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# Nonaqueous Catalytic Fluorometric Trace Determination of Vanadium Based on the Pyronine B–Hydrogen Peroxide Reaction and Flow Injection after Cloud Point Extraction

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15771, Athens, Greece.

**The catalytic effect of vanadium on the pyronine B–H<sub>2</sub>O<sub>2</sub> system is examined. Enhancement of the catalytic reaction rate along with the efficiency and selectivity against vanadium is achieved in a formic acid environment in the presence of a nonionic surfactant (Triton X-114). Elimination of drastic interference caused by inorganic acids and aqueous matrix along with a 50-fold preconcentration of vanadium are facilitated through cloud point extraction of its neutral complex with 8-quinolinol in an acidic solution. Subsequent flow injection analysis (FIA) with fluorometric detection renders the proposed method ideal for selective and cost-effective determination of as little as 0.020 µg L<sup>-1</sup> vanadium in environmental, biological, and food substrates. The preconcentration step can be applied simultaneously to multiple samples, allowing for massive preparation prior to analysis, compensating, thus, for the time-consuming procedure.**

Vanadium is an essential trace element that plays a functional role in environmental and biological systems. Its presence is widespread in water samples as well as in human and animal tissues and organs. It is also a constituent of commercial dietary supplements.<sup>1–4</sup>

Many analytical methods have been developed for its determination, including spectrophotometry,<sup>5–7</sup> fluorometry<sup>8,9</sup> and X-ray

fluorometry,<sup>10</sup> inductively coupled plasma mass spectrometry,<sup>11,12</sup> electron spin resonance spectrometry,<sup>13</sup> atomic absorption<sup>14,15</sup> and emission spectrometry,<sup>16</sup> chromatography,<sup>17</sup> neutron activation analysis,<sup>18,4</sup> thermometry,<sup>19</sup> and electrochemistry.<sup>20</sup> A substantial number of papers published hitherto are based on the catalytic effect of vanadium upon several redox systems, especially those in which an organic compound undergoes oxidation by H<sub>2</sub>O<sub>2</sub>.<sup>21–23</sup>

Although some selective catalytic reactions have been proposed for vanadium, such as those based on the oxidation of gallic acid by bromate,<sup>24,25</sup> there are still selectivity problems that appear in a lot of cases. Several metallic species, such as copper, cerium, and especially oxoanions, such as molybdates, chromates, and permanganates, have been reported to seriously interfere with the catalytic determination of vanadium, because they have similar behavior. Further interference is caused by nonmetallic anions such as nitrites, nitrates, and halides. Although proper masking produces sufficient selectivity, it may lead to a rise in detection limits.

To avoid such interferences, several extraction schemes using various complexing agents and organic solvents have been proposed,<sup>26,27</sup> resulting in increased selectivity and detectability

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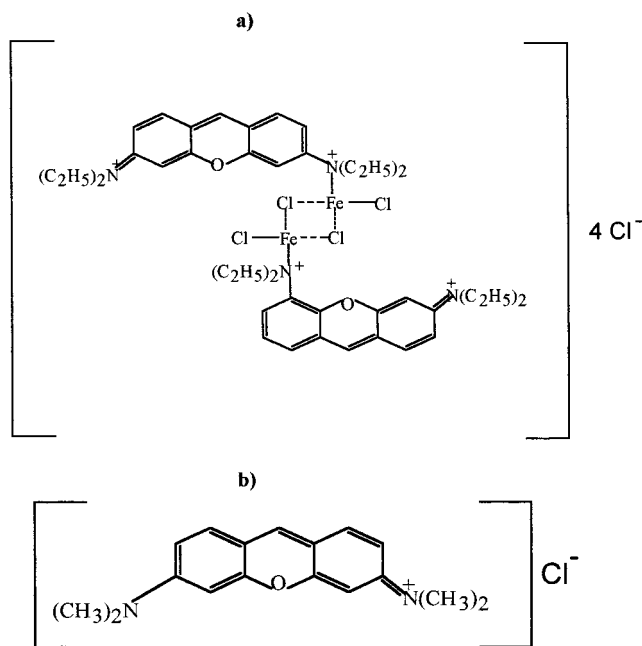


Figure 1. Structure of pyronine B(a) and pyronine Y(b).

as a result of the preconcentration. However, a large volume of sample (100–500 mL) is required along with an increased analysis time, cost, and risk of using high volumes of flammable and hazardous materials.

The proposed method is based on the preconcentration of vanadium using the so-called cloud point extraction procedure,<sup>28</sup> and its selective catalytic effect on the pyronine B–H<sub>2</sub>O<sub>2</sub> reaction in formic acid medium. The analytical reaction is monitored fluorometrically (decrease of pyronine B fluorescence) using  $\lambda_{\text{ex}}$  = 345 nm and  $\lambda_{\text{em}}$  = 565 nm in a flow injection system.

Pyronine B is an organic dye (CI 45 010) with two Fe(II) atoms in its molecule (Figure 1a) and is used as a stain for bacteria, molds, and ribonucleic acids<sup>29,30</sup> without any other analytical application. Pyronine G or Y (a dye (CI 45 005) similar to the monomer of pyronine B) (Figure 1b) has been used in some catalytic analytical schemes.<sup>31,32</sup>

The preconcentration of vanadium is based on the formation of a neutral, hydrophobic complex with 8-quinolinol, which is subsequently trapped in the micellar phase of a nonionic surfactant (Triton X-114). Utilizing the thermally induced phase extraction–separation process known as cloud point extraction (CPE),<sup>28</sup> the analyte is highly preconcentrated and free of interferences in a very small micellar phase.

Micellar systems have been widely used in analytical schemes because of their unique microenvironment, which is used for effective separation as alternatives for the conventional solvent extraction schemes.<sup>33–35</sup>

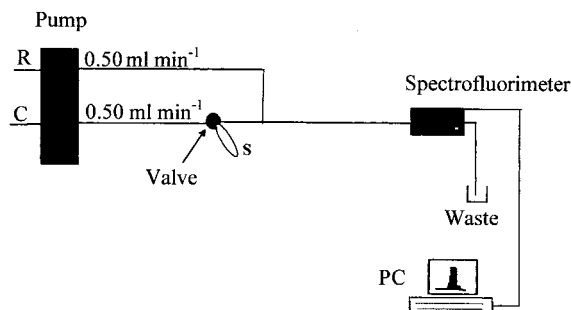


Figure 2. FIA manifold used for the determination of vanadium. C = carrier (0.25 mM pyronine B in 90% formic aqueous solution), R = reagent (200 mM H<sub>2</sub>O<sub>2</sub> in 90% formic aqueous solution), S = sample loop (20  $\mu$ L).

## EXPERIMENTAL SECTION

**Reagents.** All of the reagents were of analytical reagent grade, free from vanadium traces. Standard stock solutions of vanadium(IV) and vanadium(V) were prepared by dissolving appropriate amounts of VOSO<sub>4</sub>·5H<sub>2</sub>O and NH<sub>4</sub>VO<sub>3</sub> (Merck) in double-distilled water. Working standard solutions in the range of 0.02–2.0  $\mu$ g/L were prepared daily at the appropriate dilution. Because of its low solubility in water, 8-quinolinol (Aldrich) was dissolved in methanol 99.8% to prepare a 0.1 mol L<sup>−1</sup> solution. Triton X-114 was used without further purification to prepare a 10% w/v aqueous solution. Formic acid 98–100% (Merck) was used to prepare the carrier solution and for breaking the micellar phase. Pyronine B (Fluka) 0.001 mol L<sup>−1</sup> stock solution was prepared by dissolving the requisite amount of pyronine B in formic acid. The solutions of various cations and anions used for the interference study were obtained from the respective inorganic salts (Aldrich) by proper dilution in distilled water.

**Apparatus.** The FIA manifold designed for the catalytic spectrofluorometric determination of vanadium is shown in Figure 2. It consisted of a four-way pneumatically actuated injection valve (Rheodyne, type 50 Teflon, Cotati, CA), a multichannel peristaltic pump (Ismatec, Glattburg-Zurich, Switzerland), and a spectrofluorometer (RF-551, Shimadzu, Japan), equipped with a 12  $\mu$ L flow-through measurement cell. To be compatible with formic acid solutions, all tubing was made from Tygon.

Collection, processing, and treatment of analytical data were performed by computer, as described in previous work.<sup>36</sup> Kinetics studies were carried out spectrophotometrically using a stopped-flow apparatus (the Bio sequential SX17MV) made by Applied Photophysics, Ltd., England, connected to a spectrophotometer (Varian E-109). pH measurements were carried out using a pH meter (PHM83 Radiometer, Copenhagen).

**Procedure.** Ten mL of standard or sample solutions in the concentration range 0.02–2.00  $\mu$ g L<sup>−1</sup> of vanadium was transferred into a centrifuge tube. A 0.100-mL portion of 0.100 mol L<sup>−1</sup> 8-quinolinol solution and 0.075 mL of Triton X-114 10% w/v solution

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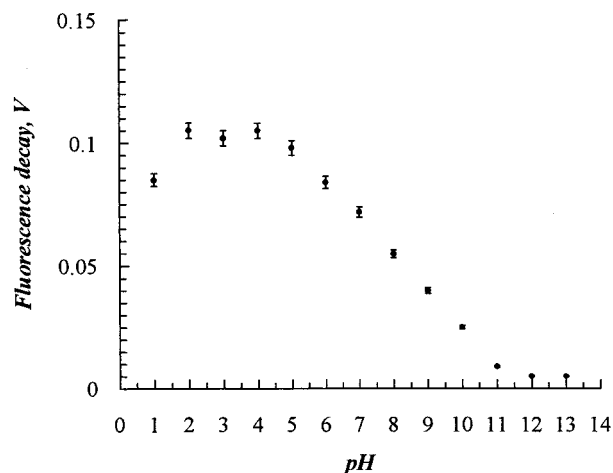


Figure 3. Effect of CPE-pH on the analytical response for  $0.4 \mu\text{g L}^{-1}$  vanadium concentration; other conditions as described in the procedure.

were then added, and the pH was adjusted to 2.5 using dilute HCl and a pH-meter. The solution was heated in a waterbath for 10 min at  $80^\circ\text{C}$  and centrifuged at 4000 rpm for 5 min. After cooling in an icebath for 5 min, the supernatant aqueous phase was discarded, and the remaining micellar phase was redissolved in  $200 \mu\text{L}$  of formic acid (90% v/v). The resulting solution was injected into the FIA manifold, and the decay of pyronine's fluorescence induced by the catalytic action of vanadium (V) was monitored, thereby obtaining FI peaks. The overall time required for the cloud point procedure was  $\sim 20$  min, but another 5 min was required to complete the measurement.

## RESULTS AND DISCUSSION

**Optimization of Cloud Point Extraction.** In the so-called cloud point extraction, several parameters play a substantial role in the performance of the surfactant system that is used and its ability to aggregate, thus entrapping the analyte species. pH, surfactant type and concentration, temperature, time, and complexing reagent concentration were studied for optimum analytical signal (negative fluorescence peak).

**pH.** The CPE procedure was carried out in the pH range 1–13 using diluted HCl and NaOH for the adjustment. The results shown in Figure 3 reveal that the optimum pH is in the range of 2–4, at which the vanadium–8-quinolinol complex is neutral. At higher pH values, the complex possesses a negative charge, and it cannot be entrapped in the nonionic micelles. This behavior is in accordance with the results of previous studies.<sup>27</sup>

**8-Quinolinol Concentration.** The effect of 8-quinolinol concentration on the analytical performance was studied using a  $0.400 \mu\text{g L}^{-1}$  vanadium solution and various concentrations of the reagent in the range of 0.01–2 mM. As is shown in Figure 4, a final concentration of 1 mM was sufficient for optimum results. This concentration ensures sufficient excess to compensate for any consumption of the reagent by other metals.

**Surfactant Type and Concentration.** Figure 5 shows the effect of the amount of the surfactant Triton X-114 ( $\mu\text{L}$  of a 10% w/v aqueous solution) on the analytical performance. It is revealed that an amount of 5–10 mg of Triton X-114 (50–100  $\mu\text{L}$  of a 10%

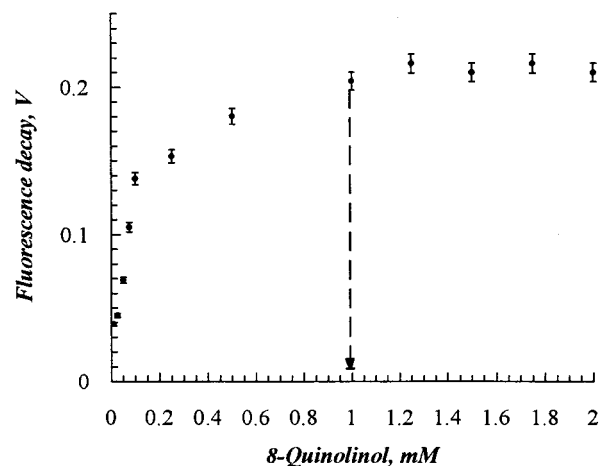


Figure 4. Effect of 8-quinolinol concentration on the extraction of  $0.4 \mu\text{g L}^{-1}$  vanadium; other conditions as described in the procedure.

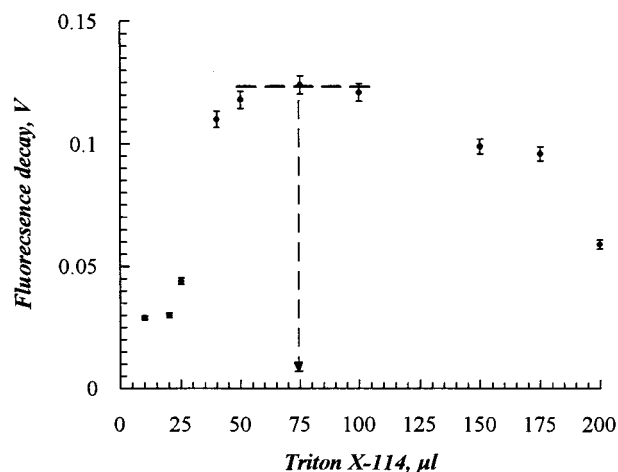


Figure 5. Effect of the amount of Triton X-114 (10% w/v solution) on the cloud point extraction efficiency of  $0.4 \mu\text{g L}^{-1}$  vanadium; other conditions as described in the procedure.

w/v solution) in 10 mL sample volume, is capable of extracting up to  $50 \mu\text{g L}^{-1}$  of vanadium. For higher concentrations, larger volumes of surfactant need to be used, but the detection limit will rise accordingly.

**Other Parameters.** The effect of ionic strength at the analytical signal was examined by establishing various concentrations of KCl in the range 0–200 mM in the sample solutions. No effect was observed.

The temperature at which the sample solution is heated was examined in the range  $30$ – $100^\circ\text{C}$ . As is shown in Figure 6, a plateau in the analytical signal was obtained from  $45$  to  $100^\circ\text{C}$ . An optimum of  $80^\circ\text{C}$  was selected.

The volume of formic acid that was used to redissolve the micellar phase with the preconcentrated vanadium was studied in the range of  $25$ – $500 \mu\text{L}$ . A  $200\text{-}\mu\text{L}$  volume was finally chosen as optimum.

The parameters concerning the analytical system were also studied thoroughly. Aqueous solutions of pyronine B exhibit a pink color and minimal fluorescence. In the presence of formic acid, a shift toward orange is observed, and fluorescence develops, reaching a maximum in a 40% formic acid solution. (Figure 7).

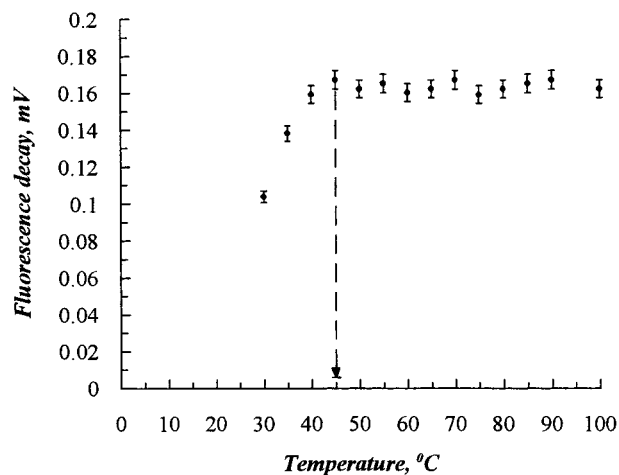


Figure 6. Effect of temperature on the analytical response for  $0.4 \mu\text{g L}^{-1}$  vanadium; other conditions as described in the procedure.

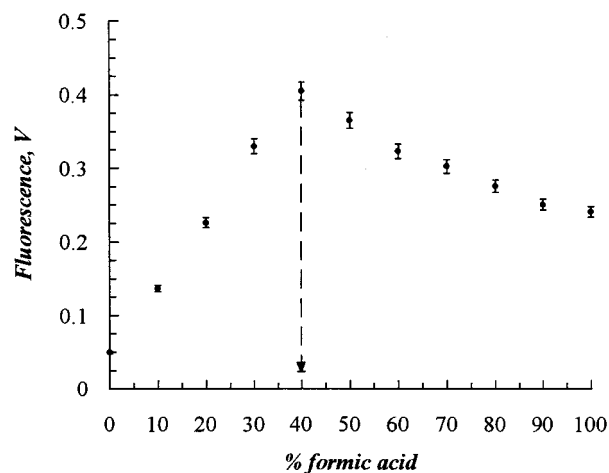


Figure 7. Effect of formic acid on the fluorescence intensity of pyronine B.

The fluorescent species of pyronine B in the presence of formic acid exhibits a very interesting redox behavior. Kinetics experiments carried out spectrophotometrically using the stopped-flow technique (Figure 8) showed that in a formic acid environment ( $>90\%$ ), the pyronine B– $\text{H}_2\text{O}_2$  system is remarkably catalyzed by vanadium, resulting in a decrease of both absorbance and fluorescence. This catalytic effect tends to retreat in formic acid  $<80\%$ , and it completely disappears in more aqueous environments. Surprisingly, though, powerful oxidants and, therefore, possible interfering agents such as Cr(VI) and Mo(VI) have no catalytic effect under these experimental conditions, even in a 500:1 ratio. The presence of Triton X-114, used in the cloud point extraction procedure, plays a substantial role in the kinetic procedure because it enhances the fluorescence intensity and accelerates the rate of the catalytic reaction. The optimized analytical parameters are presented in Table 1.

**Evaluation of the Method.** Table 2 features the analytical characteristics of the method. Under the specified experimental conditions, the calibration curve is rectilinear up to  $10 \mu\text{g L}^{-1}$  of vanadium(IV or V) with a quantitation limit of  $0.02 \mu\text{g L}^{-1}$ . The extraction coefficient holds an extremely high value ( $\sim 1$ ) because of the quantitative extraction of vanadium(V) quinolate into the surfactant-rich phase. The preconcentration factor, defined as the

Table 1. Optimized Chemical and FIA Parameters for the Catalytic Determination of Vanadium

parameter	studied range	selected optimum value
sample loop, $\mu\text{L}$	50–500	20
overall flow rate, $\text{mL min}^{-1}$	0.5–1.5	1.0
reagent flow rate, $\text{mL min}^{-1}$	0.25–0.75	0.50
temp, $^{\circ}\text{C}$	20–70	25.0
Reagents		
pyronine B, mM	0.005–1	0.25
$\text{H}_2\text{O}_2$ , mM	0.001–2000	200
$\text{HCOOH:H}_2\text{O}$ (v:v)	0:100–100:0	90:10

Table 2. Analytical Features of the Proposed Method

parameter	value
phase volume ratio <sup>a</sup>	0.010
preconcentration factor <sup>b</sup>	50
extraction coefficient <sup>c</sup>	$\sim 1$
LOD <sup>d</sup> , $\mu\text{g L}^{-1}$	0.007
QOD <sup>e</sup> , $\mu\text{g L}^{-1}$	0.02
RSD, %	1.8
regression eq	$I(\text{mV}) = (6.9 \pm 0.6) + (262 \pm 4)C (\mu\text{g L}^{-1})$
correlation coefficient, $r$	0.9996
linear range <sup>f</sup> , $\mu\text{g L}^{-1}$	0.02–10.0

<sup>a</sup> The ratio of the final volume of the surfactant-rich phase to that of the aqueous phase. <sup>b</sup> The ratio of the concentration of analyte without the application of CPE technique to that after the CPE giving the same analytical response. <sup>c</sup> The ratio of the quantity of metal in the surfactant-rich phase to that in the original solution. <sup>d</sup> Limit of detection based on  $S/N = 3$ . <sup>e</sup> Quantitation limit based on  $S/N = 10$ . <sup>f</sup> Depending on the selected surfactant concentration.

ratio of the concentration of analyte after preconcentration to that prior to preconcentration, which gives the same fluorescence inverted peak height, reaches a value of 50. The limits of detection and quantitation are sufficiently low as compared to those attained by kinetic, spectrophotometric, and even atomic absorption methods with and without preconcentration of samples.<sup>6,7,15,16,21</sup>

The time of analysis, although it may seem long, is suitable for massive analysis of multiple samples. Depending on the capacity of the centrifuge, more than 40 samples can be prepared in less than 1 h and analyzed by means of the well-established FIA rapidity and reproducibility.

**Interference Study.** The combination of the selective CPE with the selective catalytic reaction seriously decreases any interference from metal species and inorganic anions, acids, and oxo-anions. CPE procedure selectively extracts only metals forming neutral complexes with 8-quinolinol, and the selective formic acid environment diminishes the interference by other metals that might also be extracted during the CPE procedure. Experiments conducted using a  $0.4 \mu\text{g L}^{-1}$  vanadium(V) solution showed no interference by a 10 000-fold excess of Na(I), K(I), Ca(II), Mg(II), chloride, nitrite, EDTA, sulfate, phosphate, citrate, and tartrate, a 1000-fold excess of Fe(III), Al(III), Cu(II), Mn(II), Zn(II), Cr(III), Co(III), Ni(II), Cd(II), and Pb(II), and a 500-fold excess of chromates, permanganates, and molybdates.

**Mechanism of Vanadium Catalysis.** The catalytic activity of vanadium species stems from the formation of peroxyvanadate



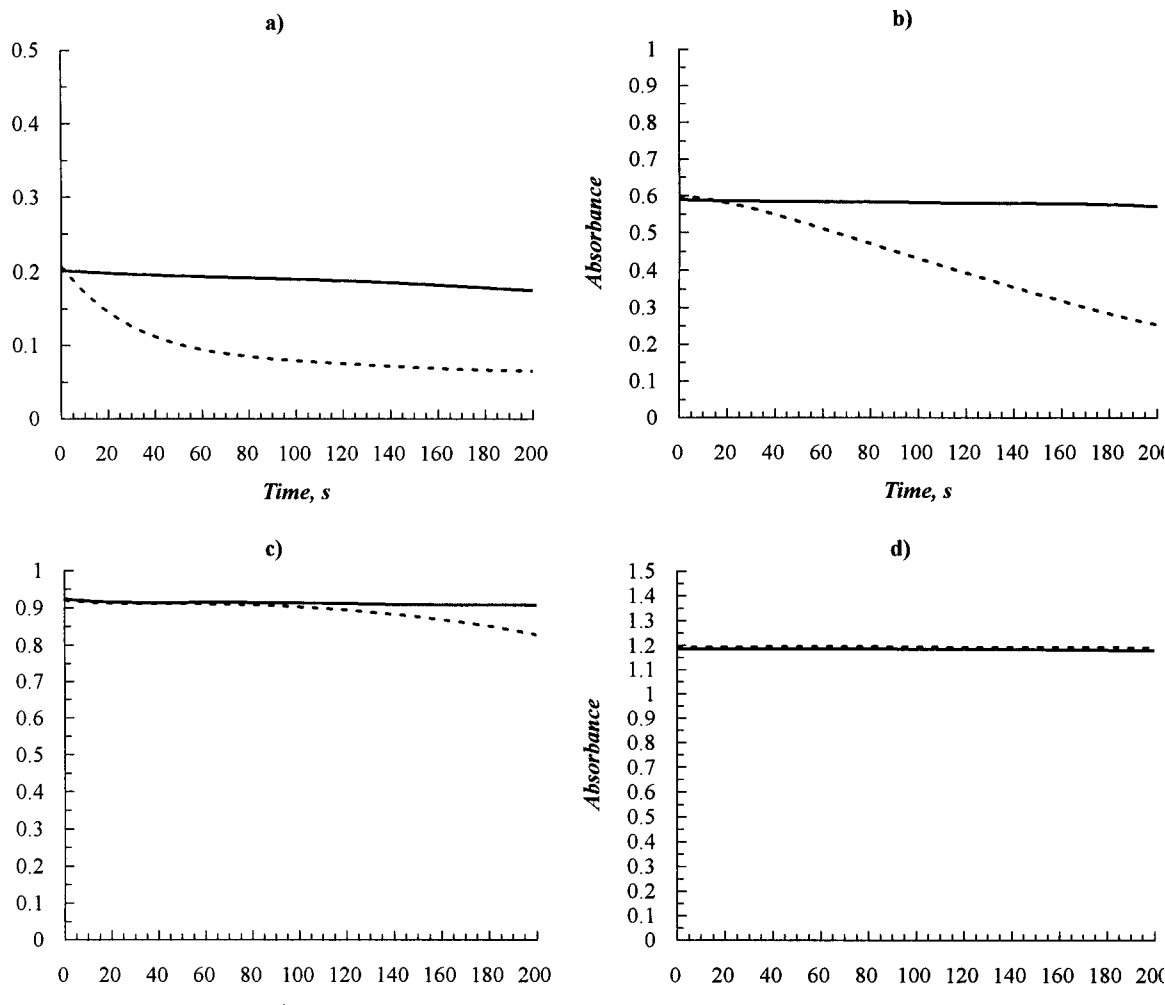
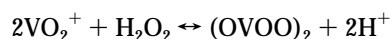
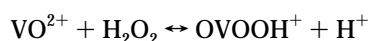


Figure 8. Kinetic data exhibiting the effect of formic acid on the catalytic action of vanadium on the pyronine B-H<sub>2</sub>O<sub>2</sub> system: (a) 100% formic acid, (b) 90% formic acid (maximum catalysis), (c) 80% formic acid, (d) 70% formic acid (no catalytic action); —, noncatalyzed reaction; ---, catalyzed reaction.

complexes (OVOOH<sup>+</sup>), which amplify the oxidative capacity of H<sub>2</sub>O<sub>2</sub> significantly.<sup>37</sup>



On the other hand, the formic acid environment binds hydrogen peroxide with hydrogen bonds, reducing its oxidative power, which in the presence of mineral acids becomes a powerful oxidant, as is proved by experiments conducted in the presence of sulfuric, nitric and hydrochloric acid. Thus, H<sub>2</sub>O<sub>2</sub> oxidizing efficiency is inhibited, allowing for the catalytic activity of a given metal to prevail.

**Analysis of Real Samples.** Water and hair samples, along with tablets of dietary supplement, were analyzed using the proposed method. Water samples were filtered through a Whatman paper filter to remove the suspended particles and then were subjected to the cloud point extraction, as previously detailed.

Table 3. Analysis of Real and Spiked Samples of Vanadium

sample	concn <sup>a</sup> μg L <sup>-1</sup>	added μg L <sup>-1</sup>	found μg L <sup>-1</sup>	recovery %
tap water	0.20 ± 0.02	0.00	0.20	100
0.05	0.25	100		
0.10	0.305	105		
0.25	0.446	98.4		
tablets	0.50 ± 0.05	0.00	0.50	100
0.1	0.60	100		
0.5	0.98	96		
2.5	3.10	104		
hair	0.54 ± 0.05	0.00	0.55	102
0.07	0.61	100		
0.32	0.88	106		

<sup>a</sup> Determined by graphite furnace atomic absorption spectrometry

Three tablets of a dietary supplement, Centrum, were pulverized and homogenized thoroughly. A 1-g portion of the sample was extracted with 30 mL hot water, and the extracts were filtered through a Whatman paper filter and diluted to 100 mL with distilled water. The extracts were subjected to the cloud point

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preconcentration process, as described above, using the optimal experimental conditions. The hair sample was treated as previously described.<sup>38,39</sup> A 10-mL portion of the solution obtained was subjected to CPE extraction and subsequent measurement. Wherever vanadium was not detected, the samples were spiked with appropriate amounts of metal to simulate real-life situations. The results of the analyses are presented in Table 3.

## CONCLUSIONS

The proposed method is composed of two steps: a cloud point extraction—preconcentration of vanadium and a catalytic spectrofluorometric approach for its measurement. The spectrofluorometric measurement in the formic acid environment offers a

unique selectivity for vanadium against other metals. It cannot be applied to pure aqueous samples, because it is dramatically intercepted by the presence of water, inorganic acids and anions. CPE extraction with 8-quinolinol, on the other hand, relieves the system of the above interference, but it is not selective toward vanadium, because 8-quinolinol reacts easily with a variety of metals. Combination of the two schemes, though, creates a powerful tool for the selective determination of vanadium at ultratrace levels, because it allows for an additional 50-fold preconcentration of vanadium. Therefore, the above method can stand as a cost-effective, selective, and safe alternative to the current methods.

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