

VANADIUM IN MEDICINAL PLANTS: NEW DATA ON THE OCCURENCE OF AN ELEMENT BOTH ESSENTIAL AND TOXIC TO PLANTS AND MAN

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Abstract. The biological importance of the trace element vanadium on a triple level – nutritional, pharmacological and toxicological – determined us to perform a large-scale investigation of medicinal plants in what their vanadium content is concerned, and to evaluate the extraction ratio of this element onto herbal teas. The analysis of 56 species, carried out through Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), revealed an average V content of 502 µg/kg dry matter in medicinal plants. The highest V content was found in flowering aerial parts, with an average of 763 µg/kg, followed by leaves (682 µg/kg), roots (600 µg/kg), flowers (352 µg/kg) and fruits (112 µg/kg). Wild thyme (*Thymus pulegioides*) has a particular capacity to accumulate this element; other V-rich species are *Geum urbanum*, *Urtica dioica*, *Hypericum perforatum* and *Valeriana officinalis*. Given the antidiabetic effect of V, wild thyme may be interesting supplement in diabetes mellitus type II. The extraction ratio of V through decoction ranges between 13% - 85%, according to the investigated species and plant organ; V from subterranean parts is best extractable. The present research presents the first large-scale analysis of Romanian plants with regard to their vanadium content.

Keywords: vanadium, medicinal plants, ICP-MS, aqueous extraction.

INTRODUCTION

Vanadium, a transitional (p) element, is with an abundance of 100 mg/kg the 22nd most frequent element in the outer Earth's crust [9]. Although it had already been discovered in the first decade of the 19th century, first mentions of its pharmacological activities were only made about hundred years later, in 1912 [16]. During the following fifty years it was found that vanadate inhibits ATPase, and in the 1980s V was identified as an insulin-mimetic agent [10]. With the advances in the research of vanadium's biological relevance, three levels could be disentangled: nutritional (intakes of µg/day), pharmacological (mg/day) and toxicological (mg/kg food dry matter). Its essentiality for animals and man was substantiated by deficiency experiments with goats [1, 20]. Administration of V-poor food resulted in growth retardation, skeletal deformations, reduction of conception rate, increased ratio of spontaneous abortion, and reduction of life expectancy [4]. However, no V-dependent enzyme could yet be isolated from animals or man, while such enzymes are known for algae (V-dependent bromoperoxidase), fungi (V-dependent chloroperoxidase [21]), and nitrogen-fixing bacteria (V-dependent nitrogenase [12]). The evidence that V is essential for the growth of higher plants is not yet conclusive. The normative V requirement for humans was estimated to be about 10 µg/day. This small amount is satisfied by regular food intake, situated in different populations between 10-50 µg V/day [5]. The most important V sources are beer and wine, which account for 75% and 40%, respectively, of the total V intake [9, 10].

Beside its physiological importance, experimental data pointed out pharmacological implications of this element, especially in the prevention and treatment of diabetes mellitus. Vanadium compounds mimic the actions of insulin and produce strong decreases in blood glucose levels in animal models of both types of diabetes [23]. These effects are based on the increase of glucose transport through the cell membrane,

stimulation of glucose oxidation and glycogen synthesis, and increasing sensitivity to insulin. Antidiabetic activities of V also include: normalization of the lipid metabolism (through inhibition of lipolysis, stimulation of lipogenesis, decreasing triglyceride and cholesterol level in blood), normalization of protein and amino acid metabolism, normalization of thyroid hormone level, and removal of secondary symptoms of this disease (retinopathy, cardiomyopathy, nephropathy) [13]. Besides their antidiabetic properties, V derivatives have also been observed to influence processes related to mitogenic cell responses (apoptosis, proliferation, neoplastic transformation).

Nevertheless, V is considered to be a toxic element in both cationic and anionic form, although the latter type has more serious side effects. In humans, the threshold for V toxicity is near 10 mg/day, representing a thousand fold of the nutritional intake [10].

The broad spectrum of vanadium's biological implications determined us to examine its contents in the main medicinal plants used in Romanian phytomedicine, and growing wild in the Western part of the country (Banat region, Aninei Mountains). To our knowledge, this is the first large-scale investigation of the V content in Romanian plants; 56 species were researched. The research had several objectives: i) to explore the potential contribution of medicinal plants to the V intake of humans, ii) to point out species prone to the accumulation of this element, iii) to assess the V-status of the flora as a reflection of environmental pollution. We also evaluated the extraction of the element onto aqueous solutions, given that this is a widespread form medicinal plants are used under.

MATERIALS AND METHODS

Plant material. Plant samples pertaining to 56 species employed in phytotherapy were collected from various areas of the Aninei Mountains (Banat region, Romania) believed to be unpolluted (far away from

roads, kilometers outside villages or towns). Samples originated from soils with different geologic origin: limestone, granite and phyllite. The naming of sites where plant samples were collected was done according to [22]. Identification of plants was carried out by Dr. D.S. Antal from the department of Pharmaceutical Botany, University of Medicine and Pharmacy Timisoara; voucher specimens were deposited in the Herbarium of the Faculty of Pharmacy. After collection, the samples were dried at ambient temperature and deposited in cotton sacks. Previous to the determination of V content, plants were brought to powder consistency using non-metallic devices, and dry mass at 105°C was determined for each plant product through heating during two hours in an oven.

Method of analysis. The assessment of the V content in was performed by inductively coupled plasma - mass spectrometry (ICP-MS). The apparatus used for this research was ThermoElemental X Series ICP-MS (Thermo Electron, Dreiech, Germany). The

parameters of the measurement were detailed previously [11]. As a first step, a semi-quantitative analysis was performed, allowing the estimation of the concentration ranges in the digestion solutions of the plant materials. The quantitative determinations were carried based on a calibration curve ($r^2 = 0.9999$) established with ICP Multi Element Standard Solution XXI CertiPUR Merck, diluted to obtain optimal measurement range (between 0.05 – 10.00 µgV/l). Internal standard was rhodium. The limit of detection for V was 0.03 µg/l.

Accuracy of the data was verified by a parallel analysis of two certified reference materials: Peach Leaves 1547 and Oriental Tobacco Leaves CTA-OTL-1. The agreement between the concentration indicated by the producer and the one obtained experimentally within the present study certifies the fact that mineralization and determination procedures were carried out quantitatively and correctly (Table 1).

Table 1. Results of vanadium determination through ICP-MS in certified reference materials.

Peach Leaves 1547		Oriental Tobacco Leaves CTA-OTL-1	
Certified value (µg V/g)	Measured value (µg V/g)	Certified value (µg V/g)	Measured value (µg V/g)
0.37 ± 0.03	0.39	3.08 ± 0.42	3.11

Sample preparation. Weighed samples of 0.3-0.4 g dried plant material were placed in Teflon crucibles and 4 ml of nitric acid (Merck, additionally purified by subboiling), 0.25 ml hydrochloric acid (Merck, ultrapur) and 1 ml hydrogen peroxide (Merck, ultrapur) were added. Mineralization was performed in a closed system with the use of microwave energy (oven MARS 5, CEM GmbH, Kamp-Lintfort Germany), at 180°C and 11 bar pressure, for 20 minutes. The digestion solutions were transferred into volumetric flasks and made-up to 15 ml with water (nanopure); 1 ml of each solution was diluted 1:10 and analyzed by ICP-MS.

Preparation of the aqueous extract. In order to evaluate the proportion in which V passes into solution, we prepared decoctions out of 17 plants, obtained as follows: 50 ml bidistilled water were added to 2.000 g dried herbal part, and heated to boiling; the temperature of 100°C was maintained for 15 minutes. After cooling and filtration, 5 ml extract were introduced in a Teflon crucible, and treated with 3 ml nitric acid subboiled and 0.250 ml hydrochloric acid ultrapur. The solution was microwave-digested, brought to 10 ml, and analyzed by ICP-MS.

Statistic analysis was performed by Windows 2003 Excel, using the functions for the calculation standard deviation, t-test and Pearson's coefficient (r).

RESULTS

The considered trace element has been identified in all the analyzed plant products (Table 2), in concentrations ranging from 13 µg /kg dry mass (hawthorn fruits), to 76.3 mg/kg (wild thyme herb). The variation intervals for the distribution of this elements' content are:

- between 10-100 µg/kg dry mass (DM): 21.6 % of samples
- between 100-500 µg/kg DM: 49.6 %
- between 500-1000 µg/kg DM: 8.0 %
- between 1000-5000 µg/kg DM: 16.0 %
- between 5000-10 000 µg/kg DM: 2.4 %
- between 10 000-50 000 µg/kg DM: 1.6 %
- between 50 000-80 000 µg/kg DM: 0.8 %

A variation span of three orders of magnitude between measured V contents could be observed, however very high V levels of over 10 mg/kg were only present in 3 samples (wild thyme from Şaua Crestăţii mountain; wood avens, Poneasca meadow; stinging nettle, Crainic meadow). In order to estimate as correctly as possible the average V content in the researched plants, the V-content of these three samples was eliminated during calculi. The average content of the investigated elements proved to be thus 502 µg/kg DM (the three eliminated values would have erroneously increased the average to 1270 µg/kg DM, a number which does not reflect that 72% of the samples contain below 500 µg V/kg DM).

The aerial parts (herbs) of medicinal plants contain the highest V amounts (Table 2); they are followed by leaves, subterranean parts, and reproductive organs (flowers and fruits). In herbs, the V content varies between 31 µg/kg DM (horsetail from Crainic meadow) and 76300 µg/kg DM (wild thyme, Şaua Crestăţii mountain), its average being 763 µg/kg DM. Vanadium concentration which greatly surpass the average content, were determined in three further wild thyme samples, a species which displayed a remarkable capacity to accumulate this element.

Table 2. The vanadium content of aerial parts (herbs) of medicinal plants ($\mu\text{g}/\text{kg}$ dry plant).

Species	Collection site; geologic substrate	V ($\mu\text{g}/\text{kg}$)	Species	Collection site; geologic substrate	V ($\mu\text{g}/\text{kg}$)
<i>Agrimonia eupatoria</i>	Lisvar Hill ; C	99	<i>Lycopus europaeus</i>	Poneasca Mount.;G	58
<i>Agrimonia eupatoria</i>	Cioplăia Hill; C	2640	<i>Lysimachia nummularia</i>	Steierdorf; C	364
<i>Anthyllis vulneraria</i>	Iabalcea; C	98	<i>Lythrum salicaria</i>	Lișcovu; F	42
<i>Artemisia absinthium</i>	Steierdorf; C	39	<i>Lythrum salicaria</i>	Poneasca mead.;G	87
<i>Artemisia absinthium</i>	Păuleasca; C	1100	<i>Melilotus officinalis</i>	Caraș mead.; C	109
<i>Centaurium erythraea</i>	Tâlva Zănei; C	187	<i>Mentha longifolia</i>	Lisovacea; C	121
<i>Chelidonium majus</i>	Lăpușnic valley; C	110	<i>Mentha pulegium</i>	Steierdorf; C	132
<i>Chelidonium majus</i>	Gârliște; C	2260	<i>Origanum vulgare</i>	Baciului Valley; C	61
<i>Cichorium intybus</i>	to Doman; C	68	<i>Origanum vulgare</i>	Secu lake; F	500
<i>Cichorium intybus</i>	Lisovacea; C	67	<i>Origanum vulgare</i>	Livada Mare; C	880
<i>Echium vulgare</i>	Carașova; C	224	<i>Origanum vulgare</i>	Mărghitaș; C	1015
<i>Epilobium parviflora</i>	Steierdorf; C	435	<i>Origanum vulgare</i>	Poiana Scocu; C	165
<i>Epilobium parviflora</i>	Goseni; F	285	<i>Potentilla anserina</i>	Golumbu; C	437
<i>Epilobium parviflora</i>	Anina; C	496	<i>Solidago virgaurea</i>	Bido Valley; C	109
<i>Equisetum arvense</i>	Scocu; C	45	<i>Taraxacum officinale</i>	Steierdorf; C	158
<i>Equisetum arvense</i>	Crainic mead.; F	31	<i>Taraxacum officinale</i>	Lisovacea; C	435
<i>Equisetum arvense</i>	Poneasca Mount; G	157	<i>Taraxacum officinale</i>	Poneasca; G	9670
<i>Equisetum arvense</i>	Carașova; C	410	<i>Thymus pulegioides</i>	Steierdorf; C	263
<i>Galium verum</i>	Clocotici; C	47	<i>Thymus pulegioides</i>	Iabalcea; C	600
<i>Genista tinctoria</i>	Iabalcea; C	212	<i>Thymus pulegioides</i>	Poneasca mead.;G	3200
<i>Hypericum perforatum</i>	Steierdorf; C	423	<i>Thymus pulegioides</i>	Secu lake; F	298
<i>Hypericum perforatum</i>	Poneasca mead.; G	92	<i>Thymus pulegioides</i>	Poiana Beții; C	1210
<i>Hypericum perforatum</i>	Crainic; F	2060	<i>Thymus pulegioides</i>	Șaua Crestății; C	76300
<i>Hypericum perforatum</i>	Poneasca Mount.;G	1470	<i>Thymus pulegioides</i>	Cioplăia Hill ; C	6050
<i>Hypericum perforatum</i>	Gornice Hill; C	237	<i>Trifolium arvense</i>	Carașova; C	185
<i>Hypericum perforatum</i>	Cuceș; C	284	<i>Verbena officinalis</i>	Mărghitaș; C	754
<i>Hypericum perforatum</i>	to Doman; C	239	<i>Viola tricolor</i>	Bârzava mead.; F	122
<i>Leonurus cardiaca</i>	Mărghitaș; C	2080	<i>Viola tricolor</i>	Carașova; C	318
<i>Leonurus cardiaca</i>	Caraș mead. ; C	163	<i>Viola tricolor</i>	Steierdorf; C	89
Average V content: 763 + 1569 $\mu\text{g}/\text{kg}$					

Note. At the calculation of the average Vanadium content, the value of 76300 (*Thymus pulegioides*, Șaua Crestății) was not included. C: limestone, F: phyllite, G: granite.

Table 3. The vanadium content of leaves of medicinal plants ($\mu\text{g}/\text{kg}$ dry plant).

Species	Collection site; geologic substrate	V ($\mu\text{g}/\text{kg}$)	Species	Collection site; geologic substrate	V ($\mu\text{g}/\text{kg}$)
<i>Allium ursinum</i>	Piatra Albă; C	43	<i>Plantago lanceolata</i>	Lisovacea; C	5630
<i>Allium ursinum</i>	Lisvar Hill; C	542	<i>Plantago lanceolata</i>	Steierdorf; C	565
<i>Allium ursinum</i>	Poneasca mead.; G	621	<i>Rubus idaeus</i>	Poneasca Mount.; G	138
<i>Allium ursinum</i>	Poiana Florii; C	1890	<i>Rubus idaeus</i>	Crainic mead.; F	1958
<i>Allium ursinum</i>	Steierdorf; C	1880	<i>Tussilago farfara</i>	Poneasca Mount.; G	166
<i>Althaea officinalis</i>	Caraș mead. ;C	246	<i>Urtica dioica</i>	Păuleasca; C	133
<i>Betula pendula</i>	Sekul; C	56	<i>Urtica dioica</i>	Poneasca Mount.; G	400
<i>Betula pendula</i>	Steierdorf; C	183	<i>Urtica dioica</i>	Crainic mead.; F	14500
<i>Betula pendula</i>	Văliug lake; F	72	<i>Urtica dioica</i>	Lisovacea mead.; C	1140
<i>Betula pendula</i>	Visochii Hill; C	114	<i>Urtica dioica</i>	Caraș mead.; C	345
<i>Corylus avellana</i>	Nermet; C	30	<i>Vaccinium myrtillus</i>	Văliug; F	85
<i>Corylus avellana</i>	Crainic mead.; F	900	<i>Viscum album</i>	Steierdorf; C	83
<i>Fragaria vesca</i>	Iabalcea; C	217	<i>Crataegus monogyna</i>	Lisovacea; C	383
<i>Fragaria vesca</i>	Sekul; C	331	<i>Crataegus monogyna</i>	Poneasca mead.;G	213
<i>Fragaria vesca</i>	Steierdorf; C	1760	<i>Crataegus monogyna</i>	Sekul; C	73
<i>Fraxinus excelsior</i>	Padina Seacă; C	26	<i>Crataegus monogyna</i>	Iabalcea; C	1210
<i>Fraxinus excelsior</i>	Ogașul Ursului; C	1820	<i>Crataegus monogyna</i>	Steierdorf; C	328
<i>Plantago lanceolata</i>	Iabalcea; C	123	<i>Malva sylvestris</i>	Carașova ; C	157
Average V content: 682 + 1062 $\mu\text{g}/\text{kg}$					

Notes. In case of *Crataegus monogyna* and *Malva sylvestris*, the samples include both flowers and leaves (as it is used in phytotherapy). At the calculation of the average Vanadium content, the value 14500 (*Urtica dioica*, Crainic) was not included.

Table 4. The vanadium content of subterranean parts of medicinal plants ($\mu\text{g}/\text{kg}$ dry plant).

Species	Collection site; geologic substrate	V ($\mu\text{g}/\text{kg}$)	Species	Collection site; geologic substrate	V ($\mu\text{g}/\text{kg}$)
<i>Angelica archangelica</i>	Văliug; F	114	<i>Primula officinalis</i>	Lisvar Hill; C	448
<i>Cichorium intybus</i>	Lisovacea; C	453	<i>Saponaria officinalis</i>	Steierdorf; C	616
<i>Geum urbanum</i>	Răcăjdianu; C	225	<i>Symphytum officinale</i>	Clocitoare; C	717
<i>Geum urbanum</i>	Poneasca mead.;G	28700	<i>Valeriana officinalis</i>	Miniș springs ; C	72
<i>Geum urbanum</i>	Lișcovu;F	230	<i>Valeriana officinalis</i>	Crainic; F	1846
<i>Ononis spinosa</i>	Carașova; C	311	<i>Valeriana officinalis</i>	Păuleasca; C	1426
<i>Primula officinalis</i>	Steierdorf; C	742	-	-	-
Average V content: 600 + 538 $\mu\text{g}/\text{kg}$					

Note. At the calculation of the average Vanadium content, the value of 28700 (*Geum urbanum*, Lișcovu) was not included. C: limestone, F: phyllite, G: granite.

Leaves are also relatively high in the investigated element, with an average content of 682 µg/kg DM (Table 3). Their V concentration varies between 26-14500 µg/kg DM, smallest in case of ash leaves from Padina Seacă, and highest in nettle leaves from Crainic meadow. Elevated V contents were determined for a second sample of nettle leaves, as well as for two samples of ramsons.

Subterranean parts contain, with an average of 600 µg V/kg DM (Table 4), a lower V content than the

aforementioned plant organs (difference not significant, $p > 0.05$). Lowest values were measured for valerian roots from Miniş springs, while wood avens (Poneasca meadow) contains two orders of magnitude more V than the average content of the element if all samples. Elevated amounts surpassing 1400 µg/kg DM were as well determined in case of two valerian samples (Crainic and Păuleasca meadows).

Table 5. The vanadium content of flowers and inflorescences of medicinal plants (µg/kg dry plant).

Species	Collection site; geologic substrate	V (µg/kg)	Species	Collection site; geologic substrate	V (µg/kg)
<i>Achillea millefolium</i>	Caraş mead.; C	228	<i>Sambucus nigra</i>	Poneasca Mount.; G	177
<i>Achillea millefolium</i>	Poneasca mead.; G	151	<i>Sambucus nigra</i>	Răcăjdianu; C	305
<i>Achillea millefolium</i>	Bârzava mead.; F	94	<i>Tilia cordata</i>	Poneasca Mount.G	25
<i>Achillea millefolium</i>	Lisovacea; C	480	<i>Tilia cordata</i>	Lisvar; C	1380
<i>Achillea millefolium</i>	Steierdorf; C	453	<i>Tilia tomentosa</i>	Valea Baciului; C	157
<i>Achillea millefolium</i>	to Doman; C	270	<i>Tilia tomentosa</i>	Secu lake; F	168
<i>Filipendula ulmaria</i>	Bârzava mead.; F	1110	<i>Verbascum phlomoides</i>	Mărghitaş; C	131
<i>Sambucus nigra</i>	Cârmeala; C	148	-	-	-
Average V content: 352 ± 386 µg/kg					

C: limestone, F: phyllite, G: granite.

Inflorescences and flowers display an average V content of 352 µg/kg DM (Table 5). Linden flowers with bracts from the Lisvar Hill and meadowsweet inflorescences from Bârzava meadow are the only samples of this type containing a V content larger than

1000 µg V/kg DM, the other samples are poor in the considered element. Fruits do not accumulate V; their average content is as low as 112 µg V/kg DM (Table 6).

Table 6. The vanadium content of fruits of medicinal plants (µg/kg dry plant).

Species	Collection site; geologic substrate	V (µg/kg)
<i>Cerasus avium (stipites)</i>	Nermet ; C	61
<i>Crataegus monogyna (fructus)</i>	Steierdorf ; C	13
<i>Juniperus communis (baccae)</i>	Poiana Mărghitaşu Mare ; C	261
Average V content: 112 ± 131 µg/kg		

C: limestone, F: phyllite, G: granite.

DISCUSSIONS

Although there is no proof regarding its essentiality to higher plants, V is easily taken up by them [10]. Its content is not regulated homeostatically, as such its content in plants reflects the V status of the soil. Vanadium is mostly concentrated in mafic rocks (200-250 mg V/kg), while granites and limestones contain lowest concentrations: 30-100 mg/kg, and 10-45 mg/kg, respectively [17]. During weathering, vanadium is adsorbed or incorporated into mineral structures of clay and iron oxides. The average V content of soils world-wide has been calculated to vary from 18-115 mg/kg [9]. The V ionic species with the highest importance is vanadyl cation (VO^{2+}); it predominates at acid pH values and is more readily taken up by plants than anions VO_3^- and HVO_4^{2-} , which are more frequent in neutral or alkaline soils [14]. In higher plants, V is biotransformed to V^{4+} [19].

The V content of the analyzed plants varies in large limits, from 13 to 76300 µg/kg DM, with a mean value of 502 µg/kg DM. Comparing these values with those obtained by other authors, it can be stated that the medicinal plants from the investigated area contain much higher amounts of V than other investigated species. In the scientific literature there are relatively

few large-scale researches on the V content of plants and animals, as well as on its importance for humans and fauna [2-4, 6-10]. Among plants, the highest V concentrations (in µg/kg DM) were determined in spices: parsley (407), dill (540), pepper (669), marjoram (2356). Fruits and grains contain generally little V: cherries (9), tomatoes (13), oranges (15), apple (19), strawberries (38), the same applies for vegetables: cabbage (20), peas (23), onion (30), broccoli (42), carrots (50), turnips (65), spinach (279), salad (377). In these researches, the average V content in fruits was 23; in legumes 41 and in spices 218 µg/kg DM. A much higher amount was found in eatable mushrooms (625). In fact, some fungi seem to be prone to accumulate extremely high amounts of V; the sporifer body of fly agaric (*Amanita muscaria*) can store up to 345 mg V/kg DM (even if the soil contains only 6.7 mg V/kg) [18]. The vanadium-containing compound found in mushrooms was named amavadine; its physiological function is not yet known.

Of the different plant parts that were researched, leaves and aerial parts (herbs) were significantly richer in V than reproductive organs. This observation is consistent with data in the literature [10].

In the present study of medicinal plants, wild thyme (*Thymus pulegioides*) demonstrated a clear capacity of

V accumulation; four of seven analyzed samples contained with at least one order of magnitude more V than the average concentration of all analyzed samples. Given the antidiabetic effect of V, wild thyme may be interesting supplement in diabetes mellitus type II, especially in association with other plants known to have a hypoglycemic effect, like *Momordica charantia* or *Vaccinium myrtillus* [15]. Other species accumulating high V amounts, according to the site of collection, were: *Geum urbanum*, *Urtica dioica*, *Hypericum perforatum* and *Valeriana officinalis*.

A correlation between the V content of plants and the lithologic substrate could not be established in the current study; for the same species collected for several substrates (lime, granite, phyllite) no significant difference could be pointed out. The literature mentions that plants grown on granite weathering soils are richer in the considered element than those vegetating on lime and phyllite [2, 5]. The absence of similar observations in the current study is probably due to very high local variations of V content in the substrate; for a given species we measured frequently differences of 1-2 orders of magnitude even when the substrate was the same rock type. Additionally, the assessment of the wild flora did not allow the unitary collection of the same species from the same site.

However, the present study could repeatedly point out unusually high V concentrations in several species gathered from the sites: Steierdorf area, Poneasca meadow and Crainic meadow. These observations can be linked to anthropogenous activities. It is known that industrial processing of certain mineral ores (ore smelters, cement, and phosphate rock factories) and burning of coal and oil increases the deposition of vanadium residues in soils. Combustion on V-rich fuels is an especially serious source of V in soils [17]. Anthropogenic V emissions are indicated even years after closure of the V source, as it was demonstrated in the vicinity of various factories [10]. The area around Steierdorf-Anina-Crivina was for many decades an

industrial site; the Crainic meadow (situated North-West of Văliug) is close to Reșița, one of the most important sites of metallurgic industry in Romania. In the third area, Poneasca valley, hosts a dam and was decades ago an important passage road for industrial purposes. Presently, even if in these sites the anthropogenic activity has dramatically decreased, the soil and the vegetation obviously show the heritage of a polluting past. The level of V-content of the plants collected here bears much resemblance to the ones measured by researchers in other polluted areas. Still, it must be stated that the V concentration in the analyzed medicinal plants poses no threats to human health, as it is very far from a toxic level (of about 10 mg/day).

Taking into account the popularity that aqueous extracts enjoy as pharmaceutical form in the phytotherapy of our country, we evaluated the proportion in which medicinal plants transmit their V charge to teas. Results indicate a large variation of the extraction yield, according to the species subjected to decoction (Table 7). The easiest passage into water (>80%) is specific to V from roots (chicory, restharrow) while V from herbs (chicory, dandelion, horsetail) can be extracted in the lowest proportion. These variations can be explained by each plant's different chemical composition, where saponins, tannins, mucilages, flavonoids etc. create specific pH values and redox potentials, or involve V in complex combinations with low solubility. A correlation between the facility of the extraction and the presence of a certain type of active principle could however not be achieved in the present study. The extraction ratio of V through decoction is medium, being mostly situated between 35-55%. Analyzing the plant organ from which the aqueous extracts were prepared, it can be noted that V can be best extracted from roots and rhizomes, suggesting that in these plant parts V can be found as compounds with high solubility in boiling water.

Table 7. The vanadium content of some aqueous extracts obtained from medicinal plants.

Species – plant part	V (µg/kg)		extraction yield (%)
	in plant product	extracted through decoction*	
<i>Cichorium intybus</i> (chicory) - roots	453	385	84.9
<i>Ononis spinosa</i> (restharrow) - roots	311	250	80.4
<i>Crataegus monogyna</i> (hawthorn) - leaves+flowers	213	150	70.4
<i>Sambucus nigra</i> (elder) - flowers	148	82	55.4
<i>Primula officinalis</i> (cowslip) - rhizomes	448	240	53.6
<i>Valeriana officinalis</i> (valerian) - rhizomes	1426	760	53.3
<i>Epilobium parviflorum</i> (willow herb) - herb	435	230	52.8
<i>Althaea officinalis</i> (marshmallow) - leaves	246	125	50.8
<i>Leonurus cardiaca</i> (motherwort) - herb	2080	985	47.4
<i>Thymus pulegioides</i> (wild thyme) - herb	263	112	42.6
<i>Viola tricolor</i> (wild pansy) - herb	122	51	41.8
<i>Filipendula ulmaria</i> (meadowsweet) - flowers	1110	421	37.9
<i>Hypericum perforatum</i> (St John's wort) – herb**	92	33	35.9
<i>Achillea millefolium</i> (yarrow) - flowers	228	79	34.6
<i>Equisetum arvense</i> (horsetail) - herb	45	11	24.4
<i>Taraxacum officinale</i> (dandelion) - herb	158	35	22.1
<i>Cichorium intybus</i> (chicory) - herb	68	9	13.2

* Values represent the extractable V amount through decoction (15 minutes) from the indicated vegetal product; preparations were made of 4% plant material in bidistilled water.

** Herbs (*herba*) represent the flowering aerial parts of medicinal plants.

Future studies are necessary for the analysis of the V-status of the Romanian flora; the present study indicates that in areas with an intense industrial background in the past or the present the V-content may be higher with one or two orders of magnitude. Establishing the relevance of this situation for grazing animals and the food chain in general will be noteworthy.

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