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Investigation of metal β-diketonates as parent materials for reference samples

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Stability of synthesized lead, cadmium and chromium (III) β-diketonates and mercury (I) dimedonate in solid state and in diluted solutions was investigated by titrimetry and inductively coupled plasma optical emission spectrometry. It was shown, that the solid samples are stable during 5 years and the solutions keep the concentration for 4 months. Metal acetylacetonates are recommended as parent substances for manufacturing of reference samples used for calibration of analytical instruments and accuracy control.

Исследована устойчивость синтезированных β-дикетонатов свинца, кадмия, хрома (III) и димедоната ртути (I) в твердом состоянии и в разбавленных растворах методами титриметрического анализа и атомно-эмиссионной спектрометрии с индукционной плазмой. Показано, что твердые образцы устойчивы в течение 5 лет, а разбавленные растворы сохраняют свою концентрацию 4 месяца. Ацетилацетонаты металлов рекомендованы в качестве исходных веществ для изготовления стандартных образцов состава при градуировке аналитических приборов и контроля правильности результатов анализа.

Nowadays, a variety of physicochemical and physical methods of analysis are widely used in ecological monitoring and for determination of microquantities of metals in foodstuffs and potable water [1]. Application of these methods requires availability of appropriate reference samples (RS) [2, 3]. The most interesting are samples suitable for calibration and accuracy control of different methods of analysis. Development of multifunctional samples is one of actual problems of modern analytical chemistry. Organic metal complexes are one of perspective classes of parent materials for reference samples preparing. Metal β-diketonates are very interesting for these purposes [4–11]. They are thermally stable, soluble enough in water and organic solvents. This is especially important for determination of metals in natural and industrial objects where they are frequently present as complexes with organic ligands [12–17].

Lead, cadmium and chromium acetylacetonates and mercury (I) dimedonate were synthesized and purified. Chromium (III) acetylacetonate was synthesized according to the following reaction:

$$Cr^{3+} + 3C_5H_8O_2 \longleftrightarrow Cr(C_5H_8O_2)_3\downarrow + 3H^+ \quad (1)$$

A known amount of chromium (III) sulphate was dissolved in 200 ml of distilled water, then acetylacetone and 60 g of carbamide were added. Reagents were heated for 4 h at 80–90°C. Purification of chromium (III) acetylacetonate was performed by its recrystallization in ethanol solution. The violet acicular crystals with the melting point of 214°C were obtained.

Lead acetylacetonate (m.p. is 206°C) was obtained by the action of a water solution

of lead acetate on an ethanol solution of acetylacetone. Reagents were heated on a bain-marie for 2 h at 80–90°C, then distilled water was added and precipitated crystals were filtered out.

Cadmium acetylacetonate (white powder, m.p. is 187°C) was synthesized in ammonia-acetate buffer media at pH 10 as given in the following consecutive reaction:

$$NaOH + C_5H_8O_2 \longleftrightarrow C_5H_7O_2Na + H_2O; \quad (2)$$

$$2C_5H_7O_2Na + Cd(NO_3)_2 \longleftrightarrow \quad (3)$$
$$\longleftrightarrow Cd(C_5H_7O_2)_2 + 2NaNO_3.$$

Mercury (I) dimedonate was prepared by the reaction of dimedonate ethanol solution and mercury (I) nitrate solution at pH 1.6. After sedimentation during 24 h the residue was filtered out and treated with ethanol in order to remove excess of dimedone. The product was dried for 1 h at 205–210°C. Thus-prepared and purified mercury (I) dimedonate was a light-gray substance with the melting point 275°C.

The contents of β-diketonates in the synthesized substances were determined in FGUP D.I.Mendeleev VNII (St. Petersburg) using "Kaskad-04" cryometer [18]. It was found that abundance of β-diketonates in all samples was more then 99.99 %. These results were verified by titrimetric determinations of metals content in the synthesized substances. Sodium thiosulfate was used as a titrant for mercury determination [19] as well as complexone (III) was used for lead and cadmium determination [20].

The solubility of β-diketonates in water at (25.0±0.1)°C was as follows: 0.46±0.03 g l^{-1} for cadmium acetylacetonate, 0.15±0.04 g l^{-1} for mercury (I) dimedonate, 1.54±0.02 g l^{-1} for chromium (III) acetylacetonate and 2.08±0.03 g l^{-1} for lead acetylacetonate.

A number of solutions contained 0.10 mg l^{-1} of lead, 0.02 mg l^{-1} of cadmium, 0.05 mg l^{-1} of chromium, 0.06 and 0.60mg l^{-1} of mercury were prepared by dissolving of exact amounts of lead, cadmium and chromium acetylacetonates and mercury (I) dimedonate in water. Stability in time of these solutions was studied using a sequential inductively coupled plasma atomic-emission spectrometer TRACE SCAN Advantage (Thermo Jarrell Ash, USA). It has axially viewed configuration, radio frequency generator crystal-controlled at 27.12 MHz with automatic tuning, purged and thermostated 0.5 meter Ebert monochromator, solar blind and infrared PMT detectors, composite grating ruled at both 2400 and 1200 lines/mm. All operations with ICP-spectrometer were controlled by the personal computer. Solution uptake rate was 1.85 ml·min^{-1}; nebulizer argon pressure was 30 psi*; radio frequency generator was 1150 W. Meinhard glass nebulizer designed for determination of low concentration of elements was used. Microstatistics was applied for data processing [21].

Table 1. Results of stability test obtained for chromium (III) acetylacetonate by tit-rimetric analysis (95 % confidence level; $n = 10$)

Date	Content of chromium in chromium (III) acetylacetonate, %	S^2
Samples stored in sealed off ampoules		
June 2000	14.9±0.1	$2.0 \cdot 10^{-2}$
January 2002	14.92±0.09	$1.6 \cdot 10^{-2}$
March 2004	14.91±0.08	$1.3 \cdot 10^{-2}$
Samples stored in laboratory glassware with ground stopper		
June 2000	14.82±0.09	$1.6 \cdot 10^{-2}$
January 2002	15.0±0.1	$2.0 \cdot 10^{-2}$
March 2004	14.96±0.09	$1.6 \cdot 10^{-2}$
$g_{max} = 0.1980$; $\frac{\overline{S^2}}{S_0^2} = 1.9$		

In order to study stability of the synthesized β-diketonates in solid state, the results of the main component (metal) determination in the samples stored during 5 years in sealed off ampoules and in the laboratory glassware with ground stopper were compared. Results obtained for chromium (III) acetylacetonate are given in Table 1.

Hypothesis checking on homogeneity of variances was performed applying Kohran's g-test at 0.05 significance level:

$$g_{\max} = \frac{S_{i\,\max}^2}{\sum_{i=1}^{m} S_i^2} \le g_{0.05}(m = 6, f_i = 9) = 0.3682,$$

where m is the number of series of experiments; $f_i = n - 1$ is the number of degrees of freedom for each series of experiments.

*Unit of USA standard used in spectrometer software. 1 psi is equal to 0.0014 kg·m^{-2}.

Table 2. Stability test results obtained by ICP-AES on diluted solutions prepared from the synthesized metal β-diketonates (P = 0.95; n = 10)

Element	Added, mg l^{-1}	Found, mg l^{-1}				
		November 2003	December 2003	January 2004	February 2004	March 2004
Pb	0.10	0.11±0.01	0.100±0.009	0.098±0.008	0.099±0.008	0.099±0.007
Hg	0.06	0.059±0.006	0.058±0.007	0.061±0.006	0.058±0.006	0.060±0.004
	0.60	0.60±0.02	0.59±0.02	0.59±0.03	0.60±0.02	0.61±0.01
Cd	0.02	0.019±0.003	0.018±0.003	0.019±0.004	0.019±0.003	0.018±0.002
Cr	0.05	0.051±0.005	0.048±0.005	0.049±0.005	0.049±0.006	0.048±0.008

Table 3. Results of statistical data treatment listed in Table 2 (P = 0.95; f_i = 9, f = 45)

Element	Initial concentration of element in solution, mg l^{-1}	S^2					g_{max}	$\frac{\overline{S^2}}{S_0^2}$
		November 2003	December 2003	January 2004	February 2004	March 2004		
Pb	0.10	$1.9 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	0.2714	1.43
Hg	0.06	$7 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$7 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	0.2941	0.23
	0.60	$7.9 \cdot 10^{-4}$	$7.9 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	$7.9 \cdot 10^{-4}$	$1.9 \cdot 10^{-4}$	0.2872	1.15
Cd	0.02	$2 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	0.3000	1.35
Cr	0.05	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$7 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	0.3714	0.03

F-test was applied to check hypotheses about the difference between mean values of concentration of metals measured during test period:

$$\frac{\overline{S^2}}{S_0^2} \le F_{0.95}(f_i = 9, f = 54) = 2.3,$$

where

$$S_0^2 = \sum_{i=1}^{m} \frac{f_i \cdot S_i^2}{f}, \quad f = \sum_{i=1}^{m} f_i \quad ,$$

$$\overline{S^2} = \frac{1}{m-1}\left[\sum_{i=1}^{m} n_i\left(\overline{x_i} - \overline{\overline{x}}\right)^2\right],$$

$\overline{\overline{x}}$ — weighted average value at given m; f — total number of degrees of freedom. One can see that variances are homogeneous and mean values of chromium (III) content in the investigated samples show a nonsignificant difference. The similar results were obtained for the rest of metal β-diketonates. It means that these substances can be stored during a long time without change of its composition not only in sealed off ampoules, but in laboratory glassware as well.

Results of stability test and statistical data treatment obtained on diluted solutions prepared from the synthesized metal β-diketonates are shown in Tables 2 and 3. The data presented in Tables 2 and 3 demonstrate that the diluted solutions of lead, cadmium and chromium (III) acetylacetonates and mercury (I) dimedonate are stable at least within four months; variances are homogeneous for each analysed element and mean values differ insignificantly.

Results of stability test of investigated substances in solid state and in diluted solutions indicate that metal β-diketonates meet the requirements for reference samples [22]. These substances can be recommended for use in chemical analysis practice as parent materials for reference samples. The standard samples of NPO "Vympel" (Moscow), NPO "Monolit" (Kharkiv), NPO "Electrotyazhmash" (Kharkiv) have been produced using lead, cadmium and chromium (III) acetylacetonates and mercury (I) dimedonate. They are applied for the calibration of analytical instruments as well as for the accuracy control.

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Дослідження β-дикетонатів металів як вихідних речовин для створення стандартних зразків складу

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Досліджено стійкість синтезованих β-дикетонатів свинцю, кадмію, хрому (III) та димедонату ртуті (I) у твердому стані та у розведених розчинах методами титриметричного аналізу та атомно-емісійної спектрометрії з індукційною плазмою. Показано, що тверді зразки є стійкими на протязі 5 років, а розведені розчини зберігають концентрацію 4 місяці. Ацетилацетонати металів рекомендовано як вихідні речовини для виготовлення стандартних зразків складу при градуюванні аналітичних приладів та проведенні контролю правильності результатів аналізу.