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Extraction System for the Spectrophotometric Determination of Tungsten(VI) with 4-Nitrocatechol and Benzalkonium Chloride

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Abstract

A novel chromogenic system for the liquid-liquid extraction and determination of trace amounts of tungsten(VI) was investigated. The system comprises 4-nitrocatechol (4NC) as a chromogenic reagent, sulfuric acid as a complexing medium, and benzalkonium chloride (BAC) as a source of bulky cations (BA^+), which readily form chloroform-extractable ion-association complexes. The impact of foreign ions and reagents was studied, and the optimal conditions for the sensitive, selective, and inexpensive determination of tungsten(VI) were identified. The limit of detection, linear working range, and molar absorptivity at λ_{max} (422 nm) were determined to be 31 ng cm^{-3}, 0.1–4.4 µg cm^{-3}, and 5.49×10^4 dm^3 mol^{-1} cm^{-1}, respectively. The composition of the extracted complex was 1:2:2 (W:4NC:BA). Two potential structures of its anionic component, $[WO_2(4NC)_2]^{2-}$, were discussed based on optimizations at the B3LYP/CEP-4G theoretical level and comparison between theoretical and experimental spectra.

Keywords: Tungsten; liquid-liquid extraction; spectrophotometric determination; 4-nitrobenzene-1,2-diol; benzalkonium chloride; TD DFT calculations

1. Introduction

Tungsten is a third-row transition metal in Group 6 of the Periodic Table. It is distinguished by a number of unique properties, including the highest melting point of all metals, high hardness, high density, excellent corrosion resistance, low coefficient of thermal expansion, high thermal shock resistance, and good electrical conductivity. These properties render it a valuable component in modern technology and necessitate its inclusion in a wide variety of end products, including steels, superalloys, tungsten carbide tools, filament wires, armor-piercing projectiles and darts, nuclear shields, heavy electrical contact points, X-ray tubes, plasma-facing materials, welding rods, glass-to-metal seals, jewelry, pigments, catalysts, chemicals, and many others.[1,2]

Tungsten is a rare element in the Earth's crust, occurring in 53 minerals.[3] It is the heaviest element ($A_r = 183.84$) with a known biological role.[4] Unlike molybdenum, its closest analogue in the periodic table, which is essential for most organisms, tungsten is primarily used by bacteria and archaea. These organisms have developed specialized enzymes that utilize tungsten instead of molybdenum.[5,6]

Tungsten is present in small amounts in food, water, and the atmosphere, but its potential to spread into the environment is increasing rapidly.[4] Humans can be exposed to tungsten through inhalation, ingestion, dermal contact, and ocular contact. The recommended exposure limits established by the National Institute for Occupational Safety and Health are 5 mg m^{-3} for insoluble tungsten and 1 mg m^{-3} for soluble tungsten per 8-hour workday.[7]

The determination of tungsten, especially in trace amounts, is more challenging than that of other metals.[8–10] There are problems associated with both the dissolution of samples and the direct analysis of solids. Commonly employed techniques, such as atomic absorption spectrometry, inductively coupled plasma mass spectrometry, and inductively coupled plasma optical emission spectrometry, face limitations due to matrix effects and difficulties in results interpretation, alongside issues of low sensitivity and high operational costs. Consequently, spectrophotometric methods have become the preferred approach, as evidenced by the extensive literature on the subject.[11–35] These methods are cost-effective and accessible to a wide range of laboratories. By selecting appropriate reagents and optimizing operational parameters, they can achieve sufficient sensitivity, selectivity, and efficiency, particularly when coupled with separation and preconcentration techniques.

The objective of this study was to examine a novel liquid-liquid extraction (LLE) system for the determination of W(VI), based on the complexation reaction of W(VI) with 4-nitrobenzene-1,2-diol (4-nitrocatechol, 4NC)[36,37] in the presence of benzalkonium chloride (BAC). The system has been designed to overcome the primary limitations associated with this widely utilized and adaptable classical technique, namely the formation of stable emulsions, incomplete extraction, poor selectivity, long extraction time, and high organic solvent consumption.[32,38]

4NC is a well-known compound[37,39] that is included in the IUPAC list of the most important analytical reagents for spectrophotometric analysis.[40] It is classified as a non-hazardous substance according to Regulation (EC) No 1272/2008.[41] BAC is a commercially available, cost-effective mixture of alkylbenzyldimethylammonium chlorides with an average molecular weight of 360.[42,43] It has been utilized in our laboratory as an ion-association reagent for LLE of molybdenum[44] and cobalt.[45] Initial studies have indicated that BAC is capable of forming a neutral, poorly water-soluble ternary complex with the anionic W(VI)–4NC species,[36–37] which can be easily extracted from acidic media (pH *ca.* 1.0–1.2) in a small volume of chloroform.

2. Experimental Section

2. 1. Chemicals and Instruments

The following chemicals were purchased and used as aqueous solutions: $Na_2WO_4{\cdot}2H_2O$ (ACS reagent, ≥99%, Merck, Schnelldorf, Germany), 4NC (>98%, Fluka AG, Buchs, Switzerland), BAC (>95.0%, Merck, Schnelldorf, Germany), disodium ethylenediaminetetraacetate dihydrate, $Na_2EDTA{\cdot}2H_2O$ (ACS reagent, 99.0–101.0%, Merck, Schnelldorf, Germany), and sulfuric acid. Their solutions were prepared at concentrations of 2×10^{-4} mol dm^{-3} (W), 7.5×10^{-3} mol dm^{-3} (4NC), 2.5×10^{-3} mol dm^{-3} (BAC), 1.0×10^{-1} mol dm^{-3} (Na_2EDTA), and 2.5 mol dm^{-3} (H_2SO_4). Distilled water was used in the experiments. Chloroform (puriss. p.a., Honeywell, Riedel-de Haën) was repeatedly utilized following the process of redistillation.

Absorbance was measured on an Ultrospec 3300 pro UV/Vis spectrophotometer (Little Chalfont, UK) equipped with 10 mm quartz semi-micro cuvettes of 0.7 cm^3 volume. The pH was checked with a WTW InoLab 720 pH meter (Weilheim, Germany). Chloroform was added to the separating funnels via a 1–5 cm^3 bottle-top dispenser (Ceramus Classic, Hirschmann, Germany).

2. 2. Optimization Procedure

The solutions of W(VI), H_2SO_4, 4NC, and BAC were combined in a separatory funnel, and the total volume was adjusted to 10 cm^3 with water. Then, 3 cm^3 of chloroform was added, and the mixture was shaken for a fixed period of time. A portion of the organic layer was poured into the cuvette, and the absorbance was measured against a similarly prepared blank.

2. 3. Calculation of the Distribution Ratio

The distribution ratio (D) at the optimal conditions (Table 1) was calculated from Equation 1 using the absorbances obtained after single extraction (A_1) and triple extraction (A_3)[44,46,47] at equal conditions. The final volume in both cases was 10 cm^3, and the initial W(VI) concentration in the aqueous phase was 1.0×10^{-5} mol dm^{-3}.

$$D = A_1/(A_3 - A_1) \quad (1)$$

2. 4. Recommended Procedure for the Determination of Tungsten(VI)

An aliquot of the analyzed solution, containing 1–44 µg W(VI), was placed in a 100 cm^3 separatory funnel. The pH was adjusted to a range of 1.0–1.2 with 2.5 mol dm^{-3} H_2SO_4. If the analyzed solution was neutral, the requisite volume of acid was 0.6 cm^3. Subsequently, 0.4 cm^3 of a 7.5 ×

Table 1. LLE-spectrophotometric optimization.[a]

Parameter	Optimization range	Recommended value
Wavelength, nm	UV/Vis	422
Concentration of H_2SO_4, mol dm^{-3}	$(0.063–5.0) \times 10^{-1}$	1.5×10^{-1}
Concentration of 4NC, mol dm^{-3}	$(0.188–7.5) \times 10^{-4}$	3.0×10^{-4}
Concentration of BAC, mol dm^{-3}	$(0.125–3.0) \times 10^{-4}$	2.0×10^{-4}
Extraction time, sec	5–300	90

[a] The volume of the aqueous phase was 10 cm^3 and that of the chloroform was 3 cm^3.

10^{-3} mol dm^{-3} 4NC solution and 0.8 cm^3 of a 2.5×10^{-3} mol dm^{-3} BAC solution were added. If necessary, a masking agent (1.6 cm^3 of a 0.1 mol dm^{-3} Na_2EDTA solution) was added prior to adjusting the volume of the aqueous phase to 10 cm^3. Finally, 3 cm^3 of chloroform was dispensed and the mixture was shaken for 1.5 minutes. Following the separation of the phases, a portion of the chloroform extract was poured into the cuvette and the absorbance was measured at 422 nm against a blank. The concentration of W(VI) was calculated from a calibration plot.

2. 5. Procedure for Dissolving Steel

The steel was dissolved using a methodology that involved treatment with acids (sulfuric and nitric) followed by treatment with NaOH to dissolve the poorly soluble tungsten compounds.[12,16,19,21,30,34] No separation of the matrix was necessary as the selectivity was sufficient, especially in the presence of Na_2EDTA as a masking agent.

A sample of the investigated steel (*ca.* 0.1 g) was treated with 20 cm^3 H_2SO_4 (1:4). Subsequently, approximately 2.5 cm^3 of concentrated HNO_3 was added dropwise. The excess HNO_3 was removed by heating the solution on a sand bath until white SO_3 vapor appeared. After cooling, the solution was alkalinized with 30 % NaOH until a stable residue was obtained. After a waiting period of 15–20 minutes, sulfuric acid (1:10) was added until the precipitate dissolved.[12,16] The solution was then transferred to a 250 cm^3 volumetric flask and made up to the mark with water.

3. Theoretical Section

The ground-state equilibrium geometries of two possible structures of the anionic component, $[WO_2(4NC)_2]^{2-}$, of the obtained complex were optimized at the B3LYP/CEP-4G theoretical level in the gas phase, with no symmetry or structural restrictions. The spin multiplicity and charge were set to 1 and −2, respectively. Subsequent frequency calculations were performed to demonstrate that the optimized structures possess no imaginary frequencies, thereby confirming their stability as minima. Additionally, vertical excitation energies were computed to simulate their UV/Vis spectra. The calculations were performed using the GAUSSIAN 03 software. The ChemCraft program, v. 1.8 was employed for the visualization of the two structures.

4. Results and Discussion

4. 1. LLE-Spectrophotometric Optimization

A single-factor optimization was conducted at room temperature (approximately 22 °C) to identify the optimal values for the following experimental parameters: sulfuric acid concentration (Fig. 1), 4NC concentration (Fig. 2, series 1), BAC concentration (Fig. 2, series 2), and extraction time (Fig. 3). The absorption maximum (λ_{max}) was observed at 422 nm, a wavelength at which the absorbance of the blank was close to zero (Fig. 4). All subsequent LLE-spectrophotometric studies were conducted under the optimal conditions shown in Table 1.

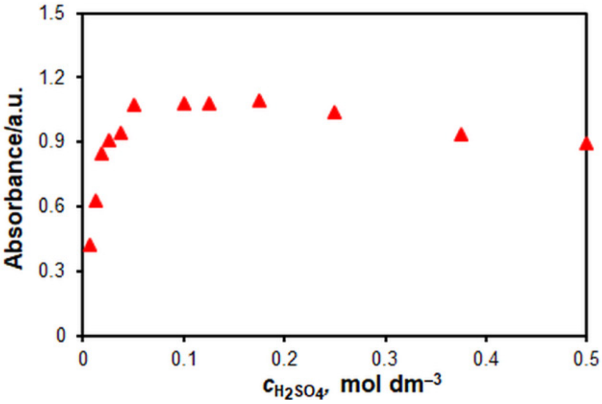

Figure 1. Effect of H_2SO_4 concentration: $c_W = 2 \times 10^{-5}$ mol dm^{-3}, $c_{4NC} = 7.5 \times 10^{-4}$ mol dm^{-3}, $c_{BAC} = 2.5 \times 10^{-4}$ mol dm^{-3}, $t_{ex} = 1.5$ min, $\lambda = 422$ nm.

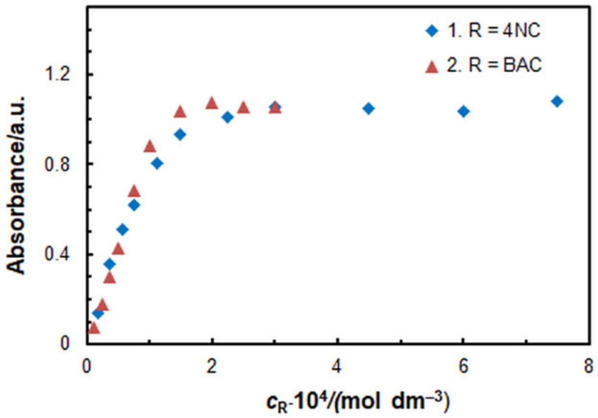

Figure 2. Effect of 4NC (1) and BAC (2) concentration: $c_W = 2 \times 10^{-5}$ mol dm^{-3}, $c_{H2SO4} = 1.5 \times 10^{-1}$ mol dm^{-3}, $t_{ex} = 1.5$ min, $\lambda = 422$ nm. 1: $c_{BAC} = 10^{-4}$ mol dm^{-3}; 2: $c_{4NC} = 3 \times 10^{-4}$ mol dm^{-3}.

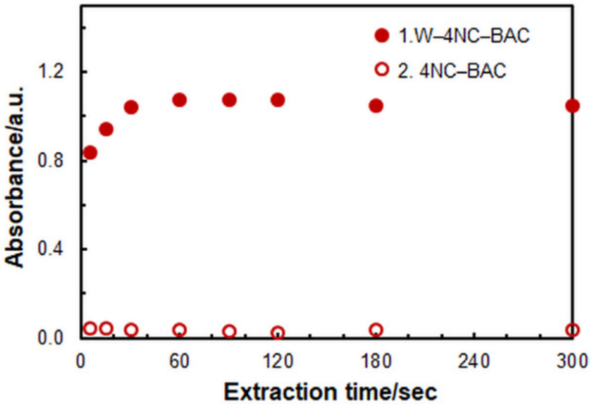

Figure 3. Effect of the extraction time: $c_W = 2 \times 10^{-5}$ mol dm^{-3}, $c_{4NC} = 3 \times 10^{-4}$ mol dm^{-3}, $c_{BAC} = 2 \times 10^{-4}$ mol dm^{-3}, $c_{H2SO4} = 1.5 \times 10^{-1}$ mol dm^{-3}, $\lambda = 422$ nm.

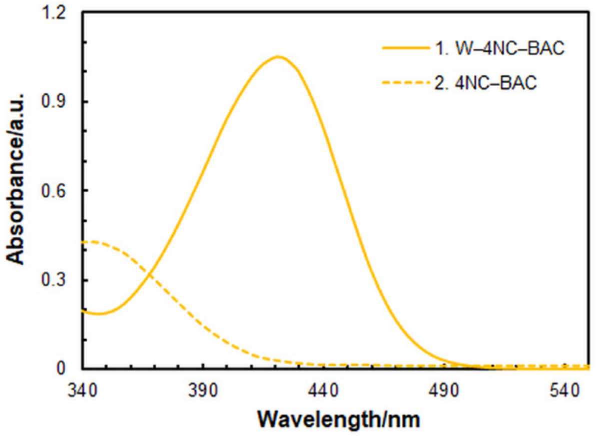

Figure 4. Absorption spectra of the ternary complex (1) and blank (2): $c_W = 2 \times 10^{-5}$ mol dm^{-3}, $c_{4NC} = 3 \times 10^{-4}$ mol dm^{-3}, $c_{BAC} = 2 \times 10^{-4}$ mol dm^{-3}, $c_{H2SO4} = 1.5 \times 10^{-1}$ mol dm^{-3}, $t_{ex} = 1.5$ min.

4. 2. Composition, Formula and Chemical Equation

Two methods were employed to ascertain the molar ratios in the extracted ternary complex. These were the mobile equilibrium method[48] (Figure 5) and the straight-line method of Asmus[49] (Figure 6 a and b). The results are consistent with the conclusion that the complex has a composition of 1:2:2 (W:4NC:BAC). This composition is identical to that reported for complexes containing tetrazolium cations instead of benzalkonium cations (BA^+).[16] Consequently, the anionic part of the complex can be represented by the formula $[WO_2(4NC)_2]^{2-}$.[16,36] Its association with BA^+ and the subsequent chloroform extraction can be represented by Equation 2.

$$[WO_2(4NC)_2]^{2-}{}_{(aq)} + 2\,BA^+{}_{(aq)} \leftrightharpoons (BA^+)_2[WO_2(4NC)_2]_{(chloroform)} \qquad (2)$$

It is noteworthy that the behavior of Mo(VI) in such a system differs from that of W(VI), despite the widely recognized similarities in the chemistry of both elements [5,36,50,51]. In fact, under analogous conditions, Mo(VI) is extracted as a 1:1:2-complex (Mo:4NC:BAC), whose established formula is $(BA^+)_2[MoO_2(OH)_2(4NC)]$.[44]

4. 3. Distribution Ratio and Extraction Constant

Table 2 presents data for the distribution ratio (D) and the extraction constant (K_{ex}) characterizing Equation 2. Several methods based on the BAC saturation curve (Figure 2) were employed to ascertain this constant. These included the Harvey-Manning method,[52] the Holme-Lanhmyhr method,[53] and the mobile equilibrium method.[48] The statistical identity of the values obtained indicates the absence of significant side processes. It is evident that the complex is suitable for analytical applications.

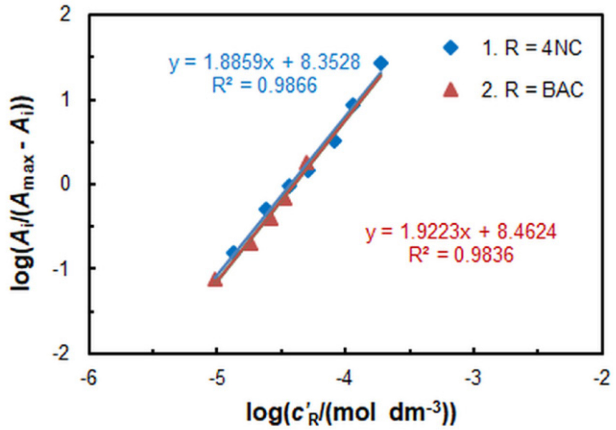

Figure 5. Determination of the 4NC : W (1) and BAC : W (2) molar ratios by the mobile equilibrium method. The resulting straight lines are based on the experimental points in Figure 2.

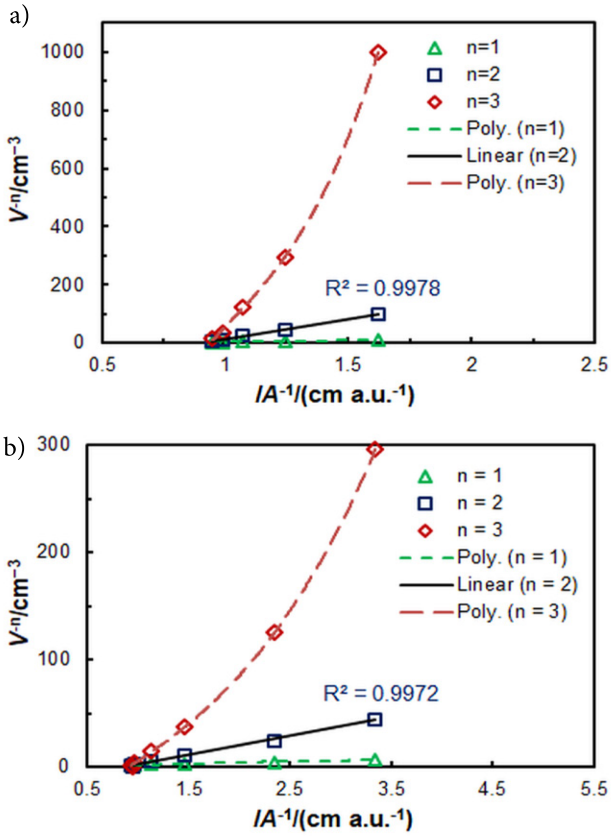

Figure 6. Determination of the 4NC : W (**a**) and BAC : W (**b**) molar ratios by the method of Asmus

Table 2. Extraction characteristics.

Characteristic	Value
Distribution ratio (log$D$)	1.03 ± 0.15 (n = 4)
Extraction constant (logK_{ex})	8.76 ± 0.05 [a]; 8.88 ± 0.14 [b]; 8.80 ± 0.70 [c]

[a] Harvey-Manning method; [b] Holme-Lanhmyhr method; [c] Mobile equilibrium method

4. 4. Ground-State Equilibrium Geometries and Spectral Comparison

It is postulated that the anionic component of the ternary complex is responsible for the spectral bands in the visible region. This is based on the fact that the benzalkonium ion (BA^+) is colorless and the complex is of the type of ionic associates.[44,45,54] To verify this assumption, the anion $[WO_2(4NC)_2]^{2-}$ was modeled using time-dependent density functional theory (TD DFT) calculations. Two isomers differing in the mutual arrangement of the NO_2 groups are theoretically possible.[55] Figure 7 illustrates their optimized ground state equilibrium geometries. The two structures, denoted as Str. 1 and Str. 2, possess octahedral symmetry, and differ slightly in bond lengths and valence angles. The aforementioned structures were employed to calculate vertical excitation energies with the time-dependent Hamiltonian, in order to simulate their theoretical absorption spectra.

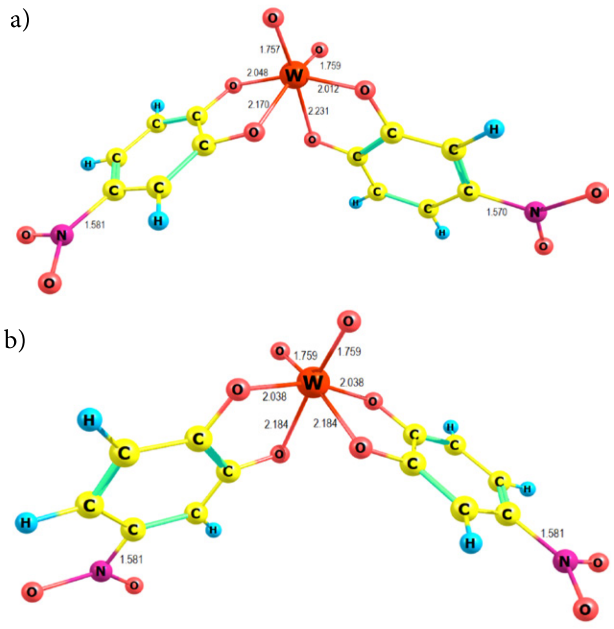

Figure 7. Optimized ground-state equilibrium geometries of the two $[WO_2(4NC)_2]^{2-}$ isomers (**a** – Str. 1; **b** – Str. 2) found at the B3LYP/CEP-4G level

Figure 8 depicts the experimental spectrum of the ternary complex and the theoretical spectra of the two isomers at a scaling factor of 1. It can be concluded that the theoretical spectrum of Str. 1 is closer to the experimental spectrum. However, the presence of Str. 2 in the extract cannot be excluded. It seems that the presence of both structures would be very probable in case their energies are close.

4. 5. Energy Analysis

The frequency calculations demonstrated that the two structures in Figure 7 are real minima. Their energy components are presented in Table 3. The Δ values were calculated as the difference between the energy components of Str. 1 and Str. 2, respectively. As can be observed, Str. 1 is slightly more stable than Str. 2. The transformation Str. 1 → Str. 2 is an endothermic reaction accompanied by an increase in the Gibbs free energy. The transformation is also accompanied by an insignificant entropy change (0.4 J mol^{-1} K^{-1}).

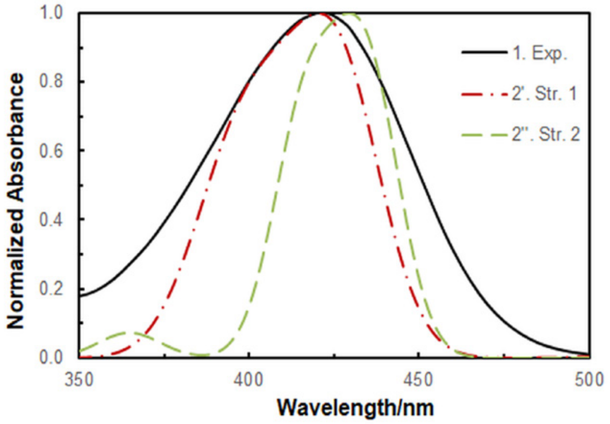

Figure 8. Comparison of the experimental spectrum (Exp.) with the two theoretical spectra (Str. 1 and Str. 2) found at the B3LYP/CEP-4G level and a scaling factor of 1

Table 3. Energy Analysis.

Energy component, a. u.	Str. 1, a. u.	Str. 2, a. u.	Δ, kJ mol^{-1}
Electron energy, *E*	−317.379176	−317.374731	11.7
E_o[a]	−317.208893	−317.204624	11.2
H[b]	−317.183715	−317.179417	11.3
G[c]	−317.265041	−317.260915	10.8

[a] Sum of electronic and zero-point energies; [b] sum of electronic and thermal enthalpies; [c] sum of electronic and thermal free energies

4. 6. Impact of Foreign Ions and Masking Agents

The impact of foreign ions and masking agents is presented in Table 4. It is evident that large amounts of many ions do not affect the absorption of the resulting extract. The presence of at least a 5000-fold excess of Na_2EDTA, which is known as an excellent masking agent, is tolerable. If necessary, this agent can additionally raise the limiting tolerance ratios for some of the ions known to form complexes with 4NC.[37] Unfortunately, Na_2EDTA was unable to cope with interferences caused by Mo(VI) and Cr(VI). Further studies demonstrated that the Cr(VI) interference problem can be readily solved through the use of ascorbic acid.

Table 4. Impact of foreign ions on the determination of 12 μg W(VI)

Foreign ion (FI)	Formula of the added salt	Amount of FI added/mg	FI : W(VI) mass ratio	Amount of W found/μg	*E*%
Acetate	$CH_3COONa\cdot 3H_2O$	12.0	1000 [a]	12.3	102
Al(III)	$Al_2(SO_4)_3\cdot 18H_2O$	12.0	1000 [a]	12.4	103
Br^-	NaBr	0.12	10	12.0	100
Ca(II)	$CaSO_4\cdot 2H_2O$	3.6	300 [a]	11.6	96.4
Cd(II)	$CdSO_4\cdot 8/3H_2O$	9.0	750	12.1	101
Citrate	$Na_3C_6H_5O_7$	0.6	50	11.5	96.2
Cl^-	NaCl	0.9	75	12.0	99.7
Co(II)	$CoSO_4\cdot 7H_2O$	0.6	50	12.4	103
Cr(III)	$Cr_2(SO_4)_3$	1.2	100	12.0	99.7
Cr(VI)	K_2CrO_4	0.006	0.5	12.4	104
		0.24 [b]	20 [b]	12.2 [b]	101 [b]
Cu(II)	$CuSO_4\cdot 5H_2O$	12.0	1000 [a]	11.6	97.1
$EDTA^{2-}$	$Na_2EDTA\cdot 2H_2O$	60.0	5000 [a]	11.8	98.7
F^-	NaF	0.6	50	11.7	97.6
Fe(II)	$(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$	0.24	20	11.9	99.2
Fe(III)	$Fe_2(SO_4)_3$	4.8	400	11.9	99.2
$H_2PO_4^-$	KH_2PO_4	12.0	1000 [a]	11.6	96.3
K^+	K_2SO_4	12.0	1000 [a]	12.1	101
Li^+	$Li_2SO_4\cdot H_2O$	12.0	1000 [a]	12.5	104
Mg(II)	$MgSO_4\cdot 7H_2O$	12.0	1000 [a]	12.1	101
Mn(II)	$MnSO_4\cdot H_2O$	0.6	50	11.9	99.0
Mo(VI)	$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	0.006	0.5	21	175
Ni(II)	$NiSO_4\cdot 7H_2O$	12.0	1000 [a]	12.1	101
NO_3^-	$NaNO_3$	0.18	10	12.4	103
		6.0	500	1.03	8.6
Pb	$Pb(CH_3COO)_2\cdot 3H_2O$	6.0	500 [a]	12.1	101
Re(VII)	NH_4ReO_4	0.12	10	12.5	104
Tartrate	$K,NaC_4H_4O_6$	0.6	50	11.8	98.3
V(V)	NH_4VO_3	0.024	2	12.1;	101
		0.36 [b]	30 [b]	12.1 [b]	101 [b]
		0.6 [c]	50 [c]	11.4 [c]	95.0 [c]
Zn(II)	$ZnSO_4\cdot 7H_2O$	2.4	200	12.2	102

[a] Higher FI-to-W(VI) ratios were not studied; [b] in the presence of 0.33 cm^3 0.2 mol dm^{-3} ascorbic acid; [c] in the presence of 1.6 cm^3 0.1 mol dm^{-3} Na_2EDTA

4. 7. Analytical Characteristics and Application

The relationship between absorbance and W(VI) concentration was linear up to 4.4 μg cm^{-3} W(VI) (R^2 = 0.9999, n = 8). The linear regression equation was $A = 0.2986\gamma + 0.0002$, where γ is the concentration in μg cm^{-3}. The standard deviation of the slope was 0.0013, while that of the intercept was 0.0031. Consequently, the intercept is statistically indistinguishable from zero. The molar absorption coefficient was 5.49 × 10^4 dm^3 mol^{-1} cm^{-1}, and the Sandall's sensitivity was 3.35 × 10^{-3} μg cm^{-2}. The limit of detection (LOD) and limit of quantification (LOQ) were calculated in two ways: 1) as three and ten times the standard deviation of the blank divided by the slope; and 2) as three and ten times the standard deviation of the ordinate intercept divided by the slope. The results were virtually identical: LOD = 31 ng cm^{-3}, and LOQ = 104 ng cm^{-3}.

The proposed analytical procedure was then applied to the analysis of a reference standard steel (RSS) and several artificial mixtures (AMs) that mimicked typical tungsten-containing alloys.[1] The results are presented in Table 5. The relative standard deviation (RSD) for these determinations was in the range of 0.94–2.25%.

It is important to note that the NaOH treatment in the RSS sample preparation stage (see above) was a critical step in obtaining reliable results. Failure to include this step may result in incomplete decomposition of the insoluble tungsten species. This is consistent with the data presented in Refs.[9,56]

4. 8. Comparison with Other Methods Involving LLE

A comparison of the present method with other published methods for tungsten determination involving LLE is presented in Table 6. The present method exhibits excellent linearity and relatively high sensitivity. It is robust and reliable due to the wide optimum ranges of the parameters

Table 5. Determination of tungsten in a referent standard steel (RSS) and artificial mixtures (AM)

	Sample			**Present method**	
	Description	**W content/%**	**Other metal components/%**	**Tungsten found[a]/%**	**RSD/ %**
RSS	Referent standard steel [b]	1.57	17.55 (Cr), 9.61 (Ni), 1.04 (V), 0.99 (Nb), 0.13 (Ta), and the balance Fe	1.58	0.94
AM-1	chromium-tungsten shock resistant steel	2.00	1.0 (Cr), and the balance Fe	2.02	1.13
AM-2	9 % tungsten hot die steel	9.00	2.5 (Cr) and the balance Fe	8.89	1.57
AM-3	Stellite	10.0	25 (Cr), 2 (Ni), 0.5 (Mn), 0.1 (Mo), and the balance Co	10.2	2.25
AM-4	18 % tungsten general purpose high-speed cutting steel	18.0	4.5 (Cr), 1.25 (V), and the balance Fe	18.2	1.81
AM-5	12% cobalt super high-speed steel	21.0	12.0 (Co), 4.5 (Cr), 1.25 (V), and the balance Fe	21.3	1.97
AM-6	Tungsten-bearing super-alloys	50.0	50.0 (Cu)	49.2	1.83

[a] Average of four replicate determinations; [b] Supplied by the Holding KCM 2000, Plovdiv, Bulgaria

Table 6. Comparison with other LLE procedures for tungsten determination

Technique	**Reagent(s)**	**Extraction solvent (ES)**	**Volume of ES/ cm^3**	**Acidity**	**Working range/ μg cm^{-3}**	**λ, nm**	**$10^{-4}\varepsilon$/ dm^3 mol^{-1} cm^{-1}**	**Sample**	**Ref. (Year)**
UV/Vis	EPH + NH_4SCN	Chloroform	10	4 mol dm^{-3} HCl	1–15	404	1.74	Steel	[13] (2002)
UV/Vis	HTB	Dichloromethane	10	0.2 mol dm^{-3} HCl	0.44–2.8	415	6.45	Synthetic samples and reverberatory flue dust	[14] (2004)
UV/Vis	4NC + MTT	Chloroform	10	pH 1.2–3.6	0.92–8.8	415	2.8	Steel and ferrotungsten	[16] (2006)
UV/Vis	CHTB	Chloroform	10	0.16–0.32 mol dm^{-3} HCl	0.5–3.0	420	4.05	Synthetic, technical, and natural samples	[17] (2008)
UV/Vis	M2B	Toluene	5	pH 3	0.2–1.8	591	7.1	Steel	[18] (2009)
UV/Vis	HCTP + HA	Chloroform	5	pH 4.2–5.4	0.5–16	465–475	2.4–2.6	Steel	[19] (2013)
UV/Vis	CHPB	Chloroform	10	0.04–0.32 mol dm^{-3} HCl	0.9–2.9	420	3.125	Synthetic and standard samples	[20] (2013)
UV/Vis	HCTP + DPG	Chloroform	5	pH 5–6	0.2–20	480	5.6	Steel, soil, and pea	[22, 23] (2015, 2016)
UV/Vis	HTPD + HA	Chloroform	5	pH 3.5–5.5	0.04–3.8	461–490	2.0–2.8	Steel and soil	[24] (2016)
UV/Vis	DTMP + HA	Chloroform	5	pH 3.9–5.2	0.4–16	476–480	2.73–2.92	Steel, soil, and plant	[26] (2017)
UV/Vis	HPMPPB	Chloroform	10	0.1 mol dm^{-3} HCl	0.36–2.0	420	9.936	Synthetic and industrial samples	[29] (2019)
UV/Vis	HBTP + HA	Chloroform	5	pH 4.1–5.6	0.2–16	470–482	2.6–3.9	Steel	[30] (2019)
UV/Vis	HMTB	Dichloromethane	10	0.1 mol dm^{-3} HCl	0.35–1.5	418	8.28	Synthetic and technical samples	[31] (2019)
AAS	HBPNAB	n-Butanol	10	pH 2–3	1–10	255.1	3.4–4.2	Steel	[57] (2022)
UV/Vis	HTPD + HA	Chloroform	5	pH 4.5–5.5	0.04–3.8	490	2.0–2.8	Steel and soil	[33] (2022)
UV/Vis	DB-18-C-6 + NH_4SCN	Chloroform	10	2.5 mol dm^{-3} HCl	1.8–183	415	1.6	Water samples and steel	[21,34] (2014, 2022)
UV/Vis	HTP + HA	Chloroform	5	pH 1.8–5.1	0.2–19	457–538	3.2–4.2	Soil	[35] (2023)
UV/Vis	4NC + BAC	Chloroform	3	0.05–0.20 mol dm^{-3} H_2SO_4	0.1–4.4	422	5.49	Synthetic samples and steel	This work

Abbreviations: 4NC, 4-nitrocatechol; BAC, benzalkonium chloride; CHPB, 6-chloro-3-hydroxy-2-phenyl-4-oxo-4*H*-1-benzopyran; CHTB, 6-chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4*H*-1-benzopyran; DB-18-C-6, dibenzo–18–C-6(2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacyclooctadeca-2,11-diene; DPG, diphenylguanidine; DTMP, 2,6-dithiol-4-methylphenol; EPH, ethopropazine hydrochloride; HA, hydrophobic amines; HBPNAB, 2-hydroxy-5-tret-butylphenol-4'-nitroazobenzene; HBTP, 2-hydroxy-5-bromothiophenol; HCTP, 2-hydroxy-5-chlorothiophenol; HMTB, 3-hydroxy-2-[2'-(5'-methylthienyl)]-4-oxo-4*H*-1-benzopyran; HPMPPB, 3-hydroxy-2-[1´-phenyl-3´-(p-methylphenyl)-4´-pyrazolyl]-4-oxo-4*H*-1-benzopyran; HTB, 3-hydroxy-2-(2'-thienyl)-4-oxo-4*H*-1-benzopyran; HTP, 2-hydroxy-5-halogenthiophenols; HTPD, o-hydroxythiophenol derivatives; M2B, methyl type 2B; MTT, 3-(4,5- dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide.

and the high tolerable levels of most of the side ions studied. The reagents used are commercially available and do not require tedious syntheses. The determination is rapid, as the extraction time is short, and no stable emulsion is formed. Moreover, the volume of organic solvent utilized ($3\ cm^3$ per sample) is less than that of the other procedures listed in Table 6.

5. Conclusions

A novel liquid-liquid extraction system for W(VI) involving inexpensive commercially available reagents (4NC and BAC) was subjected to a comprehensive study. The optimal conditions for the formation and extraction of a ternary complex, $(BA^+)_2[WO_2(4NC)_2]$, were identified. The structure of its anionic component $[WO_2(4NC)_2]^{2-}$, which is responsible for the spectral bands in the visible region, was elucidated through the use of theoretical calculations at the B3LYP/CEP-4G level. The complex is intensely colored, allowing for the determination of trace amounts of W(VI) in a simple and economical manner without the use of sophisticated instruments and expensive consumables. The developed method is sensitive, selective, rapid, and robust. Its reliability can be attributed to the high stability of the extracted complex, the low absorption of the blank, and the wide optimal ranges of the investigated parameters. The method has been successfully applied to the analysis of steel and artificial mixtures that closely resemble typical tungsten-containing alloys.

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Povzetek

Raziskovali smo nov kromogeni sistem za ekstrakcijo tekoče-tekoče in določevanje sledov volframa(VI). Sistem sestavljajo 4-nitrokatehol (4NC) kot kromogeni reagent, žveplovo kislino kot kompleksirajoči medij in benzalkonijev klorid (BAC) kot vir velikih kationov (BA^+), ki zlahka tvorijo ionske komplekse ki jih je možno ekstrahirati s kloroformom. Preučevali smo vpliv tujih ionov in reagentov in določili optimalne pogoje za občutljivo, selektivno in cenovno ugodno določanje volframa(VI). Meja detekcije, linearno področje analize in molarni absorpcijski koeficient pri λ_{max} (422 nm) znašajo 31 ng cm^{-3}, 0.1–4.4 µg cm^{-3} in 5.49×10^4 dm^3 mol^{-1} cm^{-1}. Sestava ekstrahiranega kompleksa je bila 1:2:2 (W:4NC:BA). Dve možni strukturi anionskega dela kompleksa, $[WO_2(4NC)_2]^{2-}$, smo diskutirali na osnovi optimizacije z metodo B3LYP/CEP-4G in primerjave med izračunanimi ter izmerjenimi spektri.