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Automated gas chromatographic analysis of volatile organic compounds in air

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Abstract

The performance of an automated system developed for environmental trace analysis to collect, preconcentrate and analyse organic atmospheric pollutants present in the ppb and ppt range was evaluated by taking into account the use of several detectors for identification.

Organic compounds present in air, directly taken from the atmosphere or carried to the laboratory in passivated canisters or bags, were sampled with a large volume loop, concentrated in a trap filled with different types of adsorbents, thermally desorbed and stripped by a stream of pure gas and analysed with capillary columns of different length, diameter and polarity.

A programmed temperature vaporization injector (PTV) was also used for refocusing of the sample before analysis. Flame ionization and photoionization detectors were used for the determination of aromatic and aliphatic compounds. The sensitivity and stability of the system were checked. Some examples of application to the analysis of different samples at various concentrations are described.

1. Introduction

Air monitoring for volatile organic compounds (VOC) provides information about the chemical species present in the environment which may play the role of ozone precursors, origin of the oxidizing photochemical smog, and which can be used as indicators of air quality and exposure to toxic substances. Some of the compounds, e.g. the aromatic hydrocarbons, have a direct toxic or carcinogenic action and their measurement in outdoor, indoor and working environments is required [1–4]. The analysis of these substances is generally carried out by gas chromatography, owing to the high sensitivity and/or specificity

offered by the various detectors presently available. Separation of the organic pollutants is achieved by proper selection of capillary columns of different diameter and length and filled with stationary phases of various polarities, depending on the chemical nature of the pollutants to be analysed.

Procedures used for sampling (trapping on different adsorbing materials, collection in passivated reservoirs) and analysis have been described [5,6] and official methods are provided [7–12]. The main problem is selection of the correct strategy for sample collection, which depends on many factors, such as pollutant concentration, humidity of the environment, duration and frequency of the sampling periods, location and the number of monitored points.

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Dedicated systems, often installed in working places or in pollution-monitoring stations to perform on-line continuous analysis, can be optimized to monitor selected pollutants in a well-defined concentration range and have often a rigid hardware and software configuration.

Research laboratories, however, are often requested to separate, identify and measure many different compounds over a wide range of concentrations, from thousands of ppm down to the ppb or ppt level. Possible applications which require increased sensitivity are: analysis of flue gases from the chemical industry, sewage treatment plants; control of working environments for occupational hygiene research; monitoring of the areas surrounding chemical plants or other sources of unpleasant smell or toxic vapours; identification of emission sources to highlight potential risks in the case of pollution incidents; monitoring of urban air pollution due to traffic and domestic heating; research and measurement of organic ozone precursors in areas suffering from photochemical smog.

The above list, far from being exhaustive, indicates that an analytical system suitable for many applications and over a wide range of pollutant concentrations should permit a flexible strategy of sampling and analysis methods; each of those should be applied without modification of the samples taken and analysed in the field and of samples or standard mixtures available in the laboratory, in order to permit direct comparison of the results.

We have therefore evaluated the performance of an automated system originally developed for environmental trace analysis to collect, preconcentrate and analyse many atmospheric pollutants present in the ppb range, taking into account the possibility of application to the analysis of different samples and the use of several detectors for identification purposes.

2. Experimental

Sampling and analysis were carried out by using an environmental trace analyzer Model ETA 85.21 (DANI Strumentazione Analitica

Spa, Monza, Italy), equipped with an automated sample collecting and processing unit that allows to collect a given volume of air, to trap the organic compounds, to desorb and dispatch them to the analytical unit, formed by a precolumn, by one or more packed or capillary columns, and by different types of detectors. All these operations are controlled by a flexible programming unit, which operates pneumatic valves, sets temperatures, detector sensitivities etc.

A short description of the standard process and the possible modifications is given below, with some examples of practical application.

2.1. Sample collection and processing

A schematic diagram of the sample collecting and trapping unit is shown in the left section of Fig. 1. All the surfaces that may come into contact with the sample are made of or lined with inert materials such as PTFE.

A pump provides for the aspiration of the air sample from the atmosphere, from a passivated canister or from a plastic bag; by means of automated switching valves (not shown in the figure) an air flow supplied by standard gas cylinders can be sampled at regular intervals for detector and integrator calibration. Zero air or pure inert gases can also be sampled in order to check the residual trap contamination after each analysis cycle at fixed intervals.

The thermostated sample loop, mounted on the sampling 6-ports valve V1, has a volume depending on the required amount of sample. Standard volume is 100 cm³, but samples up to 300 cm³ were used to increase sensitivity in some applications. By operating the equilibration valve, the loop pressure is equalized to atmospheric pressure; the valve V1 is then rotated and the sample sent to the trap by means of an auxiliary gas flow. This assures a constant amount of sample, independent of the different pressure of the air supplies (external air, gas cylinders, lecture bottles, canisters or bags).

The organic compounds contained in the loop volume are transferred and adsorbed in the trap mounted on the heated valve V2. Depending on the compounds to be trapped, many different

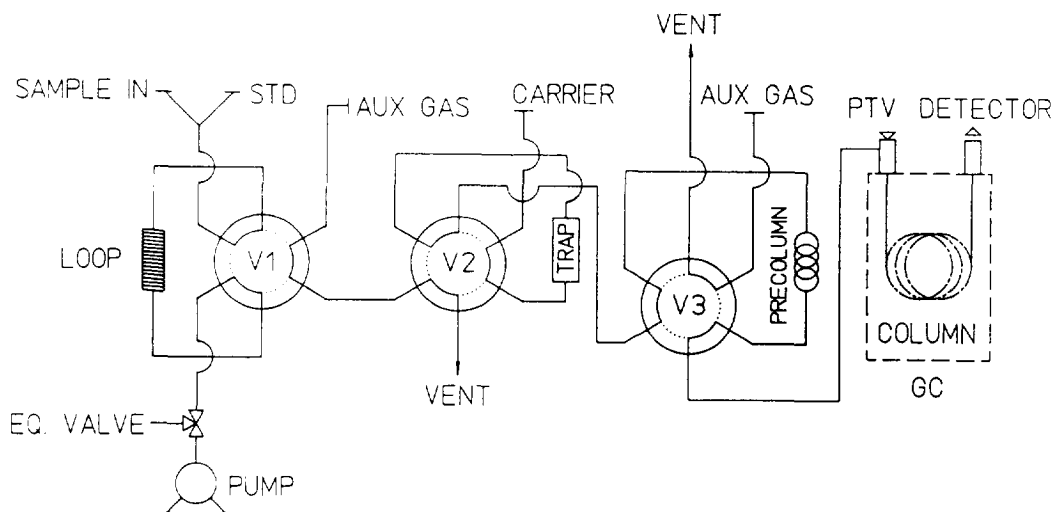


Fig. 1. Simplified diagram of the sampling and analysis system. V1 and V2: valves for loop filling and transfer of the sample to the adsorbing trap or directly to the analytical column. V3: valve for precolumn insertion and backflushing of unwanted compounds, can be replaced with an 8-port valve for multidimensional analysis with two columns.

materials can be used provided they can be effectively cleaned by the conditioning procedure and by the thermal desorption process, have a breakthrough volume large enough to trap the most volatile and less retained compounds, do not produce artifact peaks due to thermal degradation and do not irreversibly adsorb any analyte.

The following products were used: Carbo-graph (Carbochimica Romana and Alltech Associates); molecular sieves 5A, Chromosorb 106 (Johns-Manville); Graphtrap (Alltech Associates); Tenax (ENKA Research Laboratories) and Carbotrap C (Supelco).

The trap can be cooled by a cryogenic fluid circuit (liquid CO_2 or N_2) and heated by a heating mantle with a maximum speed of about $900^\circ\text{C}/\text{min}$. This procedure gives a high sensitivity also with direct sampling, because of the large volume of the loop. It is not necessary to wait a long time in order to pump enough air through the trap at low speed, to avoid saturation or breakthrough. The transfer of the sample from the loop to the trap is controlled by the flow-rate of the auxiliary gas connected to valve V1 and by the time set for the operation of the valves, and

therefore the equilibrium between gas phase and the trap material can be established, optimizing the adsorption of the sample. Integrated or averaged results can also be obtained by transferring to the trap, before thermal desorption, many samples taken at regular intervals in order to sum the amounts of pollutants, provided the breakthrough volumes of the most volatile compounds are not exceeded.

It is known that one of the main limitations in the application of adsorbing samplers is the difference in adsorptive power between different batches of sampling tubes, the initial conditioning, the contamination and artifact formation during storage [13]. In order to give ideal results, each adsorbent tube should be conditioned and tested just before sampling and its blank value checked, but this procedure obviously cannot be applied during routine work. The use of the same trap for all analyses of a given type of sample avoids fluctuation of the results due to the difference in the performance of the various samplers. After the thermal desorption of each sample the trap is clean again and can be used for the next sample. This is checked by blank sampling of pure gas at fixed intervals.

2.2. Sample analysis

When the trap (in which the total amount of VOC contained in the loop volume was collected) is heated and valve V2 is operated, a stream of carrier gas removes the trapped compounds and transfers them to the analytical unit shown in the right part of Fig. 1. Different modes of analysis are possible.

By connecting the ports 1–6 of the heated valve V3, the sample is directly sent to the injector of the gas chromatograph. For some applications (e.g. for the fast analysis of aromatic compounds such as benzene, toluene, xylenes and styrene and when resolution of xylene isomers is not required) the sample is analyzed on a wide-bore column (30 m × 0.53 mm I.D.) operated at a high carrier flow-rate (10–15 cm³/min). When higher resolution is required, a longer column must be used. When the analysis of some compounds present in the sample is not required, a precolumn can be connected to valve V3 and the heaviest compounds backflushed before entering the analytical column (see below in Section 3).

When a more complex analysis and a greater efficiency are required, longer narrow-bore columns are installed in the oven, and the programmable temperature vaporization injector

(PTV) can be refrigerated and next heated in order to trap and concentrate the compounds previously collected in the sampling trap in a narrow band (sample refocusing) [14–16].

Table 1 shows some examples of applications to different types of pollutants and lists the main characteristics of the used adsorbents, columns and detectors.

2.3. Use of precolumns and multidimensional analysis

As seen above, the 6-port valve V3 shown in the right part of the schematic diagram of Fig. 1 is used to insert a precolumn which removes the light or heavy compounds before they enter the analytical column when only few components have to be analyzed in order to shorten the total analysis time. Unwanted compounds can be backflushed by means of an auxiliary gas. This procedure is mainly used to avoid the entering into the capillary column of substances such as water and high-boiling compounds.

Multidimensional analysis, which allows to cut one or more central parts of the chromatogram and send not well resolved compounds to another more efficient column, and dual column separation, with polar and non-polar columns mounted in series [17–21], are easier obtained by

Table 1
Example of system configuration for the analysis of various contaminants in air

Sample	Trap adsorbent	(a) PTV liner (b) precolumn	Column	Detector
Ethylene oxide	Carbosphere 60/80	–	Porapak QS, 2 m × 2 mm	PID
Chlorinated hydrocarbons	80% Graphtrap 60/80 20% Molecular sieves 5A	(a) Graphtrap 60/80	Carbograph VOC 30 m × 0.32 mm	FID ECD
Volatile compounds	activated carbon	–	(a) Carbowax 20M 5 m × 0.53 mm (b) Alumina-KCl 50 m × 0.3 mm	FID
Aromatic hydrocarbons	Graphtrap 60/80	(b) Carbowax 20M 10 m × 0.53 mm	Carbowax 20M 50 m × 0.53 mm	PID
Aliphatic hydrocarbons	Graphtrap 60/80	(a) Graphtrap 60/80	PONA 50 m × 2 mm	FID

installing in the position of V3 an 8-port valve, which allows the direct or reversed connection of two columns in any requested sequence, or the separate elution of the compounds from the polar or non-polar column. Based on isothermal analysis carried out on the two independent columns and by using more or less complex calculation methods [22–26] the most efficient temperature program can be selected which allows the complete and fast separation of the compounds of interest.

Parallel arrangement is achieved by connecting, by means of a zero-volume glass press-fit union, two capillary columns of different length and/or polarity to a short piece of deactivated capillary tubing inserted in the injector. The two columns are connected to two identical detectors (FID is the best choice due to its sensitivity for all organic compounds) which permit simultaneous analysis for identification purposes. Fig. 2 shows the flow-chart for the procedure in which the results of the two parallel runs are compared and names are attributed to the peaks on the basis of the retention times within a fixed tolerance. The identification on each column is cross-confirmed by comparing the retention times and

the peak areas: correction factors are applied and the quantitative report for each column is printed. By further elaboration, the ratio between the areas or the corrected amounts of the substances identified is determined. If this ratio is equal or nearly equal to unity, the peak can be considered as free of interferences on both columns and its identity is confirmed. If the ratio is not unity, the chromatogram should be interpreted in terms of column polarity to establish what kind of interference is present and to identify the peaks correctly.

2.4. Choice of detectors

Different detectors can be installed and used separately or simultaneously after connecting them to the end of the column by proper press-fit unions and short tracts of deactivated or better methylsilicone-coated capillary tubings. Simultaneous electron-capture/flame ionization detector (ECD/FID) or FID/PID arrangements are useful for identification. The PID (photo ionization detector) is used for the analysis of aromatic compounds. In fact, notwithstanding the choice of polar columns that retard the elution of aromatic compounds, their interference with high-boiling aliphatic substances is still possible when the non-selective FID is used. However, using the PID no interference was observed (see Fig. 4).

2.5. Calibration methods

A source of standard gas can be connected to the sampling loop mounted on valve V1 of Fig. 1. Gas cylinders containing hydrocarbons and calibrated in the ppb range (SIAD, Bergamo, Italy), sampled at regular intervals, were found to give reliable results for about three months. Long-term stability of very diluted standard samples cannot be guaranteed, owing to the adsorption of the organic compounds on the walls of the cylinder. More concentrated mixtures, dynamically diluted by a stream of pure gas with a known flow-ratio, can be used in order to obtain the requested concentration. For some

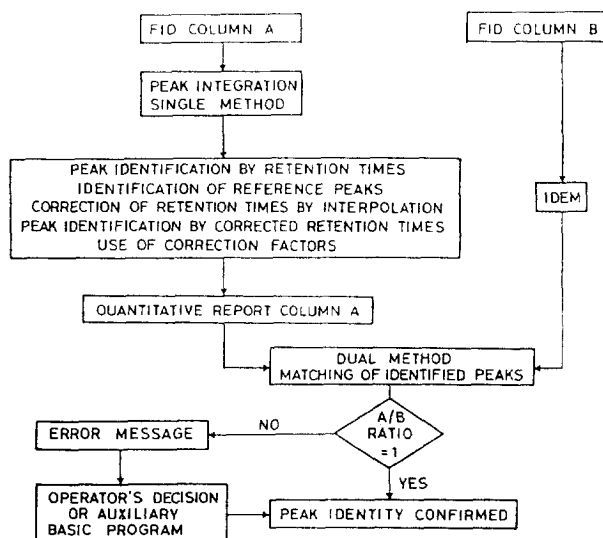


Fig. 2. Logical flow-sheet of the integrator or data system program used to identify peaks by simultaneous analysis on parallel columns of different polarity.

compounds, the use of permeation tubes is advisable.

2.6. Multiple sampling

The monitoring of urban air pollution caused by traffic often requires samples to be taken at various heights in order to study the so called canyon effect in narrow streets [27]. Fig. 3 shows how various thermostated (40°C) 300-cm^3 loops connected to sampling tubes of different height are simultaneously filled up by means of separated membrane pumps and then automatically connected in sequence to the sample input port on valve V1 of Fig. 1. While the analysis cycle described previously (filling of the calibrated loop, trapping, desorption, refocusing in the injector and GC separation) is applied to the first sample, the others are stored in the corresponding loop and will be analysed in sequence. The inertness of the lines and valves (all PTFE-

lined) is therefore essential in order to avoid sample decomposition and adsorption. In order to check if the different storage times influence the results of the analysis, three urban air samples were taken simultaneously at the same height and analysed in sequence using the PID for aromatics and the FID for all organic substances.

3. Results

The results of series of measurement carried out with some of the methods summarized in Table 1 are shown.

Fig. 4 shows the analysis of aromatic compounds obtained on a Carbowax 20M bonded-phase capillary column, $50\text{ m} \times 0.53\text{ mm}$ I.D. The upper trace shows the analysis of a reference standard (concentration 5 and 20 ppb), the second trace reports the chromatogram of a sample of urban air and the lowest trace is the result of the blank control made by repeating the complete analysis cycle with a sample of pure gas. When styrene analysis was not required, a precolumn having the same composition as the analytical column and a length of 10 m was used. After the elution of *o*-xylene the analysis was stopped by operating valve V3 at about 13 min on the 30-m and at 20–21 min on the 50-m column. The heavier compounds are then removed from the precolumn by heating and backflushing.

The reproducibility of the sampling and analysis time is of great importance for the correct automated identification of the compounds in a complex mixture. Table 2 shows the retention times averaged over a month of sampling of aromatic compounds analyzed on a Carbochrom VOC column (Carbochimica Romana and Alltech Associates) $50\text{ m} \times 0.25\text{ mm}$ I.D., filled with SP-1000 polyglycol phase. No appreciable effect of the humidity of the sampled air was observed, notwithstanding the fact that the environmental conditions during the tests changed repeatedly from warm and sunny weather to heavy rain and

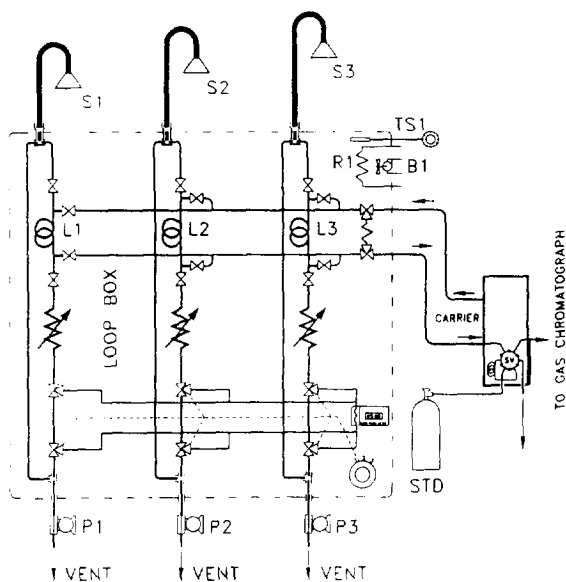


Fig. 3. Automated system for the simultaneous sampling of air at different locations or heights and transfer to the sampling loop and adsorbing trap. S1, S2, S3: sampling probes; L1, L2, L3: loops; P1, P2, P3: pumps; TS1, R1, B1: thermostating circuit.

Atmospheric aromatic hydrocarbons analysis

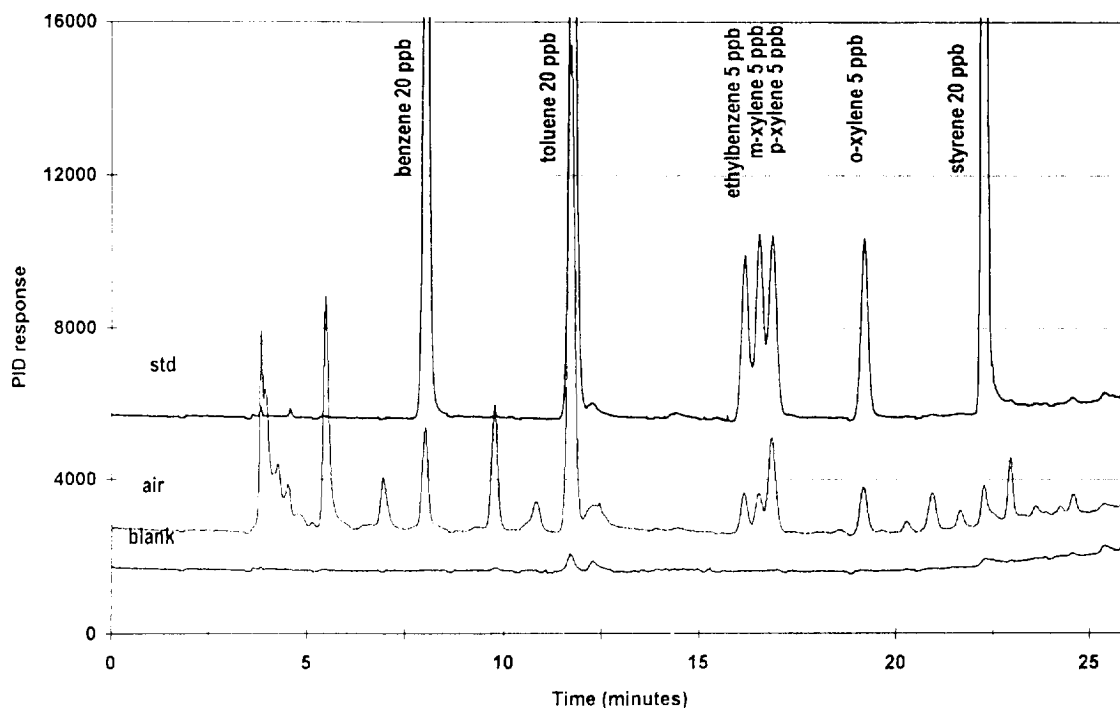


Fig. 4. Analysis of a calibration mixture of aromatic compounds (trace std), blank analysis of pure gas to check the trap cleanliness (trace blank); analysis of a real sample (trace air). Bonded polyglycol capillary column (50 m \times 0.53 mm I.D.), PID.

high humidity. The sensitivity achieved with this method for aromatic compounds with a sampling loop of 300 cm³ capacity ranges between 0.1 and 0.2 ppb.

The stability of the detectors over a wide time range is essential in order to permit comparison of the results obtained on different days. Table 3 shows the reproducibility of the response of the system to benzene, toluene, xylenes and styrene over 45 sampling, trapping, desorption and analysis cycles.

The effect of storage time in the multiple sampling procedure described in Section 2.6 is shown in Fig. 5, where the concentration of benzene measured in many consecutive analysis cycles within a car parking area is reported: the values obtained from the three lines do not show systematic scattering and therefore the different

storage times in the loops do not seem to influence the results.

4. Conclusions

The use of multiple sampling and different analysis options permits to select the best strategy depending on the nature and concentration of compounds to be detected and measured. When their concentration is relatively high, direct injection with or without injector refocusing offers the requested sensitivity.

The transfer of the sample and the concentration in the trap of the whole amount of organic substances contained in the volume of the sampling loop and the use of cryofocusing and sensitive and specific detectors permit to

Table 2
Retention times of aromatic compounds analysed over the period of one month

Compound	Averaged retention time (min)	Relative standard deviation (%)
Benzene	9.09	0.19
Toluene	10.71	0.24
Ethylbenzene	13.14	0.26
<i>p</i> -Xylene	13.76	0.27
<i>m</i> -Xylene	13.88	0.27
Isopropylbenzene	15.18	0.22
<i>o</i> -Xylene	15.40	0.24
<i>n</i> -Propylbenzene	16.67	0.17
1,3 + 1,4-Methylethylbenzene	17.40	0.15
Styrene	17.76	0.13
1,3,5-Trimethylbenzene	18.55	0.14
1-Methyl-2-ethylbenzene	18.78	0.12
<i>p</i> -Cymene	19.48	0.11
1,2,4-Trimethylbenzene	20.02	0.11
1,3-Diethylbenzene	20.64	0.10
1,4-Diethylbenzene	20.88	0.10
1,2-Diethylbenzene	21.56	0.09
1,2,3-Trimethylbenzene	21.85	0.09

Column: Carbograph VOC, 30 m × 0.53 mm I.D.; injection type, solvent split; programmable temperature vaporizing injector: 30°C for sample focusing, 300°C for evaporation; column temperature program, 40°C for 10 min, 2°C/min up to 60°C, 10°C/min up to 190°C.

increase the sensitivity of the method to the sub-ppb range. In comparison to conventional trapping in adsorbent tubes, which takes a long time and therefore does not permit instant-

Table 3
Reproducibility of the system for analysis of aromatic hydrocarbons over 45 analysis cycles

Compound	Averaged concentration (ppb)	Relative standard deviation (%)
Benzene	19.87	0.75
Toluene	19.38	1.01
Ethylbenzene	5.05	1.90
<i>p</i> -Xylene	4.99	1.72
<i>m</i> -Xylene	4.95	1.11
<i>o</i> -Xylene	4.96	0.81
Styrene	21.52	1.68

Bonded Carbowax 20M capillary, precolumn 10 m × 0.53 mm I.D., column 50 m × 0.53 mm I.D., PID (see chromatogram in Fig. 2).

aneous sampling, this technique allows more separate samples to be taken at the same time and analysed in the desired sequence and with the proper method.

Direct sampling from the atmosphere in fixed monitoring stations or the storage of the samples in passivated canisters or plastic bags for subsequent analysis in remote locations allows the use of the sampling system both for unattended automated monitoring of air pollution and for laboratory research and calibration purposes.

Although tabulated results are available for many VOC contained in air polluted by urban traffic, their identification is generally carried out on the basis of retention times on two columns of different polarity and confirmed by comparison with standard samples [28,29].

The control of pollution due to flue gas emission in industrial areas with many different plants and stacks, or due to improper disposal of industrial wastes, on the contrary, requires the identification of many and often unexpected

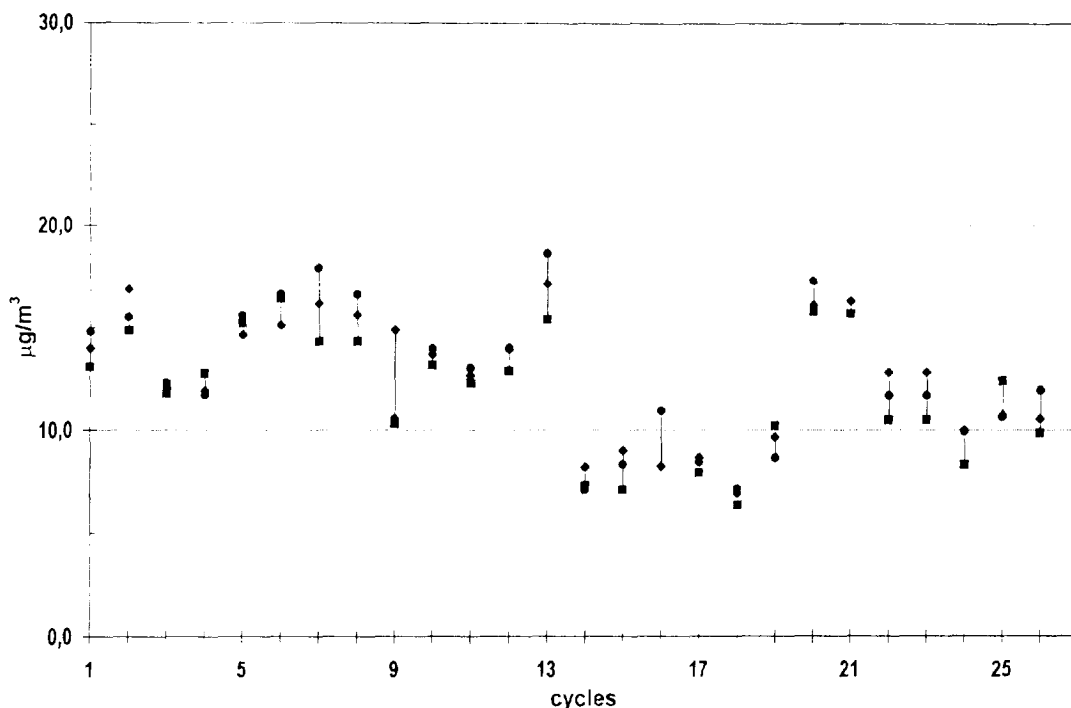


Fig. 5. Results of the analysis of benzene (PID) in many analysis cycles, sampled simultaneously with the system shown in Fig. 3. The different symbols refer to the three sampling lines.

compounds [30,31]. Coupling of conventional gas chromatographic detectors with mass spectrometers is suitable with relatively concentrated samples, as the sensitivity in the total-ion monitoring mode ranges between some nanograms for quadrupole mass analysers and about 2–10 pg for ion-trap detectors [32–36]. The selected-ion monitoring technique offers a ca. ten-fold increase of sensitivity of both detector types but, of course, can only be applied to confirm the presence of expected compounds. The possibility to increase the amount of trapped pollutants by repeated transfer of the loop volume to the refrigerated trap, described above, permits to collect enough material to detect many unknown compounds and identify them by means of automated library search algorithms.

The linearity of the sampling system and the detector can be evaluated over a concentration range of some decades by using an exponential dilution flask [37–39]. However, such a calibration method is time-consuming, does not

permit full automation and is justified only for detectors whose sensitivity does not change appreciably with time, as the FID or the PID are. In this instance, if the calibration plot is linear, by checking one or two points of the line by means of known samples, the long-term quantitative accuracy is confirmed; deviations greater than a fixed value, automatically detected by the integration system, indicate that the calibration and linearity checking must be repeated.

The overall stability of the system, however, due to sampling, storage, desorption and analysis of the sample, is high enough to permit the automated operation of the equipment over a long period of time, without the need for calibration.

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