Sediments as a Dynamic Natural Resource - From Catchment to Open Sea

**Ion-exchange chromatography as a tool for investigating vanadium speciation in sediments: preliminary studies**

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**Abstract**

Purpose: We conducted this investigation in order to develop a simple method for the determination of bioavailable vanadium, and its speciation within sediments.

Materials and methods: The method is based on the determination of acid-extractable vanadium, as this fraction is presumably bioavailable, and its subsequent speciation using IC–UV VIS (ionic chromatography with an ultraviolet-visible detector). A published method for vanadium speciation in pore water was further optimized in order to separate V(IV) and V(V) species using column EDTA derivatization on sediment samples. The developed method was applied in order to assess acid-extractable vanadium and its speciation within estuary sediments of the Krka River at the Dalmatian coast of Croatia.

Results and discussion: The obtained results are implying that the majority of vanadium within estuary sediments is in the form of less soluble fraction while the acid-extractable fraction comprises approximately 40% of the total vanadium present. In contrast, open sea sediment (station K4) was completely dominated by the acid-extractable vanadium. The extracted vanadium is in the form of V(IV).

Conclusions: Ion-exchange chromatography with an UV-VIS detector is a promising analytical method for vanadium speciation, however further optimization of the conditions (improvement of the sequential extraction procedure) is needed in order to assess speciation also within other vanadium sedimentary fractions.

**Keywords** Extractable sediment fraction, Ion chromatography Krka River estuary,Speciation,Trace metals, Vanadium chemistry

**1 Introduction**

Vanadium, V, is a transition metal and is one of the most abundant elements in Earth’s crust (among the 20) with the average content in the upper part of Earth’s crust of 60 µg g-1, reaching concentrations over 200 µg g-1 within bulk and lower continental crust (Taylor and McLennan 1995). It is the second most abundant transition metal in seawater with its concentration only being exceeded by molybdenum (~35 nmol dm-3 and 110 nmol dm-3, respectively – e.g. Emerson and Huested 1991 and references therein). The prevailing vanadium valence states in nature are vanadium(III), vanadium(IV) and vanadium(V) of which the latter two are the most soluble (Wanty and Goldhaber 1992) making the determination of vanadium speciation a challenging task. Under acidic conditions most V species display cationic character, such as the vanadyl (VO2+) and vanadate (VO2+) ions, while under less acidic to mildly alkaline conditions the vanadium species are hydrolyzed, ultimately forming in the case of vanadium(V) the anionic species HVO42- or H2VO4- (e.g. Huang et al. 2015). The vanadium (V) speciation in natural water is affected by several factors (for example pH, ionic strength and ligand forming species), including the total vanadium concentration, due to the formation of stable vanadium polymers at concentrations above 100 μmol dm-3 (e.g. Huang et al. 2015; Brookins 1988).

Vanadium concentration within sedimentary rocks echoes primarily the abundance of detrital Fe oxides, clay minerals, hydrous oxides of Fe and Mn and organic matter. The lowest average V content is characteristic for pure carbonate (up to the 15 µg g-1), with higher values in black shale, basalts and clay (reaching ca. 200µg g-1– Levison 1974; Ketris and Yudovich 2009). The high V concentration within black shale is reflecting both the affinity of the element for organic sorption sites and its relative immobility under reducing conditions due to the important role of redox regime. That is, V remains mobile under oxidizing conditions but precipitates just above the sulphate/sulphide redox zone (Brookins 1988).

Almost all reported results concerning the direct determination of vanadium species in the solid phase of environmental materials are from XAS (X-ray absorption spectroscopy) and XANES (X-ray absorption near edge structure) (e.g. Gustafsson 2019). However, the ability of Ion chromatography (IC) to quantify different metal oxidation states and stable metal complexes in sediment extracts, therefore determining transport mechanism and toxicity of metals in sediment, was prevailing advantage when choosing suitable analytical approach (Jackson 2000).For oxic environments, such as the unsaturated zone of soils, vanadate(V) is usually the most stable oxidation state. In these environments, where the surface reactions with iron(III) and aluminium(III) compounds dominate, Larsson and coworkers (2015a, 2015b, 2017) studied vanadium speciation by use of XANES spectroscopy in a number of Swedish forested and agricultural soils. The vanadyl (IV) was predominating in the morlayer (the organic surface horizon) while deeper down in the soil profile the vanadium appeared as vanadate (V). Only two studies were found that used XANES spectroscopy for V speciation in reduced natural samples showing the predominance of reduced V (III and IV) (Bennet et al. 2018; Nedrich et al. 2018).

In Krka River estuary, vanadium as a present trace metal, has been studied only once by Prohić and Kniewald(1987). In stated paper authors addressed bulk concentrations and percentage of vanadium in extractable and less extractable fraction. However, oxidation state of vanadium in investigated fractions wasn’t addressed. In order to understand biological and geochemical cycling of vanadium it is of imperative to describe and measure transformations of the vanadium among a range of chemical species that it takes form of. Moreover, usage of only bulk concentrations is insufficient indicator of mechanical pathway of specific trace element and its accumulation time in sediment (Loring et al. 1979). Present vanadium species in easily extractable fraction of sediment can originate from weathering or from anthropogenic input and it is accessible to surrounding biota, hence it represents the important part in geochemical cycling of vanadium species between sediment and water column in Krka River estuary. Furthermore, chemical speciation of vanadium is needed in order to provide information of diagenetic processes for vanadium accumulation into the sediment (Bennett et al. 2018). Taking into the account vanadium chemistry, with V(V) being most toxic and soluble species, chemical speciation of easily extracted fraction of sediment is needed.

To fully understand the geochemistry of vanadium, and to be able to predict its mobility and bioavailability, reliable information from speciation studies are of importance. Also, accumulation of vanadium in sediment can represent valid proxy for human and biological activity from local to global scale.Within this paper we introduce the use of ion-exchange chromatography with an UV detector as a tool of determining vanadium speciation in sediments. The method development and preliminary results of vanadium speciation within estuary sediment samples of the Krka River will be presented.

# 2 Materials and methods

## 2.1 Instrumentation

The used system was METROHM ECO IC; ion chromatograph with “944 Professional UV/VIS Detector Vario” and anion exchange column. The IC-UV/VIS operated at a flow rate of 0.700 mL min-1. The column temperature was ambient (~ 22 °C) and the sample injection volume was 20 µL. Used anion exchange column is Metrosepp A Supp 5-50/ 4.0, with 50.0 mm length and 4.0 mm of inner diameter.

## 2.2 Reagents

Stock standard solutions of 1.0 g dm-3V(IV) were prepared by dissolving 0.50 g of VOSO4 x 5H2O (VWR BDH Prolabo Chemicals) in 100 mL of distilled and deionized water. Stock solution of V(V) (1.0 g dm-3) was prepared by dissolving 0.23 g of ammonium metavanadate (WR BDH Prolabo Chemicals) in 2 mL concentrated HNO3(T.T.T. d.o.o.), then diluting to 100 mL with distilled and deionized water. Concentrated HCl (Fisher Chemical) was used for adjusting the pH of solutions.

The IC eluent was prepared using acetonitrile (3%)(VWR BDH Prolabo Chemicals), ethylenediaminetetraacetic acid (EDTA)(2x10-3mol dm-3)(VWR BDH Prolabo Chemicals) and ammonium hydrogen carbonate (NH4HCO3) (8x10-2mol dm-3)(VWR BDH Prolabo Chemicals). After preparation, HCl was used in order to adjust pH of the eluent to a value of 6.

## 2.3 Methods

Sediment was collected at four locations, three within the Krka River estuary and one in the open sea (Fig. 1). Gravity corer (Uwitec) equipped with Plexiglas tubes (φ = 6 cm) was used for sampling. Only the top 5 cm were retrieved and used for analysis. After the sampling, sediment samples were deep frozen (-18°C), freeze dried and sieved under 2 mm.

Total vanadium concentrations that were used for comparison, were determined in acid digested samples by using High Resolution Inductively Coupled Plasma Mass Spectrometer (HR ICP-MS, Element 2, Thermo). Sediment samples were digested as follows: 100 mg of sediment was weighted and placed in 50 mL Teflon (PTFE) bombs together with 10 mL of aqua regia (HNO3:HCl 1:3, Fisher Scientific® Trace Analysis grade) and placed in microwave oven (ANTON PAAR® Multiwave 300). After digestion, samples were filtered and diluted to 100 mL for analysis.A certified material PACS-2 (National Research Council of Canada) was used for validation of the analysis.

For the chromatographic determination of easily extractable vanadium, 1.0 g of each sediment sample was weighed in and 10 mL of deionized and distilled water containing 0.12 mol dm-3 HCl was added to each sample. Prepared samples were left to dissolve in water for approximately 40 minutes with occasional mixing. Afterwards, they were filtrated through filters with 0.2 µm filter pore size.

Prepared samples were then measured using ion chromatograph and an anion exchange column with “944 Professional UV-VIS Detector Vario”, with wavelength set at 280 nm.

# 3 Results

## 3.1 Method development

Although the use of synchrotron methods (XAS and XANES) is dominant in the determination of trace metals in sediment, in this case it is found to be unsatisfactory approach. One of the main disadvantages is the fact that XANES spectra presents wighted sum of all the species present in the analysed sample i.e. speciation of trace metals is very difficult task using stated methods (Feldmann et al. 2009). Having in mind that sediment, in general, represents a complex mixture of chemical species and that main goal of this research is vanadium speciation, by applying this method insufficient results would be obtained. As it was main goal of this research to determine bioavailable vanadium species, which are present mostly in extractable fraction, ion chromatography was found to be satisfactory approach. This method proved to be sensitive enough for determination of trace levels of vanadium, especially in complex matrix such as sediment. For determination of vanadium species in reducible, organic/sulfidic and residual fraction it is suggested optimization of sequential extraction process.

Followed method for determination of vanadium species was previously published and used for speciation in pore water (Li and Le 2007). Speciation analysis of V(IV) and V(V) in model solutions was achieved by measuring negatively charged complexed vanadium (IV) and (V) species with EDTA. During the complexation reaction with EDTA on the anion exchange column, V(IV) and V(V) form complexes of different charge [VO(EDTA)]2- and [VO2(EDTA)]3-, respectively. Charge difference between formed complexes of V(IV)-EDTA and V(V)-EDTA is the main principal of the separation of V(IV) and V(V) species on the anion exchange column, where the stationary phase is positively charged and the negatively charged [VO(EDTA)]2- and [VO2(EDTA)]3- species are attracted to it (Li and Le 2007). Figure 2A shows a chromatogram of a mixed model solution of V(IV) and V(V) species from the anion exchange chromatography separation and UV/VIS detection of these vanadium species.

Although stated method suggested that complexation of V with EDTA in the solution stabilizes formed complexes on the column, as it can be seen in Fig. 2B, when using EDTA in the solution and eluent, the peaks become more unstable due to the tendency of EDTA to reduce the V(V) species after the equilibrium of the complexation reaction was established (Kanamori et al. 1999). When comparing the kinetics of the complexation reaction between vanadium species and EDTA on different pH values, in both cases it is shown that on lower pH values complexation reactions are faster than on higher (alkaline) values. Moreover, V(IV) on lower pH values is present as stable VO2+ ion and does not oxidize to V(V) species, while on pH values higher than approximately 5.0, it can oxidize to V(V) within a few minutes. Because of the described effects, it was decided that the concentration of EDTA in eluent (2x10-3mol dm-3) would be sufficient and that complexation reaction of vanadium species with EDTA directly on column would be fast enough when the pH of measured solutions is held at acidic values (Fig. 2C). Furthermore, any transformations of vanadium species with EDTA that might occur on column are reproducible and therefore the deviations are easily calculated. Using this optimization of the method, the same peak resolution and sensitivity was accomplished as when using EDTA in the solution, but without the presence of the stated instabilities of vanadium species.

Figure 2B is also showing the effect of eluent and pH of the solution on the chromatograms. In the case when EDTA was used in-solution to determine the V(V)-EDTA complex, the eluent was acidified using HCl to pH 6.0 (dashed line), which clearly extended the retention time. Considering that the acidified eluent didnot improve the peak height and stability, and even extended the retention time, this step was avoided when treating the sediment samples. Moreover, Fig. 2B shows comparison between used EDTA in the solution, where pH of the solution was kept at 6.0, and solution where EDTA was not present as reagent where pH of the solution was reduced on 3.0. It can be seen that lowering pH accelerates complexation reaction and increases peak height and stability.

Figure 3A and 3B show measured detection limit for V(IV) and V(V) species in model solutions using described method with UV/VIS detector. Detection limit for V(IV) and V(V) species was found to be on approximate value of 5x10-6 mol dm-3 i.e. good sensitivity was accomplished and determination of vanadium species in acid extractable sediment sample was possible with the used analytical approach.

**3.2 Discussion**

The Krka River and its estuary are located in the central part of the Eastern Adriatic, in the karst region of Croatia. Since Krka River drainage area is mainly composed of carbonate rocks and it has tufa barriers along the stream, the Krka River itself brings small quantities of suspended terrigenous material to the estuary. Main suppliers of the terrigenous material to the Krka River estuary are small tributary Guduča River and Litno Spring, whose catchment areas are composed mainly of flysch and flysch-like deposits (Prohić and Juračić 1989, Juračić and Prohić 1991; Cukrov and Barišić 2006). Although this type of deposits are subordinate to carbonates in the Krka River estuary area, they play an important role in distribution of some trace elements in the estuary (Prohić and Kniewald 1987; Cukrov et al. 2009).

Figure 4 depicts chromatogram obtained after applying leaching using the 0.12 mol dm-3 solution of HCl, revealing presence of vanadyl species within all investigated samples. Having in mind used leaching conditions (mild concentrated HCl, 40 minutes) the recovered vanadyl species mostly represent the easily exchangeable fraction of the total vanadium present. Using peak height and the calibration curve for the vanadyl ion (open symbols on Fig. 3B) the determined concentration of such manner recovered vanadyl species are represented in Table 1. and were compared with the total vanadium concentration determined using the ICP-MS.

The sediment at the station K1 is under the influence of submerged freshwater inflow, bringing detrital drivensuspended matter and is characterized with the highest Al content (50933.4µg g-1) from all investigated sediments. On the hand, station K4 is not under the influence of the Krka River plume and certainly the sedimentary clay fraction is the lowest with the Al content of 18257.2 µg g-1. The total vanadium concentration is following the observed pattern, i.e. the stations under Krka River plume influence are characterized with the higher V as well as Al concentration (stations K1, K2 and K3). However, the percent of acid-extractable vanadium has opposite behavior, i.e. highest percent of extracted vanadium (almost 100% of the total vanadium present) is observed within the sample with the lowest total vanadium concentration (station K4).

Previous studies also have reported changes in a type of sediment, from Prokljan Lake seawards. For instance, total carbonate content in the estuarine sediments increases from the 55.1% in Prokljan Lake, across the 70.8% in the lower part of the estuary to the 91.7% in the open sea (Juračić and Prohić 1991). Contrariwise, the share of fine fraction (<32 μm) diminishes from Prokljan Lake (94%), via lower part of the estuary (29.1%) to the open sea (4.4%) (Juračić and Prohić1991). These differences can be attributed to the input of terrigenous material, meaning that in Prokljan Lake sediment is a mixture of a marine carbonates and terrigenous material, while in the lower part of the estuary marine biogenocarbonate sedimentation prevails (Cukrov et al. 2009).

As it can be seen, similar results are obtained on stated sampling sites in comparison with sampling sites from Krka River estuary from previous studies (Prohić and Kniewald 1987). Although previous studies had their sampling stations dominantly at high fresh water influence without comparison with open sea values, it can be seen that values for total concentration of vanadium and its carbonate fraction are somewhat alike. It is highly probable that the reducible fraction, organic/sulfidic fraction and residual fraction of vanadium concentration in Krka River estuary cannot be determined using the described chromatographic method, therefore sequential extraction is necessary.

Sequential extraction studies of different soil samples revealed that V is recovered mainly from the less soluble fractions with strong sorption properties what is in accordance with our preliminary results. Previous research on vanadium speciation in sediment fractions suggest that vanadium is present as more reduced species in less extractable fractions, due to the reduced solubility and precipitation tendencies of species at lower oxidation state, especially V(III) (Shaw et al.1990). With vanadium species being pH and Eh dependent, their transport into the sediment is controlled with lower Eh value. In the process of geochemical cycling, vanadium species are being released into the water column by oxidation into the more soluble species. Source of reduced species is thought to be detrital flux (Shaw et al. 1990).It seems very likely that Krka River plume is bringing detrital highly weathered material, i.e. clay minerals where vanadium most probably is strongly adsorbed. Also, the exchangeable fraction gives an indication of the metal bound on the particle surfaces as well as the amount of metal bound to the acid-soluble salts such as carbonates (Filgueiras et al. 2002). Also some of the Fe and Mn oxides can be recovered in this stage.

Although determining source of naturally occurring trace elements in the sediment is not straightforward because of the dependence upon multiple factors (changes in the chemistry of the source region, physical and chemical conditions during weathering, transport, deposition, diagenesis, chemistry and the movement of the ground- water), bulk concentrations in the pre-industrial era are commonly used as the background level in determination of input source of trace metals(Prohić Juračić1989). In the case of vanadium, in previous studies it is found that its distribution in Krka River estuary is generally characterized by higher background levels, where vanadium concentration is found to be around 20 mg L-1 (Prohić1987). With measured bulk concentrations being in agreement with previous studies, it can be concluded that anthropogenic input of vanadium throughout sampling stations in Krka River estuary is not significant. Moreover, despite relatively high vanadium concentrations in the sediment, bioavailability of vanadium is found to be relatively low in reference to determined vanadium species in extractable fraction.

Generally, heavy metals in the exchangeable and acid soluble fractions are considered readily and potentially bioavailable, while the reducible and oxdisable fractions are relatively stable under normal soil conditions (Filgueiras et al. 2002). Interestingly, the studies of Wisawapipat and Kretzschmar (2017) on highly weathered soils by XAEFS revealed vanadate adsorbed to goethite, ferrihydrite, gibbsite, and/or Fe(III)–natural organic matter complexes and vanadyl in the structure of goethite may be present but cannot unequivocally be distinguished by XANES spectroscopy. These authors also demonstrated that kaolinite and Fe oxides can effectively sequester V in highly weathered soils by mechanisms of adsorption and structural incorporation, and are relevant to other Fe-oxide-rich environments under acidic and oxic conditions.

**4 Conclusions**

Generally, the excess of trace metals exist in different chemical forms that tend to accumulate at exchangeable sites of various mineral components of sediment.Furthermore, the problem of bioavailability and remobilization of different chemical forms cannot be solved by trace metal analysis of the bulk sample alone, because of the wrong implication that all chemical forms have equal impact on the environment. (Prohić and Kniewald 1987.)

Preliminary studies on the developed ion-exchange chromatographic method show that this method is sufficient for the analysis of vanadium speciation. However, the method cannot be applied for the determination of vanadium speciation in less soluble fractions where it is suspected, from previous studies, that the vanadium residue is adsorbed. For a thorough determination of vanadium speciation in sediment samples the method requires improvement by employing a sequential extraction procedure. Furthermore, for determining fractions of sediment that cannot be seen chromatographically, transfer of the developed method to ICP-MS is needed, in order to offer complete information of vanadium speciation in sediment. This can lead to new conclusions with respect to the chemistry of trace metals in fresh water and marine sediments.

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**Table 1**. Vanadium concentration determined using ICP-MS and IC with UV/VIS detector. Values for each kind of measurement compared for each sampling site in Krka River estuary; K1, K2, K3 and K4. Each sampling station is characterized with Al content.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sediment sample** | **V / µg g-1 (ICP-MS)** | **V / µg g-1 (IC)** | **Al/ µg g-1** |
| K1 | 101.83 | 41.61 | 50933.4 |
| K2 | 60.64 | 28.76 | 28516.6 |
| K3 | 59.62 | 23.86 | 30076.4 |
| K4 | 41.73 | 41.00 | 182572 |

**Figure captions**

**Fig.1**The sampling area of Krka River estuary with defined sampling stations marked as: K1 (Litno- sampling site), K2, K3 and K4 (open sea sampling site).

**Fig.2 A)** Model mixed chromatograms of V(IV)-ETDA and V(V)-EDTA complexes using anion exchange chromatography separation and UV/VIS detector; speciation was achieved by measuring V(IV) and V(V) model solutions (1x10-5mol dm-3), while having EDTA in eluent (2 x 10-3mol dm-3); pH (solution)=3.0. **B)** Comparison of model chromatograms of V(V) (1x10-4mol dm-3)-EDTA complex with EDTA (1x10-4mol dm-3) in the solution (pH=6.0) (dashed line) and V(V) (1x10-5 mol dm-3) without EDTA in the solution(pH=3.0) (solid line) using anion exchange chromatography separation and UV/VIS detector. **C)** Model chromatograms of V(V)-ETDA complex using anion exchange chromatography separation and UV/VIS detector; speciation was achieved by measuring V(V) model solution (1x10-4mol dm-3), while having EDTA in eluent (2 x 10-3mol dm-3) and in the solution (1x10-4mol dm-3) at the pH of 2 (dashed line) and of 6 (solid line).

**Fig. 3. A)** Chromatograms of measured detection limit for V(IV) – EDTA and V(V) –EDTA complexes using anion exchange chromatography with UV/VIS detector. Concentrations of V(IV) and V(V) in the solutions were: 5x10-4mol dm-3, 1x10-4 mol dm-3, 5x10-5 mol dm-3, 1x10-5 mol dm-3 and 5x10-6mol dm-3, respectively. **B)** Calibration plot graphs forV(IV) and V(V) in model solutions. Measured detection limit for V(IV) and V(V) species was found to be on approximate value of 5x10-6mol dm-3.

**Fig. 4. A)** Chromatograms of selected sediment samples: station K1 (blue curve), K2 (red curve), K3 (green curve) and K4 (black curve). **B)** Chromatograms of K4 sediment sample before (solid curve) and after standard V(IV) addition (dashed curve).