

Determination of hexavalent chromium in aqueous and alkaline soil extracts

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Abstract: A fast, simple, and reliable method for determination of hexavalent chromium species in soil aqueous and alkaline extracts has been developed. The procedure is based on the ion-pair extraction of Cr(VI) with methyltrioctylammonium chloride (Aliquat 336) into xylene. The extract is analyzed by flame (FAAS) or electrothermal atomic absorption spectrometry (ETAAS). The method allows the detection of up to 2 mg kg⁻¹ Cr(VI) by FAAS and up to 25 μg kg⁻¹ Cr(VI) by ETAAS. The relative standard deviation varied in the range 2%–12% depending on the Cr(VI) levels in the samples. The analysis of certified reference material CRM041-30G Chromium VI–Soil and spike experiments showed recoveries from 91% to 106%. The procedure was applied to industrially polluted soils.

Key words: Soil, liquid phase extraction, Cr(VI), flame atomic absorption spectrometry, electrothermal atomic absorption spectrometry

1. Introduction

The ability to speciate between the oxidation states of Cr in soil samples is important as Cr(III) and Cr(VI) exhibit significant differences in toxicity. Chromium(III) is considered an essential trace nutrient for humans with an established adequate daily dietary intake range for adults from 20 to 35 μg chromium.¹ In the higher oxidation state Cr(VI) exhibits toxic, genotoxic, and carcinogenic properties.² The current soil criteria have set concentration limits for total chromium at 200 mg kg⁻¹.³ No recommended limits for Cr(VI) in soils have been agreed upon.

Current methods available for the analysis of Cr(VI) in soils include extraction in alkaline medium followed by selective separation/detection and quantification. Method EPA 3060A⁴ is considered one of most reliable extraction methods, allowing the quantitative extraction of total Cr(VI) from soils and prevention of Cr(III)–Cr(VI) interconversion.^{5,6} For selective determination of Cr(VI) in soils several ion-chromatography methods connected with UV-visible, conductivity, or inductively coupled plasma mass spectrometry (ICP-MS) detection have been proposed.^{4,7,8} These procedures are limited by laboratory available instrumentation. The diphenylcarbazide EPA7196A method applied as a common method for Cr(VI) determination in water⁹ and cement¹⁰ samples is inappropriate for soil alkaline extracts that contain humic substances acting as interfering compounds.¹¹ Solvent extraction using methyltrioctylammonium chloride (MTOACl), also known as Aliquat 336, has been used for determination of Cr(VI) in waters¹² but not in soils. The simplicity of the method

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prompts us to examine the extraction system MTOACl/xylene for determination of Cr(VI) in soil extracts in order to propose an optimized reliable procedure for fast estimation of hexavalent chromium content in soils. The accumulation of more data for Cr(VI) in soils will help to establish reasonable allowed maximum content in soils and the correct assessment of the environmental risk.

In the current study, we present a very simple, fast, and reliable procedure for determination of Cr(VI) in aqueous and alkaline soil extracts using liquid phase extraction separation of Cr(VI)–methyltrioctylammonium ion pair into xylene and FAAS/ETAAS for quantification.

2. Results and discussion

2.1. Studies on chromium desorption from soils

The leachability study was performed using 0.1 mol L^{-1} NaOH as eluent. The aim was to estimate the lowest shaking time to achieve total extraction of Cr(VI) species from soils. For this reason the total content of Cr in soil extracts was determined by flame or electrothermal AAS, assuming that the achievement of maximum total soluble chromium content will ensure quantitative elution of soluble soil Cr(VI). The dependence of total Cr leachability on the shaking time was studied. The results for chromium desorption from soils using 0.1 mol L^{-1} NaOH as extracting reagent are presented in Figure 1. It can be seen that 2 h shaking time ensures the maximum dissolvable Cr content for the three soil types. For two soil samples alkaline extracts were prepared also according to EPA3060A.

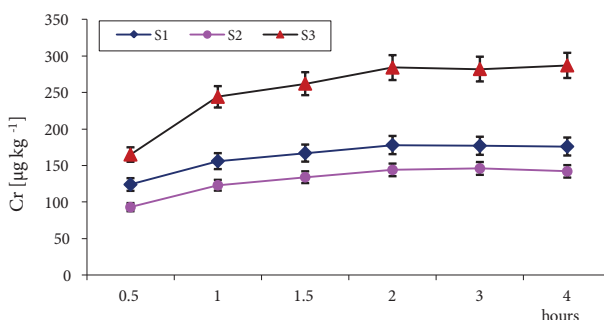


Figure 1. Leachability of Cr in 0.1 mol/L NaOH depending on shaking time for three soil samples.

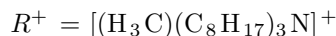
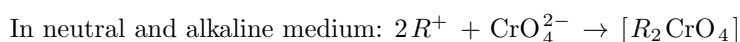
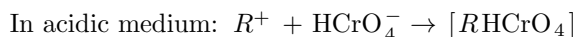
There was no statistically significant difference (Student's t-test, 95% confidence interval) between total soluble Cr content in 0.1 mol L^{-1} NaOH soil extract (0.1 mol L^{-1} NaOH, 2 h, room temperature) and EPA3060A method (0.5 mol L^{-1} NaOH + 0.28 mol L^{-1} Na_2CO_3 + 60 mg MgCl_2 , $90 \text{ }^\circ\text{C}$) soil extracts (Table 1).

Table 1. Total Cr content ($\mu\text{g kg}^{-1}$) in soil extracts obtained by elution with 0.1 mol L^{-1} NaOH and according to EPA 3060A method.

Sample	0.1 mol L^{-1} NaOH (2 h shaking at room temperature) (n = 3)	EPA 3060 A (1 h shaking with 0.5 mol L^{-1} NaOH + 0.28 mol L^{-1} Na_2CO_3 + 60 mg MgCl_2 , $90 \text{ }^\circ\text{C}$) (n = 2)
Soil 2	282 ± 14	296 ± 18
Soil 3	484 ± 18	467 ± 20

2.2. Optimization of pH for selective extraction

The mechanism of selective liquid phase extraction of Cr(VI) species consists of the formation of an ion pair of negatively charged chromate anion with long chain quaternary ammonium salt (methyltrioctylammonium chloride $[(H_3C)(C_8H_{17})_3N]Cl$ (MTOACl) known as Aliquat 336, R), which is extractable into the organic phase.



The effect of pH value on the liquid phase extraction of Cr(VI) and Cr(III) into xylene as an ion pair with methyltrioctylammonium cation was investigated separately. The pH values of water samples ranged from pH 1 (0.1 mol L⁻¹ HCl) to pH 12 (0.01 mol L⁻¹ NaOH) using diluted HCl and NaOH. The results of the effect of pH on the extraction recoveries of Cr(VI) and Cr(III) are shown in Figure 2. It can be seen that the extraction of hexavalent chromium is quantitative for the entire studied range from pH 1 to pH 12. Trivalent chromium species remain quantitatively in the aqueous phase. As positive charged ion, Cr(III) cannot form extractable ion pairs with organic cations. The strong selectivity of the investigated extraction system and the high extraction recovery for Cr(VI) independent of the pH value of the sample solution ensure the simplicity and the reliability of the procedure for nonchromatographic determination of the carcinogenic form of chromium in aqueous and alkaline soil extracts. These data for pH influence on extraction recovery do not agree with the studies by Sirinawin and Westerlud¹² indicating optimum pH 2–3 for extraction of Cr(VI) from seawater. The reason could be i) the higher content of Aliquat 336 (5%) than proposed in this work, 2% Aliquat 336, which could have as a result a different influence on the interphase tension between organic and aqueous phases and ii) isobutylmethyl ketone is a more polar solvent than xylene, which leads to a different influence on the stability of the extracted ion pair. In xylene the ion pair practically is not ionized.

The effect of pH on the extractability of Cr(VI) species using the extraction system Aliquat 336/xylene was also investigated for aqueous soil leachates. The results for three different soil types are presented in Figure 3. In slightly acidic medium at pH 5 the extraction recovery for soils with higher organic content was less than 90%. The reason could be a partial reduction of Cr(VI) to Cr(III). For quantitative extraction of Cr(VI) from soil leachates the pH value of the investigated soil solutions should be higher than pH 7.

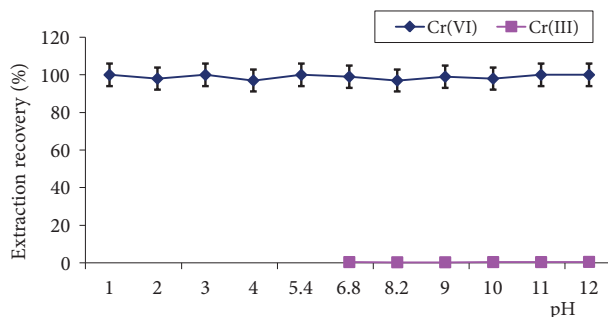


Figure 2. Extractability of chromium species from aqueous solutions with Aliquat 336 in xylene depending on pH.

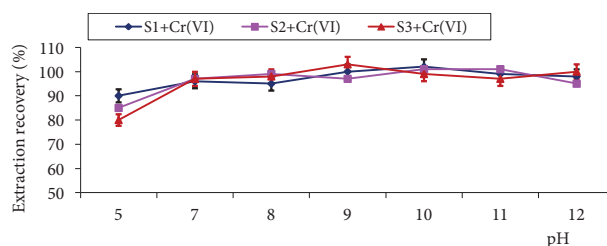


Figure 3. Effect of pH on the extraction recovery of Cr(VI) from aqueous soil leachates using the extraction system Aliquat 336/xylene. Spikes (100 ng Cr (VI)) to aqueous soil extracts.

2.3. Optimization of the liquid phase extraction time

The optimization of the liquid phase extraction procedure includes the assessment of the lowest time to achieve quantitative extraction of the Cr(VI)–MTOACl ion pair into xylene. Independent of the studied soil type the optimal extraction time was found to be 8 min.

2.4. Analytical parameters

2.4.1. Extraction-flame atomic absorption method

Determination of the chromium concentration in the organic phase by FAAS after selective extraction of Cr(VI) species was performed using external calibration with organic standards for Cr obtained by the same extraction procedure as the samples (see Section 2.2). The calibration curve was linear in the range of 0.2–10 mg L⁻¹ Cr. The determination coefficient R^2 was 0.9997 (number of points: 6). The detection limit was evaluated to be 2 mg kg⁻¹ Cr(VI) in soil by using a volume ratio of 5:2 between the aqueous/alkaline soil leachates (5.00 mL) and the xylene phase (2.00 mL). The relative standard deviation ranged from 2% at 70 mg kg⁻¹ Cr(VI) up to 10% at the 2 mg kg⁻¹ Cr(VI) level. The accuracy of the developed procedure was checked performing analysis of certified reference material CRM041-30G Chromium VI–Soil. The assigned certified value is 71.1 mg kg⁻¹ Cr(VI). From this CRM five leachates in water and six in NaOH were prepared according to the described procedure. After filtration from each soil extract three parallel 2.00-mL aliquots were taken and placed into 10-mL extraction tubes and diluted up to 10 mL with Milli-Q water. The pH of the aqueous soil extract was pH 6.9. Then the liquid phase extraction was performed with 2.00 mL 2% Aliquat 336 in xylene for 8 min. The total soluble content of Cr was measured as well. The obtained results are summarized in Table 2. The analytical recoveries are higher than 97%, which confirms the accuracy of the applied procedure. In addition, it can be seen from the results in Table 2 that for this particular soil sample (CRM041-30G Chromium VI–Soil) there exists no statistical difference (Student's t-test, 95% confidence level) between total dissolved soil chromium and the content of Cr(VI) species in all investigated soil fractions. Hence, in the CRM - soil all the soluble forms of chromium are Cr(VI) species and these species are equally soluble in water and in sodium hydroxide.

Table 2. Results from analysis of certified reference material Fluka CRM041-30G Chromium VI–Soil. Certified value for Cr(VI): 71.1 ± 3.42 mg kg⁻¹ (n – number of repetitions).

Soil fraction	Total content (mg kg ⁻¹) of Cr (mean ± SD)	Content (mg kg ⁻¹) of Cr(VI) (mean ± SD)	
		FAAS	ETAAS
H ₂ O-soluble soil fraction (n = 5)	70.4 ± 1.1	69.2 ± 1.6	70.7 ± 2.2
NaOH-soluble soil fraction (n = 6)	71.2 ± 1.5	70.2 ± 1.8	72.0 ± 3.0

2.4.2. Extraction-electrothermal atomic absorption method

Quantification was performed based on calibration using organic standards for Cr obtained by the same extraction procedure as the samples. The calibration curve was linear in the range of 2.0–40 ng mL⁻¹ Cr. The determination coefficient R^2 was 0.9994 (number of points: 5). The detection limit (evaluated as the concentration corresponding to three times the standard deviation of six replicate measurements of a blank sample) of the procedure (5.00 mL of filtrate taken for extraction) was 25 μg kg⁻¹ Cr(VI). The relative standard deviation ranged from 2.7% to 12% depending on the Cr(VI) level. Recovery studies were performed

i) using 100-fold diluted aqueous/alkaline soil extracts obtained from CRM Cr(VI)-Soil (Table 2) and ii) after spiking aqueous and alkaline soil extracts with Cr(VI) (Table 3). The mean recoveries were between 91% and 106%, i.e. in the accepted range for recovery (90%–110%).¹³ The difference between the mean results obtained for Cr(VI) after selective liquid phase extraction/ETAAS determination and the certified value for Cr(VI) was not statistically significant (Student's t-test, 95% confidence level).

Table 3. Determination of Cr(VI) in soil extracts (n = 3).

Sample	Added Cr(VI) ($\mu\text{g kg}^{-1}$)	Found Cr(VI) ($\mu\text{g kg}^{-1}$)	Recovery (%)
Soil 1 + H ₂ O	0	44 ± 5	96.8
	50	91 ± 4	
Soil 1 + 0.1 mol L ⁻¹ NaOH	0	57 ± 2	102.8
	50	110 ± 3	
Soil 2 + H ₂ O	0	74 ± 2	105.2
	100	183 ± 9	
Soil 2 + 0.1 mol L ⁻¹ NaOH	0	188 ± 8	91.2
	200	354 ± 12	
Soil 3 + H ₂ O	0	88 ± 3	93.6
	100	176 ± 13	
Soil 3 + 0.1 mol L ⁻¹ NaOH	0	425 ± 22	91.8
	200	574 ± 27	

The optimized liquid phase extraction procedure for determination of Cr(VI) in aqueous and alkaline soil extracts (described in Section 3.4) was applied to 24 soil samples taken from ferrous metallurgy areas. The results from basic statistics are presented in Table 4. The Cr(VI) content in aqueous soil extracts varied between 41 and 188 $\mu\text{g kg}^{-1}$ and in alkaline soil extracts between 43 and 586 $\mu\text{g kg}^{-1}$. As expected, the soluble soil chemical forms of chromium were mainly Cr(VI) species.

Table 4. Chromium species in soils (number of samples = 24).

Parameter	min	max	mean
Total soil Cr (mg kg^{-1})	24	158	90
Total water soluble soil Cr (Cr(III) + Cr(VI)) ($\mu\text{g kg}^{-1}$)	44	183	92
Water soluble soil Cr(VI) ($\mu\text{g kg}^{-1}$)	41	188	84
Total Cr in alkaline soil digest (Cr(III) + Cr(VI)) ($\mu\text{g kg}^{-1}$)	57	623	193
Alkaline soluble soil Cr(VI) ($\mu\text{g kg}^{-1}$)	43	586	134

3. Experimental

3.1. Experimental setup

The flame atomic absorption measurements were carried out on a PerkinElmer AAnalyst 400 spectrometer (Norwalk, CT, USA) using an air-acetylene flame. The light source was a hollow cathode lamp for Cr. The selected wavelength was 357.6 nm. The instrument parameters were set up for a maximum signal-to-noise

ratio. A PerkinElmer Zeeman 3030 spectrometer (Norwalk, CT, USA) with a HGA-600 graphite furnace was employed for the electrothermal atomic absorption determinations. The spectral bandpass was 0.2 nm. Pyrolytically coated graphite tubes were used as atomizer. The injection of 10 μL of organic phase was performed manually. Only peak areas were used for quantification. The graphite furnace operating parameters for ETAAS measurement of Cr are shown in Table 5.

Table 5. Furnace program for Cr.

Step	Drying	Pretreatment	Atomization	Cleaning
Temperature ($^{\circ}\text{C}$)	140	1500	2500	2700
Ramp/hold time (s)	10/10	15/10	0/4	2/3

3.2. Standards, reagents, and samples

All reagents used, including NaOH, methyltrioctylammonium chloride (MTOACl) (known as Aliquat 336), and xylene, were of analytical grade. High purity Milli-Q water (Milli-Q 50, Millipore, Redford, MA, USA) was used for solution preparation throughout the experiment.

For Cr(III) a ready for use standard solution for AAS (Merck, Darmstadt, Germany) with concentration of 1 g L^{-1} Cr(III) was used. The stock standard solution with concentration of 1 g L^{-1} Cr(VI) was prepared from $(\text{NH}_4)_2\text{CrO}_4$ and delivered from Sigma-Aldrich. Intermediate standard solutions with concentration 1–10 $\mu\text{g mL}^{-1}$ Cr(III) and Cr(VI) were prepared weekly by appropriate dilution. The standard solutions at ng mL^{-1} level were prepared daily. Organic standard solutions of Cr(VI) were prepared using the extraction procedure applied for soil samples. For this purpose, an exact volume of appropriate aqueous Cr(VI) standard solution was placed in a 10-mL extraction tube, followed by addition of 1 mL of 0.1 mol L^{-1} NaOH and dilution with Milli-Q water to 10 mL. Then 2.00 mL of 2% Aliquat 336 in xylene was added to the aqueous phase and the extraction was performed for 8 min. The calibration range was for FAAS 0.2–10 $\mu\text{g mL}^{-1}$ Cr in extract and for ETAAS 2–40 ng mL^{-1} Cr.

The certified reference material CRM041-30G Chromium VI–Soil (Fluka, Sigma-Aldrich) was used for proving the accuracy of the procedure.

Three types of soil samples with different total chromium and organic matter content were chosen for development and accuracy of the analytical procedure. The important characteristics of the samples are specified in Table 6. Pseudo-total chromium was determined in aqua regia soil extracts (ISO 11466).¹⁴ The pH was measured in 1:10 suspension of soil in Milli-Q water. Equivalent calcium carbonate and total organic matter content were determined by means of the usual procedures.¹⁵ For ORP the ASTM G200 standard test method was applied.¹⁶

Table 6. General characteristics of the soil samples.

Sample	Total Cr (mg kg^{-1})	pH	ORP (mV)	Organic matter (%)	CaCO_3 (%)
Soil 1(S1)	54	6.4	150	1.4	22
Soil 2(S2)	119	7.1	118	7	17
Soil 3(S3)	124	7.0	106	11	10.3

3.3. Analytical procedure

The procedure is schematically presented in Figure 4. It contains two main steps.

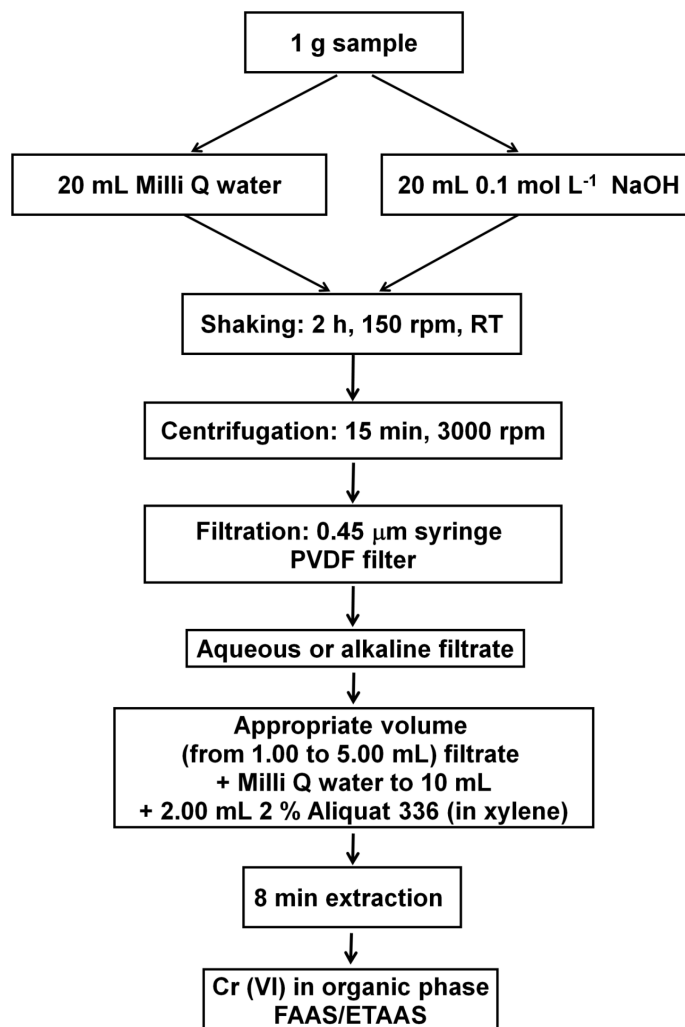


Figure 4. Schematic presentation of the analytical procedure.

3.3.1. Determination of total aqueous and alkaline dissolved chromium

A 1-g soil sample was shaken with 20 mL Milli-Q water or 20 mL 0.1 mol L⁻¹ NaOH for 2 h at 150 rpm, at room temperature. After centrifugation for 15 min at 3000 rpm, the samples were filtered through a 0.45- μ m syringe filter for determination of total dissolved chromium [Cr(III) + Cr(VI)].

3.3.2. Determination of Cr(VI) in aqueous and alkaline soil extracts

Appropriate volumes (from 1.00 to 5.00 mL) were placed into the extraction tubes. The filtrate volume used for the extraction procedure depends on the Cr(VI) content and on the linear calibration range. If necessary (pH < 7), to the tubes with aqueous leachates 1 mL of 0.1 mol L⁻¹ NaOH was added. All the samples were diluted to 10 mL with Milli-Q water. Then to each tube 2.00 mL of 2% solution of Aliquat 336 in xylene was

added and the extraction was performed by up and down shaking for 8 min. After the extraction the organic phase was directly aspirated into the flame of the spectrometer without preliminary separation from the aqueous phase. External calibration with organic Cr(VI) standard solutions (prepared as described in 3.2) was applied for quantitation. For ETAAS measurement of the Cr(VI) content in the extract, the organic phase (10 μL) was injected manually into the graphite furnace and the temperature program (Table 5) was started. The method of standard addition was applied for calibration.

3.4. Statistical analysis

For each sample, three independent analytical portions were weighed and analyzed together with corresponding procedural blanks. For each soil leachate two to four parallel extractions of Cr(VI) species were performed. The statistical data calculations were performed using the software packages Microsoft Excel (Microsoft, Redmond, WA, USA) and STATISTICA 7.0 (StatSoft, Tulsa, OK, USA).

4. Conclusion

The present paper focused on the development of an analytical procedure for simple, reliable, and rapid determination of Cr(VI) in aqueous and alkaline soil leachates. Our experimental results showed that simple shaking of soil samples with 0.1 mol L⁻¹ NaOH at room temperature for 2 h leads to the same total dissolved chromium contents as the more tedious EPA3060A procedure for preparation of alkaline soil digests for Cr(VI). The optimized procedure for subsequent liquid phase extraction of Cr(VI) species from aqueous and alkaline soil leachates as ion pair with long chain quaternary ammonium salt Aliquat 336 is selective and quantitative. Additional pH adjustment of soil extracts as well as preliminary oxidation/reduction treatments are not necessary. The quantitative determination of Cr(VI) species in the organic phase proceeds using equipment for flame/electrothermal AAS available in analytical laboratories. The accuracy of the analytical procedure is demonstrated by analysis of Fluka CRM Chromium (VI)-Soil and spiked soils. The developed method is remarkably fast and simple for performance. It can be used for rapid determination of Cr(VI) in soils independent of their type.

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References

1. Institute of Medicine, Food and Nutrition Board. RDI for Vit. A, Vit. K, As, B, Cr, Cu, I₂, Fe, Mn, Mo, Ni, Si, V and Zn. National Academy Press, DC, 2001.
2. Water Related Fate of the 129 Priority Pollutant Metals, Vol. I: Introduction and Technical Background, Metals and Inorganics, Pesticide and PCBs, EP-440/4-79-029A, 80-204373, US EPA, Washington, DC, 1980.
3. Regulation N 3 of the Bulgarian government concerning the maximum allowed content of heavy metals and metalloids in soils, 2008.
4. US Environmental Protection Agency. Method 3060A. Alkaline Digestion for Hexavalent Chromium, US Environmental Protection Agency, Washington, DC, 1996.
5. James, B. R.; Petura, J. C.; Vitale, R. J.; Mussoline, G. R. *Environ. Sci. Technol.* **1995**, *29*, 2377-2381.

6. Tirez, K.; Brusten, W.; Cluyts, A.; Patyn, J.; de Brucker, N. *J. Anal. At. Spectrom.* **2003**, *18*, 922-932.
7. Wadhawan, A. R.; Stone, A. T.; Bouwer, E. J. *Environ. Sci. Technol.* **2013**, *47*, 8220-8228.
8. Laborda, F.; Górris, M. P.; Bolea, E.; Castillo, J. R. *Intern. J. Environ. Anal. Chem.* **2007**, *87*, 227-235.
9. US Environmental Protection Agency. Method 7196A. Chromium Hexavalent (Colorimetric), US EPA, Washington, DC, 1992.
10. Kristiansen, J.; Christensen, J. M.; Byrialsen, K. *Analyst* **1997**, *122*, 1155-1159.
11. Pettine, M.; Capri, S. *Anal. Chim. Acta* **2005**, *540*, 239-246.
12. Sirinawin, W.; Westerlund, S. *Anal. Chim. Acta* **1997**, *356*, 35-40.
13. Thompson, M.; Ellison, S. L. R.; Fajgelj, A.; Willets, P.; Wood, R. Harmonised Guidelines for the use of recovery information in analytical measurement (JUPAC/ISO/AOAC International/EURACHEM, Technical Report, 1996).
14. ISO 11466:1995, Soil quality - Extraction of trace elements soluble in aqua regia.
15. Page, A. L. (Ed.), *Methods of soil analysis*, 2nd edition. American Society of Agronomy, Madison, 1982.
16. ASTM G200-09 Standard Test Method for Measurement of Oxidation-Reduction Potential (ORP) of Soil, ASTM International, West Conshohocken, PA, 2014.