Introducing CHROMATOGRAPHIA's Second Virtual Issue on Macromolecular Separations

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Three years ago, CHROMATOGRAPHIA introduced readers to its first virtual issue, guest-edited by yours truly, on the topic of macromolecular separations [1]. In it were highlighted publications in this area appearing in the journal over 2 years prior. Subsequent virtual issues, with different guest editors, have covered topics as diverse as chromatographic separations and sample extractions for polycyclic aromatic hydrocarbons [2] and the role of inductively coupled plasma mass spectrometry in separation science [3]. With the present virtual issue, we return to the topic of macromolecular separations, revisiting some of the work published in this field in the journal during the previous two calendar years.

Nine papers are included in the present virtual issue. Starting with size-exclusion chromatography (SEC), which remains the workhorse of polymer characterization, especially when coupled to a multiplicity of physicochemical detectors, we see in [4] the development of a stability-indicating SEC-photodiode array (PDA) detector method to quantify cetuximab, a potent chimeric human-murine monoclonal antibody. Cetuximab has been approved for treatment, in combination with radiation therapy or chemotherapy, of squamous cell carcinoma of the head and neck. The SEC/PDA method was shown effective in the presence of excipients or degradation products without interference.

Continuing investigations into detector orthogonalities begun in [5], the same group more recently examined both detector and wavelength orthogonalities [6]. SEC with on-line refractometry (DRI), UV/visible (UV) where the UV was a diode array detector, and fluorescence (FL) detection, of polystyrene (PS) and poly(methyl methacrylate) blends demonstrated orthogonality of DRI and UV and, within the UV spectrum, wavelength orthogonality wherein one

component of the blend was observable at one wavelength but not at another while the other blend component was observable at both wavelengths. This approach also served to examine blends with co-eluting components. SEC/DRI/FL of blends of unlabeled PS and PS center-labelled with anthracene demonstrated the orthogonality of both detection methods with respect to each other, as well as the sensitivity of FL to the presence of even minor amounts ($\approx 1\%$) of fluorescent moieties.

In [7], the authors employed SEC/DRI to determine natural rubber (polyisoprene) content in plant extract and the molar mass distribution (MMD) of the rubber. Extraction of rubber from Russian dandelion (*Taraxacum kok-saghyz* Rodin), a novel source of natural rubber which has already seen production at the pilot-plant-scale in Europe, was performed using a novel indirect sonication method which was found to be more efficient than either ambient temperature or Soxhlet extraction and less damaging to the MMD than either Soxhlet or direct ultrasonic extraction.

Rubber analysis was also performed, by a different group, employing inverse gas chromatography (IGC). In [8], IGC was used to determine the solubility and interaction parameters and their temperature dependence, and to map Hansen solubility spheres, of both natural rubber and styrene-butadiene-styrene rubber. The authors employed fourteen different probe substances, with results corroborated by both scanning electron microscopy and Fourier-transform infrared spectroscopy (FT-IR) with attenuated total reflection. In a separate study [9], IGC was also used to examine polypyrrole (PPY) after derivatization with TiO_2 . PPY is a conductive polymer (synthetic metal), the conductivity of which can be greatly enhanced by derivatization, while TiO_2 exhibits n-type semiconductor with strong electrochemical and photochemical properties, high surface area, and good electrochemical stability. Combining PPY and TiO_2 has been shown to improve physicochemical properties of the polymer such as its electrical conductivity, electrochemical and sensitivity capabilities. However, characterization of PPY

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is difficult using conventional techniques due to its insolubility in conventional solvents and to its infusible, brittle, and amorphous nature. In this study, IGC was employed to determine both the solubility parameters and the dispersive surface energy of PPY/TiO₂. Characterization of the synthesized substance was aided by FT-IR and differential scanning calorimetry.

In the realm of field-flow fractionation, Pitkänen and Tenkanen show how asymmetric flow field-flow fractionation (AF4) can be used for the analysis of cationic cellulose derivatives [10]. Coupling AF4 on-line to both DRI and multi-angle static light scattering, they evaluated the effects of eluent pH on separation, achieved near-quantitative analyte recovery (a feat in AF4), and were able to determine the molar mass, size, and solution conformation of cationic hydroxyethyl celluloses with different charge densities. The fractionation method was aided by off-line DRI experiments to determine the specific refractive index increment of the analytes. In separate work related to the characterization of charged cellulose derivatives, ion chromatography coupled with solid-phase extraction was employed to simultaneously determine trace organic acids and inorganic ions in sodium carboxymethyl cellulose [11].

In [12], we see how Macko and colleagues employed high-temperature interaction polymer chromatography using a solvent gradient to separate ethylene–vinyl acetate (EVA) copolymers based on VA content, over a 0–100% VA range, and to determine the chemical composition distribution of the copolymers based on % VA. A Hypercarb column was found to afford higher resolution than did silica gel as stationary phase.

Lastly, in [13] the authors combined flow-reversal with peak parking (stop-flow) of macromolecules, in this case human insulin, to determine band broadening occurring at both ends as well as in the bed of the packing material of a C₁₈ column packed with 2.6-μm core–shell particles. Because of the smaller diffusivity of macromolecules compared to their small-molecule counterparts, the radial heterogeneity of the column bed influences macromolecular migration less, resulting in larger band compression for polymers upon flow reversal. The column inlet (fittings, frits,

and column end structure) showed a larger contribution to band variance than did the column outlet; this is possibly due to differences in particle density and packing structure resultant from the column packing procedure.

The papers included in the *Second Virtual Issue on Macromolecular Separations* will be accessible for free until the end of this month. We encourage all our readers to take a look at what the journal has published in this and all areas of separation science. As always, we continue to welcome your submissions.

Declarations

Conflict of Interest The author has no conflict of interest nor competing interests to declare.

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