Annals of Agrarian Science

Journal homepage: http://journals.org.ge/index.php

Analysis of Heavy Metals Phases-carriers in Soils

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Received: 12 January, 2020; accepted: 19 March 2020

A B S T R A C T

A method of extractograms analysis reflecting the dissolution of heavy metals (HM) in soils by dynamic sequential extraction has been developed. The technique is based on the deconvolution of complex extractograms on a series of symmetrical or asymmetrical Gaussians, corresponding to a separate HM phases-carriers. It is possible to determine after deconvolution the number of HM phases-carriers dissolved by the reagent (n), the share of HM in each phase-carrier (S) as a percentage dissolution of the HM by this reagent to the total HM-content, relative degree of each HM phase-carrier stable to the reagent (xmax), domination of fast- or slow-soluble particles in this asymmetrical phase by its asymmetry (As), dispersion of the HM phase-carrier by its dispersion (D). It was studied the action of three reagents: acetic acid, hydroxylamine and ammonium oxalate on Cu, Pb and Zn in contaminated soils. Soils contain two groups of HM carriers-carbonates with different acetic acid solubility. Soils and sediments contain three HM phases-carriers with different rates of dissolution by hydroxylamine. The number of HM-phases dissolved by ammonium oxalate depends on metal: it ranges from two for Zn to three for Cu. In total, contaminated soils contain 7-8 HM-phases, consistently soluble by three reagents. The abundance of the phases suggests that it is desirable to perform smaller fractionation of HM, taking into account the type of pollutants.

Keywords: Heavy metals, Chemical extraction, Extractograms, Deconvolution of spectra, Pollutants, Number of HM.

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Introduction

Methods of chemical dissolution of HM phases-carriers are used in the study of heavy metals (HM) in soils and sediments. Successive schemes of HM-extraction from soils are used now. The extraction of HM is used in two modifications: static and dynamic [1-5]. Static, technically simpler system of HM fractionation is known for decades [4]. Often for the sequential HM-extraction from of soil, the liquid phase is separated from the sediment by centrifuge. But the static system of HM-fractionation has many drawbacks, among them: the duration of analysis, the impossibility of automation, the risk of incomplete extraction due to precipitation, etc. [5].

In recent years, the system of dynamic sequential fractionation of HM, based on fundamentally different, more complex equipment has been developed. In particular, dynamic sequential HM-compounds analysis is performed in a rotating spiral column, which was originally developed for counter-current chromatography [5-8].

The extracted solution is analyzed for the content of the metal, and monitoring is possible in two modes. The accumulated portions of the effluent are analyzed in off-line mode, while differential HM-extractograms are built on points [9]. On-line analysis of the effluent is almost continuous, and the kinetic extractogram is formed a continuous curve.

The system of dynamic sequential HM-fractionation allows obtaining extractograms that characterize the dynamics of metal extraction by the reagents [9]. Already simple visual viewing reveals a wide variety of extractogram forms. In some experiments, as pyrophosphate extraction of lanthanides from soils, kinetic extractograms are the only symmetrical Gaussians [10]. This simple extractogram version has not interest and it is not considered in the paper.

But often the extractogram form is a more complex, because of fact of neighboring Gaussians

superposition, that is, the effect of "overlapping fractions" [5]. Meanwhile, there are no attempts to decipher the complex forms of kinetic HM-extractograms in soils.

The aim of the work is to decipher and analyze complex kinetic extractograms of HM phase-carrier in the soil in dynamic sequential fractionation.

Objects

The HM-extractograms obtained from contaminated soil through dynamic consistent chemical treatment were studied [9].

Montana Soil No. 1 SRM 2710 was near Butte City, Montana, USA. The soil is heavily contaminated with HM, contents are: Pb = 5530, Zn = 6950, Cu = 2950 mg/kg [9]. In this soil, the world's soil Clarks [11] is exceeded 369 times for Pb, 100 times for Zn, 54 times for Cu. The Fe-content in the soil is low: 33,800 mg/kg, twice below the Fe-Clark in the Earth's crust. The Mn-content is very high: 10,100 mg/kg: 10 times higher than the Mn-Clark in the Earth's crust. The Fe/Mn-ratio is 3.3, it is much lower for Clark-ratio in the Earth's crust: 62,000/1,060 = 58 [12]. Thus, the effect of Mn-oxides in soils on HM-fixing may be comparable with the influence of Fe-oxides.

Methods

The continuous HM-fractionation was performed according the well-known Kersten-Foerstner leaching scheme [10]. Applied reactants are the next. Step 1: 1 mol/l ammonium acetate, pH 7. Step 2: 1 mol/l acetic acid + NaOH to adjust to pH 5. Step 3: 0.01 mol/l $NH_2OH{\cdot}HCl$ + 0.01 mol/l HNO_3, pH 2. Step 4: 0.1 mol/l ammonium oxalate + HNO_3, pH 3. Step 5: 30% H_2O_2 %, pH 2.4 and 1 M NH_4OAc в 6% HNO_3 (v/v = 1/3) [9]. Reagents, soluble compounds and HM- phases are presented in the Table. 1.

The continuous fractionation of HM was performed on a planetary centrifuge with a vertical one-layer coil column drum fabricated in Dortmund, Germany. The rotation speed was 550-600 rpm. The mobile phase pumping rate was 1 ml/min. Before commencing the leaching procedure, the spiral column was filled by water. Then the solid sample (~0.5 g) was introduced into the column as a suspension in 10 ml of 1 ml/l ammonium acetate in schemes of Kersten-Foerstner [10]. Then, while the column was rotated, aqueous solutions of different reagents, used as the mobile phase, were continuously fed to the column inlet. The solid sample was retained inside the rotating column as the stationary phase under the action of the centrifugal force field throughout the experiment. In most cases 40 ml of each eluent were pumped through the column. Fractions (10 ml each) of the mobile phase (effluent) were collected. The contents of the elements in the separated fractions (10 ml each) were determined by inductively coupled plasma atomic emission spectrometry [10]. The resulting HM extractograms were then processed by the deconvolution procedure.

Table 1. *Leaching scheme of Kersten-Foerstner: applied reagents and HM phases-carriers [9].*

Step	Reagent	Soluble HM-phases	HM phases-carriers
I	1 M NH_4OAc, pH 7	Exchangeable, water soluble	Sorbates
II	1 M HOAc, pH 5	Acid soluble	Carbonates
III	0.01 M $NH_2OH{\cdot}HCl$ + 0.01 M HNO_3, pH 2	Easily reducible	Mn-oxides
IV	0.1 M oxalate buffer, pH 3	Moderately reducible	Amorphous Fe-oxides
V	30% H_2O_2, pH 2 T=85°C; 1 M NH_4OAc in 6% HNO_3	Oxidizable	Organic matter and sulfides

Method of kinetic extractograms deconvolution

Considering the extractogram as kinetics of metal extraction by reagent over time, it is natural to analyze it as a complex spectrum by the conventional chemical analysis. The main drawback of analytical spectrums is the effect of overlapping signals, in this case the "phase overlap effect", which is distorted the characteristics of the signal (the content of a separate phase). The problem of spectrum "cleaning up" has received a great deal of attention, and significant progress has been made in this direction. One of the common methods of eliminating the overlapping signals in the analytical spectrum is the procedure of its deconvolution, splitting into the original components. Deconvolulation is used to decipher IR-spectrums, nuclear magnetic resonance spectrums, synchrotron X-ray analysis, X-ray fluorescent analysis, laser diffraction and other spectra [13 – 18]. For the deconvolution of spectra, the shape of individual contours is given by the functions of Gauss or Lorenz. In the paper, the function of Gauss was used for deconvolution.

Let's describe the sequence of operations for extractograms deconvolution. In the experience of kinetic dissolution of HM-phases by one reagent in off-line mode were received six test points [9]. On the original extractogram, the projection of figurative dot on the *x*-axis is reflected the volume of the effluent in the interval from 0 to 50 ml. In other words, figurative points are reflected the kinetics of the loss of HM-mass (*y*-axis) when the volume of the leaked solution on *x*-axis. When processing extractograms for each effluent, the position of the dots on the *x*-axis was rationed to the maximum, and then their position is presented in shares of 1. The ordinates of each point are given as a percentage of the HM extracted, relative to its total amount in the soil. After such initial treatment, the extractogram was approximated with a 5-th degree of polynomial. At the same time, the determination factor reached R^2 = 0.995-1.00, which indicates a fairly accurate approximation of the extractogram with a smooth polynomial function.

Then a kinetic extractogram, recorded as a polynomial, was deconvoluted on a series of symmetrical or asymmetrical Gaussians according to the relevant computer program [18].

The symmetrical Gaussian for extractograms is described by the equation:

$$Y = A \cdot \exp\{-[(x - x_{max})/D]^2\}.$$

Asymmetrical Gaussian with a linearly changing dispersion along the contour is described by the equation:

$$Y = A \cdot \exp\{-[(x - x_{max})/(D \cdot (1 + grad \cdot (x - x_{max})))]^2\}$$

where: Y – the content of extracted metal (%), A – amplitude (%); x_{max} is the position of the top of the Gaussian, grad is a gradient of dispersion. For asymmetrical Gaussians with variable dispersion: D is dispersion in the center of the contour. After deconvolution of the extractogram with the help of asymmetrical Gaussian we get its additional properties: asymmetry As, and excess Ex. Asymmetry is positive with the stretched right branch of the Gaussian and is negative in the stretched left branch. The excess has a positive value with the acute top of the Gaussian and negative with the flat top.

Deconvolution based on symmetrical Gaussian is revealed three contours in each extractogram. Is this result reliable? To answer this question, let us compare the real distance between the projections of the two adjacent contours tops on the *x*-axis with the ideal projections of the three contours, when a distance is 0.33. The greater the distance of the x_{max}, the more reason to assume that the assumption of Gaussians independence is true. In almost all studied extractograms the distance between the third and second symmetrical Gaussians is $\Delta x_{max} = x_{max-3} - x_{max-2} > 0.33$, that is, there is a high probability that these Gaussians are independent of each other.

At the same time, the distance between the centers of the first and second Gaussians is short: $\Delta x_{max} = x_{max-2} - x_{max-1} < 0.33$, which raises doubts about the independence of these Gaussians. There is a possibility that the first and second symmetrical Gaussians were formed by splitting one asymmetrical Gaussian.

Therefore, deconvolution of extractograms on the second model, with a linearly changing dispersion on the line contour was performed additionally. This more complex program was revealed the two asymmetrical Gaussians in extractograms. There are two additional characteristics: the values of asymmetry and the excesses.

The choice between the two deconvolution models is based in favor of an option with a minimum deviation from 100%. For some processing options, this minimum is obtained by modeling the extractograms by three symmetrical Gaussians. For other options, the minimum is obtained when using a model with two asymmetrical Gaussians. For example, for Cu extracted with acetic acid from the soil, the de-

viation from 100% decreased from 0.16% for three symmetrical Gaussians to 0.09 % for two asymmetrical Gaussians. This speaks in favor of splitting this extractogram into two asymmetrical Gaussians. On the contrary, for Pb extracted with hydroxylyphine from the soil deviation from 100% increased from 0.32 % for three symmetrical Gaussians to 1.55 % for two asymmetrical Gaussians. This means that the extractogram is more adequately split into three symmetrical Gaussians.

Gaussian interpretation

The deconvolulation of kinetic extractograms provides new information about the number and properties of the HM-phase in the soil. As a result of deconvolution extractograms we get the following indicators.

1) The number of Gaussian (n) as HM-phases, soluble by this reagent.

2) The share of HM-phase (S) from the total metal dissolution by the reagent.

3) The relative degree of stability of each HM-phase in relation to the reagent. It is estimated by the projection of the top of the Gaussian on the *x*-axis (x_{max}). In the weakly resistant phase: x_{max} = min, in the highly resistant to dissolution phase: x_{max} = max, in the medium resistant to dissolution phase: min < x_{max} < max. Often the main phase is the most unstable phase, but sometimes the main phase is medium-resistant.

In addition, deconvolution reveals the heterogeneity degree of particle in each phase. Different phases show different indicators.

The heterogeneity of the symmetrical phase particles can be calculated assessed through the dispersion (D), the heterogeneity of the particles increases at high D values. The heterogeneity of asymmetric phase particles can be judged by its asymmetry (As). Slow-soluble particles dominate with As > 0, and fast-soluble particles dominate with As < 0.

Results and discussion

The results of 8 complex extractograms deconvolution obtained by reagents in the II, III and IV stages of soil processing are given in Figs. 1-3 and in the Table 2. The deconvolution revealed three symmetrical or two asymmetrical HM-phases in different variants of soil chemical treatment (Figs. 1-3).

Table 2. *Properties of HM-phases, obtained by extactograms deconvolution. Source primary data from [9].*

№ phase	x_{max}	D	A, %	As	Ex	S_{phase}, %
№ 8 Acetic acid, Cu; $S_{C\text{-}decon}$ = 99.84%; **$S_{AC\text{-}decon}$ = 100.09%**						
1-C	0.14	0.10	6.19			18.4
2-C	0.20	0.22	1.47			62.6
3-C	0.67	0.18	2.22			18.8
1-AC	**0.15**	**0.18**	**7.20**	**1.08**	**1.66**	**82.5**
2-AC	**0.70**	**0.18**	**1.40**	**-0.64**	**0.65**	**17.6**
№ 9 Acetic acid, Pb, $S_{C\text{-}decon}$ = 100.67%; **$S_{AC\text{-}декон}$ = 100.26%**						
1-C	0.12	0.12	5.72			30.6
2-C	0.26	0.22	5.04			51.8
3-C	0.69	0.18	2.08			18.3
1-AC	**0.15**	**0.18**	**7.20**	**1.08**	**1.66**	**82.5**
2-AC	**0.70**	**0.18**	**1.46**	**-0.64**	**0.65**	**17.6**
№ 7 Acetic acid, Zn, $S_{C\text{-}decon}$ = 100.43%: **$S_{AC\text{-}decon}$ = 100.06%**						
1-C	0.14	0.14	1.73			40.4
2-C	0.32	0.22	0.94			37.3
3-C	0.69	0.18	0.69			22.7
1-AC	**0.15**	**0.18**	**2.15**	**1.19**	**1.89**	**72.9**
2-AC	**0.70**	**0.20**	**0.68**	**-0.81**	**0.53**	**27.2**
№4 Hydroxylamine, Cu, **$S_{C\text{-}decon}$ = 100.58%**; $S_{AC\text{-}decon}$ = **100.66%**						
1-C	**0.15**	**0.14**	**4.17**			**25.9**
2-C	**0.32**	**0.24**	**4.70**			**52.6**
3-C	**0.76**	**0.26**	**1.82**			**22.1**
1-AC	0.19	0.23	7.24	0.91	0.38	90.8
2-AC	0.78	0.22	0.92	-0.81	0.31	9.9

№5 Hydroxylamine, Pb, **$S_{C\text{-}decon}$ = 99.68%;** $S_{AC\text{-}decon}$ = 101.55%						
1-C	**0.23**	**0.14**	**1.07**			**12.0**
2-C	**0.32**	**0.52**	**2.51**			**81.5**
3-C	**0.80**	**0.14**	**0.55**			**6.2**
1-AC	0.24	0.30	3.43	0.50	-0.66	96.3
2-AC	0.81	0.14	0.35	-1.20	1.02	5.2
№6 Hydroxylamine, Zn, **$S_{C\text{-}decon}$ = 100.32%;** $S_{AC\text{-}decon}$ = 101.51%						
1-C	**0.16**	**0.16**	**3.36**			**50.0**
2-C	**0.39**	**0.16**	**1.17**			**27.3**
3-C	**0.67**	**0.20**	**0.80**			**23.0**
1-AC	0.17	0.20	2.42	1.06	0.80	80.3
2-AC	0.68	0.24	0.50	0.57	-0.43	20.2
№ 10 ammonium oxalate, Cu, **$S_{C\text{-}decon}$ = 100.22%;** $S_{AC\text{-}decon}$ = 100.28%						
1-C	**0.14**	**0.12**	**5.30**			**26.3**
2-C	**0.28**	**0.22**	**6.14**			**57.1**
3-C	**0.94**	**0.22**	**1.82**			**16.8**
1-AC	0.18	0.20	9.53	1.16	2.00	85.8
2-AC	0.96	0.18	1.84	-0.43	0.15	14.5
№ 11 ammonium oxalate, Zn, $S_{C\text{-}decon}$ = 100.39%; **$S_{AC\text{-}decon}$ = 99.78%**						
1-C	0.14	0.12	2.86			28.8
2-C	0.30	0.22	2.93			55.9
3-C	0.92	0.29	0.95			15.7
1-AC	**0.18**	**0.20**	**4.70**	**1.11**	**1.73**	**85.8**
2-AC	**0.94**	**0.16**	**0.97**	**-0.73**	**0.81**	**14.0**

Note. Highlighted are bold and stressed options of deconvolution as close as possible on the *y*-axis to 100%. Amplitude A is expressed as a percentage of the total metal content in the soil. The share of the HM-phase S_{phase} is expressed as a percentage of the metal content soluble by the reagent.

TM-phases soluble with acetic acid

The deconvolution revealed three symmetrical or two asymmetrical HM-phases (Fig. 1). Acetic acid is considered as a reagent selective to HM, fixed by carbonates (Table 1). At the same time, it is known that different metals have different degrees of affinity for carbonates. According to [19], carbonate ornstein's in the desert zone of Kazakhstan contain an average of 45 mg cu/kg, 80 mg Pb/kg, 50 mg of Zn/kg. Considering the Clarks of these metals [11], we get the magnitude of their relative affinity: Cu = 45/14 = 3.2, Pb = 80/25 = 3.2 mg, Zn = 50/62 = 0.8. Thus, it is obvious that Zn affinity to the carbonates is much lower than the affinity of Cu and Pb.

Our data are quite consistent with this difference in the extraction of metals with acetic acid. Total amplitudes of Cu- and Pb-phases are reach: 8.60 and 8.66%, but Zn-amplitude is three times less (as for carbonate ortsteins): 2.83%. Thus, the three metals studied fall into two groups: high affinity with carbonates (Cu and Pb) and low affinity with carbonates (Zn). Let's see how this difference in affinity is reflected in the properties of HM-phases.

Presence of two symmetrical Gaussians are reflected two type of carbonates as HM-phases, they differ in resistance to the action of acetic acid. We can talk about the presence of two phases of HM-carbonate with different resistance to the action of acetic acid. It is possible that it is not only Ca-carbonates, but also Mg-carbonates.

The share of rapidly soluble HM-carbonates is very high and reaches 82% for Cu and Pb, but is noticeably lower for Zn - 73%. In addition, the Zn-carbonates are differ from the Cu- and Pb-carbonates in asymmetry. For the rapidly soluble Zn-phase the positive As-values are higher than As-values for the rapidly soluble of Cu- and Pb-phases. That is, the Zn-containing phase has a higher proportion of slow-soluble carbonates. Thus, in the contaminated soil metals are fixed with carbonates with different resistance to acetic acid.

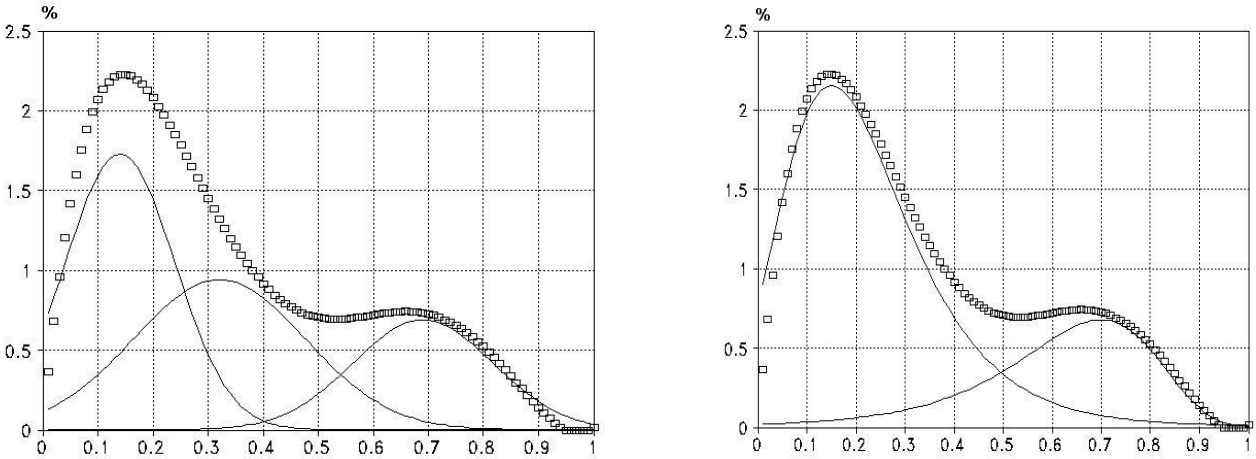

Fig 1. *Deconvolution of Zn-extractograms extracted from the soil with acetic acid. At the top: deconvolution using symmetrical Gaussians (S_{decon} = 100.43%); at the bottom: deconvolution using asymmetrical Gaussians (S_{decon} = 100.06%). The square dots reflect the shape of the original extractogram, the solid lines reflect the shape of the Gaussians..*

HM-phases soluble by hydroxylamine

The deconvolution revealed three symmetrical or two asymmetrical HM-phases (Fig. 2). Three symmetrical HM-phases, soluble during the third stage of treatment ($NH_2OH{\cdot}HCl + HNO_3$), have been identified in the soil. At the same time, there is a difference in the distribution of some metals infractions.

In the soil, the maximum Cu and Pb content falls on the second, medium soluble phase, and the maximum of the Zn falls on the first rapidly soluble phase. This indicates a difference in the solubility of HM-phases.

We will discuss the reasons for the variation of HM-phases stability to hydroxylamine. According to the Kersten-Foerstner scheme, hydroxylamine is selective in relation to HM, fixed by a single phase: Mn-oxides [9]. But obviously this phase is not the only soluble by hydroxylamine.

Here is an experience with the processing of soils of Ural, which showed that not only Mn, but also Fe is extracted by hydroxylamine solution [20]. All studied soils of Ural can be divided into three groups: soils of light and heavy texture and gley in soils of heavy texture. The Fe/Mn-ratio = (M ± m) was calculated, where M and m are average and its error of metals in hydroxylamine extracts from the soils of each group. This ratio was different in each group of soils. In extracts from the soils of the light texture, the Fe/Mn-ratio is 1.55 ± 0.22; in extracts from the soils of the heavy texture the Fe/Mn-ratio is 0.50 ± 0.04; in extracts from the gley in the heavy texture soils, the Fe/Mn-ratio is 0.25 ± 0.03. Thus manganese was extracted much more than iron only from the samples of gley by hydroxylamine. But from the rest of the soil, hydroxylamine together with Mn-oxides dissolves and a significant amount of Fe-hydroxides, which are HM-carriers. In fact, the hydroxylamine dissolves not two, but even three HM-phases.

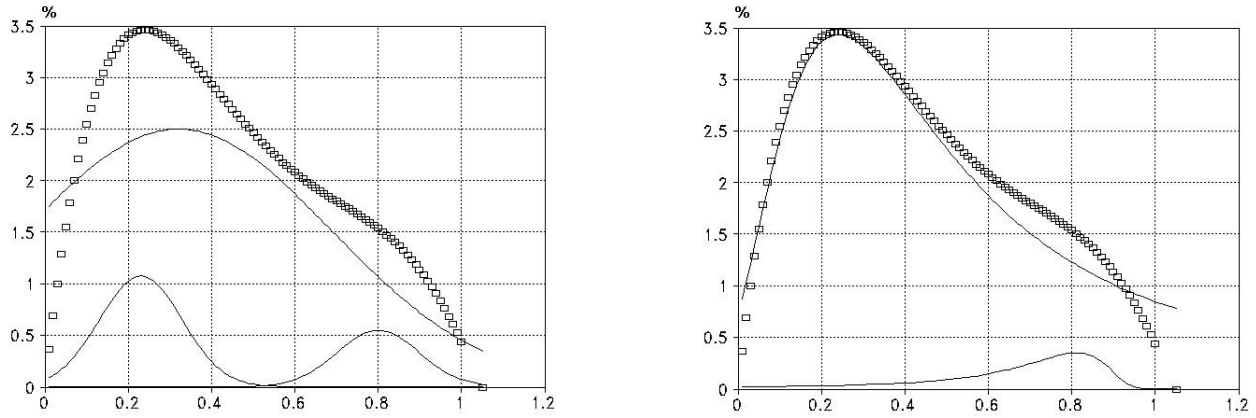

Fig. 2. *Deconvolution of Pb-extractograms extracted from the soil with hydroxylamine. At the top: deconvolution using symmetrical Gaussians (S_{decon} = 99.68%); at the bottom: deconvolution using asymmetrical Gaussians (S_{decon} = 101.55%). The square dots reflect the shape of the original extractogram, the solid lines reflect the shape of the Gaussians.*

HM-phases soluble by ammonium oxalate

The deconvolutions of HM-extractograms extracted by ammonium oxalate revealed two asymmetrical Gaussians for Zn and three symmetrical Gaussians for Cu. The deconvolution revealed three symmetrical or two asymmetrical HM-phases (Fig. 3).

The first of the asymmetrical phases accounts 86% of the Zn. The three Cu-phases are symmetrical, and the second phase accounts 57% of Cu. Thus, we can talk about the presence of two or three HM-phases with different resistance to the action of ammonium oxalate.

A large number of HM-phases are consistent to known data, that in addition to the expected X-ray aamorphous Fe-hydroxides as HM-carriers; oxalate also dissolves Fe(II)-minerals, including sulfides [21]. In addition, oxalate is able to dissolve loosely ordered silicates, such as allophanes [22].

Let us summarize. The determination of the number of TM carrier-phases makes it possible to evaluate the selectivity of each of the reagents used. There is an inverse relationship between the selectivity of the reagent and the number of phases soluble by it. This is illustrated by the action of two reagents contrasting in strength: water, with a minimum ability to dissolve solid phase particles, and royal vodka, in which this ability is expressed as much as possible. Their selectivity is very contrasting: in water, as a weak solvent, maximum selectivity, in royal vodka, which dissolves almost all minerals, there is no selectivity at all. In the schemes of sequential chemical extraction of HM, reagents are used in order of increasing their dissolving ability: from the weakest (often this is water) to the strongest (often hot nitric acid).

We calculate the average number of phases soluble by this reagent according to the formula:

$n_{cp} = (n_{Zn} + n_{Cu} + n_{Pb}) : 3.$

According to the Table 2, we obtain the average values of the number of phases soluble by acetic acid: $n_{aver(acetic)} = 2.0$, hydraxylamine: $n_{aver(hydroxylamine)} = 3.0$, ammonium oxalate $n_{aver(oxalate)} = 2.5$. As can be seen, the initial position of acetic acid in the Kersten-Foerstner scheme is quite consistent with its high selectivity (minimum $n_{aver\ (acetic)} = 2.0$). Compared with acetic acid, subsequent soil treatment with hydraxylamine showed a decrease in selectivity, since the value of $n_{aver(hydraxylamine)}$ increased to 3.0. But further soil treatment with oxalate showed an increase in selectivity: $n_{aver(oxalate)}$ decreased to 2.5. This was due to a decrease in the number of soluble Zn-phases. Thus, the selectivity of the reagent also depends on the type of HM-phases.

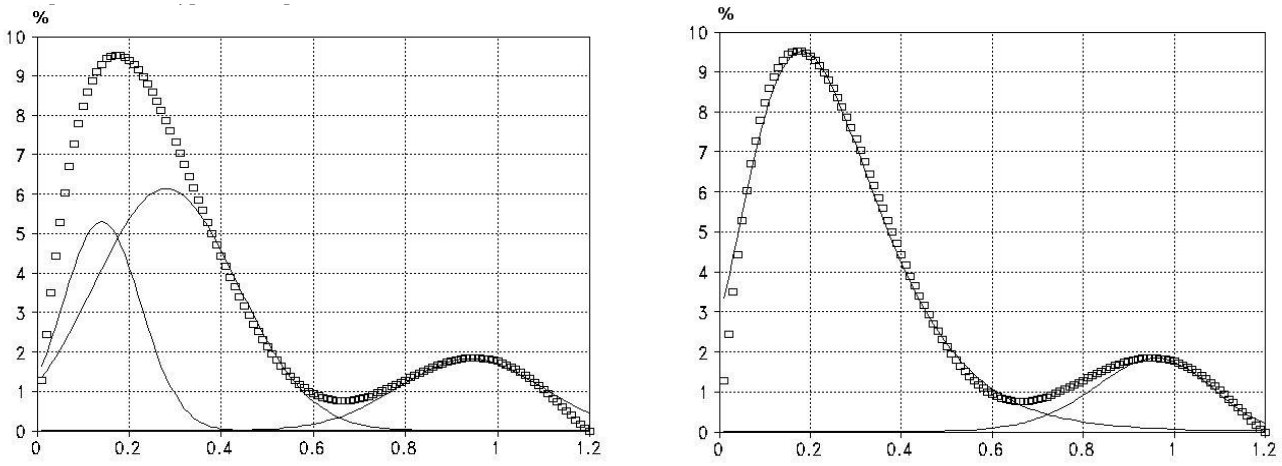

Fig. 3. *Deconvolution of Cu-extractograms extracted from the soil with oxalate. At the top: deconvolution using symmetrical Gaussians (S_{decon} = 100.39%); at the bottom: deconvolution using asymmetrical Gaussians (S_{decon} = 99.78%). The square dots reflect the shape of the original extractogram, the solid lines reflect the shape of the Gaussians.*

Conclusion

A method of extractograms analysis reflecting the dissolution of heavy metals in soils by dynamic sequential extraction has been developed. The technique is based on the deconvolution of complex extractograms on a series of symmetrical or asymmetrical Gaussian, corresponding to a separate HM phase-carrier. After deconvolition it is possible to determine the number of HM phase-carrier soluble by the reagent, the share of HM in each phase-carrier as a percentage dissolution of the HM by this reagent to the total HM-content, relative degree of each HM phase-hosted stability to the reagent (x_{max}), domination of fast- or slow-soluble particles in this asymmetric phase by its asymmetry (As), dispersion of the HM phase-carrier by its dispersion (D). It was studied the action of three reagents: acetic acid, hydroxylamine and ammonium oxalate on Cu, Pb and Zn in contaminated soil.

The soils consist of two groups of HM carbonate-carriers with different acetic acid solubility. Soils and sediments contain three HM phases-carriers with different rates of dissolution by hydroxylamine. The number of HM-phases soluble by ammonium oxalate depends on metal: it ranges from two for Zn to three for Cu. In total, the contaminated soil contains 7-8 HM-phases, consistently soluble by three reagents. The abundance of the phases suggests that it is desirable to perform smaller fractionation of HM, taking into account the type of pollutants.

The number of HM phases-carrier in soils and sediments depends on the deconvolution model of the extractograms: three symmetric and less often two asymmetric phases are detected. In any variant of deconvolution, the HM phases-carriers, fast soluble by this reagent, dominate soils and sediments. In contrast, the proportion of slowly soluble HM-phases is low, especially when exposed to ammonium oxalate: less than 18%. Judging by the presence of not one, but two or three phases, they differ in their resistance to dissolution by reagents.

So, in soils, three symmetrical Zn-phases were revealed; two of them: strongly and moderately soluble carbonates fix the main share of zinc. Two asymmetric carbonate Cu- and Pb-phases were found in soils. The presence of several phases of carbonates of HM-carriers with different resistance to acetic acid indicates the participation of Ca-, Mg-, and Fe-carbonates in the HM-fixation.

Hydroxylamine hydrochloride dissolves three symmetric HM phases-carriers in soils and sediments. Obviously, in addition to Mn-oxides, the reagent dissolves Fe-hydroxides, as well as a certain third phase. The oxalate buffer from the soil and sediment dissolves three symmetric Cu-phases and two asymmetric Zn-phases, and not the only one. It is possible that, in addition to the expected X-ray amorphous Fe-hydroxides, as HM carriers, oxalate also dissolves Fe(II)-minerals, including sulfides, as well as weakly ordered allophanes. Determination of the number and properties of HM phases-carriers allows the identification of the most suitable reagents for the extraction of different groups of TM-compounds from soils and sediments contaminated with various forms of pollutants.

Acknowledgement

The authors thank P.S. Fedotov for discussing the article and useful advices.

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