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ATOMIC ABSORPTION AND ATOMIC EMISSION WITH INDUCTIVELY COUPLED PLASMA AND X-RAY DETERMINATION OF CADMIUM AND NICKEL IN SOILS USING ULTRASOUND, TRITON X-100, AND METAL ACETYLACETONATES

Abstract: The effect of surfactant concentration (Triton X-100) on increasing the sensitivity of the atomic absorption determination of Cadmium and Nickel was studied. It is shown that after the usage of Triton X-100 ($\omega = 3\%$) sonication for 20 minutes, the sensitivity of the atomic absorption determination of Cadmium increases by 1.4 times, and Nickel does by 1.7 times. For complete extraction of analytes, ultrasonic treatment of soil samples with a power of 120 W, with a frequency of 40 kHz, was taken. The content of Cadmium and Nickel was determined by atomic absorption, atomic emission with inductively coupled plasma, and X-ray fluorescence methods in a soil sample using Cadmium and Nickel acetylacetonates as standard samples of the composition. The correctness of the results of the analysis was checked by the "injected-found" method. By varying the sample weight, the absence of substantial systematic error was confirmed. According to the Fisher criteria and Student's *t*-test, the consistency of the results obtained by two independent methods was evaluated. It is shown that the discrepancy of the means is not significant and is justified by a random scatter. The detection limits of Cadmium ($C_{min}=0,001$ mkg/ml, $C_{lit}=0,007$ mkg/ml) and Nickel ($C_{min}=0,01$ mkg/ml, $C_{lit}=0,02$ mkg/ml) were estimated by the atomic absorption method.

Key words: Cadmium, Nickel, atomic-absorption, atomic emission with inductive connected plasma spectroscopy, X ray analysis, soil, sample preparation, ultrasound, Triton X-100, metrologic characteristics.

Language: English

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Introduction

Soil pollution by heavy metals is one of the priorities of modern environmental problems. There are many methods of controlling soil contamination

with heavy metals and approaches to controlling and assessing soil contamination in different countries that differ significantly and change over time. Beginning in the 1970s, more productive and more

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"accurate" (reproducible) methods of analysis based on the transfer of samples into solution, such as atomic absorption spectroscopy (AAS), became more widespread in the field of control of biosphere objects. ICP ES / MS method. One of the methods that allows determining the gross content of heavy metals in the soil is X-ray fluorescence analysis (XRF).

Most of the heavy metals entering the soil are fixed in their upper humus layers. In soils, these metals are contained in water-soluble, ion-exchange, or weakly adsorbed forms. Water-soluble forms are usually represented by chlorides, nitrates, sulfates, and organic complexes. Besides, heavy metal ions can be associated with minerals as a part of the crystal lattice. Also, heavy metals enter the soil in the form of oxides and various salts, both soluble and insoluble in water. Among all chemical elements, heavy metals are the most toxic. They have a great affinity for physiologically critical organic compounds and can inactivate the latter. Moreover, they are capable of slow accumulation in the human body, which negatively affects its state.

The current studies report an increased concentration of heavy metals in the soil near gas wells. The mobility of these metals in the soil depends on various factors, but their retention in the soil depends on organic matter, soil pH, soil conductivity, ion exchange capacity, the presence of metal oxides that act as sorbents. In acidic soils, the mobility of Cadmium and Nickel significantly increases. Thus, the mobility of toxic elements also increases, which affects the plants in this soil, and namely, increases the contamination of plants with toxic elements by 20 times. The soil is actively exposed to anthropogenic impact, which disrupts its condition. This work is relevant, as now there are more and more objects of pollution. The study of soil cover for heavy metals is of great practical importance. Since heavy metals can be harmful, their content must be below the maximum allowable concentrations. The obtained data can become the basis for monitoring studies and comprehensive assessment of soil cover. The study results can also serve as a basis for a work plan to reduce the concentration of heavy metals. Methods of sample preparation, determination methods of analytes in environmental objects, and standard samples for determination of analytes are represented in works [1,p.50;2,p.238;3,p.2;4, p.530;5,p.6;6, p.1615;7, p.24;8,p.1566;9,p.252; 10,p.16;11, p.161; 12, p.54;13, p.74;14,p.99;15, p.80].

The main purpose of this work is to develop an ecologically safe method for determining analytes in soils using ultrasound, new media, and standard samples of the composition with improved metrological characteristics.

Experimental part

In this work, an atomic absorption spectrometer and CE333500 (flame version, lamps with hollow cathodes) were used, Cadmium was determined at $\lambda = 228.8$ nm, (C_2H_2 - air, stoichiometric, 1.2 l / min), And Nickel at $\lambda = 232.0$ nm (C_2H_2 - air, depleted, 1 l / min); atomic emission spectrometer with inductively coupled plasma and CAP 6300 DUO: speed of plasma-forming flow of argon - 12 l / min, plasma power - 1350 W, rate of additional flow of argon - 1.5 l / min, mode of observation of plasma-axial, argon flow in the atomizer - 0.55 l / min, pump speed - 50 rpm., signal integration time - 20 s, 5 parallel measurements, wavelength, nm: Cadmium - 228.8 nm, Nickel -232.0 nm. X-ray fluorescence spectrometer Elvax Light, accelerating voltage 45 kW, measurement time 100 s.

Ultrasonic bath, model PS -20, power - 120 W. frequency -40 kHz. Laboratory weighing scales OHAUS PA 64 (65 / 0.0001 g). Triton X-100, $C_{14}H_{22}O(C_2H_4O)_n$, $n=9-10$, $M_r=631$ g / mol, CCM = 2.9 mol / l. Acetylacetone, Cadmium and Nickel acetylacetonates. The initial concentration of metal solutions for the preparation of solution calibrator - 0.1 g / l. Used distilled water and chemical reagents qualification not lower than analytically pure.

Standard samples of metal solutions with a concentration of 1 g / l were used. Cadmium MSO 0502: 2003 (DZSU 022.43-96); Nickel MSO 0502: 2003 (DZSU 022.83-98).

The soil sample was taken near the gas well № 317 of "the Shebelinka Gas Production Department." The soil was dried, thoroughly grounded, and sifted through a sieve. A series of samples were taken and dissolved in 3.5 ml. of concentration HNO_3 . The solutions were evaporated to a wet residue. After cooling, 10 ml of nitric acid ($\omega = 1.5\%$) was added, treated for 15 minutes by ultrasound, and filtered into a volumetric flask with a capacity of 25 ml. 2 ml, Triton X-100 ($\omega = 4\%$), 0.5 ml Acetyl-acetone were added to the resulting solution and made up to the mark with distilled water and moved thoroughly.

Calibration solutions were prepared from standard solutions of metal ions and metal acetylacetonates. The dependences of the analytical signals in the determination of analytes on the concentration of analytes were reconstructed, and the increase in the measurement sensitivity was calculated.

Results and discussion

Metals in soils are in the form of complexes with organic ligands. The composition of inorganic standard samples significantly differs from the composition of the solutions analyzed. This issue substantially affects the results of analyte determination. Therefore, it is necessary to replace inorganic standard samples with complexes of metal ions with organic ligands. Intensification of sample preparation is achieved by using ultrasound. Adding

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Triton X-100 reduces the surface tension of the analyzed solution and increases the dispersion of the aerosol, which leads to complete atomization.

A study of the effect of Triton X-100 on the value of the analytical signal, depending on the surfactant concentration.

Thus, the highest sensitivity of the analytical signal is achieved at a surfactant concentration of Triton X-100 with $w = 3\%$.

Investigation of the influence of ultrasound processing time on the value of the analytical signal

Thus, the highest sensitivity of the analytical signal is achieved at 20 minutes of the ultrasonic treatment.

Thus, the highest sensitivity of the analytical signal is achieved at 20 minutes of the ultrasonic treatment.

The dependence of the analytical signal on the analyte concentration was obtained.

The achieved values of the analytical signals of aqueous solutions of Cadmium and solutions of Cadmium with a modifier treated with ultrasound are represented in Table 5.

The calibration dependence of the analytical signal on the Cadmium concentration is shown in Fig.1.

The obtained values of the analytical signals of aqueous solutions of Nickel and solutions of Nickel with a modifier treated with ultrasound are represented in Table 6.

The calibration dependence of the analytical signal on the Nickel concentration is presented in Fig.2.

The sensitivity factor is a numerical characteristic of sensitivity. If the calibration line is linear, then the sensitivity factor is the tangent of the angle of inclination of the calibration curve. The sensitivity of the method was determined as the slope of the linear part of the calibration curve.

The obtained results of atomic absorption determination of metals in soil samples using surfactants stabilized by ultrasound are shown in Table 8 and Table 9.

The additive method is used when checking the correctness of the results or when analyzing samples with a complex composition. The physical and chemical properties of calibration solutions may

differ from the properties of the samples, which leads to a systematic error.

Verification of the correctness of the results was determined by the method of "injected-found." The results are represented in Table 10 and Table 11.

Therefore, we can conclude that there is no significant systematic error.

By varying the weight of the samples, it was found out that the systematic error in determining Cadmium and Nickel is not significant.

The content of Cadmium and Nickel in the soil sample was determined by the atomic emission method with an inductively coupled plasma. The results are shown in Table 14.

The results of the determination of Cadmium and Nickel by atomic absorption spectroscopy and X-ray fluorescence analysis in soil samples according to Fisher and criteria and Student's t-test were compared. The results are presented in Table 15.

* $S_{1,2}$ - weighted average standard deviation for the results obtained by two independent methods.

Since $F < F_{table}$ and $t < t_{table}$ ($F_{0.95;4;4}^{table} = 6.39$; $t_{0.95;8}^{table} = 2.31$), we can conclude that the discrepancy of the averages obtained by two independent methods is insignificant and is justified by a random scatter.

Multiple measurements of the absorption signal of the zero solution. Recorded the values of 15-20 deals of the digital recording device, calculated the values of the standard deviation of the background. So, for Cadmium ($C_{min}=0,001$ mkg/ml, $C_{lit}=0,007$ mkg/ml) and for Nickel ($C_{min}=0,01$ mkg/ml, $C_{lit}=0,02$ mkg/ml).

Conclusions

The use of aqueous solutions of Triton X-100 and ultrasonic treatment eliminates the use of toxic and expensive reagents, increases the stability and homogeneity of the obtained solutions, reduces the analysis time, increases the sensitivity of analytes by 1.4 to 1.7 times. Standard samples of the composition based on metal acetylacetonates bring the chemical composition of the analyzed samples to the calibration solutions, increasing the precision and accuracy of measurements.

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Table 1. Choice of concentration of Triton X-100 for atomic absorption determination of Cadmium (n = 5, P= 0.95)

w(TritonX-100), %	Soil sample	
	$C(\text{Cd}), \text{mg/kg}$ $\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$	S_r
2	0,30±0,04	0,02
3	0,33±0,03	0,02
4	0,33±0,05	0,02
5	0,32±0,04	0,02

Table 2. Choice of Triton X-100 concentration for atomic absorption determination of Nickel (n = 5, P =0.95)

w(Triton X-100), %	Soil sample	
	$C(\text{Ni}), \text{mg/kg}$ $\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$	S_r
2	15,6±0,4	0,02
3	16,2±0,2	0,02
4	16,2±0,3	0,02
5	16,1±0,4	0,02

Table 3. The choice of ultrasonic treatment time of the analyzed solutions in the atomic absorption determination of Cadmium (n = 5, P = 0.95)

US, min.	Soil sample	
	$C(\text{Cd}), \text{mg/kg}$ $\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$	S_r
10	0,30±0,04	0,02
15	0,31±0,04	0,02
20	0,33±0,03	0,02
25	0,33±0,05	0,02

Table 4. The choice of sonication time in the atomic absorption determination of Nickel (n = 5, P = 0.95)

US, min.	Soil sample	
	$C(\text{Ni}), \text{mg/kg}$ $\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$	S_r
10	15,7±0,4	0,02
15	15,9±0,5	0,02
20	16,2±0,2	0,02
25	16,2±0,3	0,02

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Table 5. Values of analytical signals of aqueous solutions of Cadmium and Cadmium solutions with a modifier, sonicated for calibration solutions (n = 5, P = 0.95)

C(Cd), g/l	Analytical signals of aqueous solutions of Cadmium	Analytical signals of aqueous solutions of Cadmium with a modifier treated with ultrasound
0,00005	8	18
0,0001	25	42
0,0002	57	89
0,0003	91	134
0,0004	124	179

Table 6. Values of analytical signals of aqueous solutions of Nickel and solutions of Nickel with modifier, sonicated for calibration solutions (n = 5, P = 0.95)

C(Ni), g/l	Analytical signals of aqueous solutions of Nickel	Analytical signals of aqueous solutions of Nickel with a modifier treated with ultrasound
0,0001	9	15
0,0003	26	43
0,0004	34	57
0,0005	42	71
0,0007	59	98

Table 7. Values of sensitivity coefficients. The sensitivity of the atomic absorption determination of Cadmium increases by 1.4 times, Nickel – by 1.7 times.

Sample	Concentration of Cd,mg/kg $\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$	S_r
Soil sample	0,33±0,07	0,02

Table 8. The results of atomic absorption determination of Cadmium in the sample using surfactant Triton X-100 (w = 3%), stabilized by ultrasound (treatment time 20 minutes) (n = 5, P = 0.95)

Sample	Concentration of Ni,mg/kg $\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$	S_r
Soil sample	16,1±0,2	0,01

Table 9. Validation by the method of "injected-found" for Cadmium (n = 5, P = 0.95)

Sample	Cadmium content, mg/kg	Cadmium injection mg/kg	Found out mg/kg	S_r
Soil sample	0,33±0,05	0,40	0,73±0,05	0.01

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Table 10. Estimation of systematic error in atomic absorption determination of metals by varying the mass of the sample.

Sample	Nickel content, mg/kg	Nickel injection mg/kg	Found out mg/kg	S _r
Soil sample	16,1±0,2	17,0	33,1±0,4	0.01

Table 11. Estimation of systematic error in atomic absorption determination of Cadmium by varying the mass of the sample

Sample of Cd	Analytical sigal	Concentration of Cd,mg/kg $\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$	S _r
m = 4,0002 г	21	0,32±0,06	0,02
m = 4,5001 г	24	0,33±0,07	0,02
m = 5,0002 г	28	0,33±0,06	0,02
m = 5,4998 г	33	0,33±0,07	0,02
m = 6,0001 г	37	0,34±0,06	0,02
m = 6,5001 г	41	0,34±0,07	0,02

Table 12. Determination of analyte content by X-ray fluorescence analysis.

Sample of Ni	Analytical sigal	Concentration of Ni,mg/kg $\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$	S _r
m = 0,5001 г	83	16,1±0,2	0,01
m = 1,0001 г	87	16,1±0,1	0,01
m = 1,5002 г	91	16,1±0,3	0,01
m = 2,0001 г	96	16,2±0,2	0,01

Table 13. Results of X-ray fluorescence determination of Cadmium and Nickel in soil (n = 5, P = 0.95)

Element	Seria	Concentration, %	Concentration, mg/kg
Cd	K	0,000035±0,000010	0,35±0,10
Ni	K	0,0016±0,0003	16±3

Table 14. The results of atomic emission with inductively coupled plasma determination of metals in soil samples using surfactants stabilized by ultrasound (n = 5, P = 0.95)

Sample	Metal	Concentration, mg/kg $\bar{C} \pm \frac{t_{p,f}S}{\sqrt{n}}$	S _r
Soil sample	Cd	0,36±0,05	0,02
	Ni	16,2±0,1	0,01

Table 15. Comparison of the results of the determination of Cadmium and Nickel according to the criteria of Fisher F and Student t_{1,2}.

Metal	F	S _{1,2} *	t _{1,2}
Cd	1,435	0,044	1,09
Ni	1,298	0,685	1,28

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Figure 1. Dependence of the analytical signal of an aqueous solution of Cadmium and a solution of Cadmium with a modifier, treated with ultrasound, on the concentration of Cadmium in the atomic absorption determination of Cadmium.

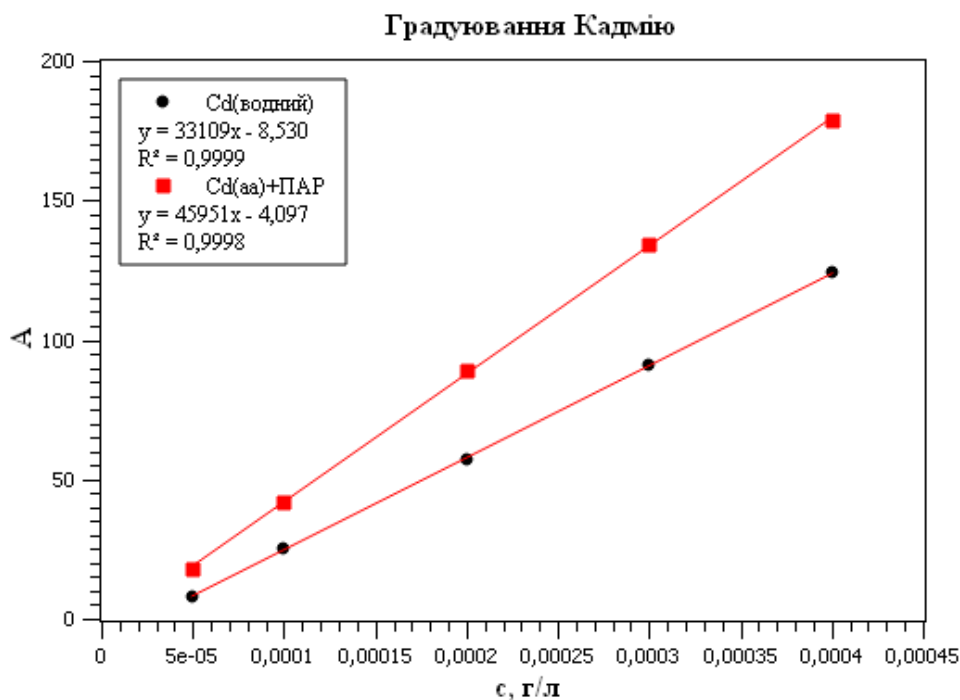
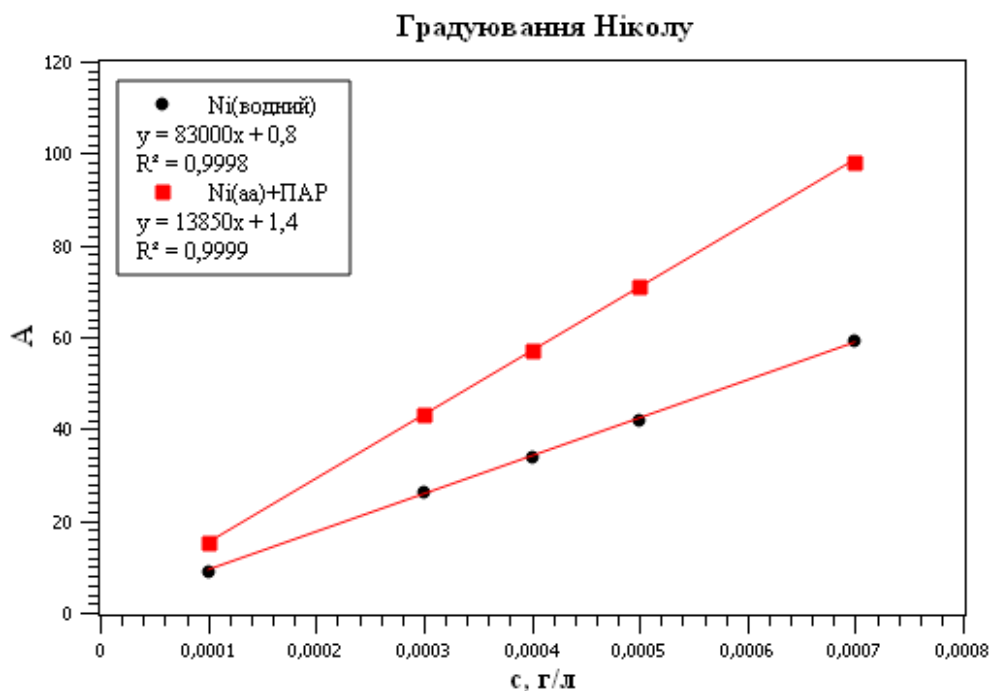


Figure 2 Dependence of the analytical signal of an aqueous solution of Nickel and a solution of Nickel with a modifier, treated with ultrasound, on the concentration of Nickel in the atomic absorption determination of Nickel.



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