SECTION 9: Chemistry and chemical technology

ATOMIC-ABSORPTION AND ATOMIC-EMISSION WITH INDUCTIVE CONNECTED PLASMA DETERMINATION OF THE ANALYTS IN OIL PRODUCTS WITH USE OF MODERN METHODS OF SAMPLE PREPARATION AND NEW STANDARD COMPOSITION SAMPLES

Abstract: An influence of concentration of surfactants and time of ultrasound treatment on value of analytical signal at atomic-absorption and atomic-emission with inductive connected plasma determination of analysts in oil products was studied. It was shown that using of our sample preparation increases sensibility in 1.5-2.0 times. These results were also proved by the new processing program. By means of by variation of the sample mass we show an absence of perfect systematical error. By the method “injected-found out” an accuracy of the results of atomic-absorption determination of Zinc and Manganese was estimated. Coherence of the results, obtained by two independent methods, was estimated by F- and t- criteria. It was shown that dispersions are homogenous and results are distinguished not sufficiently. We also estimated the limit of founding out of analytes by atomic-absorption method. It was shown that our results are lower than literature data. This is because of application of standard samples based on acetylacetanates of metals.

Key words: oil products, Zinc, Manganese, atomic-absorption and atomic-emission with inductive connected plasma spectrometry, Bridge-35, ultrasound treatment, acetylacetanates of Zinc and Manganese, analysis, methodological characteristics.

Language: English

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Introduction

The most important characteristic of oil products is the microelement content that inform us about ways of accumulation and migration, age of oil. The oil microelements, effects negatively on its refining. Use of oil refining products as fuel leads to atmospheric pollution of toxic elements.

This demonstrate us necessity to study microelement composition of oil. In order to do this the methods of the high sensitivity like atomic-absorption and atomic-emission with inductive connected plasma spectrometry are used. The procedure of samples preparation and use of standard composition samples in this method of analysis is discussed by us also. [1,p.93; 2,p.124; 3,p.9; 4,p.615;...
The main purpose of our investigation is the determination of Zinc and Manganese in oil products by methods of atomic-absorption and atomic-emission with inductive connected plasma, using of Bridge-35, ultrasound treatment and acetylacetonates analyt as standard composition samples.

Experimental

For carrying out the experiment we used atomic-absorption spectrometer C-115-MI, atomic-emission with inductive connected plasma spectrometer Trace SCAN Thermo Jarrell Ach (USA), ultrasound bath PS-20 and oil products: Okko «Exol 20w-50 economic», Okko «Exol diesel city 1540», TNK «Motor 20w-50», Lukoil «Moto 2T», VAMP «Diesel Turbo», acetylacetone, acetylacetonates of Zinc and Manganese (certified as standard samples by a number of Ukrainian companies), Bridge-35.

The analyzed solutions were prepared in such a way: to the sample weight we added 1 ml of saturated HNO₃, 4 ml of water solution of Bridge-35, 2 ml of acetylacetone and mixed by magnetic mixer within 30 min. The solution was placed into volumetric flack of 10 ml volume and diluted to scale by water SAS solution (ω = 5%) and treated by ultrasound within 10 minutes. In the result we obtained stable and homogenous emulsions which did not exfoliated for 5 days.

Results and discussion

It was established by experiment that Bridge-35 increases an analytic signal at atomic-absorption determination of Zinc and Manganese. By variation of the mass percent of Bridge-35 from 3% up to 7% it was found that the analytic signal at determination of Zinc and Manganese increase in 1,5-2 times at Bridge-35 with ω = 5%.

To obtain stable emulsions the analyzed and calibrated solutions should be treated by ultrasound. The time of the treatment was varied from 5 up to 25 minutes. It was established that maximal analytic signal is observed at ultrasound treatment of the solutions within 10 minutes. By the variation of weight of the samples from 0,1 up to 0,5 g it was found that significant systematical error at atomic-absorption determination of Zinc and Manganese is absent.

By the atomic-absorption and atomic-emission with inductive connected plasma method the determination of Zinc and Manganese was carried out in oil products at the set of next parameters: weight of the sample is 0,3 g, Bridge-35 (ω = 5%), ultrasound treatment during 10 minutes.

It was found out that the use of polyfunctional composition samples is necessary at direct atomic-absorption determination of metals in the samples with organic ligands. An approach of qualitative composition of the calibrated solutions to qualitative composition of the analyzed solutions decreases matrix effects. Using of β-dicetonates of metals in atomic-absorption spectrometry increases an accuracy of atomic-absorption determination. This results is explained by keeping atoms in flame during longer time. It was shown that application of surfactants decreases viscosity, surface tension, size of drops of the formed sol, increases efficiency of spraying of the solvent, changes redox properties of flame, character of charge distribution in the molecule, efficiency of intra-and intermolecular excitation energy transfer, interphase particles distribution, solubility, rate and equilibrium state of reaction. It was shown also the possibility to carry out analysis in low temperature flame with the increase of selectivity and sensibility in 2-3 times and decrease of limit of determination.

The results of analytes determination are in Table 1.

Verification of the validity of the results of atomic-absorption determination of the analyst in samples was done by “injected-found out” method. (Tables 2,3)

In order to find the limit of determination on “pure substances” many times measurement of analytic signal of the “zero solution” (20 values) is done.

The value of the standard deviation is calculated by formula (1)

$$S_0 = \sqrt{\frac{\sum_{i=1}^{n} (A_i - \bar{A})^2}{n-1}}$$

The limit of determination is calculated by formula (2)

$$C_{min} = \frac{3S_0}{S}$$

where S is the coefficient of sensibility.

The limits of determination of Zinc (C_{min} = 0.003) and Manganese (C_{min} = 0.003) were estimated. These limits are less than the corresponding data from literature [15, p.121].
Conclusions
The application of Bridge-35 ($\omega = 5\%$) permit us to increase the sensibility in 1.5-2.0 times and ultrasound treatment results the stable homogenous emulsions. Using of acetylacetonates of zinc and manganese as the standard composition samples, we obtain the similar results of study of chemical composition of the analyzed and calibrated solutions. The obtained results permit us to increase an accuracy of determination of Zinc and Manganese in samples.

| Sample                      | Content of Zn, mg/kg | Content of Mn, mg/kg |
|-----------------------------|----------------------|----------------------|
|                             | AAS                  | AES-ICP              |
|                             | $\bar{C} \pm \frac{t_{p,f} \cdot S}{\sqrt{n}}$ | $\bar{C} \pm \frac{t_{p,f} \cdot S}{\sqrt{n}}$ |
|                             | $S_r$                | $S_r$                |
|                             | mg/kg                | mg/kg                |
| Okko «Exol 20w-50 economic» | 464 ± 6              | 467 ± 6              |
|                             | 0.01                 | 0.01                 |
|                             | 1.85 ± 0.02          | 1.86 ± 0.02          |
|                             | 0.01                 | 0.01                 |
| Okko «Exol diesel city 1540» | 498 ± 6              | 500 ± 6              |
|                             | 0.01                 | 0.01                 |
|                             | 2.14 ± 0.02          | 2.16 ± 0.02          |
|                             | 0.01                 | 0.01                 |
| TNK «Motor 20w-50»          | 651 ± 8              | 654 ± 8              |
|                             | 0.01                 | 0.01                 |
|                             | 2.40 ± 0.03          | 2.39 ± 0.06          |
|                             | 0.01                 | 0.02                 |
| Lukoil «Moto 2T»            | 105 ± 3              | 107 ± 3              |
|                             | 0.02                 | 0.02                 |
|                             | 2.81 ± 0.03          | 2.82 ± 0.03          |
|                             | 0.01                 | 0.01                 |
| VAMP «Diesel Turbo»         | 673 ± 8              | 677 ± 8              |
|                             | 0.01                 | 0.01                 |
|                             | 2.67 ± 0.03          | 2.65 ± 0.03          |
|                             | 0.01                 | 0.01                 |
**Impact Factor:**

|        | ISRA (India) | SIS (USA) | ICB (Poland) | PII (India) | PIF (India) | RIH (Russia) | ESJI (KZ) | SJIF (Morocco) |
|--------|--------------|-----------|--------------|-------------|-------------|--------------|----------|----------------|
| Factor | 1.344        | 0.912     | 6.630        | 1.940       | 1.940       | 0.207        | 4.102    | 2.031          |

**Table 2**

Verification of the validity of atomic-absorption determination of Zink in the oil products stabilized by ultrasound treatment by “injected-found out” method (n=5, P=0.95)

| Content (Zn), mg/kg | Injected, Zn mg/kg | Found out (Zn) $\frac{\bar{C} \pm \frac{t_p \cdot s}{\sqrt{n}}}{\bar{C} \pm \frac{t_p \cdot s}{\sqrt{n}}}$, mg/kg | Sr |
|---------------------|--------------------|------------------------------------------------|----|
| Okko «Exol 20w-50 economic» | 464 | 460 | 920 ± 11 | 0.01 |
| Okko «Exol diesel city 1540» | 498 | 500 | 995 ± 12 | 0.01 |
| TNK «Motor 20w-50» | 651 | 650 | 1300 ± 16 | 0.01 |
| Lukoil «Moto 2T» | 105 | 100 | 205 ± 5 | 0.02 |
| VAMP «Diesel Turbo» | 673 | 670 | 1340 ± 17 | 0.01 |

**Table 3**

Verification of validity of Manganese determination in the oil products stabilized by ultrasound treatment by “injected-found out” method (n=5, P=0.95)

| Sample (Mn) | Injected (Mn), mg/kg | Found out $\frac{\bar{C} \pm \frac{t_p \cdot s}{\sqrt{n}}}{\bar{C} \pm \frac{t_p \cdot s}{\sqrt{n}}}$ mg/kg | Sr |
|-------------|----------------------|------------------------------------------------|----|
| Lukoil “Moro 2T” | 2.00 | 3,84±0,10 | 0.02 |
| TNK “Motor 20w-50” | 2.00 | 4,16±0,10 | 0.02 |
| Okko “Exol 20w-50 economic” | 2.00 | 4,37±0,11 | 0.02 |
| Okko “Exol diesel city 15w-40” | 2.00 | 4,85±0,12 | 0.02 |
| VAMP “Diesel Turbo” | 2.00 | 4,70±0,11 | 0.02 |

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