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## ATOMIC ABSORPTION, ATOMIC EMISSION WITH INDUCTIVELY COUPLED PLASMA, AND X-RAY FLUORESCENCE DETERMINATION OF MANGANESE AND IRON IN SOIL NEAR A GAS PRODUCTION WELL

**Abstract:** Modern soil sample preparation using an ultrasonic treatment for 20 minutes was performed by acid decomposition of the sample. The influence of surfactant concentration and ultrasound on the sensitivity of atomic absorption determination of Manganese and Iron has been studied. It was found that the most significant increase in sensitivity is achieved by adding Triton X-100 ( $w = 4\%$ ). It was also investigated that the sensitivity of the determination increased: for Manganese - 1.37 times, for Iron - 1.33 times. The content of Manganese and Iron in the soil near the gas production well was determined by atomic absorption, atomic emission with inductively coupled plasma, and X-ray fluorescence methods using manganese and iron acetylacetonates as standard samples of the composition.

The correctness of the atomic absorption determination results of analytes was checked by the "introduced-found" method. By varying the weight of the sample, it is shown that the systematic error is insignificant. A comparison of the results obtained by an independent method of analysis was made. It appeared that the scatter is not remarkable and is caused by a random scatter. The limit of detection of Manganese ( $C_{min} = 0.001 \mu\text{g} / \text{ml}$ ) and Iron ( $C_{min} = 0.008 \mu\text{g} / \text{ml}$ ) was estimated as the ones below of the literature data.

**Key words:** Manganese, Iron, atomic absorption, atomic emission with inductively coupled plasma spectrometry, X-ray fluorescence analysis, ultrasound, Triton X-100, sample preparation, metrological characteristics.

**Language:** English

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### Introduction

Many studies have reported high concentrations of metals in the soil near the gas production wells. The mobility of heavy metals in soil depends on many factors. Still, their retention in the soil depends on soil pH, organic matrix, ion exchange capacity, soil conductivity, the presence of metal oxides that act as sorbents. In acid soils, the mobility of Fe, Mn increases crucially, and this increases the mobility of toxic elements. It also affects the plants in the ground, and namely, increases the contamination of plants with toxic elements by 20 times. The mobility of heavy metals depends on many factors, chemical properties, and types of climate.

The object of the study is a soil sample taken near a gas production well. In this study, manganese and iron acetylacetonates were used to simulate the organic matrix of the soil. Modern sample preparation using ultrasonic treatment was performed.

The analysis of soil was performed near the well № 317 Gas of the production department "Shebelinkagasvydobuvannya" PAT "Ukhazvydobuvannya". Three following independent methods were used: ardent atomic absorption spectroscopy, atomic emission spectroscopy with inductively coupled plasma, and X-ray fluorescence analysis.

Nowadays, atomic absorption, atomic emission with inductively coupled plasma, spectrometry, and X-ray fluorescence analysis are the most widely used methods for the determination of analytes in multicomponent samples. A unique role is played by sample preparation, the usage of new media, and standard samples of the composition. All the methods must meet the requirements of "green chemistry" [1-15].

The aim of this work is to develop a competitive method of atomic absorption, atomic emission with inductively coupled plasma spectrometry, and X-ray fluorescence determination of analytes in soils near gas production wells using the ultrasonic treatment, surfactants, and  $\beta$ -diketonates of metals as standard samples of the composition.

An atomic absorption spectrometer and CE333500 (flame version, hollow cathodes lamps, acetylene-air flame) were used. Iron was determined at  $\lambda = 248.3$  nm,  $C_2H_2$  - depleted air, 1 l / min.  $C_2H_2$ ; Manganese was determined at 279.5 nm,  $C_2H_2$ -depleted air, 1 l / min  $C_2H_2$ . Atomic emission spectrometer with inductively coupled plasma and CAP 6300DUO: speed of plasma-forming Argon is 12 l min., plasma power - 1350 W., speed 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 - 20s., five parallel measurements, wavelength, nm: Iron - 259,940; Manganese - 257,610. X-ray fluorescence studies were performed on an Elvax Ligth spectrometer (Elvitech, Ukraine). *Accelerating*

*the voltage of 45 kV.* "Live" measurement time - 100 s. Ultrasonic bath, model PS - 20, power - 120 W, frequency - 40 kHz. Laboratory scales ONAUS 64 (65 / 0.0001 g). Triton X-100,  $C_{14}H_{22}O$  ( $C_2H_4O$ )<sub>n</sub>, n = 9-10, Mr = 631 g / mol, CMC =  $2.9 \cdot 10^{-4}$  mol / l. Acetylacetone, manganese, and iron acetyl acetonates. The initial concentration of metal solutions for the preparation of calibration solutions is 0.1 g / l. Used distilled water and chemical reagents qualification not lower than "analytically pure."

The soil sample was taken near the well № 317 of the Shebelinkagasvydobuvannya gas industry department of the state-owned public joint-stock company UkrGasVydobuvannya. The soil was dried, thoroughly powdered, and sifted through a sieve.

A series of 0.2-0.4 g weighed samples with an error of 0.0002 g was taken and dissolved in 3.5 ml of concentration of  $HNO_3$ . The dissolved samples were evaporated to a wet residue. After cooling, 10 ml of 1.5%  $HNO_3$  was added to the residue, sonicated for 20 min; the solutions were filtered. We added 2 ml of Triton X-100 solution ( $\omega = 4\%$ ), 0.5 ml of acetylacetone. The line was made up with distilled water and mixed thoroughly.

### Results and discussions

Metals in the soils near gas production wells are in the form of complexes with organic ligands. The composition of inorganic standard samples differs significantly from the composition of the solutions to be analyzed. This issue notably affects the results of analyte determination. Therefore, it is necessary to replace the inorganic standard samples for complex metal ions with organic ligands.

The intensification of sample preparation is achieved by using ultrasound.

The addition of Triton X-100 reduces the surface tension of the analyte solution and increases the dispersion of the aerosol, which leads to complete atomization. Acetylacetone was added o this solution to form acetylacetonate analytes. Calibration solutions were prepared from standard iron solutions of iron and manganese ions, as well as from metal acetylacetonates. The dependence of analytical signals in the atomic absorption determination of analytes on their concentration was constructed. The sensitivity was calculated as:

$$S = tg\alpha = dA/dC \quad (1)$$

The increase in sensitivity was determined by the following formula

$$\Delta S = tg\alpha_2 / tg\alpha_1 \quad (2)$$

where  $tg\alpha_1$  – sensitivity when using aqueous solutions of metal ions,  $tg\alpha_2$  – sensitivity in the determination of analytes by the addition of Triton X-100 and used metal acetylacetonate.

Thus, we increased the sensitivity of the determination of Iron by 1.43 times and Lead by 1.66

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times. Using metal acetylacetonates as standard samples of the composition (they are certified as standard samples of the composition of a number of Ukrainian enterprises), the composition of the analyzed samples was brought closer to the composition of the calibration solutions, which allowed to increase the precision and accuracy of measurements.

Table 1 shows the study on the choice of surfactant concentration for atomic absorption determination of analytes, and Table 2 shows the selection of the time of processing of samples by ultrasound

As can be seen from Table 1, the largest value of the analytical signal is achieved at a concentration of Triton X-100  $w = 4\%$ .

As shown in Table 2, the largest value of the analytical signal is achieved by sonication for 20 minutes.

There is in Table 3, the results of atomic absorption determination of analytes in samples are represented.

Table 4 represents the verification of the results of the atomic absorption determination of analytes. In the table. 5 represents the atomic emission spectroscopy results with inductively coupled plasma ( $n = 5, P = 0.95$ ).

The use of the method of additives is utilized to analyze samples with a complex chemical composition or to check the correctness of chemical analysis results. The chemical and physical properties of graduated solutions may differ from the properties of samples, which causes systematic error.

The results of determining the content of analytes by X-ray fluorescence analysis are shown in Table 6.

Estimation of systematic error in atomic absorption determination of metals by weight variation is shown in Table 7.8.

When varying the samples' mass, the systematic error in the determination of Iron and Manganese does not make changes as a result of research.

Comparison of the results of the determination of Iron and Manganese (Table 9.10).

Based on the obtained data, it can be concluded that the results obtained by two independent methods are comparable. According to Fisher's and Student's criteria, the AAS and AES-ICP results are consistent because the calculated value does not exceed the tabular one at ( $f_1 = 2, f_2 = 4, P = 0.95$ ).

Based on the data obtained, it can be concluded the results obtained by two independent methods can

be compared with each other. According to Fisher's and Student's criteria, the AAS and XRF results are consistent because the calculated value does not exceed the tabular one at ( $f_1 = 2, f_2 = 2, P = 0.95$ ).

Defining the boundaries of analytes

Means of reducing the detection limit:

- use of the maximum brightness of the source lighting;
- the maximum possible width of the gap, which will not lead to the overlap with other close lines;
- minimization of non-selective absorption;
- general optimization of the signal-to-noise ratio.

Multiple measurements of the absorption signal of the reference solution. The readout of 15-20 values of the digital registration device and the calculation of the value of the standard deviation of the background should be done:

$$S_0 = \sqrt{\frac{\sum(\bar{A}-A)^2}{n-1}} \quad (3)$$

where

$\bar{A}$ - the average value of the absorption signal,

A - the value of the absorption signal,

n is the number of measurements.

Calculation of the detection limit should be done by the following formula:

$$C_{min} = \frac{3S_0}{tg\alpha}. \quad (4)$$

The detection limit of Manganese:  $C_{min} = 0,001 \mu\text{g/ml}$ ,  $C_{theor} = 0,004 \mu\text{g/ml}$ ; for Iron:  $C_{min} = 0,008 \mu\text{g/ml}$ ,  $C_{theor} = 0,015 \mu\text{g/ml}$ .

## Conclusion

The usage 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 in 1.5 - 1.8 times. Standard samples of the composition based on metal acetylacetonates bring the chemical composition of the analyzed samples to the calibration solutions, and that allows increasing the precision and accuracy of measurements

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**Table 1. Choice of Triton X-100 concentration for the increase of the sensitivity of atomic absorption determination of Iron and Manganese (n = 5, P = 0.95).**

w (Triton X-100),%	Soil sample		
	C(Fe), mg/kg $\bar{C} \pm \frac{t_{p,f} S}{\sqrt{n}}$	C(Mn), mg/kg $\bar{C} \pm \frac{t_{p,f} S}{\sqrt{n}}$	S <sub>r</sub>
3	11000 ± 17	349 ± 8	0,01
4	11666±13	360±5	0,01
5	10650±14	327±11	0,01
6	10500±16	327±13	0,01

**Table 2. The choice of ultrasonic treatment time in the atomic absorption determination of Iron (n = 5, P = 0.95).**

t,min	Soil sample		
	C(Fe), mg/kg $\bar{C} \pm \frac{t_{p,f} S}{\sqrt{n}}$	C(Mn), mg/kg $\bar{C} \pm \frac{t_{p,f} S}{\sqrt{n}}$	S <sub>r</sub>
10	11457 ± 24	355 ± 9	0,01
15	11603±32	327±7	0,01
20	10650±26	3±11	0,01
25	10500±27	327±13	0,01

**Table 3. The results of atomic absorption determination of Iron and Manganese using Triton X-100 (w = 4%), stabilized by ultrasound (treatment time is 20 min) (n = 5, P = 0.95).**

Sample	C(Fe), mg/kg $\bar{C} \pm \frac{t_{p,f} S}{\sqrt{n}}$	S <sub>r</sub>	C(Mn), mg/kg $\bar{C} \pm \frac{t_{p,f} S}{\sqrt{n}}$	S <sub>r</sub>
Soil sample	11666 ± 13	0,05	360±5	0,03

**Table 4. Validation by the method of "entered-found" for Iron (n = 5, P = 0.95).**

Sample	Fe content, 10 <sup>-4</sup> g/l	Injected Fe, 10 <sup>-4</sup> g/l	Found out Fe, 10 <sup>-4</sup> g/l	Mn content, 10 <sup>-4</sup> g/l	Injected Mn, 10 <sup>-4</sup> g/l	Found out Mn, 10 <sup>-4</sup> g/l	S <sub>r</sub>
Soil sample	6,40± 0,03	12,00	18,24± 0,05	5,80± 0,04	11,00	16,71± 0,07	0,02
Soil sample	6,40± 0,03	3,00	9,43± 0,02	5,80± 0,04	3,00	8,92± 0,03	0,02

**Table 5. The results of determining Iron and Manganese content in the soils of atomic emission spectroscopic inductively coupled plasma (n = 5, P = 0.95).**

C(Fe), mg/kg	S <sub>r</sub>	C(Mn), mg/kg	S <sub>r</sub>
11646 ± 9	0,05	355±8	0,02

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**Table 6. Concentrations of Iron and Manganese were obtained by X-ray fluorescence method (n = 5, P = 0.95).**

Element	Series	C(Mn), mg/kg $\bar{C} \pm \frac{t_{p,f} S}{\sqrt{n}}$
Fe	K	11646 ± 91
Mn	K	348±6

**Table 7. Estimation of the systematic error in the atomic absorption determination of Iron by varying the mass of the sample.**

Sample	Analytical signal	C(Fe), mg/kg	S <sub>r</sub>
m=0,2134	31	11600 ± 11	0,05
m=0,3247	33	11612 ± 10	0,05
m=0,4222	35	11608 ± 12	0,05

**Table 8. Estimation of systematic error in the atomic absorption determination of Manganese by varying the mass of the sample.**

Sample	Analytical signal	C(Mn), mg/kg	S <sub>r</sub>
m=0,2134	97	360 ± 7	0,03
m=0,3247	100	363 ± 6	0,03
m=0,4222	99	365 ± 8	0,03

**Table 9. Comparison of the results of determination of metals by AAS and AES-ICP methods in the soil sample according to Fisher's and Student's criteria.**

Metal	F	F <sub>tabl</sub>	t	t <sub>tabl</sub>
Fe	1,44	6,94	1,77	2,45
Mn	1,60		2,41	

**Table 10. Comparison of the results of determination of metals by AAS and X-ray fluorescence methods in a soil sample according to Fisher's and Student's criteria.**

Metal	F	F <sub>tabl</sub>	t	t <sub>tabl</sub>
Fe	10,16	19	2,54	2,78
Mn	1,21		2,67	

## References:

- Mao, J., Liu, X., Chen, B., Luo, F., Wu, X., Jiang, D., & Luo, Z. (2017). *Electronics Science Technology and Application*, V.4 (1), pp.23-31.
- Macros, D.R., Parsons, J., Garcia, H., Corral, A., Cruz, J. G., Campos, T.A., Duarte, M.A., & Gardea-Torresdey, J. (2011). *Physical Review and Research International*, V.1(2), pp. 29-44.
- Jing, Y., Jingwen, B., Meiyu, L., Yang, C., Shoutong, W., & Qiyong, Y. (2018). *Journal of Analytical Methods in chemistry*, V.4, pp.7-15.

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4. Asoh, K., & Ebihara, M. (2013). *Analytical Chimica Acta*, V.779, pp.8-13.
5. Ramsey, M.H., & Thompson, M. (1985). *Analyst*, V.110 (5), pp.510-519
6. Anzano, J., Abia, L., Aragoes, M., Ballano, E., Lomero, L., Pena, C., & Perez, A. (2014). *J. Lab. Chem. Educ.* V.2 (1), pp. 4-9.
7. Buzina, I.M. (2012). *Visnyk ZNAEU*. V. 2, pp. 232-241.
8. Singh, V., Padalia, D., & Devlal, K. (2017). *J. Nucl. Phus.* V.4(2), pp.383-391.
9. Vlasova, I.V. (2011). *Journ. Anal. Chem.* V. 66 (1), pp.24-33.
10. Vershinin, V.I. (2011). *Vestnyk Omskogo universiteta*, V.2, pp.113-117.
11. Baena, J.R., & Valcarcel, M. (2003). V.22 (10), pp.641-646.
12. Vershinin, V.I. (2012). *Vestnyk Omskogo universiteta*. V.5, pp.14-17.
13. Budnikov, G.K. (1998). *Sorosovskii obrazovatelni journal*, V.5, pp.23-29.
14. Revenko, A.G. (2005). *Ukr.him.journ.* V.71 (9), pp.39-44.
15. Puhovskii, A.V. (2013). *Prirodoobustroistvo*, V.2, pp.11-14.