Lecture Mo(VI)

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“STUDY ON THE COMPLEX FORMATION OF THE ANIONIC CHELATE OF MO(VI) WITH BIDENTATE LIGAND AND THE CATION OF MONOTETRAZOLIUM SALT FOR ITS POTENTIAL DETERMINATION IN BIOLOGICAL SYSTEMS„

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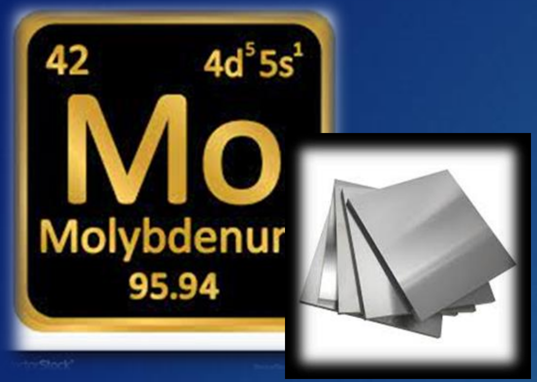
Molybdenum

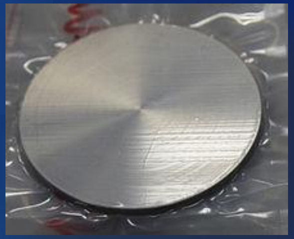
Molybdenum - the secret of the sharpness and strength of ancient samurai swords

- Scientists in Europe for several centuries failed to detected the mystery of the sharpness and strength of ancient samurai swords. Just in the 19th century in swords of the 14th century an admixture of Mo was found, which determines their high strength.
- Due to its refractoriness and low coefficient of thermal expansion, Mo is widely used in electrical engineering, radio electronics and high temperature technology.



Molybdenum characterization

- **Molybdenum** - position 42 in the periodic table; the second-row transition metal; belongs to group 6;
- **Molybdenum** is a soft, ductile, lustrous, silvery-white metal



✓ high thermal and electrical conductivity,

✓ low vapor pressure, low coefficient of thermal expansion,

✓ and good alloyability with ferrous and nonferrous metals.

- Molybdenum's role in such materials is to improve the hardness, strength, ductility, and resistance to shock, fatigue, and creep, especially at elevated temperatures. The main application is in metallurgy.
- There are 31 known isotopes of molybdenum. Occur naturally – 7 isotopes. The most common isotopic molybdenum application involves ^{99}Mo used in various imaging applications in medicine.

Molybdenum occurrence

Molybdenum is not widely distributed in nature.

- In the Earth's crust – 0.0003% by weight (average content – 1.2 mg kg^{-1});
- In the water of the oceans – 8,9 to 12,2 mg L^{-1};
- About 20 molybdenum minerals are known.
- The most important of them: molybdenite MoS_2 (60 % Mo), povelite $CaMoO_4$ (48 % Mo), molibdit $Fe(MoO_4)_3 \cdot nH_2O$ (60 % Mo) и wulfenite $PbMoO_4$.

Molybdenum essentiality

Although Mo is a relatively rare element, it is essential for microorganisms, plants, and animals. More than 50 molybdenum-dependent enzymes are known in all kingdoms of life.

Molybdenum in the body of plants, animals and humans is constantly present as a microelement involved mainly in nitrogen metabolism.

Molybdenum is essential for the activity of a number of redox enzymes.

In plants, Molybdenum stimulates the biosynthesis of nucleic acids and proteins, increases the content of chlorophyll and vitamins.

In the absence of Molybdenum legumes, oats, tomatoes, lettuce and other plants get sick, do not bear fruit and die.

In a high percentage of cases, people who took 10-15 mg of Mo a day developed gout.

Terms concerning molybdenum intake

The WHO and European Commission's Directorate-General for Health and Food Safety introduces:

Recommended Dietary Allowances (RDAs)

- for adults – 20-50 year – 45 µg/day for males and females;

Average dietary intake

- for adults – 20-50 year – 109 µg/day for males;
- for adults – 20-50 year – 76 µg/day for females;

Tolerable upper intake level (UL)

- for adults – 14-70 year – 2 mg/day.

Excessive accumulation of molybdenum in the body is toxic.

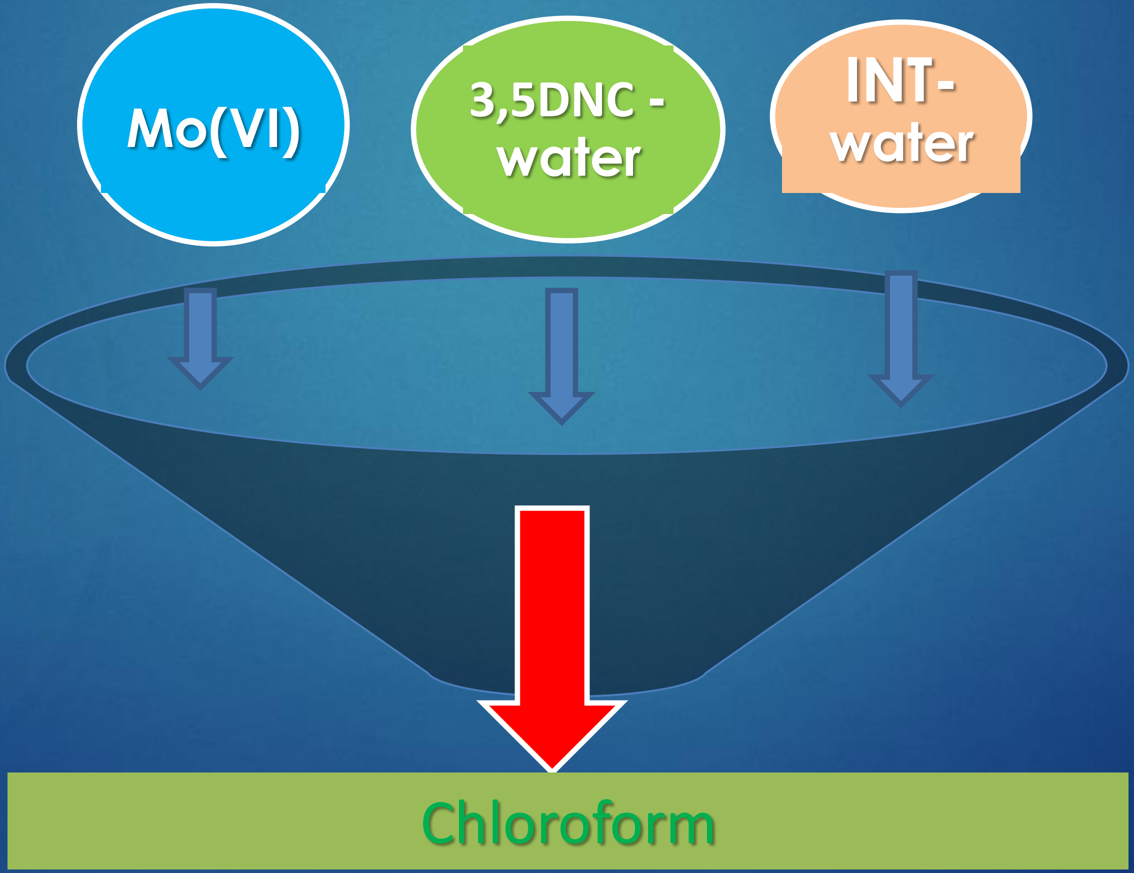
Molybdenum in analytical techniques

Methods involving spectrophotometry

- simple and low-cost;
- can be easily combined with procedures for preliminary separation and concentration;
- can be easily combined with cloud point extraction;
- can be easily combined with liquid-liquid extraction.

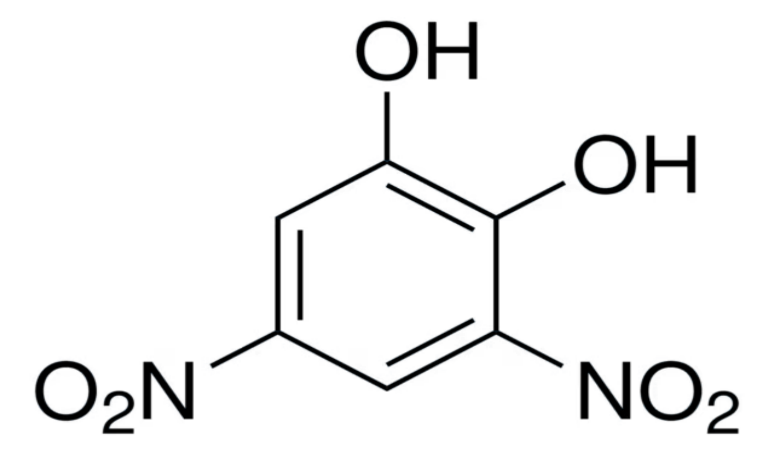
The aim of the present work is:

To develop a sensitive and selective extractive spectrophotometric procedure for the determination of molybdenum in alloys, biological, medical and pharmaceutical samples with 3,5-Dinitrocatechol (3,5-DNC) and 2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT).

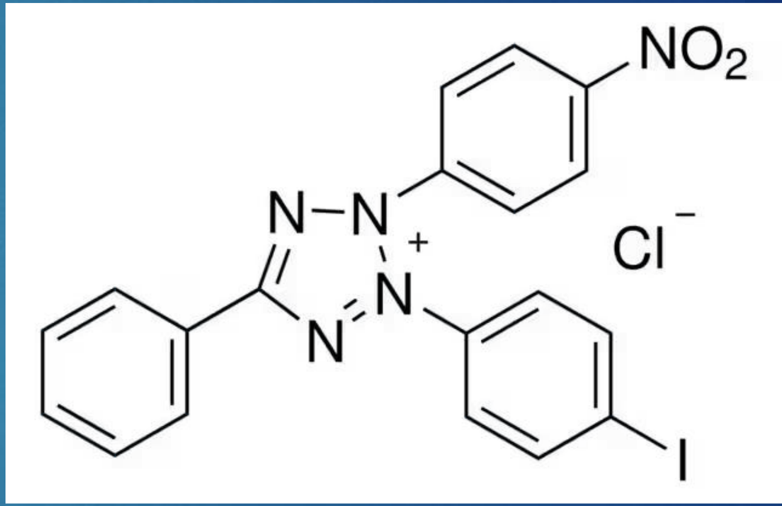


Reagents and apparatus

- . 3,5-Dinitrocatechol (3,5-DNC) – a well-known analytical reagent;
- . 2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) – has been used in biological and analytical practice.



3,5-Dinitrocatechol (3,5-DNC)
Molecular formula: $C_6H_4N_2O_6$



2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT)
Molecular formula: $C_{19}H_{13}ClIN_5O_2$

Reagents and apparatus

- Solution of Mo^{VI} (2×10^{-4} mol dm^{-3}) was prepared by dissolving $Na_2MoO_4\cdot2H_2O$ (purum, 99.98% trace metals basis, Fluka, Germany) – aqueous solutions 1.04×10^{-2} mol dm^{-3} in distilled water containing H_2SO_4 were used.
- 3,5-Dinitrocatechol (3,5-DNC) (Sigma–Aldrich GmbH, Germany) – solutions in $CHCl_3$ with concentrations of 1×10^{-3} mol dm^{-3}.
- 2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) (p.a., Sigma–Aldrich GmbH, Germany) – aqueous solutions with concentrations of 2.0×10^{-3} mol dm^{-3} were used.
- H_2SO_4 (95-97% for analysis, Merck) – 2 mol dm^{-3} solution was prepared.
- Absorbance measurements were performed by using a Camspec M508 (UK).

Results and Discussion

1. Liquid–liquid extraction–spectrophotometric optimization
1.1. Absorption spectra of complex in chloroform

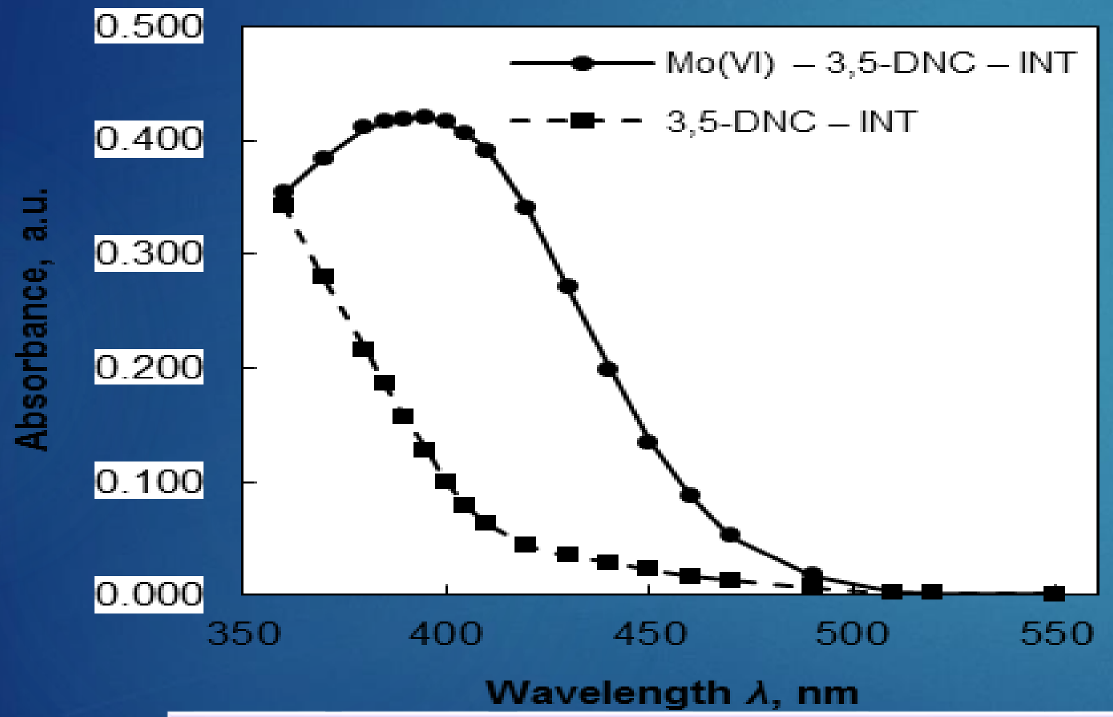


Figure 1. Absorption spectra of the complex Mo(VI)–3,5-DNC–INT and of the blank sample 3,5-DNC–INT in $CHCl_3$
$C_{Mo(VI)} = 2.08 \times 10^{-5}$ mol L^{-1}; $C_{3,5\text{-}DNC} = 2.0 \times 10^{-4}$ mol L^{-1}, $C_{INT} = 2.0 \times 10^{-4}$ mol L^{-1}; $C_{H2SO4} = 4.0 \times 10^{-1}$ mol L^{-1}; $\lambda = 395$ nm; $\tau = 1$ min

Under the optimum conditions (Table 1), the complex has an absorption maximum at 395 nm, where the blank absorbs insignificantly.

Results and Discussion

1.2. Optimum extraction-spectrophotometric conditions

Optimum conditions	Analytical characteristic
Absorption maximum (λ_{max}) 395 nm	Apparent molar absorptivity (ε') $(2.05 \pm 0.06)\times10^4$ L mol^{-1}cm^{-1}
Volume of the aqueous phase 10 cm^3	True molar absorptivity (ε) $(1.92 \pm 0.07)\times10^4$ L mol^{-1}cm^{-1}
Volume of the organic phase 10 cm^3	Sandell's sensitivity (SS) 4.68 ng cm^{-2}
Concentration of H_2SO_4 in the aqueous phase $(1.6\div6.0)\times 10^{-1}$ mol L^{-1}	Adherence to Beer's law up to 4.99 μg cm^{-3}
Shaking time (τ) 1 min	Relative standard deviation (RSD) 1.92%
Concentration of 3,5-DNC $C_{3,5\text{-}DNC} \geq 1.0 \times 10^{-4}$ mol L^{-1}	Limit of detection (LOD) 0.31 μg cm^{-3}
Concentration of INT $C_{INT} \geq 2.0 \times 10^{-4}$ mol L^{-1}	Limit of quantification (LOQ) 1.03 μg cm^{-3}

Table 1. Optimum extraction-spectrophotometric conditions and analytical characteristics of the system

Effect of co-existing ions and reagents on the complex formation of the ion-associate Mo(VI)–3,5-DNC–INT for extraction in the presence of 20 μg Mo(VI)

Table 2.

Co-existing ion and reagent	Co-existing ion and reagent, μg/10 cm^3 aqueous phase	Mo(VI) found, μg	R, %
Na^+	10000	20.45	102.25
K^+	10000	20.21	101.05
Mg^{2+}	10000	20.55	102.75
Ca^{2+}	10000	20.07	100.35
Cu^{2+}	10000	19.54	97.68
Zn^{2+}	10000	19.98	99.92
Cd^{2+}	10000	20.39	101.95
Ni^{2+}	10000	19.77	98.86
Co^{2+}	10000	20.39	101.95
Al^{3+}	2000	20.09	100.45
Cr^{3+}	10000	19.94	99.68
Fe^{2+}	750	19.61	98.05
Fe^{3+}	100	16.21	81.03
V(V)	100	21.83	109.14
Cr(VI)	100	20.39	101.96
W(VI)	50	25.95	129.75

Effect of co-existing ions and reagents on the complex formation of the ion-associate Mo(VI)–3,5-DNC–INT for extraction in the presence of 20 µg Mo(VI)

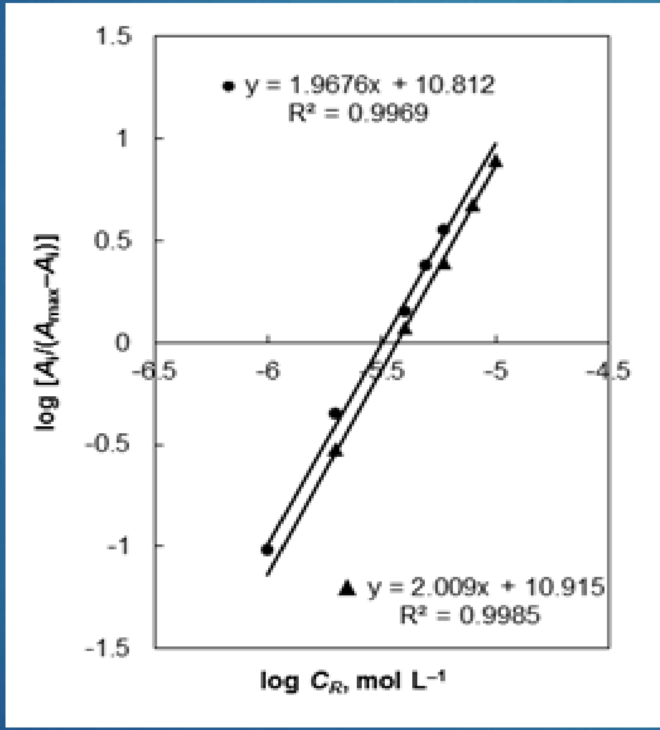
Table 4.

Co-existing ion and reagent	Co-existing ion and reagent, µg/10 cm^3 aqueous phase	Mo(VI) found, µg	R, %
F^{-}	10000	20.53	102.65
Br^{-}	10000	20.55	102.77
PO_4^{3-}	10000	20.19	100.97
$P_2O_7^{4-}$	10000	19.84	99.18
$C_2O_4^{2-}$	10000	13.98	69.89
CH_3COO^{-}	10000	20.55	102.74
$C_4H_4O_6^{2-}$	10000	20.22	101.11
$C_6H_5O_7^{3-}$	10000	20.24	100.21
Complexone III	10000	20.07	100.35
Complexone IV	10000	20.41	102.03
L- Ascorbic acid	1000	20.04	100.18

Mo(VI) – 3,5-DNC – INT

2. Molar Ratios

2.1. Molar ratios, formulae and equations



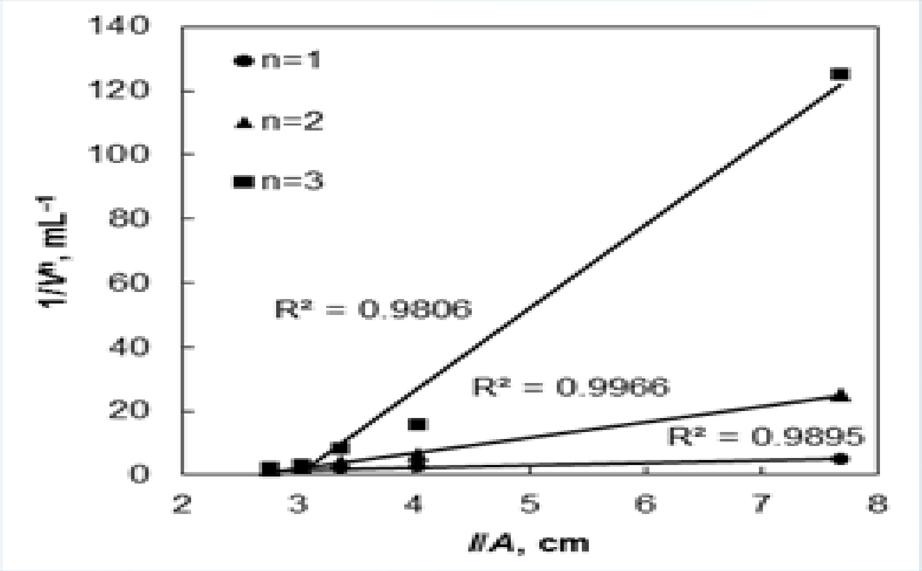
Mo(VI):3,5-DTC and **Mo(VI):INT** **molar ratio**

Figure 2. Straight lines by the mobile equilibrium method for determination of the molar ratios Mo(VI):3,5-DTC and Mo(VI):INT

Mo(VI) – 3,5-DNC – INT

2. Molar Ratios

2.2. Molar ratios, formulae and equations



Mo(VI):3,5-DNC molar ratio

Figure 3. Determination of molar ratio (n) Mo(VI):3,5-DNC by the method of Asmus

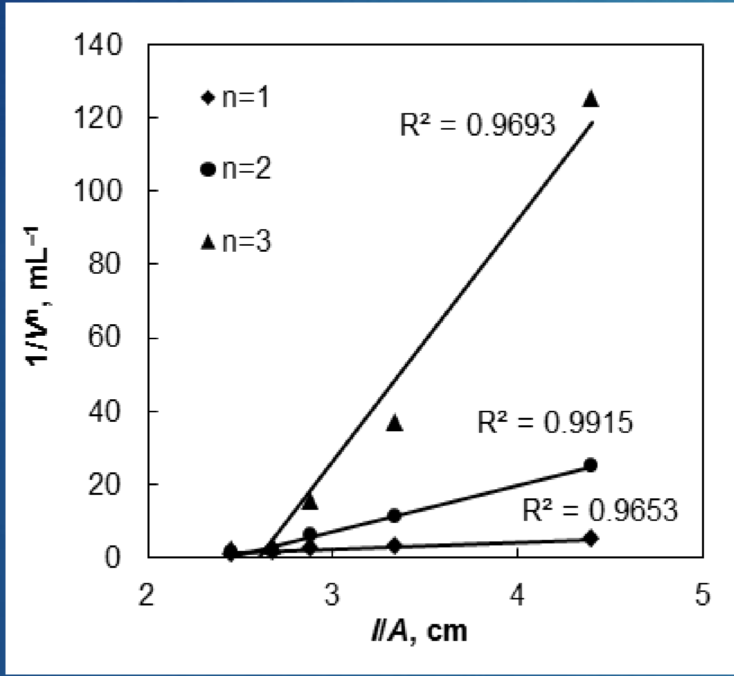
$C_{Mo(VI)} = 2.08 \times 10^{-5}$ mol L^{-1}; $C_{INT} = 2.0 \times 10^{-4}$ mol L^{-1};

$C_{H2SO4} = 4{,}0 \times 10^{-1}$ mol L^{-1}; $\lambda = 395$ nm; $\tau = 1$ min

Mo(VI) – 3,5-DNC – INT

2. Molar Ratios

2.3. Molar ratios, formulae and equations



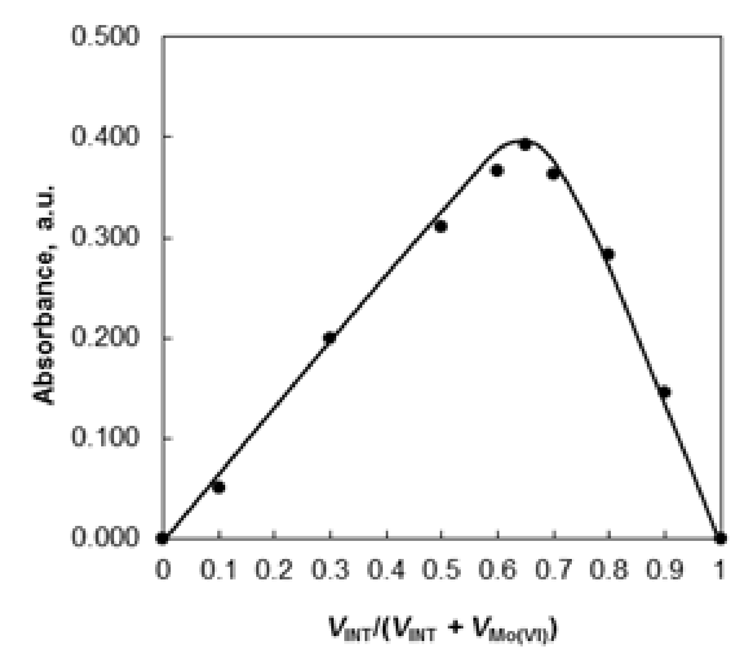


Figure 4. Determination of the molar ratio (n) Mo(VI):INT by the method of Asmus
$C_{Mo(VI)} = 2.08 \times 10^{-5}$ *mol L*$^{-1}$; $C_{3,5\text{-}DNC} = 2.0 \times 10^{-4}$ *mol L*$^{-1}$; $C_{H2SO4} = 4,0 \times 10^{-1}$ *mol L*$^{-1}$; $\lambda = 395$ *nm*; $\tau = 1$ *min*

Figure 5. Determination of the molar ratio (n) Mo(VI):INT by the method of continuous variations
$C_{Mo(VI)} + C_{INT} = 8.0 \times 10^{-5}$ *mol L*$^{-1}$; $C_{3,5\text{-}DNC} = 2.0 \times 10^{-4}$ *mol L*$^{-1}$; $C_{H2SO4} = 4.0 \times 10^{-1}$ *mol L*$^{-1}$; $\lambda = 395$ *nm*; $\tau = 1$ *min)*

Mo(VI) – 3,5-DNC – INT

2. Molar Ratios

2.4. Molar ratios, formulae and equations

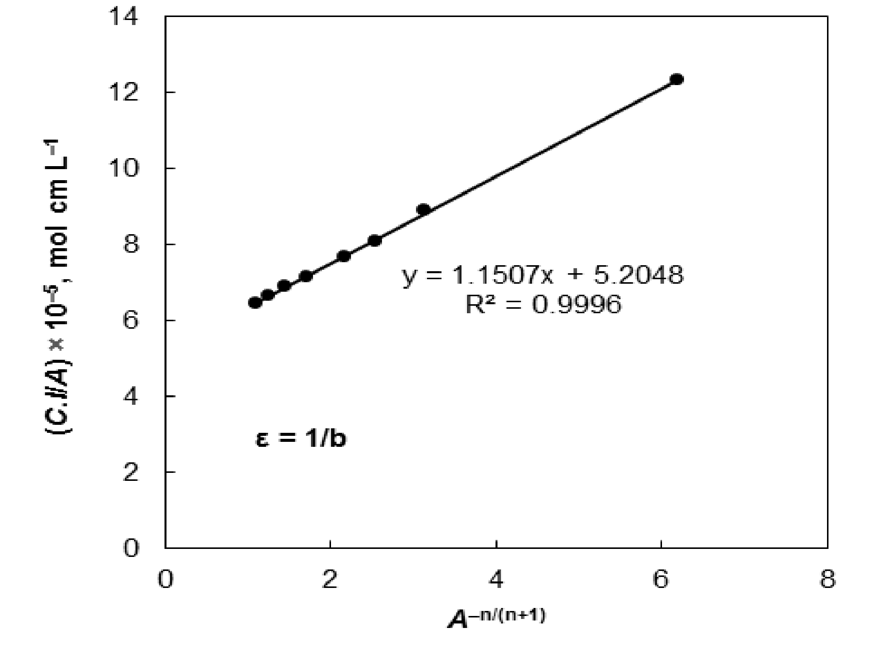


Figure 6. Dependency of ($C.l/A$) on $A^{-n/(n+1)}$ (method of Komar–Tolmachev)
$C = C_{Mo(VI)}$ mol L^{-1}; $C_{INT} = 2\ C_{Mo(VI)}$ mol L^{-1}; $C_{3,5\text{-}DNC} = 2.0 \times 10^{-4}$ mol L^{-1};
A – absorbance; l – cell thickness, l = 1 cm; n = 2

Mo(VI) – 3,5-DNC – INT

3. Extraction Constant, Distribution Ratio and Fraction Extracted

Equilibrium constant and recovery factor	Value
Equilibrium (equation 3) - Association constant β $\beta = (INT)_2\{MoO_2[O_2C_6H_2(NO_2)_2]_2\}_{(aq)} / \{[(INT)^+]^2_{(aq)} \times \{MoO_2[O_2C_6H_2(NO_2)_2]_2\}^{2-}\}_{(aq)}\}$	$\log \beta = (9.93 \pm 1.38)^a$
Equilibrium (equation 4) - Distribution constant K_D $K_D = \{(INT)_2\{MoO_2[O_2C_6H_2(NO_2)_2]_2\}\}_{(org)} / \{(INT)_2\{MoO_2[O_2C_6H_2(NO_2)_2]_2\}\}_{(aq)}$	$\log K_D = (1.23 \pm 0.01)^b$
Equilibrium (equation 5) - Extraction constant K_{ex} $K_{ex} = \{(INT)_2\{MoO_2[O_2C_6H_2(NO_2)_2]_2\}\}_{(org)} / \{\{[INT]^+\}^2_{(aq)} \times \{MoO_2[O_2C_6H_2(NO_2)_2]_2\}^{2-}\}_{(aq)}\}$	$\log K_{ex} = (11.16 \pm 1.39)^c$ $\log K_{ex} = (10.95 \pm 0.15)^d$
Recovery factor *R*%	$R = (94.39 \pm 0.05)\%^e$

[a] Calculated by Komar–Tolmachev method (equation 6);
[b] Calculated by equation (7);
[c] Calculated by equation (9), where β is determined by the Komar–Tolmachev method;
[d] Calculated by Likussar–Boltz method (equation (10));
[e] Calculated by equation (8).

Table 3. Values of the equilibrium constants and the recovery factor

Mo(VI) – 3,5-DNC – INT

4. Analytical Characteristics and Application

- The relationship between the absorbance and the Mo(VI) concentration (**Beer's Law**) was studied.
- Under the optimum conditions (Table 1), Mo^{VI} is extracted as an ion-association complex, with the general formula $(INT^{+})_2\{Mo^{VI}O_2[O_2C_6H_2(NO_2)_2]_2\}$.
- Its molar absorptivity at λ_{max} (ε_{395} = (2.05±0.06)×10^4 dm^3 mol^{-1} cm^{-1}).
- The linear regression equation was $A = 0.2081\gamma + 0.0098$, where γ is the mass concentration (µg cm^{-3}).
- The standard deviations of the slope and intercept were 0.004 and 0.008, respectively.
- The limit of detection (LOD) and limit of quantitation (LOQ) calculated as 3- and 10-times standard deviation of the blank divided by the slope, were 0.31 µg cm^{-3} and 1.03 µ g cm^{-3}, respectively.

Mo(VI) – 3,5-DNC – INT

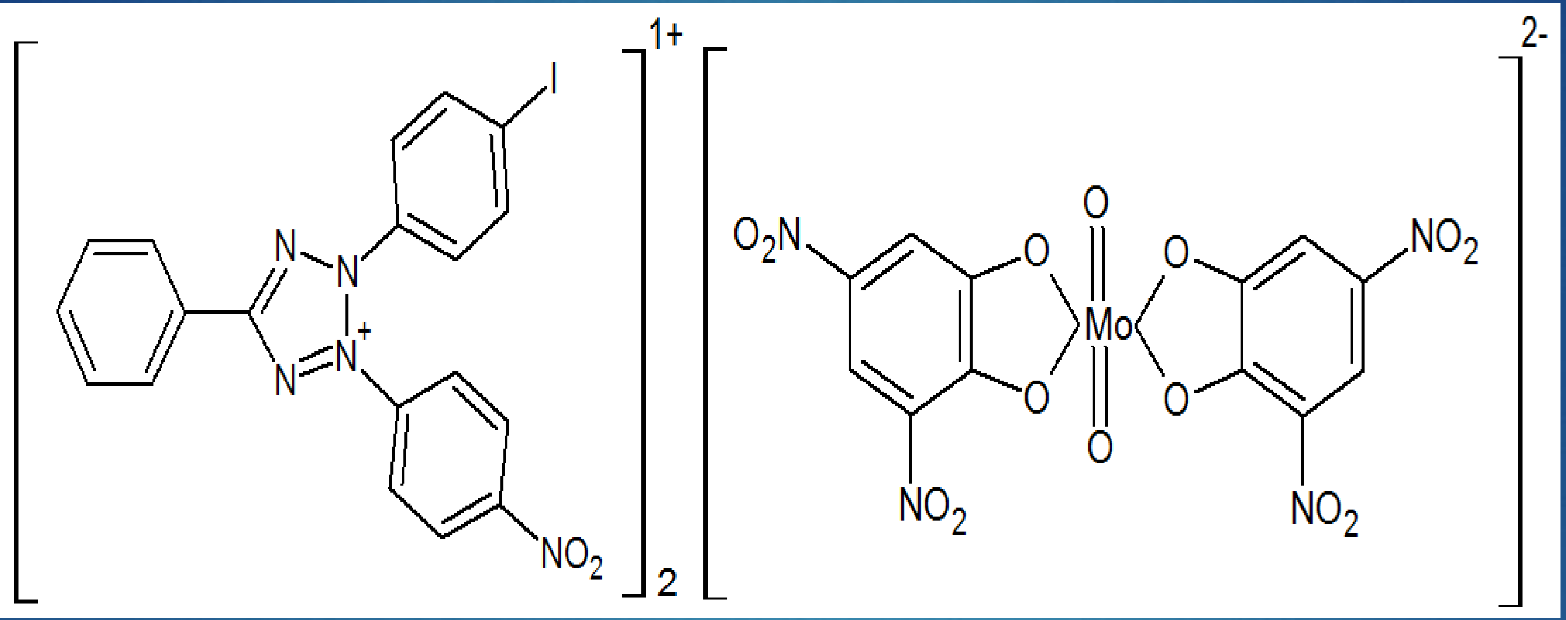


Figure 7. Structure of the ion-associated complex Mo(VI)–3,5-DNC–INT

$$(INT^{+})_2\{Mo^{VI}O_2[O_2C_6H_2(NO_2)_2]_2\}$$

Mo(VI) – 3,5-DNC – INT

5. Conclusions

- New liquid-liquid extraction-chromogenic system for Mo(VI) involving 3,5-DNC and INT was studied.
- Under the optimum conditions, Mo^{VI} is extracted as a 1:1:2 complex (Mo:4NC:BZC) with λ_{max} = 395 nm and formula $(INT^+)_2\{Mo^{VI}O_2[O_2C_6H_2(NO_2)_2]_2\}_2$.
- The structure of its anionic part was clarified with the help of theoretical calculations.
- The complex is intensely colored and allows the determination of trace Mo(VI) in a simple and economical way, without the use of sophisticated instruments.
- The developed analytical procedure is characterized by a low LOD, good linearity. It is fast, selective, and robust.

Thank you for your attention