

APPLICATION OF APDC FOR SEPARATION OF CHROMIUM, THALLIUM AND ARSENIC FORMS FROM WATER SAMPLES – PRELIMINARY RESULTS

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Introduction

Arsenic, thallium and chromium belong to a group of potentially very toxic elements. They are listed as priority hazardous substances and are considered within the top 20 contaminants by the US-EPA. Arsenic toxicity depends on chemical forms and redox states of the elements. The most toxic forms of arsenic are non-organic compounds, while arsenic organic compounds are non-toxic. Cr(III) is an essential dietary nutrient, required to potentiate the metabolism of insulin and normalizes glucose, protein and lipid levels, while Cr(VI) is toxic and carcinogen. Both forms of Tl are toxic but Tl(III) is more toxic than Tl(I). Toxicological properties depend not only on the total amount, but mainly on their oxidation state.

The cations As(III), Cr(III), and Tl(III) have some similar chemical properties and can react with dithiocarbamates (DTCs). According to the ‘Hard and Soft Acid and Bases Theory’ (Pearson 1968), Tl(III) is soft acid and create covalent chemical bond with sulfur. Not only soft acids can create chemical bond with soft basic. Cr(III) and As(III) are hard acids and probably create chemical bond with sulfuric too. As, Tl and Cr compounds with DTCs can be selectively separated in water samples and soil extracts using solid phase extraction (SPE). SPE have been applied for years, but becomes more and more popular due to the small cost of SPE-chambers and easiness of application. The separation of matrix could be performed in mode *off-line* as well as *on-line* SPE.

Previous experience with diethylenedithiocarbamate (DDTC) application in speciation analysis of Tl(III) was very promising (Krasnodebska-Ostrega et al. 2013). But for use of DTCs molecules in simultaneous separation and pre-concentration of the Me(III) from a water matrix, it required the use of another compound. The solubility of the complexes of trivalent ions with ammonium pyrrolidinedithiocarbamate (APDC) are much lower than with DDTC. Therefore, APDC was proposed for simultaneously precipitation of Me(III)APDC (Me = As(III), Tl(III) and Cr(III)).

Methods

The aim of this study was to develop a method for separation of As(III)/As(V), Cr(III)/Cr(VI) and Tl(I)/Tl(III) in water samples on a SPE column. Octadecyl silica gel (SGX C18) modified with ammonium pyrrolidinedithiocarbamate (APDC) was applied as sorbent. The method is based on the differences in chelation of metals on different oxidation states and APDC depending on the selected conditions, especially pH. Cr(III), As(III), Tl(I) and Tl(III) can precipitate with APDC in acetic acid solution (pH 5) (Hulanicki 1968). Based on literature data ions: As(III), Tl(III) and Cr(III) should be retained on the sorbent as complexes with APDC. The sorbent should be leached using organic solvent, according to hydrophobic properties of the compounds. In turn, ions of As(V), Tl(I) and Cr(VI) are instable in nitric acid solution and using this acid should lead to leaching of the species of studied elements.

The first two steps were applying the nitric acid and water on the column to clean up the sorbent. The third step was washing the sorbent with APDC solution in order to deposit APDC on the sorbent. Finally, it was necessary the introduction of the sample on the column. In order to wash the metalloid forms, which should not retain on a sorbent (complexes As(V), Tl(I) and Cr(VI) with APDC), water or 0.1 mol L⁻¹ HNO₃ was applied. On the other hand, complexes As(III), Tl(III), Cr(III) with APDC were eluted with 96% EtOH. The content of analyte in the eluent was determined by inductively coupled plasma mass spectrometry (ICP MS).

Results

This preliminary study indicated that complex Tl(I)APDC (37% recovery) is much better eluted from the sorbent using 0.1 mol L⁻¹ HNO₃ than Tl(III)APDC, which was leached in next step (92% recovery); both forms of Cr were retained on the sorbent. Cr(III) was retained on the sorbent, but more than 40% passed to the filtrate. Cr(III) was strongly hydrated, therefore its reaction with APDC was slower. The best results were obtained for arsenic. As(III) was retained on the column (90%), while only 15% of As(V) was retained. In addition, As(V) was effectively eluted by water or 0.1 mol L⁻¹ HNO₃ (approx. 10 - 15% of volume of the applied samples), but As(III) was not efficiently eluted (recovery 20-40%).

Conclusion

In summary, the proposed conditions of conducting simultaneous speciation analysis of As, Tl and Cr are not enough selective. The method proposed needs further modifications and at the moment can be applied successfully only for arsenic speciation.

References

- Pearson, R.G. (1968). Hard and Soft Acid and Bases Theory. *J. Chem. Educ.*, 45, 581–587
- Krasnodębska-Ostręga, B.; Sadowska, M.; Piotrowska, K.; Wojda, M. (2013). Thallium (III) determination in Baltic seawater samples by ICP MS after preconcentration on SGX C18 modified with DDTC. *Talanta*, 112, 73 -79.
- Hulanicki, A. (1967). Complexation reactions of dithiocarbamates. *Talanta*, 14, 1371 – 1392.