



Review

Application of the evaporative light scattering detector to analytical problems in polymer science



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ABSTRACT

Over the last two decades the evaporative light scattering detector (ELSD) has found more and more use in liquid chromatography (LC) of synthetic polymers. The reason behind this is that it can be used for a significantly wider variety of analyte/solvent combinations. Although in many of the applications the ELSD has been used in a qualitative manner, it can also be used quantitatively. For quantitative interpretation of analyses it is, in the case of synthetic polymers, essential to know how parameters, which characterize a polymer sample (i.e., molar mass and chemical composition), as well as parameters, which are a consequence of the LC separation (i.e., composition and flow rate of the mobile phase, its composition), influence the response of the ELSD. This review gives a tabulated overview over applications of ELS detectors in polymer analysis. The influence of parameters arising from either the polymer side or the chromatographic separation is discussed in detail and, in addition, the influence of the ELS detector's running conditions, i.e. type and flow rate of gas and temperature of nebulizer and evaporator, will be reviewed. This information will prove valuable whenever the calibration of an ELSD for the quantitative analysis of synthetic polymers is attempted.

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1. Introduction

In polymer analytics, each polymer sample, as a rule, has to be regarded as a blend of macromolecules which may differ in their molar mass as well as in their chemical composition. A separation of these macromolecules according to their size in solution, i.e. the hydrodynamic volume, is realized by size exclusion

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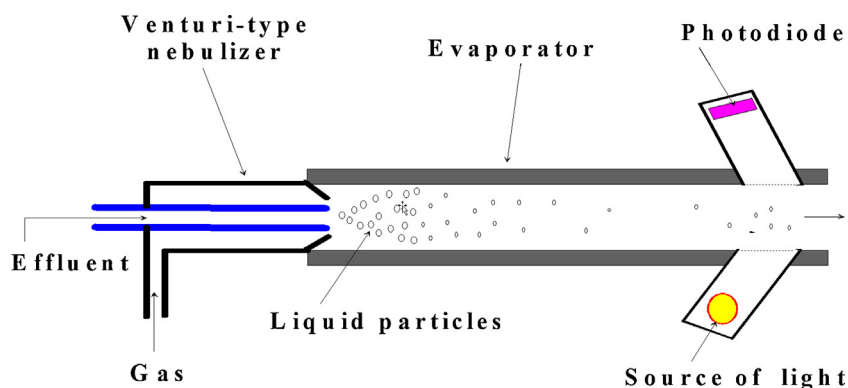


Fig. 1. Schematic representation of an ELSD and the processes inside it.

chromatography (SEC), also known as gel permeation chromatography (GPC). For this technique commonly employed concentration sensitive detectors are the refractive index (RI) – (in various forms) and the UV–visible detector. Although the infrared (IR) detector is primarily used for the determination of the chemical composition, it has been used as a concentration sensitive detector as well, especially in high temperature chromatography of polyolefins [1–5].

A determination of the molar mass of the polymer components after separation in the GPC can either be achieved through calibration of the elution volume with standards of known molar mass and the possible application of universal calibration [6] or by adding mass sensitive detectors such as multi angle laser light scattering (MALLS) detector and viscometer to the chromatographic setup in a multiple detection approach [1,7].

Another task often requested in practice in the analysis of synthetic polymers is the separation of macromolecules into groups, which differ in their chemical composition, and liquid chromatography using gradients of mobile phases has been often used for this purpose. Differences in the elution volumes enable to confirm (or exclude) the presence of a specific polymer in a sample. More detailed information about the chemical composition can be acquired by using a LC-transform module which allows analyzing the separated polymer fractions in the absence of the solvent.

In a LC-transform module the effluent from the chromatographic separation is sprayed on a germanium disk where the mobile phase is evaporated leaving the analyte on the disk. As germanium is transparent to infrared radiation, the analyte can then be analyzed by offline FTIR. As the disk rotates while the liquid is sprayed onto it, and the rotation speed is known, a correlation between HPLC elution volume and chemical composition found in the FTIR analysis can be established [8].

A quantitative detection can, however, be more challenging in interactive chromatography as the changing composition of the mobile phase along the chromatographic run excludes the use of a RI detector, and the UV–visible detector requires the presence of UV-absorbing groups in the polymer, while the IR detector requires a sufficient contrast between the mobile phase and the analyte, i.e. an IR absorption of the polymer which is not present in the spectrum of the solvent. A LC-transform module could be used for quantification as well but it is laborious and time consuming as the concentration can only be determined offline, using this approach. Therefore, if it is not possible to employ an UV–visible detector or an IR detector, a removal of the mobile phase (analogous to the LC-transform approach) in the detector itself is desirable.

The removal of the mobile phase prior to the actual detection is realized in the evaporative light scattering detector's (ELSD) detection principle which is a concentration sensitive detector of quasi-universal applicability in high performance liquid chromatography (HPLC) [9–11], field flow fractionation (FFF) [12]

and supercritical fluid chromatography (SFC) [9,13]. This detector has also been termed evaporative mass detector (EMD) or simply evaporative-type detector [2]. Although the term evaporative light scattering detector and its acronym ELSD have their shortcomings, throughout this review the term will be used. It is most commonly found throughout the literature, avoids confusion about the ELSD being a true mass detector and prevents mix-ups with either mass spectrometers or charged aerosol detectors (CADs) and other evaporation-based detectors (cf. Section 3).

The ELSD was first described by Ford and Kennard in 1966 [9,14,15] and can detect virtually any analyte which is of lower volatility than the mobile phase in which it is analyzed in.

The working principle of the ELSD is quite complex and was described by several authors, for example by Megoulas and Kouparris in their extensive review [9]. In short, the effluent from a LC separation is nebulized into tiny droplets by a Venturi-nozzle using a stream of inert gas, which may be heated, depending on detector type and settings. The solvent is then evaporated from the resulting aerosol in a heated drift tube. As a result the analyte, formerly contained in the effluent, forms tiny particles which pass through a beam of light and scatter the latter. The scattered light is then detected by a photodiode, usually a photodiode and the output voltage forms then the analytical signal [9,15,16]. A schematic representation of an ELSD and the processes inside it is shown in Fig. 1. The reader is referred to Refs. [9,15,16] for more extensive information on the subject of the ELSD working principle.

Applications of the ELSD on detection of various analytes have been summarized in Refs. [9,11,17,18]. However, only a small number of publications which are dealing with the application of ELSD on detection of polymeric substances are listed in reviews [9,17,18], e.g. Refs. [19–23].

The ELSD has, nonetheless, been extensively used for the detection of synthetic polymers in the last two decades. Several producers offer ELSD instruments, which differ in construction and operational parameters (Table 1). An overview of papers dealing with the use of ELSD in the analysis of synthetic polymers is given in Table 2.

In this work we will examine the application of ELSD detection to the analysis of synthetic polymers, where analysts are confronted with changes in mobile phase composition due to either preferential solvation phenomena or both continuous and local gradients. In the latter cases, the ELSD is often the only feasible option for the detection of macromolecules. A particular focus will be given to issues arising from the distributions present in synthetic polymers, i.e. the molar mass dependence of the ELSD response and the influence of the chemical composition of a polymer on the detector signal, as these effects are highly relevant for a quantitative interpretation of a chromatographic analysis. In the following sections we will also discuss all other experimental variables which

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