EKSTRAKCIJA METALA I METALOIDA IZ UZORAKA TLA VODENIM OTOPINAMA AMONIJEVIH SOLI

EXTRACTION OF METALS AND METALLOIDS FROM SOIL SAMPLES BY AQUEOUS SOLUTIONS OF AMMONIUM SALTS

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I N T R O D U C T I O N

Soil is a very powerful reservoir of various chemicals due to its ability to bind such substances onto the surface of the soil particles [1]. Trace metals and metalloids are amongst such substances. Through their uptake of by plants, the metals and metalloids can enter food chain and thus pose a risk to human health [2].

An assessment of mobility and bioavailability of trace elements that are present in soil requires determination of those elements in soil samples by an appropriate methodology. The most of the methods for trace metals and metalloids analysis in the soils samples, that are described in the scientific literature and/or are present in wide professional practice, consist of a transfer of the analytes into solution with subsequent quantification of the elements in the prepared solutions (extracts or digestates) by means of some of the atomic spectrometric techniques.

The most applied method for preparation of soil samples for toxic elements quantification includes digestion of the soil samples by *aqua regia* [3]. This is a quite aggressive digestion reagent, it does not simulate natural conditions in soil and, often does not allow to draw reliable conclusions about mobility of the analysed elements in soil. Therefore, the use of milder extraction reagents for transferring of the analytes into solution is recommended [4,5].

This work describes two different methods for analysis of 24 selected chemical elements in soil samples that consists of the extraction by aqueous solution of an ammonium salt (NH_4Cl or NH_4NO_3). The selected elements were quantified by means of inductively coupled plasma-atomic emission spectrometry (ICP-AES). As a model soil sample the certified reference material Metranal-33 was used.

E X P E R I M E N T A L

1.) Extraction:
- ~ 1.00000 g CRM soil sample / 10 mL of each extraction solution in 20 mL-polypropylene vessels
- extraction solution: NH_4Cl or NH_4NO_3, 0.1 mol dm^{-3}
- room temperature
- 24 h / orbital shaker
- filtration: syringe-type filters (0.45 µm)
- acidification of the extracts: HNO_3 (65 %), *supra pur*, ψ = 1 %

2.) Quantification of the analytes in the extracts:
- ICP-AES: Thermo Fischer iCAP6300 Duo
- measured lines (nm):
  Al-167.079, As-189.042, B-208.959, Ba-455.403, Be-234.861, Cd-214.438, Co-228.616, Cr-205.552, Cu-324.754, Fe-238.204, K-766.490, Li-670.784, Mg-279.553, Mn-257.610, Mo-202.030, Na-589.592, Ni-231.604, Pb-220.353, Sb-217.581, Se-196.090, Sr-407.771, Ti-334.941, Tl-190.856, Zn-213.856
- external calibration (multi-elemental standard solutions):
  - 0 µg L^{-1} (all elements)
  - 1 µg L^{-1} and 10 µg L^{-1} (trace metals and metalloids)
  - 100 µg L^{-1} (trace metals and metalloids)
  - 2000 µg L^{-1} Ca, 200 µg L^{-1} K, 400 µg L^{-1} Mg, 1000 µg L^{-1} Na.

R E S U L T S

Table 1. Results of the quantification of the selected elements in the soil certified reference material Metranal-33 (Analytika, Czech Republic) after the extraction done by aqueous solutions of ammonium salts (N=5, each)

		Extractant: ammonium chloride (NH_4Cl), 0.1 mol dm^{-3}				Extractant: ammonium nitrate (NH_4NO_3), 0.1 mol dm^{-3}			
	Certified total content	MDL*	Found**			MDL*	Found**		
			Mean ± Std.dev.	Recovery	RSD		Mean ± Std.dev.	Recovery	RSD
	mg/kg	mg/kg		%	%	mg/kg		%	%
Al	65095	0.016	0.041 ± 0.009	0.00006	22.6	0.027	0.038 ± 0.002	0.00006	5.4
As	-	0.020	0.028 ± 0.004	0.17	12.8	0.012	0.036 ± 0.006	0.22	15.7
B	-	0.012	0.642 ± 0.007	n.d.	1.0	0.010	0.677 ± 0.020	n.d.	2.9
Ba	495	0.030	10.7 ± 0.1	2.17	1.2	0.007	12.5 ± 0.3	2.53	2.2
Be	2.18 ± 0.16	0.015	< 0.015	n.d.	n.d.	0.009	< 0.009	n.d.	n.d.
Ca	9863	0.328	n.d.	n.d.	n.d.	0.299	n.d.	n.d.	n.d.
Cd	0.32 ± 0.04	0.001	0.0039 ± 0.0002	1.21	4.4	0.0005	0.0011 ± 0.0002	0.36	16.4
Co	11.5 ± 0.7	0.001	0.023 ± 0.001	0.20	2.7	0.002	0.018 ± 0.001	0.16	4.5
Cr	79.8 ± 6.7	0.001	0.004 ± 0.001	0.01	17.9	0.001	0.005 ± 0.000	0.01	10.0
Cu	29.1 ± 0.8	0.125	0.245 ± 0.058	0.84	23.6	0.038	0.256 ± 0.020	0.88	7.8
Fe	29027	0.146	< 0.146	n.d.	n.d.	0.107	0.131 ± 0.040	0.016	30.6
K	18350	1.05	306 ± 3	22.3	1.0	0.810	327 ± 3	23.9	1.0
Li	-	0.033	0.242 ± 0.010	n.d.	4.0	0.025	0.266 ± 0.009	n.d.	3.4
Mg	6151	0.236	162 ± 2	2.63	1.4	0.014	125 ± 2	2.04	1.2
Mn	600 ± 37	0.032	10.3 ± 0.2	1.71	2.4	0.005	9.07 ± 0.13	1.51	1.4
Mo	-	0.002	0.055 ± 0.002	n.d.	3.1	0.004	0.052 ± 0.002	n.d.	4.7
Na	5490	1.86	145 ± 6	2.65	4.4	0.221	39.2 ± 0.4	0.71	1.0
Ni	31.3 ± 1.5	0.005	0.072 ± 0.002	0.23	3.0	0.003	0.067 ± 0.003	0.21	4.5
Pb	33.5 ± 2.4	0.007	< 0.007	n.d.	n.d.	0.011	< 0.011	n.d.	n.d.
Sb	-	0.018	0.025 ± 0.009	n.d.	34.3	0.009	0.021 ± 0.001	n.d.	5.7
Se	-	0.018	< 0.018	n.d.	n.d.	0.009	0.012 ± 0.003	n.d.	26.5
Sr	-	0.001	8.18 ± 0.11	n.d.	1.4	0.003	8.52 ± 0.10	n.d.	1.1
Ti	4076	0.033	0.179 ± 0.014	0.004	7.7	0.028	0.178 ± 0.011	0.004	6.1
Tl	-	0.017	< 0.017	n.d.	n.d.	0.007	0.019 ± 0.006	n.d.	30.4
Zn	81.0 ± 7.6	0.017	< 0.017	n.d.	n.d.	0.008	0.011 ± 0.010	0.045	88.7

* Method detection limit = 3 × σ(procedural blanks) × dillution factor
** N = 5

C O N C L U S I O N R E M A R K S

The obtained results permit to draw these conclusions:
1) Ba, K, Mg, Mn, Na, and Sr can be reliably quantified in soil extracts that are prepared by the two extraction reagents.
2) High RSD values for the elements Al, As, Cr, Cu, and Sb suggest low reliability of their results (due to relatively high MDL values).
3) Ca was strongly extracted so for its quantification subsequent dilution of the extracts should be performed.
4) There was not possible to quantify some of the tested elements (Be, Fe, Pb, Se, Tl, Zn), because their mass fractions are lower than their MDLs.

R E F E R E N C E S

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