UvA-DARE (Digital Academic Repository)

Comparison of sample concentration methods and correlation chromatography for polymer dynamic head-space studies.

Kaljurand, M.; Smit, H.C.

DOI

[10.1007/BF02274502](https://doi.org/10.1007/BF02274502)

Publication date

1994

Published in

Chromatographia

[Link to publication](#)

Citation for published version (APA):

Kaljurand, M., & Smit, H. C. (1994). Comparison of sample concentration methods and correlation chromatography for polymer dynamic head-space studies. *Chromatographia*, 39, 210-215. <https://doi.org/10.1007/BF02274502>

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

Comparison of Sample Concentration Methods and Correlation Chromatography for Polymer Dynamic Head-Space Studies

M. Kaljurand*¹ / H. C. Smit²

¹Institute of Chemistry, Estonian Academy of Sciences, Akadeemia tee 15, Tallinn, EE0026, Estonia

²Laboratory of Analytical Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV, Amsterdam, The Netherlands

Key Words

Gas chromatography
Correlation chromatography
Concentration methods
Polymer dynamic head-space sampling

Summary

Gas chromatography has been used to study the kinetics of evolution of volatiles from polypropylene samples (at 70 °C). Correlation chromatography (CC) and the trapping of volatiles on Tenax sorbents 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 head-space gas on a GC column. The results of trapping differed from those obtained by single injection. However, the data from single injections and CC were in good agreement. The CC method was found to offer far more operator convenience for dynamic head-space analysis than sample trapping, being less subject to operator errors.

Introduction

Determination of the quantitative and qualitative composition of polymer volatiles ("head-space") is of utmost importance in estimating the suitability and applicability of a given polymer material to, for example, the food or pharmaceutical industry [1]. Dynamic head-space analysis of solid material involves 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 and releasing the components evolved. Trapping is either on adsorbents or in a cryogenic trap, the compounds trapped being released by extraction or heating.

While the total amount of compounds evolved is of importance from an analytical point of view, the kinetics of gas evolution from a polymer matrix also has a theoretical value in 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 head-space into the GC does not guarantee the necessary detection limit hence 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 and releasing procedure are well-known. These are fog formation in cryogenic traps, a danger of trapped-compound degrading during heating, the possibility of selective and irreversible adsorption of sample gases on the trap surface or catalytic activity of the surface [7].

As an alternative to trapping, correlation chromatography [8] offers direct introduction of sample to the chromatograph, using pseudo random injection of the sample. As a noise suppression method, CC enables a decrease in the detection limit down to two orders of magnitude 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, CC has its own problems, it is critically sensitive to sampling device quality which means that it needs a stable and perfect injection device. The level of perfection required can be estimated [8] but, in general, the variation in the amount of gas injected should be < 5 %. Also, the injection profile should be reproducible or, if the sample flow is modulated by a sampling device, changes in sample concentration in the column input from maximum to zero and vice versa should be taken negligible time. All deviations from perfection 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 low usage of CC. However, recent studies have demonstrated that at least a Valco 10-port HPLC sampling valve can be applied in liquid CC without causing problems with "ghost" peaks [10]. It has also been shown that a Deans-type pneumatic sampling valve can be successfully applied to GC [11] together with thermal and chemical modulators [12, 13].

Although the possibilities and limitations of CC as a trace analysis method compared to classical techniques have been discussed [14], no studies are available on the application of trapping-desorption and CC to the same subject under conditions as similar as possible. In this respect the dynamic head-space of polymers offers a good subject for comparative studies because by choosing the proper heating temperature for a polymer, the gas evolved can be adjusted to a convenient amount for single direct injections, CC and trapping. In the present paper, a polypropylene sample was chosen as a source of low level gas. We analysed only the qualitative composition of the polypropylene head-space gas (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 by a Carlo Erba 4200 chromatograph with a flame ionisation detector. The column was a metal capillary (15 m $\times$ 0.5 mm, Perkin-Elmer) coated with 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 valve were on-line with the capillary column. The reactor consists of a quartz tube (150 $\times$ 4 mm) whose temperature can be kept constant or programmed from ambient to 600 °C at a rate of 1 to 20 °C/min. The pneumatic valve makes use of the pressure switching idea for sample introduction proposed by Deans [16]. The valve geometry is given in [17].

Equipment Control and Data Acquisition

Experimental control and data acquisition were by an Apple IIe computer using home-made interface cards and software. The detector signal was recorded with a digitisation interval of 0.5 s using a 23 bit analogue-to-digital converter (Design Bureau, Institute of Cybernetics, Estonian Academy of Science). The software enables control of the sampling of evolved products from the reactor to the column either at equal intervals or pseudo-randomly as required in CC. In all CC experiments, a pseudo random sequence of 511 elements was used which theoretically enables us to decrease the detection limit by a factor of $\sqrt{512/2} = 11.3$

times. A chromatogram was computed from the detector output via a fast Hadamard transform.

Purge and Trapping

The purge and trapping of polymer head-space gas was performed in a thermostatted quartz tube. The products evolved were carried to the sorbent tube (30 $\times$ 2 mm quartz) by N₂. The carrier gas was dried by silica gel and filtered through molecular sieves before entering the purge and trap reactor.

Materials

The polypropylene sample studied has the following characteristics: density 0.900 g $\cdot$ cm⁻³, isotactic, 90.3, relative molecular mass 186 000, melting point 158 °C, ethylene content 4.9 % and crystallinity 40.1 %. Two sorbents were used: Tenax (Ohio Valley Spec. Chem. Inc.), 7 g and activated charcoal, 27 g, (SKT, USSR). SKT is a peat based product used as adsorbent for inorganic gas and light hydrocarbon separations in chromatography [18]. Its specific surface is not known to the authors.

Procedure

In case of direct single injections and CC a 30 mg polypropylene sample in the thermochromatographic reactor was heated at 70 °C for several hours. The gas stream released passed the Deans' valve to the vent. Every hour a single injection chromatogram or a correlogram was recorded by sampling the evolved gas flow to the column.

In the purge and trap procedure, the sample was not heated in the thermochromatographic reactor but in the purge and trap device for many hours. Every hour the evolved products were trapped by the adsorbent during the time necessary for performing a correlation experiment (usually 4 min). Then the sorbent tube was removed from the output line of the purge and trap device and placed in the thermochromatographic reactor in the chromatograph, the trapped compounds were desorbed using the temperature program of 20 °C $\cdot$ min⁻¹. The final temperature for Tenax was 270 °C and for charcoal 350 °C. The desorbed components were carried to the vent through the Deans' sampling valve by N₂ flow. During the desorption cycle, samples were taken from this stream to the column at equal intervals (2 min) and chromatograms recorded. The sorbent tube was kept at the final temperature for 45 min to release all gas from the sorbent. The level of the residual, exponentially decreasing signal was monitored chromatographically and when it was negligible compared to that from the desorbed gas, the tube was taken off the reactor and put into the head space gas flow to start the next desorption cycle. When the cycle was complete, all the chromatograms were added by computer. In theory this 'total' chromatogram pattern should be proportional to the that obtained by conventional purge and trap procedure.

This desorption technique was applied for two reasons. First, although in principle a few commercially available instruments are suitable for dynamic head space analysis, it is difficult to find one meeting all requirements [19]. Having no commercial purge-trap device in the author's laboratory the approach however enables us to implement the thermochromatographic reactor (available in one author's laboratory) as a device for the controlled slow heating of the sorbent tube. Desorbing the bulk of gas to vent and simultaneously performing short duration injections of the flow to the column at regular intervals, the required chromatographic separation of head-space components can be maintained. A conventional approach is to collect all the evolved gas to a cryogenic trap and after that release all the gas by fast desorption (applying heat pulse to trap) to the chromatographic column. However, the trap is an additional source of errors which we tried to avoid at the time. In our approach, most of the trapped head-space gas is lost, thus the method is not acceptable as a standard analytical procedure but should be tolerable for our study where only the chromatographic pattern and head-space gas evolution kinetics are compared. We compensated the loss of signal by increasing the polymer in the purge-trap reactor by a factor of 10–100 compared to that used in CC – assuming that this will not cause a significant increase in reaction rates between the gas components evolved.

The authors realise that this approach makes it difficult to compare detector limits for CC and trapping and hence, as already mentioned in the "Introduction", such comparison was left for further studies.

Check for Trap Breakthrough

The trap breakthrough time was tested by collecting the gas evolved from the polymer and trapped into the sorbent over 5, 10, 15, 30 and 45 min. Dependence of the peak areas of desorbed compounds on heating time was found to be linear (correlation coefficient 0.965 for Tenax and 0.997 for charcoal) within the time intervals used. This is the condition for conservation trapping where the amount of gas adsorbed is proportional to the trapping time [20] and, in principle, quantification of the adsorbed gas should be possible.

Results

Kinetics of Evolution

The rate of evolution of the polypropylene head-space gas with time is shown in Figure 1. The curves represent relative intensities and have an arbitrary y axis offset for clarity.

The experimental points obtained by single injection and CC can be approximated by an empirical function proportional to $t^{-0.53}$ with correlation coefficient 0.988, for both the sets, where t = time. Scatter of points on the curves obtained using sorbents is very wide and

Figure 1

Kinetic curves for evolved gases recorded by different methods.

although for charcoal some decay is apparent (correlation coefficient about 0.5), there is little evidence of any functional relation behind the set of points.

Chromatograms of the products evolved after a 1, 2, and 13 h heating of polypropylene are in Figure 2. The better resolution of the correlograms peaks results from the fact that the injection time was shorter by a factor of 4 in the case of CC. Compared to single injection chromatograms, the correlograms still have a higher signal to noise ratio. This results from the multiplex advantage of CC [21]. Chromatograms obtained from Tenax generally exhibit some resemblance to the single injection chromatogram pattern, although the peak intensity distribution does not coincide with that of single injection chromatogram. The pattern of chromatograms obtained using charcoal is rather different from the others. The good signal-to-noise ratio obtained from Tenax and activated charcoal is (an explained above) due to the amount of polymer being 100 times higher (3 g), than that used in the CC experiment.

Influence of Background

In determining ultra low concentrations of target compounds in evolved gas flows the purity of carrier gas and amount of gas adsorbed on reactor vessel walls are of even greater 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

Figure 2

Normalized chromatograms of evolved gases obtained by different methods. Number on each chromatogram represents relative amplitude of highest peak. Polymer amount for CC and single injection measurements – 30 mg and for Tenax and activated charcoal measurements – 3 g. (SI – single injection, CC – correlation chromatography, TX – Tenax, AC – activated charcoal); a) – blank reactor chromatogram, b, c, d) – chromatograms obtained after 1, 7, and 13 h heating of polymer, respectively.

their peaks on the chromatograms. To investigate the influence of the background signal to the chromatograms of the evolved products the injection time and the polymer sample amount in the purge and trap reactor was reduced to a value comparable to that used in CC experiments (45 mg). As in the previous case, the trapped and released gas amounts did not follow any trend during heating of the polymer. Chromatograms obtained after 1, 7, and 13 h heating are in Figure 3. The pattern known from a single injection chromatogram can hardly be recognised in the noisy chromatograms from Tenax. Chromatograms from charcoal have a high signal-to-noise ratio but the pattern does not resemble a single injection chromatogram at all. Comparing it with the blank signal of the purge and trap reactor it is evident that what was trapped by activated charcoal is the reactor blank.

Figure 3

Normalised chromatograms of evolved gases measured by different methods. Number on each chromatogram represents relative amplitude of highest peak. Polymer amount – 45 mg. (TX – Tenax, AC – activated charcoal; a) – blank reactor chromatogram, b, c, d) – chromatograms obtained after 1, 7 and 13 h heating of polymer, respectively.

Discussion

Considering the direct injection of polymer head-space gas as a reference signal representing correctly the qualitative and quantitative composition of evolved gas, it follows from our measurement that CC can also correctly represent composition. Problems arise when trapping is used. As already mentioned, it follows from Figures 2 and 3 that Tenax releases the adsorbed components approximately correctly although the distribution of peak intensities does not necessarily coincide with that of a single injection. The trapped amounts of gas, however, are widely dispersed indicating no decay (Figure 1). This behaviour is not clear because, as demonstrated under „Experimental“, it cannot be explained by trap breakthrough during the desorption cycle. One reason may be some unknown factor on performing measurements. For example, despite careful control of carrier pressures and flow rates over polymer and sorbent tubes in purge-trap and thermochromatographic reactors some minor leaks in fittings and sealing may occur. Also, operations with adsorbents require care and are labour-intensive, thus human errors can not be ruled out. However, it is unlikely that even more care will improve results.

What has been said for Tenax holds also for activated charcoal. This adsorbent seems to be suitable for the analysis of light, non-polar components but irreversibly adsorbs more heavier polar ones. Tenax appears to be more suitable for trapping higher molecular mass gases. This behaviour of both adsorbents is well-known.

The results obtained are an indication of the difficulties in determining polymer head-space gas using adsorbents. As head-space instruments are mostly home-made then, as stated in [19], difficulties arise mainly from manipulations of apparatus. Our experience conforms this conclusion. Problems with the catalytic activity of the adsorbent surface and irreversible

adsorption also remains when using these instruments. We, however, realize that using commercial instruments with different analysis methodology the advantage of CC over trapping may be somewhat less dramatic as follows from our results. Nevertheless, it demonstrates even more 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 reorganising the measurement process itself, not by chemical manipulations on samples. Theoretical predictions of noise suppression property of CC follows also in results (compare results of single injection and CC).

Carrier matrix impurity peaks do not appear in the chromatograms even in the reactor blank signal (Figure 2 CC.a) because the concentration of impurities in the pure carrier and the sample is the same. The possibility of differential measurements was first pointed out in Ref. [22]. This property of CC enables us to construct measurement systems where some classes of impurity are pseudo-randomly filtered out by suitable selective adsorbents applying some physical or chemical action on adsorbent. As a simple example of this kind of action may serve an application of thermal pulse to the adsorbent. This idea is implemented by chemical modulation input systems [23]. 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 adsorbent as long as it adsorbs the necessary components completely.

Several disadvantages of the CC method have already been pointed out above. Introducing CC into a labora-

Table I. Comparison of CC and trapping methods for polymer head-space analysis.

Advantages	
Trapping	Correlation chromatography
1 Commercial equipment available	Direct method: no sample pre treatment necessary
2 Wide experience of analysts	Fool-proof procedure: no operator experience needed
3 High sensitivity can be obtained	Convenient method: analysis automated
	Influence of impurities in carrier gas excluded
Disadvantages	
Trapping	Correlation chromatography
1 Catalytic activity and irreversible adsorption of sorbents changes sample composition	No commercial equipment available
2 Procedure involves much manipulation with traps that require extreme care	Basic ideas of CC are too complicated for acceptance by general analytical community
3 Signal enhancement factor (usually one to two orders of magnitude) limited by trap breakthrough and reactions between sample components	Difficult to improve detection limits using CC below two orders of magnitude compared to single injection chromatography
4 Not all factors generating the signal known to the analyst	

tory when there is no ready-made instruments in the market is a somewhat challenging task requiring (besides knowledge of computational mathematics, and system identification theory) good motivation.

Conclusions

The results of comparison of trapping and CC for polymer head space analyses are summarised in Table I.

Acknowledgements

The authors would like to thank V. Takjas for performing measurements and M. Koel and E. Urbas (Inst. of Chemistry, Estonian Academy of Sciences) for help in performing sorption measurements and fruitful discussions in preparing the paper, and Matti Elomaa (Department of Polymer Chemistry, Helsinki University, Finland) for providing the polypropylene sample.

References

- [1] B. V. Ioffe, A. G. Vittenberg, *Head-Space Analysis and Related Methods in Gas Chromatography*, J. Wiley & Sons, NY, 1984.
- [2] E. R. Adlard, I. N. Davenport, *Chromatographia* **17**, 421 (1983).
- [3] G. I. Rudenko, V. V. Maltsev, V. N. Studenchik, E. P. Ustinov, *Russian J. Anal. Chem.* **40**, 421 (1983).
- [4] I. Delcourt, I. P. Guerier, I. Muller, *Chromatographia* **17**, 88 (1983).
- [5] R. P. M. Doper, *Crompack News* **11**, 1 (1984).
- [6] Anonymous, *The Supelco Reporter* **8**, 1 (1989).
- [7] J. S. Drugov, V. G. Berjoskin, *Gas Chromatographic Analysis of Air Pollution*, "Chimija", Moscow, 1981, p. 36 (in Russian).
- [8] M. Kaljurand, E. Küllik, *Computerised Multiple Input Chromatography*, Ellis Horwood Ltd., Chichester, 1989, 225 p.
- [9] R. Mulder, P. I. Hoogerbrugge, H. C. Smit, *Chemometrics and Intelligent Laboratory Systems* **1**, 243 (1987).
- [10] C. Mars, H. C. Smit, *Anal. Chim. Acta* **228**, 193 (1990).
- [11] M. Kaljurand, M. Elomaa, L. Plit, *Anal. Chim. Acta* **248**, 271 (1991).
- [12] M. Engelsma, W. Th. Kok, H. C. Smit, *J. Chromatogr.* **506**, 201 (1990).
- [13] J. B. Phillips, D. Luu, I. Pawliszin, G. C. Carle, *Anal. Chem.* **57**, 2779 (1985).
- [14] R. Annino, *ACS Symp. Ser.* **284**, 83 (1985).
- [15] E. Küllik, M. Kaljurand, M. Lamberg, *Intern. Lab. Jan/Febr 80* (1987).
- [16] D. R. Deans, *J. Chromatogr.* **289**, 43 (1984).
- [17] M. Kaljurand, *Proc. Estonian Acad. Sci., Chemistry* **38**, 25 (1989).
- [18] J. Jashin, *Physical-Chemical Foundations of Chromatographic Separations*, "Chimija", Moscow, 1976, 235 p. (in Russian).
- [19] A. Venema, *JHRC* **13**, 537 (1990).
- [20] J. M. P. M. Curvers, *Qualitative and quantitative aspects of trace analyses by capillary gas chromatography*. Thesis, Eindhoven Techn. Univ. 1985, 183 p.
- [21] M. Kaljurand, M. Koel, E. Küllik, *Anal. Chem. Acta* **239**, 3173 (1990).
- [22] J. M. Laeven, H. C. Smit, J. C. Kraak, *Anal. Chem. Acta* **194**, 11 (1987).
- [23] J. H. Valentin, G. C. Garle, J. B. Phillips, *Anal. Chem.* **57**, 1035 (1985).
- [24] M. Engelsma, *Chemical Concentration Modulation in Correlation Chromatography*, Thesis, Univ. Amsterdam, 1991, 146 p.

Received: Mar 30, 1994
 Revised manuscript
 received: May 25, 1994
 Accepted: Jun 5, 1994