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**Citation for published version (APA):**

Staal, W. J., Cools, P. J. C. H., Herk, van, A. M., & German, A. L. (1993). On-line extraction of polymers, oligomers, additives and monomers by multiple solvents on packed HPLC columns. *Chromatographia*, 37(3-4), 218-220. <https://doi.org/10.1007/BF02275864>

**DOI:**

[10.1007/BF02275864](https://doi.org/10.1007/BF02275864)

**Document status and date:**

Published: 01/01/1993

**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.

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# On-line Extraction of Polymers, Oligomers, Additives and Monomers by Multiple Solvents on Packed HPLC Columns

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## Key Words

Column liquid chromatography  
On-line extraction of polymer additives  
Gradient elution of polymers

## Summary

Extraction of monomers, additives, oligomers, and polymers from a blend is very time consuming and labor intensive. Now by use of a special guard column and multi-solvent gradient liquid chromatograph (HPLC), the extraction and analysis can be performed in one step.

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## Introduction

The classic Soxhlet extraction of additives in a polymer takes 7–24 hours and needs large amounts of solvents. The more modern extraction technologies with supercritical fluids, microwave oven and ultrasonic bath take shorter times (20–60 min) [1].

The problem with these new and relatively severe extraction technologies is that some polymers will degrade under such conditions. In general the greatest problems with extraction technologies are the recovery, the selectivity of the extraction solvent and the limited automation possibilities. Because of the limited selectivity a chromatographic analysis is needed after the extraction [2]. The multiple solvent extraction method based on an HPLC instrument does not have these disadvantages. Extraction and analysis are also performed in one step on-line. The principle of this method is to dissolve the sample in a good solvent and precipitate or suspend the polymer sample in the HPLC instrument with a non-solvent. This precipitate or suspension will adsorb onto a guard column with a special flow distributor to prevent column plugging. By

adding a solvent to the adsorbed suspension with a gradient system, the monomers, additives and polymers will redissolve and elute from the column.

## Experimental

### HPLC Equipment

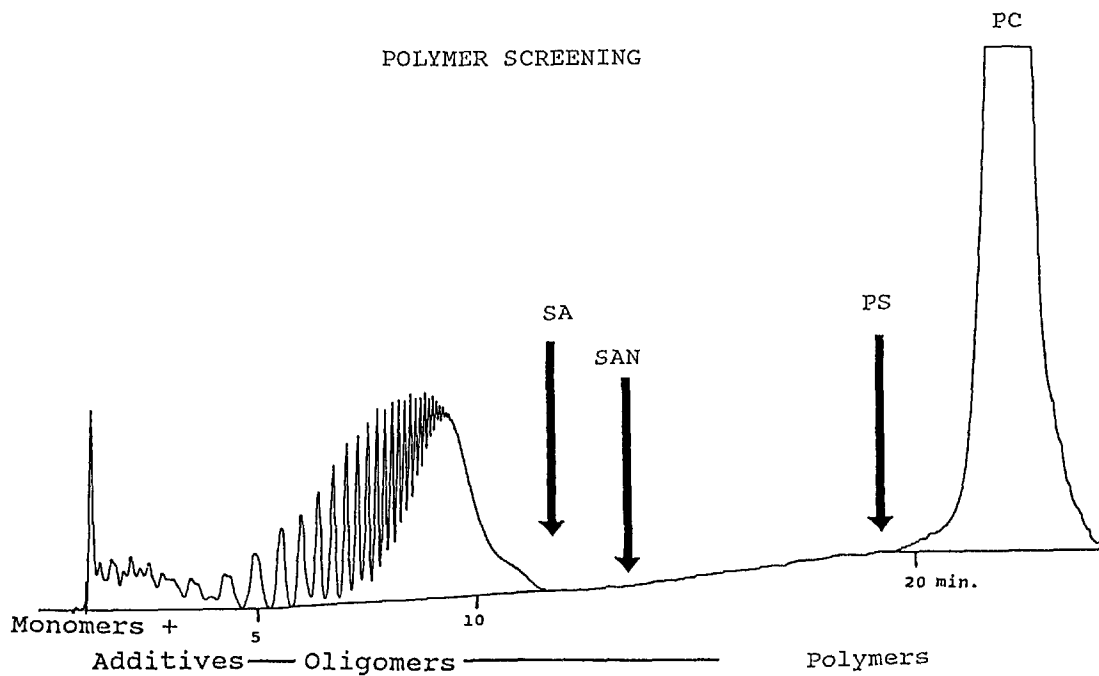
Gradient elution was performed with a 4 solvent gradient pump (Model 600). A Waters intelligent sample processor (WISP, Model 712) was used to inject 5 µl samples (conc. 1 % w/v). A Waters variable wavelength detector (Model 486) was used to monitor the eluent at a wavelength of 261 nm. The chromatogram was recorded with an integrator (Waters, Model 741). The water was purified with a Milli-Q system from the Millipore Corporation. Tetrahydrofuran (THF) without stabilizer was obtained from Rathburn.

### HPLC Conditions

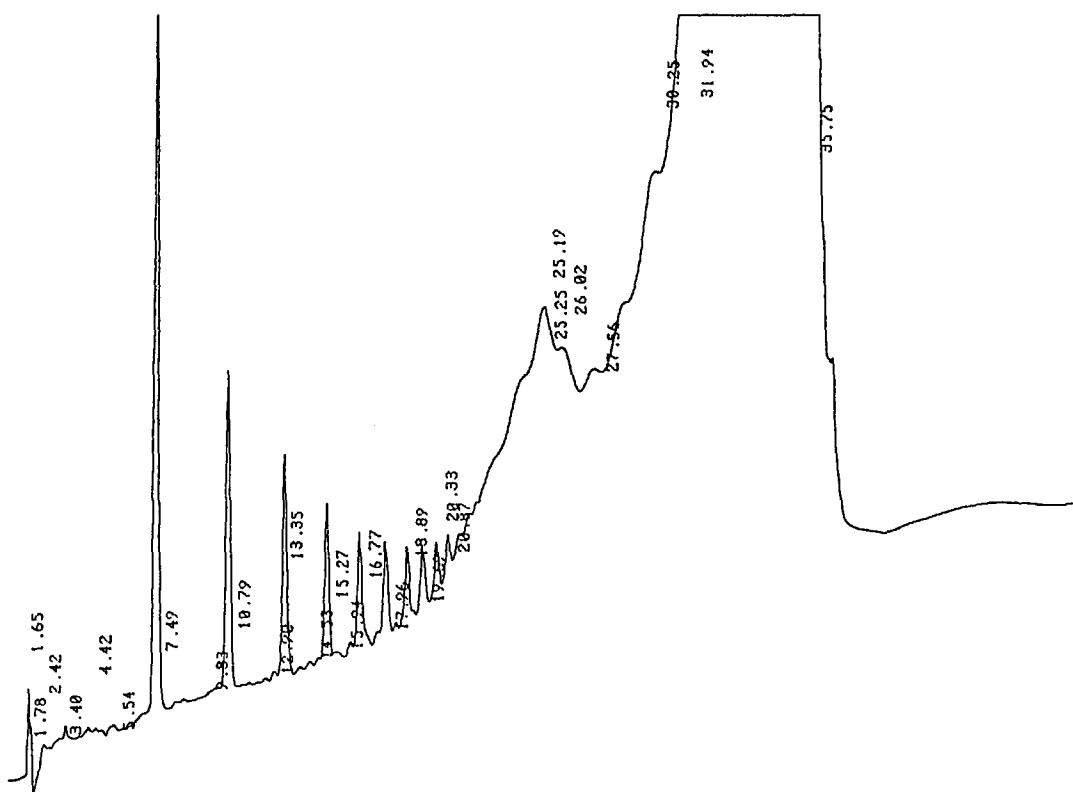
All polymer samples were dissolved in THF prior to analysis. A linear gradient was used starting with 50/50 water/THF as nonsolvent to 100 % THF as good solvent in 30 or 60 minutes. The eluent flow was 1 ml/min. The guard column was a Guard-Pak module (Waters) with Nova-Pak C18, 4 µ inserts. This guard column has a special flow distributor to prevent plugging. The main column was radial-packed (100 × 8 mm, Nova-Pak C18, 4 µm Waters) and placed in a radial compression chamber (Waters). With this column semi-preparative separations can also be achieved. The polymers were from Scientific Polymer Products, inc. US.

## Results and Discussion

Many researchers have published successful HPLC separations of monomers, additives, oligomers and polymers [3–6]. In this study the experimental and



**Figure 1**  
 Gradient separation of polycarbonate oligomers, polycarbonate polymer and the elution position of other polymers in a polycarbonate blend.



**Figure 2**  
 Gradient separation of polysulfone containing oligomers. Concentration 1 mg/ml THF. Injection volume 5  $\mu$ l Column. Radial-Pak Nova-Pak C18, 100  $\times$  8 mm, 4  $\mu$ m. Eluent 50/50 water-THF to 100 % THF in 30 min. linear. Flow 1 ml/min.

instrumental conditions for monomers, additives, oligomers and polymers are all combined in the one method.

An impression of the extraction and separation power is given in Figure 1. The elution position of different monomers, additives and polymers in a polycarbonate blend is shown. During the polymerization of polysulfone, some oligomers are formed (Figure 2). With the strong solvent, (THF) all of the polymer material is eluted from the column. The amount of oligomers can be calculated relative to the polymer peak. The success of this application is based on the large adsorption or adhesion power of the suspension on the guard column. This guard column is packed with spherical particles (110 mg) having a surface area of 120 m<sup>2</sup>/g. That means that the injected amount of polymer (50 µg) is spread over 1–12 m<sup>2</sup>. This layer is so thin that extraction and redissolution is immediate. Due to this large surface area, this method can be scaled-up to preparative (mg → g) scale.

## Future Improvements

By reducing the gradient speed (%/min) impressive improvements can be made on the separation capabilities. Improvements can be made also by using a larger number of selective solvents and column packings. With more selective detectors (fluorescence) and universal mass detectors, detection improvements can be made.

## References

- [1] R. Nielson, *Journal of Liquid Chrom.*, **14**(3), 503 (1991)
- [2] F. P. B. van der Maeden, M. E. F. Biemond, P. C. G. M. Janssen, *J. Chromatogr.* **149**, 539 (1978)
- [3] J. J. Lewis, L. B. Rogers, R. E. Pauls, *J. of Chromatogr.*, **264**, 339 (1983)
- [4] G. Glöckner, *Chromatographia*, **25**, 854 (1988)
- [5] R. Schultz, H. Engelhardt, *Chromatographia*, **29**, 205 (1990)
- [6] W. J. Staal, *Proceedings of the international technical symposium on GPC and LC analysis of polymers and related materials*, Oct. 1989, Boston, Mass., USA, p. 518

Received: Apr 13, 1993

Accepted: May 17, 1993