

## Impact Factor:

ISRA (India) = 1.344	SIS (USA) = 0.912	ICV (Poland) = 6.630
ISI (Dubai, UAE) = 0.829	PIHII (Russia) = 0.156	PIF (India) = 1.940
GIF (Australia) = 0.564	ESJI (KZ) = 4.102	IBI (India) = 4.260
JIF = 1.500	SJIF (Morocco) = 2.031	

SOI: [1.1/TAS](#) DOI: [10.15863/TAS](#)

## International Scientific Journal Theoretical & Applied Science

p-ISSN: 2308-4944 (print) e-ISSN: 2409-0085 (online)

Year: 2018 Issue: 07 Volume: 63

Published: 19.07.2018 <http://T-Science.org>

**Oleg Ivanovych Yurchenko**

Kharkiv V.N. Karazin  
National University, PhD, Full Professor of  
Chemical Metrology Department,  
[yurchenko@karazin.ua](mailto:yurchenko@karazin.ua)

**Tetyana Vasylivna Chernozhuk**

Kharkiv V.N.  
Karazin National University, PhD, Associate  
Professor of Inorganic Chemistry Department,  
[tanya.chernozhuk@gmail.com](mailto:tanya.chernozhuk@gmail.com)

**Oleksii Andriovych Kravchenko**

Kharkiv V.N.  
Karazin National University, PhD, Associate  
Professor of Chemical Metrology Department,  
[alekseykravch@ukr.net](mailto:alekseykravch@ukr.net)

### SECTION 9. Chemistry and chemical technology

## NEW STANDARD COMPOSITION SAMPLES, SURFACTANTS AND ULTRASOUND TREATMENT AT ATOMIC-ABSORPTION AND ATOMIC-EMISSION WITH INDUCTIVE CONNECTED PLASMA DETERMINATION OF CADMIUM AND COPPER IN OIL PRODUCTS

**Abstract:** An influence of concentration of twin 20 and time of ultrasound treatment on value of analytical signal at atomic-absorption and atomic-emission with inductive connected plasma determination of cadmium and copper in oil products was studied. It was shown that using of our sample preparation increases sensibility in 1,5-2,0 times due to formation of the homogenous emulsions. Using of new standard samples based on cadmium and copper acetylacetonates maximally approximate the samples to the calibration solutions. This increases the precision of definitions. By varying the weight of the analyzed samples it was established that the method didn't contain significant systematic errors. By the method "injected-found out" an accuracy of the received results 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. The distribution of results is justified by random distribution. We also estimated the limit of founding out of analytes. It was shown that our results are lower than literature data.

**Key words:** cadmium, copper, acetylacetonates of cadmium and copper, ultrasound treatment, twin-20, atomic-absorption and atomic-emission with inductive connected plasma spectrometry, oil products, analysis, metrological characteristics.

**Language:** English

**Citation:** Yurchenko OI, Chernozhuk TV, Kravchenko OA (2018) NEW STANDARD COMPOSITION SAMPLES, SURFACTANTS AND ULTRASOUND TREATMENT AT ATOMIC-ABSORPTION AND ATOMIC-EMISSION WITH INDUCTIVE CONNECTED PLASMA DETERMINATION OF CADMIUM AND COPPER IN OIL PRODUCTS. ISJ Theoretical & Applied Science, 07 (63): 112-118.

**Soi:** <http://s-o-i.org/1.1/TAS-07-63-15> **Doi:**  <https://dx.doi.org/10.15863/TAS.2018.07.63.15>

### Introduction

Heavy metals are found in oil products in the form of complex mixtures, in the form of solid metal oxides and organometallic particles formed after the mechanical processing of oxidative and chemical corrosion, respectively [1, p.353]. The disadvantages of early techniques are the limited amount of detectable metals and the lack of universality [2,p.7].

More than 95% of all analyzes are performed by comparative methods, including 90% by spectroscopic methods. The total uncertainty of the results of the analysis affects the general uncertainty associated with calibration. However, it is possible to

reduce this uncertainty by using the standard samples of  $\beta$ -diketonates of metals for calibration [3,p.5]. Using of spectroscopic methods of analysis and sample preparation of petroleum products were described in papers [4, p.2; 5,p.97; 6,p.553; 7,p.1980; 8,p.400;9,p.161;10,p.460].

The purpose of our investigation was using of new standard samples, twin-20 and ultrasound treatment to obtain reliable data by methods of atomic-absorption and atomic-emission with inductive connected plasma for analytes determination in oil products.



## Impact Factor:

ISRA (India) = 1.344	SIS (USA) = 0.912	ICV (Poland) = 6.630
ISI (Dubai, UAE) = 0.829	PIIHQ (Russia) = 0.156	PIF (India) = 1.940
GIF (Australia) = 0.564	ESJI (KZ) = 4.102	IBI (India) = 4.260
JIF = 1.500	SJIF (Morocco) = 2.031	

### Experimental

For carrying out the experiment we used atomic-absorption spectrometer C-115-MI, atomic-emission with inductive connected plasma spectrometer Trace Scan advantage (USA), ultrasound bath PS-20 and oil products: Okko «Exol 20w-50 economic», Okko «Exol diesel city 15w-40», TNK «Motor 20w-50», Lukoil «Moto 2T», VAMP «Diesel Turbo», acetylacetone, acetylacetonates of Cadmium and Copper, twin-20 (4% for Cadmium determination, 2% for Copper determination).

The analyzed solutions were prepared in such a way: to the sample weight we added 1 ml of saturated HNO<sub>3</sub>, 4 ml of water solution of twin-20, 2 ml of acetylacetone and mixed by magnetic mixer within 30 min. The solution was placed into volumetric flask of 10 ml volume and diluted to scale by twin-20 water solution ( $\omega=2\%$ (Cu) and  $\omega=4\%$ (Cd)) and treated by ultrasound within 20 min (Cd) and 15 min (Cu). In the result we obtained stable and homogenous emulsions which did not exfoliated for 5 days.

*Preparation of the calibration solutions based on standard composition samples of aqueous solutions of Cadmium and Copper.*

In a volumetric flask of 50 ml volume we transferred 2.5 ml of the initial solution with a concentration of Cadmium and Copper 0.1 g/l, diluted to scale by distilled water and mixed thoroughly. Obtained intermediate solution has the concentration of Cadmium and Copper  $5 \times 10^{-3}$  g/l.

To prepare the calibration solution with concentration  $1 \times 10^{-4}$  g/l, 0.2 ml of intermediate solution with concentration  $5 \times 10^{-3}$  g/l was taken, transferred to a flask of 10 ml volume, diluted to scale by distilled water and mixed thoroughly.

To prepare the calibration solution with concentration  $3 \times 10^{-4}$  g/l, 0.6 ml of intermediate solution with concentration  $5 \times 10^{-3}$  g/l was taken, transferred to a flask of 10 ml volume, diluted to scale by distilled water and mixed thoroughly.

To prepare the calibration solution with concentration  $5 \times 10^{-4}$  g/l, 1 ml of intermediate solution with concentration  $5 \times 10^{-3}$  g/l was taken, transferred to a flask of 10 ml volume, diluted to scale by distilled water and mixed thoroughly.

To prepare the calibration solution with concentration  $7 \times 10^{-4}$  g/l, 1.4 ml of intermediate solution with concentration  $5 \times 10^{-3}$  g/l was taken, transferred to a flask of 10 ml volume, diluted to scale by distilled water and mixed thoroughly.

To prepare the calibration solution with concentration  $1 \times 10^{-3}$  g/l, 2 ml of intermediate solution with concentration  $5 \times 10^{-3}$  g/l was taken, transferred to a flask of 10 ml volume, diluted to scale by distilled water and mixed thoroughly.

*Preparation of the calibration solutions based on Cadmium and Copper acetylacetonates with additives of twin-20.*

To prepare the calibration solution with Cadmium or Copper concentration  $1 \times 10^{-4}$  g/l, 0.2 ml of intermediate solution with concentration  $5 \times 10^{-3}$  g/l was taken, transferred to a flask of 10 ml volume, added 4 ml of twin-20 solution (the appropriate concentration for Cadmium or Copper), diluted to scale by distilled water and mixed thoroughly.

To prepare the calibration solution with Cadmium or Copper concentration  $3 \times 10^{-4}$  g/l, 0.6 ml of intermediate solution with concentration  $5 \times 10^{-3}$  g/l was taken, transferred to a flask of 10 ml volume, added 4 ml of twin-20 solution (the appropriate concentration for Cadmium or Copper), diluted to scale by distilled water and mixed thoroughly.

To prepare the calibration solution with Cadmium or Copper concentration  $5 \times 10^{-4}$  g/l, 1 ml of intermediate solution with concentration  $5 \times 10^{-3}$  g/l was taken, transferred to a flask of 10 ml volume, added 4 ml of twin-20 solution (the appropriate concentration for Cadmium or Copper), diluted to scale by distilled water and mixed thoroughly.

To prepare the calibration solution with Cadmium or Copper concentration  $7 \times 10^{-4}$  g/l, 1.4 ml of intermediate solution with concentration  $5 \times 10^{-3}$  g/l was taken, transferred to a flask of 10 ml volume, added 4 ml of twin-20 solution (the appropriate concentration for Cadmium or Copper), diluted to scale by distilled water and mixed thoroughly.

To prepare the calibration solution with Cadmium or Copper concentration  $1 \times 10^{-3}$  g/l, 2 ml of intermediate solution with concentration  $5 \times 10^{-3}$  g/l was taken, transferred to a flask of 10 ml volume, added 4 ml of twin-20 solution (the appropriate concentration for Cadmium or Copper), diluted to scale by distilled water and mixed thoroughly.

### Results and discussion

The first stage of choosing the optimal conditions for the analysis was determination of the twin-20 concentration. The dependence of the analytical signal from the twin-20 concentration was investigated (Table 1).

From the obtained results, we can conclude that the twin-20 with  $\omega = 4.0\%$  gives the largest analytical signal for Cadmium, and  $\omega = 2.0\%$  for Copper. At the same time, the sensitivity of atomic-absorption determination of Copper and Cadmium increased 1.5-2.0 times, respectively. When applying twin-20, the density of the solution, the surface tension and the size of the aerosol droplets that were formed decreased, while the efficiency of the solution spray and the reaction rate increased.

The second stage of our study was determination of ultrasound treatment time of the prepared emulsion. For this, the emulsion was treated by ultrasound for different periods of time. US is

## Impact Factor:

ISRA (India) = 1.344	SIS (USA) = 0.912	ICV (Poland) = 6.630
ISI (Dubai, UAE) = 0.829	PIIHQ (Russia) = 0.156	PIF (India) = 1.940
GIF (Australia) = 0.564	ESJI (KZ) = 4.102	IBI (India) = 4.260
JIF = 1.500	SJIF (Morocco) = 2.031	

used to create stable emulsions of oil products which did not exfoliated for 5 days. The resulting emulsions are transparent and homogeneous. Dependence of Cadmium and Copper concentration in oil products from the ultrasound treatment time of analyzed solutions for atomic-absorption determination of Cadmium and Copper ( $n = 5$ ;  $P = 0.95$ ) (Table 2). As can be seen from Table 2, the optimal time for Cadmium determination is 20 min, and for Copper determination is 15 min.

Table 3 shows the results of atomic-absorption determination of Cadmium and Copper in oil products emulsions with using twin-20, Cadmium and Copper acetylacetonates and ultrasound.

In order to verify the accuracy of the metals determination in oil products, the "injected-found out" method was used. The results of the measurements are given in Table 4.

Systematic error of Cadmium and Copper determination was estimated by varying the sample mass of oil products. The results of investigation are presented in Table 5.

As can be seen from Table 5, there is no linear systematic error.

In addition to the atomic-absorption method, the determination of the metals was also carried out by atomic-emission method with inductive connected plasma (Table 6).

Coherence of Cadmium and Copper determination results with atomic-absorption and atomic-emission with inductive connected plasma methods was determined by F- and t-criteria. The results are shown in Table 7.

Similar results were obtained for Copper determination.

To determine the detection limit of these methods, 20 blank solutions were used for calculation of  $C_{min}$ . The results are shown in Table 8. As can be seen from Table 8, the obtained results are lower than literature data.

## Conclusions

The use of new standard composition samples of surfactants as new media and ultrasound treatment during sample preparation of oil products significantly increases metrological characteristics of atomic-absorption and atomic-emission with inductive connected plasma methods for Cadmium and Copper determination.

Table 1

Selection of twin-20 concentration for atomic-absorption determination of Cadmium and Copper.

w(SAS Twin-20), %	C Cd , mg/kg	$S_r$
3	0,18 0,03	0.03
4	0,30 0,003	0.04
5	0,22 0,02	0.02
6	0,20 0,02	0.01

w(SAS Twin-20), %	C Cu , mg/kg	$S_r$
1	2,36 0,06	0.03
2	2,68 0,11	0.04
3	1,68 0,03	0.02
4	1,42 0,01	0.01
5	1,27 0,04	0.03

**Impact Factor:**

<b>ISRA</b> (India) = <b>1.344</b>	<b>SIS</b> (USA) = <b>0.912</b>	<b>ICV</b> (Poland) = <b>6.630</b>
<b>ISI</b> (Dubai, UAE) = <b>0.829</b>	<b>PIHHI</b> (Russia) = <b>0.156</b>	<b>PIF</b> (India) = <b>1.940</b>
<b>GIF</b> (Australia) = <b>0.564</b>	<b>ESJI</b> (KZ) = <b>4.102</b>	<b>IBI</b> (India) = <b>4.260</b>
<b>JIF</b> = <b>1.500</b>	<b>SJIF</b> (Morocco) = <b>2.031</b>	

**Table 2****Time of US treatment of the samples.**

US, min	C Cd mg/kg	S <sub>r</sub>
10	0,24 0,001	0.01
15	0,26 0,001	0.01
20	0,27 0,001	0.01
25	0,27 0,001	0.01

US, min	C Cu mg/kg	S <sub>r</sub>
5	2,66 0,06	0.02
10	2,83 0,03	0.01
15	4,39 0,04	0.01
20	2,39 0,08	0.03

**Table 3****Results of determination of Cadmium and Copper by the AAS method in oil products (n = 5; P = 0.95).**

	C Cd,mg/kg	S <sub>r</sub>
Lukoil «Moto 2T»	0,28 0,01	0.01
THK «Motor 20w-50»	0,29 0,01	0.01
WAMP	0,36 0,01	0.02
Okko «Exol diesel city 1540»	0,37 0,01	0.01
Okko «Exol 20w-50 economic	0,22 0,01	0.01

	C Cu,mg/kg	S <sub>r</sub>
Lukoil «Moto 2T»	3,54 0,04	0.02
Okko «Exol diesel city 1540»	4,39 0,04	0.01
Okko «Exol 20w-50 economic	5,94 0,06	0.01

**Table 4****Verification of the accuracy of atomic-absorption determination of Cadmium and Copper in ultrasound stabilized emulsions by the "injected-found out" method (n = 5; P = 0.95).**

Sample	Contain of Cd, mg/kg	Injected , mg/kg	Found out mg/kg	S <sub>r</sub>
Lukoil "Moto 2T"	0,28	0,25	0,52±0,01	0,01
TNK "Motor 20w-50"	0,29	0,30	0,59±0,01	0,01
VAMP "Diesel Turbo"	0,36	0,35	0,70±0,01	0,01

## Impact Factor:

ISRA (India) = 1.344	SIS (USA) = 0.912	ICV (Poland) = 6.630
ISI (Dubai, UAE) = 0.829	PIHII (Russia) = 0.156	PIF (India) = 1.940
GIF (Australia) = 0.564	ESJI (KZ) = 4.102	IBI (India) = 4.260
JIF = 1.500	SJIF (Morocco) = 2.031	

Okko "Exol diesel city 15w-40"	0,37	0,35	0,71±0,01	0,01
"Okko "Exol 20w-50 economic	0,22	0,25	0,46±0,01	0,02

Sample	Contain of Cd, mg/kg	Injected, mg/kg	Found out mg/kg	S <sub>r</sub>
Exol diesel city	4,39	3,5	7,89±0,16	0,02
"Exol 20w-50 economic	5,94	6,5	12,02±0,12	0,01
"Diesel Turbo"	3,54	4,00	7,6±0,15	0,02

Table 5

Estimation of the systematic error in the atomic-absorption determination of Cadmium and Copper by varying the sample mass (n = 5; P = 0.95).

M of the sample, g	C Cd, mg/l	S <sub>r</sub>
0,2	0,2517	0,02
0,3	0,2769	0,02
0,4	0,3072	0,02

M of the sample, g	C Cu, mg/l	S <sub>r</sub>
0,2	1,42 ± 0,03	0,02
0,3	1,45 ± 0,03	0,02
0,4	1,4 ± 0,03	0,02

Table 6

Results of atomic-emission with inductive connected plasma determination of Cadmium and Copper in oil products (n = 5; P = 0.95).

	C Cd, mg/kg	S <sub>r</sub>
Lukoil «Moto 2T»	0,278 0,02	0.01
THK «Motor 20w-50»	0,289 0,01	0.01
WAMP	0,36 0,01	0.02
Okko «Exol diesel city 1540»	0,37 0,01	0.02
Okko «Exol 20w-50 economic	0,22 0,01	0.01

	C Cu, mg/kg	S <sub>r</sub>
Lukoil «Moto 2T»	4,54 0,04	0.02
Okko «Exol diesel city 1540»	4,359 0,04	0.01
Okko «Exol 20w-50 economic	5,974 0,06	0.02

**Impact Factor:**

ISRA (India) = 1.344	SIS (USA) = 0.912	ICV (Poland) = 6.630
ISI (Dubai, UAE) = 0.829	PIHII (Russia) = 0.156	PIF (India) = 1.940
GIF (Australia) = 0.564	ESJI (KZ) = 4.102	IBI (India) = 4.260
JIF = 1.500	SJIF (Morocco) = 2.031	

**Table 7**

Coherence of Cadmium and Copper determination results by the methods of AAS and AES-ICP in oil products stabilized by ultrasound treatment, according to Fisher and Student criteria at n = 5; P = 0.95.

	F	t <sub>1/2</sub>
Lukoil «Moto 2T»	1,75	1.59
THK «Motor 20w-50»	2,23	1.78
WAMP	2,54	2.15
Okko «Exol diesel city 1540»	1,01	1.79
Okko «Exol 20w-50 economic	1,29	2.55

**Table 8**

Estimation of the detection limit of Cadmium and Copper in oil products.

№	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	A <sub>cp</sub>	S <sub>0</sub>	C <sub>min</sub> Cd
1	1	2	0	1	0	2	1	0.03	0.006
2	1	1	2	2	2	0	1.16	C <sub>lit</sub> =0,007	
3	2	1	2	1	1	0	1.16		
4	1	3	0	3	0	2	1		
5	3	1	2	5	2	1	1.5		
6	2	1	1	2	0	2	1		
7	1	2	0	5	0	1	1.16		
8	1	2	3	2	2	1	1.5		
9	2	1	2	4	1	2	1		
10	3	2	3	5	0	1	1.16		
11	1	1	2	3	1	2	11		
12	1	3	0	2	1	2	1.5		
13	3	2	3	6	2	1	1		
14	2	0	1	5	0	2	1.16		
15	3	1	1	3	0	2	1		
16	2	1	1	3	1	3	1		
17	4	2	2	1	1	0	1.16		
18	2	1	2	2	1	2	1.5		
19	1	3	0	1	2	0	1.5		
20	2	1	1	3	2	0	1.5		

№	A <sub>1</sub>	A <sub>2</sub>	A <sub>3</sub>	A <sub>4</sub>	A <sub>5</sub>	A <sub>6</sub>	A <sub>cp</sub>	S <sub>0</sub>	C <sub>min</sub> Cu
1	3	4	3	4	1	3	2.8	0.06	0.001
2	3	4	3	4	5	3	3.7	C <sub>lit</sub> =0,002	
3	2	3	4	3	1	2	2.5		
4	3	5	4	3	4	1	3.3		
5	3	2	1	3	4	3	2.7		
6	4	1	2	3	2	3	2.3		

**Impact Factor:**

<b>ISRA (India)</b> = <b>1.344</b>	<b>SIS (USA)</b> = <b>0.912</b>	<b>ICV (Poland)</b> = <b>6.630</b>
<b>ISI (Dubai, UAE)</b> = <b>0.829</b>	<b>PIHHI (Russia)</b> = <b>0.207</b>	<b>PIF (India)</b> = <b>1.940</b>
<b>GIF (Australia)</b> = <b>0.564</b>	<b>ESJI (KZ)</b> = <b>4.102</b>	<b>IBI (India)</b> = <b>4.260</b>
<b>JIF</b> = <b>1.500</b>	<b>SJIF (Morocco)</b> = <b>2.031</b>	

7	2	3	1	5	3	4	3.0		
8	3	2	5	4	5	4	2.7		
9	4	3	4	3	1	2	2.8		
10	4	3	4	5	4	2	3.8		
11	3	4	3	4	4	3	3.5		
12	5	3	5	4	5	4	4.3		
13	4	3	5	4	5	4	4.2		
14	2	3	5	4	2	1	3.7		
15	4	1	3	2	1	4	2.2		
16	3	4	3	4	3	4	3.5		
17	4	6	4	3	5	3	4.3		
18	4	3	4	5	4	5	4.2		
19	4	2	4	2	3	4	3.0		
20	4	2	3	2	3	6	2.8		

**References:**

1. Soura R.M. (2004) Analytical sciences, V.20, pp.351-355.
2. Rastova N.V. (1992) Journ. Anal. Chem, V.47, pp.4-14.
3. Yurchenko O.I. (2010) Visnyk Kharkivskogo university, V. 895, pp. 3-9 .
4. Kolesnikova L.S. (1976) Izvestia Tomskogo polytechnicnogo instituta, V.275,pp.1-3.
5. Kolodyajny A. (2006) Metody i objekty himicheskogo analiza, V.57, pp. 90-104.
6. Saint Pierre T.D., Dias L.F. (2004) Spectracing Acts, V.59,pp.551-558.
7. Duych C., Miekely N., C.L.P da Silereera, Syatma P.T (2002) Spectrochim act, V.51, pp.1979-1990.
8. Kahrn K., Strubingen A., Chirines J.R., Mostraser A. (2003) Spectrochim, V.58, pp.397-413.
9. Bings N.M., (2002) Spectrochim, V.17, pp. 759-765.
10. Wodimu T., Goesser W., Irgolic K.J., (2000) Spectrochim, V.157, pp. 456-467.

