In solution antimony exists either in the pentavalent or trivalent oxidation state. As Sb(III) is more toxic than Sb(V), it is important to be able to perform a quantitative speciation analysis of Sb’s oxidation state. The most commonly applied chromatographic methods used for this redox speciation analysis do, however, often show a low chromatographic Sb recovery when samples of environmental or biological origin are analysed. In this study we explored basal chemistry of antimony and found that formation of macromolecules, presumably oligomeric and polymeric Sb(V) species, is the primary cause of low chromatographic recoveries. A combination of HPLC-ICP-MS, AFFF-ICP-MS and spinfiltration was applied for analysis of model compounds and biological samples. Quantitative chromatographic Sb redox speciation analysis was possible by acidic hydrolysis of the antimony polymers prior to analysis. Sample treatment procedures were studied and the optimum solution was acidic hydrolysis by 1 M HCl in the presence of chelating ligands (EDTA, citrate), which stabilise the trivalent oxidation state of Sb.