-month period

	Peak height for ethylene expressed as % F.S.D. calibration mixture prepared from pure gas	Peak height for 1,1-dichloroethane expressed as % F.S.D. calibration mixture prepared from pure liquid
	73	62
	75	64
	74	63.5
	74	65
	68	63.5
	74.5	60.5
	76	58
	74	62
	74.5	59.5
	70	58
	68	59.5
	72	62
	74.5	62
	75.5	62
	73	65
	75	65.5
	75	63.5
	81	59.5
$\bar{x}$	73.7	61.9
σ%	4.0	3.8

the laboratory. The overall procedure was controlled by a number of simultaneous samplings at the same place, performed arbitrarily throughout the campaigns. Duplicate measurements resulting in detectable amounts of pollutants were used to calculate reproducibility which was between 3,8 and 9,5% (Table VI). Before interpreting the results summarized in Table VII it must be known that sample collection for laboratory analysis was always performed according to the mini-max principle, i.e. most of the samples were collected simultaneously at different places in the plume of the polluting sources, while only one or two of them were taken in the opposite direction, serving as a background control.

A detailed study of the situation in the vinyl chloride plant area pointed out that heavy pollution by chlorinated hydrocarbons ($C > 1000\,\mu g \cdot m^{-3}$ for 1,1- and 1,2-dichloroethane; $C > 500\,\mu g \cdot m^{-3}$ for vinyl chloride) was essentially restricted to an area within 1 km from the source (Figure 8).

TABLE V

Detection limits and coefficients of variation for g.c. analysis reached for the pollutants when quantitated as described in Table III

Pollutant	Detection limit $\left(\frac{\text{signal}}{\text{noise}}=3\right)$ ppbv	Detection limit $\left(\frac{\text{signal}}{\text{noise}}=3\right)$ $\mu g \cdot m^{-3}$	Coefficient of variation for g.c.-analysis (per cent)
Ethylene	4	5	0.8
Vinyl chloride	12	30	1
1,1-dichloroethane	25	100	2.5
1,2-dichloroethane	74	300	3
Dichloromethane	17	60	0.4
1,1,1-trichloroethane	0.073	0.4	0.4
Trichloroethylene	0.37	2	0.6
Tetrachloroethylene	0.15	1	0.9
Benzene	9	30	1.4
Toluene	21	80	3
Ethyl benzene	58	250	3
$(m+p)$ xylene	75	325	4.8

Pollution by 1,1-dichloroethane was found to differ from that of the other members of the group by its very irregular occurrence in time and space. In addition its appearance was always marked by an abrupt modification of the g.c. fingerprint (Figures 9 and 10) accompanied by spike pollution. All these observations point to the fact that pollution by 1,1-dichlorethane only occurs in case of "accidents".

For ethylene, important pollution was systematically detected in two zones. The first is identical with that found for the chlorinated hydrocarbons, the second is situated 2 to 3 km from the plant in the predominating wind direction (Figure 8). These findings indicate that, in favorable meteorological conditions, an appreciable ethylene pollution might occur in locations relatively far away from the polluting source. This far reaching effect of ethylene pollution in a mostly agrarian region poses severe problems. The validity of this conclusion was proved by the coincidence of pollution episodes detected with complaints deposited at the local authorities by surrounding farmers.

A comparison of these results with those obtained from the field control station, which performs 48 analyses each day, is only possible when

TABLE VI

Duplicate measurements resulting in detectable pollutant concentrations ($\mu g \cdot m^{-3}$)

C_2H_4	10	10	18	30	35	40	45	435	620	635	745
	10	10	18	30	35	40	45	445	550	640	660
	745	945	1075	1370	4000	coefficient of variation = 3.8 %†					
	665	890	1070	1230	4490						
C_2H_3Cl	105	135	150	180	240	290	370	410	540	620	
	115	135	170	170	200	340	350	435	530	590	
	coefficient of variation = 4.9 %										
1,2-$C_2H_4Cl_2$	325	330	440	440	590	610	700	795	5880		
	310	390	395	440	630	610	840	835	6180		
	coefficient of variation = 9.5 %										
CH_2Cl_2	210	225	237	333	330	365	440	751	840	1050	1897
	225	240	260	346	390	470	480	942	840	1020	1851
	coefficient of variation = 8.8 %										
1,1,1-$C_2H_3Cl_3$	4.5	14	19	20	22	34	65	182	237	369	751
	4.0	17	21	22	23	34	85	182	261	379	754
	coefficient of variation = 8.7 %										
C_2HCl_3	9	18	18	32	36	90	150	188	199	231	838
	10	16	23	36	40	100	142	192	200	198	921
	coefficient of variation = 8.4 %										
$C_6H_5CH_3$	118	130	208	233	233	265	368	380	422	492	853
	118	150	229	304	241	266	371	446	441	547	942
	923	coefficient of variation = 8.1 %									
	1026										

†Coefficient of variation $= 100\sqrt{\left(\frac{2\Sigma d^2}{n}\right)}$

n = number of duplicate measurements

$$d = \frac{\text{1st reading} - \text{2nd reading}}{\text{1st reading} + \text{2nd reading}}$$

meteorological conditions are favorable. In addition, differences in sampling place and periods covered should be taken into account. As can be expected on the basis of these differences, analyses performed in the laboratory and in the field always showed the same tendency (same maxima, same minima) but not the same pollutant concentrations (Table VIII). The validity of the information accumulated by the fixed control station more clearly shows from the results summarized over a six-months' period (Table IX) immediately following the mini-max campaign.

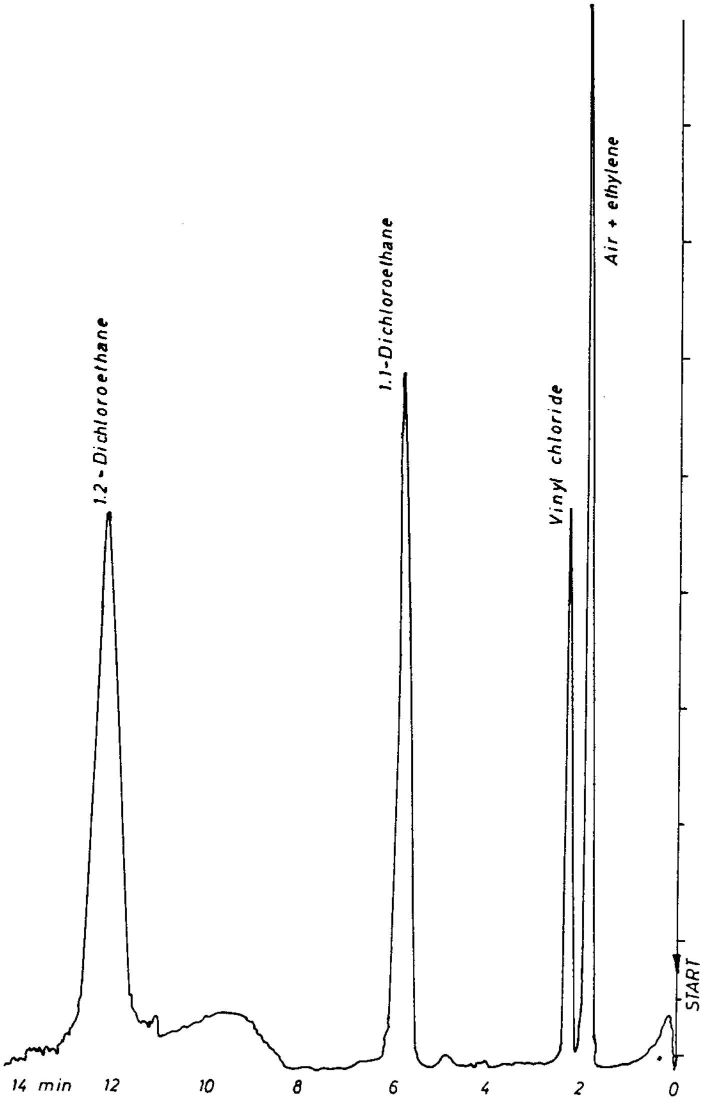


FIGURE 5 Separation of vinyl chloride, 1,1-dichloroethane and 1,2-dichloroethane in conditions described in Table I.

All information was fitted into a suitable mathematical model which permitted the formulation of requirements concerning reorganization of immission sources or the prediction of the impact on environmental pollution caused by industrial expansion. The effectiveness of the reorganization imposed was followed by the field control station and is illustrated in Table X, which summarizes the results obtained throughout 1976.

The importance of the pollutant levels detected can be better appreciated by comparing them to the maximum permissible levels for ambient

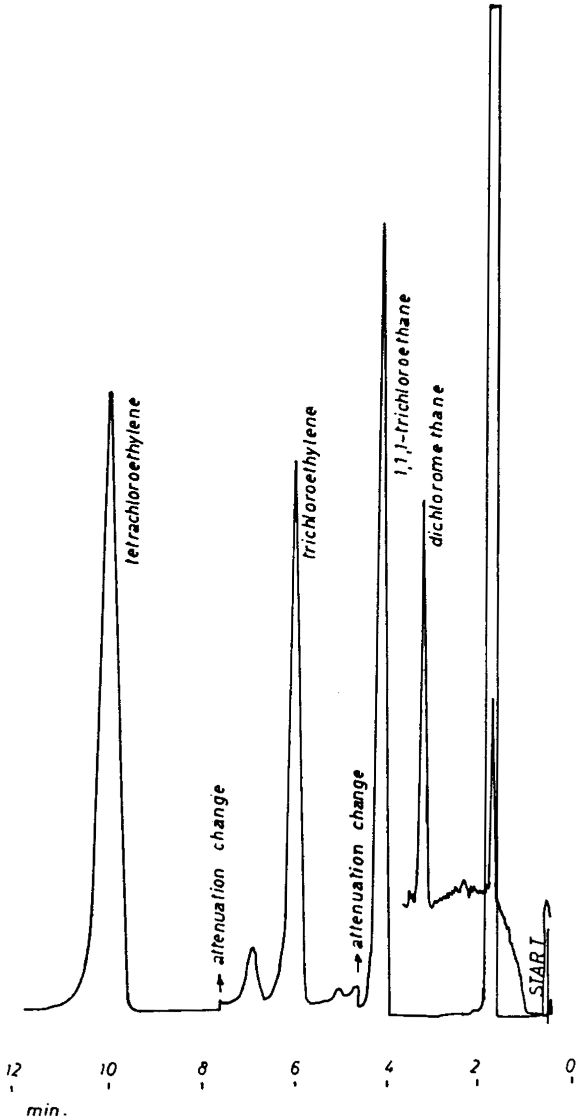


FIGURE 6 Separation of dichloroethane, 1,1,1-trichloroethane, trichloroethylene and tetrachloroethylene as described in Table I.

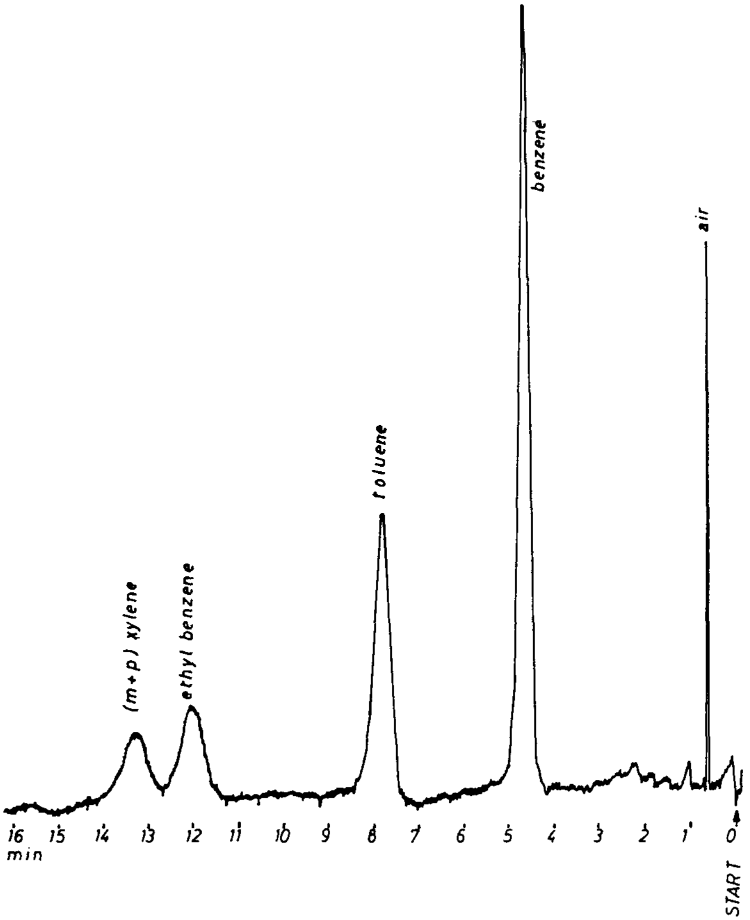


FIGURE 7 Separation of lower aromatics in conditions indicated in Table I.

air found in literature. For ethylene the American Industrial Hygiene Association recommends limits of 250 ppb over 1 hour and 50 ppb over 8 hours in agrarian zones, 500 ppb over 1 hour and 100 ppb over 8 hours in residential zones.[13] Concerning vinyl chloride the majority of instances in the U.S.A. is in favour of no detectable levels.[14] For 1,1- and 1,2-dichloroethane our only reference is the limit imposed in Russia which amounts to 3000 $\mu g \cdot m^{-3}$ for instantaneous measurements and 1000 $\mu g \cdot m^{-3}$ as 24 hours' average.[15]

The second campaign was performed in an area covered by a very intensive industry, where paint solvents and additives appeared to be the

TABLE VII

Frequency of occurrence and maximum levels found by mini-max campaigns and laboratory analysis, summarized over six months

Source	Prior pollutants	Total number of samples analysed	% with[a] C > D.L.	% with C > 500 $\mu g \cdot m^{-3}$	% with C > 1000 $\mu g \cdot m^{-3}$	Maximum levels detected in $\mu g \cdot m^{-3}$
Vinyl chloride plant	Ethylene	570	72	18	7	5 000
	Vinyl chloride		12	4	2	7 000
	1,1-dichloroethane		5	1	0,5	4 700
	1,2-dichloroethane		19	13	6	17 000
Paint industry	*Dichloromethane*	410	39	7	3	3 200
	1,1,1-trichloroethane		71	3,5	1,5	4 200
	Trichloroethylene		50	3	0,5	1 500
	Tetrachloroethylene		65	1	0,7	21 000
	Benzene		15	1	0,5	2 000
	Toluene		57	11	3	4 600
	Ethyl benzene		9	2,5	0,7	1 600
	$(m+p)$ xylene		18	10,5	3,5	4 300

[a] C = concentration, D.L. = detection limit

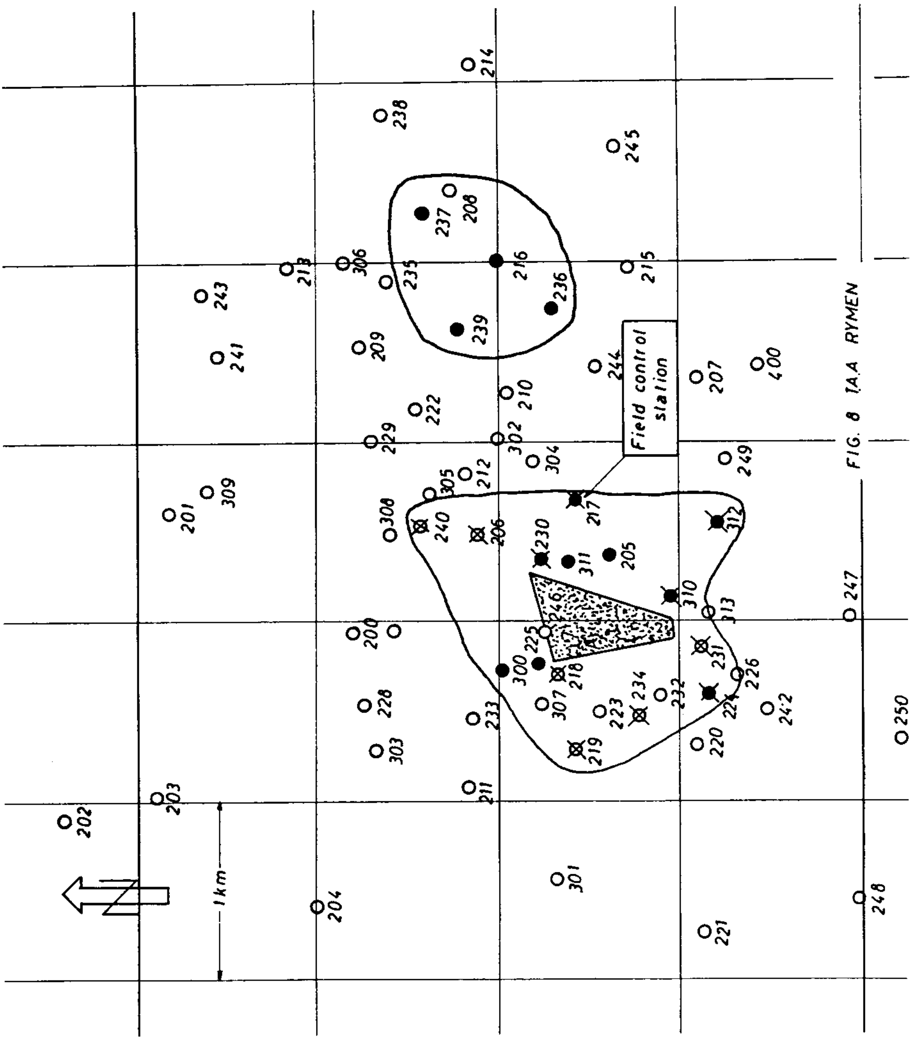


FIGURE 8 Schematic representation of results obtained during the mini-max campaign around the vinylchloride plant:

○ sampling places

● places with important ethylene pollution

x places with important pollution by chlorinated hydrocarbons

numbers: sampling point identities.

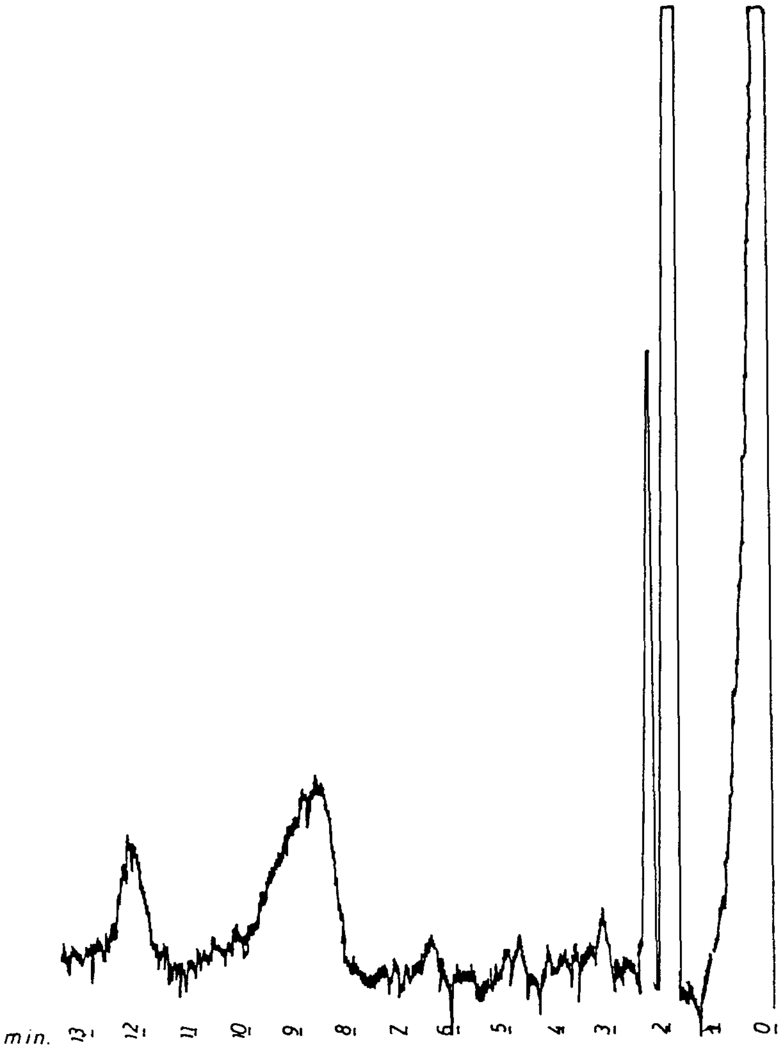


FIGURE 9 Fingerprint showing "normal" pollution by chlorinated hydrocarbons in the vinyl chloride plant area.

major organic pollutants. For all pollutants detected (Table V) pollution was restricted to two zones each of them immediately adjacent to one of the two sets of polluting sources present. A schematic representation of sources and sampling points where $C > 500\,\mu g \cdot m^{-3}$ was regularly detected, is shown in Figure 11. The hazardous nature of the pollution levels present is very difficult to be evaluated because of the wide range of

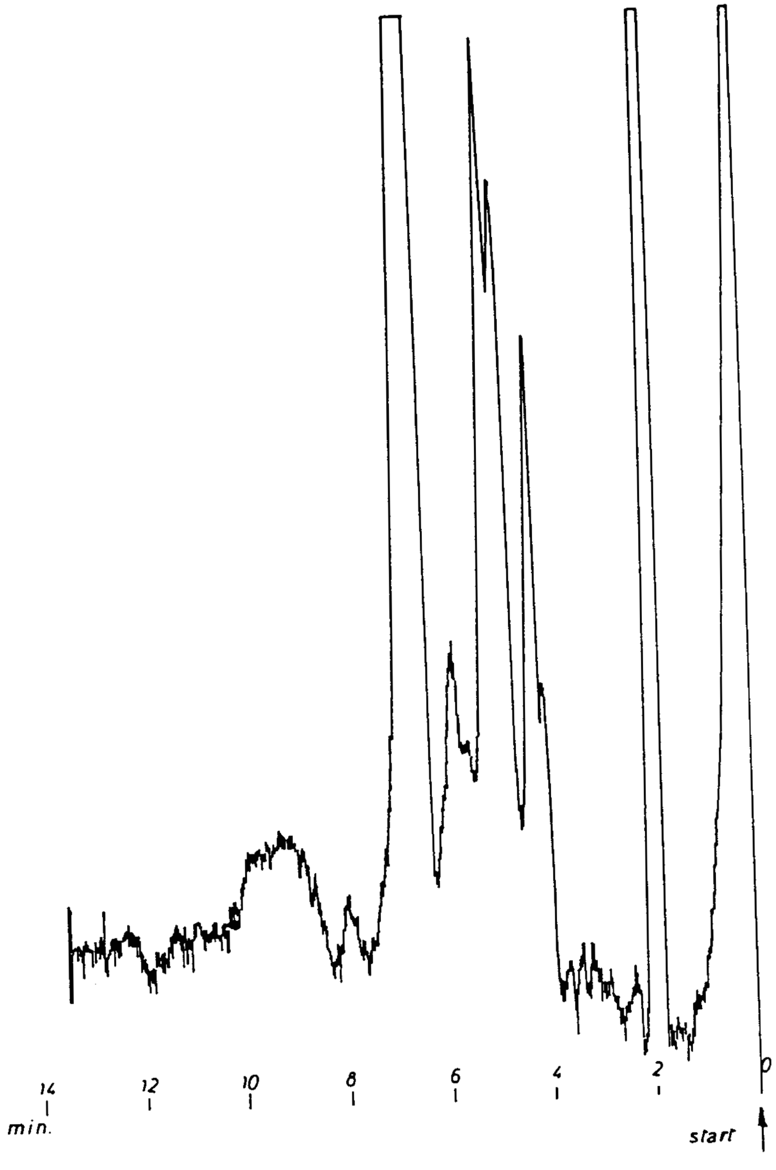


FIGURE 10 Fingerprint showing "accidental" pollution by chlorinated hydrocarbons in the vinyl chloride plant area.

TABLE VIII

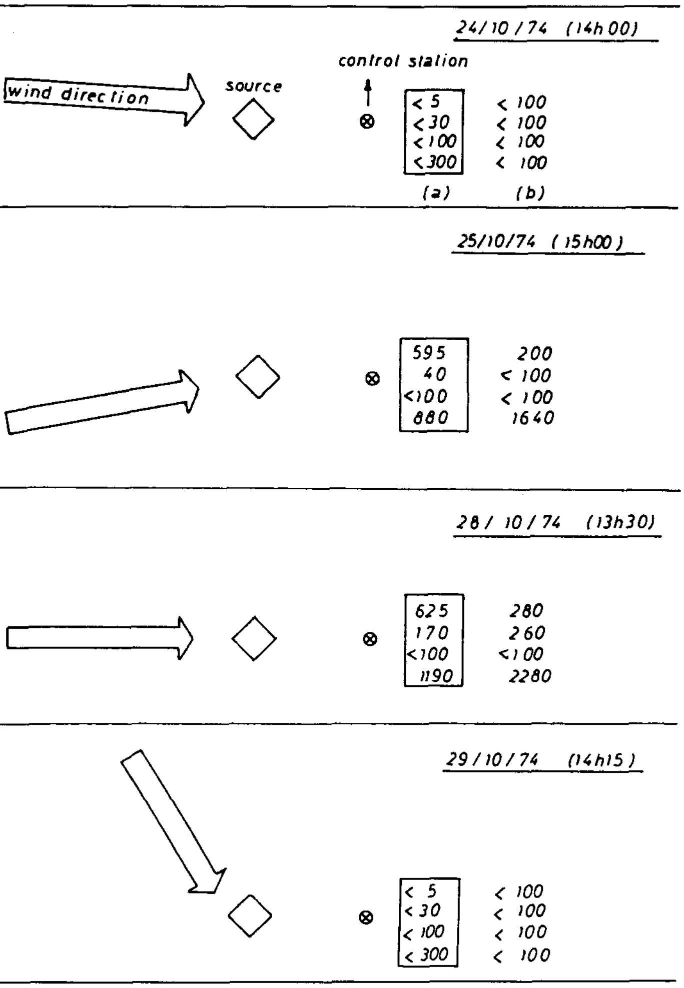
Illustration of correlation between results from the laboratory and the fixed control station

a) laboratory: 30 minutes averages

b) station: instantaneous injections

concentrations are given in $\mu g \cdot m^{-3}$ and in the order

$C_2H_4 - C_2H_3Cl - 1,1\text{-}C_2H_4Cl_2 - 1,2\text{-}C_2H_4Cl_2$



recommended maximum immissible concentrations cited in literature. However, bearing in mind the vinyl chloride story, maximum care should be the general principle.

TABLE IX

Frequency of occurrence and maximum levels detected by the field control station over the six months' period immediately following the mini-max campaign

Pollutant	Number of days controlled	% with[a] C>D.L.	% with $C>500\,\mu g\cdot m^{-3}$	% with $C>1000\,\mu g\cdot m^{-3}$	Maximum levels detected in $\mu g\cdot m^{-3}$
Ethylene		29	18	11	8 300
Vinyl chloride	170	29	7	4	7 680
1,1-dichloroethane		3	1	0	580
1,2,-dichloroethane		4	3	3	5 700

[a] C = concentration, D.L. = detection limit.

TABLE X

Frequency of occurrence and maximum levels detected by the field control station during 1976, illustrating the effectiveness of the reorganization performed

Pollutant	Number of days controlled	% with[a] C>D.L.	% with $C>500\,\mu g\cdot m^{-3}$	% with $C>1000\,\mu g\cdot m^{-3}$	Maximum levels detected in $\mu g\cdot m^{-3}$
Ethylene		5	2	0,[illegible]	1 160
Vinyl chloride	340	1	0,9	0,6	1 560
1,1-dichloroethane		0	0	0	<100
1,2-dichloroethane		2	2	1	4 780

[a] C = *concentration*, D.L. = *detection limit*

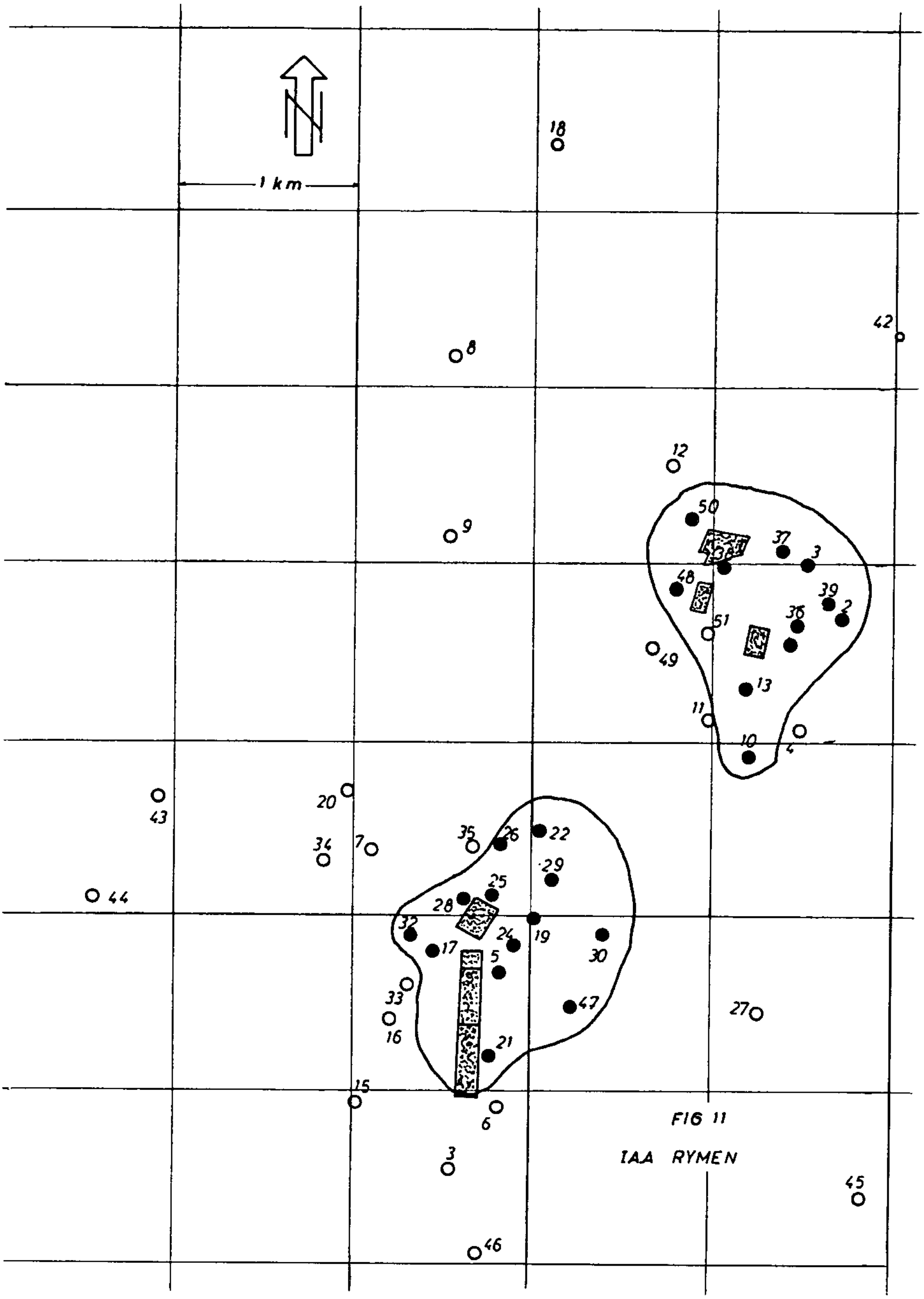


FIGURE 11 Zones showing important pollution by chlorinated hydrocarbons and aromatics as they were detected during the mini-max campaign in the second area under investigation.

Numbers: sampling point identities.

CONCLUSION

Provided some special care is taken regarding sampling and calibration, the combination of gas-solid or gas-liquid chromatography with one of the presently available highly sensitive detectors offers a versatile method of analysis for organic air pollution measurements. A careful selection of columns and g.c. operating conditions soon results in a detailed g.c. pattern, specific for the area under investigation. As ppb levels are easily reached for most compounds, analyses can be carried out directly, on air samples excluding laborious preconcentration procedures. The only disadvantage of the method consists in its limitation in time and space. On one hand analyses performed discontinuously in the laboratory permit selection of sampling places according to meteorological conditions, but only cover a restricted period of time. On the other hand the technique poses no severe problems to be automated and used in a fixed control station. In this case survey might be continuous but the validity of the results obtained will be dependent upon meteorological conditions. However, this disadvantage can be partly anticipated by a careful selection of field station implantation according to predominating meteorological conditions. The combination of both concepts seems to be a good approximation of the ideal solution.

References

1. P. A. Leighton, *Photochemistry of Air Pollution* (Academic Press, New York, 1961).
2. A. J. Haagen-Smit and L. G. Wayne, *Air Pollution* (A. C. Stern, ed.), 2nd ed., Vol. 1, (Academic Press, New York, 1967), p. 111.
3. A. P. Altshuller, *J. Air Pollut. Contr. Ass.* **16**, 257 (1966).
4. A. P. Altshuller and T. A. Bellar, *J. Air Pollut. Contr. Ass.* **13**, 81 (1963).
5. Q. R. Stahl, Air pollution aspects of ethylene, preparation for N.A.P.C.A., Consumer Protection Env. Health Science, Dept. of Health, Education and Welfare, Litton Systems Inc., Env. Systems, Dd Bethesda, Maryland.
6. S. P. Levine, K. G. Hebel, K. Bolton and R. E. Kugel, *Anal. Chem.* **47**, 1075 A (1975).
7. K. Yamagiwa and K. Ichikawa, *Mitt. Med. Fak. Tokio* **15**, 295 (1915).
8. E. L. Kennaway, *Brit. Med. J.* **1**, 564 (1924).
9. J. W. Cook *et al.*, *J. Chem. Soc.* (1933) 395–405.
10. U.S. Environmental Protection Agency, Air quality data for 1968 Publication APTD-0978 (1972).
11. K. Grob and L. Grob, *J. Chrom.* **62**, 1 (1971).
12. E. Burghardt and R. Jeltes, Report H 216-11, IG-TNO, Delft (1974).
13. IG-TNO, Delft, "Analyse van de smogsituatie in de Randstad Holland," Werkrapport G 500, December 1971.
14. "ACS for strict vinyl chloride limits," *Chemical Eng. News*, July 15, 1974, p. 4.
15. N. F. Izmerov, "Control of Air Pollution in the USSR," Public Health Papers No. 54, WHO, Geneva, 1973.
16. Maximale Immissions-Konzentrationen (MIK)—Organische Verbindungen—VDI 2306—März 1966.