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COMPARISON OF SAMPLE CONCENTRATION METHODS AND CORRELATION CHROMATOGRAPHY FOR POLYMER DYNAMIC HEADSPACE-STUDIES

Abstract. Gas chromatography (GC) was used to study the kinetics of the evolution of volatile substances from the polypropylene sample (at 70 °C). Correlation chromatography (CC) and the trapping of volatile substances onto sorbents Tenax and activated charcoal were employed to improve the detector signal. As a reference, the kinetics of gas evolution was studied by making a series of direct single injections of polymer headspace gas to the GC column. The results of trapping differed from those obtained by CC. However, the data collected by single injections and CC were in good agreement. The CC method was found to offer far more operator convenience for dynamic headspace analysis than sample trapping, thus being less subject to errors due to the operator's mistakes.

Introduction

Analysis of the quantitative and qualitative composition of polymer volatile substances ("headspace") is of utmost importance in estimating the suitability and applicability of a given polymer material to e. g. the food or the pharmaceutical industry [1]. Dynamic headspace analysis of solid material involves a continuous removal of the gas phase above the condensed phase by means of a gas flow followed by sampling of the evolved gases to an analytical device (such as gas chromatograph) directly from the flow or after trapping/releasing the evolved components. The trapping is performed either onto sorbents or into a cryogenic trap, the compounds trapped being released by extraction or by heating the trap.

While the total amount of the evolved compounds is of importance from an analytical point of view, the kinetics of gas evolution from a polymer matrix has a theoretical value in view of the understanding of many physical and chemical properties of the material under study. Frequently, the amount of gas evolved from a polymer is so small that a direct single injection of polymer headspace to the GC does not quarantee the necessary detection limit and the concentration of the evolved gas by trapping is inevitable. Trapping techniques have been extensively studied (e. g. [2-4]). Also, proper equipment is available on the market [5, 6]. Despite its wide application, disadvantages of the trapping/releasing procedure are well known. These are fog formation in cryogenic traps, the danger of trapped compounds degradation during heating, the possibility of selective and irreversible adsorption of sample gases on the trap surface or its catalytic activity [7].

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As an alternative to trapping, correlation chromatography [8] offers direct introduction of a sample to the chromatograph, using a pseudo-random injection of the sample gas. As a noise suppression method, CC enables a decrease in the detection limit down to two orders which is sufficient in practice. The advantage of CC is that the result can be obtained without any physical or chemical modification of the sample. On the other hand, however, CC has its own problems. The method is critically sensitive to sampling device quality: CC needs a stable and perfect injection device. The degree of perfection required can be estimated [8], though in general the variation of the amount of the gas to be injected should be lower than 5%. Also, the injection profile should be reproducible or if the sample flow is modulated by a sampling device, transitions in the sample concentration in the column input from maximum to zero and vice versa should be done during an infinitely short period of time. All the deviations from ideality generate "ghost" peaks on correlograms, i. e. chromatograms calculated from the detector output. The CC theory can predict the pattern and intensity of ghost peaks very precisely [8, 9]. The absence of commercially available instrumentation with a proper input system and software is, in our opinion, the main reason for a low use of CC. However, recent studies have demonstrated that at least a Valco ten port HPLC sampling valve can be applied to liquid CC without causing any problems with "ghost" peaks [10]. It has also been shown that a pneumatic sampling valve of Dean's type can be successfully applied to GC [11] together with thermal and chemical modulators [12, 13].

Although possibilities and limitations of CC as a trace analysis method as compared to classical techniques have been discussed and criticized in literature [14], no studies are available on the application of trapping/desorption and CC to the same object in conditions as similar as possible. In this respect the dynamic headspace of polymers offers a good object for comparative studies because by choosing a proper heating temperature of a polymer, the amount of the gas evolved can be adjusted to a convenient level of measurement for direct single injections, CC, and trapping. In the present paper, a polypropylene sample was chosen as a model. We analysed only the qualitative composition of polypropylene headspace (reflected in the chromatogram patterns) and its evolution kinetics. Estimation of absolute quantities of the evolved gases that can be detected by both methods and comparison of CC and cryogenic trapping will be the subject of further studies.

Experimental

Chromatography. Chromatographic analysis was made by a Carlo Erba 4200 chromatograph with a flame-ionization detector. The column was a metal capillary column (15 m × 0.5 mm, Perkin-Elmer) coated with liquid phase Carbowax 20M. The injector port of the chromatograph was replaced by the reactor used for thermochromatographic measurements [15] and a home-made pneumatic valve. The reactor and the valve were on line with the capillary column. The reactor consists of a quartz tube (15 cm × 4 mm) whose temperature can be kept constant or programmed from ambient to 600 °C at a rate of 1—20 °C. The pneumatic valve makes use of the pressure switching idea for sample introduction (proposed by Deans [16]). The valve geometry is given in [17].

Experiment control and data acquisition. Experiment control and data acquisition were performed with an Apple IIe computer through home-

made interface cards and software. The detector signal was recorded with a digitization interval of 0.5 s using a 23-bit analog-to-digital converter (Design Bureau, Institute of Cybernetics, Estonian Academy of Sciences). The software enables to control the sampling of the products evolved from the reactor to the column either at equal intervals or pseudorandomly as required in CC. In all CC experiments, a pseudorandom sequence of 511 elements was used which enables to theoretically decrease the detection limit by a factor of $\sqrt{511}/2 = 11.3$. A chromatogram was computed from the detector output via a fast Hadamard transform.

Purge and trapping. The purge and trapping of polymer headspace gas was performed in a thermostated quartz tube. The evolved products were carried to the sorbent tube (3 cm $\times$ 2 mm quartz) by N_2. The carrier gas was dried by silica gel and filtered by molecular sieves before entering the purge and trap reactor.
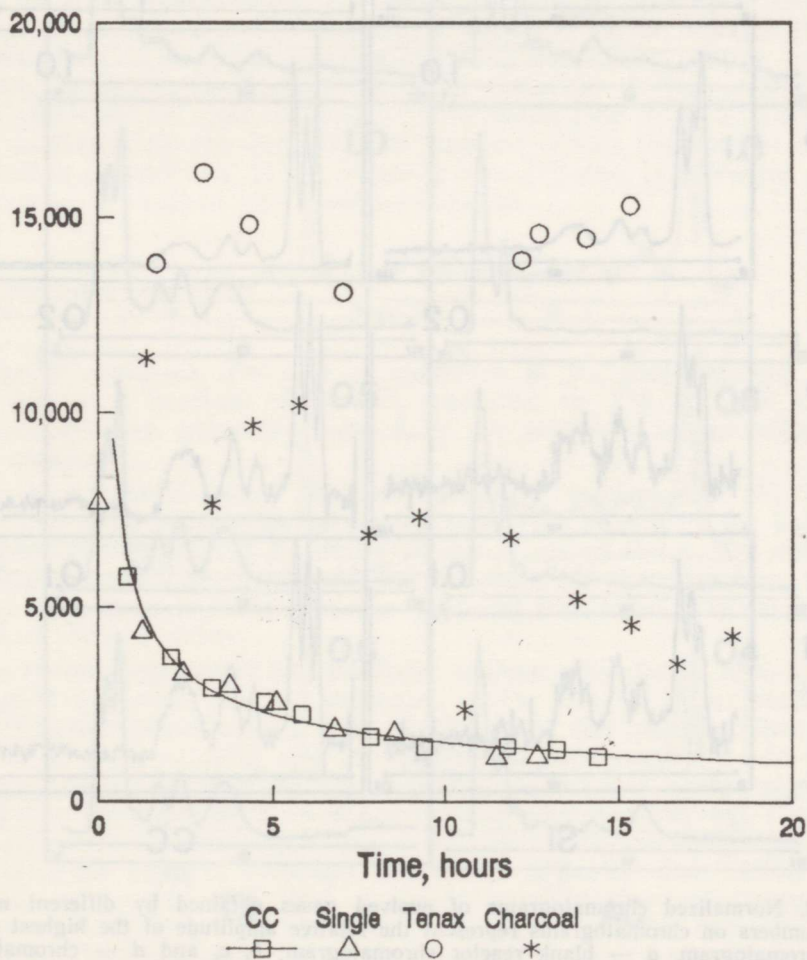

Fig. 1. Kinetic curves for evolved gases recorded by different methods.

Materials. The polypropylene sample studied has the following characteristics: density 0.900 g/cm³, molecular weight 186 000, melting point 158 °C, ethylene amount 4.9%, and crystallinity 40.1%. Two sorbents were used: Tenax (Ohio Valley Spec. Chem. Inc.), 7 g, and activated charcoal, 27 g, (SKT, made in USSR). SKT is a peat-based product used as sorbent for inorganic gas and light hydrocarbon separations in chromatography [18]. Its surface area is not available to the authors.

Procedure. In case of direct single injections and CC, a 30-mg polypropylene sample was in the thermochromatographic reactor which was heated at 70 °C for several hours. Every hour a single injection chromatogram or a correlogram was recorded.
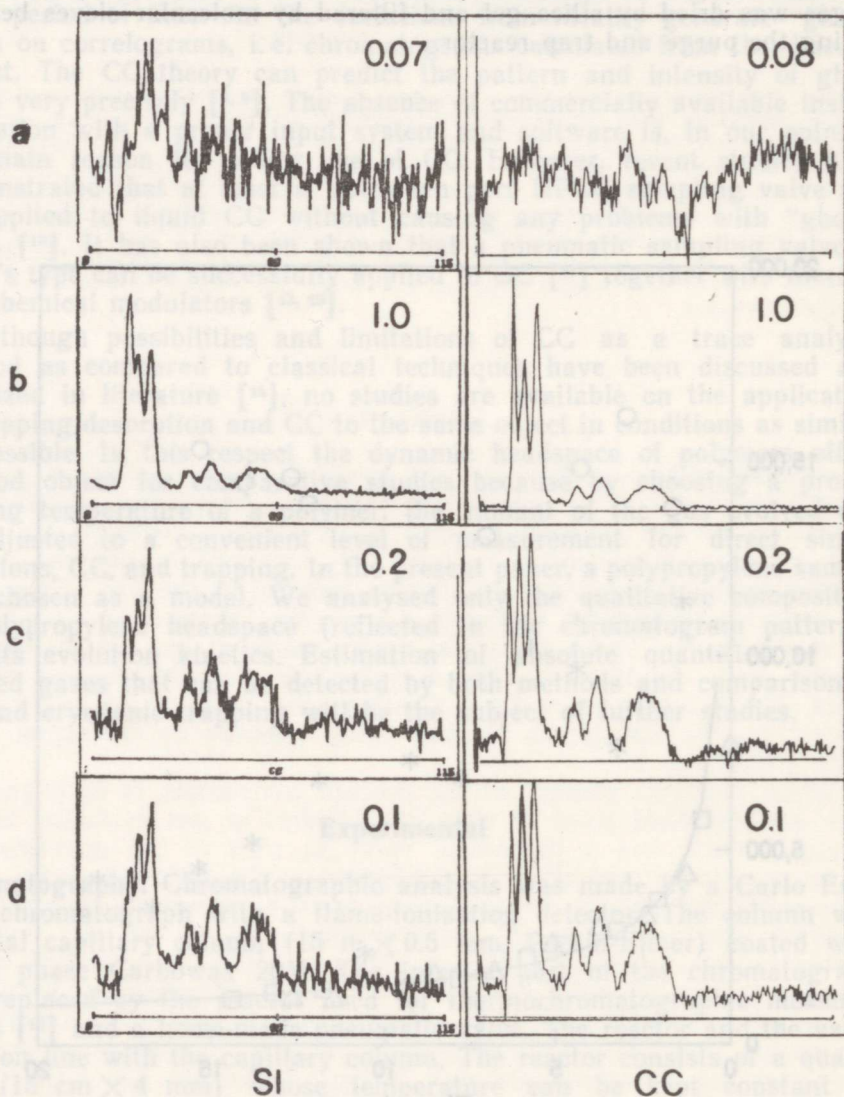

Fig. 2. Normalized chromatograms of evolved gases obtained by different methods. The numbers on chromatograms represent the relative amplitude of the highest peak of the chromatogram. *a* — blank reactor chromatogram; *b*, *c*, and *d* — chromatograms obtained after 1-, 7-, and 13-hour heating of the polymer, respectively.

SI — single injection, CC — correlation chromatography. Polymer amount — 30 mg.

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In the purge and trapping procedure, the sample was also heated in the purge and trapping device for many hours. Every hour the evolved products were trapped to the sorbent during the time equal to that necessary for performing a correlation experiment (usually 4 min). Then the sorbent tube was replaced by a hollow tube to maintain the set pressure and carrier flow rate in the purge and trap device. The sorbent tube was placed into the thermochromatographic reactor in the chromatograph and the trapped compounds were desorbed using the temperature program of 20°C/min. The final temperature for Tenax was 270 and for charcoal 350°C. The desorbed components were carried to the vent through the Deans sampling valve by an N_2 flow. In this way
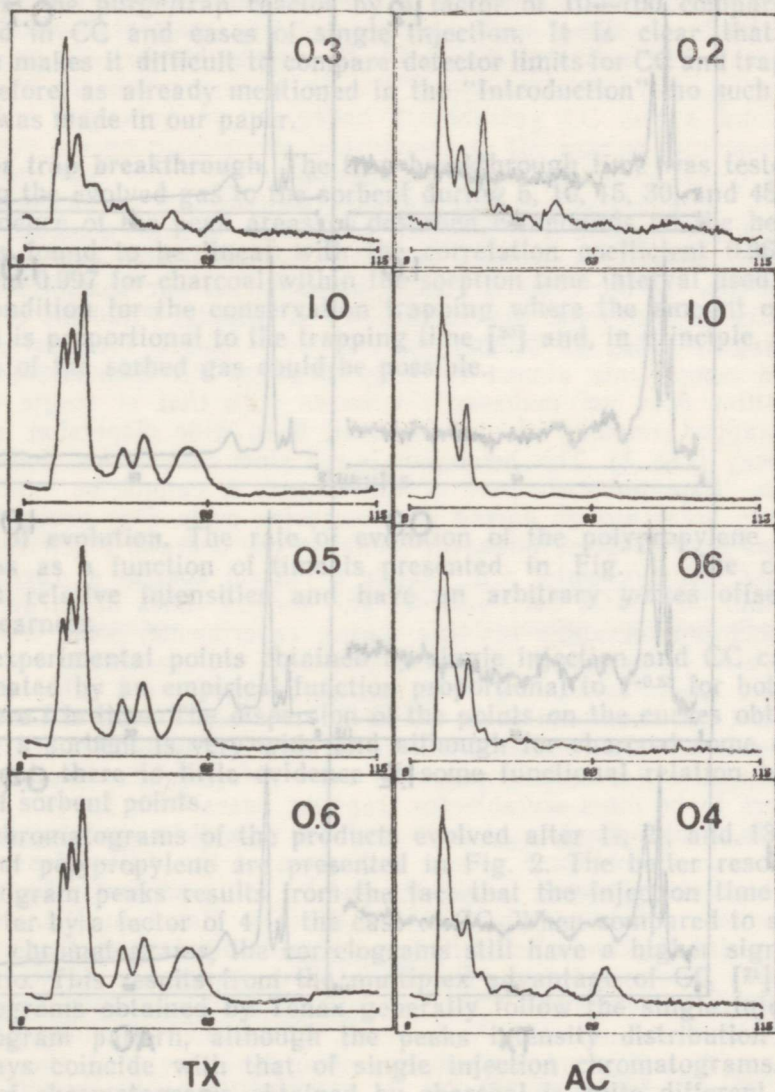

Fig. 2 — contd. TX — Tenax, AC — activated charcoal. Polymer amount — 3 g.

we have a gas stream with desorbed components in it. During the desorption cycle, the samples were taken from this stream to the column at equal time intervals (2 min) and the chromatograms were recorded. When the desorption cycle was over, all the chromatograms were added by computer to get a total chromatogram of the desorbed products. The sorbent tube was kept at the final temperature for 45 min to release the small amount of the gas remaining in the sorbent. The level of the residual exponentially decreasing signal was monitored chromatographically and when the signal was negligible compared to that from the desorbed gas, the tube was taken off the reactor and put into the headspace gas flow to start the next desorption cycle.
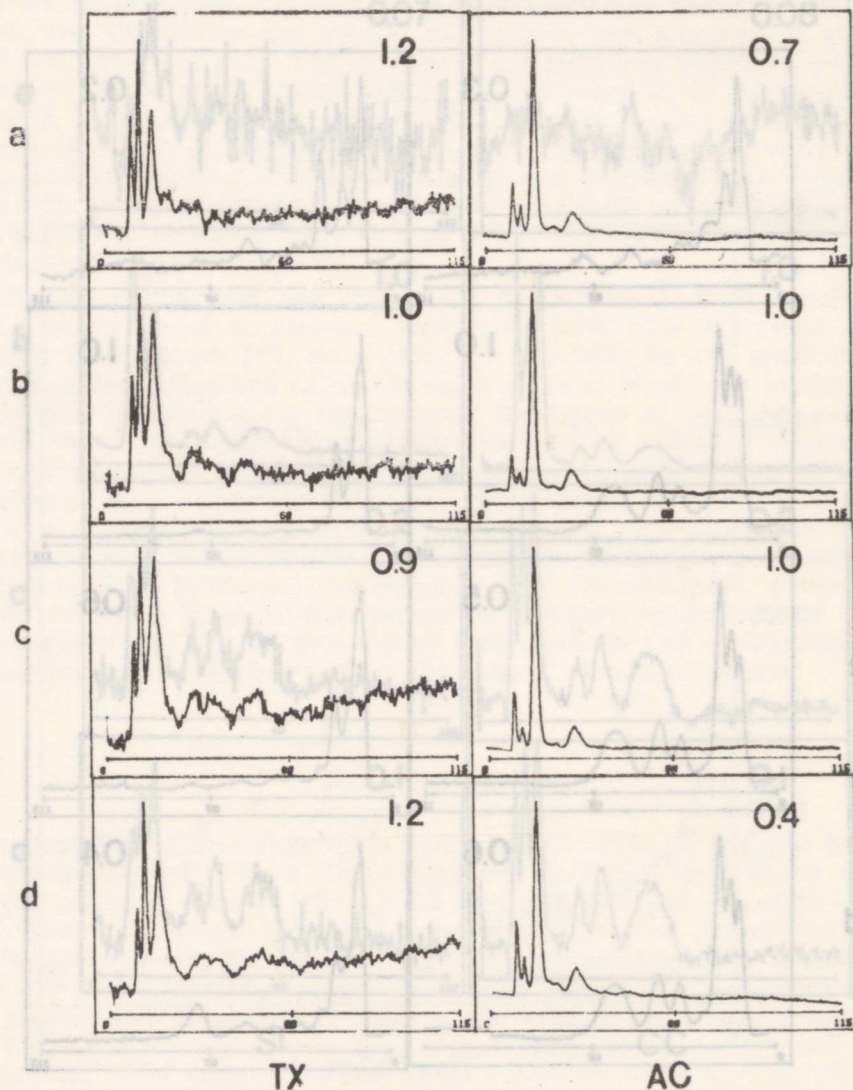

Fig. 3. Normalized chromatograms of evolved gases measured by different methods. Polymer amount — 45 mg. See Fig. 2 for explanation of symbols.

This kind of desorption technique was applied for two reasons. First, although in principle a few commercially available instruments are suitable for dynamic headspace analysis, it is difficult to find one meeting all the requirements [19]. Though the authors have no commercial purge/trap device in their laboratory, this approach enables to implement our thermochromatographic reactor for the controlled heating of the sorbent tube. Secondly, desorbing the bulk of the gas to the vent and simultaneously performing short-duration injections of the flow to the column at regular intervals, the required resolution of headspace component peaks can be maintained. A conventional approach is to collect all the gas released to the cryogenic trap, but the trap is an additional source of errors which we tried to avoid this time. In our approach, most of the trapped headspace gas is lost, thus the method is not acceptable as a usual analytical procedure, but it should be tolerable for our comparative study for the reasons already mentioned. We compensated for the loss of signal by increasing the polymer amount in the purge/trap reactor by a factor of 10—100 compared to that used in CC and cases of single injection. It is clear that this approach makes it difficult to compare detector limits for CC and trapping and therefore, as already mentioned in the "Introduction", no such comparison was made in our paper.

Check for trap breakthrough. The trap breakthrough time was tested by collecting the evolved gas to the sorbent during 5, 10, 15, 30, and 45 min. A dependence of the peak areas of desorbed compounds on the heating time was found to be linear with the correlation coefficient 0.965 for Tenax and 0.997 for charcoal within the sorption time interval used. This is the condition for the conservation trapping where the amount of gas adsorbed is proportional to the trapping time [20] and, in principle, quantification of the sorbed gas could be possible.

Results

Kinetics of evolution. The rate of evolution of the polypropylene headspace gas as a function of time is presented in Fig. 1. The curves represent relative intensities and have an arbitrary y-axes offset for graph clearness.

The experimental points obtained by single injection and CC can be approximated by an empirical function proportional to $t^{-0.53}$ for both the sets, where t is time. The dispersion of the points on the curves obtained by using a sorbent is very wide and although for charcoal some decay is apparent, there is little evidence of some functional relation behind the set of sorbent points.

The chromatograms of the products evolved after 1-, 2-, and 13-hour heating of polypropylene are presented in Fig. 2. The better resolution of correlogram peaks results from the fact that the injection time used was shorter by a factor of 4 in the case of CC. When compared to single injection chromatograms, the correlograms still have a higher signal to noise ratio. This results from the multiplex advantage of CC [21]. The chromatograms obtained by Tenax generally follow the single injection chromatogram pattern, although the peaks intensity distribution does not always coincide with that of single injection chromatograms. The pattern of chromatograms obtained by charcoal is quite different from the others. The good signal to noise ratio of the chromatograms obtained by Tenax and activated charcoal is due to the fact that the amount of the polymer (3 g) is 100 times bigger than that used in the CC experiment.

Influence of background. In determining ultra low concentrations of target compounds in the evolved gas flows the purity of the carrier gas and the amount of the gas sorbed on the reactor vessel walls are of even higher importance than the overall detector noise power value because peaks of the components existing in the carrier matrix in higher concentrations than target components can easily mask target component peaks on chromatograms. To investigate the influence of the background signal to the chromatograms of the evolved products, the injection time and the polymer sample amount were reduced to the values comparable to those used in CC experiments. As in the previous case, the trapped and released gas amounts did not follow any tendency during the heating of the polymer. The chromatograms obtained after 1-, 7-, and 13-hour heating are presented in Fig. 3. The pattern known from a single injection chromatogram can be hardly recognized in the noisy chromatograms obtained from Tenax. The chromatograms obtained from charcoal have a high signal to noise ratio, but the pattern does not resemble single injection chromatograms at all. Its comparison with the blank signal of the purge and trap reactor shows that what was trapped by activated charcoal is the reactor blank.

Discussion

If direct injection of polymer headspace gas is considered as a reference signal representing correctly the qualitative and quantitative composition of the evolved gas, it follows from our measurements that also CC can represent the composition accurately. Problems arise when trapping is used. As follows from Figs. 2 and 3, Tenax releases the sorbed components almost correctly although the distribution of peak intensities does not necessarily coincide with that of single injection. The trapped amounts of gas, however, have wide dispersion indicating no decay (Fig. 1). This behaviour is not clear because, as demonstrated in the "Experimental" part of this paper, it cannot be explained by the trap breakthrough during the desorption cycle. One probable reason for this may be some unknown factor in the operator's activity on performing measurements; e. g. despite a careful control of carrier pressures and flow rates over polymer and sorbent tubes in purge/trap and thermochromatographic reactors during experiments, some leaks of fittings and sealing may happen. Operations with sorbents require care and are labour-consuming, thus human errors are not ruled out.

What has been said about Tenax is valid also for activated charcoal. This sorbent seems to be suitable for the analysis of light nonpolar components but adsorbs irreversibly more polar and heavier ones. Tenax appears to be more suitable for trapping gases with heavier molecular weights. Such behaviour of these sorbents is well known.

The results obtained are an indication of the difficulties appearing in determining polymer headspace gas by using sorbents. As headspace instruments are mostly home made then, as stated in [19], difficulties arise mainly in connection with apparatus manipulations. Our experience confirms this conclusion. Problems of the influence of the catalytic activity of sorbent surface and irreversible adsorption also remain when using these instruments. We, however, realize that if commercial instruments with a different methodology of analysis are used, the advantage of CC over trapping might not be so dramatic as our results indicate. Nevertheless, this demonstrates even more vividly the critical dependence of the trapping results on the materials and equipment used, as well as the analyst's experience. CC as a completely automatic direct method

of analysis is less prone to operator errors. Especially for kinetic measurements the result can be obtained simply by reorganizing the measurement process itself, not by chemical manipulations on the sample. Theoretical predictions that CC can suppress noise are also confirmed by our results (compare results of single injection and CC).

Carrier matrix impurities peaks do not appear in the chromatograms even in the reactor blank signal (Fig. 2 CC.*a*) because the concentrations of impurities in the pure carrier and the sample are the same. This possibility of differential measurements was first pointed out in [22]. This property of CC enables to construct measurement systems where some classes of impurities are pseudorandomly filtered out by suitable selective sorbents applying some physical/chemical action on sorbent. This idea is implemented by chemical modulation input systems [23, 24]. The idea can be developed even further by imaging input systems where the sample is introduced into the column by modulating between two sample flows: one with the class of impurities of interest and the other without them. The advantage of this system should be that there is no need to worry about the processes taking place on the sorbent as far as it adsorbs the necessary components completely.

Several disadvantages of the CC method were already pointed out in the beginning of the paper. Introducing CC into a laboratory when there are no ready-made instruments in the market is a somewhat challenging task requiring (besides knowledge of computational mathematics and system identification theory) a good motivation.

Conclusions

The results of comparison of trapping and CC for polymer headspace analysis are summarized in the Table.

Comparison of CC and trapping methods for polymer headspace analysis

Trapping	Correlation chromatography
Advantages	
1. Commercial equipment is available	1. Direct method: no sample pretreatment
2. Wide experience of analysts	2. Fool-proof procedure: no operator's experience is needed
3. High sensitivity can be obtained	3. Convenient method: analysis is automated
	4. Influence of the impurities in the carrier gas is excluded
Disadvantages	
1. Catalytic activity and irreversible adsorption of sorbents changes the sample composition	1. No commercial equipment is available
2. The procedure involves a lot of manipulations with traps that require extreme care	2. The theoretical basis still requires research
3. Not all factors generating the signal are known to the analyst	3. The signal enhancement practically reaches two orders only

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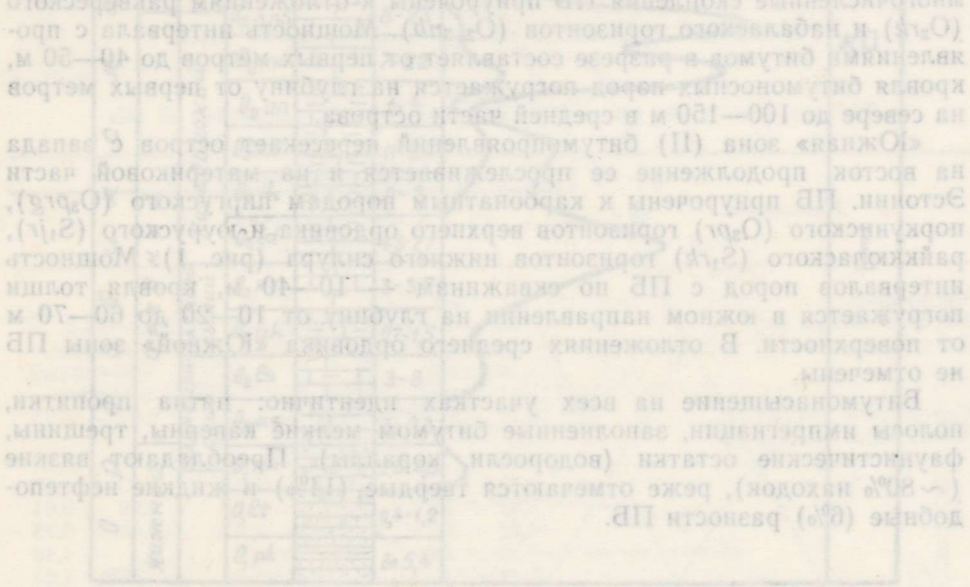*Mihkel KALJURAND, Vaike TAKJAS*

KORRELATSIOONKROMATOGRAAFIA JA PROOVI KONTSENTREERIMISE KUI POLÜMEERIDE AURUFAASI DÜNAAMILISE ANALÜÜSI MEETODITE VÕRDLUS

Polüpropüleenist eralduvate gaaside aurufaasi lendumise kineetika uurimiseks kasutati gaasikromatograafia meetodit. Detektori signaal—müra suhte parandamiseks kasutati korrelatsioonkromatograafiat (KK) ja lenduvate produktide püüdmist sorbentidele «Tenax» ja aktiivsüsi. Kontrolliks mõõdeti gaaside eraldumise kineetikat proovi sisestamisel kolonni üksiksüstide jadana. Tulemused, mis saadi aurufaasi sorbeerimisega «Tenaxile» ja aktiivsöele, erinesid nendest tulemustest, mis saadi KK abil. Viimase meetodi puhul saadud tulemused olid aga heas kooskõlas üksiksüstide jada sisestamisel saadud tulemustega. Ka osutus KK-meetodi kasutamine analüütikule palju mugavamaks kui proovi sorbeerimine «Tenaxile» ja aktiivsöele. Selle tõttu on analüütiku subjektiivsete eksimuste oht korrelatsioonkromatograafia kasutamise korral palju väiksem kui sorbentide kasutamisel.

Михкель КАЛЬЮРАНД, Вайке ТАКЯС

СРАВНЕНИЕ МЕТОДОВ КОНЦЕНТРИРОВАНИЯ И КОРРЕЛЯЦИОННОЙ ХРОМАТОГРАФИИ ПРИ ДИНАМИЧЕСКОМ ПАРОФАЗНОМ АНАЛИЗЕ ПОЛИМЕРОВ

Изучена кинетика выделения летучих продуктов из полипропилена при 70° С методом газовой хроматографии. Для уменьшения предела детектирования применены методы концентрирования и корреляционная хроматография. Показано, что последняя обеспечивает получение более надежных результатов.