The Influence of Sampling Methods and Different Gas Chromatographic Systems on the Determination of Concentrations of Volatile Hydrocarbons in Air Samples

A. Juszkiewicz, B. Kijak

Jagiellonian University, Faculty of Chemistry, Department of General Chemistry, Ingardena 3, 30-060 Krakow, Poland

Abstract

A study was performed in order to compare two techniques of air sampling, i.e. with use of SUMMA canisters and with use of sorption tubes. Analyzed air was collected in Krakow and Vienna together with calibration mixtures containing 7 and 27 hydrocarbons of known concentrations. The samples were analyzed using two different gas chromatographs equipped with different columns and with FID detectors.

Introduction

Large quantities of volatile organic compounds are emitted into the atmosphere as a result of antropogenic and biogenic processes [1, 2]. These compounds are closely related to photochemical oxidant formation [3-5]. Over the past 20-30 years much experimental work has been carried out all over the world concerning the physical and chemical processes occurring in the atmosphere [6, 7]. But unfortunately, analytical and statistical approaches will influence reported levels since a standard approach is not adopted by all research.

Chemical analysts agree that material sampling and its preparation for analysis plays an important role in the whole process of analysis and consequently affects the final results. Atmospheric air, being a mixture of a high number of substances, can be sampled either directly to special tanks (isolation method) or while sampled can be subjected to partial separation of its components and concentration of the substances to be analyzed (aspiration and sedimentation methods) [8, 9]. Which sampling method is chosen depends on a number of factors such as properties of the analyzed substances, the purpose of the analysis, and availability of equipment and means.

The choice of the best sampling method and the correct execution of this analytical step constitutes an introduction to obtaining correct results. However, it is commonly known that the analysis of the same sample in two different laboratories does not necessarily produce the same results. The origin of the observed discrepancies is complex, and authors commonly avoid comparing results that were obtained using different analytical methods.

The aim of this work was to compare two air sampling methods, one with the use of SUMMA canisters and the other with the use of sorption tubes, in terms of their usefulness for determinations of non-methane hydrocarbons in ambient air, as well as to determine the effects of the sampling methods and of the applied chromatographic set-ups on the final results of the determination of concentrations of volatile non-methane hydrocarbons in ambient air.

Experimental

Analytical Equipment and Methods

Two gas chromatographs were used: Varian (type STAR 3600CX) and Hewlett Packard (type HP 3890), equipped with flame-ionization detectors (FID), capillary columns and cryogenic traps to concentrate the samples.

Table 1. Characteristics of gas chromatographs: HP 3890 and Varian Star 3600CX.

	GC Hewlett Packard 3890	GC Varian Star 3600CX
detector	FID (250ºC)	FID (250ºC)
column	PLOT GS-Alumina Al_2O_3/KCl length 30 m, diameter 0.53 mm	DB-1 film 3 μm, length 60 m, diameter 0.32 mm
carried gas	helium (6 ml/min)	helium (2.5 ml/min)
column temperature program	40ºC for 2 min, 10ºC/min up to 190ºC	-60ºC for 1 min, 8ºC/min up to 20ºC, 5ºC/min up to 180ºC
sample concentration	cryogenic trap cooled with liquid nitrogen	cryogenic trap cooled with liquid nitrogen
mean volume of analyzed air sample	2000 cm³	160 cm³
time of analysis	25 min termodesorption of sorption tube, 1 min cryogenic concentration, 40 min chromatographic analysis	4 min cryogenic concentration, 50 min chromatographic analysis
sampling	sorption tubes	canisters, sorption tubes

Hewlett Packard 3890 Gas Chromatograph

The Hewlett Packard gas chromatograph was equipped with a GS-Alumina PLOT capillary column, 30 m long, 0.53 mm in diameter. The column is applied for separation of aliphatic hydrocarbons containing up to 6 carbon atoms in their molecules. Specification of the chromatograph is presented in Table 1.

With this chromatograph only samples collected with the sorption tubes were analyzed. The sorption tube was attached to the set-up in such a way that a carrier gas flowed consecutively through the tube, a Nafion drier and the cryogenic trap. Drying of the samples was necessary because of the sensitivity of the applied column to water vapour [10, 11]. In order to desorb the adsorbed substances, the sorption tube was heated at 230°C for 25 minutes. During thermodesorption the trap was cooled with liquid nitrogen in order to collect the analyzed substances. Next the valve was closed, the trap was heated and the substances from the trap were dosed to the chromatographic column for separation.

Sorption tubes. The tube sorption materials were selected in such a way that both the most volatile and less volatile hydrocarbons were retained in the tubes while passing air samples through them. Since at present a substance that would adsorb hydrocarbons of 2 to 10 carbon atoms is not available, the tubes are commonly filled with several layers of different adsorbents [12, 13].

The sorption tubes, made of glass 1 mm thick, 15 cm long and 4 mm in inner diameter, were filled with the following layers of adsorbents:

I layer: Tenax TA, 35-60 mesh (Chrompack); 2,6-diphenyl-p-phenylethylene based macro- porous poly mer adsorbing organic compounds having at least 6 carbon atom chains,

II layer: Carbotrap (Supelco), activated carbon adsor bing hydrocarbons having 4 to 8 carbon atom chains,

III layer: a mixture of Carbosieve S-II 60/80 mesh (Supelco) and Molsieve 5 A 60/80 mesh (Chrompack) - molecular sieves strongly binding the most volatile hydrocarbons.

Each layer of about 300 mg adsorbent was separated with silanized glass wool in order to prevent the layers from mixing. The openings of the tubes were closed with metal screws (Swagelock) with gaskets (Supeltex M-2A Vespel-Ferrules).

During air sampling air was first blown through the Nafion dryer (Molsieve 5L, Pellets, Fa. Supelco), and next through the sorption tube in the direction indicated in Fig. 1. The flow rate and sampling time were measured. The applied flow rate was 70-90 cm³/min and the sampling time was 20-30 min.
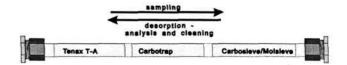

Fig. 1. Sorption tube.

Cleaning of sorption tubes. The tubes were cleaned before use by heating at 240°C overnight, in pure helium flowing through the tubes at a rate of approximately 20 ml/min. The cleaned tubes were hermetically closed, and in the case of their storage longer than 1 day they were placed in air-tight containers filled with helium. After each cleaning the degree of cleaning was checked at randomly chosen tubes. It was found that independent of the time of cleaning, considerable amounts of ethene, propene and toluene were present in the cleaned tubes. By repeating the process of thermodesorption without detaching the tube

from the system, concentrations of all the substances lower by about 20% were obtained. This indicates that only a part of contamination originates from adsorption of substances taking place while manipulating the open tube, and that its considerable part is continuously liberated from the sorbent [14].

Calibration of HP 3890 system. The system was calibrated with use of a calibration mixture containing 7 hydrocarbons in nitrogen, each of concentration 15 ppm: ethane, acetylene, n-propane, n-butane, n-pentane, n-hexane, n-heptane (Messer Austria GmBH). To measure the volume of the calibration mixture a 1 ml gas syringe was used. The calibration mixture was dosed directly to the chromatographic set-up as well as through the sorption tubes, taking into consideration adsorption and desorption. Reproduction of dosing was checked and the calibration coefficients of each component of the calibration mixture were determined. The dosing reproduction error was within 10%. The direct dosing of the calibration mixture allowed us to eliminate the contribution of tube contamination to the detected signal as well to determine the degree of recovery of hydrocarbons from the sorption tubes. For all the examined compounds the degree was close to 100 %. The highest relative standard deviation was noted for ethylene, which is the compound present in the cleaned tube in the highest amounts.

As a result of the chromatographic analysis of ambient air a sequence of peaks and their surface areas were obtained. Peaks were identified with use of retention times. Peak surface areas were calculated into concentrations, taking into account the volume of the air sample and mean concentration of contamination in the cleaned tube. Since in the case of hydrocarbons the FID signal practically does not depend on the structure of hydrocarbons, depending mainly on amounts of detected substances [15, 16], in calculations the mean calibration coefficient, i.e. that of propane, was used for all the examined hydrocarbons.

Varian Star 3600CX Gas Chromatograph

The Varian gas chromatograph type Star 3600CX is equipped with a cryogenic trap, a nonpolar column DB-1 (60 m long, 0.32 mm in diameter, 3 µm film) and a flame-ionization detector. The work of the chromatograph, detection of signals and all the calculations are operated by a "Star Chromatography Workstation" program, version 4.5. Samples are dosed to the set-up with use of a pump (Sierra Instrument Inc.) and a flow regulator (Side-Trak, Sierra Instrument Inc.) [17]. With this set-up

samples collected in the sorption tubes and in metal SUMMA canisters were analyzed. The characteristics of the chromatograph are presented in Table 1.

SUMMA canisters. SUMMA canisters are containers 6 dm^3 in volume, made of electropolished stainless steel, having the internal surface passivated in the SUMMA process [18, 19]. They are containers of multiple reuse; they are washed by blowing either pure air or nitrogen, and pumping out the gas up to the pressure of 10^5 times lower than the atmosphere. For air sampling the canister valve (Nupro SS-4HS) is opened, and as a result of pressure difference air is aspirated into the canister. Each canister has a paper filter used to avoid collecting dust.

Calibration of the set-up. The set-up was calibrated with a calibration mixture of 27 hydrocarbons in nitrogen (National Physical Laboratory, UK) of concentrations between 5 and 68.5 ppbv. Peaks were identified with use of both retention times and Kovatc temperature indexes of retention [20, 21]. In order to identify a higher number of compounds, temperature indices of retention available in the literature were applied to an appropriate chromatographic column. This extended the number of the analyzed compounds to 56. Similarly to the HP 3980 analysis, one calibration coefficient (i.e. that of propane) was used in calculations for all the hydrocarbons.

Comparative Experiment

The materials used for a comparative experiment included a mixture of 27 hydrocarbons in nitrogen and ambient air collected in Cracow in the morning of 14 August 98. The mixture of 27 hydrocarbons was first analyzed directly on the Varian Star 3600CX chromatograph (reference point), and then the mixture was collected in the sorption tubes and analyzed with the two gas chromatograph. The amount of the mixture sorbed in the tubes for analysis with the Varian Star 3600 CX chromatograph was about 160 cm^3, and that for analysis with the HP3890 was about 1000 cm^3. The analyses were performed both on the day of sampling and after 3 days of storage of the tubes with the adsorbed gases.

Ambient air was sampled at the height of the second floor from the Faculty of Chemistry of Jagiellonian University. The air was collected in 10 sorption tubes and in 10 canisters. The samples were collected at 30 min. intervals simultaneously to 2 sorption tubes and to 2 canisters. The former were analyzed with the Hewlett Packard chromatograph, the latter with the Varian Star 3600CX chromatograph.

Table 2. Performed measurements.

Sample	Sampling method	Chromatographic analysis
mixture of 27 hydrocarbons	direct introduction to the set-up	Varian Star 3600CX
	sorption tubes	Varian Star 3600CX
	sorption tubes	Hawlett Packard 3890
ambient air in Cracow	SUMMA canisters	Varian Star 3600CX
	sorption tubes	Hawlett Packard 3890
ambient air in Vienna	sorption tubes	Hawlett Packard 3890

Ambient air was also collected in Vienna in the centre of the city, at the height of the third floor, at a distance of 10 m from the street of considerable flow of traffic. The samples were collected in the sorption tubes and analyzed with the Hewlett Packard 3890 gas chromatograph. The samples were collected every day for 2 weeks in September 1998 between 1 and 2 p.m., and additionally in the same period for 2 days the samples were collected every hour. The results are listed in Table 2.

Results and Discussion

The Mixture of 27 Hydrocarbons - Analysis with Use of the Varian Star 3600 CX Gas Chromatograph

The volumes of 160 cm^3 calibration mixture containing 27 hydrocarbons were sorbed in the sorption tubes and analyzed both directly after sorption and after 3 days of storage. The same volume of the mixture was analyzed after direct collection in the cryogenic trap. The results of the measurements, i.e. concentrations of all the analyzed compounds, are presented in Fig. 2.
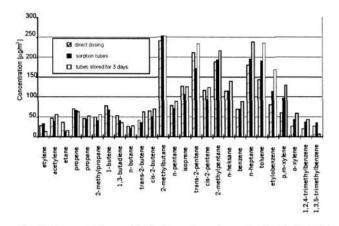

Fig. 2. Concentrations of 27 hydrocarbons determined with the GC Varian Star 3600CX: (▨) direct dosing, (■) sampling with use of sorption tubes; analysis performed immediately after sorption, (□)sampling with use of sorption tubes; analysis after 3 days of storage.

The best agreement between the two studied sampling methods was obtained for aliphatic hydrocarbons. The total alkane concentration determined in the sorption tubes decreased by about 1% as compared to their concentrations determined directly. The highest losses at the process of adsorption were observed for ethane (-62%), which results from its high volatility. Adsorption is a process dependent on temperature of the sorbent, and in the case of more volatile compounds this temperature plays an important role. It was suggested in [22] that better results could be obtained if the sorption is carried out at lower temperature.

In the case of alkenes concentrations obtained after adsoqition and desorption in the sorption tubes were lower by about 16% than those obtained with direct dosing. The only compound whose concentration increased is ethylene. However, this increase can result from the high level of this compound in the cleaned tubes.

The concentrations of aromatic hydrocarbons increased considerably after the sorption-desorption process in the tubes. For benzene a close value was obtained (increase by 1%), but with an increasing number of functional groups in the aromatic ring this increase grows, e.g. for toluene an increase by 44% was observed, and for xylenes the increase was by more than 90%.

In the case of the stored tubes with adsorbed gases, it was found that the concentrations of the majority of compounds increased after 3 days of storage. The biggest changes were noted for aromatic compounds, next for alkenes, and the smallest for alkanes. Only for 5 compounds, i.e. ethylene, propene, 1-butene, 1,3-butadiene and 1,3,5-trimethylbenzene, the concentrations decrease.

The comparison of the content of the tubes determined after 3 days of storage with the concentrations of the compounds determined directly shows that the increase in concentration occurring as a result of storage compensates the losses of alkenes taking place at sorption. Alkanes on the other hand, which demonstrated a good agreement in concentrations regardless of the sampling method do not confirm this same agreement. For aromatic compounds a further increase in concentration was observed making the differences in the determined concentrations higher. The only exception is 1,2,4-trimethylbenzene, whose concentration initially increases and then decreases.

Summing up the above results it can be stated that there exists a considerable agreement between the results obtained with use of the two examined sampling methods for a limited number of compounds. This agreement was not observed for the most volatile compounds such as ethane and ethylene, which require lower sorption temperature, and for aromatic compounds whose concentrations determined in the sorption tubes were considerably higher than those determined with direct dosing.

The Mixture of 27 Hydrocarbons - Comparison of the Results Obtained from Two Different Gas Chromatographs

The volumes of approximately 1000 cm^3 of the mixture of 27 hydrocarbons were sorbed in the sorption tubes for the analysis performed with the Hewlett Packard 3890 gas chromatograph. The chromatograph was equipped with a GS-Alumina PLOT column, different from the one used in the Varian Star 3600CX chromatograph. This is why it was necessary to determine the sequence at which the compounds leave the column and to identify the peaks on the chromatogram. For identification the application notes of a given column [23] and the other calibration mixture containing 7 hydrocarbons were used. For a not very high number of compounds such identification is possible, as the retention times of hydrocarbons depend mainly on boiling points of compounds, and the boiling point in turn depends on the length of a carbon chain, on kinds of functional groups and chemical bonds [24]. Having identified the peaks, the concentrations of the compounds were calculated. Next, the mean values of concentrations were calculated and compared with the results obtained from the Varian Star chromatograph. The results are presented in Fig. 3.
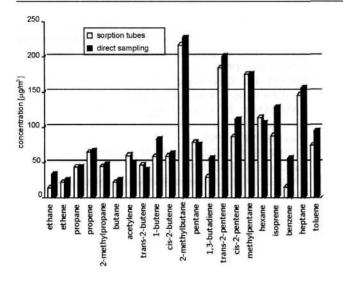
Fig. 3. Concentration of hydrocarbons of the hydrocarbon mixture analyzed after direct dosing (GC Varian Star 3600 CX) and with use of sorption tubes (HP 3890).

Fig. 4. Percentage of selected hydrocarbons in ambient air in Cracow and Vienna (as 100% a sum of the listed compounds was assumed).

In the chromatogram of the hydrocarbon mixture obtained from the GS-Alumina PLOT column the number of peaks is lower than the number of the analyzed substances. The peaks of substances such as ethylbenzene, xylenes and trimethylbenzenes are missing. The only aromatic compounds visible in the chromatogram are benzene and toluene. The reason for that is that the applied column is intended for separation of hydrocarbons of carbon chains not longer than 6 carbon atoms.

The concentrations of the majority of hydrocarbons were found lower as compared to those obtained from the Varian Star 3600CX. This concerns in the first place the above mentioned aromatic compounds, and also alkenes. The overall concentration of alkenes decreased by 15 %, although in this group there is a compound whose concentration was determined to be higher, i.e. fran.s-2-butene. The best agreement between the concentrations determined by the two studied methods was obtained for alkanes. The determined total concentration of these compounds was lower by 4 % than the values assumed as a reference point, with the biggest losses detected for ethane. For this compound it is recommended to carry out the sorption at temperatures lower than the ambient because of its volatility.

Some compounds were found not to be well separated on the Alumina PLOT column. In the case of the calibration mixture these were acetylene and n-butane. In some chromatograms they appeared as two peaks and in some as one broadened peak. Also, the efficiency of separation of this column was checked at different flow rates and different temperature programmes, but these parameters were found to have little effect on efficiency of separation.

Ambient Air Collected Simultaneously in SUMMA Canisters and Sorption Tubes

Air was sampled simultaneously to canisters and sorption tubes. The former were analyzed with the Hewlett Packard 3890 gas chromatograph, and the latter with the Varian Star 3600CX gas chromatograph.
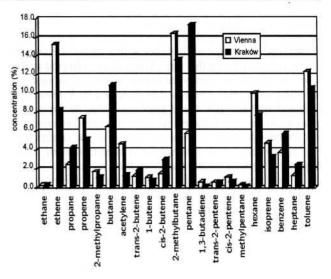
The most striking differences observed are:
- with use of the canisters and the GC Varian a higher number of compounds was identified, a higher number of peaks was registered in chromatograms, and better separation was obtained;
- the concentrations of the identified substances are higher in air collected in the sorption tubes;
- the changes in concentrations of all hydrocarbons collected in the sorption tubes occurring on storage are higher (i.e. the canisters seem to be more stable).

The basic origin of the observed differences are the different columns used in the set-ups. As mentioned before, the GS-Alumina column is mainly used for the analysis of hydrocarbons of not more than 6 carbon atoms in the molecule. This is why a big group of hydrocarbons of bigger molecules could not be determined with this column. Besides, it is suspected that some compounds which could be separated on one column could not be separated on the other one. Furthermore, there occurred a problem with the separation of 4-carbon compounds on the GS-Alumina PLOT column. The shape of the peaks indicates that the mixture was not completely separated.

On the other hand, the differences in the concentrations determined with use of the sorption tubes also originated from the contamination of the tubes. In the case of ethylene the level of contamination was higher than the determined concentration! The only indicator comparatively consistent with the two methods are mean changes in the concentrations.

Comparison of Hydrocarbon Levels in Ambient Air in Cracow and Vienna

Ambient air was collected in both cities in similar conditions, i.e. in summer in the city centre, in the close vicinity of streets of heavy traffic. The concentrations of the majority of the identified compounds are similar in both cities. The highest discrepancy was noted for n-butane and n-pentane. Their concentrations in Cracow are about twice those in Vienna. On the other hand a considerably higher

concentration of ethylene was found in Vienna. However, the measurements presented in 3.1 indicate that the losses of ethylene on storage of the tubes with a sorbed air sample can be responsible for this fact. Ambient air collected in the tubes in Cracow was analyzed either on the second or third day after sampling, whereas that collected in Vienna was analyzed within a few hours after sampling. As far as the concentrations of n-butane and n-pentane are concerned, it was found that their increase on storage is not significant. The differences in the determined concentrations of n-butane and acetylene could stem from their incomplete separation. In some chromatograms their peaks were not well separated. Aromatic compounds represented by benzene and toluene have comparable concentrations. Fig. 4 presents the concentrations of the discussed compounds in both the cities.

In sumary it can be stated that the level of hydrocarbons in ambient air in Cracow and Vienna is similar [25], and the observed differences reflect the real existing differences or too little precision of the measurements.

Conclusions

Canisters and sorption tubes are the most common tools used for air sampling. Each of them have advantages and disadvantages discussed in the literature [22, 26]. They are compared in respect of operating costs and easiness of transportation and storage, but the crucial criterion determining their usefulness seems to be the effectiveness of their cleaning, so that their contamination does not interfere with analysis.

The presented study confirms the common opinion that it is very hard to obtain the same results with different analytical methods and different analytical set-ups. Therefore, there exists a need for further development of analytical equipment and analytical methods in order to obtain more accurate and more precise results.

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