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Liquid–liquid extraction and quantitative determination of tungsten (VI) using macrocyclic reagent (DB-18-C-6) as a thiocyanate complex $[WO\ (SCN)_5]^{2-}$

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ABSTRACT

In recent years, the extraction using crown ethers has reached a resounding success in different scientific and technical fields. In this work, the authors report the results of the main steps of extraction and determination (proportioning) of the tungsten ion (VI) using a chloroformed solution of crown ether. The dibenzo–18–C-6(2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene according to the IUPAC systematic nomenclature). The identification and quantification of W(VI) using the absorption spectrum, the influence of the necessary reagents, the needed acidity level for complete extraction and complexation of W (VI) using a crown ether, and the influence of multivalent metal ions were examined, considering that the sensitivity, selectivity, and detection limits have been determined. This system obeys Beer's law in the range of 0.18–18.3 $\mu g\,cm^{-3}$of tungsten with a molar absorption of $1.6 \times 10^4\,mol^{-1}\,cm^{-1}$ at 415 nm and the detection, quantification limits were, respectively, equal to 0.7–1.8 $\mu g\,cm^{-3}$. The developed method was applied for the extraction of W(VI) in the high speed steel (HSS): HS2–9–1–8 containing 2% W, 9% Mo, 1% V, and 8% Co.

Keywords: Dibenzo-18-crown-6; Tungsten; Complexation; Extraction; High speed steel

1. Introduction

There are several methods for the extraction and the quantification of tungsten. Each method has its advantages and disadvantages. In many cases, the majority of heavy metals interfere with the extraction and quantification of tungsten by existing methods: hydrochloric acid solutions by neutral organophosphorus compounds and high molecular weight amines, with mesityl oxide, electrothermal atomic absorption spectrometry after hydrolysis and selective removal of tungsten by liquid–liquid extraction, using the ion pairing reagent procaine hydrochloride, etc. [1–4]. For this reason, these metals must previously be complexed or eliminated.

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The importance of this work is related to the fact that a liquid–liquid extraction method for the quantification of W(VI) has been developed, as well as a spectrophotometric method that allows control of the amount of tungsten in tungsten-contaminated waters, as well as in the analysis of steels.

The crown ethers selectively extract cations such as Li^+, Na^+, K^+, NH_4^+, by taking a positive charge. This favors the extraction of highly polarized anions of iodides, cyanides, and thiocyanates of heavy metals (Bi(III), Co(II), Mo(V), W(V), etc.). Synthesis of crown ether 4-acrylamidobenzo-18-crown-6 (ABCE) functionalized polyacrylamide (PAAm) gel beads. In nitric acid, the extraction efficiency is found to be high (>80%) when the number of hydrogen ions in aqueous phase is less than that of ABCE molecules attached to hydrogel backbone.

Among many crown ethers synthesized for the extraction, the most frequent ones used are 15C5, B15C5, 18C6, DCH18C6, DB24C8, and the DB18C6 [5–12].

The extraction mechanism may be presented as follows:

$$\underset{\text{organic phase}}{\text{DB-18-C-6}} + \underset{\text{aqueous phase}}{NH_4^+} \longrightarrow \underset{\text{organic phase}}{[\text{DB-18-C-6}\cdot NH_4]^+}$$

$$\longrightarrow 2\underset{\text{organic phase}}{[\text{DB-18-C-6}\cdot NH_4]^+} + \underset{\text{aqueous phase}}{[WO(SCN)_5]^{2-}}$$

$$\longrightarrow \underset{\text{organic phase}}{[\text{DB-18-C-6}\cdot NH_4]_2^+\cdot[WO(SCN)_5]^{2-}}$$

The effect of structural studies of the crown's ring size variation, lipophilic, and acidic group attachments for lariat ethers with carboxylic and other acidic groups on the selectivity and efficiency of metal cations transport has also been presented. The effect of a counter anion presence is also discussed. Examples of metal ions' selective removal using various other ion carriers such as calixarenes, calixcrown ethers, cyclodextrins and their polymers, as well as acyclic polyethers are also examined [13].

Facilitated transport of Zn(II), Cd(II), and Pb(II) across polymer inclusion membranes doped with imidazole azocrown ethers. The influence of azocrown ether concentration on metal ions transport across PIM was studied. The initial fluxes of transported metal ions depend on the hydrophile–lipophile balance and the molecular volumes of azocrown ethers. Cellulose triacetate membranes doped with imidazole azocrown derivatives as fixed carriers have been prepared and applied for the investigation of facilitated transport of Zn(II), Cd(II), and Pb(II) ions from aqueous nitrate source phase ($C_{Me} = 10^{-3}$ M, pH = 5.0), the transport selectivity of the polymer inclusion membranes [14,15].

The extraction of uranium from the concentrated brine rejected by integrated nuclear desalination systems, three innovative and efficient methods of uranium extraction have been proposed: Resin grafted with calixarene; magnetic separations; and canal system with braid adsorbents. The resin grafted with calixarene; this method has the advantage of very high selectivity. Its performances, especially for large-scale extraction, still need further R&D and optimization [16].

5-(4-Pyridyl) nonane was evaluated as a solvent for trace amounts ($<5\times10^{-5}$ M) tungsten (VI) from aqueous chloride-thiocyanate solutions. Remarkable improvements in metal extractability have been observed on the addition of SCN^- to aqueous solutions of hydrochloric acid. Extreme partition coefficients are obtained from 0.1 M HCl in 0.2 M KSCN. Decreases in the extractability of metal are produced by relatively high (>0.5 M) SCN^- concentration and increased concentration of acid in support. Data analysis of slope, under the optimal conditions, indicates the most probable composition of the extractable species to be WO_2 (SCN) 2.2 PYN. Neutral anions have no significant effect on the *D* values (complex extraction, %). Behavior of a number of metal ions was tested considering the optimal conditions for water extraction. The survey shows that the reagent has great potential for the preconcentration of a number of metal ions, including the common toxins [17].

In our work, we have developed the extraction method which is accurate and sensitive and presents the advantage of progressing rapidly and is characterized by a high selectivity and specificity. In addition, a prior separation of the mixture's components is not needed.

2. Experimental

2.1. Materials and methodology

To optimize the process, the following solutions were used: $Na_2WO_4{\cdot}2H_2O$ at 10^{-4} M, DB-18-C-6 at 0.005 M (chloroformed solution), solution of $SnCl_2$ at 40%, solution of NH_4SCN at 20%, concentrated hydrochloric acid and acetone(All reagents used are chemically pure), and Spectrophotometer Pye Unicam UV-visible 87000.

The experience has shown that crown ethers 18-C-6 and DB-18-C-6 form the most stable cationic complex with K^+ and NH_4^+ in an organic phase. In the case of the complexation of the K^+ ion and using the

DB-18-C-6, the size (diameter) of K^+ ions (0.267 nm) and NH_4^+ (0.278 nm) is consistent with the size of the crown ethers molecules cavity (0.26–0.32 nm). These cationic complexes strongly attract the anionic complexes found in the aqueous phase $[BiI_4]^-$, $[Co(SCN)_4]^{2-}$, $[MoO(SCN)_5]^{2-}$, $[WO(SCN)_5]^{2-}$, etc.

To quantify the W(VI) in a solution using a crown ether it is necessary to determine the following factors: the maximum adsorption of the associate of $[\text{DB-18-C-6} \cdot NH_4]_2^+ \cdot [WO(SCN)_5]^{2-}$, to determine the efficiency of crown ethers for the extraction of the anionic complex of $[WO(SCN)_5]^{2-}$, to study the influence of different solvents on the performance of the extraction of anionic complex $[WO(SCN)_5]^{2-}$, to study the influence of different solvents on the yield of the extraction process of the anionic complex $[WO(SCN)_5]^{2-}$, the evaluation of the influence of the molar ratio of reagents on the absorbance of the associate, the evaluation of the influence of acidity on the complexation and quantitative extraction of the anionic complex $[WO(SCN)_5]^{2-}$, and the evaluation of the influence of bivalent and trivalent metal ions.

2.2. Procedures

2.2.1. Procedure 1: Absorption spectrum of the complex $[\text{DB-18-C-6} \cdot NH_4]_2^+ \cdot [WO(SCN)_5]^{2-}$

In order to determine the maximum adsorption experimentally, the following experiments have been realized: in a 50 cm^3 separating funnel, 10.00 cm^3 of calibrated solution of W(VI) at 1.10^{-4} M have been transferred (1.00 cm^3 of this solution contains 18.385 µg of tungsten). About 10 cm^3 of concentrated HCl, 3.0 cm^3 of 40% $SnCl_2$ solution, and 5.0 cm^3 of 20% NH_4SCN solution were taken and diluted to 30 cm^3 (using water). After 15 min, add 1.00 cm^3 of acetone and 10.00 cm^3 of chloroformed solution of DB-18-C-6 at 5×10^{-3} M were added, and the mixture was agitated for 10 s to separate the organic phase (yellow) and the maximum absorption of the organic phase was determined.

2.2.2. Procedure 2: Calibration curve

In six separating funnels, add respectively, 1.00, 3.00, 5.00, 8.00, and 10.00 cm^3 of a calibrated solution of W(VI) at 10^{-4} M (1.0 cm^3 of this solution contains 18.38 µg of W(VI)). The optimized reagents are introduced and then the extraction and the measurement of the absorbance at the wavelength of 415 nm were performed, as described above.

2.2.3. Procedure 3: determination of tungsten in HS2–9-1–8

In a 100 cm^3 glass, 1 g of pulverized high speed steel (with an accuracy of 0.0002 g) was taken and then 20 cm^3 of concentrated HNO_3 and 1 cm^3 of 10% H_2O_2 were added. A slow heating until the dissolution of the taken sample was carried out. A yellowish precipitate of H_2WO_4 was obtained. The filtered precipitate obtained with glass filter No 3 was filtered, and then the precipitate deposited on the filter (2–3 times) was washed with small portions of HNO_3 (1:4). About 20 cm^3 of NaOH solution at 1 M was added and the obtained liquid was recovered in a 50 cm^3 gaged flask and diluted to the graduation gage (the mark) by distilled water; 1 cm^3 of this solution theoretically contains 0.4 mg of tungsten. In a 25 cm^3 gaged flasks take 1 cm^3 of the solution obtained and dilute it with distilled water to the mark of the flask. About 1 cm^3 of this diluted solution contains 16 µg of tungsten, so the final tungsten solution recovered was at a concentration of 10^{-4} mole l^{-1}. About 10.00 cm^3 of the prepared solution was then transferred in a 50 cm^3 separating funnel; 10 cm^3 of concentrated HCl, 3.0 cm^3 of 40% $SnCI_2$ solution, and 5.0 cm^3 of 20% NH_4SCN solution were added and the mixture was diluted to 30 cm^3 using water. After 15 min, add 1.00 cm^3 of acetone and 10.00 cm^3 of a chloroformed solution of DB-18-C-6 at 5×10^{-3} M were added. The mixture was mixed for 10 s and the organic phase (yellow) was separated. The measurement of the organic phase absorbance in comparison with the chloroformed solution of DB-18-C-6 was determined and the amount of W was deduced from the calibration curve.

3. Results and discussion

3.1. Absorption spectrum of the complex

The absorption spectrum of the complex $[\text{DB-18-C-6} \cdot NH_4]_2^+ \cdot [WO(SCN)_5]^{2-}$ was shown by procedure 1. The results are presented in Fig. 1. The maximum absorption of the ionic associate $[\text{DB-18- \textbackslash C-6} \cdot NH_4]_2^+ \cdot [WO(SCN)_5]^{2-}$ was 415 nm. The molar absorption coefficient (factor) of the colored complex was $\varepsilon \approx 1.6 \times 10^4$ $mol^{-1} cm^{-1}$ at the wavelength $\lambda = 415$ nm.

3.2. The choice of crown ethers for the complete extraction of the anionic complex $[WO(SCN)_5]^{2-}$

Using the same method of operation mentioned above, a series of crown ethers with different concentrations (from 1×10^{-3} to 5×10^{-3} M) were used to

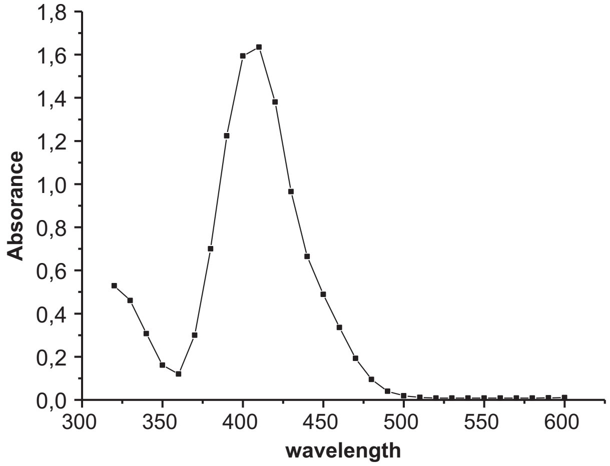

Fig. 1. Absorption spectrum of the complex $[\text{DB-18-C-6} \cdot NH_4]_2^+ \cdot [WO(SCN)_5]^{2-}$.

determine the reagent adequate for our manipulation. The results are presented in Fig. 2 showing that the crown ethers, DB-18-C-6, were more effective than 15-C-5, Benzo-15-C-5, DCH-18-C-6, 18-C-6.

(D: Complex extraction, %).

3.3. *Effects of different solvents on the extraction yield of the anionic complex $[WO(SCN)_5]^{2-}$*

Using the same method of operation mentioned above, a series of organic solvents were used to determine the reagent adequate for our manipulation. The extraction of the complex $[WO(SCN)_5]^{2-}$ from certain solutions, depends on the nature of the solvents. To mark this influence, different solutions of DB-18-C-6 were used in the following solvents: chloroform, dichloroethane, dibutylether, and butanol.

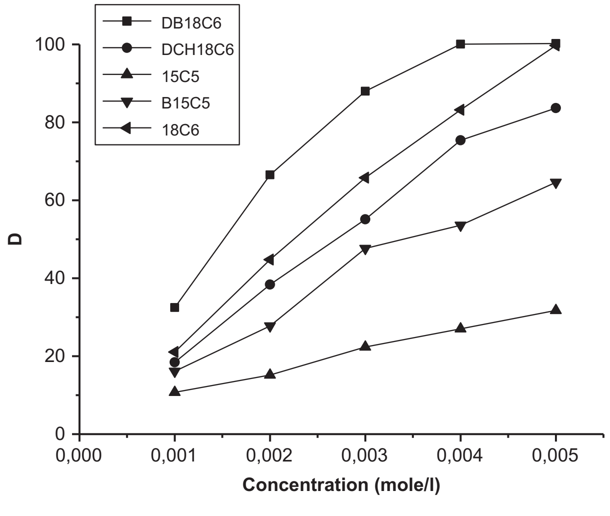

Fig. 2. Study of the dependence between the extraction degree of the anionic complex $[WO\ (SCN)_5]^{2-}$ and certain crown ethers of different concentrations.

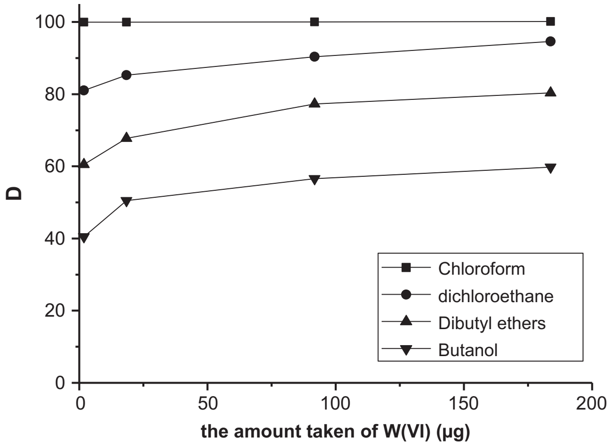

Fig. 3. Effects of different solvents on the extraction yield.

For this purpose, a series of samples have been initially prepared of the anionic complex $[WO(SCN)_5]^{2-}$ from a calibrated solution of W(VI) at 1×10^{-4} M, for a given concentration of DB-18-C-6 (5×10^{-3} M) in the various solvents mentioned above. The results are presented in Fig. 3 showing that among the solvents used, the most effective was chloroform.

3.4. *The effect of the concentration of the crown ether DB-18-C-6*

Using the same operating method mentioned previously, the concentration (10^{-3}–5×10^{-3} M) of the solution of DB-18-C-6 was varied to determine the optimal concentration. The results are presented in Fig. 4 showing that the optimal concentration of the

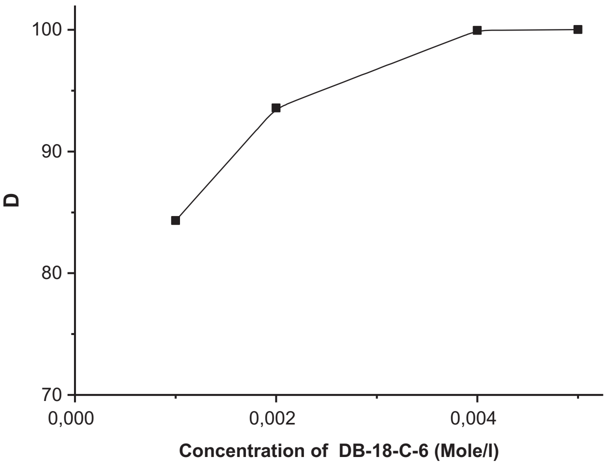

Fig. 4. Influence of the concentration of DB-18-C-6 on the extraction degree of W(V).

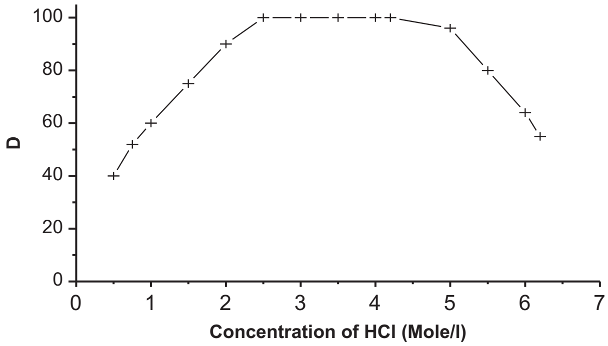

Fig. 5. Optimization of medium acidity for the extraction of [WO $(SCN)_5]^{2-}$.

crown ether *DB-18-C-6* reagents was used for a complete extraction of $[WO(SCN)_5]^{2-}$.

3.4.1. Choice of reducing agents for the reduction of W(VI) to W(V)

For the reduction of W(VI) various reducing agents have been suggested such as the amalgam of tin, Sn^{2+} in a concentrated hydrochloric acid environment, a mixture of Sn^{2+} and Ti (III) in acidic environment (HCl at 4 M). As a reducing agent, a solution of $SnCl_2$ was used. It was experimentally found that for the reduction of W(VI), it is necessary to introduce 3.0 cm^3 (5.4×10^{-3} M)/4.0 cm^3 (7.2×10^{-3} M) of $SnCl_2$ solution at 40%.

3.4.2. Optimization of the medium acidity for the extraction of the anionic complex $[WO(SCN)_5]^{2-}$

Using the same operating method as mentioned above, the amount of hydrochloric acid (1–15 cm^3) can be varied and the corresponding results are presented in Fig. 5 showing that the optimal amount of acid was 3 cm^3. A complete extraction of $[WO(SCN)_5]^{2-}$ was achieved at a starting HCl concentration of 2.5 M. At this level of acidity, the W(VI) was reduced to W(V) causing the formation of tungstyl ion WO^{3+} and its complexion occurred in the presence of NH_4SCN. On the other hand, as this acidity stabilizes the positive charge of the crown ether and the fixed ion complex formed [WO $(SCN)_5]^{2-}$. It should be taken into consideration that the use of a large amount of HCl negatively affected the extraction; this can be explained by the gradual substitution of ligands (SCN^-) by the Cl^- ions, after which the coloration(staining) intensity decreased and the WO^{3+} ions transformed progressively into WCl_5 or $[WOCl_5]^{2-}$.

3.4.3. Optimization of the amount of NH_4SCN

Using the same procedure as mentioned above, the amount of NH_4SCN can be varied thereby leading to an optimal amount of NH_4SCN is 4.0 cm^3 or 5.2×10^{-3} mole.

Table 1
Comparison of the developed method with other methods

Reagents	Blue thiazolyl, MTT	Hydrochloride ethopropazine (EPH) and thiocyanate	3-hydroxy-2 – (2´-thienyl)-4-oxo-4H-1-benzopyran (HTB) ligand—metal = 1:2	Crown ether and thiocyanate *2DB-18-C-6: W*
λ_{max} (nm)	415	404	415	415
ε ($dm^3 mol^{-1} cm^{-1}$)	2.8×10^4	1.2×10^4	6.65×10^4	1.6×10^4
Obeys Beer's law in the range (μg cm^{-3})	0–8.8	2.3–12.9	0–2.8	0.18–18.3
Detection limit (μg cm^{-3})	0.27	–	–	0.7
Quantification limit (μg cm^{-3})	0.92	–	–	1.8
Sandell's sensitivity (μg cm^{-2})	–	0.02003	0.0029	0.0306
Solvent	Chloroform	Chloroform	Dichloromethane	Chloroform
Interfering ions	Mo(VI), V (V), Cu(II), U(VI), Pt(IV)	Mo(VI), V(V), Pt (IV)	Pt(IV), U(VI), Mo(VI), Re (VII), PO_4^{3-}	Pt(IV),U(VI), Re(VII), Au(III) and PO_4^{3-} less than 50 μg/ml^{-1} do not interfere
Ref.	[5]	[6]	[7]	

Table 2
Determination of W(VI) in high-speed steel: HS2-9-1-8

Exp.	X_i	$\bar{X}$	$X_i - \bar{X}$	$(X_i - \bar{X})^2$	S	$S_{\bar{X}}$	S_r	$tS_{\bar{X}}$	$tS_X, \%$
1	99.85	99.88	−0.30	0.0900	0.1872	0.0764	0.0019	0.1963	0.1945
2	100.07		+0.19	0.0361					
3	99.78		−0.10	0.0100					
4	99.75		−0.13	0.0039					
5	99.80		−0.08	0.0064					
6	100.05		+0.17	0.0290					
			0.97	0.1754					

Note: X_i: Content in W(VI) %; $\bar{X}$: Arithmetic mean; Σd^2: The sum of the square deviations of the mean value; S: Standard deviation; S_r: Standard deviation relative; $S_{\bar{X}}$: Standard deviation means; and $tS_{\bar{X}}$: Interval probability.

3.5. Calibration curve

After having optimized the necessary amounts of reagents, a plot of the calibration curve can be realized. The experiment is shown by procedure 2. The detection limit and the quantification limit are, respectively equal to 0.7 and 1.8 μg cm^{-3}. The relative error is 0.65%. The method thereby elaborated (developed) allowed the determination (dosage) of certain amounts of W(VI) in the range of 1.838–183.85 μg. The molar extinction coefficient corresponding to 415 nm was equal to $\varepsilon = 16{,}000$.

3.6. Influence of the presence of other metal ions

It was experimentally determined that the hundredfold addition of Mg^{2+}, Ca^{2+}, Ba^{2+}, Sn^{2+}, Mn^{2+}, Zn^{2+},Co^{2+}, Ni^{2+}; Hg^{2+}, Ag^{+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, and Bi(III) to the solution of W(VI) did not interfere with its identification and dosage. This is confirmed by the identical results obtained in both cases (the presence and absence of these ions).

However, it has been observed that thiocyanate complexes of Fe(III) and Bi(III) are extracted simultaneously. However, the Fe(III) is reduced during the formation of the complex of W(V) in the presence of reducing agent used Sn(II). On the opposite side, a small concentration of Bi(III) and Vanadium (V) did not interfere with the determination of W(V). The Co (II) in the conditions of the dosage of W(V) did not form a complex with the thiocyanate ions (on the one hand, the environment is strongly acidic, and on the other hand the concentration of the thiocyanate was not sufficient).

Copper ions are reduced during the determination of W(V) and precipitated in the form of CuSNC (it was separated by filtration). Molybdenum (VI) must be extracted first from a solution of HCl at 6 N using diethyl ether or hexane. Vanadium (V) and W(VI) remain completely in the aqueous solution. The presence of small amounts of Pt(IV), U(VI), Re(VII), and Au(III) ions (50 μg) did not interfere with the determination of W(VI).

3.7. Comparison of the developed method with other methods

There are several existing spectrophotometric methods for the determination of W(VI), the comparative study between our method of work and previous work is represented in Table 1.

3.8. Determination of tungsten in high speed steel HS2–9-1–8

The method for the determination of tungsten in high speed steel HS2–9-1–8 containing 2% of W, 9% of Mo, 1% of V, and 8% of Co, is shown by procedure 3.

Note: The volume of the diluted solution taken is 10.00 cm^3 and contains theoretically 160 μg of W(VI). When performing the analysis, six parallel results were found: 99.65, 100.05, 99.75, 99.80, 99.84, and 100.02, the results of mathematical treatment dosage of W(VI) in high speed steel HS2–9-1–8 are given in Table 2.

Using the criterion value t with the liberty degree $f = n-1$ and probability equal to 0.95, the confidence interval: $tS_{\bar{X}} = S_X.\ t_{0.95} = 0.0764 \times 2.57 = 0.1963$, $\%\ tS_X = 0.1963 \times 100/99.88 = 0.1965$. The results found were considered with a confidence interval of: 99.88 at 100.07.

The analysis of the results obtained indicated that the results were in the range of 99.68–100.07% with a probability of 0.95.

4. Conclusion

A method for the identification and dosage of W(VI) based on the formation of the ionic associate of yellow colored $[\mathrm{DB\text{-}18\text{-}C\text{-}6 \cdot NH_4}]_2^+ \cdot [\mathrm{WO(SCN)_5}]^{2-}$ was developed for the determination of W(VI) in the presence of bivalent and trivalent metal ions. The maximum absorption of this complex was 415 nm.

The molar absorption coefficient of the colored complex was $\varepsilon \approx 1.6 \times 10^4$ mol^{-1}cm^{-1} at the wavelength $\lambda = 415$ nm. The detection limit and quantification limit are, respectively, equal to 0.7–1.8 μg.cm^{-3}. By this method the dosage in the range of 1.8–183 μg of W(VI) was realized.

The method developed was applied for the determination of tungsten (VI) in the HSS (high speed steel): HS2–9-1–8 containing 2% of tungsten. The results were processed by a statistical method. The results of the analysis were in the range of 99.66–100.04% with a probability of 0.95.

Symbols

$\lambda_{\max}$ — the wavelength, nm

ε — the molar absorption coefficient, dm^3 mol^{-1} cm^{-1}

References

[1] T. Sato, K. Sato, Liquid–liquid extraction of tungsten (VI) from hydrochloric acid solutions by neutral organophosphorus compounds and high molecular weight amines, Hydrometallurgy 37 (1995) 253–266.

[2] V.M. Shinde, S.M. Khopkar, Liquid–liquid extraction of tungsten(VI) with mesityl oxide application to an alloy steel, Talanta 16 (1969) 525–529.

[3] W. Saab, A. Sarda, G. Cote, Determination of trace metals in high-purity tungsten hexafluoride by electrothermal atomic absorion spectrometry after hydrolysis and selective removal of tungsten by liquid–liquid extraction, Anal. Chim. Acta 248 (1991) 235–239.

[4] M.S. El-Shahawi, L.A. Al Khateeb, Spectrofluorometric determination and chemical speciation of trace concentrations of tungsten species in water using the ion pairing reagent procaine hydrochloride, Talanta 88 (2012) 587–592.

[5] V.D. Lekova, K.B. Gavazov, A.N. Dimitrov, Application of a ternary complex of tungsten(VI) with 4-nitrocatechol and thiazolyl blue for extraction-spectrophotometric determination of tungsten, Chem. Pap. 60 (2006) 283–287.

[6] P.M. Saraswati, J.S. Haramappa, Extractive spectrophotometric determination of tungsten (VI) in alloy steels using ethopropazine hydrochloride, Anal. Sci. 18 (2002) 913.

[7] N. Agnihotri, J.R. Mehta, Extractive spektrophotometric determination of tungsten(VI) using 3-hydroxy-2-(2′-thienyl)-4-oxo-4H-1-benzopyran, J. Anal. Chem. 94 (2004) 341–345.

[8] M. Nabiev, K. Hammoudi, Mise au point d'une méthode de dosage de la vitamine B_{12} à l'aide des éthers couronnes [Development method of vitamin B_{12} determination using crown ethers], STP Pharma Pratiques, Paris, Société Française des Sciences et Techniques Pharmaceutiques 10 (2000) 145–148.

[9] A. Saoud, M. Nabiev, A. Nabieva, B. Hamada, Extraction spectrofotometric method of determiningmolybdinum by dibenzo-18-C-6, Azerbaijan J. Chem. 4 (2009) 158–162.

[10] M. Sivanatham, B. Venkata Rao Tata, C. Anand Babu, Synthesis of crown ether functionalized polyacrylamide gel beads and their extraction behaviour for strontium ions, Desalin. Water Treat. 38 (2012) 8–14.

[11] N. Papadoyannis, G.K. Sarris, Determination of dibenzo-18-crown-6-potassium ferricyanide and ferrocyanide complexes by combined liquid chromatography-flame atomic absorption spectrometry, Anal. Lett. 21 (1988) 21–28.

[12] M. Lauth, P.H. Gramain, Ion chromatographic separation on silica grafted with benzo-18-C-6 crown ether, J. Liq. Chromatogr. 8 (1985) 2403–2415.

[13] W. Walkowiak, C.A. Kozlowski, Macrocycle carriers for separation of metal ions in liquid membrane processes, Desalination 240 (2009) 186–197.

[14] M. Ulewicz, K. Sadowska, J.F. Biernat, Facilitated transport of Zn(II), Cd(II) and Pb(II) across polymer inclusion membranes doped with imidazole azocrownethers, Desalination 214 (2007) 352–364.

[15] J. Ramkumar, B. Maiti, P.K. Mathur, K. Dhole, Crown ethers as carriers for the transport of anionic thiocyanate complex of uranyl ion across a bulk liquid membrane, Sep. Sci. Technol. 35 (2000) 2535–2541.

[16] H. Sodaye, S. Nisan, C. Poletiko, S. Prabhakar, P.K. Tewari, Extraction of uranium from the concentrated brine rejected by integrated nuclear desalination plants, Desalination 235 (2009) 9–32.

[17] M.I. Butt, A. Mamoon, R. Siddique, M. Ejaz, Solvatation of thiocyanate complexe of tungsten(VI) (by 5-(4-pyridyl) nonane) from aqueous hydrochloric acid solutions, J. Radioanal. Nucl. Chem. 88 (2005) 231–239.