

[PP 1.3]

The Chromatographic Trapping and Separation of Chromium Species Prior to Atomic Absorption Spectrometric Detection

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The form or species the metal is in is very important, because of the effect it may have on the environment, as some forms of the same metal are more toxic. Chromium(VI), for example, is carcinogenic and chromium(III) is found to be involved in some enzyme systems. It is therefore important to be able to separate these two species in a water sample and to determine how much of each is present. A solid phase extraction device (SPE-NH₂) was used for the separation and preconcentration of Cr(VI) from Cr(III), prior to flame atomic absorption spectrometric detection. If it is necessary to determine only Cr(VI) by separation and preconcentration from Cr(III), a single micro-column packed with 3-aminopropyl silica can be used. This is then conditioned prior to use with MeOH and 1.00M HCl. The chromium(VI) can then be eluted with 2.00M HCl directly to the flame AAS. The concentration of Cr(III) is then obtained by the difference between the total concentration of Cr and the determined concentration of Cr(VI). If two micro-columns are used in this system packed with 3-aminopropyl silica using a different preconditioning stage, the method can be used to preconcentrate

and separate both Cr species. The first micro-column was protonated with MeOH and 1.00M HCl to trap Cr(VI) and the second micro-column was conditioned with only MeOH to trap Cr(III). Using this method, Cr(VI) and Cr(III) in a water sample can be preconcentrated and separated. 2.00M HCl was used to elute Cr(VI) and H₂O₂/NaOH was used to elute Cr(III) on-line detected by FAAS. The function of H₂O₂/NaOH was not only as an eluent for removing Cr(III) from the -NH₂ functional group, but also as an oxidizing agent to oxidize Cr(III) to CrO₄²⁻. The CrO₄²⁻ form cannot be trapped with the -NH₂ functional group and can easily pass out of the non-protonated aminopropyl micro-column directly through to the FAAS. This on-line method using two micro-columns coupled with FAAS can be used to preconcentrate and separate both Cr(III) and Cr(VI) species, and the total concentration of chromium concentrations less than 1 ppm in water samples. The method can also be modified to determine inorganic arsenic speciation (As(III) and As(VI)) in environmental samples.

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Oriented Chemical-Thermodynamic Modelling of the Speciations of Heavy Metals (Cu, Cd, Pb) in Fresh-Water Reservoirs

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The migration, bioavailability and toxicity of heavy metals (HM) in natural waters depend on their distribution on separate fractions (so-called 'forms of maintenance'). Usually 'dissolved' and 'suspended' parts are distinguished, with the state and amount of the latter, including plankton community, being essential in the dynamics of pollutants deposition into the bottom sediments (BS). However, the 'dissolved' part frequently prevails, and HM speciation in it plays a key role in all the mentioned relations. In turn, the last depends on ion composition, Eh, pH, temperature of waters, nature and concentration of the dissolved organic matter (DOM).

Our approach to a description of the HM state in the form of a 'dissolved' part, i.e. quote distribution under the formed of HM chemical forms (speciation) is based on the oriented chemical-thermodynamic modelling (taking into account the constructive principle of locality and partiality of any internal equilibria [1]). The last is carried out with an addition of the selected reference data on an inorganic subsystem, analytical data and experimentally obtained integral parameters (K^* and C^*_L) of HM ions bound to fragments of a DOM in conditions of a particular reservoir [2]. HM distribution between 'dissolved' and 'suspended' parts is also analysed. The method was realized for study of a state of Cu(II), Pb(II), Cd(II) in the fresh reservoirs of Western Siberia: In Novosibirsk Reservoir (NR), located in the south (zone of high technogenic loading), and small northern lakes (SNL). Besides ion composition and total HM content, K^* and C^*_L were determined by ionometry with ISE on Cu²⁺, Cd²⁺, Pb²⁺. It was found [3] that the 'dissolved' part of more alkaline (pH=8.9±0.3)

and mineralised ($\Sigma_{\text{ion}}=140\pm 10$ mg/l) NR hydroxo and carbonate forms (with the small contribution of binding with DOM) dominate in the summer period, and is bonded with DOM forms for Cu(II), Pb(II) and aqua-ions for Cd(II) in SNL (pH 4.5±6.5 and $\Sigma_{\text{ion}} 2\pm 30$ mg/l). In the winter period, in reservoirs of both types, there is a downturn of pH and an increase in mineralisation that reduces the amount of hydroxoforms. For SNL, a significant (of 1.5-10 times) increase in the total HM concentrations of both 'dissolved' and 'suspended' part is observed. The fact of approximately equal average annual total HM concentrations in both types of reservoirs (in spite of the difference of technogenic loads) is also of interest.

For SNL, besides the level of total HM concentrations, the significant amount of their aqua-ions can be an essential factor of negative influence on aquatic organisms.

Thus, the oriented chemical-thermodynamic modelling allows one to receive the detailed information on the chemical forms of HM in natural waters and, on this basis, to predict an ecological risk of pollution of particular reservoirs in their current condition.

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- [1] BELEVANTSEV, V.I. (1998): Journal of Structural Chemistry 39, 224
- [2] SMOLYAKOV, B.S. et. al. (1996): Chemistry for Sustainable Development 4, 539
- [3] SMOLYAKOV, B.S. et. al. (1999): Chemistry for Sustainable Development 7, 575