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# Solidified floating organic drop microextraction and spectrophotometric determination of vanadium in water samples

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Solidified floating organic drop microextraction (SFODME) was used as a sample preparation method prior to spectrophotometric determination of trace amounts of vanadium in water samples. 8-Hydroxyquinoline (oxine) was used as the chelating agent. The main parameters affecting the performance of SFODME, such as pH, concentration of oxine, extraction time, sample and organic phase volume, extraction temperature, and the nature of the organic solvent, were optimized. Under the optimized conditions, an enhancement factor of 38, detection limit of 0.97 $\mu$g $L^{-1}$, and good relative standard deviation of $\pm$3.9% at 10 $\mu$g $L^{-1}$ were obtained. The method was successfully applied to the determination of vanadium in tap water, well water, river water, and sea water. The accuracy of the method was assessed through a recovery experiment and independent analysis by graphite furnace atomic absorption spectrometry.

**Key Words:** Vanadium determination, solidified floating organic drop microextraction, preconcentration/separation, spectrophotometry

## Introduction

Vanadium is highly distributed in the Earth's crust but is never found unbound in nature. Vanadium occurs in about 65 different minerals and in carbon-containing deposits such as crude oil, coal, oil shale, and tar sands. Watering is an important way in which vanadium is redistributed throughout the environment because venedates are generally very soluble. Vanadium is present in natural water in concentrations ranging between $1 \times 10^{-7}$ and $5 \times 10^{-7}$ mol $L^{-1}$.[1] Vanadium can be found in the environment and in algae, plants, invertebrates, fishes, and many other species. In mussels and crabs, vanadium strongly bioaccumulates, which

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can lead to concentrations about $10^5$ to $10^6$ times greater than the concentrations that are found in seawater.[2] Vanadium atoms are an essential component of some enzymes, particularly the vanadium nitrogenase used by some nitrogen-fixing microorganisms. Vanadium compounds are not regarded as serious hazards, but at high concentrations they could be highly toxic to humans and animals.[3] Therefore, determination of trace amounts of vanadium in water and environmental samples has received increasing attention.

Several analytical techniques have been reported for the determination of vanadium in water samples, including inductively coupled plasma mass spectrometry (ICP-MS),[4] inductively coupled plasma emission spectroscopy (ICP-OES),[5] electrothermal atomic absorption spectrometry (ETAAS),[6–9] and flame atomic absorption spectrometry (FAAS).[10] However, many of these methods are expensive and time-consuming, and they require skillful operators. The spectrophotometric method, a relatively inexpensive and easily handled technique, has been used for determination of vanadium,[11–14] but in many cases where the level of vanadium in the natural sample is very low or the matrices are complex, a separation/enrichment step is necessary to improve the precision and detection limit of the method. Different methods, such as liquid-liquid extraction (LLE),[11,15] solid phase extraction (SPE),[13,16,17] coprecipitation,[18] cloud point extraction (CPE),[9,19] and microextraction,[5,8,9,14] have been used for the separation and preconcentration of vanadium from different matrices. Liquid phase microextraction (LPME) has emerged as a new and attractive alternative for sample preparation. LPME is a miniaturized implementation of the conventional LLE in which the amount of organic solvent is greatly reduced. LPME was introduced in 1996[20] and has been performed in different modes, including single drop microextraction (SDME),[20–22] hollow fiber liquid phase microextraction (HF-LPME),[23] temperature-controlled ionic liquid dispersive liquid phase microextraction (TILDLME),[24] dispersive liquid-liquid microextraction (DLLME),[25–29] and solidification of floating organic drop microextraction (SFODME).[30–33] Recently, we reviewed these LPME techniques and their application to metal analysis.[34] Among the methods, SFODME is a new microextraction method introduced in 2007.[30] It is a simple, fast, and inexpensive liquid phase microextraction mode in which a small volume of an extraction solvent with a density lower than water and a melting point near room temperature (10-30 °C) is floated on the surface of an aqueous solution containing the analyte. The mixture is agitated to maximize the contact area between the 2 solutions. After the extraction is done for a prescribed time, the floated extractant droplet is easily collated by solidifying it at a low temperature. The advantages of this method are simplicity, high efficiency, low cost, a simple extraction apparatus, and consumption of a very small amount of low-toxicity organic solvent. This method had been used for the extraction of metal ions from water samples followed by their determination with atomic spectroscopy.[31–33,35–38]

In this study, the possibility of implementation of SFODME in combination with spectrophotometry for trace element determination was considered. Vanadium in the aqueous phase was extracted as its complex with oxine in 1-undecanol and determined by measuring its absorption at 383 nm with a spectrophotometer.

# Experimental

## Materials and instruments

All reagents used were of the highest purity available and of at least analytical reagent grade. A stock solution (100 mg $L^{-1}$) of vanadium was prepared by dissolving an appropriate mass of $NH_4VO_3$ into a small amount

of ammonia solution in a 100-mL flask and diluting it to the mark with distilled water. Standard solutions were prepared daily from the stock solution by serial dilution with water. Deionized water was used throughout in sample preparation and all solutions were stored in precleaned polypropylene containers (Nalgene, Lima, OH, USA). 1-Undecanol, 1-dodecanol, 1,10-dichlorodecane, and n-hexadecane were obtained from Merck (Darmstadt, Germany). 8-Hydroxyquinoline (oxine) was also obtained from Merck and the solution of oxine in 1-undecanol ($6.8 \times 10^{-3}$ mol $L^{-1}$) was prepared by dissolving the proper amount of oxine in 1-undecanol.

The spectra and absorbance were measured with a double beam spectrophotometer (JASCO, model 7800; Tokyo, Japan) using a glass cell (b = 1 cm) with a volume of approximately 1 mL. The pH measurements were carried out with a Metrohm 691 pH meter (Herisau, Switzerland) using a combined glass calomel electrode.

### Sample preparation

The water samples were filtered through a 0.45-$\mu$m Millipore filter; the pH was adjusted to approximately 5 and was treated according to the given procedure.

### Procedure

The pH and ionic strength of the sample or standard solution with a concentration of vanadium in the range of 3-100 $\mu$g $L^{-1}$ were adjusted to approximately 5 and 0.01 mol $L^{-1}$, using 1% nitric acid (or ammonium hydroxide) and sodium chloride, respectively. Thereafter, 50 mL of this solution was transferred to a vial of approximately 52 mL containing a stirring bar, and 300 $\mu$L of oxine in 1-undecanol ($6.8 \times 10^{-3}$ mol $L^{-1}$) was added. The magnetic stirrer was turned on and the solution was mixed for 20 min at 1000 rpm. In this step, the vanadium ions reacted with oxine and extracted into 1-undecanol. After the extraction time was complete, the sample vial was kept in an ice bath until the organic solvent was solidified. The solidified solvent was then transferred into a conical vial, where it melted immediately. The extract was then diluted to 500 $\mu$L with ethanol and its absorption was measured at 383 nm against a reagent blank treated in the same way.

## Results and discussion

8-Hydroxyquinoline (oxine) is an amphoteric chelon that dissolves in alkaline solutions as the oxinate ion and in acidic solutions as the oxinium cation. Oxine forms a stable chelate with certain metals that are extractable into chloroform and similar solvents. 8-Hydroxyquinoline has been used for the extraction spectrophotometric determination of some metal ions, including vanadium.[39] In the preliminary experiments, it was observed that vanadium from the aqueous phase could be extracted into a small volume of oxine in 1-undecanol. The base of the extraction is the formation of a pink chelate, which has a maximum absorption at 383 nm (Figure 1). To attain a high enrichment factor, the influence of different parameters that affect the chelate formation and the extraction conditions were optimized in a univariable approach. Furthermore, the extraction efficiency and enrichment factor were calculated according to Eqs. (1) and (2), as described before.[30–33]

$$\text{Extraction efficiency} = (C_o \times V_o / C_{aq} \times V_{aq}) \times 100 \quad (1)$$

$$\text{Enrichment factor} = C_o / C_{aq} \quad (2)$$

Here, $V_o$, $C_o$ and $V_{aq}$, $C_{aq}$ are the volume and concentration of the analyte in the organic and the initial aqueous phases, respectively. $C_o$ was calculated from the calibration graph of the standard solution of the relevant chelate of vanadium in ethanol.

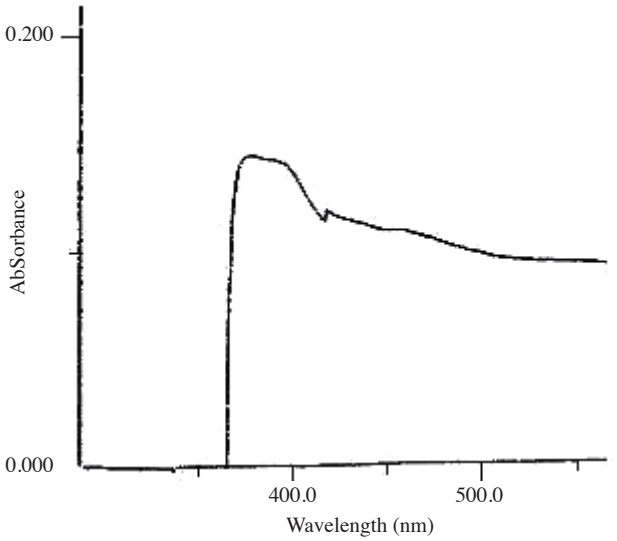


**Figure 1.** Absorption spectrum of vanadium-oxine chelate.

## Selection of organic solvent

The extracting solvent for SFODME must satisfy several requirements. It should have low volatility, low toxicity, low water solubility, and a melting point near room temperature (10-30 °C), and it must not interfere in the analytical techniques used for the determination of analytes. According to these criteria, several extracting solvents, including 1-undecanol (mp 13-15 °C), 2-dodecanol (mp 22-24 °C), 1,10-dichlorodecane (mp 14-16 °C), and n-hexadecane (mp 18 °C), were investigated. The order of extraction efficiency was found to be 1-undecanol > 2-dodecanol > 1,10-dichlorodecane > n-hexadecane. According to the LLE equation, the rate of transport of analyte into the organic phase is directly related to the interfacial area between the 2 liquid phases. As the melting point of 2-dodecanol is close to room temperature, it did not disperse properly in the aqueous solution; thus, its interfacial area was lower, and under a fixed extraction time, the amount of chelate extracted was lower. The lower extraction efficiency of 1,10-dichlorodecane and n-hexadecane in comparison to 1-undecanol is due to their lower polarities. Thus, in the present study, 1-undecanol was selected as an extracting solvent because of its sensitivity, stability, low water solubility, low vapor pressure, and lower price.

## Effect of pH

The separation and preconcentration of metal ions by SFODME involves the formation of chelates with sufficient hydrophobicity to be extracted into small volumes of the organic phase. It is obvious that the sample's pH has a unique role in the formation of vanadium oxine chelate and its subsequent extraction. Therefore, the influence of pH on the extraction of 0.5 $\mu$g of vanadium from 50 mL of aqueous phase into 300 $\mu$L of 1-undecanol containing oxine ($6.8 \times 10^{-3}$ mol $L^{-1}$) was studied in the pH range of 1-9. The pH was adjusted by using

either diluted nitric acid or a sodium hydroxide solution. Figure 2 shows the influence of pH on the analytical signal absorbance. As is shown, the extraction efficiency of vanadium with oxine into 1-undecanol is maximized in the pH range of 4-6. The decrease in extraction efficiency at lower or higher pH levels is due to the amphoteric character of oxine; thus, its distribution between water and organic solvents is strongly dependent on the pH of the aqueous phase. Accordingly, a pH of approximately 5 was selected for subsequent work and real sample analysis.

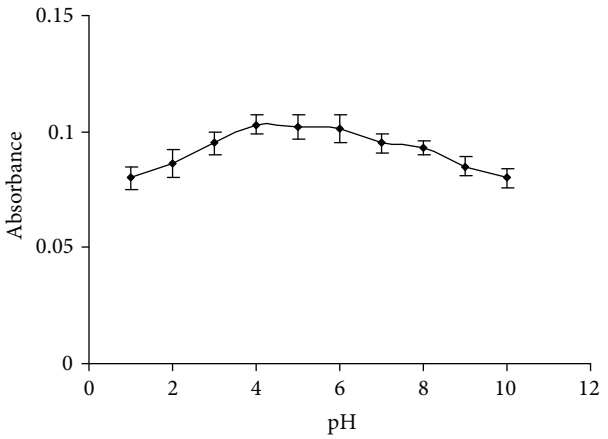


**Figure 2.** Effect of pH on the extraction of vanadium by SFODME method. Extraction conditions: sample volume, 50 mL; vanadium concentration, 10 $\mu$g $L^{-1}$; organic phase volume, 300 $\mu$L; oxine concentration, 6.8 $\times$ $10^{-3}$ mol $L^{-1}$; extraction time, 20 min.

## Effect of concentration of oxine

The efficiency of analyte extraction is dependent on the distribution ratio of the metal chelate between the 2 phases. At a constant aqueous phase pH, up to the solubility limit of the chelate in the organic phase, the value of the distribution ratio and consequently the extraction efficiency will increase as the concentration of the chelate increases.[40] Therefore, the influence of the oxine concentration on the extraction efficiency was studied by varying its concentration between 4.0 $\times$ $10^{-3}$ and 2.0 $\times$ $10^{-2}$ mol $L^{-1}$. As shown in Figure 3, the absorbance signal was increased when the oxine concentration was increased up to 6.0 $\times$ $10^{-3}$ mol $L^{-1}$, and after that the absorbance and thus the extraction efficiency remained nearly constant. A concentration of 6.0 $\times$ $10^{-3}$ mol $L^{-1}$ of oxine was selected as optimum for further studies.

## Effect of extraction time and stirring rate

Extraction time is an important factor influencing the extraction efficiency and speed of analysis. In order to have good precision, sensitivity, and speed, it is necessary to select an extraction time that guarantees the achievement of equilibrium between the aqueous and organic phases. The effect of extraction time on the extraction efficiency was examined by varying the extraction time from 15 to 60 min at constant experimental conditions. The results showed that the formation of chelate and its extraction was relatively fast, and after 20

min, the absorbance signal of vanadium was independent of extraction time (Figure 4). An optimum stirring period of 20 min was selected.

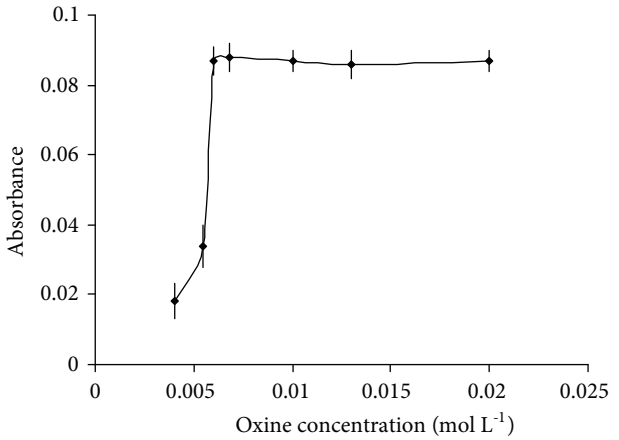


**Figure 3**. Effect of oxine concentration on the extraction of vanadium by SFODME method. Extraction conditions: sample volume, 50 mL; vanadium concentration, 10 $\mu$g $L^{-1}$; organic phase volume, 300 $\mu$L; pH, approximately 5; extraction time, 20 min.

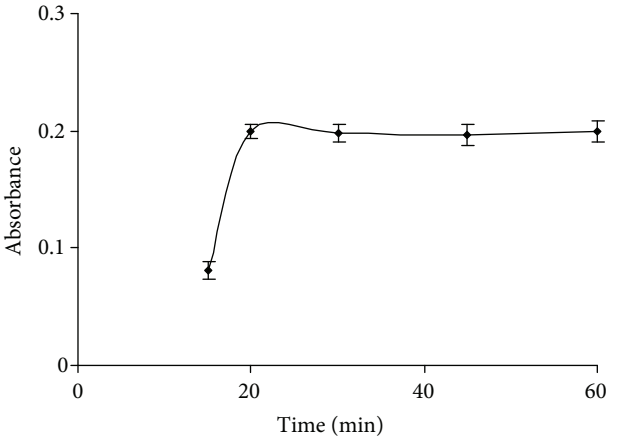


**Figure 4.** Effect of time on the extraction of vanadium by SFODME method. Extraction conditions: sample volume, 50 mL; vanadium concentration, 10 $\mu$g $L^{-1}$; organic phase volume, 300 $\mu$L; oxine concentration, $6.8 \times 10^{-3}$ mol $L^{-1}$; NaCl concentration, 0.01 mol $L^{-1}$; pH, approximately 5.

The stirring rate is another important parameter of SFODME that enhances the kinetics of chelate formation and its extraction. According to the film theory of convective-diffusive mass transfer in the LPME system, the faster the sample agitation, the lower the thickness of diffusion film in the aqueous phase and consequently the higher the mass-transfer coefficient in the aqueous phase.[20] In this study, the stirring rate was varied between 500-1250 rpm at a constant extraction time of 20 min. The extraction efficiency was found to increase as the stirring rate was increased up to 1000 rpm, and then it remained constant. Hence, a stirring rate of 1000 rpm was adopted for further study.

## Effect of temperature

The magnitude of equilibrium constants that are involved in the extraction procedure are temperature-dependent, so temperature is a factor that affects the percentage of the metal ion that is extracted. In the present study, the effect of the sample solution's temperature on the extraction efficiency was studied at different temperature (18, 25, 30, and 40 °C). The experimental results showed that the extraction efficiency was constant at temperatures higher than 25 °C. The lower extraction efficiency at 18 °C may be due to the increase in viscosity and the decrease in the dispersion of 1-undecanol at a temperature close to its melting point.

## Effect of salt

In order to investigate the effect of ionic strength on the SFODME performance, several experiments were performed with different NaCl concentrations (0.0-1.0 mol $L^{-1}$) while keeping other experimental parameters constant. The results confirmed that salt addition up to a concentration of 0.005 mol $L^{-1}$ caused an increase in absorbance, and then it leveled off. This observation suggests the possibility of using this method for the separation and determination of vanadium from saline solutions.

## Effect of extraction and sample volume

Demonstration of the preconcentration capability of the SFODME system is an important aspect of the method's development. An increase in the ratio of the volume of the aqueous phase to the organic phase will increase the preconcentration factor, but it may reduce the extraction efficiency in a given extraction time. For this purpose, the volume of extracting solvent was varied from 150-400 $\mu$L, the extraction was done, the extract was diluted to 500 $\mu$L with ethanol, and its absorption was measured against a reagent blank. The results (Figure 5) showed that by increasing the volume of 1-undecanol up to 300 $\mu$L, the extraction efficiency was increased and then became constant at higher volumes of extracting solvent. Therefore, an organic volume of 300 $\mu$L was selected as optimum.

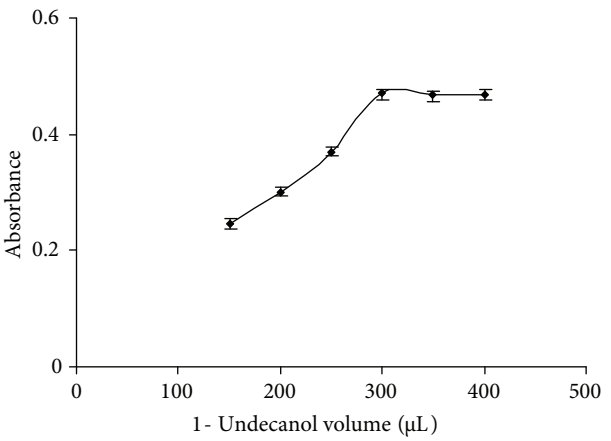


**Figure 5.** Effect of volume of organic phase on extraction of vanadium by SFODME method. Extraction conditions: sample volume, 50 mL; vanadium concentration, 10 $\mu$g $L^{-1}$; organic phase volume, 300 $\mu$L; oxine concentration, $6.8 \times 10^{-3}$ mol $L^{-1}$; extraction time, 20 min; NaCl concentration, 0.01 mol $L^{-1}$; pH, approximately 5.

Furthermore, in order to explore the possibility of enriching low concentrations of the vanadium from a large volume, the effect of sample volume on extraction of 0.5 $\mu$g of vanadium from different aqueous volumes (20-60 mL) at optimum conditions was examined using a properly sized vial. The extract was then separated and diluted to 500 $\mu$L with ethanol and the concentration of the analyte was determined by measuring its absorption against a reagent blank in 383 nm. The results showed that quantitative recovery ($>95\%$) was obtained for sample volumes up to 50 mL.

## Interference study

The sensitivity and utility of the SFODME in the preconcentration of vanadium in the presence of potential interfering ions in natural water samples at an initial mole ratio of 1000 (ion/vanadium) was examined. When interference was observed, the concentration of the interfering ion was lowered. The results of this investigation are given in Table 1. A relative error of less than 5% was considered to be within the range of experimental error. As is shown, the presence of high concentrations of alkali, alkali earth cations, and chloride, sulfate, and nitrate anions did not cause interference, but the presence of some metals that form oxinates in a slightly acidic medium did interfere in the determination of vanadium. However, addition of EDTA ($1 \times 10^{-4}$ mol $L^{-1}$) increased the selectivity of the system, and the tolerance limit of $Zn^{2+}$, $Ni^{2+}$, and $Co^{2+}$ ions in the presence of EDTA was found to 200, 250, and 200, respectively. The interference of $Fe^{+3}$, $Al^{+3}$, and $Cu^{+2}$

**Table 1.** Effect of diverse ions on the recovery of vanadium. Concentrated volume, 50 mL; vanadium concentration, 20 $\mu$g $L^{-1}$.

| Ion | Molar ratio (ion/V) | Recovery (%) |
|---|---|---|
| $Ca^{2+}$ | 1000 | 96 ± 2 |
| $K^{+}$ | 1000 | 102 ± 2 |
| $Zn^{2+}$ | 200[a] | 98 ± 3 |
| $Ni^{2+}$ | 250[a] | 97 ± 1 |
| $Co^{2+}$ | 200[a] | 96 ± 2 |
| $Mg^{2+}$ | 100 | 95 ± 3 |
| $Cr^{3+}$ | 100 | 104 ± 2 |
| $Fe^{3+}$ | 10[b] | 98 ± 2 |
| $Al^{3+}$ | 10[b] | 99 ± 3 |
| $Cu^{2+}$ | 10[b] | 97 ± 1 |
| $Ba^{2+}$ | 1000 | 103 ± 2 |
| $Na^{+}$ | 1000 | 99 ± 2 |
| $Cl^{-}$ | 1000 | 99 ± 2 |
| $SO_4^{2-}$ | 1000 | 103 ± 3 |
| $NO_3^{-}$ | 1000 | 97 ± 1 |

[a]In the presence of EDTA ($1.0 \times 10^{-4}$ mol $L^{-1}$); [b]after back extraction at pH = 9.

was eliminated according to the procedure described in the liquid-liquid extraction of vanadium with oxine;[39] in other words, the 1-undecanol extract that contained the vanadium and the interfering ions was shaken with an alkali solution (pH approximately 9), thereby stripping the vanadium into the aqueous phase and leaving behind the other metals in the 1-undecanol. The pH of the aqueous phase was then adjusted to approximately 5 and the vanadium was extracted and determined according to the given procedure. Thus, in this manner, the method becomes specific for vanadium.

## Figures of merit

Under the optimum conditions described above, the analytical performance characteristics of the proposed method are listed in Table 2. The calibration graph was linear in the vanadium concentration range of 3-100 $\mu$g $L^{-1}$ and had an equation of A = 0.009C + 0.080 with $r^2$ = 0.9997, where A is the absorbance of the extract and C is the concentration of vanadium ($\mu$g $L^{-1}$) in the initial solution. The limit of detection, defined as DL = $3S_B/m$ (where DL, $S_B$, and m are the limit of detection, the standard deviation of the blank, and the slope of the calibration curve, respectively), was 0.94 $\mu$g $L^{-1}$. The relative standard deviation (RSD) for 7 replicate measurements of 10 $\mu$g $L^{-1}$ of vanadium was 3.9%. The enhancement factor, calculated as the ratio of the slopes of the calibration graphs with and without preconcentration, was about 38; however, a higher enrichment factor can be obtained by the use of a microcell for the measurement of the absorbance of the analyte.

**Table 2.** Analytical characteristics of SFODME-spectrophotometry for determination of vanadium.

| Parameter | Analytical feature |
|---|---|
| Linear range (µg $L^{-1}$) | 3-100 |
| $r^2$ | 0.9997 |
| Limit of detection (µg $L^{-1}$) | 0.94 |
| RSD % (n = 7, 10 µg $L^{-1}$) | 3.9 |
| Enhancement factor[a] | 38 |
| Sample volume (mL) | 50 |

[a]Enhancement factor calculated as the ratio of the slope of the preconcentration samples to that obtained without preconcentration.

## Natural water analysis

To test the reliability of the recommended procedure, the method was applied to the determination of vanadium in tap, well, river, and sea water samples. For this purpose, a volume of 50 mL of each sample was preconcentrated with 300 $\mu$L of a solution of oxine ($6.8\times10^{-3}$ mol $L^{-1}$) in 1-undecanol according to the proposed method. The results are given in Table 3. The accuracy of the method was verified by the analysis of the samples spiked with 2 known levels of vanadium and by comparing the results with the data obtained by means of independent analysis of the samples with graphite furnace atomic absorption spectrometry (GFAAS) under

the conditions recommended by the manufacturer. The relative recoveries at the spiking levels were in the range of 96%-102%, and as the results of GFAAS show, the concentration of vanadium in these sample was lower than the detection limit of the developed method; in other words, at a 95% confidence level, there was no significant difference between these results. This demonstrates that the matrices of the tap, well, river, and sea water samples had no effect on the SFODME method for the determination of vanadium.

**Table 3.** Determination of vanadium in tap, well, river, and sea water samples.

| Sample | Added vanadium ($\mu g\ L^{-1}$) | Found vanadium Mean ± SD[a] ($\mu g\ L^{-1}$) | Recovery (%) | GFAAS Mean ± SD[a] ($\mu g\ L^{-1}$) |
|---|---|---|---|---|
| Tap water | - | ND[b] | | 0.28 ± 0.01 |
| | 10 | 10.2 ± 0.3 | 102 | |
| | 40 | 38.3 ± 0.8 | 96 | |
| Well water | - | ND[b] | | 0.44 ± 0.02 |
| | 10 | 9.8 ± 0.3 | 98 | |
| | 40 | 38.8 ± 0.6 | 97 | |
| River water | - | ND[b] | | 0.21 ± 0.01 |
| | 10 | 10.1 ± 0.4 | 101 | |
| | 40 | 39.0 ± 0.8 | 98 | |
| Sea water[c] | - | ND[b] | | 0.68 ± 0.01 |
| | 10 | 9.7 ± 0.4 | 97 | |
| | 40 | 40.4 ± 0.7 | 101 | |

[a]Standard deviation (n = 3); [b]not detected, [c]after back extraction at pH = 9 and in the presence of EDTA ($1 \times 10^{-4}$ mol $L^{-1}$).

## Conclusion

The results of this investigation demonstrate that solidified floating organic drop microextraction (SFODME) combined with spectrophotometry can be used as a simple and powerful tool for the preconcentration and determination of metal ions from aqueous samples. It has also been shown that the colored complex of vanadium with oxine can be extracted into 1-undecanol. Furthermore, the proposed SFODME method permits the effective separation and preconcentration of vanadium and final determination by spectrophotometry in several categories of natural waters. The sample preparation time as well as the consumption of organic solvent is minimized and the figures of merit of the developed method are comparable to other reported preconcentration-spectrophotometry methods for the determination of vanadium.[11–14]

The main benefits of the system are the enhancement of spectrophotometric sensitivity, minimum organic

solvent consumption, rejection of matrix constituent, low cost, and high enrichment factor. Future work will be directed toward the extraction of other metals using various ligands and the assessment of the capability of the method for determination of other metal ions.

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