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Technetium and Rhenium sulfide nanodispersion size speciation by SAXS, nanosizer and ultramicrocentrifugation.

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Technetium and rhenium heptasulfides were among the first synthesized compounds of these elements as considered the convenient route for Tc and Re separation from aqueous solutions. Although in the first works its composition was established as M₂S₇ (M = Tc, Re) it was rather surprising in view of Tc and Re redox potentials being in contradiction with those of S²⁻. No reasonable thermodynamic data is available on the solubility of these compounds mostly due to the variety of chemical nature ascribed to these compounds and difficulties in its nano- and micro- size speciation/attribution. Only the formation kinetics and colloidal particle size speciation studies [1-3] provided with some reliable information on Tc concentration dependences. Structure unit fragment Tc₃S₁₃ for technetium sulfide acc. to EXAFS studies [4] contained trinuclear Tc(IV) cluster with 3-S atom inside it and the planar vacancies filled with multiple disulfide ligands, thus explaining the excesses of S in this compound. In the growing process of Tc-S colloid system, the size of colloid particles was shown to increase by deposition of Tc sulfide on the particle surface, not by coagulation of the particles [3]. Recently mixed oxo-sulfide species of Tc were characterized [5].

Here we continue microcentrifuge size speciation in course of the reaction of Tc(VII) and Re(VII) with sulfide and follow it with size speciation of generated particles in the solution by SAXS at specialized small angle diffractometer SAXSess (Anton Paar (Austria), CuK α (1.54 Å), transmission analysis after collimation correction mode, sealed glass capillaries, registration with ImagingPlate). Based on Log(I) = f(s²) plots, $s = 4\pi\sin(\Theta)/\lambda$ for the aged samples two types of species were observed in Re sulfide colloidal solution by SAXS. Small particles were monodisperse and quite isotropic with $R_g = 0.31 - 0.45$ nm. Large particles were disc shaped with 40 nm in diameter and 5 nm height. Both methods supported induction period and kinetic dependent on the [Na₂S] in the solution and the order of mixing the reagents. Based on the similarity of chemical behavior we suggest similarity in composition of technetium and rhenium species obtained in the identical conditions. The stability of M₃S₁₀ (M = Tc, Re) in the resulting solution was dependent of the S²⁻ concentration in it. When higher than 0.06M Na₂S, further growth of Tc and Re sulfide particles occurred for $t \geq 150$ h similar to observations made in [3]. For [Na₂S] ≤ 0.04 M, the M₃S₁₀ was reoxidized by present air to Tc(VII) within 175-200 hours thus being resolubilized. The determination of the free Tc and Re species concentration with separation of ionic or nanocolloidal particles with 5 kD "Sartorius" ultramicrocentrifuge tubes gave evidence on the M₃S₁₀ nanosulfide formation similar to that observed in [4]. The equation for the Tc sulfide solubility based on these figures was evaluated.

References

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