Sorption Preconcentration and Determination of Molybdenum(VI) by Diffuse Reflection Spectroscopy

Olga N. KONONOVA[1][*], **Sergey V. KACHIN** [1], **Anastasiya E. CHAIKOVSKAYA**[1],
Alexander G. KHOLMOGOROV[2], **Olga P. KALYAKINA**[1]
[1]*Department of Chemistry, Krasnoyarsk State University,*
660041 Krasnoyarsk, Svobodny Pr., 79, Russian Federation
e-mail: cm2@ktk.ru
[2]*Institute of Chemistry and Chemical Technology, Siberian Department of the*
Academy of Science, Karl Marx Pr. 42, 660049 Krasnoyarsk, Russian Federation

The present work focuses on the preconcentration of molybdenum and its determination in aqueous solutions by means of diffuse reflection spectroscopy. The preconcentration of Mo(VI) was carried out using the macroporous strong basic anion exchanger AV-17-10P synthesized on the basis of styrene and divinylbenzene. The method for Mo determination with this collector in industrial solutions and natural water was developed using solid-phase spectroscopy. The colored surface compound to be determined was obtained by a preceding Mo(VI) sorption on the resin and by subsequent treatment of the concentrate obtained with definite amounts of pyrocatechol violet. The calibration curve is linear at the Mo (VI) concentration range 0.05-2.5 mg·dm^{-3} with a sample volume of 50.0 cm^3. The detection limit is 0.002 mg·dm^{-3}.

Key Words: Sorption, Preconcentration, Molybdenum(VI), Pyrocatechol violet, Aqueous solutions

Introduction

Molybdenum and its derivatives show different physico-chemical and biological properties, which allow them to be usedwidely in various fields of modern engineering, science and agriculture[1,2]. However, the elevated content of Mo in the environment is hazardous for humans, animals and plants[3]. For example, Mo(VI) ions cause decreases in catalase activity, which results in increases in uric acid concentrations in organisms and leads to a podagric syndrome. Moreover, these ions raise the lability of blood pressure and reduce cholesterol transportation[1,2]. Therefore, the determination of the microcontents of Mo and its compounds in the environment is a matter of vital importance.

At present several up-to-date methods as neutron activation, mass-spectrometry, and atomic emission with inductively coupled plasma are used for Mo determination[4]. All these methods require expensive stationary equipment. The other physical-chemico methods, which are also suitable for the above-mentioned

---

[*]Corresponding author

purpose[5−11], are easier to carry out, but they also have some limitations: for instance, some methods require extraction, masking or other separation processes. Moreover, in order to obtain the analytical signal, reducing agents are often used. Such a multistage process hinders analysis.

Therefore, it is a matter of practical interest to develop relatively simple and sensitive methods for Mo(VI) determination, i.e. combined methods based on the preconcentration and determination of the components in the sorbent phase by means of solid-phase spectroscopy[12], in particular by diffusion reflection spectroscopy[13].

The possibility of sorption-photometrical Mo(VI) determination with organic reagents in the phase of different sorbents in aqueous solutions by means of quantitative or test methods was shown previously[14−18].

The present work is devoted to an ion exchange equilibrium investigation of analytical systems containing Mo(VI) as well as anion exchanger AV-17-10P and organic reagent pyrocatechol violet (PCV), with the aim of developing a sorption-spectroscopic method for Mo(VI) determination in aqueous solutions, in particular under field-work conditions.

Experimental

A strong basic macroporous anion exchanger, AV-17-10P, synthesized by the TOKEM Company (Kemerovo, Russia) was preliminary prepared in accordance to the standard procedure [19]and loaded with chloride ions by means of 2M HCl.

A stock Mo(VI) solution was prepared from accurately weighed samples of pure salt, $Na_2MoO_4 \cdot 2H_2O$. The initial Mo(VI) concentration was 10 g·dm^{-3} (0.1 mol·dm^{-3}). Working Mo(VI) solutions with lower metal concentrations (0.05-2.5 mg·dm^{-3}) were prepared from this solution by dilution with distilled water. The necessary acidity was achieved by adding HCl or NaOH solutions and controlled using a pH-meter (pH-340, Russia). All reagents were of analytical grade.

The preconcentration of Mo(VI) was carried out under batch experiment conditions. For this purpose, anion exchanger samples (0.2 g of dry substance) were swollen for 4 h in weak acidic HCl solutions (pH 3.0-3.5). After swelling, the resins were placed in graduated flasks (v = 50.0 cm^3). Then 10.0 cm^3 of HCl (pH 3.0-3.5) and a Mo(VI) aliquot of the necessary concentration were added to the exchanger samples. After that, HCl solutions were added up to the flask mark and the contents were stirred for 15 min. Then the resins were separated from solutions and the filtrates were subjected to analysis. The Mo (VI) concentration in these solutions was determined by a photometrical method (alizarin S as reagent) [20] using a photocolorimeter (KFK-3, Russia) or spectrophotometer (Specord M 40, Germany). The sorption was carried out at (20 ± 1) °C.

Static exchange capacity (amount of ions sorbed in mg or mmol/g of the resin) as well as Mo recovery degree Q and distribution ratio D were calculated from experimental data:

$$Q = [(C_o\text{-}C)/C_o] \cdot 100\%, \tag{1}$$

$$D = [\overline{Mo(VI)}]/[Mo(VI)], \tag{2}$$

where $[\overline{Mo(VI)}]$ and [Mo(VI)] are the equilibrium Mo(VI) concentrations in the resin phase (mmol/g) and in solution (mmol·cm^{-3}), respectively; C_o is the Mo(VI) concentration in the solution before sorption, g·dm^{-3};

and C is the Mo(VI) concentration in the solution after sorption, $g \cdot dm^{-3}$.

The concentration of Mo absorbed was determined in this case from the difference between initial and equilibrium Mo concentrations in the solutions.

The electron absorption spectra of the solutions investigated were registered using spectrophotometer (Specord M 40, Germany). The anion exchanger samples for IR spectroscopy were prepared according to the following procedure. After the saturation of samples with Mo ions, the sorbents were dried by filter paper (no washing with water to avoid changing the Mo ionic state in the resin phase). Then the air-dried samples were ground in a vibration mill. The tableting of resins was carried out with KBr (0.3 mg of resin to 200 mg of KBr). The IR-spectra detection was carried out with an IR spectrometer (Specord M 80, Germany).

The colored reaction on the sorbent surface was obtained by means of PCV solutions prepared from accurately weighed samples of pure reagent (analytical grade). The initial concentration of these solutions was $0.05 \ mol \cdot dm^{-3}$.

The PCV solutions were added both to the anion exchanger in the Cl^- -form and to the sorbent with the preconcentrated Mo(VI) ions. In the first case the resin acquires an orange color. The Mo compound with PCV obtained in the sorbent phase is blue.

For the solid-phase spectroscopy method, the change in the Gurevich-Kubelka-Munk function $\Delta F(R)$ is used as an analytical signal:

$$\Delta F(R) = [(1-R)^2/(2R)]-[(1-R_0)^2/(2R_0)], \tag{3}$$

where R and R_0 are diffusion reflection coefficients (quantities of dimension 1) of the chelate of metal ions with organic reagents in the ion exchanger phase and of the ion exchanger, respectively.

The diffusion reflection coefficients were measured on a colorimeter (Pulsar, Russia). The average relative error of 5 parallel experiments statistically processed by the standard method [21] does not exceed 2.5%.

Results and Discussion

The strong basic macroporous anion exchanger AV-17-10P was chosen for our investigation, since this sorbent was proved to be effective previously for the recovery of Mo(VI) from copper-containing solutions[22]. The physico-chemical and sorption properties of AV-17-10P are presented in Table 1.
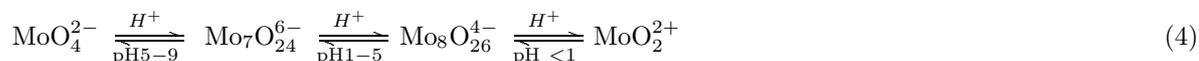
Table 1. Physical-chemico and sorption properties of anion exchanger AV-17-10P.

Copolymer	Functional group	Static exchange capacity in the Cl^- form, mmol/g	Specific swelling volume, cm^2/g	Total pore volume, cm^3/g	Pore size, nm	Specific surface, m^2/g
Styrene, DVB	$-N^+(CH_3)_3$	4.0	3.8	0.59	1.5×10^6- 1.0×10^5	23.0

DVB – divinylbenzene

To carry out the preconcentration of Mo(VI) on the anion exchanger AV-17-10P effectively, we studied the ion exchange equilibrium in this system at the range of Mo concentrations from $0.0005 \ mmol \cdot dm^{-3}$ to $0.1 \ mol \cdot dm^{-3}$ and at pH 1-12. It is known[22−24] that the Mo ionic state in aqueous solutions depends on the pH

value and Mo concentration. The basic solutions contain only MoO_4^{2-} ions, but the addition of acids leads to the formation of different polymeric ions: $Mo_7O_{24}^{6-}$, $Mo_8O_{26}^{4-}$ etc. This complex polymerization process takes place when the Mo concentration is higher than 10^{-4} mol·dm^{-3}. It can be presented as follows:

$$MoO_4^{2-} \underset{\text{pH5-9}}{\overset{H^+}{\rightleftharpoons}} Mo_7O_{24}^{6-} \underset{\text{pH1-5}}{\overset{H^+}{\rightleftharpoons}} Mo_8O_{26}^{4-} \underset{\text{pH } <1}{\overset{H^+}{\rightleftharpoons}} MoO_2^{2+} \tag{4}$$

The boundaries for anion formation depend on the Mo concentration, which influences both the ion exchange process and the changes in composition of polyanions[22,24].

We determined that the optimal pH value for Mo(VI) sorption is 3.0-3.5. Under these conditions, the anion exchanger, due to its macroporous structure, recovers the Mo(VI) polyanions $Mo_7O_{24}^{6-}$ and $Mo_8O_{26}^{4-}$. The IR spectra of this system are presented in Figure 1. IR spectrum 1, which is characteristic for AV-17-10P in the Cl$^-$ - form, has the following bands: 970 cm^{-1} = planeness vibrations of C–H-groups of benzene ring disubstituted; 890 cm^{-1} = vibrations of N$^+$(CH$_3$)$_3$-groups; and 827 and 768 cm^{-1} = external planeness vibrations of C–H groups of benzene ring disubstituted[22,25]. IR-spectrum 2, presenting the anion exchanger saturated with Mo(VI) ions, has bands at 942, 906, 852, 718 and 657 cm^{-1}, characterizing polyanions in the sorbent phase[22,25].
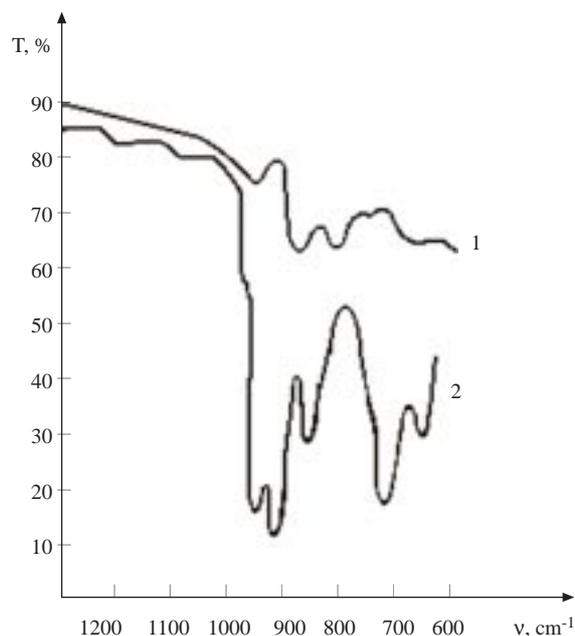

**Figure 1.** IR-spectra fragments of sorption systems based on anion exchanger AV-17-10P:

1 = anion exchanger in the chloride form;
2 = anion exchanger after saturation with Mo(VI) ions.
Mo(VI) concentration is 0.1 mol·dm^{-3}. Sorption time is 24 h.

It is important to note that the macroporous anion exchanger AV-17-10P shows the best sorption properties during the recovery of large Mo polyanions (the exchange capacity is 1460 mg/g under these conditions).

Mo(VI) sorption proceeds under optimal conditions according to the following anion exchange reactions:

$$\overline{6RCl} + Mo_7O_{24}^{6-} \rightleftharpoons \overline{R_6Mo_7 + O_{24}} + 6Cl^-, \tag{5}$$

$$\overline{4RCl} + Mo_8O_{26}^{4-} \rightleftharpoons \overline{R_4Mo_8 + O_{26}} + 4Cl^-. \tag{6}$$

During these processes, complex Mo polycompounds with bridge hydrogen bonds are formed in the resin phase [22]:
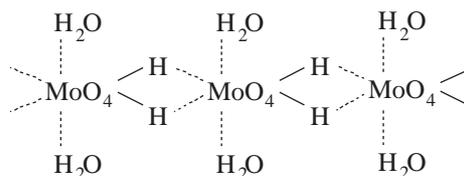
These compounds consist of MoO_4^{2-} and H_2MoO_4. With the decrease in the pH of the solution from 7.0 to 3.0, the exchange capacity of AV-17-10P grows because of the reduction in the specific charge values of the sorbed ions. For instance, if 0.5 Mo corresponds to 1 charge of MoO_4^{2-} ion, then 2 Mo correspond to 1 charge of $Mo_8O_{26}^{4-}$ polyanion, i.e. the exchange capacity of the resin increases up to 4 times during the sorption of the $Mo_8O_{26}^{4-}$ ion[2,22,24]. Therefore, the macroporous anion exchanger has an advantage over gel resins due to its ability to sorb large Mo polyanions.

If the concentration of Mo(VI) in solutions is less than 10 mmol·dm^{-3} (which is characteristic for natural water), the dominating ions are MoO_4^{2-}:

$$\overline{2RCl} + MoO_4^{2-} \rightleftharpoons \overline{R_2MoO_4} + 2Cl^-. \tag{7}$$

The quantitative Mo(VI) recovery proceeds in this case for 15 min. The diffuse reflection spectrum of the concentrate obtained has no maxima in the visual region. Thus, it can be stated that AV-17-10P is the appropriate collector for Mo(VI).

In order to obtain a colored reaction on the sorbent surface, pyrocatechol violet (pyrocatecholsulfophtaleine) (PCV) was investigated.

It is known [13,17] that the colored compounds in the sorbent phase can be obtained in 3 ways. Firstly, the complex compound of reagent and determined metal ions is formed in solution and then is sorbed on a suitable support material. Secondly, the reagent is sorbed and then its reaction with the determined metal ions takes place in the sorbent phase. Thirdly, the preliminary sorption of metal ions occurs and then they interact with the reagent in the sorbent phase. The method for the preparation of samples is chosen in accordance with the specific features of an analytical system.

We determined that the optimal way to obtain the colored compound is to sorb Mo(VI) on AV-17-10P first and then to carry out the interaction between the concentrate obtained and the reagent in the anion exchanger phase. This method is characterized by high selectivity due to the preliminary separation of the components determined.

Using potentiometric titration data, we determined that the molar ratio of Mo and PCV in the phase of AV-17-10P is 1:2. The optimal pH value for the complex-forming reaction in the sorbent phase is 3.0.

The Mo(VI)-PCV complex in the resin phase is blue (its color develops over 20 min) and has an absorption maximum at a wavelength of 660 nm (Figure 2).
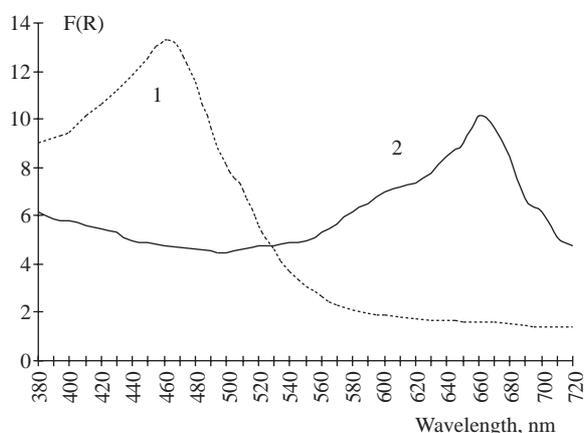

Figure 2. Dependence of Gurevich-Kubelka-Munk function F(R) on wavelength.
1 = anion exchanger modified with PCV;
2 = (Mo(VI)-PCV)-complex compound in the anion exchanger phase.
Initial Mo(VI) concentration is 1×10^{-3} mol·dm^{-3}; solution volume is 50.0 cm^3; sorbent mass is 0.2 g.

The IR spectrum of the Mo(VI)-PCV complex compound in the resin phase is characterized by a wide absorption band at 600-1000 cm^{-1} (Figure 3, spectrum 2; spectrum 1 concerning the resin in the Mo(VI) form was described above).The isolated peaks, which are characteristic for the spectrum of Mo(VI) in the phase of the same sorbent, are not observed, but the general peak appears with the absorption maximum at 807 cm^{-1}. Moreover, the peak at 970 cm^{-1} can be attributed to vibrations of the end Mo = O bonds[22,25]. Therefore, Mo(VI)-PCV-complex in the anion exchanger phase is formed and the question regarding its kind of binding with the resin needs to be studied additionally. It is known[14,15,26] that PCV complex with Mo in solution has the following structure:
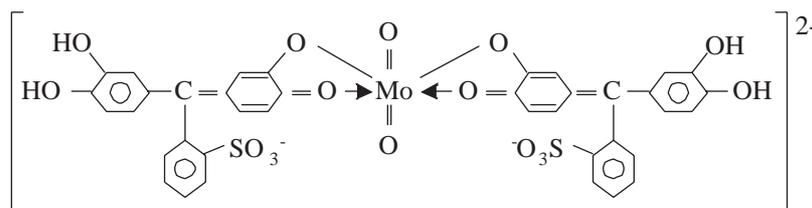
Probably a similar complex is formed in the AV-17-10P phase, since the diffusion reflection spectra of the complexes of Mo(VI)-PVC in the solution and resin are similar to each other[14,15].

The investigation of the Mo(VI) concentration effect on the formation of analytical signal showed that the calibration curve is linear at the concentration range 0.05-2.5 mg·dm^{-3} ($5.2 \times 10^{-4} - 2.6 \times 10^{-2}$ mmol·dm^{-3}) at the solution volume 50.0 cm^3.

The moisture content in the anion exchanger phase has the following effect on the amplitude of the analytical signal: the diffusion reflection coefficients are higher for the wet samples than those for the dry ones. This effect can be probably be attributed to the presence of reflecting particles enhancing the reflecting ability of the samples. In the present paper, the diffusion reflection coefficients were registered for the wet resins only.
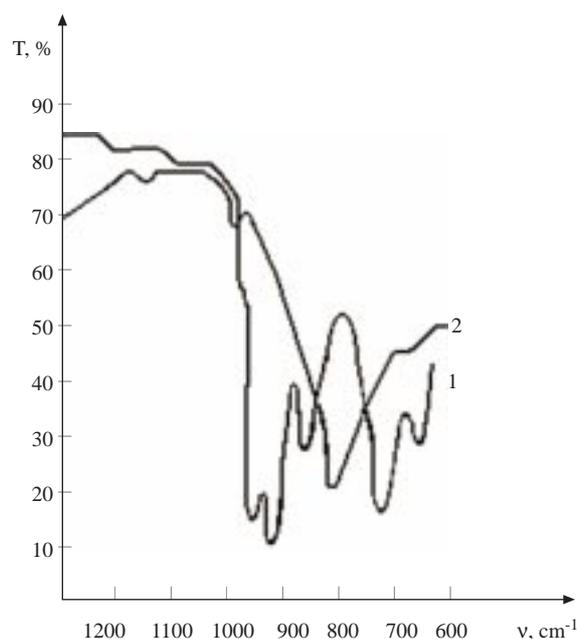
Figure 3. IR-spectra fragments of sorption systems based on anion exchanger AV-17-10P:

1 = anion exchanger after saturation with Mo(VI) ions;
2 = anion exchanger after reaction between Mo(VI) and PV.
Mo(VI) concentration is 0.1 mol·dm^{-3}. Sorption time is 24 h.

The size of resins beads has an effect on the amplitude of the analytical signal as well. The values of the Gurevich-Kubelka-Munk function F(R) increase when the size of beads is falling. This effect can be explained by the fact that the diffusion coefficients for the samples with small beads are lower than those for the samples with large beads. It is known [13] that the values of the Gurevich-Kubelka-Munk function depend on diffusion coefficients in accordance with the following formula:

$$(1\text{-}R)^2/2R = \beta/s, \tag{8}$$

where R, s and β are the diffusion reflection, diffusion and absorption coefficients, respectively.

In the present paper, the anion exchanger fraction of size $5 \times 10^5 - 1 \times 10^6$ nm was chosen for investigation.

It is known [26] that the presence of such ions as Cu^{2+}, WO_4^{2-}, Al^{3+} and Sn(IV), which form the colored compounds with PCV, as well as the presence of different acids (H_3PO_4, H_2SiO_3, $H_2C_2O_4$, HF, EDTA, ascorbic acid) can interfere with the molybdenum determination. That is why we have studied the effect of these compounds.

Table 2 presents the results of sorption-spectroscopic Mo(VI) determination in the presence of the above-mentioned components. It can be seen from these data that Mo(VI) can be determined in the presence of Cu^{2+}, WO_4^{2-} and Al^{3+} (up to 500-, 700- and 1000-fold surplus, respectively). The anions of complex-forming acids (ethanediodic, phosphoric, silicic and hydrofluoric) as well as the masking acids (EDTA, ascorbic acid) cause practically no hinderence Mo(VI) determination. Sn(IV) ions form complex compound at pH 3-5 a with PCV at a wavelength of 550 nm. This reaction develops over 10 min[27], and therefore Sn(IV) ions do not hinder Mo determination.

Table 2. Sorption-spectroscopic Mo(VI) determination with pyrocatechol violet in the presence of interfering components.

Mo(VI) initial concentration is 1.5×10^{-2} mmol·dm^{-3}; n = 5; p = 0.95

Macrocomponent (MC)	Concentration Mo:MC	The concentration of Mo(VI) found, mmol·dm^{-3}	The average relative error, %
Cu^{2+}	1:500	1.57×10^{-2}	5
WO_4^{2-}	1:700	1.48×10^{-2}	-2
Al^{3+}	1:1000	1.62×10^{-2}	8
F^-	1:300	1.43×10^{-2}	-5
$C_2O_4^{2-}$	1:400	1.45×10^{-2}	-3
SiO_3^{2-}	1:2500	1.58×10^{-2}	5
PO_4^{3-}	1:300	1.47×10^{-2}	-2
EDTA	1:2500	1.48×10^{-2}	-1
Ascorbic acid	1:2000	1.56×10^{-2}	4

It should be noted that the macrocomponents of natural fresh water (Na^+, K^+, Ca^{2+}, Mg^{2+}) also do not hinder sorption-spectroscopic Mo(VI) determination (up to 10,000-fold surplus) because they are not absorbed on the anion exchanger.

Table 2 supports the conclusion that the selectivity of Mo(VI) determination with PCV in the anion exchanger phase is satisfactory.

The calibration curve equation has the following form:

$$\Delta F(R) = (1.57 \pm 0.04) \cdot C_{Mo} + (0.5 \pm 0.01). \tag{9}$$

The detection limit calculated according to 3S-criterion[28] is 0.002 mg·dm^{-3} (2×10^{-5} mmol·dm^{-3}) at the solution volume 50.0 cm^3.

The suggested method for Mo(VI) sorption-spectroscopic determination has an error of 7.5% (P = 0.95) statistically processed by standard methods[21].

Therefore the following procedure for Mo(VI) sorption-spectroscopic determination can be proposed: 0.2 g of anion exchanger AV-17-10P in the Cl$^-$-form preswollen at pH 3.0 are placed into a graduated flask (v = 50.0 cm^3) and the analyzed Mo (VI)-containing aqueous solution is added. Then the HCl solution (pH 3.0) is added up to the flask's mark. The content is stirred for 15 min. After that the resin is separated and 0.2 cm^3 of pyrocatechol violet (0.0125 mol·dm^{-3}) is added drop-by-drop to the sorbent. After 20 min, the diffusion reflection coefficients are measured at $\lambda = 660$ nm relative to a comparison sample.

The content of Mo(VI) in the analyzed solution is calculated from the calibration curve plotted for the stock Mo(VI) solutions (aliquots with a Mo content of 2.5-125 μg).

The correctness and reproducibility of the method proposed in the present paper were tested on model solutions, the concentration and composition of which were close to those of natural water. Moreover, industrial solutions obtained after the processing of spent catalysts were used for comparison. The results are summarized in Table 3. It can be seen from these data that Mo(VI) determination in aqueous solutions by means of the proposed method is correct and reproducible to a satisfactory extent.

Table 3. Sorption-spectroscopic Mo(VI) determination in the model (MS) and industrial (IS) solutions.

(n = 5; p = 0.95; $t_{0.95}$ = 2.78)

Analysis object	Mo (VI) content, mg·dm^{-3}		S	$\pm t_p \cdot \frac{S}{\sqrt{n}}$
	Initial	Found		
MS 1	0.35	0.35	0.025	0.03
MS 2	1.75	1.74	0.019	0.02
MS 3	2.35	2.35	0.026	0.03
IS 1*	0.50	0.54	0.017	0.02
IS 2**	0.50	0.54	0.024	0.03

* Industrial solution obtained after processing of spent Ni-Mo catalysts on the basis of aluminum oxide

** Industrial solution obtained after processing of spent Co-Mo catalysts on the basis of aluminum oxide

Taking into account the high selectivity of determination, the wide linear range of Mo(VI) contents determined, and the accessibility and stability of the reagents used, the proposed method can be recommended for the analysis of Mo-containing aqueous solutions (for example, natural and industrial water and sewage), including analysis under field-work conditions.

References

1. **"Boolshoy Entsiklopedicheskiy Slovar"**. Ed. by I.L. Knunyants, pp. 350-351. Bolshaya Rossiyskaya Entsiklopediya, Moscow, 1998. (**"The Great Encyclopedia Dictionary"**, in Russian).

2. A.G. Kholmogorov, O.N. Kononova, G.L. Pashkov, S.V. Kachin, O.N. Panchenko and O.P. Kalyakina, **The European J. of Mineral and Environmental Processing 2,** 82-93 (2002).

3. N.F. Reymers, **"Okhrana Prirody I Okrushaushchey Sredy"**. Prosveshchenie, Moscow, 1990. (**"Nature Conservation and Environmental Control"**, in Russian).

4. Z. Marczenko, **"Photometricheskoe Opredelenie Elementov".** Mir, Moscow, 1971. (**"Photometrical Analysis of Elements"**, in Russian).

5. T. Chen, Z. Chen and Z. Zhou, **Phys. Test. and Chem. Anal**. **B 29,** 336-341 (1993).

6. X. Song, **Phys. Test. and Chem. Anal**. **B 29**, 355-59 (1993).

7. R. Dass and J.R. Mehta, **Bull. Chem. Soc. Jap**. **67,** 2103-08 (1994).

8. J. Rameshwar and J.R. Mehta, **Fresenius' J. Anal. Chem**. **349,** 520-25 (1994).

9. C.K. Rao, V.K. Reddy and T.S. Reddy, **Proc. Indian. Nat. Sci. Acad**. **A 59,** 449-52 (1993).

10. R. Dass and J.R. Mehta, **J. Indian. Chem. Soc**. **72,** 512-17 (1997).

11. K. Susumi, H. Suzuki and I. Masaaki, **Anal. Sci. 12,** 761-64 (1996).

12. K. Yoshimura, H. Waki and S. Ohashi, **Talanta 23,** 449-55 (1976).

13. V.K. Runov and V.V. Tropina, **J. Anal. Chem. (Moscow) 52,** 71-76 (1996).

14. Y.V. Barbalat, V.M. Ivanov, T.V. Polenova and N.V. Feodorova, **Vestnik Moskovskogo Universiteta 39,** 174-77 (1998).

15. V.M. Ivanov, A.V. Rybakov, V.N. Figurovskaya, G.V. Prokhorova and G.A. Kochelaeva, **Vestnik Moskovskogo Universiteta 39**, 258-60 (1998).

16. I.B. Yuferova, T.I. Tikhomirova and V.I. Fadeeva, **J. Anal. Chem. (Moscow) 44,** 1068-72 (1989).

17. K. Yoshimura, S. Matsuoka and H. Waki, **Anal. Chim. Acta 225,** 313-19 (1989).

18. A.A. Lurie **"Chromatograficheskie Materialy. Spravochnik" ("Materials for Chromatography"**, in Russian). Khhimiya, Moscow, 1978.

19. **"Laboratornoe Rukovodstvo po Khromatograficheskim i Smezhnym Metodam"**, ed. by O. Mikes, pp. 251-72, Mir, Moscow, 1982. (**"Laboratory Handbook of Chromatographic and Allied Methods"**, in Russian).

20. K.N. Bagdasarov and A.G. Kovaleva, **"Analiz metallov" ("Analysis of Metals"**, in Russian). Izdatelstvo Rostovskogo Universiteta, Rostov na Donu, 1972.

21. J.H. Pollard, **"A Handbook of Numerical and Statistical Techniques**". Cambridge University Press, Cambridge, London, New York, Melbourne, 1977.

22. A.G. Kholmogorov, M.V. Mokhosoev and E.L. Zonkhoeva, **"Modificirovannye Ionity v Technologii Molibdena i Volframa" ("Modified Ion Exchangers in Molybdenum and Tungsten Technology"**, in Russian). Nauka, Novosibirsk, 1985.

23. F.A. Cotton and G.F.R.S. Wilkinson, **"Sovremennaya Neorganicheskaya Khimiya".** Mir, Moscow, 1972. (**"Advanced Inorganic Chemistry. A Comprehensive Text",** Interscience Publishers: a division of John Wiley & Sons, New York – London – Sydney, 1966).

24. M.Th. Pope, **"Geteropoli I Isopolioksometallaty".** Nauka, Novosibirsk, 1990. (**"Heteropoly and Isopoly Oxometalates"**, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo, 1982).

25. K. Nakamoto, **"IK-spectry i Spectry KR Neorganicheskikh i Coordinatsionnykh Soedineniy" ("IR- and Raman Scattering Spectra of Inorganic and Complex Compounds"**, in Russian). Mir, Moscow, 1991.

26. F. Umland, A. Janssen, D. Thierig and G. Wünsch, **"Theorie und praktische Anwendung von Komplexbildnern".** Akademische Verlagsgesellschaft, Frankfurt am Main, 1971.

27. K. Burger, **"Organic Reagents in Metal Analysis".** Akademial Kiado, Budapest, 1973.

28. K. Doerffel, **"Statistika v Analiticheskoy Khimii" ("Statistics in Analytical Chemistry"**, in Russian). Mir, Moscow, 1994.