DOI: https://doi.org/10.26896/1028-6861-2019-85-6-5-10

METAL-ORGANIC COMPLEXES IN ENVIRONMENTAL SOLID SAMPLES: ON THE SELECTIVITY OF PYROPHOSPHATE EXTRACTION

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Received March 23, 2019. Revised April 17, 2019. Accepted April 29, 2019.

Sequential extraction procedures (SEP) have been widely used for the fractionation of trace elements in soils according to their physicochemical mobility and bioaccessibility. Potassium/sodium pyrophosphate in alkaline medium may be considered as the most appropriate extracting reagent for the recovery of amorphous metal-organic complexes, which play a very important role in biological, physical, and chemical processes in soil. However, the selectivity of pyrophosphate has been poorly studied. In the present work the ability of pyrophosphate to attack mineral inorganic phases of environmental solids was assessed using dynamic extraction, which allows one to minimize artifacts and mimic natural conditions. Samples of gabbro and granite containing nearly no organic compounds were taken as example. The eluents applied addressed exchangeable, specifically sorbed, bound to Mn oxides, and bound to metal-organic complexes fractions extractable by 0.05 M $Ca(NO_3)_2$, 0.43 M CH_3COOH, 0.1 M $NH_2OH \cdot HCl$, and 0.1 M $K_4P_2O_7$ at pH 11, respectively. As expected, pyrophosphate extraction leads to a partial dissolution of elements bound to inorganic compounds. The recovery of aluminum, iron, manganese, and rare earth elements by pyrophosphate is up to 4% of their total concentrations in samples. The results were discussed on the basis of coordination chemistry of pyrophosphate complexes. In general, pyrophosphate extraction could be further regarded to be sufficiently selective for the dissolution of metal-organic complexes while using SEP in environmental analysis, soil science, and biogeochemistry. Nevertheless, in the interpretation of the fractionation results, a partial dissolution of mineral inorganic phases should be taken into consideration, especially for soils with low content of organic compounds.

Keywords: fractionation analysis; soils; metals; dynamic extraction; metal-organic complexes; pyrophosphate.

Introduction

Fractionation of trace metals (TM) into operationally defined forms under the sequential action of leachants (extracting reagents) with increasing aggressiveness is a common approach in biogeochemical studies for distinguishing various species of TM according to their physico-chemical mobility and bioaccessibility [1, 2]. The identification and quantification of TM associated with different components and phases of soil or sediments is defined as “fractionation analysis” according to the IUPAC recommendation [3].

Sequential extraction procedures (SEP) for TM were first proposed in the late sixties [4]. Then, a few dozens of different SEP have been developed [5, 6]. There are a few schemes that have received wide acceptance. One of the most “popular” four-step protocols was introduced by Tessier et al. [7]. The European Commission through the BCR (Community Bureau of Reference) Programme and its successor (Standards, Measurements, and Testing Programme, SM&T) designed a simplified three-step SEP [8, 9] used for the certification of extractable metals in reference materials of lake sediment. However, none of SEP can be considered to be absolutely preferable.

With regard to the organic compounds in sediments and soils, they are mainly of complex macromolecular material, e.g., humic and fulvic acids, carbohydrates, and peptides. Under aerobic conditions, the organic compounds can degrade resulting in the release (mobilization) of bound TM [10]. Oxidising reagents such as sodium hypochlorite in an alkaline medium [11, 12] and hydrogen peroxide heated at 85°C [2], or strong complexing reagents such as salts of ethylenediaminetetraacetic acid (EDTA) [4, 13] have been used for the extraction of TM bound to organic compounds. However, the selectivity of these reagents to metal-organic complexes of soils was found to be rather poor [10]. A “mild” reagent used for the extraction of metals bound to organic compounds is potassium/sodium pyrophosphate at pH 10 [12, 14, 15]. This reagent is considered to be relatively selective to the easily oxidisable organic fraction (i.e. metals bound to humic and fulvic acids). However, the extraction efficiency is low [16]. In order to increase the solubility of organic soil components, a 0.1 mol/L $K_4P_2O_7$ + 0.1 mol/L KOH mixture has been recommended instead of 0.1 mol/L $K_4P_2O_7$ (pH 10) [4]. Potassium/sodium pyrophosphate in alkaline medium was used not only in SEP [17] but also as a single extractant for the separation of amorphous metal oxide-organic complexes, in particular, humic and fulvic acids from soil [18, 19]. Fractions of organic compounds were as well extracted sequentially from the soils using water in the first step and 0.1 M sodium pyrophosphate (pH = 10) in the second one [20]. Nevertheless, the selectivity of pyrophosphate extraction to metal-organic complexes still remains debatable since the formation of stable phosphate complex compounds may lead to the partial leaching of metals from other mineral phases of soil.

The aim of this work is to assess the selectivity of using pyrophosphate extractants in SEP for the separation of metal oxide-organic complexes. The extraction is performed under dynamic (continuous flow) conditions, which allow one to minimize two main problems of batchwise SEP, namely (I) the phase overlapping (the possibility of releasing metals associated to different geological phases by a single leaching agent), and (II) the metal readsorption phenomenon (TM released by one extractant could associate with other undissolved solid components or freshly exposed surfaces within the time-scale of the extraction step) [10]. Certified reference materials of gabbro and granite, which contain nearly no organic compounds, are used to study the ability of pyrophosphate to attack mineral inorganic phases of environmental solids.

Experimental

Samples and reagents. Russian certified reference materials SG-3 (agpaitic granite) and SGD-2a (essexite gabbro) with grain size less than 50 µm were under study. The samples were purchased from the Institute of Geochemistry (Irkutsk, Siberian Branch of the Russian Academy of Sciences, Russia).

All the reagents used were of analytical grade. Calcium nitrate, acetic acid, hydroxylamine hydrochloride, potassium pyrophosphate, potassium hydroxide, nitric, perchloric, and hydrofluoric acids were purchased from Merck (Germany). Leaching solutions were prepared every month. Ultrapure deionized water with resistivity 18.2 MΩ · cm (Millipore Simplicity) was used for the preparation of solutions.

Dynamic leaching of elements using rotating coiled column (RCC). The extraction and fractionation of elements were performed on a planetary centrifuge furnished with a vertical one-layer coiled polytetrafluoroethylene (PTFE) column. The device was fabricated in the Institute of Analytical Instrumentation (St. Petersburg, Russia). During the experimental protocol the spiral column rotates around its axis and simultaneously revolves around the central axis of the unit with the aid of a planetary gear. The two axes are parallel. The planetary centrifuge has a revolution radius $R = 90$ mm and a rotation radius $r = 50$ mm. The β value ($\beta = r/R$) is therefore 0.55. The separation column is made of PTFE tube with an inner diameter of 1.6 mm and a total inner capacity of 20 mL. The tube volume is approximately 10 mL.

Before commencing the leaching procedure, the spiral PTFE column was filled with water, after that the solid sample (500 mg) was introduced into the column (in the stationary mode) as a suspension in 5 mL of 0.05 M $Ca(NO_3)_2$. Then, extra 5 ml of 0.05 M $Ca(NO_3)_2$ were added into the sample test-tube and injected into the column. Then, while the column was rotated (the rotation and revolution speeds were 600 rpm), extracting reagents used as eluents were continuously fed to the column inlet (1.0 mL/min). The eluents applied addressed exchangeable, specifically sorbed, bound to Mn oxides, and bound to metal-organic complexes fractions extractable by 0.05 M $Ca(NO_3)_2$, 0.43 M CH_3COOH, 0.1 M $NH_2OH \cdot HCl$, and 0.1 M $K_4P_2O_7$ at pH 11, respectively. The fractionation was achieved by successive changing the eluents. Each of first two reagents (calcium nitrate and acetic acid) was pumped through the column during 120 min. Each other reagent was pumped during 60 min. Throughout the experiment, the solid sample was retained inside the rotating column by the centrifugal force. The collected sub-fractions of effluent were directly analyzed by ICP-MS and ICP-AES without filtration. After the extraction, the solid residue was removed from the stopped column by pumping water at a flow rate of

30 mL/min. All the extractions were made in triplicate.

Elemental analysis of extracts and residual fractions. The elements in extracts were determined using an ICP-MS (X-7, Thermo Scientific, USA). The measurements were made using the standard parameters: a RF generator power of 1250 W; a PolyCon nebulizer; a plasma-forming Ar flow rate of 12 L/min; an auxiliary Ar flow rate of 0.9 L/min; an Ar flow rate into the nebulizer of 0.9 L/min; an analyzed sample flow rate of 0.8 mL/min. The selected elements (Li, Na, Mg, Al, P, S, K, Ca, V, Mn, Fe, Cu, Zn, Sr, and Ba) were also determined by ICP-AES (iCAP 6500, Thermo Scientific, USA). The measurements were made using the standard parameters: a RF generator power of 1250 W; a PolyCon nebulizer; a plasma-forming Ar flow rate of 13 L/min; an auxiliary Ar flow rate of 0.6 L/min; an Ar flow rate into the nebulizer of 0.8 L/min; an analyzed sample flow rate of 1.2 mL/min. For Li, V, Mn, Cu, Zn, Sr, and Ba, which were determined both by ICP-AES and ICP-MS, average values of contents were used. It should be noted that the data for these elements confirmed the accuracy of the results obtained by both methods.

The elemental analysis of residual fractions was performed using a certified procedure described in detail earlier [21 – 23]. Samples were digested in an open beaker using a combination of perchloric, hydrofluoric, and nitric acids.

Results and discussion

Dynamic fractionation of trace elements. As outlined in the introduction, the dynamic extraction is an attractive alternative to the conventional batchwise SEP. Microcolumn extraction and RCC extraction are regarded as the most promising techniques [24]. Since planetary centrifuges equipped with one-layer and multi-layer rotating columns are extensively used in countercurrent chromatography, they are fabricated and commercially available in many countries.

The dynamic fractionation of trace elements was performed according to the leaching procedure proposed and tested in our previous works [25, 26]. The sequence of extractants was developed according to studies [4, 27, 28] on the selectivity of leachants to dissolved phases of soils and sediments. 0.05 M calcium nitrate was used as a prospective reagent for the recovery of exchangeable (retained by weak electrostatic interactions) fraction [4].

TABLE 1. Concentrations of elements in essexite gabbro (Russian certified reference material SGD-2a), mg/kg ($n = 3$; $P = 0.95$)

Element	Pyrophosphate extractable fraction	Sum of residual and four extractable fractions	Total concentration (certified value)
Al	40 ± 5	$(41.2 \pm 2.8) \cdot 10^3$	$(39.5 \pm 1.6) \cdot 10^3$
Cr	n.d.*	65 ± 5	58 ± 5
Mn	0.5 ± 0.1	$(1.32 \pm 0.35) \cdot 10^3$	$(1.30 \pm 0.08) \cdot 10^3$
Fe	72 ± 6	$(36.2 \pm 8.2) \cdot 10^3$	$(39.6 \pm 1.2) \cdot 10^3$
Co	n.d.	40 ± 7	40 ± 4
Cu	n.d.	50 ± 8	58 ± 5
La	0.43 ± 0.02	80 ± 10	82 ± 10
Ce	0.96 ± 0.08	145 ± 30	163 ± 20
Pr	0.14 ± 0.04	18 ± 5	20.7 ± 3.7
Nd	0.412 ± 0.007	77 ± 15	89 ± 11
Sm	0.06 ± 0.01	15 ± 4	17 ± 2
Eu	0.017 ± 0.001	2.8 ± 0.6	3.9 ± 0.5
Gd	0.035 ± 0.006	11 ± 3	11.5 ± 2.0
Tb	0.005 ± 0.001	1.4 ± 0.2	1.5 ± 0.2
Dy	0.020 ± 0.005	7.1 ± 0.2	6.2 ± 1
Ho	0.004 ± 0.001	1.16 ± 0.16	1.1 ± 0.2
Er	0.011 ± 0.002	3.1 ± 0.3	2.8 ± 0.6
Tm	n.d.	0.36 ± 0.03	0.35
Yb	0.005 ± 0.001	2.4 ± 0.1	2.5 ± 0.3
Lu	n.d.	0.32 ± 0.06	0.30 ± 0.05

* not determined.

Non-buffered acetic acid solutions (usually 0.1 – 0.43 M) are commonly applied to leach the acid soluble fraction (carbonates, or other specifically adsorbed species of trace elements for non-calcareous samples) [5, 6]. The recommended concentration of 0.43 M [4] was used in the present work. A non-acidified 0.1 M hydroxylamine solution at pH 3.6 as an extracting reagent [27] was used for the selective dissolution of manganese oxides without a notable attack to iron oxides, organic compounds or Al-containing mineral phases. The mixture 0.1 M $K_4P_2O_7$ + 0.1 M KOH (pH 11) was used to leach metals bound to metal-organic complexes.

The most important results of the dynamic extraction of trace and some major elements from gabbro and granite samples are shown in Tables 1 and 2, correspondingly. As seen, the sum of extractable and residual fractions of trace and major elements and certified values of their total concentrations are in good agreement. This confirms the accuracy of the results obtained.

The distribution of elements between extractable and residual fractions in gabbro and granite samples is clearly illustrated in the Figure. In major cases the residual fraction of elements is the most representative one, as it can be expected for gabbro and granite. The exchangeable fraction of gabbro sample contains nearly no extractable elements. At the same time notable amounts of major elements (such as Al, Fe, Mn) and trace elements (such as Cu, Cr, rare earth elements) were found in acid soluble and easily reducible fractions. Pyrophosphate extractable fraction of gabbro sample is also not free from Al, Fe, and REE. In the sample of granite, trace and major elements are distributed between all four extractable fractions. It should be noted that the exchangeable fraction is characterized by relatively high concentrations of Al, Fe, Mn, and REE. These elements were also found in acid soluble, easily reducible, and pyrophosphate extractable fractions.

Pyrophosphate extractable fraction. For gabbro sample, relative contents of elements in pyrophosphate extractable fraction are less than 1% (Figure). For granite samples, these values are higher (up to 4% for rare earth elements and 13% for Cr). This phenomenon needs a special consideration and might be explained on the basis of coordination chemistry of pyrophosphate complexes.

Pyrophosphate ion is the result of condensation of two hydrophosphate units. The pi-bonding stabilizes di- and polyphosphate species in solution much more than analogous sulphates. The first protonation constant of the pyrophosphate ion at

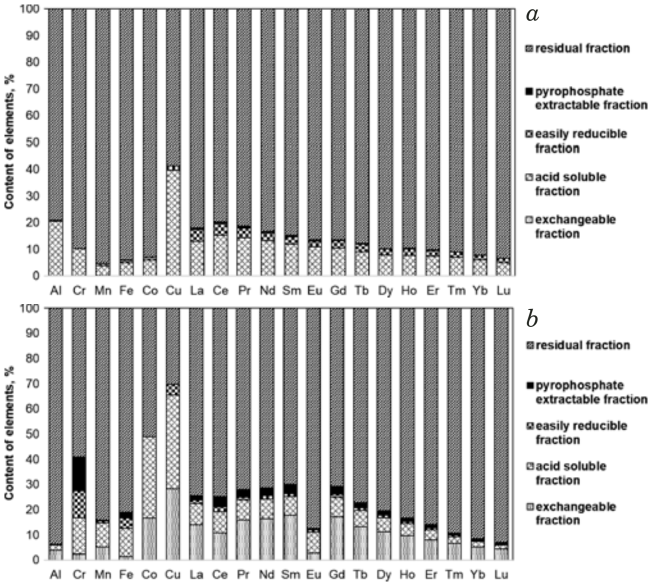
TABLE 2. Concentrations of elements in agpaitic granite (Russian certified reference material SG-3), mg/kg ($n = 3$; $P = 0.95$)

Element	Pyrophosphate extractable fraction	Sum of residual and four extractable fractions	Total concentration (certified value)
Al	75 ± 10	$(29.7 \pm 3.5) \cdot 10^3$	$(28.1 \pm 0.2) \cdot 10^3$
Cr	5.1 ± 1.0	38.9 ± 8.3	31 ± 3
Mn	4.1 ± 0.8	$(1.09 \pm 0.05) \cdot 10^3$	930 ± 40
Fe	400 ± 90	$(17.4 \pm 2.4) \cdot 10^3$	$(15.7 \pm 0.2) \cdot 10^3$
Co	n.d.*	0.84 ± 0.17	1.3 ± 0.3
Cu	n.d.	15 ± 4	12 ± 1
La	0.66 ± 0.07	40 ± 3	45 ± 5
Ce	3.5 ± 0.7	87 ± 7	90 ± 10
Pr	0.38 ± 0.10	12.3 ± 0.6	—
Nd	1.7 ± 0.3	52 ± 3	50 ± 10
Sm	0.42 ± 0.07	11 ± 1	10 ± 1
Eu	0.0020 ± 0.0005	0.30 ± 0.03	0.4 ± 0.1
Gd	0.32 ± 0.06	10 ± 1	—
Tb	0.035 ± 0.005	1.7 ± 0.3	1.7 ± 0.3
Dy	0.17 ± 0.03	10 ± 1	10
Ho	0.025 ± 0.007	1.9 ± 0.2	—
Er	0.08 ± 0.01	6.4 ± 0.6	6
Tm	0.007 ± 0.001	0.92 ± 0.10	—
Yb	0.055 ± 0.012	6.7 ± 0.7	7 ± 1
Lu	0.007 ± 0.001	1.1 ± 0.1	0.9 ± 0.2

* not determined.

25°C is $2.29 \cdot 10^7\ M^{-1}$ in 1 M $NaClO_4$ [29] and $3.39 \cdot 10^7\ M^{-1}$ in 1 M $NaNO_3$ [30]. The rate of hydrolysis reaction $P_2O_7^{2-} + H_2O = 2HPO_4^-$ increases at low pH and under heating. The high metal ion concentration prevents hydrolysis due to the complex formation. The stability of metal complexes with di- and polyphosphates increases in alkaline media due to the deprotonation of anion [31]. Diphosphate ions form complexes with a large number of cations including alkali and alkaline earth metals. The values of stability constants are, e.g., $K_1 = 12.6\ M^{-1}$ for $[NaP_2O_7]^{3-}$ and $1.6 \cdot 10^3\ M^{-1}$ for $[Pb(P_2O_7)_2]^{6-}$ (25°C, 1 M $NaNO_3$) [32]. It is well known that pyro- and triphosphates of rare earth elements dissolve in an excess of sodium pyrophosphate in both acidic and alkaline media. The lowest solubility of $LnPO_4$ occurs in neutral solution. The addition of $HP_2O_7^{3-}$ to a metal salt solution results in the decrease of pH due to the liberation of free H^+ ions. Large excess of pyrophosphate is required to dissolve the pyrophosphates of di- and trivalent metals. The complexes that present in acidic solutions generally contain two or three chelating pyrophosphate units [33]. The extraction of metals by pyrophosphate increases in alkaline solution with the excess of extraction agent.

Taking into consideration the coordination chemistry of pyrophosphate complexes, it becomes clear that apart from metal-organic complexes, pyrophosphate in alkaline solution may also slightly attack inorganic compounds of trace and major elements. As it is seen from the results obtained, the partial dissolution of rare earth and other elements bound to inorganic compounds (including oxyhydroxides and aluminosilicates) is dependent on the geochemical composition of minerals. For gabbro sample, the recovery of REE, aluminum, iron, and manganese is nearly negligible (less than 1% of their total contents). For granite sample, the recovery of trace REE may be up to 4%, whereas the recovery of major elements (iron, aluminum, and manganese) is less than 2%. Chromium is an exception and its recovery in pyrophosphate extractable fraction is more than 10%. A lower extractability of elements from gabbro might be attributed to the geochemical peculiarities of this mineral. It consists primarily of plagioclase and pyroxene and may be considered as an analogue of basalt. Highly crystalline structure of gabbro makes the elements nearly unavailable for “mild” pyrophosphate extraction. Granites, which contain primarily feldspar, quartz and biotite, are less crystalline and may reflect to some extent the primary minerals composition of acid soils in the context of the present research, though in fact soils consists of a great number of different minerals.



Distribution of elements between extractable and residual fractions in essexite gabbro SGD-2a (*a*) and agpaitic granite SG-3 (*b*)

Conclusion

It may be concluded that potassium pyrophosphate in alkaline medium could be further regarded as a sufficiently selective extracting reagent for the dissolution of metal-organic complexes while using SEP for the speciation analysis of environmental solids. Nevertheless, in the interpretation of the results obtained it should be always taken into consideration that due to the formation of stable pyrophosphate complexes, inorganic compounds (including oxyhydroxides and aluminosilicates) might be also partially dissolved, that leads to the mobilization of elements bound to mineral phases of samples under investigation. For soils with high content of organic compounds, the contribution of dissolution of inorganic compounds by pyrophosphate to the results of fractionation analysis may be negligible. However, if the content of organic compounds in soil is low, this contribution may be crucial. The conclusion made is of importance for the fractionation analysis of soil and sediments and its applications to soil science and biogeochemistry.

Acknowledgements

The authors would like to acknowledge the financial support from the Russian Science Foundation (project No. 16-13-10417). The authors are also grateful to Dr. Olga B. Rogova for useful discussions.

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