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**INVESTIGATIONS OF THE POSSIBILITIES  
OF DETERMINING VANADIUM IN WATER BY ABSORPTION  
ATOMIC SPECTROMETRY USING INITIAL CONCENTRATION  
BY THE CHELATE FORMATION AND EXTRACTION METHODS**

**Abstract**

*Possibilities of determining low concentrations of vanadium in underground and surface waters using the absorptive atomic spectrometry with flame excitation method were tested.*

*Due to the very low level of concentration of the determined element in water, initial condensation was necessary by chelate formation with 1-ammonium-pyrrolidin-dithiocarbamat (APDC) at pH = 4, and by extracting to the isobutyl methyl ketone (MIBK). Spectrometric measurements were made in the obtained extract. After optimising the conditions of measurement, investigating and determining the influence of disturbing substances, and determining the limit of detectability, it was found that using the developed method vanadium can be determined in water in the range of concentrations between 0.004 and 0.050 mg/dm<sup>3</sup>. Determination becomes impossible if concentrations of iron of over 0.5 mg/dm<sup>3</sup> are present.*

**1. Introduction**

Vanadium is one of the biophilous elements. In natural waters it occurs at very low concentrations. In underground waters with low level of mineralisation, most often vanadium concentrations in an oxidising environment are 0.0005 to 0.002 mg/dm<sup>3</sup> [3]. In Poland, in the Białystok voivodship, which is one of the least degraded areas of Poland, concentrations of this element in underground waters range between 0.0002 and 0.006 mg/dm<sup>3</sup>. Vanadium commonly occurs in surface and underground waters. Its natural source in underground water are some components of magmatic rocks, enriched with that element, such as titanium magnetites and mica minerals.

Water may contain also vanadium coming from industrial waste [2] and from atmospheric pollution resulting from burning bioliths.

Vanadium content in water is determined by colorimetric methods or using absorption spectrometry methods with atomising in a graphite oven, or by atomic emission spectrometry with inductively coupled plasma (ICP). The Polish Standard recommends that vanadium in natural waters and in waste water should be determined by spectrophotometric methods [4]. Colorimetric (spectrophotometric) methods are very labour- and time-consuming [1]. They require many operations, which makes high accuracy and precision difficult to attain. The other mentioned above spectrophotometric methods allow quick, direct determination of low concentrations of vanadium in water, they are very sensitive and accurate, but due to the high cost of apparatus their availability is rather limited.

This paper presents an attempt at developing a method for determining vanadium using cheaper equipment, such as atomic absorption spectrometers with flame excitation. The boundary of detectability in water was lowered by determining it in the organic phase, after prior condensation using the chelate formation and extraction method.

## 2. Methodology of investigations

### 2.1. Apparatus

All measurements were carried out by flame technique, using the atomic absorption spectrometer manufactured by VARIAN, "model SpektrAA - 250 Plus".

### 2.2. Reagents

- ammonium-pyrrolidin-dithiocarbamat (APDC), manufactured by BDH, of 99% purity - 2% water solution, purified with isobutyl methyl ketone;
- isobutyl methyl ketone (MIBK) of Merck with 99.9% purity;
- acetate buffer with pH = 4, purified with the isobutyl methyl ketone;
- methyl orange - 0.1% water solution;
- nitric acid, "Merck" production;
- sodium hydroxide - 10% water solution;
- potassium nitrate - water solution of  $-20 \text{ mg K/cm}^3$  concentration.

### 2.3. Conditions of measurements

The following optimum conditions for measurements of vanadium in water solutions in organic phase were established:

Table 1. Conditions for vanadium measurements

It.	Parameters	Water	Organic phase
1	Type of flame	nitrous oxide/acetylene	nitrous oxide/acetylene
2	Mode of work	integration	integration
3	Wave length	318.5 nm	318.5 nm
4	Lamp current	18 mA	18 mA
5	Slit width	0.2 nm	0.2 nm
6	Acetylene flow	8.55 dm <sup>3</sup> /min	7.05 dm <sup>3</sup> /min
7	N <sub>2</sub> O flow	11.0 dm <sup>3</sup> /min	11.0 dm <sup>3</sup> /min
8	Burner height	11 mm	12 mm
9	Uptake rate	9.1 cm <sup>3</sup> /min	5.2 cm <sup>3</sup> /min
10	Delay time	3 s	3 s
11	Time of measurement	3 s	5 s
12	Replicates	3	3

Background correction is not necessary, though it may be preferable in measurements of natural samples.

## 2.4. Determination of vanadium

### 2.4.1. Method of direct determination of vanadium in water

In the first stage, the possibilities of direct determination of vanadium in water were checked. After acidification, water samples were concentrated by a factor of 10 by vapourisation in an open system. To the samples and standards 2 mgK/dm<sup>3</sup> of potassium (solution of KNO<sub>3</sub>) was added to reduce ionisation of vanadium in the flame and to obtain a linear relationship between absorption and concentration (standard curve).

Table 2. Results of vanadium calibration in water phase

Concentration of standard [mgV/dm <sup>3</sup> ]	Absorption			Mean absorption (A)	RSD [%]
		(A)			
0.00	0.000	0.001	0.000	0.000	
0.10	0.001	0.001	0.001	0.001	27.3
0.50	0.005	0.005	0.005	0.005	7.2
1.00	0.010	0.010	0.010	0.010	4.3
5.00	0.056	0.055	0.056	0.056	0.8
10.00	0.106	0.106	0.106	0.106	0.2

RSD - relative standard deviation

Direct measurement of the vanadium content in water solutions is possible for concentrations exceeding 0.2 mg/dm<sup>3</sup>. Measurements made at the limit of detectability are loaded with a large error (Table 2). Therefore, the concentration of 0.5 mg V/dm<sup>3</sup> should be adopted as the safe lower limit for direct determination. This limitation excludes the use of this method in investigations of natural waters.



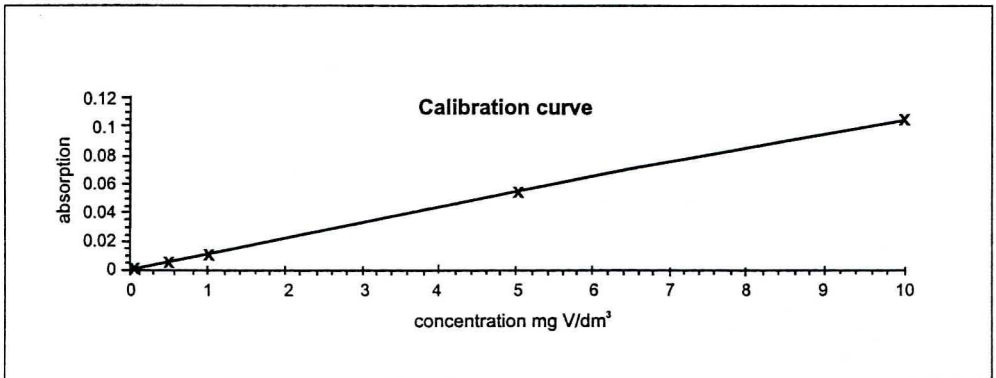


Fig. 1. Relationship between absorption and concentration of vanadium in water solutions

10-fold concentration allows to make vanadium concentrations at the  $0.05 \text{ mg/dm}^3$  level. Therefore it becomes possible to find whether vanadium concentration does or does not exceed allowable values, which for inland surface waters is  $1.0 \text{ mg/dm}^3$ , and for sewage waters discharged into water or soil - is  $2.0 \text{ mg/dm}^3$ .

Considering that the average concentration of vanadium in natural waters is  $0.002 \text{ mg/dm}^3$ , in order to determine such low concentrations it was necessary to thicken the sample using the chelate formation and extraction method. Such a procedure allows further lowering of the boundary of detectability of vanadium.

## 2.4.2. Method of determining vanadium in the organic phase

In the next stage of investigations vanadium determination was attempted in the organic phase, after thickening by chelate formation and extracting the element from the water phase [5].

### 2.4.2.1. Chelate formation and extraction of vanadium

In order to thicken the vanadium, chelate formation was utilised with the use of  $5 \text{ cm}^3$  of ammonium-pyrrolidin-dithiocarbamat (APDC) at  $\text{pH} = 4$ , and extraction of  $10 \text{ cm}^3$  of isobutyl methyl ketone (MIBK). The spectrometric measurement of vanadium content was carried out in the obtained extract.

At the earlier given parameters, the limit of detectability of vanadium is  $0.005 \text{ mgV/dm}^3$ , which means that it is of the same order as the average concentration in natural groundwater.

For conditions of measurement given in Table 1, the following results of calibration were obtained.

Table 3. Results of vanadium calibration in the organic phase

Concentration of standard [mgV/dm <sup>3</sup> ]	Absorption			Mean absorption (A)	RSD [%]
	(A)				
0.000	0.000	0.000	0.000	0.000	
0.005	0.005	0.005	0.004	0.005	5.7
0.007	0.007	0.007	0.007	0.007	0.0
0.010	0.010	0.010	0.010	0.010	1.4
0.020	0.020	0.020	0.020	0.020	0.0
0.025	0.025	0.025	0.025	0.025	0.8

RSD - relative standard deviation

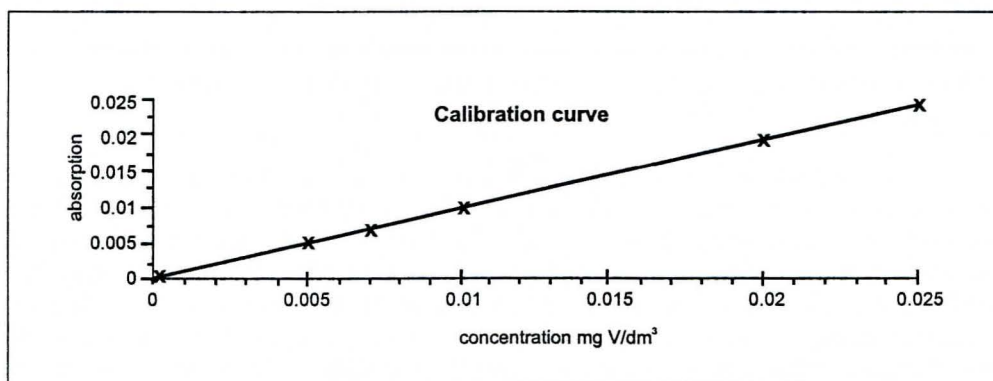


Fig. 2. Relationship between absorption and concentration of vanadium in the organic phase

#### 2.4.2.2. Determination of vanadium in groundwater

##### *Preparation of samples for investigations*

Determination of vanadium was carried out on samples of groundwater, in which earlier vanadium was determined by the atomic absorption method with atomisation in a graphite oven. Except samples 15a, concentration of vanadium in these samples was below 0.001 mgV/dm<sup>3</sup>. To 1 dm<sup>3</sup> of each sample various amounts of the vanadium standard were added. Next, the samples were evaporated to less than 100 cm<sup>3</sup> and transferred to 200 cm<sup>3</sup> measuring flasks, and pH = 4 was established with the acetate buffer with respect to methyl orange. After this the samples were chelated with APDC (5 cm<sup>3</sup>) and extracted to 10 cm<sup>3</sup> MIBK. Water was added to the flasks, so that the whole organic phase was in the neck of the flask. Measurements were made in the organic phase without earlier separation of the water phase.

##### *Results of determinations*

Measurements of vanadium content in the organic phase were carried out at earlier selected optimum conditions (Table 1).

Table 4. Percentage of retrieved vanadium in groundwater

lt.	No. of sample	Introduced addition of vanadium standard [mg/dm <sup>3</sup> ]	Obtained result [mg/dm <sup>3</sup> ]	% retrieved	Fe content in water [mg/dm <sup>3</sup> ]
1	P1	0.005	0.002	40	6.02
2	P1'	0.005	0.003	60	6.02
3	P19	0.010	0.007	70	6.40
4	P19'	0.010	0.006	60	6.40
5	P13a	0.050	0.020	40	7.51
6	P13a'	0.050	0.006	12	7.51
7	P5	0.100	0.003	3	16.34
8	P5'	0.100	0.002	2	16.34
9	P15a	0.0036*	0.003	75	0.49

\* Real vanadium content in the sample, determined by atomic absorption with activation in graphite oven.

As can be seen, very low percentage of retrieval of vanadium from the samples was attained (from 70 to 2%). For sample 15a, in which the concentration of the investigated element was 0.004 mg/dm<sup>3</sup>, 75% retrieval was obtained. The agents which may hinder determination of vanadium by this method are compounds of iron and organic substances. The degree of retrieval of vanadium decreases with increasing iron content (Table 4). In sample P5, in which the content of iron was 16.34 mg/dm<sup>3</sup>, the percentage of retrieved vanadium was only 2-3%. Whereas, in sample 15a, where iron content was only 0.49 mg/dm<sup>3</sup>, vanadium retrieval was 75%.

Table 5. Influence of iron on determination of vanadium in groundwater

lt.	No. of sample	Concentration of iron [mg/dm <sup>3</sup> ]	Addition of vanadium standard [mg/dm <sup>3</sup> ]	Retrieval of vanadium [mg/dm <sup>3</sup> ]	Retrieval of vanadium [%]
1	P14b	0.38	0.100	0.108	108
2	P14b	0.38	0.200	0.222	111
3	P16N	1.53	0.050	0.051	102
4	P16N	1.53	0.100	0.104	104
5	P6N	1.53	0.200	0.191	95
6	P8	2.06	0.050	0.053	106
7	P8	2.06	0.100	0.078	78
8	P8	2.06	0.200	0.180	90
9	P13	3.31	0.050	0.055	110
10	P13	3.31	0.100	0.107	107
11	P13	3.31	0.200	0.160	80
12	XIV	4.49	0.050	0.039	78
13	XIV	4.49	0.100	0.110	110
14	XIV	4.49	0.200	0.178	89
15	Vla	5.38	0.050	0.040	80
16	P14	6.33	0.100	0.120	120



The next step was an attempt to test the influence of iron content on the retrieval of vanadium. Water samples with iron content ranging from 0.38 to 7.38 mg/dm<sup>3</sup> were selected. No thickening of the samples was executed. From each acidified sample a volume of 100 cm<sup>3</sup> was placed in a 200 cm<sup>3</sup> measuring flask and appropriate amounts of vanadium were added. Further procedure was the same as for evaporated samples. Obtained results are shown in Table 5.

It was found that retrieval of vanadium in samples with low iron content is much higher. Satisfactory results were obtained for samples with iron content between 0.38 and 5.0 mg/dm<sup>3</sup> (which corresponds to iron content in water before 10-fold concentration from 0.038 to 0.50 mg/dm<sup>3</sup>), at which retrieval of vanadium was 78 to 110%. Average retrieval was 98%.

Table 5. Influence of iron on determination of vanadium in groundwater

It.	No. of sample	Concentration of iron [mg/dm <sup>3</sup> ]	Addition of vanadium standard [mg/dm <sup>3</sup> ]	Retrieval of vanadium [mg/dm <sup>3</sup> ]	Retrieval of vanadium [%]
1	P14b	0.38	0.100	0.108	108
2	P14b	0.38	0.200	0.222	111
3	P16N	1.53	0.050	0.051	102
4	P16N	1.53	0.100	0.104	104
5	P6N	1.53	0.200	0.191	95
6	P8	2.06	0.050	0.053	106
7	P8	2.06	0.100	0.078	78
8	P8	2.06	0.200	0.180	90
9	P13	3.31	0.050	0.055	110
10	P13	3.31	0.100	0.107	107
11	P13	3.31	0.200	0.160	80
12	XIV	4.49	0.050	0.039	78
13	XIV	4.49	0.100	0.110	110
14	XIV	4.49	0.200	0.178	89
15	VIa	5.38	0.050	0.040	80
16	P14	6.33	0.100	0.120	120

For natural waters with large iron content, the presented method cannot be used.

### 3. Summary

1. In result of the investigations, the possibilities of using spectrometers for atomic absorption with excitation in flame for the determination of vanadium in natural waters.
2. By the method of atomic absorption spectrometry with atomisation in nitrous monoxide/acetylene, vanadium can be determined directly from water phase, if its content in natural water is over 0.050 mg/dm<sup>3</sup>, at 10-fold concentration by evaporation and presence of 2 mg/dm<sup>3</sup> of potassium.
3. If the vanadium content is in the 0.004-0.050 mg/dm<sup>3</sup> range, then it can be determined using concentration by chelate formation and extraction. Chelating

was realised with ammonium-pyrrolidin-dithiocarbamat at pH 4, and extraction with the isobutyl methyl ketone. With this procedure, vanadium retrieval is about 98%.

4. In the future the problem of removing iron salts or masking their influence on the level of vanadium retrieval will be investigated in order to widen the range of applicability of the method.

### References

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