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Review

Determination of vanadium species in environmental samples

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Abstract

The distribution of vanadium between different oxidation states plays an important role in its environmental chemistry. As its two most commons forms, vanadium(IV) and vanadium(V) have different toxicity, speciation analysis of this element is necessary for environmental and biological samples. This paper presents recent research on the determination of vanadium species. Some important problems concerning stability of vanadium forms and proposed separation techniques are discussed.

Keywords: Vanadium; Speciation; Environmental samples

1. Introduction

Vanadium is widely distributed in the earth's crust but in low abundance. Vanadium at trace amounts represents an essential element for normal cell growth, but can be toxic when present at higher concentration. It can exist in many oxidation states as well as the oxyanions and oxycations, which are formed in the solutions. The multiple oxidation states, ready hydrolysis and polymerization confer a level of complexity to the chemistry of vanadium well above that of many metals. Vanadium dissolves in natural waters in natural waters as V(IV) and V(V). Both species have different nutritional and toxic properties. Tests carried out on yeast cells have proved that the vanadate ion is strong inhibitor of the enzyme Na and K-ATPase, while V(IV) appeared to be a weaker inhibitor [1]. Therefore, an accurate determination of vanadium species on different oxidation states is more important than the total metal content when a correct evaluation of human exposure and related risks are required.

Vanadium is used widely in industrial processes including the production of special steels, temperature-resistant alloys, in glass industry, in the manufacture of pigments and paints, for lining arc welding electrodes and as catalyst. Its use with non-ferrous metals is of particular importance in the atomic energy industry, air-craft construction and space technology. Vanadium compounds released in large quantities, mainly by burning fossil fuels and also from various industrial processes, are precipitated on the soil drained by rain and groundwater and may be directly adsorbed by plants.

The mean vanadium air concentrations of $0.1\,ng\,m^{-3}$ (the eastern Pacific ocean) to $0.72\,ng\,m^{-3}$ (rural northwest Canada) can be regarded as natural background levels. Typical concentrations in urban air vary over a wide range of about $0.25–300\,ng\,m^{-3}$, with markedly higher concentrations during the winter months compared to summer season.

Vanadium(V), which exists as VO_2^+ in acid media and VO_4^{3-} in alkaline solution, is expected to be the prevailing form in waters exposed to the atmospheric oxygen. Vanadium(IV), as the vanadyl cation VO^{2+}, may be present in reducing environment. It is stable in acidic solution below pH 2, but is oxidized to the pentavalent state by atmospheric oxygen at higher pH values. It complicates the determination of V(IV) in natural samples with pH above 2, since stabilization of this form is necessary. The coexistence of these species depends on the pH, redox potential and the ionic strength of the system [2–5].

The vanadium contents of soils are related to those of the parent rocks from which they are formed and range from 10 to $220\,mg\,kg^{-1}$, the highest concentrations being found in shales and clays [6]. The concentration of vanadium in soil is about 10 times higher that in plants. The aerial por-

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tions of plants have the lowest content, while the roots have nearly the same levels as the soil in which the plants are grown.

Vanadium is present in most cells of plants and animals. Intercellularly, it tends to be present as vanadyl, bound to glutathione, catecholamines or other small peptides [7]. In plasma vanadium is usually found bound to transferring and in red cells to hemoglobin. In spite of being a nutritional element, vanadium is not accumulated by the biota; the only organisms known to bioaccumulate it to any significant degree being some mushrooms, tunicates and sea squirts. The occurrence of vanadium in sea squirts is supposed to be one of the main sources of this metal contents in crude oil and oil shales, which can contain vanadium in the form of vanadyl porphyrins [8] up to 4%.

Like molybdenum, vanadium assumes an exceptional position among the biometals in that both its anionic and cationic forms can participate in biological processes. In its anionic forms, vanadates, it strongly resembles phosphates, but in its cationic forms—mainly as VO^{2+}, and in certain cases as vanadium(III)—it behaves like typical transition metal ion, which competes with others in coordination to biogenic ligands and compounds. Among vanadium compounds, tetra- and pentavalent forms are the most studied because both are capable of reacting with genetic machinery; they can interact with the phosphate groups and the sugar alcohol groups of nucleotides to form complexes that inhibit or stimulate the activity of many DNA or RNA enzymes. Vanadium and its compounds are generally known to have insulin-mimetic activity, both in vitro and in vivo and may become useful in the future treatment of diabetes [9,10]. However, questions regarding the possible toxicity of these compounds, in particular following prolonged administration for the treatment of diabetes, are thus a serious concern. Vanadium is know to be more toxic when inhaled and relatively less when ingested.

Speciation analysis of trace heavy metals in environmental samples concerns their presence in various oxidation states, in different protonated and polymerized forms, in complexes with various ligands as well as various of homogeneous and heterogeneous association with constituents of natural samples. For vanadium in natural waters, most speciation studies deal with the determination of the total amount of dissolved V(IV) and V(V), owing to the different interactions of these two forms with living organism. The aim of this review was to cover general aspects of vanadium speciation analysis and to highlight the most important ideas, such as stability of vanadium species and separation/preconcentration techniques.

2. Stability of vanadium species

Stock solution containing a given metal of known oxidation state and chemical composition at appropriate concentration is an important requirement for speciation analysis. Commercially available standard solutions of metals could be used for this purpose or this solution can be prepared by dissolving pure metal in concentrated acid. Dissolution of vanadium is usually carried out with pure concentrated nitric acid or HNO_3–H_2O_2 mixture. Gàspàr and Posta [11] found that pure vanadium(V) could only be achieved when the dissolution was carried out with pure HNO_3 without hydrogen peroxide. The small amount of H_2O_2 (1–2 ml) results in the presence of V(IV) in the range of 10–20%. When 10 ml of H_2O_2 was added to HNO_3 and the mixture was heated the ratio of V(IV) to total metal content was about 1/3.

Generally, the storage of the acidified sample solution (pH < 2) is recommended due to the possibility of adsorption on the container walls. However, acidification could modify the chemical forms of the analyte or disturb the equilibrium between the various species present. It was found [12] that solution of vanadium(V), prepared in deionised water, was stable in the pH range of 2–9. By contrast, solution of V(IV) was stable only at pH 2. At pH 5.6 was gradually oxidized and fully transformed into V(V) within 3 min at pH 9. The oxidation rates of vanadium(IV) added to natural lake water (pH 7.7) and seawater (pH 7.9) were slower; half-lives of about 15 and 7 min, respectively, were observed. These results indicated that vanadium could not exist as V(IV) in neutral and/or basic natural waters [12–14]. However, there have been several papers describing the existence of V(IV) in natural waters [15,16]. Our studies showed that oxidation of V(IV) added to lake water was slower when a sample (at natural pH 7.1) was degassed before determination (Fig. 1). Vanadium(V) was gradually reduced to V(IV) both in lake water and seawater acidified to pH 2, although this reaction was not observed in deionised water at the same pH [12]. These results are consistent with those obtained by Nukatsuka et al. [14], but the half live of V(V) found by them was shorter. Redox studies of vanadium species suggest that

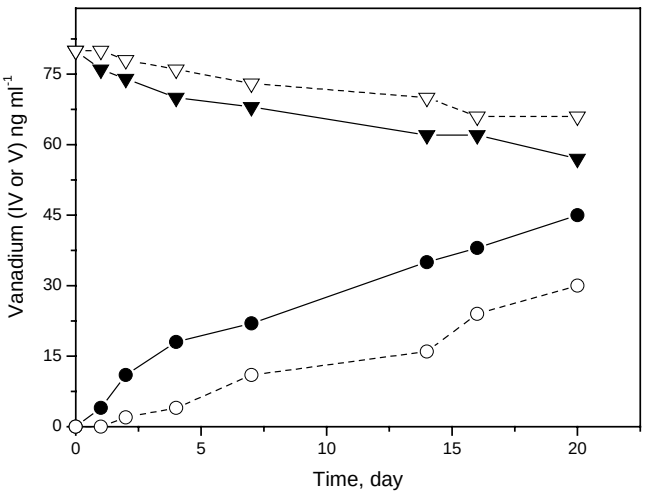

Fig. 1. Behavior of vanadium species in spiking lake water (pH 7.1) after addition of V(IV) (▼, ▽) or V(V) (●, ○) (degassing time: 20 min, temperature: 20 °C).

natural water samples should be analyzed immediately after sampling without acidification.

Wang and Jang [4] determined the content of vanadium species in some water certified reference materials (prepared by Institute for National Measurement Standards NRC) using liquid chromatography with ICP-MS detection (Fig. 2). These materials have only the certified values for total dissolved vanadium. In the nearshore seawater reference material CASS-3 the ratio of V(IV) to V(V) was 9/5, while in the riverine water reference sample SLRS-3 only vanadium(IV) was found at concentration of $(0.38 \pm 0.05)\,\mathrm{ng\,ml^{-1}}$. The samples, after collection and filtration, were acidified to pH 1.6 with ultrapure nitric acid, thus according to the previous papers [12,14], vanadium(V) could be reduced.

In biological samples the vanadium-protein binding is also very sensitive to changes in its environment. Even small changes from the original pH value to a more acidic medium could disrupt the binding of vanadium(V) to transferrin or increase the percentage of vanadium(V) bound to albumin [16]. Thus, for the speciation of vanadium in serum or other biological fluids it is necessary to adhere as close as possible to the physiological pH value of the fluid.

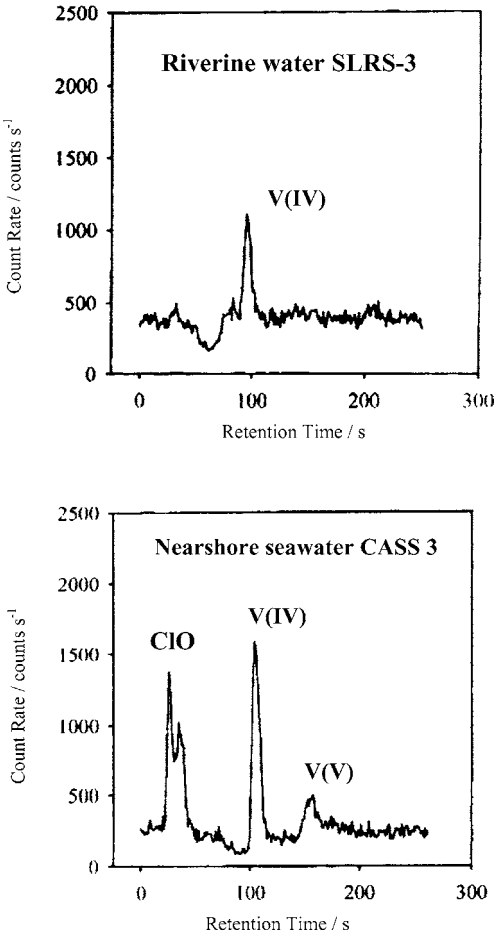

Fig. 2. Chromatograms of riverine water SLRS-3 and nearshore seawater CASS-3 reference materials for trace metals. (Reprinted from ref. [4] with permission from Elsevier.)

3. Preconcentration/separation techniques

To determine trace content of vanadium a preconcentration technique is frequently required before its determination. Many such techniques have been proposed, including coprecipitation, solvent extraction and ion exchange. However, for separation of vanadium species, mainly V(IV) and V(V), liquid as well as solid phase extractions mainly have been applied. Some of the proposed procedures collected both vanadium species together or only one form. The other species was then determined after its conversion (reduction or oxidation) or by the difference after total vanadium measurement. Simultaneous separation and subsequent determination of the two oxidation states of this metal would lead to more reliable results, particularly when the ratio of V(IV)/V(V) or V(V)/V(IV) is large.

The extraction procedures for the separation of V(IV) and V(V) using *N*-cinnamoyl-*N*-(2,3-xylyl)hydroxylamine and toluene [17] as well as 2-hydroxyacetophenone oxime and CH_3Cl [18] at different pH values have been proposed. Garazov et al. [19] developed the method based on the formation ad subsequent extraction into chloroform of the ternary ion association complex of V(V) with pyridylazo resorcinol and iodo-nitro-tetrazolium chloride. The formation of the ternary ion-association complex vanadium-5,7-dichlorooxime-rhodamine 6G followed by extraction with toluene was applied for the separation of vanadium(IV) [20] and vanadium(V) [21]. Moreover, in both papers similar pH ranges and wavelengths for spectrophotometric detection of vanadium were proposed.

Solid phase extraction is now widely used preconcentration/separation method in analytical chemistry. Anchoring the active site to a solid support in a polymer matrix provides an immobilized active surface capable of selective and quantitative separation of different species from aqueous solution The solid phase extraction approach has some advantages in comparison with liquid extraction, e.g. higher preconcentration factor, greater efficiency and handling simplicity [22]. The application of chelating resin became very popular with the introduction of various chelating groups, like imidazole 4,5-dicarboxylic acid [23], dicyandiamine [24], aminothiourea [25], 3-aminopropyltriethoxysilane [26] and acylphenylhydrazine [27] for preconcentration and separation of vanadium(V). Moreover, the suitable chelating ligands were immobilized on the surface of the polymeric supports [12,17,28,29]. In these schemes only one vanadium form was enriched on the microcolumn.

For selective preconcentration and separation of vanadium species, several conventional ion-exchange resins, functionalised cellulose sorbents and chelating resin were examined [30]. Cellulose sorbent with phosphonic acid exchange groups (Cellex P) was found to be superior for enrichment of both vanadium(IV) and vanadium(V). They could be simultaneously eluted using EDTA solution. An enrichment factor of 150 was obtained. The speciation

study of vanadium has been tested using CDTA added to the sample or as a selective eluent for V(IV).

A simple and rapid two-step method for the separation and determination of V(IV)) and V(V) using Sephadex DEAE A-25 with Eriochrome Cyanide R (ECR) was proposed by Bosque-Sendra et al. [31]. In the first step, vanadium(IV) was retained on the solid support as V(IV)-ECR complex and then determined by solid phase spectrometry. Subsequently, in the second stage, ascorbic acid and ECR were added to the resulting solution and the content of V(V), thus transforming into V(IV)-ECR complex, was measured (Fig. 3). Also complexation of vanadium species with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol [32] and dithizone or 8-hydroxyquinoline (8-HQ) [33] followed the sorption onto a C_{18} microcolumn or XAD-7 resin were applied. The quantitative retention of V(V) on a microcolumn packed with 8-HQ immobilized on silica gel requires the application of much lower flow rate (0.3–1 ml min^{-1}) in comparison to sorption of vanadium–8HQ complex (~5 ml min^{-1}). Moreover, stronger acid solution in greater volume (8 ml of 2 mol l^{-1} HNO_3 + 0.5 ml l^{-1} HCl) is required for complete recovery of the sorbed vanadium on this resin.

The Gibbs–Donnan model was used to predict conditions for separation of vanadium species applying very popular chelating resin Chelex 100 containing the iminodiacetate groups [34]. The method consists of sorbing both V(IV) and V(V) at pH about 4.5 and stripping V(V) at basic conditions (pH 10), and then V(IV) at acidic media (pH 0.8). However, the equilibrium time was 2 h. It was observed that that oxidation state of vanadium(IV) is highly stabilized one sorbed on Chelex 100, so that after sorption the procedure could be carried out in air.

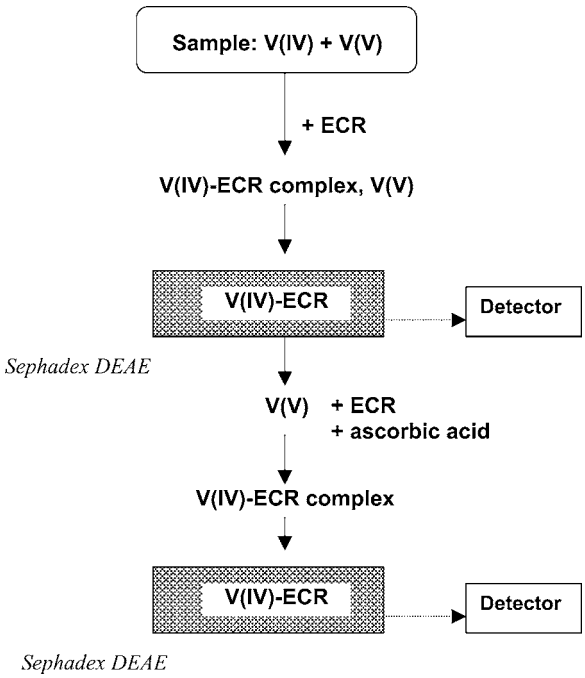

Fig. 3. Diagram for the separation and determination of V(IV) and V(V) in two steps using Eriochrome Cyanide R (ECR) and solid phase spectrometry. (Reprinted from ref. [31] with permission from Springer-Verlag.)

4. Chromatographic and electrophoretic separation

The predominant trend in the proposed methods for vanadium speciation is the use of liquid chromatography (LC) and capillary electrophoresis (CE). Coupled methods combining LC with AAS detection [11], atomic emission spectrometry [15], inductively coupled plasma mass spectrometry [4,35] and visible spectrophotometry with post-column derivatisation [13,29,36,37] have been developed. Recently, chelation ion chromatography has received considerable attention for the determination of trace metals in complex sample matrices [38,39]. The main principle of this approach is based on the formation of metal complexes on the surface of a chelating stationary phase and separation occurring as a result of differences in conditional stability constants between metal complexes. A high efficiency chelating stationary phases can be formed by chemical bonding, impregnation or dynamic loading, either on polystyrene or silica based substrates. Cowan et al. [29] dynamically modified neutral polystyrene resin with dipicolinic acid for the separation of V(V), while Huang et al. [35] tested two kind of synthesized chelating stationary phases, bis(2-aminoethylthio) methylated resin and γ-aminobutyro hydroxamate resin, for the determination of vanadium species spiked in artificial seawater samples.

Capillary electrophoresis is an alternative method to liquid chromatography for the separation of vanadium species due to its high efficiency and rapid separation. Usually for modification of metal ions mobility, complexation with suitable ligands is used. Two main approached are applied in speciation analysis of vanadium. One is on-capillary complexation, in which a soluble ligand is added to the running electrolyte and weak complexes are rapidly formed. Vanadium species were chelated with aminopolycarboxylic acids, such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentacetic acid (DTPA), nitrilotriacetic acid (NTA) and *N*-2-hydroxyethylethylendiaminetriacetic acid (HEDTA), to form anionic complexes which were separated by CE with UV detection [40,41]. Another approach is pre-capillary complexation, in which the excess of a strong ligand is added to the sample to form complexes before CE analysis. Pre-capillary derivatisation was carried out also with aminocarboxylic acids [42] as well with 4-(2-pyridylazo)resorcinol (PAR) [42,43]. Despite many advantages with respect to simplicity and selectivity, this approach suffers from some disadvantages such as incomplete complexation and time-consuming processing of real samples. Moreover, less stable vanadium(V) chelates were partially decomposed in the capillary during the separation process [40]. It is possible to use aminocarboxylic acids as both ligand and the electrolyte for on-capillary complex-

ation. New reagents that can form kinetically stable complexes with vanadium species are being searched to improve the sensitivity of the pre-capillary CE method. The application of the anionic ternary complexes V(V)–PAR–H_2O_2 and V(V)–PAR–tartaric acid provided better results because of the high absorptivity and stability [43,44]. Recently, a Mo(VI)–P(V) reagent has been proposed for pre-capillary complex formation [45]. In this method, vanadium oxoanions were incorporated in the peripheral structure of the molybdophosphate complex forming stable kinetically species with different mobilities. Since both vanadium species have high molar absorptivity in the UV region, the Mo(VI)–P(V) reagent method brought an increase in the sensitivity by an order of magnitude.

5. Analytical methods for vanadium determination

The content of vanadium in natural samples is very low in the range of a few $\mu g\,l^{-1}$, hence powerful analytical methods are required. Only a few of them show sufficient sensitivity, such as neutron activation analysis (NAA), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and mass spectrometry (ICP-MS) as well as some UV–vis spectrophotometric methods.

Most of the direct spectrophotometric methods for determination of vanadium in environmental samples lack the necessary sensitivity and/or selectivity without sample pretreatment [46–48]. The use of solid phase spectrometry has produced a higher sensitivity and a lower detection limit with respect to solution methods [31,49]. Kinetic methods using vanadium-catalyzed redox reactions are simple and inexpensive. They are based on its catalysis of organic compounds oxidation with bromate, persulfate or chlorate [50–52]. Highly selective and sensitive methods for determination of V(IV) in the presence of large excess of vanadium(V) has been reported by Safavi et al. [52]. This method, based on the catalytic effect of V(IV) on the oxidation of aniline blue by bromate, has very wide linear range (5–1200 $\mu g\,l^{-1}$) with the detection limit of 2 $\mu g\,l^{-1}$. Application of flow injection analysis for the catalytic methods, when the reaction time should be strictly controlled, improved their accuracy [53,54].

Also flow injection analysis methodology with chemiluminescence detection has been proposed for successive determination of trace amounts of V(IV) and total vanadium [54]. The method utilized the catalytic effect of vanadium(IV) on the oxidation of purpurogallin by periodate to produce light emission. Vanadium(V) can be determined after on-line reduction using silver-reducing column. The detection limit of 50 $\mu g\,l^{-1}$ was obtained with the sampling rate of about 50 h^{-1}.

ETAAS has been used on a routine basis for the determination of trace amounts of vanadium. Some problems, mainly concerned with tailing of the absorbance signal, carbide formation and acid interferences have been encountered [56–60]. It was found that the presence of mineral acids improved the signal profile of vanadium, smoothing the tailing effect [60]. The enhancement of the signal (peak area) was more pronounced with hydrochloric than with nitric acid. The best results for vanadium determination were obtained using an untreated graphite tube [59]. The coated tubes not only gave poor sensitivity but also increased the memory effect. A number of matrix modifiers was testing for vanadium determination by ETAAS in different kind of samples [59,61]. Usually, the position of the element peak in relation to that of the matrix was taken for comparison and the slopes of the calibration curves were used as selection criteria. Su and Huang [59] found that magnesium nitrate gave the lowest detection limit (0.42 $\mu g\,l^{-1}$) for vanadium determination in seawater samples, while for biological materials a mixture of citric acid, palladium nitrate, magnesium nitrate and diammonium-hydrogen phosphate was sufficient [61].

ICP-MS detection offered better sensitivity for determination of vanadium than ETAAS [62–69]. However, the diatomic ions $^{35}Cl^{16}O^+$ and $^{34}S^{16}OH^+$ (arising from the sample matrix) overlapped with the most abundant isotope of vanadium at $m/z = 51$. Moreover, the high content of organic components may cause problems with torch clogging and carbon deposition. Cryogenic desolvation reduced both the solvent load on the plasma and the abundance of oxide ions by removing water vapor [62]. Chloride can be also removed as hydrogen chloride by the same method. By coupling electrothermal vaporization (ETV) with ICP-MS, most of the solvent and a large part of the matrix components can be removed prior to introduction of the analyte species into plasma by means of chemical modification and temperature programming of the vaporization cell [63,65,69]. ETV–ICP-MS offered about an order of magnitude lower detection limit (0.08–0.3 $\mu g\,l^{-1}$) than pneumatic nebulization ICP-MS [63]. The best solution to isobaric interference problem was to analyze the samples under high mass spectral resolution ICP-MS [68,70]. At a resolution of $m/\Delta m = 3000$, the signal for ClO^+ was readily resolved from that for $^{51}V^+$, if only trace amount of this analyte were to be determined. However, only a few laboratories use this technique for routine analyses, due to complexity and high cost. The dynamic reaction cell (DCR) technique has proved to be an effective method for elimination of spectroscopic interferences [66,68]. Liu and Jiang [66], using NH_3 as the reaction cell gas reduced the signal to noise ratio approximately by four orders of magnitude. The detection limit for vanadium determination in their work (0.006 $\mu g\,l^{-1}$) was comparable to the high resolution ICP-MS results [64]. DCR–ICP-MS approach was routinely applied in the speciation analysis of various vanadium complexes under study for their insulin-like properties [71]. It enabled to detect vanadium on-line in serum after size exclusion chromatography in the presence of a buffer at physiological salinity (0.15 M NaCl) with a detection limit of 40 $ng\,l^{-1}$.

Table 1
Analytical methods for vanadium speciation

Separation method	Reagent/sorbent	Solvent/eluent	Detection method (range or detection limit)	Reference
Solvent extraction	*N*-Cinnamoyl-*N*-(2,3-xylyl)hydroxylamine	Toluene; pH 2—V(V), pH 5.5—V(IV)	555 nm (0.1–1 $\mu g\,l^{-1}$)	[17]
	2-Hydroxyacetophenone	Chloroform	350 nm—total vanadium, 400 nm—V(V) (1–6 $\mu g\,l^{-1}$)	[18]
	Pyridylazo resorcinol + iodo-nitro-tetrazolium chloride	Chloroform	V(V) at 560 nm, V(IV)—after oxidation by $NaBrO_3$	[19]
Solid phase extraction	Cellex P	V(IV)—0.3 $mol\,l^{-1}$ CDTA, V(V)—0.2 $mol\,l^{-1}$ EDTA	ETAAS	[30]
	Sephadex DEAE + Eriochrome Cyanide R	V(IV)—in eluate, V(V)—after reduction by ascorbic acid	595 nm (1.5 $\mu g\,l^{-1}$)	[31]
	5-Br-PADAP + CDTA sorption on Amberlite XAD-7	V(IV)—in eluate, V(V)—25% (v/v) HNO_3	ICP-AES (19 $ng\,l^{-1}$)	[32]
	Chelex 100	V(V)—0.001 $mol\,l^{-1}$ NH_3, V(IV)—0.16 $mol\,l^{-1}$ HNO_3	ETAAS	[34]
HPLC	IC-cation	EDTA + tartaric buffer	720 nm (10.2 $ng\,l^{-1}$)	[13]
	C_{18}	KH-phthalate	FAAS (0.16 $mg\,l^{-1}$)	[11]
	Bis(2-aminoethylthio) methylated resin	Nitric acid, pH 1.5	ICP-MS (0.01 $\mu g\,l^{-1}$)	[35]
CE	EDTA complexes	EDTA at pH 4	UV at 185 nm (0.03–0.1 $mg\,l^{-1}$)	[40,41]
	Mo(VI)–P(V) reagent	Monochloroacetic acid	UV at 220 nm (10.1 $ng\,l^{-1}$)	[45]
	Oxidation of purpurogallin by periodate	V(V) directly, V(IV) after reduction on Ag-column	Chemiluminescence (0.05 $\mu g\,l^{-1}$)	[55]

6. Conclusion

Number of studies have been recently addressed to the understanding the biological and physiological function of vanadium as well as its potential toxicity. The speciation analysis of this element is of great importance due to the versality of vanadium forms and their respective properties. However, the analysis is complicated by several drawbacks. One of them is the possibility of redistribution of vanadium species, particularly when the environment of the sample, such as acidity, salinity or redox potential, is changing. Another problem is its very low content in environmental and biological samples. Despite of recent advances in instrumental analysis, direct determination of trace vanadium in complexes matrix is still very difficult. Thus, a separation/preconcentration technique is frequently required before measurement. The procedures which separate the individual species, followed by their direct determination, are preferred due to the need for only minimal sample pretreatment. The last factor is particularly important because prolonged sample manipulation may affect distribution of vanadium species significantly. The hyphenated systems consisting of separation modules (LC or EC) and element-selective detection is obvious but factors such as separation mechanisms, mobile phase, pH and the steps involving sample preparation must be carefully considered to prevent the interconversion of species and to ensure accurate characterization of sample. Table 1 summarizes the methods for the vanadium speciation described in the text.

It is evident that high accuracy is needed in the quantitative measurement of the trace element species. Quality assurance of the analytical procedure is therefore of prime importance. It can be only performed with representative reference materials, certified for the relevant species. Although several certified reference materials for vanadium with different matrices are available, they are only certified for total metal content. The complexity of the system restricts a possibility of application of the recovery tests for validation of the method. Therefore such validation must be based on the comparison of different procedures and very careful interpretation of all steps.

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