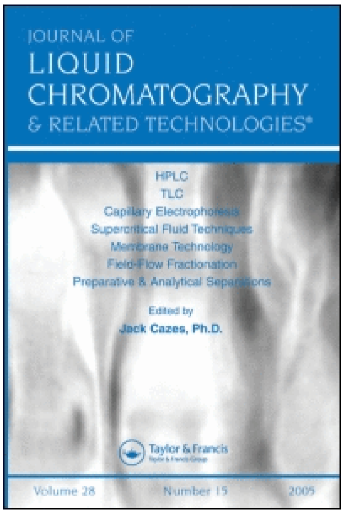

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# Determination of Chemical Composition of Polymers by Sec with Coupled Density and Ri Detection. I. Polyethylene Glycol and Polypropylene Glycol

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# DETERMINATION OF CHEMICAL COMPOSITION OF POLYMERS BY SEC WITH COUPLED DENSITY AND RI DETECTION. I. POLYETHYLENE GLYCOL AND POLYPROPYLENE GLYCOL

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## SUMMARY:

It is shown, that the chemical composition of copolymers and polymer blends can be determined for any point of the molecular weight distribution using size exclusion chromatography (SEC) with two universal detectors: a density detector and a RI detector.

Mixtures of polyethylene glycols and polypropylene glycols have been analyzed using the new method.

## INTRODUCTION:

In the analysis of copolymers an important problem is the variation of the chemical composition with molecular weight, which may influence product properties very strongly. By conventional analytical methods (such as elemental analysis, IR- or NMR-spectroscopy etc.)[1] one may obtain only the overall composition. Fractionation according to molecular weight and/or chemical composition and subsequent determination of molecular weight and chemical composition is, however, a rather laborious task[2].

Several authors have applied two-dimensional ("orthogonal") chromatography[4-10], i.e. a combination of size exclusion chromatography (SEC), which separates according to molecular dimensions, with liquid adsorption chromatography, which separates according to chemical composition.

Another approach is the use of size exclusion chromatography (SEC) with two detectors, the sensitivity of which for both monomer units is sufficiently different. Basically, there are two possible cases:

1. One of the detectors is selective (which means, it detects only one of the components), the other one is universal (which means, that it will detect both monomer units). Many examples have been described in the literature[11-19], although it works only with a small number of copolymers: if one of the monomer units is UV-active (such as styrene), one may use a photometer as the selective detector and a differential refractometer as the universal detector. Infrared detection may also be applied, which combines a universal and a selective detector in one instrument[20- 22].
2. Both detectors are universal, that means, each detector detects both of the components, but with a different sensitivity. This would be very important for the numerous non-UV-absorbing copolymers, but as the only commonly used universal detector in SEC is the RI - detector, only a few examples have been described in the literature[23-25].Since the density detector[23-35] has proven to be a real alternative to the RI - detector, the second approach seemed to be a solution of this problem.

The aim of this paper was to evaluate the performance of SEC with coupled universal detectors in the analysis of non-UV-absorbing polymers. Instead of copolymers mixtures of unipolymers were used as well defined standard materials. Polyethylene glycols and polypropylene glycols were chosen for three reasons: they are commercially available in a wide range of molecular weight, their copolymers are important products, and they have already been studied in previous communications[27,35].

## INSTRUMENTATION AND MATERIALS:

A density detection system DDS 70 (A.PAAR KG, Graz, Austria) was used, which is shown schematically in Fig.1.

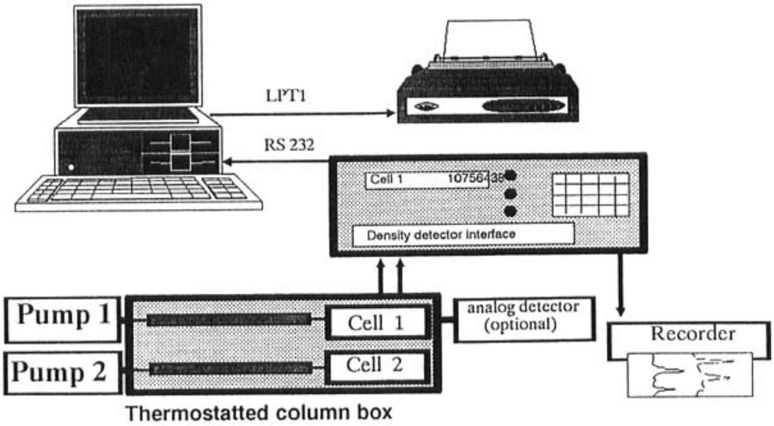

*Fig 1: Chromatographic system using the density detector (schematically)*

A thermostated box contains the columns and up to two (indepentent) density measuring cells, which are connected to an intelligent interface. A second detector (in this case a differential refractometer SICON LCD 201) is connected to the analog input of the interface and coupled to one of the density cells. Raw data are collected in the interface and transferred to a MS-DOS computer. Data acquisition and processing is performed using the software package CHROMA.

A column set of three 30 cm - columns filled with PL Microgel ($10^4$-$10^3$-500 A) was used for all chromatograms. Chloroform (Merck, LiChroSolv grade) was used as mobile phase. Polyethylene glycols with molecular weights of 2000, 1500, and 1000 and polypropylene glycol (m.w. 2000) (purchased from Merck) were used without any further purification.

## THEORY:

A concentration $c_i$ of a solute passing the measuring cell of a RI detector causes a change $\Delta n$ in the refractive index :

$$\Delta n = c_i \cdot \nu_i + c_i^2 \cdot A \tag{1}$$

wherein $\nu_i$ is the refractive index increment.

Since the concentrations in SEC are very low, the second term is negligible, and one may write

$$\Delta n = c_i \cdot \nu_i \tag{2}$$

In a similar way, a density change $\Delta d$ represents the concentration of a solute

$$\Delta d = c_i \cdot a_i \tag{3}$$

For a copolymer containing the monomer units A and B with the corresponding response factors $\nu_A$, $\nu_B$ and $a_A$, $a_B$, respectively, the corresponding changes in RI and density are

$$\Delta n = c_i . ( \nu_A . w_A + \nu_B . w_A ) \tag{4}$$

and

$$\Delta d = c_i . ( a_A . w_A + a_B . w_A ) \tag{5}$$

wherein $w_A$ and $w_B$ are the weight fractions of A and B.

Division of equations (4) and (5) yields

$$\Delta n/\Delta d = ( \nu_A . w_A + \nu_B . w_A ) / ( a_A . w_A + a_B . w_A ) \tag{6}$$

With

$$w_B = 1 - w_A \tag{7}$$

one may write

$$\Delta n/\Delta d = [w_A . (\nu_A - \nu_B) + \nu_B] / [w_A . (a_A - a_B) + a_B] \tag{8}$$

A simple transformation yields

$$1/w_A = 1 - (a_A . \Delta n/\Delta d - \nu_A) / (a_B . \Delta n/\Delta d - \nu_B) \tag{9}$$

Using this equation, the weight fractions of A and B can be calculated from $\Delta n$ and $\Delta d$.

Conversion of the signals from the detectors into refractive index or density changes, respectively, requires understanding of data acquisition and processing. Hence the working principle of the instrument used for these investigations shall be explained briefly.

The signal $x_d$ from the density detector is - due to the special measuring principle - inherently digital and represents the mass $m_i$ eluted within each measuring interval:

$$x_d = a_i . m_i / [2.10^{-7}.(d_0 + B).F] \tag{10}$$

wherein $d_0$ is the density of the mobile phase, B the cell constant, F the flow rate, and $a_i$ the response factor, which is given for each sample component by

$$\Delta d = c_i \, . \, (1 - d_0 . \bar{v}^*{}_i) = a_i . \, m_i / V \qquad (11)$$

wherein $\bar{v}^*{}_i$ is the apparent specific volume and V the volume passing the measuring cell during one measuring interval.

The signal from the RI - detector ( +- 1V) has to be digitalized using the AD-converter of the interface to yield a digital signal ( +- 20000 digits).

In CHROMA the response factor $f_R$ of the RI-detector is defined as the response (in digits) per $\mu$g of sample (or peak area per sample size):

$$x_R = f_R \, . \, m_i \qquad (11)$$

Using the signals defined above instead of the density and RI - changes and $f_R$ instead of the refractive index increment, one may easily calculate the weight fraction of the monomer units at each point of the MWD.

For this purpose, molecular weight tables (obtained using CHROMA) are written to ASCII-files, from which the $w_A$ and $w_B$ can be calculated using Symphony.

As soon as $w_A$ and $w_B$ are known, one may calculate the corrected chromatogram (using equation 4 or 5), and therefrom the corrected MWD, which is absolutely necessary, if the response factors for the monomer units are considerably different and the chemical composition varies with molecular weight.

## RESULTS AND DISCUSSION:

The determination of response factors was performed by repeated injections of varying sample sizes. As has been shown in a previous communication[35], the

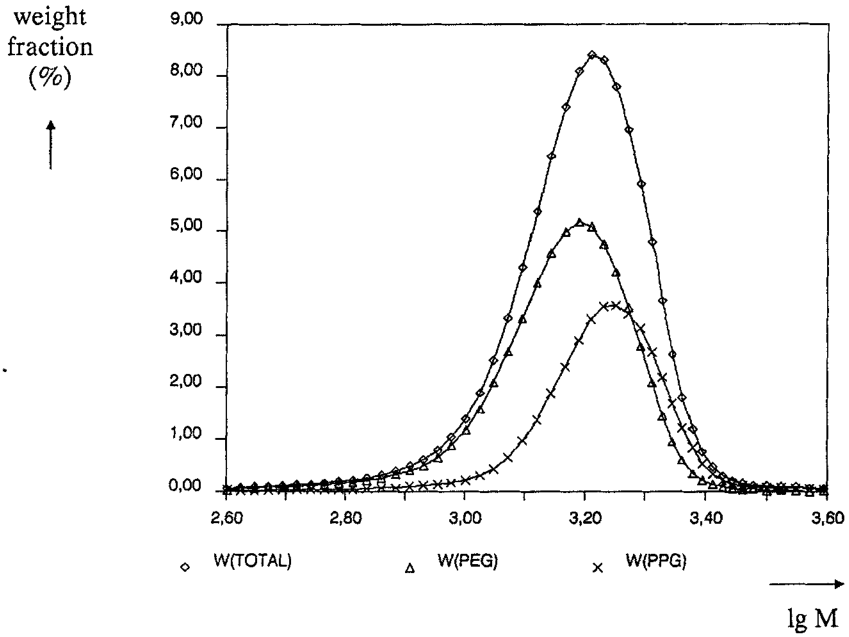

*Fig.2: Molecular weight distribution and weight fraction of monomer units from a chromatogram of a mixture of polypropylene glycol 2000 and polyethylene glycol 1500 obtained with density and RI detection.*

*Tab.1: Response factors of polyethylene glycols and polypropylene glycols in density and RI-detection*

| Sample | mol.weight | density | RI |
|---|---|---|---|
| PPG | 2000 | -0.450 | -6.43 |
| PEG | 2000 | -0.260 | -15.15 |
| PEG | 1500 | -0.262 | -15.37 |
| PEG | 1000 | -0.262 | -15.13 |

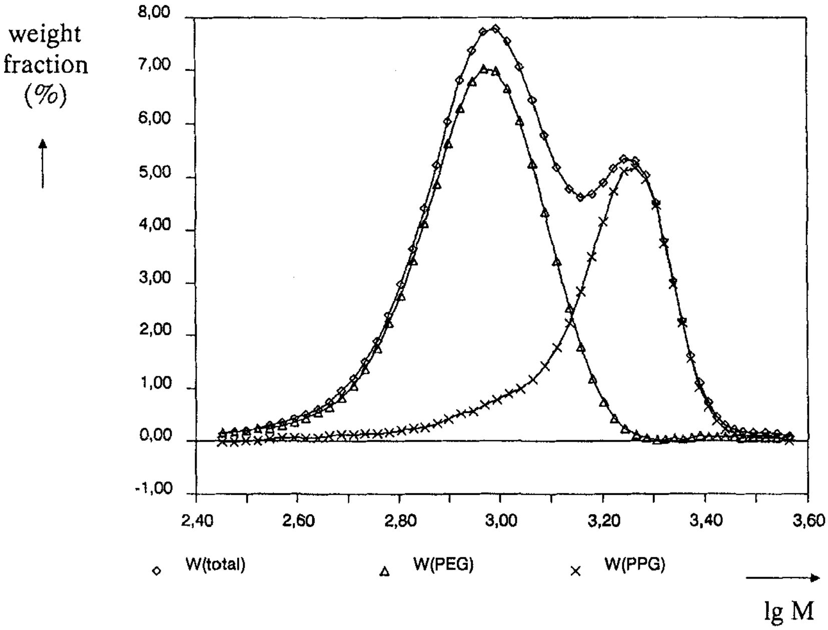

*Fig.3: Molecular weight distribution and weight fraction of monomer units from a chromatogram of a mixture of polypropylene glycol 2000 and polyethylene glycol 1000 obtained with density and RI detection.*

response factors can be considered as constant, their dependence on molecular weight has, however, to be taken into account for the lower oligomers.

In Tab. 1 the response factors of all samples are given for density and RI-detection :

As a test for the performance of the method, three limiting cases of copolymers or polymer blends were simulated using the following mixtures:

1. polypropylene glycol 2000 + polyethylene glycol 1500
2. polypropylene glycol 2000 + polyethylene glycol 1000
3. polyethylene glycol 2000 + polyethylene glycol 1000

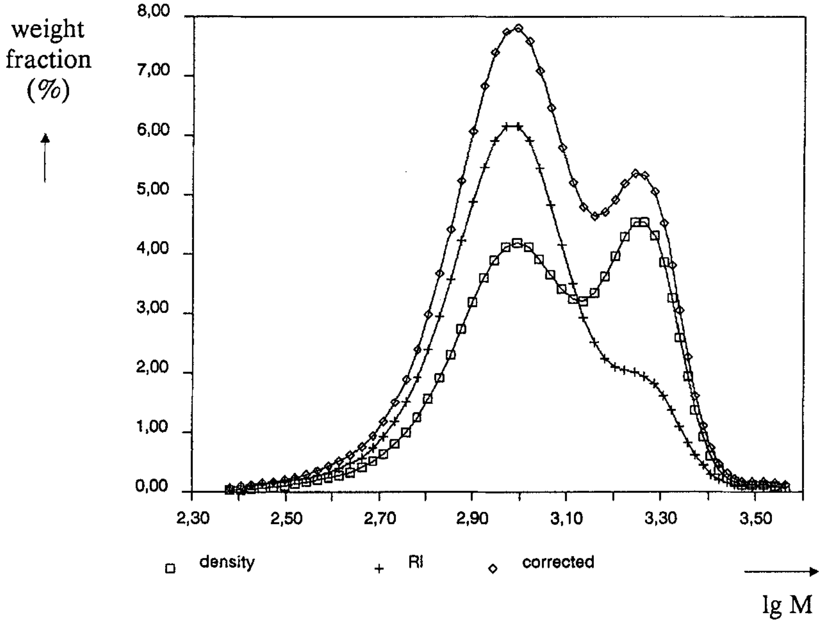

*Fig.4: Molecular weight distribution from density and RI detection, respectively, and corrected molecular weight distribution of a mixture of polypropylene glycol 2000 and polyethylene glycol 1000.*

In the first case, a single peak is obtained, the composition of which should vary only slightly with molecular weight, which is really observed, as can be seen from Fig. 2:

In case 2 a double peak results, the composition of which varies strongly with molecular weight: at higher molecular weight almost pure polypropylene glycol should be found, at lower molecular weight almost pure polyethylene glycol. Indeed the weight fraction of A is found close to zero at low molecular weight, the weight fraction of B at high molecular weight, as can be seen from Fig. 3:

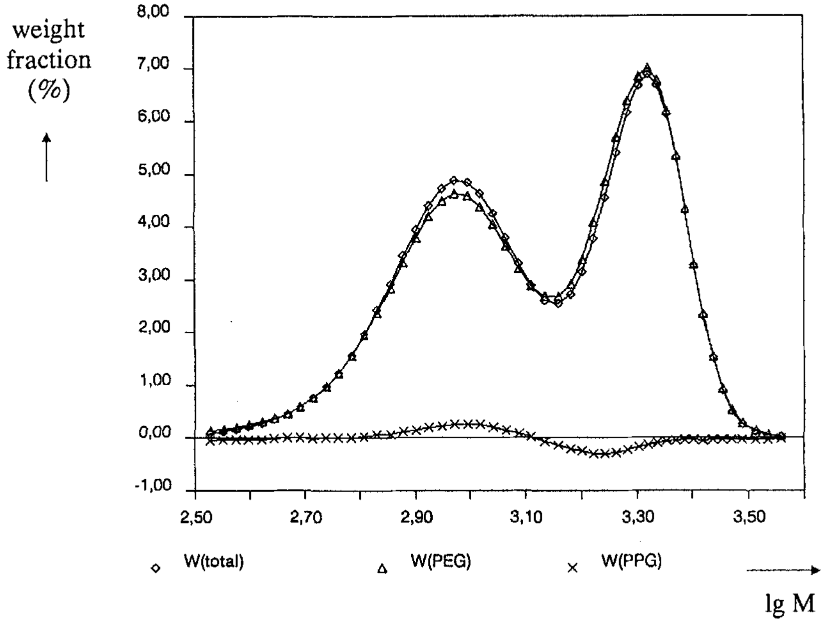

*Fig.5: Molecular weight distribution and weight fraction of monomer units from a chromatogram of a mixture of polyethylene glycol 2000 and polyethylene glycol 1000 obtained with density and RI detection.*

As soon as the weight fractions of A and B have been determined over the entire MWD, the corrected distribution can be calculated. In Fig.4 the distributions from both of the detectors and the corrected molecular weight distribution are shown.

The chromatogram obtained in case 3 looks quite similar, but here the weight fraction of polypropylene glycol is found to be close to zero over the entire range of molecular weight, and the weight fraction of polyethylene glycol is identical with the overall distribution curve, as can be seen from Fig. 5.

## CONCLUSIONS:

The new method proves to yield the chemical composition of a copolymer for any point of the molecular weight distribution. Corrected chromatograms (and molecular weight distributions) can also be obtained by compensation for changes in chemical composition along the distribution curve.

Further investigations shall evaluate scope and limitations of the method. The effects of chemical structure (statistical, random, alternating, graft, and block copolymers), block length, end groups etc. will have to be studied as well as the applicability to various other types of copolymers.

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