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Adaption of a parallel-path poly(tetrafluoroethylene) nebulizer to an evaporative light scattering detector: Optimization and application to studies of poly(dimethylsiloxane) oligomers as a model polymer

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ABSTRACT

The adaption of an parallel-path poly(tetrafluoroethylene)(PTFE) ICP-nebulizer to an evaporative light scattering detector (ELSD) was realized. This was done by substituting the originally installed concentric glass nebulizer of the ELSD. The performance of both nebulizers was compared regarding nebulizer temperature, evaporator temperature, flow rate of nebulizing gas and flow rate of mobile phase of different solvents using caffeine and poly(dimethylsiloxane) (PDMS) as analytes. Both nebulizers showed similar performances but for the parallel-path PTFE nebulizer the performance was considerably better at low LC flow rates and the nebulizer lifetime was substantially increased. In general, for both nebulizers the highest sensitivity was obtained by applying the lowest possible evaporator temperature in combination with the highest possible nebulizer temperature at preferably low gas flow rates. Besides the optimization of detector parameters, response factors for various PDMS oligomers were determined and the dependency of the detector signal on molar mass of the analytes was studied. The significant improvement regarding long-term stability made the modified ELSD much more robust and saved time and money by reducing the maintenance efforts. Thus, especially in polymer HPLC, associated with a complex matrix situation, the PTFE-based parallel-path nebulizer exhibits attractive characteristics for analytical studies of polymers.

1. Introduction

With evaporative light scattering detectors (ELSD), it is possible to detect analytes without chromophores. Therefore, this universal HPLC detector, exhibiting good suitability for gradient elution protocols, is an attractive alternative to the typically used diode array detector in HPLC or refractive index detector in size exclusion chromatography (SEC). An important field of application is the investigation of polymers [1,2]. The use of ELSD for studies of carbohydrates [3], poly(dimethylsiloxane) [4] or poly(ethylene glycol) [5,6] is already well established. Nevertheless, the ELSD also has some constraints, i.e. the non-linear dependence of the ELSD signal on sample concentration and restriction to volatile or semi-volatile mobile phases and correspondingly to analytes which are not vaporable through the detection process [7,8]. For understanding the potentials and limitations of the device a detailed analysis of the process associated with this detection principle is necessary. The signal generation is determined by the following three steps: Initially the liquid effluent from liquid chromatography is nebulized, followed by evaporation of the mobile phase and finally the remaining analyte particles are transferred to a measurement cell where a light beam is scattered by the latter and detected with a photomultiplier [9–12].

Mojsiewicz-Pieńkowska [13] classified four groups of factors which influence the signal response of an ELSD: (i) parameters determining the separation procedure (e.g. flow and composition of mobile phase); (ii) parameters which can be modified by the user without influencing the actual separation in liquid chromatography (e.g. detector temperatures, nebulizer type); (iii) chemical and physical properties of the investigated analyte (e.g. molecular weight, vapor pressure) and (iv) types of different nebulization gases (e.g. different heat conductivities [14]). The most important

Abbreviations: ACN, acetonitrile; ELSD, evaporative light scattering detector; MeOH, methanol; PDMS, poly(dimethylsiloxane); PTFE, poly(tetrafluoroethylene); SEC, size exclusion chromatography; THF, tetrahydrofuran.

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Table 1
Overview of selected data of relevant solvents; *) data taken from [20], all other data out of [21].

Solvent	Viscosity (T = 25 °C) [mPa s]	Density (T = 30 °C) [g mL^{-1}]	Vapor pressure (T = 25 °C) [kPa]	Boiling temperature [°C]	Surface tension (T = 25 °C) [mN m^{-1}]
Acetonitrile	0.369	0.7707	11.9	81.6	28.66
Tetrahydrofuran	0.456	0.8833	21.6	66.0	26.4 *)
Acetone	0.306	0.7796	30.8	56.1	22.71
Methanol	0.544	0.7815	16.9	64.5	22.17

parameters which can be varied for optimization of the detector response are factors one and two. Thus, the nebulizer and evaporator temperature, ELSD gas flow, type of nebulizer and the detection parameters of the scattered light are the aspects the analytical chemist should properly adjust because the complexity of the detector is mostly determined by these interactions [15,16]. Additionally, parameters like the choice of mobile phase and flow rate also affect the ELSD response significantly.

In the initial detection step, the effluent of the LC system gets nebulized to a primary aerosol, which shows a narrow polydispersity and particle distribution [11]. The amount of nebulization gas has to be adjusted carefully to generate an ideal aerosol, consisting of the majority of analyte particles and adequate amount of mobile phase. Furthermore, the aerosol formation should be robust and thus generate a flat baseline with low noise. For organic solvents, a low gas flow is usually preferred. As soon as the mobile phase contains small amounts of water, a higher gas flow or evaporator temperature is necessary for complete nebulization of the droplets. An appropriate and uniform aerosol is an important prerequisite for a robust detector performance. After nebulization, the remaining mobile phase in the primary aerosol is evaporated in a heated drift tube. In ideal case only analyte particles pass the drift tube. Small aerosol droplets facilitate an efficient evaporation because of their larger surface-to-volume ratio [7] compared to large droplets.

Apart from this, special attention needs to be paid to prevent the evaporation of easily vaporizable analytes. For these substances, it might be advisable to decrease the evaporation temperature if possible in order to obtain sufficient detector response. After evaporation of the mobile phase, the primary aerosol is essentially changed to an aerosol containing only large analyte particles that ideally scatter light. In general, three different kinds of light scattering are taken into account: reflection-refraction, Rayleigh and Mie scattering. The entire scattering process is dominated by the wavelength λ of the incident light beam and the particle diameter d. Rayleigh scattering occurs from particles which are much smaller than the wavelength of the incident light while scattering by reflection and refraction is dominated by larger particles. In between, Mie scattering, which is slightly asymmetric in comparison to Rayleigh scattering, occurs. The asymmetry in direction of propagation leads to decreased light intensity in the light measuring angle [15]. At a ratio of d/λ of about 3.5 the detector sensitivity is in an optimum [17]. A further comprehensive theoretical discussion is beyond the scope of this work and can be found elsewhere [15–18]. An unfavorable ratio of surface area to volume results in a reduced detector performance. Monochromatic light sources, like LED or laser with a short wavelength radiation are used in the most cases to obtain an appropriate detector signal. In conclusion, scattering processes due to particle distributions result in a non-linear behavior of the ELSD [7,8,17].

In addition to parameters discussed above, the mobile phase also affects the detection process. Thus different optimizations for improvement of the signal intensity are described. Stolyhwo et al. [14] and Mathews et al. [19] proposed an adaption of ELSD parameters during gradient elution, due to the change of mobile phase composition. The complex process of signal generation leads to various optimized settings for different solvents, but to our knowledge, it is not completely understood yet which solvent parameter is significant for an alteration in sensitivity. Viscosity, density, surface tension, vapor pressure or boiling point (summarized in Table 1) might influence the detection process [12].

The investigation of analytes like PDMS is commonly done with ELSD and could be used as typical model substance in polymer HPLC, and thus a detailed analysis of these species shows the influences of molar mass and polymer matrix. In the recent years, applications of PDMS in various areas, e.g. in cosmetics, medicine or pharmacy showed increasing importance. Siloxanes are used as detergents, coating excipients in various pharmaceuticals or as implants [22–24].

With polymer HPLC, a detailed analysis of silicone oils and a separation of several particular oligomers are possible. Furthermore, detailed information about the influence of molar mass and polymer matrix on the detection process is obtained. In a recent publication, Mojsiewicz-Pieńkowska [13] analyzed linear siloxanes of different viscosities with SEC and investigated the influence of flow rate of nebulizer gas, temperature of drift tube and flow rate of mobile phase on the ELSD signal. Based on these results, further investigations can contribute to a more detailed understanding of this polymer type.

Since its invention by Charlesworth [15], various types of ELSDs were investigated. As each manufacturer uses a slightly different setup of the detector, it is difficult to compare different detector models. Reports on comparative characterization are very rare [2,7,8]. The nebulization step is a very crucial point and especially in case of polymer analysis the issue of decreasing signal occurs, when high amounts of sample matrix prevail. In this case, polymer matrix includes both, other polymers than the analyte polymer and high molecular weight constituents of the investigated polymer. The challenge of these types of matrices occurs at the tip of the nebulizer where small amounts thereof remain as fragments and may lead to nebulizer clogging after several measurement series. Especially in case of a concentric glass nebulizer which is installed in some commercially available ELSDs, polymer sample components can clog the tip of the thin capillary within the nebulizer. In order to overcome these problems, a more robust type of nebulizer is desirable. The comparison with different nebulization based techniques, as for example inductively coupled plasma mass spectrometry (ICP-MS), shows similar concerns regarding high amounts of matrix. For ICP-based techniques, it is recommended to use a parallel-path poly(tetrafluoroethylene) (PTFE) nebulizer in place of a concentric glass nebulizer to avoid capillary clogging [26–29]. For the compatibility with ELSD, the given dimensions of the nebulizer have to be taken into account as well as its shape, diameter and range of flow rate. These constraints were fulfilled by a parallel-path PTFE nebulizer developed by Burgener [30–32]. In the present work, a comparison of both nebulizers is done with caffeine as model analyte and PDMS as an important practical application in the field of polymer analysis. Detector parameters were optimized for both ELSD configurations. Furthermore, the application of the parallel-path PTFE nebulizer for PDMS analysis and ELSD response factors concerning different molar mass oligomers were determined.

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