

## Extraction–Photometric Determination of Vanadium in Natural Waters

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**Abstract**—The procedure for the extraction–photometric determination of vanadium from *N*-benzoyl-*N*-phenylhydroxylamine (*N*-BPHA) is improved for the analysis of natural waters. The dependence of the absorbance of extracts on the concentration of vanadium(V) in aqueous solution is linear in the range of 0–1500 µg/L and can be described by the equation  $A = (10.70 \pm 0.02) \times 10^{-4} c_V$  (µg/L). The molar absorption coefficient of the complex in chloroform is  $5450 \pm 10$  and its partition coefficient between the phases is equal to  $26.1 \pm 0.5$ . It is shown that vanadium in natural waters occurs in the free and bound forms. The prevailing anionic forms of vanadium(V) are, probably, free and the cationic species of vanadium(IV) are bound with organic components of natural waters. For the decomposition of the last named compounds, the authors recommend the oxidative digestion of samples by boiling with 1 mL conc. HClO<sub>4</sub> to the appearance of fumes.

**Keywords:** vanadium, determination, substance analysis, natural waters

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The vanadium ingress to the environment occurs both naturally from polymetallic and iron ores and as a result of human activity from wastes of heavy and oil-processing industry. The toxicity of vanadium depends on its valence, the dispersity of particles, and the solubility of compounds in biological media. The concentration of vanadium in the Earth crust was estimated at  $1.5 \times 10^{-2}\%$ ; in soil,  $10^{-2}\%$ ; and in uncontaminated natural waters, at  $2 \times 10^{-6}\%$ . The conventional concentration of vanadium in underground waters is 0.5–2.5 µg/L; however, in certain volcanic regions it can be as high as 140 and even 2470 µg/L [1, 2]. In determining vanadium in natural waters, analysts often assess the total concentration of vanadium(V) and neglect the determination of its speciation.

The most efficient and sensitive analytical methods currently used for the determination of vanadium in natural waters are as follows: capillary electrophoresis (CE) [3, 4], various versions of chromatography [1–3, 5–7], optical emission spectrometry with inductively coupled plasma (ICP) [8], and ICP MS [3]. The attained limit of detection is 0.02 µg/L [7]. However, the ambiguity of the data on the composition of the complex forms of vanadium present at natural waters complicates their identification in chromatographic and CE separation. In the use of MS detection, the determination of the <sup>51</sup>V<sup>+</sup> ion interferes with the [<sup>35</sup>Cl<sup>16</sup>O]<sup>+</sup> ion. Methods of atomic spectroscopy are often used in combination with preconcentration operations (extraction, ion exchange, coprecipitation)

[9]. Vanadium can also be determined by kinetic methods (limit of detection 0.01 µg/L) [10].

Vanadium is most often determined by photometric procedures using hydroxamic acids and oximes. Benzohydroxamic acid and *N*-BPHA were recommended for the determination of vanadium in waters. *N*-benzoyl-*N*-phenylhydroxylamine and its compound with vanadium(V) dissolve in organic solvents, so that the analysts can use this reagent for the extraction–photometric determination of vanadium(V) traces. Extraction offers a possibility of not only preventing hydrolysis and polymerization, but also of increasing the selectivity of vanadium determination. The selectivity attains a maximum in extraction with chloroform from highly acid (3–6 M HCl) solutions at a 10-fold excess of the reagent. The stoichiometry of the complex formed is V(*N*-BPHA)<sub>2</sub>; its absorption maximum lies at 510 nm and molar absorption coefficient is 4650. The Beer law for the extraction–photometric determination of vanadium with *N*-BPHA is obeyed in the range 0.7–12 µg/L of vanadium. Vanadium(IV) in strongly acid solutions does not react with *N*-BPHA; therefore, under these conditions, *N*-BPHA is a specific and a highly sensitive reagent for determining vanadium(V). The works [11, 12] were devoted to the determination of small amounts of vanadium with *N*-BPHA.

Along with vanadium, niobium, tantalum, zirconium, plutonium(IV), titanium, tin(IV), cerium, molybdenum(VI), and tungsten (VI) are extracted with chloroform from strongly acid solutions as com-

plexes with *N*-BPHA. These ions do not interfere with the determination of vanadium in natural water samples, because their concentrations are either insignificantly low in comparison to that of vanadium (the first four elements) or the complexes they form with *N*-BPHA do not absorb light in the visible region (the other elements). The usually present cations do not interfere with the determination of vanadium.

The toxicity of vanadium compounds depends on its species present in waters. Studies of the state of vanadium in natural waters are complicated, on one hand, by numerous oxidation states of vanadium occur, its trend to acid-base interactions and complex formation, and, on the other hand, by the low rate of establishment of equilibria in the systems. It is believed that 98–99% of vanadium in underground waters is present in the form of vanadium(V) [7]. At concentrations about  $10^{-5}$  M and  $\text{pH} < 6$ , only mononuclear species  $\text{VO}_2^+$ ,  $\text{HVO}_3$  and  $\text{VO}_3^-$  can occur [13]. However, in surface waters in the presence of large amounts of organic substances of biological origin, one cannot neglect the possibility of the reduction of vanadium(V) with the formation of cationic forms of vanadium(IV) and their stable complexes with humic and fulvic acids. The composition of these complex forms is unknown, which complicates their determination.

The aim of this work was the development of a procedure with various versions of sample preparation for the extraction-photometric determination of vanadium species in natural waters.

## EXPERIMENTAL

Photometric measurements were performed on a Shimadzu UV mini 1240 spectrophotometer in the wavelength region 400–700 nm using 10-mm cells. Samples of natural waters were evaporated on an electric hotplate. Weighed portions were taken using a VLR-200 analytical balance. We used the following reagents: ammonium metavanadate of analytical grade, Mohr's salt of chemically pure grade, phenylanthranilic acid of reagent grade,  $\text{H}_3\text{PO}_4$  of chemically pure grade,  $\text{HClO}_4$  of chemically pure grade, HCl of chemically pure grade, chloroform of reagent grade, (purified by distillation at  $64^\circ\text{C}$ ), a KU-2 ion exchanger in the *N*-form, and an Amberlit ion exchanger in the Cl-form. A stock solution of vanadium(V) (0.829 g/L) was prepared by dissolving 2.3934 g of ammonium vanadate in 60 mL of 0.5 M  $\text{H}_2\text{SO}_4$  followed by dilution to 1 L with distilled water. The solution was standardized by titration with a standard solution of Mohr's salt using phenylanthranilic acid. Working solutions were prepared by diluting the stock solution with distilled water immediately before use. A *N*-benzoyl-*N*-phenylhydroxylamine solution was prepared by dissolving 0.1000 g of a dry reagent in 50 mL of chloroform.

## RESULTS AND DISCUSSION

The procedure for the extraction-photometric determination of vanadium with *N*-BPHA is based on the formation of a complex compound  $\text{V}(\text{N-BPHA})_2$  of violet color. The concentration of HCl considerably affects the completeness of complex formation of vanadium(V) with *N*-BPHA. To create the optimum acidity of solutions ( $\geq 2.4$  M HCl), we consecutively added 12 mL of 6 M HCl, distilled water to 30 mL, and 3 mL of a reagent solution in chloroform to the sample. After careful stirring and settling, the extract was separated and its absorbance was measured against the reagent solution in chloroform at 530 nm [14].

The data [15, 16] on the time of color development and the stability of extracts of the vanadium(V) complex in time are contradictory. According to our data, the color of the extract developed completely within less than 1 min. In the further experiments, the absorbance of extracts was measured immediately after phase segregation. The color of the extract remained stable for at least 4 h; its intensity noticeably decreased only after one day, probably, because of the proceeding of an intramolecular redox reaction. The partition ratio of the complex between chloroform and water phase was equal to  $26.1 \pm 0.5$ . The dependence of the absorbance of extracts on the concentration of vanadium(V) in an aqueous solution was linear in the range 0–1500  $\mu\text{g/L}$  and can be described by the equation  $A = (10.70 \pm 0.02) \times 10^{-4} c_v$  ( $\mu\text{g/L}$ ); the molar absorption coefficient of the complex in chloroform was equal to  $5450 \pm 10$ .

The concentration of vanadium in natural waters is very low, so that vanadium preconcentration is necessary. In this work, we used preconcentration by the evaporation of samples on heating. Vanadium in natural waters can occur in an inactive complex form; therefore, its correct determination is possible only after the complete acid digestion of samples with the oxidation of organic substances present in the sample. This is usually done by adding 5–10 mL of a mixture of  $\text{HNO}_3$  with  $\text{H}_2\text{SO}_4$  [17].

It was found that, for the decomposition of organic substances in the sample, sample evaporation with 1 mL of conc.  $\text{HClO}_4$  is quite sufficient. To confirm the completeness of sample digestion by the proposed method, we compared the results of vanadium determination with sample evaporation to a volume of 25 mL in the presence of  $\text{HClO}_4$  until the appearance of  $\text{HClO}_4$  fumes. In the course of sample evaporation, the color consecutively changed from almost clear to yellow, then to brown, and again to tintless with the reduction of the volume of solution to 1 mL, the appearance of  $\text{HClO}_4$  fumes, and the complete decomposition of organic substances. Judging from the data obtained (Table 1), from 10 to  $> 60\%$  of vanadium in samples of natural waters was, probably, bound into complexes. Therefore, the correct determination of the total concentration of vanadium in

**Table 1.** Determination of vanadium ( $\mu\text{g/mL}$ ) in water samples before the oxidation decomposition of organic substances with perchloric acid ( $n = 3$ ,  $P = 0.95$ )

Water sample	Without oxidation	After oxidation
River Smolenka, St. Petersburg, sample 1	$7.7 \pm 0.2$	$10.4 \pm 0.6$
River Okhta, St. Petersburg, sample 1	$17.0 \pm 0.7$	$18.8 \pm 1.4$
Snow, Staryi Peterhof, sample 2	$9.1 \pm 0.6$	$11.4 \pm 0.7$
Snow, Staryi Peterhof, sample 3	$4.9 \pm 0.7$	$13.6 \pm 1.1$
Snow, Staryi Peterhof, sample 4	$13.7 \pm 1.6$	$27.4 \pm 1.7$

**Table 2.** Verification of the procedure for the determination of vanadium in natural waters by the standard addition method ( $n = 3$ ,  $P = 0.95$ )

Water sample	Added, $\mu\text{g/L}$	Found, $\mu\text{g/L}$
River Karpovka, St. Petersburg, sample 2	5.3	$5.6 \pm 0.5$
River Moika, St. Petersburg, sample 2	10.0	$10.0 \pm 0.7$
River Neva, St. Petersburg, sample 3	17.6	$17.6 \pm 0.8$
River Fontanka, St. Petersburg, sample 4	20.0	$20.1 \pm 1.7$
Lake Chudskoe, Pskov oblast, sample 2	26.5	$26.8 \pm 0.7$
River Volga, Saratov oblast, sample 2	30.1	$29.9 \pm 0.7$

natural waters can be possible only after the decomposition of samples with the complete oxidation of vanadium and organic substances present in waters.

Vanadium(IV), aluminum, manganese, lead, and cobalt in the ratios 1 : 100 did not interfere with the determination of vanadium(V) with *N*-BPHA. Iron, chromium, and zinc in the ratios higher than 1 : 1 affected the determination of vanadium. These ions can be efficiently masked with phosphoric acid to form of stable ortho phosphates. In the analysis of natural waters, the concomitant elements were masked by adding 1 mL of conc.  $\text{H}_3\text{PO}_4$  to a solution. As a result, we proposed the following procedure of sample preparation: filtering of a water sample (a little more than 1 L) through a paper filter; exact measurement of the volume of water sample (1 L); addition of 1 mL of  $\text{HClO}_4$  to the analyzed sample; sample evaporation to the appearance of  $\text{HClO}_4$  fumes; addition of 1 mL of  $\text{H}_3\text{PO}_4$  to the evaporated sample for masking concomitant elements; and sample dilution to 25 mL with distilled water.

We analyzed 5-mL aliquot portions of samples prepared as described above. The accuracy of the results obtained was checked by the added–found method: we introduced a known additive of vanadium into a sample of natural water and determined it after all steps of sample preparation (Table 2). The found additives for all of the studied samples corresponded to the introduced ones, which confirmed the accuracy of the results obtained.

The results of analyses of various samples of natural and tap waters using the modified procedure with pre-

liminary sample digestion by boiling with  $\text{HClO}_4$  are listed in Table 3. The range of found vanadium concentrations in various types of natural waters (river, lake, snow) was rather narrow (2–35  $\mu\text{g/L}$ ); the maximum values did not exceed the maximum concentration limit for sanitary waters (100  $\mu\text{g/L}$ ). Samples were taken in the northwest region of Russia; however, the results of analysis of samples 16–19 confirmed the typicality of the values obtained for Russia in general. The influence of the anthropogenic factor can be illustrated by comparing samples taken in city (1–9) and suburban (10–15) reservoirs. In the first case, the average concentration of vanadium was as high as  $13 \pm 4 \mu\text{g/L}$ , whereas in the last case, it was  $7.0 \pm 1.8 \mu\text{g/L}$ .

The question about the sign of charge of vanadium species present in natural waters can be resolved by preliminarily passing the analyzed samples through ion exchangers. The sample portion passed through a cation exchanger will contain only anionic forms of vanadium and, vice versa, the sample portion passed through an anion exchanger will contain only its cationic forms. The samples were passed through two chromatographic columns (layer 10 cm) filled with a KU-2 cation exchanger in the H-form and with an Amberlit IRA-401 anion exchanger in the Cl-form at a rate of 5 mL/min. Then the samples were evaporated and subjected to complete acid digestion.

The results of analyses of various samples of natural waters are presented in Table 4. It can be seen that, in natural waters, vanadium is present both in cationic and anionic forms, and the last ones are prevailing (61 and 33%, respectively); neutral (first of all, hydrophobic) forms of vanadium in the samples comprised, on

**Table 3.** Results of analysis of water samples ( $n = 3$ ,  $P = 0.95$ )

Sample no.	Water sample	Found vanadium, $\mu\text{g/L}$
1	River Neva, St. Petersburg, sample 2	$15.9 \pm 0.2$
2	River Fontanka, St. Petersburg, sample 3	$19.3 \pm 3.2$
3	River Moika, St. Petersburg	$7.7 \pm 0.4$
4	Griboedov Canal, St. Petersburg, sample 2	$6.0 \pm 0.2$
5	Obvodnyi Canal, St. Petersburg, sample 2	$8.1 \pm 0.6$
6	River Smolenka, St. Petersburg, sample 3	$13.8 \pm 1.1$
7	River Karpovka, St. Petersburg	$7.4 \pm 0.7$
8	River Okhta, St. Petersburg, sample 2	$35.0 \pm 1.4$
9	River Okkervil, St. Petersburg	$5.6 \pm 0.7$
10	River Mga, Kirov region, Leningrad oblast	$10.4 \pm 0.6$
11	Lake Omchino, Luga region, Leningrad oblast, sample 2	$6.3 \pm 0.6$
12	River Obla, Luga region, Leningrad oblast	$5.5 \pm 0.6$
13	Well, Luga region, Leningrad oblast	$5.6 \pm 0.6$
14	Water conduct, Novyi Peterhof, Leningrad oblast	$1.7 \pm 0.7$
15	Lake Chudskoe, Pskov oblast	$12.5 \pm 0.7$
16	Lake Krugloe, Moscow oblast	$3.8 \pm 0.7$
17	River Volga, Saratov oblast	$37.0 \pm 1.1$
18	River Irgiz, Saratov oblast	$11.8 \pm 0.4$
19	River Bol'shoi Yugan, Khanty-Mansiysk Autonomous region	$14.7 \pm 0.7$
20	Snow, Staryi Peterhof, sample 6	$3.1 \pm 0.6$
21	Snow, Universitet railway station, sample 2	$8.5 \pm 0.6$
22	Tap water, Staryi Peterhof, sample 2	$3.5 \pm 0.7$
23	Tap water, St. Petersburg	$2.4 \pm 0.3$

**Table 4.** Concentrations of different vanadium forms in water samples ( $n = 3$ ,  $P = 0.95$ )

Water sample	Concentration of vanadium forms, $\mu\text{g/L}$ (%)		Total concentration of vanadium, $\mu\text{g/L}$
	cationic	anionic	
River Fontanka, sample 2	$2.4 \pm 0.6$ (24)	$7.0 \pm 0.6$ (69)	$10.1 \pm 1.4$
River Smolenka, sample 2	$4.0 \pm 0.6$ (39)	$6.0 \pm 0.2$ (59)	$10.2 \pm 0.6$
Griboedov Canal, sample 1	$1.8 \pm 0.2$ (30)	$4.0 \pm 1.0$ (66)	$6.1 \pm 0.2$
Obvodnyi Canal, sample 1	$7.0 \pm 0.7$ (47)	$7.7 \pm 0.2$ (51)	$15.0 \pm 0.8$
River Krasnen'kaya, St. Petersburg	$1.9 \pm 0.7$ (35)	$2.6 \pm 0.8$ (48)	$5.4 \pm 0.7$
River Novaya, St. Petersburg	$2.5 \pm 0.6$ (45)	$2.8 \pm 0.8$ (50)	$5.6 \pm 0.9$
Angliyskii Pond, Novyi Peterhof	$0.9 \pm 0.4$ (35)	$1.5 \pm 0.6$ (58)	$2.6 \pm 0.7$
Krasnyi Pond, Novyi Peterhof	$0.9 \pm 0.5$ (30)	$2.2 \pm 0.7$ (73)	$3.0 \pm 0.7$
Olgin Pond, Novyi Peterhof	$0.8 \pm 0.4$ (17)	$3.4 \pm 0.5$ (74)	$4.6 \pm 0.8$
Pond, Park Sergievka, Staryi Peterhof	$1.3 \pm 0.6$ (27)	$3.0 \pm 0.6$ (61)	$4.9 \pm 1.5$
River Narova, pos. Perevolok, Leningrad Oblast	$1.8 \pm 0.7$ (24)	$5.3 \pm 0.9$ (70)	$7.6 \pm 0.9$
Lake Omchino, Leningrad oblast, sample 1	$2.5 \pm 0.2$ (37)	$3.6 \pm 0.6$ (53)	$6.8 \pm 0.6$
Gulf of Finland, Staryi Peterhof	$1.5 \pm 0.6$ (41)	$2.0 \pm 0.6$ (54)	$3.7 \pm 0.7$
Snow, Universitet Station, sample 1	$2.8 \pm 0.2$ (34)	$5.6 \pm 0.6$ (67)	$8.3 \pm 0.6$
Snow, Staryi Peterhof, sample 5	$2.7 \pm 0.2$ (36)	$4.9 \pm 0.2$ (64)	$7.6 \pm 0.4$
Tap water, Staryi Peterhof, sample 1	$0.05 \pm 0.03$ (2)	$2.7 \pm 0.2$ (90)	$3.0 \pm 1.3$
Tap water, Staryi Peterhof, sample 1	$1.7 \pm 0.9$ (23)	$4.5 \pm 0.2$ (62)	$7.3 \pm 1.5$

the average, 6%. The anionic forms of vanadium(V) cannot form complexes and can, therefore, be determined in the sample even without its acid digestion (Table 1). The cationic forms of vanadium(IV), probably, occur in natural waters as stable complexes with humic and fulvic acids and their determination requires the acid digestion of samples.

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