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DETERMINATION OF BARIUM IN DIFFERENT SOIL MATRICES

OZNACZANIE BARU W RÓŻNYCH MATRYCACH GLEBOWYCH

Abstract: Barium mobility and toxicity depend on the speciation forms in which barium occurs in a given environment. The dominant form is the carbonate – barite one. There are also other significant forms in this element's cycle – the organic one, so-called reduced or lithogenic. The speciation forms of occurrence and their amount in soils and solid waste may be assessed using sequence extraction. The subject of the paper was to carry out research on the determination of so-called barium fractions in various soil matrices: agriculturally utilized or used for recreation, polluted with motor vehicles and soil-waste contaminants (from brown coal and bituminous shales recovery). On the basis of the present research, the individual barium loads existing in various fractions – exchangeable, carbonate, reduced, organic and residual – were determined. In research procedures, Tessier's methodology was used for sequence extraction.

Keywords: barium, barium speciation forms in soils and waste, sequence extraction

Barium is an element which occurs in the barite form (BaSO_4) and the witherite one (BaCO_3) [1–4]. The range of its content, *eg* in magmatic rocks ranges from 0.5–1200 mg/dm^3 and is higher than in acidic rocks while in sedimentary rocks it is dispersed in the range 50–800 mg/dm^3 , indicating the tendency to concentrate in the mudstone [1]. In soils, this element migrates together with circulating waters and is leached inside the soil profile (mainly in the form of aqua complexes $[\text{Ba}(\text{aq})_n]^{2+}$ and ion pairs $\text{Ba}^{2+} \cdot \text{SO}_4^{2-}$ and $\text{Ba}^{2+} \cdot \text{CO}_3^{2-}$) or is subject to concentration in the thin surface layer [2, 3], binding ionically and coordinating together with the contained humus substance [3]. The barium content in soils most frequently ranges from 20–1000 mg/dm^3 [1] and 1350 mg/kg in the industrial development areas [5]. The interesting problem is the analytical determination of this element's concentrations in various environmental matrices and waste substances and its speciation forms [6, 7]. It is the issue which is relatively little known, especially as far as the occurrence of functional dependencies between speciation forms and specific properties of mineral – organic matrices is concerned. From literature data we know that this issue is taken with the use of various leaching

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procedures [6, 8]. Barium speciation forms, especially the ones leached from different waste substances are the subject of interest due to the various toxicity for biocenoses [9–13].

The purpose of the work was barium fractions determination in the soils which were agriculturally utilized, used for recreation, polluted with motor vehicles and contaminated with post-mineral wastes. The obtained results were discussed and compared with literature data.

Materials and methods

Barium was determined in five extrahent solutions with the use of *flame atomic absorption spectrometry* (FAAS); the wavelength of 553.6 nm. This element's content was analyzed in soil samples (collected from sub-surface soil layer) from the vegetable garden located on the outskirts of the city (P1 – average soil, pH 7.51), farmland located near the urbanized area (P2 – heavy, pH 9.35) and from the recreational park area located near a big city (P3 – light, pH 7.56) (Table 1). The areas of taking the soil samples loaded with waste substances were: P4 – located near excavation from brown coal recovery and P5 – from bituminous shales recovery (Table 2). The remaining two series of samples came from the crossroads of the big city (P6) and the bus depot (P7) from this city. Samples P1–P3 and P6 and P7 were taken from places located on the territory of the same district self-government, and the maximum distance between collection points did not exceed 7.0 km. Samples were taken from the area of 20.0 m² in each case and were subject to sequence extraction in accordance with Tessier's methodology [14–17], applying air – dried surplus (40.0 g each) which was treated with extracting solutions of the increasing strength according to procedures given below:

A) fraction I. In order to determine barium content in fraction I (so-called exchangeable barium forms), samples were treated with 20.0 cm³ (1.0 M) of CaCl₂ and after intensive shaking (at pH 7.0), shaken out for 1 hour at room temperature. After separating the solid components in the filtration process, the filtrate was subject to the analysis of this element's content. The residued solid soil samples were washed with distilled water and dried.

B) fraction II. Dried soil samples, which remained after running the procedure in accordance with point A, were subject to extraction (so-called barium forms bonded with carbonates – fraction II) adding 40.0 cm³ (1.0 M) CH₃COONH₄ and acidating it with 80 % of CH₃COOH to pH 7.0.

After mixing, it was shaken for 5.0 hours at room temperature. During this operation the reaction was controlled: when pH > 7.0 – it was acidified. The filtrate was subject to analysis, and the washed and dried samples of the solid phase were used for the 3rd stage of extraction (to determine the so-called barium forms connected with aqueous ferric and manganese oxides).

C) fraction III. At this stage (determination of fraction bounded with Fe/Mn oxides) to the dried sample of the solid phase, residual was added and mixed after taking the procedure in accordance with point B, 40.0 cm³ (0.04 M) solution of NH₂OH · HCl in

25 % CH_3COOH . Samples (pH 2.0) were shaken for 5.0 hours at the temperature of 96 ± 3 °C. The filtrate was subject to analysis, and the washed and dried solid material was directed to the 4th stage of extraction (so-called barium bounded with organic matter – fraction IV) to constant residues.

D) fraction IV. 10.0 cm^3 (0.02 M) HNO_3 and 10.0 cm^3 30 % aqueous solution of H_2O_2 , were added to the material sample from the stage given in point C. They were mixed (pH 2.0) and shaken for 135.0 minutes at the temperature of 85 ± 2 °C. Next, 10.0 cm^3 30 % H_2O_2 was added and shaken for 135.0 minutes. After that time, 20.0 cm^3 (3.0 M) of $\text{CH}_3\text{COONH}_4$ in 20 % HNO_3 (v/v) was added and shaken for 30.0 min at the room temperature (pH 2.0). The filtrate was subject to analysis, and the residual washed and dried soil samples were subject to 5-stage of extraction (residual barium forms – fraction V).

E) fraction V. 6.0 cm^3 of HNO_3 and 4.0 cm^3 of 30 % H_2O_2 , were added to the residues from the solid phase in point D, and then mixed (pH 2.0). They were shaken at the boiling point for one hour, adding HNO_3 and H_2O_2 twice until white ashes were released. Next, 20.0 cm^3 of 30 % H_2O_2 were added and shaken for 30.0 minutes at the boiling point. The results of the analyses for barium content in the individual fractions are presented in Tables 1–3.

Results and discussion

The aim was to apply Tessier's procedure to determine barium fractions occurring in the selected samples of clean soils and the soils contaminated with substances of anthropogenic origin (post-mineral wastes and motor vehicle contaminations) (Tables 2 and 3).

In soil samples taken from the same area (samples P1–P3, P6 and P7), despite the motor vehicle pollutions (samples P6 and P7), similar concentrations of the given fractions were determined (Tables 1 and 3) and no evident influence of motor vehicle traffic on the fractional content of this element was found.

Table 1

Average concentrations of barium fraction in mg/kg dry mass determined in the selected soil samples with the use of sequence extraction method*

Barium fractions	P1 samples (RSD [%])		P2 samples (RSD [%])		P3 samples (RSD [%])	
(I) exchangeable	17.76	(2.1)	42.59	(0.6)	16.18	(2.7)
(II) carbonate	31.71	(0.7)	27.21	(1.6)	29.11	(0.1)
(III) Fe/Mn oxides	10.63	(1.8)	15.64	(2.1)	8.97	(1.1)
(IV) organic	12.13	(0.9)	14.33	(1.5)	9.14	(1.9)
(V) residual	33.26	(2.0)	38.60	(3.0)	29.70	(2.5)

* P1 samples – average soil (pH 7.51), P2 samples – heavy soil (pH 9.35), P3 samples – light (pH 7.56); RSD – relative standard deviations.

Table 2

Average concentrations of barium fractions in mg/kg dry mass determined in soil samples contaminated with solid substances (mixture of post-mineral wastes and soil*) with the use of sequence extraction method

Barium fractions	P4 samples, (RSD [%])		P5 samples (RSD [%])	
(I) exchangeable	20.84	(0.8)	32.03	(0.1)
(II) carbonate	128.00	(1.2)	64.12	(0.9)
(III) Fe/Mn oxides	192.10	(1.7)	160.21	(1.3)
(IV) organic	32.13	(0.6)	31.99	(0.5)
(V) residual	284.82	(2.8)	291.22	(1.9)

* Area of taking the samples (pH 7.11) located close to post-mineral depot from brown coal recovery and close to post-mineral depot from bituminous shales recovery (pH 6.80) (samples P7).

Table 3

Average concentrations of barium fractions in mg/kg dry mass determined in soil samples overloaded with motor vehicle pollution with the use of sequence extraction method*

Barium fractions	P6 samples (RSD [%])		P7 samples (RSD [%])	
(I) exchangeable	48.33	(1.2)	16.13	(1.2)
(II) carbonate	22.92	(2.2)	11.10	(1.8)
(III) Fe/Mn oxides	16.77	(2.4)	12.61	(2.0)
(IV) organic	14.07	(1.7)	7.93	(1.8)
(V) residual	30.59	(2.8)	20.31	(2.0)

* P6 samples – light soil (pH 6.69), P7 samples – light (pH 7.39).

Changeable fraction, which naturally occurs mainly in the form of aqua complexes $[\text{Ba}(\text{aq})_n]^{2+}$ and ionic pairs of $\text{Ba}^{2+} \cdot \text{SO}_4^{2-}$ and $\text{Ba}^{2+} \cdot \text{CO}_3^{2-}$ were determined at the similar quantity level in soil samples of reduction pH = 7.3–7.6, mainly in light soils (samples P1, P3 and P5). In these samples, the content of the changeable fraction did not exceed 25 % of the total content of this element. The highest content of this fraction compared with the total content was determined in soil samples taken from the farmland (heavy soil) and from the crossroads; and they were respectively: 30.8 and 36.4 % at the similar, average barium content respectively: 138.37 and 132.68 mg/kg dry mass.

Assessing the barium fraction bound with Fe/Mn oxides in samples P1–P3, P6 and P7, a similar content level was found in clean samples and loaded with motor vehicle pollutions (Tables 1 and 3). Such level of the fraction compared with the iron content, particularly manganese towards oxides, for which barium shows particular preference, can be explained due to a slight distance of the sample recovery points [18–21]. However, in case of soil samples contaminated with brown coal and bituminous shale waste, high total content of this element and the specific content of the matrices (significant content of oxide iron and manganese forms) results in extremely high concentrations of this barium fraction, amounting to about 30 % of the total barium content.

The significant difference in concentrations of the given fractions for clean soils samples (Samples P1–P3) and the ones overloaded with motor vehicle pollutions

(samples P4 and P5) is evident in case of organic fraction – (P4). The concentration level of this fraction for clean soils is similar, despite the different content of humus substances and at the same time 3 times lower than the one registered in case of soils polluted with waste. This phenomenon can be interpreted by the presence of high-molecular organic substances of humin type (Hum), which are present in brown coal and bituminous shales fragments contaminating the examined soil samples. The presence of these substances results in forming very constant bonds of covalent type $Ba_a(R)_b$ (where: R – organic ligand, a and b – coefficients resulting from stoichiometry rules) or to a smaller extent – the coordinating one, certainly resulting in complex structures, which can be described by a simplified formula $[Ba(Hum)_x]^{(+2-y)}$ (where: Hum – high-molecular organic ligands which are the natural humification products, x – number of coordinated ligands (Hum), y – ligand's valency) [22, 23]. From the comparison of the content level of the fraction for the given sample categories we may conclude that coordinating barium occurs under the influence of the determined class of the high-molecular organic compounds, which are many times lower than in samples P1–P3, P6 and P7 than in contaminated samples P4 and P5.

The content of the so-called residual fraction (fraction V) in the determined soil samples was different – in clean soil samples and in ones overloaded with motor vehicle pollutions it amounted to 20–30 %, and in soil samples polluted with post-mineral residues – over 40 % of the total barium content just as in drilling mud [15].

Conclusion

On the basis of the conducted research it was found that soils contaminated with post-mineral waste are characterized with a higher amount of barium determined in the fractions: bound with Fe/Mn oxides and the so-called residual one. The registered concentration of this element in organic fraction, in samples containing post-mineral residues is higher than the values registered for the rest of the soil samples. In case of soil samples overloaded with motor vehicle pollutions, no evident difference in barium fractional content was found in relation with the fractional content determined in clean soil samples.

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OZNACZANIE BARU W RÓŻNYCH MATRYCACH GLEBOWYCH

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Abstrakt: Mobilność oraz toksyczność baru zależy od form specyjalnych, w jakich występuje w danym środowisku. Dominującą jest węglanowa – barytowa. Istnieją również inne, istotne w obiegu tego pierwiastka

– organiczna, tzw. zredukowana czy litogenna. Specyjalne formy występowania oraz ich ilość w glebach i stałych substancjach odpadowych można oszacować, wykorzystując ekstrakcję sekwencyjną. Przedmiotem pracy były badania nad oznaczalnością tzw. frakcji baru w różnych matrycach glebowych: użytkowanych rolniczo i rekreacyjnie, obciążonych zanieczyszczeniami komunikacyjnymi oraz glebowo-odpadowych (z terenu pozyskiwania węgla brunatnego i łupek bitumicznych). Na podstawie przeprowadzonych badań oznaczono poszczególne pule baru występujące w różnych frakcjach – jonowymiennej, węglanowej, zredukowanej, organicznej oraz pozostałej. W procedurach badawczych wykorzystano do ekstrakcji sekwencyjnej metodykę Tessiera.

Słowa kluczowe: bar, formy specyjalne baru w glebach i odpadach, ekstrakcja sekwencyjna