Problems caused by the activity of Al₂O₃-PLOT columns in the capillary gas chromatographic analysis of volatile organic compounds

Citation for published version (APA):

Noij, T. H. M., Rijks, J. A., & Cramers, C. A. M. G. (1988). Problems caused by the activity of Al₂O₃-PLOT columns in the capillary gas chromatographic analysis of volatile organic compounds. *Chromatographia*, 26(1), 139-141. <https://doi.org/10.1007/BF02268138>

DOI:

[10.1007/BF02268138](https://doi.org/10.1007/BF02268138)

Document status and date:

Published: 01/01/1988

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Problems Caused by the Activity of Al_2O_3 -PLOT Columns in the Capillary Gas Chromatographic Analysis of Volatile Organic Compounds

Th. Noij²/J. A. Rijks¹/C. A. Cramers^{*1}

¹ Eindhoven University of Technology, Lab. Instrumental Analysis, P. O. Box 513, NL-5600 MB Eindhoven, The Netherlands,

² Present address: The Netherlands Waterworks' Testing & Research Institute, KIWA N. V., PO Box 1072, NL-3430 BB Nieuwegein, The Netherlands

Key Words

Capillary gas chromatography
 Al_2O_3 -PLOT columns
Catalytic activity
Halocarbons

Summary

Al_2O_3 -PLOT columns are used with great advantage for the analysis of volatiles, because of the increased capacity ratio and selectivity compared to WCOT-columns. Their applicability is limited to relatively non-polar components with relatively low boiling points i.e. eluting before n-decane.

In the analysis of the halocarbons in stratospheric air, the decomposition of certain compounds was observed.

In this study the stability of a number of volatile organic compounds was determined in function dependence of the column temperature using a two-dimensional GC-system.

A possible reaction mechanism for the decomposition is proposed and confirmed for several chlorinated ethanes.

selectivity, and peak resolution is improved. On the other hand, the highly active alumina restricts the applicability of this type of column in gas chromatographic analyses. The practical use is limited to compounds eluting before n-decane. Polar solutes like ethanol and methanol do not elute at all, while slightly polar compounds often elute with bad peak shapes. The retention mechanism is very sensitive to the water content of the carrier gas, although the effect is reduced by a KCl deactivation of the alumina stationary phase [3]. It was observed that at elevated temperatures some halogenated compounds reacted during the chromatographic process [11]. Moreover, under supercritical chromatographic conditions ($T > 200^\circ\text{C}$, $P > 30$ Bar) Asche observed the decomposition of certain halocarbon mobile phases $\text{C}_2\text{Cl}_3\text{F}_3$, CCl_4 , CH_2Cl_2 and $\text{C}_2\text{H}_4\text{Cl}_2$ on alumina stationary phases in packed columns [12]. This had led to great concern about the quantitative results of the analyses of traces of halogenated organic compounds on this type of column. Here general rules are provided with respect to the catalytic destruction of organics on Al_2O_3 -PLOT columns. For this purpose, several volatile organic compounds were examined by comparison of their peak areas after separation on a WCOT and a PLOT column at various temperatures in a two-dimensional GC system. A possible reaction mechanism is suggested and experimentally confirmed.

Introduction

In environmental monitoring, the analysis of volatile organic compounds by capillary gas chromatography has become increasingly important. Porous Layer Open Tubular (PLOT) columns with Al_2O_3 as the stationary phase have proven to be very suitable for the separation of light hydrocarbons [1–6], $\text{C}_1 - \text{C}_2$ halocarbons [6, 7] and perfluoroalkanes [8]. The combination of PLOT columns with packed or WCOT columns in multidimensional GC systems has been reported as well [9, 10].

On an Al_2O_3 -PLOT column volatile compounds can be separated at considerably higher temperatures than on a thin film WCOT column. Thus the need of sub-ambient oven temperatures is avoided. Compared to thick film WCOT columns Al_2O_3 -PLOT columns offer a higher

Experimental

Gas standards were prepared by the addition of an internal standard (CCl_2F_2 , except for C_2H_4 and cyclo- C_3H_8 , where C_3H_8 was the internal standard) and 2 to 4 organic compounds to 100 ml of helium contained in a glass vessel. Final concentrations ranged between 0.5 and 10 % (v/v). In order to eliminate errors due to concentration changes during storage, the injected sample was divided into two parts with the gas chromatographic equipment shown in Fig. 1 (Sichromat-2, Siemens AG, Karlsruhe, FRG). One part (~ 60 %) is separated on the first column (WCOT, $L = 26$ m, i. d. = 0.32 mm, CP SIL 5CB, $d_f = 1.1 \mu\text{m}$; Chrompack, Middelburg, NL) and detected by the first FID in order to determine the actual compound concentrations in

Fig. 1

Experimental configuration of the two-dimensional capillary GC system. I = splitter injector; S = "Life switching system"; CC₁ = WCOT column; CC₂ = Al₂O₃/KCl PLOT column; FID₁, FID₂ = Flame Ionisation Detectors; DATA = data system.

Fig. 2

Chromatograms of a hydrocarbon gas standard; (a) WCOT column, (b) PLOT column. 1 = C₂H₄; 2 = C₃H₈ (s); 3 = cyclo-C₃H₆; 4 = C₂H₂.

the sample. After passage of the WCOT column, the other part is transferred to the second column (Al₂O₃/KCl-PLOT, L = 50 m, i. d. = 0.32 mm; Chrompack, Middelburg, NL) and detected by the second FID. The ratio of the observed relative response factors reveals the effect of the Al₂O₃-PLOT column on the composition of the gas sample. An example of the separations on both columns is shown in Fig. 2.

Results and Discussion

Calculations

The stability factor K_s is a measure for the inertness of the compound with respect to the reactivity of the Al₂O₃ stationary phase and is expressed as:

$$K_s = \frac{(A_i/A_s)_2}{(A_i/A_s)_1} \quad (1)$$

where A is the peak area of the compound studied (j) resp. the internal standard compound (s) for the WCOT/FID system (1) and the Al₂O₃-PLOT/FID system (2). It follows

that K_s is equal to the ratio of the observed relative response factors for both systems:

$$K_s = \left[\frac{(f_j)_2}{(f_j)_1} \right]_{\text{obs.}} \quad (2)$$

Irreversible adsorption by the Al₂O₃-PLOT column is indicated by $K_s = 0$ and catalytic decomposition by decreasing K_s with increasing column temperatures or eventually $K_s = 0$.

In a separate study it was shown, that the internal standard compounds, i.e. C₃H₈ and CCl₂F₂, are not destructed by the Al₂O₃ stationary phase. When no reaction occurs the factor K_s is not necessarily equal to unity. It was shown by Gough and coworkers [13, 14] as well as by Dressler [15], that the detector response of e.g. halogenated hydrocarbons depends on the hydrogen flow rate of the FID, and this will definitely be different for both detectors used here. For the inert compounds K_s ranged from 0.6 up to 1.3. Consequently changes of K_s have to be regarded rather than deviations from unity.

Reproducibility

The reproducibility of the K_s -factor was determined when no sample degradation occurred (C₂H₂ at 175 °C), as well as when decomposition reactions were observed (C₂H₂ at 250 °C). The corresponding relative standard deviations were 1.6 % respectively 5.6 %.

Although it was not recognized as a result of decomposition processes, similar observations were reported by Reineke and Bächmann [6]. At an elution temperature of 265 °C, they found a poor FID response for C₂H₂.

Influence of the Temperature

For a selected number of compounds the K_s values at different temperatures of the Al₂O₃-PLOT column are presented in Table I. Roughly, three categories can be distinguished: A. components that react strongly, even at moderate temperatures; B. compounds that react only at high temperatures; C. compounds that do not react at the temperatures studied (Note that for CCl₄ no clear tendency is observed).

Apparently partly halogenated compounds interact strongly with the Al₂O₃ stationary phase, whereas completely halogenated and saturated hydrocarbons are not affected. Apart from the compounds listed in Table I, it was also shown by separate investigations using a different experimental set-up that SF₆, CClF₃, CBrF₃ and C₂ClF₅ are not decomposed. Of special interest is the behaviour of CH₃CCl₃ on the Al₂O₃ stationary phase at high temperatures. Fig. 3 clearly shows the formation of a reaction product (peak 3), when the temperature increases. By using a Mass Selective Detection (Hewlett Packard, Avondale, PA, USA), this compound was identified as CH₂CCl₂. Although it is far beyond the scope of this study to present a detailed discussion on the catalytic activity of alumina, a short outline is given here. It is a well-known fact in catalysis that alumina behaves as an acidic catalyst [16]. The acidity of alumina is enhanced by the presence of water or chloride,

Table I. The influence of the column temperature on K_s .

Cat.	Compound	Temperature °C							
		75	100	125	150	175	200	225	250
A.	CHClF ₂	0.6	0.3	0.1	0	0	0	—	—
	CHCl ₂ F	—	—	0	0	0	0	—	—
	CH ₂ Cl ₂	—	—	0	0	0	0	0	0
	CHCl ₃	—	—	0.5	0.2	0	0	—	—
	CH ₃ CCl ₃	—	—	0	0	0	0	1.0*	1.1*
B.	C ₂ HCl ₃	—	—	—	1.0	1.0	1.0	0.8	0.7
	C ₂ H ₂	—	—	0.9	0.9	0.9	0.8	0.7	0.6
C.	CCl ₃ F	—	—	0.8	1.0	0.9	0.9	0.8	1.0
	C ₂ Cl ₂ F ₄	1.0	0.9	0.9	1.0	1.0	1.0	—	—
	C ₂ Cl ₃ F ₃	—	—	—	1.1	1.0	1.1	1.0	1.0
	C ₂ Cl ₄	—	—	1.1	1.0	1.0	1.1	1.1	1.2
	C ₂ H ₄	—	—	0.7	0.6	0.6	0.7	0.6	0.6
	cyclo-C ₃ H ₆	—	—	0.9	0.9	0.9	0.9	0.9	0.9
	n-C ₅ H ₁₂	—	—	1.2	1.3	1.2	1.3	1.3	—
	n-C ₆ H ₁₄	—	—	—	1.3	1.2	1.3	1.3	—
	n-C ₇ H ₁₆	—	—	—	—	1.1	1.3	1.3	—
	CCl ₄	—	—	0.5	0.3	0.4	0.2	—	—

*peak area of a reaction product.

Fig. 3

Chromatograms showing the formation of CH₂CCl₂ from CH₃CCl₃ on Al₂O₃ at different temperatures. a = 175 °C; b = 200 °C; c = 225 °C; d = 250 °C; 1 = CCl₂F₂ (s); 2 = CCl₃F; 3 = CH₂CCl₂; 4 = C₂Cl₄.

thus forming a strong Brönsted acid. Such an acidic catalyst may abstract HCl from halogenated hydrocarbons and thus forming carbenium-ions, e.g.

Through intra- or intermolecular rearrangements, several products may be formed, both as final reaction products or as intermediates. In industrial processes these principles are applied in hydrocracking, polymerisation and alkylation [17].

A logical explanation for the presence of CH₂CCl₂ as a reaction product is the HCl abstraction from CH₃CCl₃.

Similar reactions were observed for CHCl₂CH₃ (to give CHClCH₂) as well as for CH₂ClCHCl₂ (to give CH₂CCl₂). For the other compounds, however, no reaction products could be detected by the MSD.

Conclusions

Although Al₂O₃/KCl-PLOT columns are very suitable for the gas chromatographic separation of volatile organic compounds, the catalytic activity of alumina may cause false identifications as well as erroneous quantitative results. It was shown that at elevated temperatures partly halogenated compounds are decomposed by the Al₂O₃/KCl stationary phase. The proposed mechanism of catalytic HCl abstraction was confirmed for 1,1,1-trichloroethane, 1,1,2-trichloroethane and 1,1-dichloroethane.

References

- [1] W. Schneider, J. C. Frohne, H. Bruderreck, J. Chromatogr. 155, 311 (1978).
- [2] R. C. M. de Nijs, J. HRC & CC, 4, 612 (1981).
- [3] R. C. M. de Nijs, J. de Zeeuw, J. Chromatogr., 279, 41 (1983).
- [4] N. Schmidbauer, M. Oehme, J. HRC & CC, 8, 404 (1985).
- [5] N. Schmidbauer, M. Oehme, J. HRC & CC, 9, 502 (1986).
- [6] F. J. Reineke, K. Bächmann, J. Chromatogr., 323, 323 (1985).
- [7] K. Ballschmiter, P. Mayer, Th. Class, Fres. Z. Anal. Chem. 323, 334 (1986).
- [8] L. Ghaoui, E. Dessai, W. E. Wentworth, S. Weisner, A. Zlatkis, E. C. M. Chen, Chromatographia, 20, 75 (1985).
- [9] F. Poy, L. Cobelli, J. Chromatogr., 349, 17 (1985).
- [10] H. Tani, M. Furuno, J. HRC & CC, 9, 712 (1986).
- [11] H. Stöl, private communication.
- [12] W. Asche, Chromatographia, 11, 411–412 (1978).
- [13] T. A. Gough, M. A. Pringuer, C. J. Woollam, J. Chromatogr., 150, 533 (1978).
- [14] M. A. Pringuer, J. Porter, T. A. Gough, C. F. Simpson, J. Chromatogr. Sci., 17, 387 (1979).
- [15] M. Dressler, J. Chromatogr., 42, 408 (1969).
- [16] K. Tanabe, Solid Acids and Bases, Acad. Press, New York, 1970.
- [17] P. H. Emmett, Ed., Catalysis, Vol. VI., Reinhold, New York, 1959.

Received: Sept. 27, 1988

Accepted: Nov. 4, 1988
G