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Determination of molybdenum in extracts of soil and sewage sludge CRMs after fractionation by means of BCR modified sequential extraction procedure

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ABSTRACT

A modified three-step sequential extraction procedure proposed by the Commission of European Communities Bureau of Reference (BCR) was applied to certified reference materials of three different soil groups (rendzina, luvisol, and cambisol) and sewage sludge of different compositions originating from a municipal water treatment plant in order to assess potential mobility and the distribution of molybdenum in the resulting fractions. In the soils examined, molybdenum was present almost entirely in the mineral lattice, the content of molybdenum in the fractions of the studied reference materials of sludges was predominant in the fraction, represents Mo bound to organic matter and sulphide.

The internal check of accuracy was performed on the results of the sequential extraction by comparing of the extractable amounts of molybdenum in the sequential procedure with the results of the pseudototal digestion of original samples. The recovery ranged from 96 to 101% and the precision (RSD) in the extracts was below 10%.

1. Introduction

Molybdenum plays a complex role in our ecosystems. The element has multiple roles metallurgically, it is a cofactor of enzymes which are essential in plants and animals, and in recent years molybdenum has been recognized as important in human health. The biological antagonism between molybdenum and copper has been extensively investigated [1]. Molybdenum is an essential trace element for both plants and animals, including humans. In plants, this element is necessary for the fixation of atmospheric nitrogen by bacteria at the start of protein synthesis. It appears to be toxic when its concentration in plants is higher than 5 $\mu g\,g^{-1}$ [2,3]. It is unknown which tissue best reflects eventual toxic exposure. In human serum molybdenum concentration lower than 1 $\mu g\,L^{-1}$ was reported [4], mean concentration in urine was 42.5 $\mu g\,L^{-1}$ [5]. Molybdenum in soils is primarily in the oxyanion form and is chemisorbed by iron oxides, noncrystalline aluminosilicates and organic matter [6]. Under reducing conditions molybdenum is easily bioaccessible by formation of soluble thiomolybdates, e.g. MoS^{2-} and $MoO_2S_2{}^{2-}$. Phosphate additions to soil may release $MoO_4{}^{2-}$ from binding sites. Monitoring the Mo content in environmental samples is desirable and highly recommended [7]. The molybdenum content in soils varies from 0.1 to 40 $mg\,kg^{-1}$ and depends on the parent material and the pedogenic process associated with its development [8]. In order to improve the quality of soils, sewage sludge and bottom sediments are often applied to soil due to their high content of nutrients and organic matter. Therefore, some of these potentially toxic elements in all the above environmental matrices should be monitored. The results relating to speciation of molybdenum in soils provide detailed data on molybdenum mobility and transport and have to date only be described in a few papers mostly are devoting to total or pseudototal determination of molybdenum [9–14]. Chemical speciation strongly influences the mobility of metals in soils and sludges. Operational methods of speciation, such as the use of single or sequential extraction are commonly applied. Sequential extraction methods may provide useful information on the association of metals with different soil phases. To harmonize methodology for extraction tests, the European Community has developed a BCR-three stage sequential extraction protocol, which was modified by Rauret et al. [15,16]. To our knowledge, the three-step sequential extraction procedure in accordance with the modified BCR Protocol has not been applied to sewage sludge. The usefulness and limitation of sequential extraction and its future role is reviewed by Bacon and Davidson [17]. In our work, this BCR extraction scheme was applied to soil CRMs of different origins (orthic luvisol, rendzina, and eutric cambisol) and CRMs of sewage sludge one of them provided with a certified total content of molybdenum in order to: (1) investigate the distribution of molybdeum in the respective phases, (2) acquire information about the mobility of molybdenum, (3) provide indicative contents of the extractable molybdenum in the respective fractions in the above soil and sewage sludge CRMs

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Table 1
Instrumental parameters and temperature programme for the determination of molybdenum by ET-AAS.

Wavelength (nm)	313.3
Lamp current (mA)	30
Bandpass (nm)	0.7

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow rate (mL min^{-1})
Drying	110	10	20	250
Drying	130	10	30	250
Pyrolysis	1500/1700[a]	10	20	250
Atomization	2500	0	5	0
Cleaning	2600	1	2	250

[a] Mixed modifier $Pd(NO_3)_2 + Mg(NO_3)_2$ was used.

and also (4) add data on molybdenum to the already existing data on other elements in the soil CRMs [18,19]. The frequent low concentrations of molybdenum in environmental samples require highly sensitive techniques, such as ET-AAS. ET-AAS with transversely heated graphite atomizers (THGA) was applied to the determination of Mo in the soil and sewage sludge extracts. The mixture of $Pd(NO_3)_2 + Mg(NO_3)_2$ was used as chemical modifier. Pseudototal molybdenum content in soils and sludges was determined after digestion with aqua regia. This dissolution procedure was compared with another decomposition method, decomposition with acid mixture HNO_3–$HClO_4$–HF at atmospheric pressure. The interfering effects of major and minor concomitants of soils and sludges on Mo signals were evaluated.

2. Experimental

2.1. Apparatus and instrumental parameters

Molybdenum concentrations in the extracts were determined by graphite furnace atomic absorption spectrometry with Zeeman-effect background correction 5100ZL, using Perkin-Elmer Zeeman atomic absorption spectrometer 5100PC, fitted with AS 71 furnace autosampler. The operational instrumental parameters and optimum charring and atomization temperatures for the determination of molybdenum are given in Table 1. Recommended modifiers, magnesium nitrate and palladium (0.005 mg Pd + 0.003 mg $Mg(NO_3)_2$) were used for the determination using THGA tubes with integrated L'vov platform. The injection volume was 30 μL (20 μL of the extract + 10 μL of the modifier).

A KS125 basic IKA-shaker (IKA Labortechnik Germany) and a K70D centrifuge (MLW, Germany) were used for extraction and to separate extracts from residues resulting from the sequential extraction procedure. Vessels made from PTFE were used throughout the whole procedure. The aqua-regia digestion of the soil and sewage sludge residues after the sequential extraction and the original soil and sewage sludge CRMs was performed using the recommended procedure ISO 11466. All glass-ware and plastic containers were previously soaked in 10% (v/v) nitric acid overnight and rinsed with deionized water. PRO-PS Labconco (Kansas City, KS, USA) was used for producing deionized water.

2.2. Reagents and samples

All reagents were obtained from Merck, Darmstadt, Germany. Calibrants were prepared by a serial dilution of 1000 μg mL^{-1} Merck solution of molybdenum in 0.2% (v/v) nitric acid and in the respective extracting solutions.

The detailed information for the certified reference materials of soils S-VM (Soil Eutric Cambisol), S-SP (Soil Rendzina), S-MS (Soil Orthic Luvisols) is introduced in [18], total values of molybdenum are not certified. In the certified reference materials of sewage sludge from a city water treatment plant the certified total value of molybdenum in the sludge WT-H is 78.4 ± 5.0 and indicative values of molybdenum in sludges WT-L and WT-M are 3.65 ± 1.47 and 4.27 ± 1.42 mg kg^{-1}, respectively.

2.3. Sequential extraction procedure

Sequential extraction procedure was performed using the modified three-stage procedure recommended by BCR [16] on 1 g of soil (sewage sludge) certified reference materials.

Three-stage sequential extraction procedure was designed based on acetic acid extraction (step 1), hydroxylamine hydrochloride extraction (step 2) and hydrogenperoxide/ammonium acetate extraction (step 3).

Step 1. A 40 mL volume of acetic acid (0.11 mol L^{-1}) was added to 1 g of soil (sludge) in a PTFE vessel. The vessel was shaken for 16 h (overnight) at room temperature in a mechanical shaker operating at 300 motions min^{-1} for 20 min, the shaking speed was adapted in order to ensure a continuous suspension of the mixture. The extract was separated from the solid residue by centrifugation for 20 min and decanted into a polyethylene container and stored in a refrigerator at 4 °C for analysis. The residue was washed with 20 mL of distilled water by shaking for 20 min, centrifuged and the washings discarded.

Step 2. To the residue from step 1, 40 mL of a freshly prepared hydroxylamine hydrochloride, 0.5 mol L^{-1} (pH was adjusted by adding of 25 mL of 2 mol L^{-1} HNO_3 to 1 L volumetric flask to the dissolved hydroxylamine hydrochloride (34.75 g)) in deionized water. The extraction procedure was then performed as described above.

Step 3. A 10 mL of hydrogen peroxide (8.8 mol L^{-1}) was added carefully in small aliquots to the residue from step 2. The vessel was loosely covered with the watch glass and digested at room temperature for 1 h with occasional manual shaking. Digestion was continued by heating the vessel to 85 °C in a water bath for 1 h, and then reduced the volume to less than 3 mL by further heating of the uncovered vessel. A second 10 mL of aliquot of hydrogen peroxide was added and the digestion procedure was repeated. Fifty milliliters of ammonium acetate (1 mol L^{-1}, adjusted to pH 2 with nitric acid) was added to the cool moist residue. The sample was shaken, centrifuged and the extract was separated as described in step 1. The solid residue was retained for aqua-regia digestion.

Sequential extraction was performed in PTFE vessels (100 mL volume) with PTFE covers (originally used for digestion under elevated pressure in autoclave):

2.4. Aqua-regia digestion

Pseudototal metal content was determined by digestion with aqua regia, according to the ISO Norm (11466). One gram of the soil (0.5 g sludge) was weighed into the reaction vessel, 0.5–1.0 mL of water was added to obtain a slurry, then 7.0 mL of 12.0 mol L^{-1} HCl followed by 2.3 mL of 15.8 mol L^{-1} HNO_3, drop by drop, to reduce foaming, was added. The reaction vessel was allowed to stand for 16 h (overnight) at room temperature for slow oxidation of the organic matter of the soil. Then the sample was digested using microwave oven. The digests were filtered through Whatman No. 541 filter paper into 50 mL volumetric flasks, the insoluble residue onto the filter paper was washed with a 0.5 mol L^{-1} HNO_3 and the volumetric flask was filled with 0.5 mol L^{-1} HNO_3 up to the mark. Residual material remaining after step 3 of the sequential extraction was digested in the same manner after quantitative transferring of the residual from PTFE vessel.

2.5. Decomposition of soils and sewage sludge for the determination of total molybdenum

Total molybdenum content was determined after decomposition with HNO_3, HF and $HClO_4$. 0.5 g of homogenized soil (sewage sludge) sample was weighed into a home-made PTFE vessel (thickness of the wall was 0.5 mm) and 10 mL of HNO_3 was added. The reaction vessel was allowed to stand for 16 h (overnight) at room temperature to allow for slow oxidation of organic matter. The mixture was gently heated and evaporated on a sand bath (150–160 °C) to 1–2 mL. After cooling, 3 mL of $HClO_4$ was added and evaporated to 1–2 mL. After addition of 20 mL of HF, the mixture was slowly evaporated to dryness. The residue was dissolved by 2 mL of HCl, heated, then 10 mL of deionized water was added, heated and filtered to a 50 mL volumetric flask. Rinsing with deionized water was repeated three times. The sample was then made up to 50 mL with deionized water.

Limits of detection – LODs (three times the standard deviation of the blank, divided by the slope of the calibration graph) for molybdenum in the extraction reagents of BCR sequential extraction procedure for 1st fraction, 2nd fraction, 3rd fraction and residue were 0.037; 0.056; 0.112 and 0.052 (in $\mu g\,g^{-1}$), respectively, and limits of quantification – LOQs (ten times the standard deviation of the blank, divided by the slope of the calibration graph) for 1st fraction, 2nd fraction, 3rd fraction and residue were 0.124; 0.188; 0.374 and 0.174 (in $\mu g\,g^{-1}$), respectively.

3. Results and discussion

3.1. Temperature programme

The pyrolysis and atomization temperatures for the determination of molybdenum in the THGA tube were optimized and the optimum conditions either for the extracts or the solutions obtained after sample digestion are presented in Table 1. It was proved that the thermal pretreatment temperature of 1500 °C without modifier was optimum for all the soils and sewage sludge extracts (1700 °C with the use of the mixture of $Pd(NO_3)_2 + Mg(NO_3)_2$ as chemical modifier).

3.2. Interference effects

The interference effect of extracting agents was examined by comparison of the slopes of the calibration curves constructed on the basis of data obtained with the molybdenum calibration solutions prepared in 0.2% (v/v) HNO_3 and those prepared in the extracting solutions (0.11 mol L^{-1} CH_3COOH, 0.5 mol L^{-1} $NH_2OH{\cdot}HCl$, and 1 mol L^{-1} CH_3COONH_4). The slopes were as follows: 0.0065, 0.0063, 0.0052, and 0.0042, respectively. It can be concluded that slopes differ and the atomization of molybdenum is slightly affected by the extracting agents.

Matrix effects associated with the components of soils and sludges were investigated using “simple” and “mixed” model solutions. The “simple” model solutions contained 20 $\mu g\,L^{-1}$ of molybdenum and a potentially interfering ion (each at four concentration levels: 0.01 mg L^{-1}, 0.10 mg L^{-1}, 1.00 mg L^{-1}, and 10.0 mg L^{-1}). Studied elements were: Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Si, and Zn (all as nitrate). In this case, no differences were observed between atomization signals achieved for molybdenum prepared in 0.2% (v/v) HNO_3 and molybdenum in the presence of the potentially interfering ion studied. The “mixed” model solution contained a mixture of Al, As, Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Na, Ni, Pb, Si, Fe, and Zn. The element concentrations were as follows: 50; 0.03; 10; 0.01; 0.06; 0.30; 0.70; 1.20; 1.20; 0.70; 0.06; 0.20; 0.50; 0.01; 3.50; 1.30 (in mg L^{-1}), respectively. The contents in this model solution were similar to the contents in the sewage sludge WT-H (with maximal contents of the matrix elements). The prepared model solution was spiked with different molybdenum concentrations. In this case, comparison of the results obtained by external calibration with the results obtained by the standard addition technique has shown a substantial difference in the slopes. Based on these observations, the method of standard addition was applied for evaluation of molybdenum in the all samples studied.

Another troubles usually related to the determination of refractory elements by ET-AAS, such as peak-tailing, carbide formation and memory effect had also to be resolved. The differences in slopes (in %) of calibration curves for the determination of molybdenum in 0.2% (v/v) HNO_3 in the presence of the mixed modifier $Pd(NO_3)_2 + Mg(NO_3)_2$, measured in a new graphite tube and a graphite tube after 80, 160, and 240 atomization cycles were 6, 12, and 25%, respectively. In order to minimize memory effects, an extra clean-up step was incorporated between the measurements.

3.3. Determination of molybdenum in the extracts of soils and sewage sludge and in the solution following sample digestion

Molybdenum content in the soil and sewage sludge extracts and the extraction residue which underwent aqua-regia dissolution was quantified using the technique of standard addition. The results are given in Table 2 and they represent mean values ± standard deviation (SD) of 4 replicate analyses (4 repeated extraction pro-

Table 2
Summary of results of molybdenum ($\mu g\,g^{-1}$)[a] in soils and sewage sludge obtained by sequential extraction (1–3), aqua-regia digestion of residue (4); aqua-regia digestion of original samples (determined pseudototal content) and total content.

CRMs	1	2	3	4	$\sum 1+2+3+4$	Determined “Pseudototal Content”	Certified (indicative[c])/ determined total content	Rec. %[d]
	$Mo_{step\,1}$[b]	$Mo_{step\,2}$	$Mo_{step\,3}$	$Mo_{residual}$				
Soil								
S-MS	<0.124	<0.188	<0.374	0.619 ± 0.050	0.619 ± 0.050	0.612 ± 0.008	N.c./0.806 ± 0.069	101
S-SP	<0.124	<0.188	<0.374	0.928 ± 0.037	0.928 ± 0.037	0.934 ± 0.129	N.c./1.05 ± 0.11	99
S-VM	<0.124	<0.188	<0.374	0.696 ± 0.047	0.696 ± 0.047	0.705 ± 0.123	N.c./0.960 ± 0.092	99
Sludge								
WT-H	0.337 ± 0.011	<0.188	69.3 ± 3.3	0.276 ± 0.009	69.9 ± 3.3	70.7 ± 1.8	78.4 ± 5.0/78.7 ± 4.7	99
WT-M	<0.124	<0.188	3.53 ± 0.28	<0.174	3.53 ± 0.28	3.56 ± 0.05	4.27 ± 1.42[c]/4.37 ± 1.01	99
WT-L	0.335 ± 0.017	<0.188	2.05 ± 0.21	0.285 ± 0.017	2.67 ± 0.24	2.69 ± .0.11	3.65 ± 1.47[c]/3.38 ± 0.69	99

[a] Mean values ± standard deviation (SD) of 4 replicate analyses (4 repeated extraction procedures).

[b] Content of molybdenum is below the LOQ in step 1; 2; 3; residual (LOQ = 0.124; 0.188; 0.374; 0.174 $\mu g\,g^{-1}$ Mo, respectively).

[c] Indicative value.

[d] Recovery = ($\sum 1+2+3+4$/pseudototal content from original sample) × 100%.

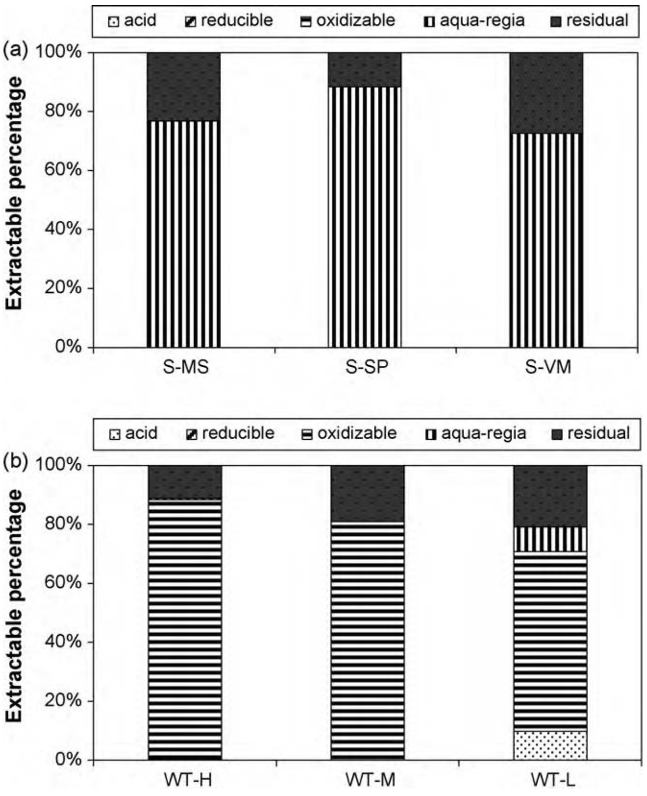

Fig. 1. Molybdenum distribution obtained for the soils S-MS, S-SP, S-VM (a) and the sludge WT-H, WT-M, WT-L (b) using the modified BCR sequential extraction procedure.

cedures). Since no data are available for the molybdenum content in a certified reference material in accordance with the modified BCR three-step extraction procedure, the accuracy of the determination of molybdenum in line with this procedure was verified by comparing the sum of the molybdenum content in the extracts and aqua-regia leachable contents in the residue with the pseudototal aqua-regia leachable contents in the original sample. These results are included in Table 2. A very good agreement was achieved with recoveries ranging from 99–101%.

The content of extractable molybdenum from all the steps of the sequential extraction procedure as applied to S-SP, S-VM, S-MS soils and WT-H, WT-M and WT-L sewage sludge is compared with the aqua-regia leachable contents and the distribution of molybdenum in the respective fractions: (1) exchangeable and associated with carbonates, (2) associated with easily and moderately reducible iron and manganese oxyhydroxides, (3) associated with organic matter and sulphides, (4) molybdenum in the residue—bound in mineral lattice. The largest proportion of molybdenum in the soil certified reference materials studied originating from unpolluted areas was found exclusively in the residual fraction (99–101%) bound to mineral lattice, and its release is unlikely under environmental conditions. In all three soils, the content of molybdenum in the 1st, 2nd, and 3rd fractions was below the limit of quantification. Although these soils represent different soil groups, molybdenum is strongly incorporated in their minerals and immobile, hence not accessible to plants. Extractable percentage relating to the total determined content of Mo is presented in Fig. 1.

Sewage sludge is the insoluble residue from the treatment of waste waters undergoing either aerobic or anaerobic digestion processes. Sludge comprises resistant organic compounds (60% organic matter), nitrogen (3% N), phosphorus (2% P_2O_5), other macronutrients (0.5% K_2O, 5% CaO, 1.5% MgO) [20], a wide range of micronutrients and non-essential trace metals. The typical concentration of molybdenum in sewage sludge is 1–40 mg kg^{-1} dry weight [21]. The certified total contents and the indicative values of Mo in the certified reference materials of sewage sludge studied were in a range of 3.65–78.4 mg kg^{-1}. These materials had a very similar matrix as far as the major elements were concerned (e.g. approximately 3% Al; 1.7% Fe; 0.6% K; 0.6–0.8% Mg; 0.8–1.4% P and 1% S) but they differed mainly in the content of trace elements. Major content of molybdenum was found associated with organic matter and sulphides. From Fig. 1b, where molybdenum distribution obtained for the sludge WT-H, WT-M, and WT-L using modified BCR sequential extraction procedure is illustrated, it can be seen the fact, that mostly Mo is bound to the organic matter and sulphide. Because sewage sludge products are commonly higher in total and potentially available Mo than soils, amendment of soils with sludge could cause health problems and must be controlled.

4. Conclusions

The three-step sequential extraction procedure validated by the Measurement and Testing Programme – M&T (formerly BCR) – of the European Commission, was applied to the pedologically different groups of soil and sewage sludge certified reference materials using three extracting solutions – diluted acetic acid, hydroxylammonium chloride and ammonium acetate. In soils, regardless of the soil group, molybdenum was present almost exclusively in mineral lattice, in an immobile form non-accessible to plants. In sewage sludge, molybdenum followed a different pattern with association to organic matter and sulphides.

It was shown that this sequential procedure is also applicable to environmental matrices other than sediments, as described in the modified BCR Protocol; it is repeatable, appropriate and sufficiently reproducible for environmental monitoring purposes.

The data resulting from the modified BCR sequential extraction scheme carried out on the certified reference materials of soils S-MS, S-SP, and S-VM and sewage sludge WT-L, WT-M, and WT-H can serve as indicative concentrations of molybdenum in these certified reference materials. Although the number of samples analysed was limited, they represent various soil groups and sewage sludge. The data acquired provide valuable information about the mobility and distribution of molybdenum in real environmental samples (sewage sludge and soil) based on the modified BCR extraction Protocol.

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