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CAPILLARY ZONE ELECTROPHORESIS FOR THE DESCRIPTION OF POLYELECTROLYTES

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High molecular polyelectrolytes find a high range of interest in modern chemistry and biochemistry. Functionalized colloids are not only small entities presenting a huge exchange surface but also have pH-dependent aggregation potentials, creating "compartments" that can possess own specific architectures and functions. The best examples are given by macromolecular systems like collagen, hyaluronic acids or lignin in living systems. In the environment, poly(hydroxycarboxylates) like dissolved humic substances (HS) are the main constituents of the dissolved natural organic carbon (DOC) pool in surface, ground and soil pore water. The degree of ionization of these macromolecules is governed by the amount of ionized phenolic and carboxylic groups of the humic core, which is a function of solution pH. Compared to the operationally defined fulvic acids (FA - soluble in both alkali and acid solutions), the humic acids (HA - soluble in alkali, insoluble in acid solutions) are of higher molecular size and lower acidity. Capillary electrophoretic methods were shown ideal investigation techniques for charged macromolecules and choosing the right buffer allows fingerprinting of these complex mixtures and the description of structural properties or of their oligomeric distributions. The characterization of such complex mixtures possessing a wide dispersity in molecular sizes and in net charges, can be done by the description of the signal distribution, i.e. the effective mobility distribution. Parameters were defined to describe such polydispersity in analogy to parameters from classical chromatography. This presentation is intended to illustrate the use of polydispersity descriptors in the characterization of polyelectrolytes like well defined poly(styrene-4-sulfonates) materials compared to the more heterogeneous natural humic substances.

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IMPROVEMENT OF PRECISION IN CAPILLARY ELECTROPHORESIS BY MOBILITY SCALE TRANSFORMATIONS: A REPRODUCIBILITY STUDY.

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The transformation of the raw electrophoretic time data in effective electrophoretic mobilities (µ-scale) taking account of the endoosmotic flow (EOF) was proposed. With this new µ-scaling, the obtained electropherograms are more representative of the velocity based separation phenomena than with the migration time and a very reproducible direct comparison of electropherograms is possible. This is very important when analyzing molecules in real complex samples where alteration in EOF stability can occur or when comparing electrophoretic runs from different experimental setups (column length, voltage).

Besides possible qualitative peak tracking, a quantitative improvements can be achieved with the peak integration in the µ-scale leading to significant better peak area reproducibility and more precise quantitative analysis than with the primary time-scale integration.

Reproducibility in migration time and mobility was studied at different voltages and sample concentrations; we investigated about 50 consecutive runs of several pesticides (phenoxy acids, triazines) with p-hydroxybenzoic acid as internal standard and mesityloxide as EOF-marker. Each electropherogram was transformed from migration time in mobility scale with referring to the EOF or to the internal standard. The reproducibility of qualitative and quantitative parameters like the migration-times (t), the effective mobility (µ), the areas in migration-time scale (A_t), the time corrected