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Direct determination of vanadium in high saline produced waters from offshore petroleum exploration by electrothermal atomic absorption spectrometry

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Abstract

The present work reports the development of a methodology for the direct determination of vanadium in high saline waters derived from offshore petroleum exploration employing electrothermal atomic absorption spectrometry. Such waters, usually called produced waters, present complex composition containing various organic and inorganic substances. In order to attain best conditions (highest sensitivity besides lowest background) for the methodology, studies about the effects of several variables (evaluation of pyrolysis and atomization temperatures, type of chemical modifier, concentration of modifier and pyrolysis time) and the convenient calibration strategy were performed. Best conditions were reached with the addition of 10 μg of $NH_4H_2PO_4$ as chemical modifier employing pyrolysis (during 10 s) and atomization temperatures of 1500 and 2700 °C, respectively. Obtained results indicated that, in this kind of sample, vanadium can be determined by standard addition method or employing an external calibration approach with standard solutions prepared in 0.8 mol l^{-1} NaCl medium. In order to evaluate possible matrix interferences, a recovery test was performed with five spiked samples of produced waters. The limit of detection, limit of quantification and relative standard deviation in 0.8 mol l^{-1} NaCl medium were also calculated and the derived values were 1.9 $\mu g\,l^{-1}$, 6.3 $\mu g\,l^{-1}$ and 5.6% (at 10 $\mu g\,l^{-1}$ level), respectively.

Keywords: Vanadium; Produced waters; Electrothermal atomic absorption spectrometry; Chemical modifiers

1. Introduction

In last few decades, the exploration of petroleum in offshore environments has increased in importance due to the fast depletion of the deposits on land. One of the main characteristics of the petroleum exploration in offshore platforms is the large amount of water extracted together with the oil, since the deposits are surrounded by seawater that percolates through sedimentary environment where petroleum is located. Besides, after elapsed a certain time, water is pumped into the well in order to maintain its pressure, enhancing the oil recovery in a process called secondary recovery of petroleum. The water found along with the petroleum in the well is called *formation water* while the *produced water* is the effluent obtained by mixing *formation water* with the water injected into the well [1].

The main features of produced waters obtained in offshore operations is their high salinity and complex composition [2]. Depending on their origin, produced waters can contain a wide range of chemical substances, such as organic salts, aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), heavy metals and occasionally, radioactive materials usually called normally occurred radioactive materials (NORM) [3]. In general, much more water is yielded in an offshore operation than oil. Depending on the dimensions of the reservoir, the explored area and the capacity of the exploration unity, the volume of produced water extracted can reach around 2000–40,000 m^3/day [4]. This fact can be considered a great problem in the petroleum industry because this water must be characterized and treated before discharging, including the evaluation of metals concentration. However, this task is complex and laborious because of the high salinity of samples, which makes it difficult to employ current techniques utilizing trace level determination of metals such as ICP-MS, ICP-OES or even ETAAS.

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Speaking of vanadium, certainly ETAAS is one of the most popular analytical techniques used for its determination in different kinds of samples, such as soil extracts [5], biological fluids [6–12], oils [13–15], wines [16], acid digests from biological materials [17,18] and hair [19], detergentless microemulsions of diesel oil [20], slurries [21,22] and others [23–27]. However, the direct application of ETAAS for vanadium determination in saline samples like seawater is currently limited to few papers [28–31]. Also, nothing could still be found in the specialized literature concerning vanadium determination in any kind of produced water.

As mentioned above, in terms of vanadium determination in saline samples by ETAAS, only some research works were cited. Tominaga and Bansho [28] employed a solution of 10% (w/v) ascorbic acid as chemical modifier in order to minimize matrix effects on direct determination of vanadium (among others analytes) in coastal seawater. Working on optimized conditions, the authors achieved a detection limit of 18 $\mu g\,l^{-1}$ and R.S.D. always better than 12%.

Su and Huang [29] related the simultaneous determination of vanadium together with molybdenum in seawater by using a multielemental electrothermal atomic absorption spectrometer. Different chemical modifiers ($Pd(NO_3)_2$, $Mg(NO_3)_2$ and a mixture of both) were tested for matrix removal. In the case of vanadium, standard addition method was used with $Pd(NO_3)_2$ or the mixture as modifiers. Detection limits between 0.32 and 0.51 $\mu g\,l^{-1}$ were achieved in the analysis of certified seawater samples CASS-3 and NASS-4. In turn, Segar and González [30] did not use any chemical modifier for the direct determination of vanadium in seawater by ETAAS. However, in this situation a poor detection limit of 50 $\mu g\,l^{-1}$ was obtained. In another approach for the same task, Segar [31] employed a static analysis method in ETAAS. Although the detection limit was improved to 30 $\mu g\,l^{-1}$, the author recognized that it was impossible to determine vanadium directly in unpolluted seawater since its concentrations of 2 $\mu g\,l^{-1}$ are far lower than detection limit.

The aim of this work was to provide new possibilities for the direct determination of vanadium in very high saline samples employing ETAAS as analytical technique. For this purpose, different chemical modifiers (HF, $NH_4H_2PO_4$ and a mixture of both) usually employed to minimize chloride interference were tested as well as operational conditions for the heating program. Also, calibration strategy was carefully evaluated in order to achieve best accuracy for vanadium determination in real samples of produced waters from offshore petroleum exploration. It is important to remark that no similar work was found in the literature regarding to ETAAS determination of any trace element in saline produced waters obtained along petroleum prospecting.

2. Experimental

2.1. Apparatus

A Hitachi (Tokyo, Japan) polarized Zeeman-effect electrothermal atomic absorption spectrometer, model Z-8200, equipped with universal vanadium hollow cathode lamp from Hitachi was used throughout the experimental work. The spectrometer was coupled with auto-sampler Hitachi SSC-300. Integrated absorbance measurements were made by using Hitachi 190-6003 Pyro tube-type cuvettes and atomization was performed on tube walls. Argon was always used as protective gas and the instrumental operating conditions were: 12.5 mA lamp current, 0.4 nm slit width and 318.4 nm wavelength.

The salinity of the samples was measured with a hand-held refractometer model S/Mill-E furnished by Atago (Saitama, Japan).

2.2. Reagents and solutions

All water (18 MΩ cm resistivity) used in the preparation of solutions was obtained in a Simplicity Milli-Q Water System (Millipore, Milford, MA, USA). The reagents were of analytical grade and used as received.

Vanadium stock solution with a concentration of 1000 $\mu g\,ml^{-1}$ was obtained from Merck (Darmstadt, Germany). Vanadium standard solutions were always prepared by suitable dilution of the stock solution.

$NH_4H_2PO_4$ modifier solutions of different concentrations were prepared by adequate dilution of a commercially available stock solution of 1000 $\mu g\,ml^{-1}$ $NH_4H_2PO_4$ (Merck, Darmstadt, Germany) with purified water. As the same way, $NH_4H_2PO_4$-HF modifier solution (500 $\mu g\,ml^{-1}$ $NH_4H_2PO_4$ and 50% (v/v) HF) was prepared by mixing 1.0 ml of a 1000 $\mu g\,ml^{-1}$ $NH_4H_2PO_4$ stock solution with 1 ml of concentrated HF (Merck, Darmstadt, Germany) in a 5 ml PTFE stopped flask. Concentrated nitric acid (used in this work for sample preservation and decontamination of collection flasks) was supplied by Merck (Darmstadt, Germany).

Hydrofluoric acid solution (50%, v/v) was prepared by mixing 1.0 ml of purified water with 1.0 ml of concentrated HF (Merck, Darmstadt, Germany) in a 5 ml PTFE stopped flask. This solution was prepared daily just before use.

2.3. General procedure

For the measurement of V in the solutions, 20 μl of sample or standard solution was inserted into a graphite furnace, immediately followed by the injection of 10 μl of a 1000 $\mu g\,ml^{-1}$ $NH_4H_2PO_4$ modifier solution. Then, the temperature program was run and integrated absorbance was measured under the conditions suggested by the manufacturer. The temperature program used is listed in Table 1. It is important to remark that the atomization was always carried out on tube wall.

Table 1
Temperature program used for the direct determination of V in produced waters by ETAAS

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar flow rate ($ml\,min^{-1}$)
Drying	80–140	40	0	200
Pyrolysis	[a]	0	[a]	200
Atomization	[a]	0	10	0
Cleaning	2800	0	4	200

[a] Parameters under study.

2.4. Sample collection and storage

After collecting high saline produced waters with decontaminated polyethylene flasks (48 h soaked in 10%, v/v HNO_3 solution), the samples were acidified with concentrated nitric acid to pH 1.5 and stored in the refrigerator until analysis.

3. Results and discussion

3.1. Pyrolysis and atomization curves

The first part of the experimental work was to build up pyrolysis and atomization curves to set best instrumental conditions for the measurement of vanadium in the samples of produced waters. Both pyrolysis and atomization curves were always constructed using vanadium standard solutions prepared in purified water and 0.8 mol l^{-1} NaCl (40‰ salinity) solution, in order to simulate saline conditions usually found in produced waters obtained in offshore petroleum extraction. Also, different chemical modifiers ($NH_4H_2PO_4$, HF and $NH_4H_2PO_4$ + HF) were evaluated in order to choose the best modification approach for the system under study.

It is well known that vanadium is a carbide-forming element, which atomizes at very high temperatures in the graphite tube [32]. Thus, the literature recommends the use of tubes coated with pyrolytical graphite to minimize the formation of vanadium carbide [6]. Taking these information into account and considering that main characteristic of produced waters is their high salinity, the modification study was focused on the matrix elimination before atomization step (virtually in the pyrolysis) in order to decrease background signal. This way, firstly, a pyrolysis curve was constructed with a 50 μg l^{-1} V solution employing all modifiers cited above and without modifier addition. Obtained results shown in the Fig. 1, demonstrate that, in water, all modifiers have similar efficiency that allows the pyrolysis temperature to be elevated up to 1500 °C without analyte losses. Although vanadium is recognized to be having higher thermal stability, a decrease in the sensitivity around 25% was noted when no modifier was added indicating that some vanadium atoms are lost during pyrolysis step. It is important to remark that no differentiation between efficiency of the modifiers tested was possible in this experiment since the observed values of background were always very low. Also, as stated previously, the behavior of vanadium was similar for all modifiers tested.

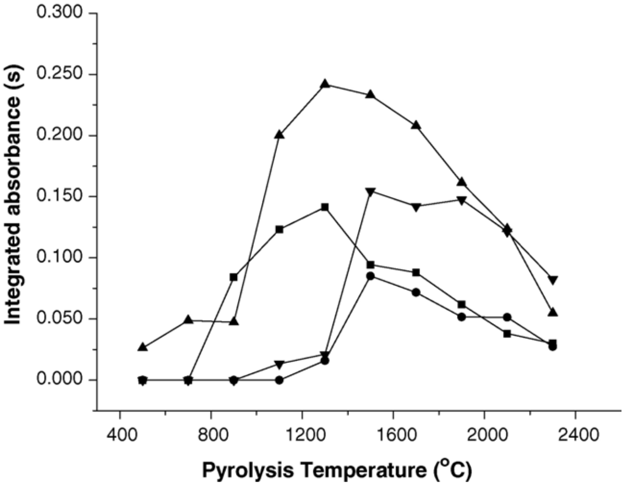

Fig. 2. Pyrolysis curves with different modifiers in NaCl 0.8 mol l^{-1} medium: (■) without modifier; (●) 10 μl of a 50% (v/v) HF solution; (▲) 10 μl of a 1000 mg l^{-1} $NH_4H_2PO_4$ solution (10 μg) and (▼) $NH_4H_2PO_4$ (10 μg) + HF 50% (v/v); [V] = 50 μg l^{-1}; atomization temperature = 2700 °C; pyrolysis time = 10 s.

When vanadium standard solution (also 50 μg l^{-1}) was prepared in 0.8 mol l^{-1} NaCl medium the analyte behavior was completely different. As can be seen in Fig. 2, at pyrolysis temperatures lower than 1100 °C, the absorbance of vanadium was low for any modifier. This happens due to the highest background signal observed at these temperatures (Fig. 3), which

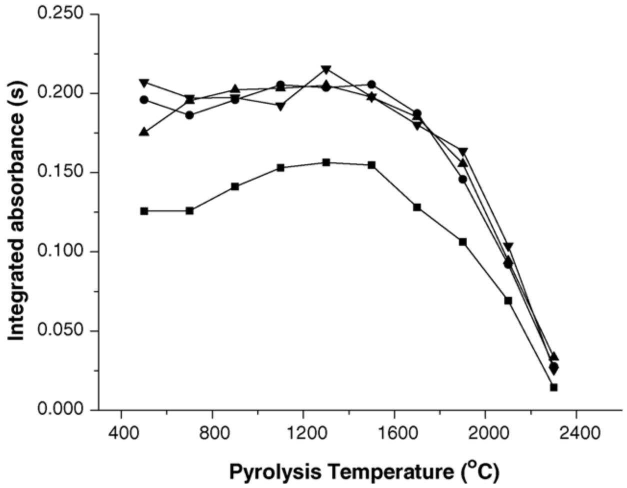

Fig. 1. Pyrolysis curves with different modifiers in purified water medium: (■) without modifier; (●) 10 μl of a 50% (v/v) HF solution; (▲) 10 μl of a 1000 mg l^{-1} $NH_4H_2PO_4$ solution (10 μg); (▼) $NH_4H_2PO_4$ (10 μg) + HF 50% (v/v); [V] = 50 μg l^{-1}; atomization temperature = 2700 °C; pyrolysis time = 10 s.

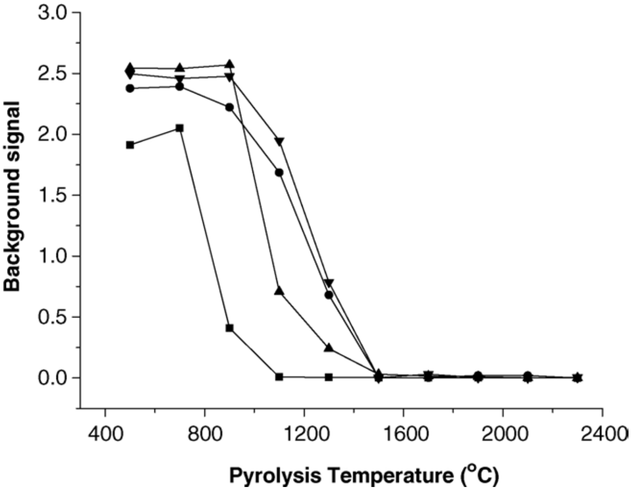

Fig. 3. Background signals obtained in the built up of the pyrolysis curve for vanadium in 0.8 mol l^{-1} NaCl medium: (■) without modifier; (●) 10 μl of a 50% (v/v) HF solution; (▲) 10 μl of a 1000 mg l^{-1} $NH_4H_2PO_4$ solution (10 μg) and (▼) $NH_4H_2PO_4$ (10 μg) + HF 50% (v/v); [V] = 50 μg l^{-1}; atomization temperature = 2700 °C; pyrolysis time = 10 s.

overpass the correcting capacity of Zeeman-effect based corrector employed. Besides, when HF was added as a modifier (alone or together with $NH_4H_2PO_4$) a reduction in the analytical signals of vanadium was observed, denoting that some volatile compounds of V are formed in this situation. In order to explain this phenomenon, two alternatives were considered: (1) direct formation of fluoride volatile species of vanadium and (2) secondary formation of chloride volatile species of vanadium due to the hydrochloric acid released from matrix after addition of HF. The former phenomenon was considered taking into consideration the work of Cabon [33–35]. He supports that addition of high amounts of hydrofluoric acid to solutions containing high concentrations of NaCl converts chloride matrix into corresponding fluoride, releasing hydrochloric acid.

Best results were obtained when $NH_4H_2PO_4$ was added as modifier. In NaCl medium, the formation of volatile NH_4Cl was enhanced with this modifier, making it possible to minimize chloride concentrations present in the matrix. Also, as most prominent effect, the stabilization of vanadium by phosphate added as modifier allowed the pyrolysis temperature to be raised up to 1500 °C without losses, providing the direct volatilization of NaCl (boiling point = 1413 °C) [32] present. At temperatures higher than 1500 °C a decrease in the analytical signal was observed due to the regular volatilization of the analyte in the pyrolysis step, while at pyrolysis temperature below 1100 °C, lowest analytical signals were verified as result of high background values recorded, which were not conveniently corrected, as already mentioned. This way, $NH_4H_2PO_4$ was chosen as modifier employing a pyrolysis temperature of 1500 °C since at this temperature background signal was reduced near to zero (see Fig. 3) and sensitivity similar to that obtained in purified water was observed.

Once the optimum pyrolysis temperature was established, an atomization curve was created after checking atomization conditions for vanadium. As can be seen in Fig. 4, setting pyrolysis temperature at 1500 °C resulted in atomization curves very similar for vanadium in both water and chloride matrices. Analytical signal increased through entire temperature range tested (2400–2700 °C), and the atomization temperature of 2700 °C was chosen because at this level, higher sensitivity was attained besides faster completion of analytical peak.

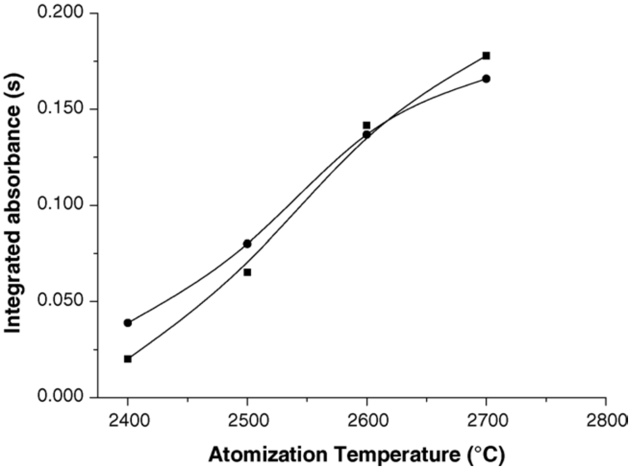

Fig. 4. Atomization curves built up in (■) pure water and (●) 0.8 mol l^{-1} NaCl media using 10 μg of $NH_4H_2PO_4$ as modifier. [V] = 50 μg l^{-1}; pyrolysis temperature = 1500 °C; pyrolysis time = 10 s.

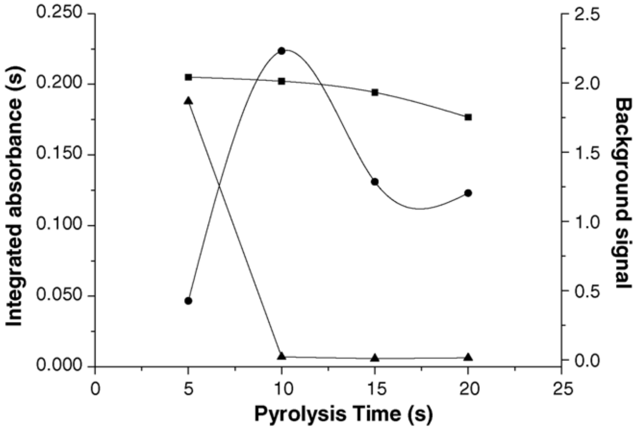

Fig. 5. Influence of pyrolysis time on the analytical signal of vanadium in (■) pure water and (●) 0.8 mol l^{-1} NaCl solution using 10 μg of $NH_4H_2PO_4$ as modifier and on (▲) background signal observed in the measurement of vanadium in saline solution. [V] = 50 μg l^{-1}; pyrolysis temperature = 1500 °C; atomization temperature = 2700 °C.

3.2. *Study of the influence of pyrolysis time*

Following the optimization of instrumental conditions for vanadium determination by ETAAS, the influence of pyrolysis time was investigated. This parameter was studied in a range of 5–20 s, maintaining the pyrolysis temperature at 1500 °C during whole pyrolysis, without ramping and testing vanadium standard solutions prepared in purified water and 0.8 mol l^{-1} NaCl media. As can be seen in the Fig. 5, in water medium a slight decrease in vanadium signal was observed when pyrolysis time was increased, indicating that a little portion of the analyte is volatilized when graphite tube is heated for longer periods. In chloride medium the behavior was quite different. Adjusting pyrolysis time at 5 s, vanadium signal was very low, again as result of the high background attained in this situation, because this pyrolysis time was not enough to eliminate considerable amounts of NaCl inserted into the tube. However, increasing it up to 10 s, the analytical signal reached its maximum value and, at same time, background was almost reduced to zero, indicating that 10 s pyrolysis time is sufficient to eliminate matrix without promote vanadium volatilization. This observation reinforces the hypothesis raised before that the direct volatilization of NaCl at 1500 °C is the most important effect for background signal minimization.

For times higher than 10 s, although background remained near to zero, vanadium signal suffered stronger reduction than in water, probably as result of volatilization of vanadium-chloride species (note that, in this case, HF is not added). This result reinforced the hypothesis raised previously in the construction of pyrolysis curve that some vanadium can be lost as chloride volatile compounds. This way, a pyrolysis time of 10 s was chosen for all further experiments.

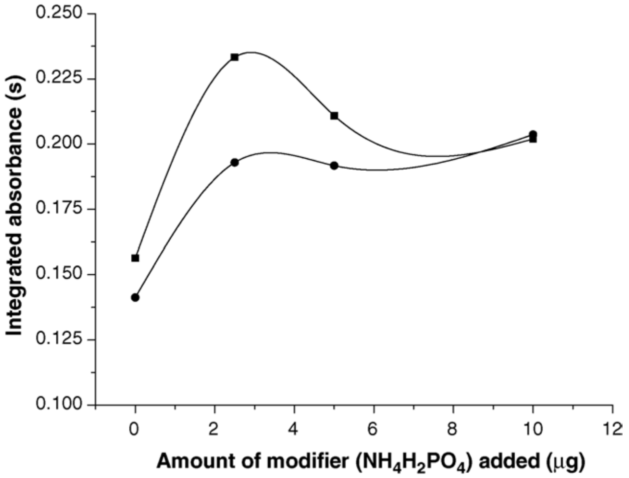

Fig. 6. Influence of the amount of modifier added on the absorbance of vanadium in (■) pure water and (●) 0.8 mol l^{-1} NaCl solution. [V] = 50 µg l^{-1}; pyrolysis temperature = 1500 °C; atomization temperature = 2700 °C; pyrolysis time = 10 s.

3.3. *Study of the influence of the amount of modifier added*

In the present method, the modifier added to the samples play an important role because it is responsible for the conversion of NaCl into volatiles NH_4Cl which is volatilized during pyrolysis, and also for vanadium thermal stabilization. Due to the high salinity usually observed in produced waters (up to 120‰), the amount of $NH_4H_2PO_4$ inserted together with the sample must be carefully examined. The study was performed measuring vanadium (1 ng) absorbance in presence of variable amounts of modifier, which ranged between 0 and 10 µg. Again, vanadium behavior was tested in purified water and chloride media (0.8 mol l^{-1} NaCl). Results are shown in Fig. 6. As expected when no modifier was added the vanadium signal was lowest in both situations. Sensitivity obtained in water medium was better than that observed in NaCl solution between 2.5 and 5 µg modifier added, indicating the deleterious effect of chloride over vanadium signal and that the amount of modifier added in this range is not enough to promote analyte stabilization during pyrolysis and to provide elimination of remarkable amounts of chloride. When 10 µg of modifier were added no difference between signals obtained for vanadium in water and chloride media was observed. This effect was previously verified when pyrolysis curves were constructed, indicating that at this situation chloride interference can be overcome during heating program. So, it was decided that 10 µg of $NH_4H_2PO_4$ (10 µl of a 1000 µg ml^{-1} solution) modifier would be inserted together with 20 µl of sample.

3.4. *Application of the methodology—external calibration versus analyte addition*

After optimization of operational parameters the developed methodology was applied for the determination of V in real samples of produced waters. During this application, a comparison between external calibration and standard addition approaches was performed in order to set the best calibration strategy for the methodology.

Firstly, different external calibration approaches were tested by analyzing samples using analytical curves built up with standards solutions prepared in both purified water and 0.8 mol l^{-1} NaCl. Also, samples were spiked with vanadium at concentrations of 10 and 25 µg l^{-1} in order to evaluate recovery level employing both curves. As can be seen in the results shown in Table 2, no noticeable difference was observed between vanadium concentrations determined with the two approaches utilized. Applying a paired *t*-Student test to compare such results, it was possible to observe that, at 95% confidence level, there was no statistical difference between vanadium concentrations. As mentioned before, recovery percentages (Table 3) were calculated using the two analytical curves as reference and results between 88.2 and 126% were attained with an average value of

Table 2
Results obtained in the analysis of real samples of produced waters by analytical curve and standard addition methods

Method	Medium	Equation	V found (µg l^{-1})
Analytical curve (10–75 µg l^{-1})	Purified water	$A = 0.0051\ [V] + 0.001$; $r = 0.9997$	$PW_1 = 32.0 \pm 0.9$ $PW_2 = 34.5 \pm 0.5$ $PW_3 = 16.7 \pm 0.6$ $PW_4 = 12.7 \pm 0.4$ $PW_5 = 4.31 \pm 0.28$
	0.8 mol l^{-1} NaCl	$A = 0.0049\ [V] + 0.002$; $r = 0.9994$	$PW_1 = 33.1 \pm 0.7$ $PW_2 = 35.7 \pm 0.8$ $PW_3 = 17.1 \pm 0.6$ $PW_4 = 13.1 \pm 0.4$ $PW_5 = 4.29 \pm 0.14$
Standard addition (10–25 µg l^{-1})	PW_1 (74 ‰)	$A = 0.0048\ [V] + 0.163$; $r = 0.9998$	35.0 ± 1.5
	PW_2 (78 ‰)	$A = 0.0051\ [V] + 0.179$; $r = 0.9992$	34.2 ± 1.1
	PW_3 (34 ‰)	$A = 0.0049\ [V] + 0.090$; $r = 0.9962$	18.3 ± 0.7
	PW_4 (38 ‰)	$A = 0.0048\ [V] + 0.065$; $r = 0.9996$	13.5 ± 0.5
	PW_5 (14 ‰)	$A = 0.0050\ [V] + 0.023$; $r = 0.9999$	4.67 ± 0.30

Values are expressed as media of three independent determinations ± standard deviation. [V]: vanadium concentration in µg l^{-1}; PW_1, PW_2, PW_3, PW_4 and PW_5 are produced water samples with their respective salinities in parenthesis.

Table 3
Results obtained in the recovery tests for V executed with real produced water samples

Sample	V added ($\mu g\,l^{-1}$)	Recovery A[a] (%)	Recovery B[a] (%)
PW_1 (74‰)	0	–	–
	10	90.2	105
	25	93.3	101
PW_2 (78‰)	0	–	–
	10	110	126
	25	101	110
PW_3 (34‰)	0	–	–
	10	116	125
	25	97.3	103
PW_4 (38‰)	0	–	–
	10	88.2	95.0
	25	94.1	99.2
PW_5 (14‰)	0	–	–
	10	98.0	102
	25	97.3	101

[a] Recovery A refers to the recoveries calculated from external calibration with standard solutions prepared in water and recovery B refers to the recoveries calculated when standard solutions were prepared in 0.8 mol l^{-1} NaCl.

102 ± 10%, indicating that no matrix interference is observed for the method developed.

Another test done was the determination of vanadium in the samples using the standard addition method. Table 2 also shows the results obtained, including the equations of all standard addition curves. It is interesting to remark that sample salinity had no influence on the slopes of the curves, which varied from 0.0048 to 0.0051, reinforcing the idea raised previously that matrix is completely removed during heating program without vanadium losses when 10 μg of $NH_4H_2PO_4$ is added as chemical modifier. Comparing the results obtained by standard addition with those obtained by external calibration using the paired *t*-Student test, it was possible to realize that there was no statistical difference between standard addition and external calibration (in water or chloride media) approaches. Testing the correlation between vanadium concentrations determined by all procedures, curves with following equations were derived:

$$AC_{NaCl} = (1.040 \pm 0.025)AC_{H_2O} - (0.184 \pm 0.059), \quad r = 0.9999$$

$$SAD = (0.989 \pm 0.024)AC_{H_2O} + (0.911 \pm 0.051), \quad r = 0.9991$$

$$AC_{NaCl} = (0.951 \pm 0.024)SAD - (1.089 \pm 0.058), \quad r = 0.9990$$

where AC_{NaCl}, AC_{H_2O} and SAD are vanadium concentrations determined by analytical curve with standard solutions prepared in purified water, analytical curve prepared with standard solutions prepared in 0.8 mol l^{-1} NaCl and standard addition, respectively. Slopes were always very close to 1.0 and correlation coefficients were always better than 0.999. Moreover, curves passed through to origin. These values indicated that there was no statistical difference between procedures adopted for vanadium determination in produced water samples.

4. Analytical features of the methodology

After all studies performed, it was verified that the direct V determination in produced waters from petroleum exploration by ETAAS can be carried out by employing $NH_4H_2PO_4$ modifier. The addition of 10 μg of this chemical modifier on the sample leads to an atomization temperature of 2700 °C and a pyrolysis temperature of 1500 °C. In such conditions, pseudoanalytical curves were built up in both purified water and 0.8 mol l^{-1} NaCl media to derive the general equations and the detection limits of the methodology. Such equations are shown in Table 2. The detection (3 s criterion) and quantification (10 s criterion) limits, estimated from the measurement of vanadium standard solution with 10 $\mu g\,l^{-1}$ concentration were 1.8 and 6.0 $\mu g\,l^{-1}$, respectively, for purified water medium and 1.9 and 6.3 $\mu g\,l^{-1}$, respectively, for 0.8 mol l^{-1} NaCl medium. Characteristic masses, taken from these same analytical curves, were 17.2 pg for purified water medium and 17.9 for 0.8 mol l^{-1} NaCl medium. The R.S.D., calculated after 10 measurements of 10 $\mu g\,l^{-1}$ vanadium solutions was 6.0 and 5.6% for water and 0.8 mol l^{-1} NaCl media, respectively.

5. Conclusions

According to the results observed in the present study, the direct determination of vanadium in highly saline produced waters obtained from petroleum exploration by electrothermal atomic absorption spectrometry can be carried out using 10 μg of $NH_4H_2PO_4$ as chemical modifier. Using such amount of modifier, a pyrolysis temperature of 1500 °C during 10 s could be set together with an atomization temperature of 2700 °C.

Calibration strategy did not show relevant importance in the direct vanadium determination in produced waters since, by using operational conditions optimized in this study, no difference was observed between standard addition and external calibration (with vanadium standard solutions prepared in water or 0.8 mol l^{-1} NaCl) approaches.

The method developed presented a detection limit of 1.9 $\mu g\,l^{-1}$ and a quantification limit of 6.3 $\mu g\,l^{-1}$ when calibration was performed employing vanadium standard solutions prepared in 0.8 mol l^{-1} NaCl medium, which is suitable for the determination of vanadium in real samples of produced waters. Also, at such conditions, a precision of 5.6% was attained.

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