Speciation of Chromium and Vanadium in Medicinal Plants

Isiaka A. Owolabi, Khakhathi L. Mandiwana* and Nikolai Panichev

Department of Chemistry, Tshwane University of Technology, P.O. Box 56208, Arcadia Pretoria, 0007, South Africa.

Received 15 October 2015, revised 16 February 2016, accepted 1 March 2016.

ABSTRACT

In this study, Cr(VI) and V(V) were determined in medicinal plants collected from the farm located between two smelters. Chromium(VI) and vanadium(V) were leached from medicinal plants with 0.1 M Na_2CO_3 prior their determination by ETAAS. The concentration of Cr(VI) in medicinal plants varied between 3.1 ± 0.5 $\mu g\ g^{-1}$ and 9.4 ± 0.2 $\mu g\ g^{-1}$ and that of V(V) ranged from 1.1 ± 0.08 $\mu g\ g^{-1}$ to 17 ± 1.7 $\mu g\ g^{-1}$. It was established that element species taken up by plants do not depend on metal content in soil but is a function of plant properties. Results of the determination of water-soluble (hot water) Cr(VI) and V(V) concentrations showed that consumption of three cups of tea prepared from medicinal plants from Zizameleni farm is safe since recommended maximum limits is not exceeded through normal consumption of tea infusion.

KEYWORDS

Speciation, leaching, medicinal plants, sodium carbonate, electrothermal atomic absorption spectrometry.

1. Introduction

Medicinal plants are plants that provide health-promoting characteristics and have curative properties. They are used in the preparation of natural medicinal products and have been used throughout human history.[1–2] The World Health Organization (WHO) has reported that approximately 75 % of the world's population use medicinal herbs as alternative remedies to modern medicine.[3] The plant medical applications depends on the traditional experience introduced by local people.[4–5]

The growing awareness among researchers on the importance and uses of medicinal plants in the health care systems has popularized the use of medicinal plants because of the belief that they are safe.[6–10] The widespread use of herbal medicine comes with the risk of overdoses through inappropriate consumption.[11]

Zizameleni farm (25.5717°S, 27.7959°E) specializes in the cultivation of medicinal plants. It is located between ferrochrome smelter (25.3938°S, 27.5070°E) and vanadium smelter (25.3427°S, 27.5325°E) and therefore is exposed to smelter emissions. Chromium(VI) is formed during ferrochrome production due to the oxidation of Cr(III) due to the presence of oxygen (O_2) at high temperature.[12] Therefore, Cr(VI) is released into the atmosphere with smelter emissions.

$$2CR_2O_3\,(s)+4Na_2CO_3\,(aq)+3O_2\,(s) \rightarrow 4NaCrO_4(aq)+4CO_2\,(g)$$

Similarly, pentavalent vanadium, V(V), is emitted to the atmosphere during V_2O_5 production by vanadium smelters.

Both Cr(VI) and V(V) compounds are toxic and carcinogenic. Smelter emissions to the atmosphere settle in soil and penetrate through deep layers of soil where they are accumulated by plants. Chromium (VI) in the form chromate ions (CrO_4^{2-}) is easily accumulated by plants because it resembles sulphate ions (SO_4^{2-}).[13] Similarly, V(V) in the form of VO_4^{3-} is easily accumulated by plants because VO_4^{3-} ions resemble the most important nutritional PO_4^{3-} ions.[14]

The World Health Organization (WHO) recognized Cr(VI) as a carcinogenic agent whereas overexposure to V(V) compounds is linked to kidney, heart and liver damage.[15] The location of Zizameleni farm between the ferrochrome and vanadium smelters make it a suitable case study to assess the effects of smelter emissions on medicinal plants. Therefore, the objective of this study was to determine the concentration of Cr(VI) and V(V) in medicinal plants from Zizameleni farm to verify their suitability for human consumption.

* To whom correspondence should be addressed. E-mail: mandiwanakl@tut.ac.za

2. Experimental

2.1. Equipment and Reagents

A Perkin-Elmer Atomic Absorption Spectrometer model AAnalyst 600 which employs Zeeman-effect background correction system was used for all measurements. The spectrometer was equipped with an AS-800 autosampler and the whole system was controlled by means of AA Winlab software with Microsoft Windows 2010 program. Perkin Elmer hollow cathode lamps of vanadium and chromium operating at 318.4 nm and 357.9 nm have been used for the determination of V and Cr, respectively. Transversely heated graphite furnace tubes (THGA) fitted with integrated L'vov platforms (Perkin-Elmer, part N B050-4033) was used as the atomization source.

The stock solutions containing 1000 g L^{-1} Cr(III) (as $CrCl_3$) or Cr(VI) (as K_2CrO_4) (Merck, South Africa) and 1000 mg L^{-1} V(V) as NH_4VO_3 (Merck, South Africa), were used for the preparation of working standards through serial dilution of the stock solutions. Ultra-pure water with a resistivity of 18.2 MΩ cm^{-1} was obtained with a Milli-Q water purification system (Millipore Corporation, U.S.A.), and was used for all dilutions and sample preparations. Argon, 99 % pure (Afrox, South Africa), was used as the protective and purging gas.

2.2. Quality Assurance

The analytical results for the determination of chromium and vanadium were validated through the analysis of certified reference materials (CRM 545, MESS-3 and PACS-2). The result of the determination of Cr(VI) was validated by the analysis of CRM 545 and good agreement between certified (40.2 ± 0.6 $\mu g\ g^{-1}$) and found (39 ± 1.3 $\mu g\ g^{-1}$) values was established. The total content of chromium was determined after complete digestion of the MESS-3 and there was good agreement between the certified value (243 ± 10 $\mu g\ g^{-1}$) and found value (245 ± 4.2 $\mu g\ g^{-1}$). Similarly, for PACS-2, good agreement between the certified value

ISSN 0379-4350 Online / ©2016 South African Chemical Institute / http://saci.co.za/journal
DOI: http://dx.doi.org/10.17159/0379-4350/2016/v69a8

(90.7 ± 4.6 μg g^{-}1) and found value (91.3 ± 2.6 μg g^{-1}) was established.

Certified reference materials with certified V(V) content are currently not available. Therefore, the results of V(V) determination in samples were validated through spiking of samples with V(V) standard solutions and followed by the determination of percentage recoveries. The % recoveries of the spiked analytes ranged between 98 % and 105 %. The results of total vanadium determination also show good agreement between the found (MESS-3: 234 ± 10 μg g^{-1}; PACS-2: 133 ± 5 μg g^{-1}) and certified values (MESS-3: 236 ± 9 μg g^{-1}; PACS-2: 131 ± 3 μg g^{-1}).

2.3. Samples

Samples were collected from Zizameleni farm (25.5717°S, 27.7959°E) in August 2013. The farm is located approximately 3 km from the vanadium smelter (Vametco Alloy, 25.3427°S, 27.5325°E) and 8 km from the ferrochrome smelter (Hernic ferrochrome, 25.3938°S, 27.5070°E). Twenty species of medicinal plants were collected within 500 m^2 area. Soil samples representing the upper soil layer with a thickness of 20 cm were collected inside the 500 m^2 where medicinal plants are planted. Medicinal plants were washed with ultrapure water. All samples were air dried at room temperature and ground to a particle size of less than 200 μm with an IKA A11 milling system.

2.4. Leaching of Metal Species from Solid Samples

Twenty-five millilitres (25.00 mL) of 0.1 mol L^{-1} Na_2CO_3 was added to approximately 0.25 g powdered sample and the content was boiled for 15 min. The samples were then allowed to cool to room temperature before being transferred to 50 mL polypropylene tubes. The final volumes of sample solutions were adjusted to 25.00 mL with ultra-pure water. The samples were filtered through 0.45 μm hydrophilic PVDF filter prior the determination of Cr(VI) or V(V) by ET-AAS.

2.5. Determination of Total Metal Concentrations in Soil Samples

In order to determine the total concentration of chromium and vanadium, complete digestion of samples was carried out. For this purpose, approximately 0.25 g of soil was first digested in a 10:1 mixture of concentrated HF (5 mL) and concentrated H_2SO_4 (0.5 mL), and heated till near dryness. Furthermore, 1 mL concentrated $HClO_4$ and 2 mL concentrated HF were added and again the mixture was heated to near dryness to evaporate excess acids. Finally, 1 mL concentrated $HClO_4$ was added, and the sample was evaporated until the appearance of white fumes. The residue was then dissolved in 5 mL of 6 M HCl and diluted to 25.0 mL with ultrapure water. The resulting solution was then analyzed by ET-AAS for total Cr and total V concentrations.

2.6. Determination of Total Metal Concentrations in Medicinal Plants

Approximately 0.25 g of plant samples were placed in a porcelain crucible. The temperature of the furnace was slowly increased from room temperature to 650 °C using muffle furnace. The samples were ashed at this temperature until a white or grey residue ash was formed. The ashes were allowed to cool to room temperature, dissolved in 1 mL of a mixture 1:1 concentrated HNO_3 and concentrated HCl, and diluted to 25.00 mL with ultra-pure water prior the determination of total Cr and total V by ET-AAS.

2.7. Determination of Cr(VI) and V(V) in Medicinal Teas

Approximately 2 g of samples was transferred into 500 mL beaker and 200 mL ultra-pure water was added. The mixture was boiled for 15 min. The sample solutions were allowed to cool to room temperature before diluting to 200 mL. Alternatively, 2 g sample was soaked in 200 mL of hot water for 15 min. In order to determine Cr(VI) and V(V), the sample solutions were filtered through 0.45 μm hydrophillic PVDF filter prior analysis with ET-AAS. The total Cr and V concentrations that is available after boiling medicinal plants in water was determined by analyzing the prepared tea without filtration.

3. Results and Discussion

3.1. Results of the Determination of Cr and V in Soil

The separation of Cr(VI) from Cr(III) during leaching is accomplished because Cr(VI) exist as insoluble Cr compounds in solid, e.g. $CaCrO_4$, and therefore by treating solid samples with solution of Na_2CO_3, Cr(VI) is transferred into solution as Na_2CrO_4. That way, Cr(VI) as Na_2CrO_4 will pass through the filter and Cr(III) will remain in the precipitates as $Cr(OH)_3$.

$$CaCrO_4\,(s) + Na_2CO_3\,(aq) \rightarrow CO_3\,(s) + Na_2CrO_4\,(aq)$$

Because V(V) and Cr(VI) have similar chemical properties, both of them can be separated from V(IV) and Cr(III) compounds, respectively, by treatment with a solution of Na_2CO_3.

$$Ca_3(VO_4)_2\,(s) + 3Na_2CO_3\,(aq) \rightarrow 3CaCO_3\,(s) + 2Na_3VO_4\,(aq)$$

Table 1 summarizes results for the determination of Cr(VI) and V(V) concentration in soil. It was found that the concentration of Cr(VI) in soil ranged between 4.0 ± 0.2 μg g^{-1} and 10 ± 0.8 μg g^{-1} and that of V(V) ranged between 11 ± 0.5 μg g^{-1} and 45 ± 2.0 μg g^{-1}.

The correlation curve between Cr(VI) and total Cr in soil was plotted as a function of their concentrations. The correlation curve was linear (R^2 = 0.9999) indicating that Cr(VI) and total Cr originated from the same source as their concentrations increases together (Fig. 1a). Similar results were observed for vanadium (Fig. 1b). Therefore, the differences in concentration of Cr(VI) and total Cr or V(V) and total V in medicinal plants as compared to that in soil depend on individual plant properties.

3.2. Results for the Determination of Cr and V in Medicinal Plants

The concentration of Cr(VI) in medicinal plants varied from 3.1 ± 0.2 μg g^{-1} to 9.4 ± 0.6 μg g^{-1} and that of total Cr were in the range between 65 ± 5 μg g^{-1} and 368 ± 20 μg g^{-1}. The highest Cr(VI) concentrations were found in *Capsicum annuum* and *Artemisia afra* species. The results also showed that *Echinacea purpurea* has lower uptake of Cr(VI) (3.1 ± 0.1 μg g^{-1}) but in contrast accumulated high level of total chromium (104 ± 9 μg g^{-1}). This study also showed that *Nepeta cataria* (9.4 ± 0.6 μg g^{-1}) is the plant that accumulate higher levels while *Capsicum annuum* accummulated

Table 1 Results for the determination of Cr and V in soil (n = 6).

	[Cr(VI)] /μg g^{-1}	Total [Cr] /μg g^{-1}	[V(V)], /μg g^{-1}	Total [V] /μg g^{-1}
Soil 1	10 ± 0.8	1723 ± 86	19 ± 1.0	802 ± 25
Soil 2	4.0 ± 0.2	714 ± 35	11 ± 0.5	525 ± 14
Soil 3	6.2 ± 0.4	1021 ± 41	45 ± 2.0	1775 ± 90
Soil 4	8.0 ± 0.6	1400 ± 70	32 ± 1.5	1300 ± 40
Means	7.1 ± 0.5	1215 ± 58	27 ± 1.3	1001 ± 40

$$\text{Mean} \pm t_{0.05} \times \frac{s}{\sqrt{n}}$$

$$\bar{x} \pm t_{0.05} \times s/\sqrt{n}$$

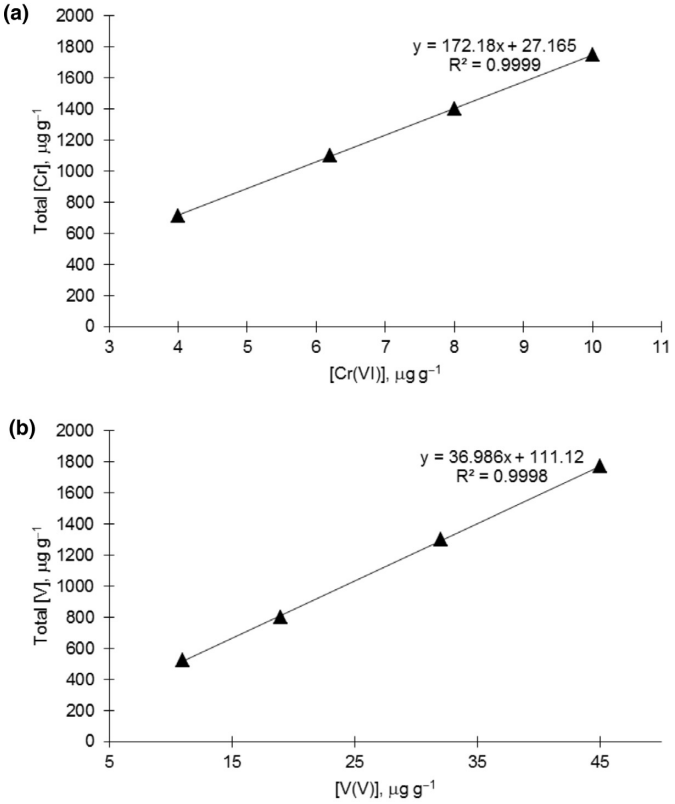

Figure 1 Correlation curve between concentration of metal species and total metal concentration: (**a**), chromium; (**b**), vanadium.

higher levels of total Cr (368 ± 20 μg g^{-1}) (Table 2). The concentration of Cr(VI) in *Rosmarinus officinalis* in this study (4.1 ± 0.2 μg g^{-1}) was 8 times higher than those collected from different herbalists in Hatay region (0.49 ± 0.01 μg g^{-1}) in Turkey.[16] The results of vanadium determination in medicinal plants indicated that low amount of vanadium is present as V(V) species.

The results also shows that V(V) content is only a fraction of the total vanadium content. The concentrations of V(V) leached from plants in *Artemisia afra*, *Nepeta cataria* and *Salvia officinalis* were equal at 95 % level of confidence but in contrast have different total vanadium concentration of 66 ± 3.0 μg g^{-1}, 104 ± 8.0 μg g^{-1} and 439 ± 2.0 μg g^{-1}, respectively. It was also found that *Bidens pilosa* (27 ± 1.6 μg g^{-1}) accumulate the highest levels of V(V) while *Salvia officinalis* (439 ± 2.0 μg g^{-1}) accumulated the highest total vanadium (Table 3). It was not possible to compare results of vanadium determination with those in literature due to limited data available and differences in medicinal plants species.[17]

3.3. Results for the Determination of Cr(VI) and V(V) in Medicinal Teas

According to the World Health Organization (WHO), the maximum recommended concentration of Cr(VI) that should be consumed is 50 μg day^{-1} and that of V(V) is 60 μg day^{-1}.[15,18–19] Therefore, to assess whether Cr(VI) in medicinal plants from Zizameleni does not exceed these limits, one medicinal cup of tea was prepared as normally recommended on most medicinal packages. Two grams (2 g) of medicinal plants (leaves or roots) were boiled in 200 mL ultra-pure water or soaked in 200 mL of hot ultra-pure water for 15 min prior the determination of analytes. To determine Cr(VI) and V(V) that could be consumed per cup of medicinal tea, the samples were filtered through 0.45 μm hydrophilic filter before analysis. The results of the determination of Cr(VI) in medicinal plants showed that hot water leach a small fraction of Cr(VI) and V(V). Approximately 0.1 μg g^{-1} was found in each gram medicinal plant tea soaked implying that a person could consume a maximum of 0.6 μg day^{-1} of Cr(VI) by drinking a maximum of three cups of medicinal tea per day (Table 4). Therefore, it can be concluded that a person can only exceed the recommended daily Cr(VI) limit by drinking at least 83 cups of medicinal teas. Similarly, the maximum of 3.6 μg day^{-1} of V(V) could be consumed per day by drinking three cups of medicinal tea (Table 4). Therefore, it would require drinking at least 17cups of medicinal tea to exceed the maximum

Table 2 Results of the determination of Cr(VI) and total chromium in medicinal plants (n = 6, Mean ± $t_{0.05} \times \frac{s}{\sqrt{n}}$).

Common name	Botanical name	Part used	[Cr(VI)]/μg g^{-1}	Total [Cr]/μg g^{-1}	% Cr(VI)
African potato	*Hypoxis hemerocallidea*	Seed	8.3 ± 0.4	178 ± 10	4.7
Aloe vera	*Aloe barbadensis miller*	Leaves	4.5 ± 0.2	67 ± 4	6.7
Beetroot	*Beta vulgaris*	Root	4.4 ± 0.2	106 ± 4	4.2
Blackjack	*Bidens pilosa*	Leaves	5.9 ± 0.3	105 ± 8	5.6
Buffalo thorn	*Ziziphus mucronata*	Leaves	4.6 ± 0.4	65 ± 5	7.1
Catmint	*Nepeta cataria*	Leaves	9.4 ± 0.6	73 ± 6	13
Chillies	*Capsicum annuum*	Seed	9.2 ± 0.4	368 ± 20	2.5
Coneflower	*Echinacea purpurea*	Leaves and flower	3.1 ± 0.2	104 ± 9	2.9
Garden sage	*Salvia officinalis*	Leaves	8.3 ± 0.5	91 ± 7	9.1
Golden rods	*Solidago virgaurea*	Leaves and flower	5.0 ± 0.2	86 ± 5	5.8
Karee	*Rhus lancea*	Leaves	5.0 ± 0.1	188 ± 10	2.7
Kie apple	*Dovyalis caffra*	Seed	5.6 ± 0.3	109 ± 9	5.1
Lemon grass	*Cymbopogon*	Leaves	6.0 ± 0.4	144 ± 17	4.2
Lemon verbena	*Aloysia citrodora*	Leaves	9.1 ± 0.6	223 ± 20	4.1
Pepper-bark tree	*Warburgia salutaris*	Leaves	7.2 ± 0.3	97 ± 7	7.4
Rosemary	*Rosmarinus officinalis*	Leaves	4.1 ± 0.1	152 ± 10	2.7
Stinging nettle	*Urtica dioca*	Leaves	8.0 ± 0.4	186 ± 24	4.3
Thyme	*Thymus vulgaris*	Leaves	6.4 ± 0.3	84 ± 7	7.6
Tomato	*Solanum lycopersicum*	Seed	8.3 ± 0.4	228 ± 15	3.6
Wild wormwood	*Artemisia afra*	Leaves	8.2 ± 0.6	229 ± 25	3.6

Table 3 Results of determination for V(V) and total vanadium in plants ($n = 6$; Mean $\pm t_{0.05} \times \frac{s}{\sqrt{n}}$).

Common name	Botanical name	Part used	[V(V)]/μg g^{-1}	Total [V]/μg g^{-1}	%V(V)
African potato	*Hypoxis hemerocallidea*	Seed	17 ± 0.8	112 ± 10	16
Aloe vera	*Aloe barbadensis miller*	Leaves	6.9 ± 0.5	61 ± 0.8	11
Beetroot	*Beta vulgaris*	Root	2.3 ± 0.2	46 ± 0.5	5
Blackjack	*Bidens pilosa*	Leaves	27 ± 2.0	89 ± 5.0	30
Buffalo thorn	*Ziziphus mucronata*	Leaves	17 ± 1.0	122 ± 6.0	14
Catmint	*Nepeta cataria*	Leaves	16 ± 0.8	104 ± 8.0	15
Chillies	*Capsicum annuum*	Seed	5.0 ± 0.3	146 ± 10	3.4
Coneflower	*Echinacea purpurea*	Leaves & flower	12.4 ± 1.0	44 ± 0.8	27
Garden sage	*Salvia officinalis*	Leaves	16 ± 0.8	439 ± 20	4
Golden rods	*Solidago virgaurea*	Leaves & flower	4.0 ± 0.4	35 ± 2.0	11
Karee	*Rhus lancea*	Leaves	17 ± 1.7	84 ± 4.0	20
Kie apple	*Dovyalis caffra*	Seed	4.4 ± 0.5	19 ± 1.0	23
Lemon grass	*Cymbopogon*	Leaves	6.4 ± 0.4	22 ± 1.5	29
Lemon verbena	*Aloysia citrodora*	Leaves	15 ± 0.8	63 ± 2.5	24
Pepper bark	*Warburgia salutaris*	Leaves	1.1 ± 0.8	25 ± 1.0	4.4
Rosemary	*Rosmarinus officinalis*	Leaves	1.4 ± 0.1	33 ± 1.5	4.2
Stinging nettle	*Urtica dioca*	Leaves	4.5 ± 0.5	18 ± 0.8	25
Thyme	*Thymus vulgaris*	Leaves	12 ± 0.6	44 ± 1.0	27
Tomato	*Solanum lycopersicum*	Seed	13 ± 1.0	51 ± 2.0	21
Wild wormwood	*Artemisia afra*	Leaves	16 ± 0.8	66 ± 3.0	24

Table 4 Results of the determination of Cr(VI) and V(V) in medicinal teas (n=6).

Common name	Botanical name	[Cr(VI)] /μg day^{-1}	[V(VI)] /μg day^{-1}
African potato	*Hypoxis hemerocallidea*	0.1 ± 0.01	0.2 ± 0.01
Aloe vera	*Aloe barbadensis miller*	0.1 ± 0.01	0.3 ± 0.01
Beetroot	*Beta vulgaris*	0.1 ± 0.01	0.1 ± 0.01
Blackjack	*Bidens pilosa*	0.1 ± 0.01	0.1 ± 0.01
Buffalo thorn	*Ziziphus mucronata*	0.1 ± 0.01	0.2 ± 0.01
Catmint	*Nepeta cataria*	0.1 ± 0.01	0.1 ± 0.01
Chillies	*Capsicum annuum*	0.1 ± 0.01	0.1 ± 0.01
Coneflower	*Echinacea purpurea*	0.1 ± 0.01	0.2 ± 0.01
Garden sage	*Salvia officinalis*	0.1 ± 0.01	0.2 ± 0.01
Golden rods	*Solidago virgaurea*	0.1 ± 0.01	0.1 ± 0.01
Karee	*Rhus lancea*	0.1 ± 0.01	0.1 ± 0.01
Kie apple	*Dovyalis caffra*	0.1 ± 0.01	0.1 ± 0.01
Lemon grass	*Cymbopogon*	0.1 ± 0.01	0.4 ± 0.01
Lemon verbena	*Aloysia citrodora*	0.1 ± 0.01	0.2 ± 0.01
Pepper bark	*Warburgia salutaris*	0.1 ± 0.01	0.2 ± 0.01
Rosemary	*Rosmarinus officinalis*	0.1 ± 0.01	0.1 ± 0.01
Stinging nettle	*Urtica dioca*	0.1 ± 0.01	0.3 ± 0.01
Thyme	*Thymus vulgaris*	0.1 ± 0.01	0.1 ± 0.01
Tomato	*Solanum lycopersicum*	0.1 ± 0.01	0.6 ± 0.01
Wild wormwood	*Artemisia afra*	0.1 ± 0.01	0.1 ± 0.01

recommended daily limit of V(V). It is practically impossible to exceed these limits and therefore, teas prepared from medicinal plants from Zizameleni farm are safe for human consumption.

4. Conclusions

Analysis of medicinal plants collected in the farm between Cr and V smelters showed that Cr(VI) and V(V) contents accumulated by plants depends on individual plant species and is not a function of metal species concentration in soil. It was also found that an individual cannot exceed the recommended maximum daily limits of Cr(VI) and V(V) by consuming three cups of medicinal tea per day.

References

1 M.J. Jordán, J. Castillo, S. Bañón, C. Martínez-Conesa and J.A. Sotomayor, Relevance of the carnosic acid/carnosol ratio for the level of rosemary diterpene transfer and for improving lamb meat antioxidant status, *Food Chem.*, 2014, **151**, 212–218.

2 M.M. Iwu, *Handbook of African Medicinal Plants*, 2nd edn., CRC Press, Boca Raton, 2014.

3 I. Ujváry, Pest control agents from natural products, in *Hayes' Handbook of Pesticide Toxicology*, (R. Krieger, ed.), 3rd edn., Academic Press, New York, 2010, pp. 119–229.

4 M. Leonti, The future is written: impact of scripts on the cognition, selection, knowledge and transmission of medicinal plant use and its implications for ethnobotanyand ethnopharmacology, *J. Ethnopharmacol.*, 2011, **134**, 542–555.

5 B. Kamsu-Foguem, G. Diallo and C. Foguem, Conceptual graph based knowledge representation for supporting reasoning in African traditional medicine, *Eng. Appl. Artif. Intel.*, 2013, **26**, 1348–1365.

6 A. Maroyi, An ethnobotanical survey of medicinal plants used by the people in Nhema communal area, Zimbabwe, *J. Ethnopharmacol.*, 2011, **136**, 347–354.

7 S.S. Ningthoujam, A.D. Talukdar, K.S. Potsangbam and M.D. Choudhury, Challenges in developing medicinal plant databases for sharing ethnopharmacological knowledge, *J. Ethnopharmacol.*, 2012, **141**, 9–32.

8 G.O. Barney, Environment projections, in The Global 2000 Report to the President of the U.S., (G.O. Barney, ed.), *Pergamon*, 2013, **13**, 227–449.

9 E. Bignante and N. Tecco, Is indigenous health knowledge converging to herbalism? Healing practices among the Meru and the Maasai of the Ngarenyanyuki ward, Northern Tanzania, *Geoforum*, 2013, **48**, 177–186.

10 A. Filipiak-Szok, M. Kurzawa and E. Szlyk, Determination of toxic metals by ICP-MS in Asiatic and European medicinal plants and dietary supplements, *J. Trace Elem. Med. Biol.*, 2015, **30**, 54–58.

11 S. Mcwhorter, C. Read, G. Ordaz and N. Stetson, Materials-based hydrogen storage: Attributes for near-term, early market PEM fuel cells, *Curr. Opin. Solid State Mater. Sci.*, 2011, **15**, 29–38.

12 J.M. Pacyna and J.O. Nriagu, Atmospheric emissions of chromium from natural and anthropogenic sources, in *Chromium in the Natural*

and Human Environment, (J.O. Nriagu and E. Nieboer, eds.), John Wiley & Sons, Toronto, 1988, pp. 105–124.

13 G. Svehla, *Vogel's Qualitative Inorganic Analysis*, 7th edn., Longman Singapore Publishers, Singapore, 1996.

14 R.R. Moskalyk and A.M. Alfantazi, Processing of vanadium: a review, *Miner. Eng.*, 2003, **16**, 793–805.

15 WHO, World Health Organization, Safety evaluation of certain food additives and contaminants. WHO Food Additives Series: Safety evaluation of certain food additives and contaminants. Prepared by the Seventy-fourth meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA), Geneva, 2012, **65**: 81–86.

16 S. Sungu, Y. Kilboz and M.M. Atan, Determination of chromium species in various medicinal plants consumed in Hatay region in Turkey, *Int. J. Food Prop.*, 2013, **16**, 1711–1716.

17 D.S. Antal, C.A. Dehelean, C.M. Canciu and M. Anke, Vanadium in medicinal plants: new data on the occurrence of an element both essential and toxic to plants and men, Analele Universităţii din Oradea, Fascicula Biologie, **XVI/2**, pp. 5–10. 2009.

18 M. Jović and S. Stanković, Human exposure to trace metals and possible public health risks via consumption of mussels *Mytilus galloprovincialis* from the Adriatic coastal area. *Food Chem. Toxicol.*, 2014, **8**: 241–251.

19 Y. Qian, F.J. Gallagher, H. Feng, M. Wu and Q. Zhu, Q., Vanadium uptake and translocation in dominant plant species on an urban coastal brown field site, *Sci. Total Environ.*, 2014, **4**, 696–704.