



Short communication

Separation and flame atomic absorption spectrometric determination of total chromium and chromium (III) in phosphate rock used for production of fertilizer



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ABSTRACT

Due to the commercial value of phosphate rock (PR) as a fertilizer precursor, it is necessary to investigate its heavy metals content. Chromium (Cr) may present as Cr(III) or Cr(VI) in PR; but quantitative differentiation between them is not an easy task. This is due to possible interconversion of Cr species during the digestion/leaching process. In this work, ultrasound digestion (USD) of PR was optimized (300 mg PR, 4.0 mL of 4.0 mol L⁻¹ nitric acid, 15 min sonication) for the sake of leaching Cr species prior to their determination by flame atomic absorption spectroscopy. Using multi-walled carbon nanotube (MWCNT) as adsorbent, solid phase extraction (SPE) was used to separate Cr(III) from the digestate at pH 9, while total Cr was estimated after reducing Cr(VI) into Cr(III). The optimum USD/SPE method gave LOQ and LOD of Cr(III) of 0.96 mg kg⁻¹ and 0.288 mg kg⁻¹, respectively. The method sensitivity was 1.44×10^{-3} AU kg mg⁻¹ within the studied Cr concentration range (5–400 mg kg⁻¹). The USD/SPE method was validated by analyzing lake sediments LKSD-4 certified reference material, and by comparison with classical digestion method (CD). Application of USD/SPE on Jordanian PR samples gave total Cr rang 29.1–122.0 mg kg⁻¹ (± 1.4 –6.3), while Cr(III) ranged between 23.8 and 101.7 mg kg⁻¹ (± 1.3 –5.5). AFPC Rock Check Program samples gave total Cr range 238.9–394.7 mg kg⁻¹ (± 11.5 –24.1), while Cr(III) ranged between 202.4 and 335.8 mg kg⁻¹ (± 11.4 –18.3). These results were very close to the results obtained by the CD method.

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1. Introduction

Phosphate rock (PR) is a non-renewable resource that is used as the raw material for production of artificial fertilizers [1]. Jordan reserves millions of tons of PR, mostly in Eshdyia, in which the principal phosphate mineral is apatite (Ca₅(PO₄)₃F) [2]. Unfortunately, PR may contain various contaminants, such as beryllium, manganese, chromium, arsenic, lead, mercury, cadmium and vanadium [3]. The range of contaminants concentration depends on the geological origin and the mining location of PR [4–7]. This may reduce the PR quality so that continuous monitoring of contaminants in PR is necessary.

Chromium (Cr) is the 24th most abundant element in the Earth's crust; its average concentration is 100 ppm [8] and its concentrations range is between 1 and 3000 mg kg⁻¹. Kotas and Stasicka [9] reported a survey of Cr occurrence in different environmental compartments.

Cr is one of seven elements which were classified in the fertilizer industry as being harmful to plants and biological systems [10]. Cr can exist in PR as Cr(III) or Cr(VI); while Cr(III) is a useful micronutrient, Cr(VI) is a toxic species. The relation between Cr(III) and Cr(VI) strongly depends on the pH and the oxidative properties of the location, but usually Cr(III) is predominant [9].

Although some analytical techniques may analyze solid samples as it is, most other analytical techniques require dissolution of the sample into some solvent [11–13]. The classical method of choice for PR decomposition is usually heating in mixed mineral acid [6,7,10,14]. This method suffers from several drawbacks; it is time-consuming and requires large amounts of reagents and power. Some studies reported unfamiliar leaching methods of elements from PR. For example, Al-Othman and Sweileh [11] developed a simple and fast leaching method for the potentiometric determination of fluoride in PR using 0.5 M citric acid solution. In another study, fusion of PR with lithium tetra-borate [13] caused total dissolution of the sample in a glass matrix which was then analyzed by X-ray fluorescence spectroscopy. Macedo et al. [15] determined total arsenic and arsenic (III) in phosphate fertilizers and PR using slurry preparation with hydrochloric acid

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in an ultrasonic bath. Al-Shawi and Dahl [10] determined total Cr in PR after digestion with nitric acid followed by oxidation of the sample with potassium peroxosulphate to convert all Cr into hexavalent state. Mar and Okazaki [6] investigated cadmium content in several PRs used for the production of fertilizers. Javied et al. [7] investigated heavy metals pollution in PRs used for production of fertilizer in Pakistan but Cr was not included in their study. Aydin et al. [16] reported a study for hazardous metal geochemistry of sedimentary phosphate rock used for fertilizer production but Cr was not included in their study as well. Borges et al. [17] developed a method for cadmium determination in fertilizer samples using graphite furnace atomic absorption spectrometry and slurry sampling. Jesus et al. [18] determined mercury in phosphate fertilizers by cold vapor atomic absorption spectrometry.

Thermal heating can be replaced by auxiliary energy, such as microwave and ultrasound (US), to accelerate the sample digestion process [19]. The two methods are safe, efficient and powerful sources of energy that may be used in digesting solid samples [20]. Ultrasound-assisted digestion (USD) has been used for elemental analysis of many particulate materials such as contaminated soil, coal fly ash, street dust, biological samples, plant materials and sediments [21–24]. It was reported that exposure of solid samples to US lead to changes in their structural surface morphology. The impact of US jet and its associated shock wave erodes the solid leading to localized fragmentation of particles [21,23]. The main benefits of USD over other methods are the speed of digestion, high sample treatment capacity and low reagent usage. US can assist digestion by mechanical and chemical effects. The dissolution kinetics of PR in HCl solution in the presence of US was investigated by Tekin [25]. Unceta et al. [26] reviewed Cr speciation in solid matrices, in which some US digestion procedures were reported for Cr determination in environmental waters.

The direct speciation of Cr species is not always possible by common instrumental methods. This may be due to limitations of the method selectivity and ability to distinguish between different species and/or the detection limits provided by the method. Kotas and Stasicka [9] reviewed the most common methods of Cr speciation. Recently solid phase extraction (SPE) proved itself as a powerful tool for selective separation of Cr species from solutions [27]. This was due to its simplicity, speed, low-cost, and ease of automation. Multi-walled carbon nanotube (MWCNT) was extensively used for sorption and extraction of heavy metals. Sorption of divalent metal ions from aqueous solution by MWCNT was reviewed by Rao et al. [28]. The sorption mechanism was mainly attributed to chemical interactions between the metal ions and the surface functional groups of the MWCNT. So that it was not surprising that sorption capacity of MWCNTs remarkably increased after MWCNT oxidation. Preconcentration of inorganic metals by MWCNT was reviewed by Lemos et al. [29] and by Pyrzynska [30]. Tuzen and Soylak [31] reported a Cr speciation procedure in water samples using MWCNT. They extracted Cr(VI) after complexation with ammonium pyrrolidine dithiocarbamate chelate. Total Cr was estimated after oxidizing Cr(III) into Cr(VI) while Cr(III) was estimated by difference. Actually, dealing with solid samples (as in the present work) is more difficult since there is a possibility of inter-conversion of oxidation states during the digestion process.

The purpose of the present work was to optimize an USD method for leaching Cr species from PR. The digestate was passed through MWCNT to separate and quantify Cr(III). Total Cr was estimated similarly after reducing all Cr species into Cr(III). The optimum method was used to determine total Cr and Cr(III) in Jordanian and AFPC Rock Check Program samples. This work reported for the first time separation and determination of Cr(III) and total Cr in PR under mild digestion conditions (4.0 M HNO₃) which will preserve Cr species as it is. This is the contrary to

classical digestion method which uses vigorous digestion conditions and may convert one Cr species into another.

2. Experimental

2.1. Chemicals and materials

Stock standard solutions of Cr(III) and Cr(VI), each contained 1000 mg L⁻¹, were purchased from Aldrich. Sodium meta-bisulfite (Na₂S₂O₅) was purchased from GCC. Working standard solutions were freshly prepared by appropriate dilution of the stock standard solutions. All the reagents involved in this work were of analytical grade. Distilled water was used in this work. The following buffers (0.050 M each) were used to control the desired pH of the solution: hydrochloric acid–potassium chloride (pH 1.0), hydrochloric acid–glycine (pH 3.0), sodium acetate–acetic acid (pH 5.0), disodium hydrogen phosphate–sodium dihydrogen phosphate (pH 7.0), and ammonium chloride–ammonia (pH 9.0). Multi-walled carbon nanotube (MWCNT) was purchased from Shenzhen Nanotech port Co. Ltd., Shenzhen, China. MWCNT had the following characteristics as provided by the manufacturer: external diameter range: 10–30 nm, length range: 5–15 μm, purity > 95%; ash ≤ 0.2 wt%; amorphous carbon 2%; specific surface area 40–300 m² g⁻¹. Before use, MWCNT was dried at 70–80 °C for 2 h; then it was oxidized with concentrated nitric acid at room temperature for 24 h; and then it was washed with water several times to remove any water-soluble contaminants. Lake Sediments Reference Material LKSD-4 was purchased from Canadian Certified Reference Materials Project CCRMP (Ottawa, Canada).

2.2. Sampling and preparation of phosphate rock (PR) samples

All PR samples were supplied by the Jordan Phosphate Mines Company (JPMC)/Jordan. The PR samples were of two categories: the first category consisted of PR samples from local Jordanian phosphate mines (samples names: Eshydia1, Eshydia2, Eshydia3, Eshydia4, Hassa and Abiad); the second category consisted of PR samples from the AFPC Rock Check Program (AFPC (2009–07), AFPC (2009–09), AFPC (2008–11), and AFPC (2009–12)). All PR samples were crushed, ground to powder, homogenized and passed through a 30 mesh sieve, and kept in an oven at 110 °C for 1 day to remove any moisture.

2.3. Instrumentation

An Analyst 300 Perkin Elmer flame atomic absorption spectrometer “FAAS” (Waltham, MA, USA) was used for determination of Cr concentrations in the eluate under the following instrument conditions: wavelength: 357.9 nm; slit width: 0.5 nm; lamp current: 10 mA; flame type: air–C₂H₂; fuel flow: 1.4 L min⁻¹; burner height: 16.3 mm. The major and some trace elemental composition of PR samples were estimated semi-quantitatively by using a Diano (model 2023) X-ray fluorescence (XRF) spectrometer following the operating conditions provided by the manufacturer. An ultrasonic water bath (Soniclean 120T, Australia) was used for assisting PR digestion and Cr leaching with the following instrument specifications: bath size: 153 × 138 × 100 mm³; bath capacity: 2.0 L; pulse swept power: 60 W; weight: 1.5 kg. A HERMLE LABORATORY centrifuge (type Z200A, Germany), which has a speed range from 0 to 6000 rpm, was used for separation of the un-digested PR from the digestate “leachate”. Solid phase extraction (SPE) of the leached Cr onto MWCNT was performed using a visiprep-12-port vacuum manifold (Supelco, Germany). The outlet tip of the manifold was connected to a vacuum pump

(Heidolph, Germany) to control the sample loading flow rate during the SPE process.

2.4. US-assisted digestion/leaching procedure (USD)

US-assisted leaching of Cr from PR was performed by placing 300 mg of PR and 4.0 mL of 4.0 mol L⁻¹ nitric acid into a 10 mL screw-capped microwaveable centrifuge tube. The tube was placed in the center of the ultrasonic bath and the instrument was switched on for 15 min. The digestion mixture was then centrifuged for 4 min at 3000 rpm. The supernatant was then decanted and sent for separation and determination of Cr(III) and total Cr as described in Section 2.5. The solid residue from digestion was filtered, dried and then weighed for determination of the mass% digested of PR, which was calculated as follows:

$$\text{mass\% digested} = \frac{(\text{mass before digestion} - \text{mass after digestion})}{\text{mass before digestion}} \times 100\%.$$

2.5. SPE/separation and determination of Cr(III) and total Cr

SPE cartridge was prepared by placing 200 mg of MWCNT in an empty 6-mL polypropylene SPE-tube (Supelco, USA). Polyethylene frits were used to hold the adsorbent packing in the cartridge. The cartridge was preconditioned by washing with 6 mL of 1.0 mol L⁻¹ HNO₃, then 12 mL distilled water, and then with 12 mL of pH 9.0 buffer solution.

2.5.1. SPE of Cr(III)

The digestate obtained from Section 2.4 (which contained the leached Cr species) was buffered to pH 9 and diluted to 50 mL. It was passed through the pre-conditioned MWCNT cartridge under the force of water suction. The retained Cr(III) ions were eluted with 5 mL of 1.0 mol L⁻¹ HNO₃, which were determined directly by flame atomic absorption spectrometry.

2.5.2. SPE of total Cr species

Total Cr was determined by using another digestate sample (from Section 4). Two drops of 0.10 mol L⁻¹ sodium meta-bisulfite were added to reduce Cr(VI) into Cr(III). A similar procedure as in Section 2.5.1 was then followed, and total Cr concentration was determined.

2.6. Classical digestion method (CD)

Classical digestion procedure was similar to the procedure described by Mar and Okazaki [6]. The digestate was cooled and centrifuged at 3000 rpm. The supernatant was separated and transferred into a 100 mL volumetric flask and the volume was completed to the mark. This procedure converted all Cr species into Cr(VI) due to vigorous oxidation conditions. So that total Cr concentration was determined directly using FAAS.

3. Results and discussion

3.1. Elemental composition of PR samples

The major elements compositions of PR samples are shown in Table 1. It is clear that PR samples composed mainly of CaO, P₂O₅, SiO₂, F, Al₂O₃, Fe₂O₃ and MgO, where CaO, P₂O₅ and F were the most abundant species in all the studied PR samples. Their concentration range was as follows: CaO: 43.2–52.7%; P₂O₅: 28.5–36.0%; F: 3.1–4.0%. These results agree with the literature values of the main element contents [6,7]. Other elements were

Table 1

Origin and chemical composition (%) of PR samples

	P ₂ O ₅	CaO	F	Al ₂ O ₃	Fe ₂ O ₃	MgO	SiO ₂
Jordanian PR samples supplied by JPRMC^a							
Eshydia 1	32.8	46.7	–	0.5	0.5	0.3	–
Eshydia 2	33.5	52.7	4.0	0.2	0.1	0.3	2.0
Eshydia 3	31.6	51.0	3.6	0.4	0.2	0.3	4.8
Eshydia 4	32.7	48.2	3.7	0.7	0.4	0.3	9.5
Hassa	34.6	51.4	–	0.1	0.2	0.3	–
Abiad	33.7	50.3	–	0.2	0.2	0.3	–
AFPC^b Rock Check Program							
AFPC (2009–07)	33.5	48.5	3.7	1.3	1.0	0.3	–
AFPC (2009–09)	36.0	52.1	4.0	0.4	0.1	0.1	–
AFPC (2008–11)	29.0	43.2	3.2	0.8	0.6	0.4	–
AFPC (2009–12)	28.5	46.1	3.1	0.9	0.7	0.3	–

^a JPRMC: Jordan phosphate mines company.

^b AFPC: Association of Fertilizer and Phosphate Chemists.

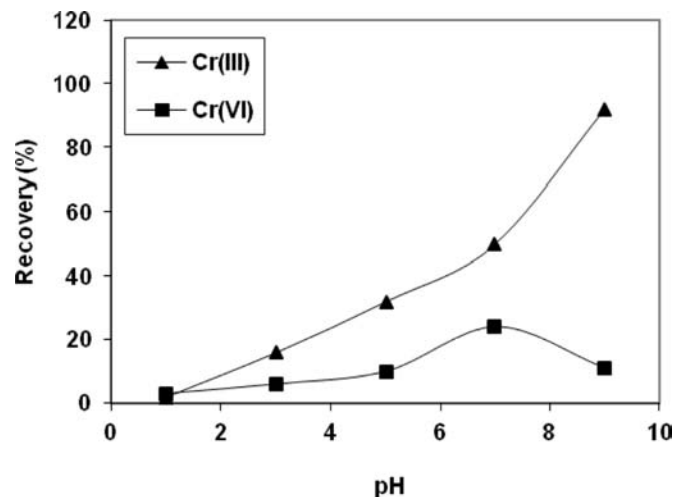


Fig. 1. Effect of solution pH on chromium SPE using MWCNT.

also detected as minor constituents: Na₂O < 0.60%; K₂O < 0.050%; Cl < 0.040%; TiO₂ < 0.021%; MnO < 0.034%.

3.2. Solid-phase extraction and separation of Cr(III) from the digestate

Solid phase extraction of Cr(III) from the digestate was performed using oxidized MWCNT as the solid extractant. Oxidation of MWCNT usually generates carboxylic and phenolic groups on the MWCNT surface [32], which is expected to improve the adsorption efficiency of Cr(III) on the oxidized surface. According to the procedures described in a previous work [32], the total acidic groups on MWCNT after nitric acid oxidation was 36.0 μmol g⁻¹; while the adsorption capacity of Cr(III) on MWCNT was 1.68 μmol g⁻¹.

To study the effect of pH on SPE of Cr(III) from the digestate, the pH of the digestate was adjusted to various values (viz. 1, 3, 5, 7 and 9) prior to the SPE process. It is known that the pH of the aqueous solution affects the chemical nature of the adsorbent surface [32]. At acidic pH values, protonated functional groups predominate; while at basic pH values, deprotonated functional groups predominate. The chemical nature of the adsorbate is also affected by the solution pH. The species distribution curves of Cr(III)–H₂O and Cr(VI)–H₂O system as a function of pH were presented by Stewart and Olesik [33] and Saha et al. [34]. In the pH range of 3–7, the possible Cr(III) species are Cr³⁺, Cr(OH)²⁺, Cr(OH)₂⁺ and Cr(OH)₃. From Fig. 1, it is clear that the recovery of

Cr(III) increased with increasing pH values. This was probably due to that Cr(III) retention occurred through H-bonding between Cr-hydroxo and carboxylic group on the MWCNT surface. At pH 9 the % recovery of Cr(III) increased significantly due to maximum H-bonding of the predominant Cr(OH)_4^- species at pH 9 with the carboxylic and phenolic groups on the MWCNT surface. Since MWCNT can strongly retain Cr(III) rather than Cr(VI) at pH 9, so that this pH was selected as the optimum digestate pH to separate Cr(III) from other Cr species in the digestate matrix. Recovery of Cr(III) at pH 9 reached ~95%, while Cr(VI) gave recovery < 8% at this pH. Total Cr was determined after reduction of the digestate contents with sodium meta-bisulfite to convert all Cr species into Cr(III) and then SPE at pH 9 using MWCNT. The recovery of total Cr was above 95%.

3.3. US-assisted digestion of PR/Cr leaching

Cr compounds are found in the environment due to erosion of Cr-containing rocks; they are then distributed by volcanic eruptions [9]. Cr is mined as chromite ore (FeCr_2O_4) [35]. The ideal chemical formula of chromite mineral is $\text{FeO}(\text{Cr}_2\text{O}_3)$. However substitution of (Mg^{2+} , Ca^{2+} or Mn^{2+}) for Fe^{2+} and of (Al^{3+} or Fe^{3+}) for Cr^{3+} is possible. On the other hand, metal ions in sediments may generally present in the organic matter as oxy-hydroxides of iron, aluminum or manganese; or in phyllosilicate minerals; or as carbonates or sulfides [24]. The metal ions may be retained in the solid phase by different mechanisms, such as: ion-exchange, outer and inner sphere surface complexation, adsorption, precipitation or co-precipitation [24]. These issues may significantly affect the ability of leaching Cr from the PR matrix.

Sample Eshydia4 was used for optimization of US-assisted digestion/leaching procedure. The USD method was based on the use of moderate acid concentrations (4.0 mol L^{-1} and less) without heating. This is expected to maintain the oxidation states of Cr ions during the leaching process. The relation between Cr(III) and Cr(VI) strongly depends on pH and oxidative properties of the location, but in most cases, the Cr(III) is the dominating species [9]. US was used as an efficient source of mechanical energy at room temperature that facilitated and speeded-up the mass transfer process instead of normal mechanical stirring. Optimization and evaluation of the USD procedure was evaluated by determining the concentration of Cr(III) and total Cr recovered after digestion and the percentage of PR mass digested. USD was optimized in terms of time of sonication, type and concentration of the digestion medium. From Table 2, it was noted that acids other than nitric acid gave worse results in which less Cr was leached and less mass was digested. It was also noted that sonication of the digestion mixture has significantly improved Cr leaching and PR digestion compared to digestion/leaching without sonication (see Table 2). It was interesting to note that 10 min of sonication in nitric acid was enough to leach the maximum amount of Cr but 15 min of sonication increased mass digested of PR. Furthermore it was noted (Table 2) that 2.0 mol L^{-1} of nitric acid was sufficient to leach maximum amount of Cr from PR; 4.0 mol L^{-1} of nitric acid did not leach more Cr but digested more mass of the PR. In this work, we were interested in maximum Cr leaching from PR; however, 15 min sonication of PR in 4.0 mol L^{-1} nitric acid was selected in the USD procedure to ensure maximum Cr leaching from PR samples of higher Cr concentrations. These results indicated that both chemical and mechanical effects played significant roles in PR digestion and Cr leaching.

3.4. Validation studies

In order to characterize the proposed USD/SPE: 300 mg samples of Eshydia4, which contains $29.1 \pm 1.4 \text{ mg kg}^{-1}$ of total Cr and

Table 2

Effect of various factors on USD of PR.

Digestion/ leaching parameters	Cr(III) (mg kg^{-1}) (mean \pm sd) ^a	Total Cr (mg kg^{-1}) (mean \pm sd) ^a	Mass digested (%) (mean \pm sd) ^a
Digestion medium (4.0 mL, 2.0 M, 10 min sonication)			
Nitric acid	23.2 ± 1.2	28.5 ± 1.3	58.6 ± 5.0
Hydrochloric acid	22.1 ± 1.3	26.4 ± 1.4	39.2 ± 1.6
acetic acid	10.0 ± 0.6	11.7 ± 0.4	12.8 ± 0.3
citric acid	6.1 ± 0.4	7.2 ± 0.4	9.0 ± 1.3
Time of sonication (4 mL of 2.0 M HNO_3)			
No sonication	4.1 ± 0.4	4.6 ± 0.4	41.3 ± 2.2
2 min	14.1 ± 0.6	17.9 ± 1.1	48.6 ± 4.3
5 min	14.5 ± 0.7	18.5 ± 0.5	52.7 ± 4.5
10 min	23.8 ± 1.3	29.2 ± 1.6	58.3 ± 5.3
15 min	23.9 ± 1.2	29.5 ± 1.5	64.2 ± 2.8
Concentration nitric acid (4.0 mL, 10 min sonication)			
1.0 M	18.1 ± 0.8	23.6 ± 0.9	34.5 ± 3.4
2.0 M	23.4 ± 1.1	28.9 ± 1.3	58.8 ± 5.1
4.0 M	23.9 ± 1.3	28.8 ± 0.9	75.7 ± 3.8

^a Standard deviation.

$23.9 \pm 1.3 \text{ mg kg}^{-1}$ of Cr(III), were spiked simultaneously with Cr(III) and Cr(VI) to get various spiked levels of total Cr: 0, 5, 10, 20, 40, 80, 120, 160, 200, 250 and 300 and 400 mg kg^{-1} . In each spiked sample, 20% of the spiked Cr was Cr(VI); while 80% of the spiked Cr was Cr(III). The samples were then treated using the proposed USD/SPE method (see Sections 2.4 and 2.5). The unspiked PR sample was used as the blank. The recovery of Cr(III) from the eluate ranged between 95.3 and 103.2% (%RSD: 2.2–7.5%), while the recovery of Cr(VI) was less than 5.0%. This indicated that the SPE method was almost selective for Cr(III) in the presence of Cr(VI). After reducing Cr species in the digestate, it was found that the recovery of total Cr ranged between 97.1 and 99.8%.

Using the unspiked PR sample as blank, the average absorbance of Cr(III) was plotted against the added concentration of Cr (mg kg^{-1}). By linear regression of the data, the r^2 value (0.9972) revealed that the method was linear within the studied concentration range. The slope of the calibration curve (method sensitivity) was $1.488 \times 10^{-3} \text{ AU kg mg}^{-1}$. Since no real PR blank was available, the limit of quantification (LOQ) of Cr(III) was estimated based on 10 times the standard deviation of the unspiked PR sample; the LOQ was found to be 0.96 mg kg^{-1} .

3.4.1. Application of the USD/SPE method on CRM

The proposed USD/SPE method was applied for determination of total Cr in Lake Sediments LKSD-4 certified reference material. The average result for total Cr in Lake Sediments LKSD-4 ($21.9 \pm 1.4 \text{ mg kg}^{-1}$, $n=3$) was in good agreement with the certified value (21.0 mg kg^{-1}). This result indicated that the proposed method could be used for determination of total Cr in LKSD-1 certified reference material. The analysis certificate reported the certified concentration of Cr without any indication to the Cr(III) content.

3.5. Determination of Cr(III) and total Cr in Jordanian and AFPC rock check program

The optimum USD/SPE method was applied for determination of Cr(III) and total Cr in Jordanian and AFPC phosphate rock samples. The results are shown in Table 3. USD/SPE method could detect $29.1\text{--}122.0 \text{ mg kg}^{-1}$ ($\pm 1.4\text{--}6.3$) of total Cr and $23.8\text{--}101.7 \text{ mg kg}^{-1}$ ($\pm 1.3\text{--}5.5$) of Cr(III) in Jordanian PR samples. The USD/SPE method could detect $238.9\text{--}394.7 \text{ mg kg}^{-1}$ ($\pm 11.5\text{--}24.1$)

Table 3

Application of the optimum USD/SPE method on various PR samples (n=4) and comparison with classical digestion method (CD)

	USD method		CD method
	Total Cr (mg kg ⁻¹) (mean ± sd) ^a	Cr(III) (mg kg ⁻¹)(mean ± sd) ^a	Total Cr (mg kg ⁻¹)(mean ± sd) ^a
Jordanian PR			
Hassa	93.9 ± 2.1	75.3 ± 3.4	95.5
Abiad	122.0 ± 6.3	101.7 ± 5.5	128.5
Eshydia1	75.6 ± 2.8	63.7 ± 2.7	64.8
Eshydia2	83.0 ± 3.2	68.9 ± 2.8	86.1
Eshydia3	101.6 ± 3.3	82.4 ± 4.8	105.6
Eshydia4	29.1 ± 1.4	23.8 ± 1.3	28.9
AFPC Rock Check Program samples			
AFPC (2009–07)	317.2 ± 16.3	261.7 ± 13.8	329.8
AFPC (2009–09)	238.9 ± 12.8	202.4 ± 12.6	234.2
AFPC (2008–11)	394.7 ± 24.1	335.8 ± 18.3	388.2
AFPC (2009–12)	285.3 ± 11.5	229.7 ± 11.4	293.4

^a Standard deviation.

of total Cr and 202.4–335.8 mg kg⁻¹ (± 11.4–18.3) of Cr(III) in AFPC Rock Check Program samples. To make sure that the method was free from interferences, standard addition method was followed. It was found that the addition of 15% of the found Cr in the sample matrix gave 99.2% recovery, while addition of 85% of the found Cr gave 98.5% recovery. Javied et al. [7] reported Cr content in PR in many countries in the world. For example, they reported 291 mg kg⁻¹ in Moroccan PR and 129 mg kg⁻¹ in the Middle Eastern PR. Our results for AFPC Rock Check Program samples were comparable to the reported values of Moroccan PR; while our results of Jordanian PR samples were comparable to the reported values of the Middle Eastern PR. Javied et al. [7] also reported Cr contents in PRs from other origins, such as Syrian PR: 136 mg kg⁻¹; Saudi Arabian PR: 176 mg kg⁻¹; USA PR: 142 mg kg⁻¹; Algerian PR: 208 mg kg⁻¹; Russian PR: 23.3 mg kg⁻¹; Pakistani PR: 17 mg kg⁻¹.

3.5.1. Comparison with classical digestion method (CD)

For the sake of comparison with the proposed USD/SPE method, classical digestion method (CD) described by Mar and Okazaki [6] was also tested in this work as an independent digestion method for determination of total Cr in Jordanian and AFPC phosphate rock samples. Due to vigorous oxidation conditions involved in Mar and Okazaki method, differentiation between different Cr species was not possible due to conversion of all Cr forms into Cr(VI). The total Cr obtained from CD method was compared with total Cr obtained by USD/SPE method. The results are shown in Table 3. Application of the student's t-test showed that there was no significant difference (within 95% confidence level) between the USD/SPE method and the CD method in terms of total Cr estimated.

4. Conclusion

USD of PR followed by solid-phase extraction using MWCNT as the extractant and then FAAS determination was an efficient, sensitive and accurate method for effective leaching, extraction and determination of total Cr and Cr(III) in PR. The method was applicable within a wide range of Cr concentration in which low LOQ was achieved. The method was tested for both total Cr and Cr(III) determination based on spike recovery. Based on analysis of CRM (lake sediments), only total Cr determination was validated. The results obtained by USD/SPE for analysis of Jordanian and

AFPC Rock Check Program PR samples were comparable to CD method.

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