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J. Rudolph^a; C. Jebsen^a

^a Institut für Chemie 3: Atmosphärische Chemie der Kernforschungsanlage Jülich GmbH, Jülich, FRG

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The Use of Photoionization, Flameionization and Electron Capture Detectors in Series for the Determination of Low Molecular Weight Trace Components in the Non Urban Atmospheret

J. RUDOLPH AND C. JEBSEN

Institut für Chemie 3: Atmosphärische Chemie der Kernforschungsanlage Jülich GmbH, D-5170 Jülich, FRG

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The set-up of a gaschromatograph with three different detectors in series is presented. The application of such a system for the analysis of light organic trace compounds in the atmosphere at low concentration levels is described. The analytical procedure combines an enrichment step at ≈ 100 K on porous glass beads, separation on a 9 m long 0.8 mm inner diameter stainless steel column packed with Duropack *n*-octane/Porosil C and detection with a photoionization, an electron capture and a flameionization detector in series. This combination does not adversely effect the performance of the detectors or the separation efficiency of the system with the exception of unstable compounds which may decompose in the ionization chambers of the PID or ECD. For the trace species under consideration in this work—light hydrocarbons and halocarbons—the detection system proved to be very useful. It combines the possibility of measuring a great variety of species with detection limits in the low ppt range with additional information on the identity of a given peak from the signal ratio of the different detectors.

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INTRODUCTION

The spectrum of organic compounds in the atmosphere—as well in polluted urban and industrial areas as in non urban regions—is very complex and their abundance may vary considerably, especially for the more reactive species with short atmospheric residence time. In addition the mixing ratios of many important trace gases are low, a few ppb (10^{-9}) to a fraction of a ppb. The most widely used technique for the measurement of organic species in the atmosphere is gaschromatography combined with ionization detectors or mass spectrometry. Although gaschromatography combined with mass spectrometry—especially in the specific ion monitoring mode—is a very selective and sensitive analytical method, the expense of a GC-MS system is inadequate high for a routine environmental monitoring instrument. Very often a specific combination of separation column and detector is used for the determination of certain compounds or groups of components—e.g. the analysis of chlorofluorocarbons by gaschromatography with electron capture detection (EC-GC). For the analysis of complex mixtures of various types¹⁻³ often different detectors are used either simultaneously or in different measurements.

Simultaneous detection with detectors of different selectivity can give additional informations on the functional groups of the individual substances, help to confirm the identity of a certain peak and increase the number of species which can be detected with sufficient sensitivity from a single gaschromatographic analysis. In most of these applications the detectors are combined in a parallel configuration by splitting the column effluent, but also the use of different detectors in series (tandem configuration) is possible.⁴ The advantages of a parallel configuration for a multidetector unit are the possibility to use more than one destructive detector (e.g. a flame photometric and flameionization detector), the ease of adjusting each detector to optimum operation conditions (temperature, gas flow rate) and reduced problems with peak broadening due to detector dead volumes. Disadvantages of a parallel connection of detectors to the column by means of an effluent splitter are the problem of a constant and reproducible split ratio—especially for temperature programming—and the decrease of the effective detection limit according to the split ratios. Since the object of our measurements is the determination of low molecular weight trace gases in the non urban atmosphere the sensitivity of the analytical method is of prime importance and thus we felt that a tandem configuration of the detectors would be best suited for the problem at hand.

The types of detectors were selected with respect to three considerations:

- 1) optimum sensitivity of the detectors
- 2) the possibility to detect a broad spectrum of light trace gases relevant for the non urban atmosphere
- 3) sufficiently different selectivity of the detectors to give some additional information on the identity of the chromatographic peaks.

Also the condition that for different detectors in series only one destructive detector is possible has to be observed. We decided to use a photoionization, a flameionization and an electron capture detector. Especially the photoionization detector promises to be valuable due to the possible change of selectivity by the use of lamps with different photon energies and its high sensitivity for unsaturated hydrocarbons.^{2,4,5}

In this paper the set up of this triple detector system is described and the advantages and difficulties in the application of such a system for the analysis of low molecular weight trace gases in the non urban atmosphere are discussed.

EXPERIMENTAL

A schematic drawing of the experimental set up is shown in Figure 1. The gaschromatograph is a Siemens L 402 equipped with an electron capture—and a flameionization detector. Additionally mounted is a HNU PI-52 photoionization detector with independent power supply, temperature control and amplifier. The detectors are connected with each other by stainless steel tubing of 0.3mm inner diameter. Only the connection of the ECD outlet with the stainless steel tubing is made of teflon in order to provide electrical insulation. All other connections including the make up gas tee pieces are stainless steel. Each detector has its own make up gas regulation in order to enable independent flow rate changes.

The detectors are connected with each other in the order of increasing optimum gas optimum gas flow rate (PID, ECD, FID) and the optimum flow rates are adjusted by means of the make up gases I-III. Flow rate is $13 \text{ cm}^3 \text{ min}^{-1} \text{ N}_2$ for the PID, $25 \text{ cm}^3 \text{ min}^{-1} \text{ N}_2$ for the ECD and for the FID $30 \text{ cm}^3 \text{ min}^{-1} \text{ N}_2$. Temperature of the photoionization detector is 360 K if a 11.7 eV lamp is used and 460 K for other photon energies. Both the electron capture and the flameionization detector are kept at 570 K. All the transfer lines between the detectors are heated to $\approx 380 \text{ K}$.

As separation column we use stainless steel tubing of 0.8 mm i.e. (1/16" o.d.) packed with Durapack *n*-octane/Porasil C (100/120 mesh). Similar

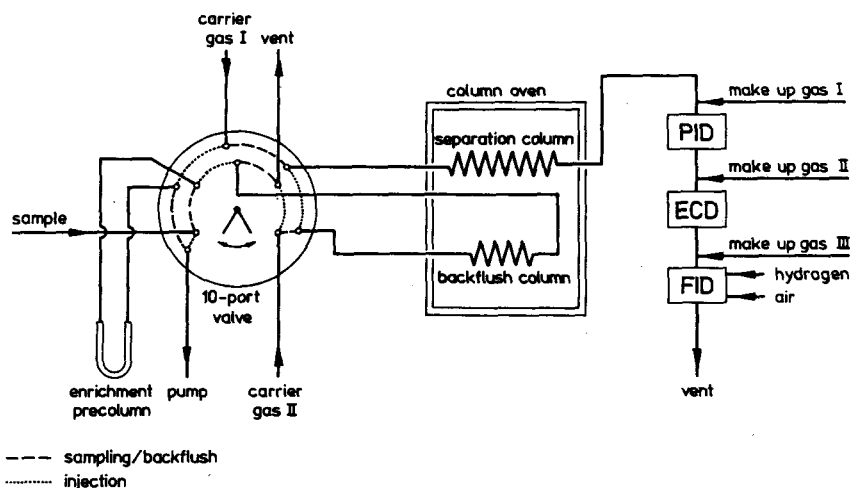


FIGURE 1 Schematic diagram of gas chromatograph and inlet system.

columns have been used for the determination of hydrocarbons by flame ionization gaschromatography⁶ and for halocarbon measurements by GC-MS in the selective ion monitoring mode.⁷ This column packing was selected because of its relatively low bleeding, its suitability for the separation of a variety of low molecular weight compounds and the possibility to operate this column at subambient temperatures down to 170 K. The separation column consists of two parts, one of 6 m length and one of 3 m length. The 3 m piece is used for backflush in order to avoid the accumulation of species of low volatility on the separation column which would result in increased baseline noise and drift. For the backflush system a ten port switching valve—which simultaneously serves as sample injection valve—is used. Since—with the exception of a few species—sample volumes of some cm³ are not sufficient for the determination of trace species in the non urban atmosphere, the sample loop of the 10 port valve is substituted by an enrichment precolumn. Various adsorbents are described in the literature for the enrichment of trace gases from air samples.^{6,8-10} We decided to use porous glass beads (≈ 60 mesh) in a 10 cm long 1/8" stainless steel precolumn at ≈ 100 K for sample preconcentration. Since the packing of the separation column is sensitive to moisture and in order to prevent the separation column to be clogged by water, the air samples are dried by means of a tube packed with magnesium perchlorate. The measurements of light halocarbons and hydrocarbons are not adversely affected by this drying procedure. For

smaller air samples the drying tube is installed between enrichment and separation column. Larger air samples are dried previous to the enrichment step. After sample concentration the rotary valve is switched into the "injection" position and the temperature of the precolumn is raised—by direct resistance heating—to about 530 K. During sample desorption the separation column is kept at 170 K to prevent peakbroadening during injection. The column is heated programmed from 170 K to 320 K with 25 K min^{-1} and from 320 K to 400 K with 2 K min^{-1} and finally kept at 400 K for up to 30 minutes if a complete chromatogram is run.

Qualitative peak identification is made according to the retention times and by co-chromatography. In addition, the peak identity can be confirmed by the signal ratios for the different detectors (see below). For quantitative evaluations, the peak heights (or sometimes the peak areas) are compared with those from standards of known trace gas mixing ratios. Appropriate standards are prepared by dilution of the pure compounds with purified synthetic air in a static dilution system (two or three dilution steps).

The air samples are collected in 2 dm^3 stainless steel containers (in special cases also containers of 10 dm^3 volume are used) and transferred into the laboratory for analysis. The design and conditioning of such sample containers have already been described in detail.¹¹

RESULTS AND DISCUSSION

An example for a chromatogram from an air sample collected in a semi-rural area in central Europe (some km outside the small town of Jülich in Western Germany) is shown in Figure 2 a-c. The FID trace is shown in 2a, ECD and PID (117. eV photonenergy) trace in 2b and 2c. In Figure 2d the trace of the PID with a 10.2 eV lamp from a different run is shown. The sample and the sample volume are the same as for Figure 2a-c. As expected, the possibilities to detect and identify different trace species are significantly increased by the use of a multidetector system, compared to a single detector.

The primary question is, whether such a multidetector system meets the requirements for the analysis of light trace species in the non urban atmosphere (e.g. linearity, reproducibility, detection limits). Table I lists the average and the standard deviation of the peakheights from seven repetitive measurements of the same air sample (0.5 dm^3 sample volume). These seven measurements were made within three days, thus the standard deviation includes also any variation due to instrument drifts. For most

TABLE I
 Reproducibility of peakheights for some selected trace gases†

Compound	Peakheight (mV)			Volume†† mixing ratios (10^{-9})
	ECD	PID (11.7 eV lamp)	FID	
CH ₃ Cl	102 ± 7%	1.8 ± 8%	0.05 ± 10%	0.7
CHCl ₃	151 ± 8%	—	—	0.15
CCl ₄	594 ± 7%	—	—	0.4
CH ₃ -CCl ₃	1925 ± 2.2%	9.6 ± 3.4%	0.56 ± 3.3%	1.5
CF ₂ Cl ₂	1900 ± 2.5%	—	—	0.8
C ₆ H ₆	—	2.6 ± 6%	0.33 ± 3.6%	0.2
C ₃ H ₆	—	1.9 ± 8%	0.42 ± 11%	2.5
n-C ₄ H ₁₀	—	6.8 ± 2.2%	0.99 ± 2.3%	1.8
CS ₂	61 ± 9%	2.7 ± 3.0%	—	0.1

†The data represent the average of seven measurements within three days and their relative standard deviation. Sample volume was 0.5 dm³.

††Errors of the absolute calibration are not included in the standard deviations listed in this table.

problems of atmospheric trace analysis the reproducibility of the measurements is sufficient, especially if it is considered that the trace gas mixing ratios are in the lower ppb and sub-ppb region. To some extent the precision of such an analysis can be increased by frequently running a standard of known composition and thus correct for instrument drifts. With this equipment it is generally sufficient to run one standard each day in order to check the instrument's performance and the stability of the calibration. For most of the compounds the relative errors obtained for different detectors are comparable. The large difference in the precision of the CS₂ analysis between the electron capture—and the photoionization detector is probably due to the interference of CFCl₃ which causes some difficulties in the evaluation of the CS₂ peak in the ECD chromatogram.

The linearity of the detector response was checked by injecting different volumes of the same air sample, In Figure 3 a plot (in a log-log scale) of the peakheight versus the amount of the individual sample is shown. For most of the species the slope is essentially unity, indicating a detector response which is proportional to the amount of substance. An exception is observed for the ECD. For signals of more than one volt the detector is overloaded, a result of the limited linear range of electron capture detectors. This occurs for some species already at sample sizes of as little as one nanogram. Thus the ECD signals cannot be evaluated quantitatively for species with extremely high response if the mixing ratios (or the sample volumes) exceed certain limits. In this case direct injection of a small sample volume without a preconcentration step should be

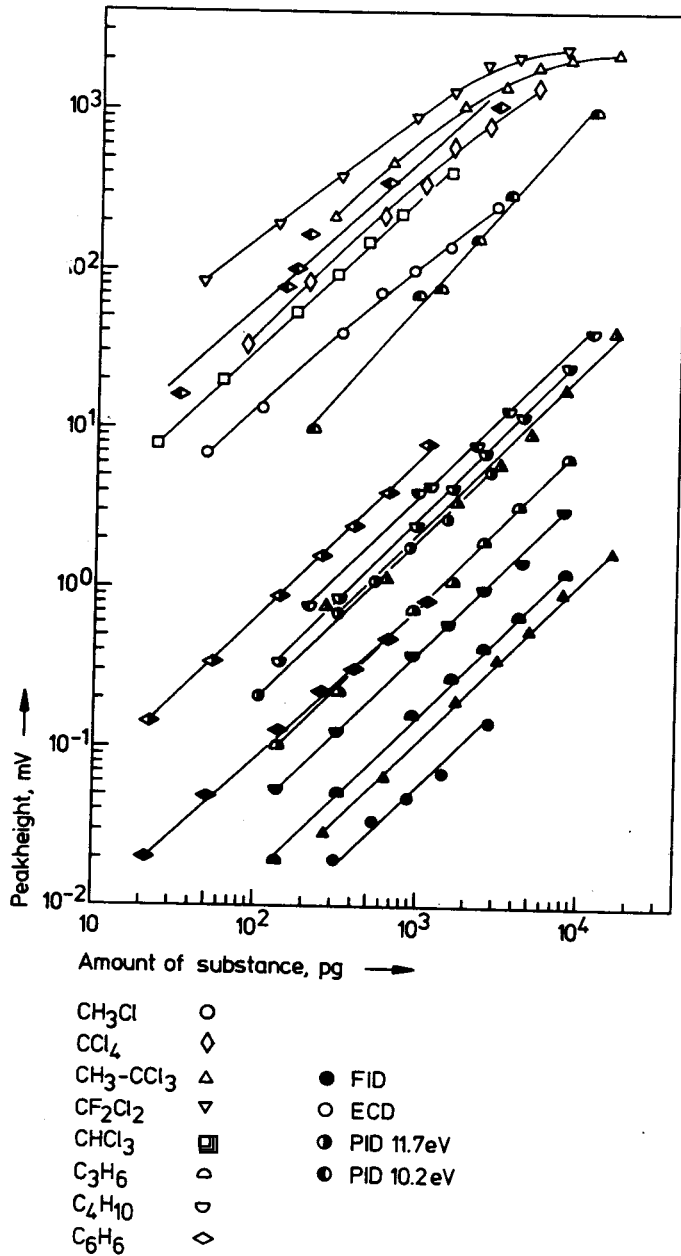


FIGURE 3 Dependence of peakheight from amount of sample for some atmospheric trace components and different detectors.

preferred. Both the PID and the FID have a significantly wider range of linearity, generally more than sufficient for the analysis of trace gases in the atmosphere. As expected, there are significant differences in the response of different detectors for the same compound. This cannot only be used to identify certain peaks, but also has the consequence that the detection limits of the same compound may differ by orders of magnitude between the different detectors. Since the noise levels of the detectors also vary by orders of magnitudes (some 10^{-6} V for the FID, but for the ECD nearly half a millivolt) the detection limit for a given species is not just proportional to the response factors for the different detectors.

TABLE II
Detection limits† of some selected atmospheric trace constituents for different detectors in a 1 dm³ air sample

Compound	ECD	Detection limit $\times 10^{12}$		
		FID	PID (11.7 eV)	PID (10.2 eV)
C ₃ H ₆	—	20	20	3
n-C ₄ H ₁₀	—	10	10	70
C ₆ H ₆	—	5	2	0.2
CS ₂	2	—	2	1
CH ₃ Cl	3	50	5	—
2-Methyl Butadiene	—	7	5	0.7
CHCl ₃	1	—	—	—
CCl ₄	1	—	—	—
CCl ₄	1	—	—	—
CH ₃ -CCl ₃	1	25	10	—
C ₂ HCl ₃	0.5	10	15	3
CF ₂ Cl ₂	0.2	—	—	—

†based on three times the baseline noise level
—not detectable in the low nanogram level

In table II the mixing ratios of several trace species are listed which in a 1 dm³ sample still show a peak with a height of three times the baseline noise level. Generally the detection limits are in the low ppt-range and thus sufficient for measurements in the unpolluted atmosphere. It should be noted that the lower detection limit for alkenes and aromatics for a PID with 10.2 eV lamp compared to a 11.7 eV lamp are caused by the higher photon intensity of the 10.2 eV lamp and are not due to differences in photoionization efficiency. The better detection limits for alkanes with a 11.7 eV lamp however are due to the strong dependence of the photoionization efficiency from the photon energy, especially for the light alkanes (cf. (2)). The detection limit of 0.2 ppt for benzene in a 1 dm³

sample with a PID at 10.2 eV photonenergy corresponds to ≈ 0.7 pg benzene absolut. This is slightly less than the value of 0.3 ppb with 1 cm^3 air sample and a signal to noise ratio of 2:1 reported by Hester and Meyer¹² for measurements with a 1/8" separation column under isothermal conditions in combination with a photoionization detector of identical type. This improvement is probably due to the use of a separation column with only 0.8 mm i.d. and of a stationary phase with an extremely low bleeding.

The chromatograms in Figure 2 clearly demonstrate the different response of the various detectors for the same compound. For a considerable number of species valuable qualitative informations on the type of compound (e.g. halocarbon, unsaturated hydrocarbon etc.) can be directly obtained from a comparison of the signals of the different detectors. The differences in the signal ratios are not only valuable in order to identify the individual compounds, but can also be used to test if there are any significant interferences from other species, provided their response ratios are sufficiently different. Since the errors of the peakheights are only a few percent, the presence of 10% of an interfering substance in a chromatographic peak could already be recognized if the response ratios for two detectors of the two compounds differ by more than a factor of 2. For most compounds the differences in the response ratios for the various detectors are even larger, as can be seen from the chromatograms in Figure 2.

The main problem with the use of several detectors in series is the possible decomposition of part of the compounds in one of the detectors, except the last one. For most of the trace species we tested in this work (that is mainly hydrocarbons and halocarbons) no such effects were observed. However, there is one surprising exception, ethyne—also present and detectable in the PID (11.7 eV lamp)—cannot be measured by the FID. Tests showed that this is most probably due to a reaction of ethyne with the surface of the gold plated ionization chamber of the PID.

CONCLUSIONS

The described system of three detectors in series meets the requirements for the analysis of the unpolluted atmosphere for light trace gases like halocarbons and hydrocarbons. The performance of the detectors and the separation efficiency of the chromatographic system is not adversely effected by the detector coupling. Compared to a single detector system the scope of species which can be determined in a single run is considerably expanded and a comparison of the different detector signals gives valuable information with respect to the identification of the

chromatographic peaks and the detection of interferences. A series configuration of detectors should not be used for the determination of unstable species—e.g. aldehydes, alcohols etc.—which can be decomposed in the ionization chamber of the detectors. For such species a split of the column effluent—with the resulting loss in the effective detection limits—cannot be avoided.

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