

Ultra-low Current Electrospray Ionization of Chloroform Solution for the Analysis of Perfluorinated Sulfonic Acids

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Abstract

Rationale. Femtoamp and picoamp electrospray ionization characteristics of a non-polar solvent were explored. The direct ESI-MS analysis of chloroform extract solution enabled rapid analysis of perfluorinated sulfonic acid (PFS) analytes in drinking water. **Methods.** Neat chloroform solvent and extracts were directly used in a typical wire-in ESI setup using micrometer emitter tips. Ionization currents were measured with femtoamp sensitivity while ramping the spray voltage from 0 to -5000 V. Methanol was used to illustrate the characteristics of spraying chloroform. The effect of spray voltage and inlet temperature was studied. A liquid-liquid extraction workflow was developed to analyze PFOS in drinking water using an ion trap mass spectrometer. **Results.** The ionization onset of chloroform solution was 41 ± 17 fA at 300 V. The ionization current gradually increased with voltage while remaining below 100 pA when using voltage up to -5000 V. PFOS ion signal was significantly enhanced to improve the detection limit to 25 ppt in chloroform. Coupled with a liquid-liquid extraction workflow, detection limits of 0.38-5.1 ppt, and a quantitation range of 5-400 ppt were achieved for perfluorinated sulfonic compounds in 1 mL drinking water samples. **Conclusions.** Femtoamp and picoamp modes expand the solvent compatibility range of electrospray ionization and can enable quantitative analysis in ppt concentrations.

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