Coulometric determination of chromium, molybdenum, and tungsten by generated lead(II)

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The conditions of electrochemical generation of Pb(II) in the media of KNO_3, NH_4NO_3 or NH_4ClO_4 and in the media with pH adjusted within the range 7.7—8.1 were studied for the use of precipitation reactions of Pb(II) with CrO_4^{2-}, MoO_4^{2-}, and WO_4^{2-} in the volumetric analysis.

The developed procedures of determination were tested with respect to standard solutions of K_2CrO_4, Na_2MoO_4, and Na_2WO_4.

The results of coulometric determination of Mo and W in ferromolybdenum and ferrotungsten obtained under proposed conditions were confronted with the results obtained by other methods or by the use of standard ferroalloys.

В работе изучаются условия электрохимического генерирования Pb(II) в средах KNO_3, NH_4NO_3 и NH_4ClO_4, а также в средах с измененным pH в интервале 7,7—8,1 с целью использования реакций осаждения Pb(II) с CrO_4^{2-}, MoO_4^{2-} и WO_4^{2-} в весовом анализе.

Разработанные методы определения были опробованы на стандартных растворах K_2CrO_4, Na_2MoO_4 и Na_2WO_4.

Результаты кулонометрического определения Mo и W в ферромолибдене и ферровольфраме при предложенных условиях сравниваются с результатами других методов анализа или проверяются с помощью стандартных ферросплавов.

This study has arisen from the need for a rapid and reliable method of determination of Cr, Mo, and W in ferroalloys without the use of toxic mercury salts.

In practice [1], the gravimetric determination of MoO_4^{2-} and WO_4^{2-} [1—3], classical titrimetric determination of MoO_4^{2-} [4] or redox determination of $Cr(VI) \rightleftarrows Cr(III)$ [4] are still in use. The usual determination of W is based on the precipitation reaction of WO_4^{2-} with Hg_2^{2+} [2, 3]. The separated precipitate Hg_2WO_4 is annealed to give WO_3. This method requires a great consumption of mercury salt which is more and more expensive without regard to slowness of determination and contamination of laboratory with mercury vapour. Besides the gravimetric determination in the form of $PbMoO_4$, molybdenum is frequently

determined by reverse chelatometric titration after preceding filtration of $PbMnO_4$ [4, 5]. As for the determination of Cr in ferrochromium, the titration with Fe(II) is recommended [1, 6]. However, this titration is not very selective and the result is dependent on quantitative removal of a great excess of O_2^{2-} and necessitates a frequent ascertainment of rapidly varying titre of the volumetric solution.

The authors of paper [7] used the precipitation of CrO_4^{2-} with volumetric solution of Pb(II) salt in the medium of 20 % ethanol with pH 5.7 and amperometric indication exhibiting a relative standard deviation of 1.2 %.

As for coulometric studies, we must mention communication [8] describing the generation of Pb(II) from a lead anode in the medium of KNO_3 with pH 6—7 and papers [9—11] dealing with the generation of Pb(II) from an amalgam anode.

Experimental

Instruments and equipment

The pH measurements were carried out with a pH-meter PHM 22r equipped with a pair of electrodes, *i.e.* G 202 B and K 100 (Radiometer, Copenhagen).

The coulometric measurements were performed with a coulometer OH 404 (Radelkis, Budapest). Lead amalgam (2 %) prepared by dissolving fine lead shavings in mercury (purity for polarography) served as a generating electrode. The electrode of about 3.5 cm^2 surface was placed in a frame of poly(vinyl chloride). The lead electrode of 4 cm^2 surface was prepared by casting lead (of 99.999 % purity) (Matthey—Johnson, England) into a porcelain form of convenient shape. A Pt cathode of 5 cm^2 surface OH 935 delivered as accessories to coulometer OH 404 was used as an auxiliary electrode.

A dropping mercury cathode in amperometric connection was employed as a polarizable indicator electrode. This cathode consisted of spectral carbon and was paraffined *in vacuo* before use [12]. Its effective area was about 20 mm^2 and a mercury drop of about 8 mm^2 was placed in a glass bed with Pt contact. All electrodes were polarized at -800 mV against SCE. A recorder of polarograph OH 102 (Radelkis, Budapest) connected as microampere-meter was used for recording the indicating curves. The indicating signal transformed in indicating unit OH 404 in square-wave voltage was carried to the recorder through a galvanic separator (of original construction [13]) comprising a transformer-coupled synchronous detector.

All measurements were carried out in nitrogen atmosphere under constant stirring.

Chemicals and solutions

All chemicals were at least anal. grade reagents (Lachema, Brno) and were recrystallized and dried before use. The standard solutions of K_2CrO_4, Na_2MoO_4, and Na_2WO_4 of

2×10^{-2} mol dm^{-3} concentration were prepared from those chemicals. The concentration of these solutions was checked plumbometrically by using potentiometric indication and a lead ion-selective electrode Crytur 82-17 (Monocrystals, Turnov). The standard solutions of ferroalloys were obtained from Orava Ferroalloy Works in Istebné where these preparations are used as standards. The contents of main components of these preparations were verified by several methods. The solution of triethanolamine (TEA) (Loba-Chemie, Austria) was used in 1 % concentration.

Working procedure

As for the work with the solutions of K_2CrO_4, Na_2MoO_4, and Na_2WO_4 we used media which contained additions of KNO_3, NH_4NO_3, and NH_4ClO_4 in 1 mol dm^{-3} concentration and a small addition of TEA (*ca.* 1 ml of 1 % TEA) for adjustment of pH. These media were satisfactory for the potentiometric as well as coulometric titrations.

For processing ferroalloys, we developed and optimized the following procedure: 2.5 g of fine powder of a certain ferroalloy is mixed in a nickel crucible with 15 g of Na_2O_2 and 10 g of Na_2CO_3 and allowed to melt (for about 30 min). The melt is extracted and boiled for about 3 min. After cooling the mixture is filtered through a white-band filter and diluted to the volume of 500 ml. We take 0.5—2.0 ml of this solution for the titration itself. We sensibly acidify this portion with an addition of about 1—2 ml of concentrated HNO_3 or $HClO_4$ and remove the arising CO_2 by 1 min boiling. The surplus of acids is neutralized with concentrated solution of NH_4OH the excess of which is removed by boiling. In the medium of NH_4NO_3 or NH_4ClO_4 thus formed we immediately determine Mo and Cr after preceding dilution to a volume of about 40 ml. If we want to determine tungsten, we add about 1 ml of 1 % solution of TEA into this solution in order to attain pH 7.7—8.1.

We thoroughly remove oxygen from the solutions by bubbling with nitrogen for 10 min. We insert the lead generation electrode, platinum cathode separated with a salt bridge filled with the corresponding 1 M solution of electrolyte (KNO_3, NH_4NO_3, NH_4ClO_4), and the pair of indicator electrodes into the electrolytic cell.

Results and discussion

The optimum method of volumetric determination of Cr, Mo, and W was selected on the basis of described methods [14, 15]. From the view-point of plant operation, we consider the redox determinations based on preceding reduction of Cr(VI), Mo(VI), and W(VI) to the degree of oxidation equal to 2—5 by means of different reduction agents or coulometric reduction at constant potential [16] to be intricate. Precipitation determinations with generated Ag(I) are also not convenient because of a rather high solubility of silver products ($[Ag_2X] \approx 3 \times 10^{-5}$ mol dm^{-3}) as well as the results published in paper [17]. The authors of this paper revealed a complicated mechanism catalyzed by silver salts giving rise to mixed products.

The conditions of quantitative generation of Pb(II) and precipitation were verified by us with standard solutions of K_2CrO_4, Na_2MoO_4, and Na_2WO_4 in the media of KNO_3, NH_4NO_3, and NH_4ClO_4 as well as in the media with adjusted pH (urotropine, acetate, and triethanolamine buffer solution). While even weak-acid medium up to pH 4 is suited to precipitation and determination of Cr and Mo, the determination of W necessitates to adjust the pH of solution to the value varying in the interval 7.7—8.1 and to use 0.5—2.0 ml of a 2×10^{-2} M solution of W compound in total volume of 40 ml. The influence of temperature up to 55 °C and addition of ethanol was verified. The investigated anions are quantitatively precipitated in the temperature interval between 20 and 50 °C and no addition of organic solvent is necessary in the above-mentioned media and dilutions (the solubility of Pb products in aqueous solutions is about 10^{-6} mol dm^{-3}). On the contrary, an increased temperature has negative influence at higher dilutions. For coulometric generation we used currents of 5—25 mA (current density was 1—6 mA cm^{-2}). If W is determined with lower generating currents, the indicating curve does not exhibit such a rapid change in current after reaching the equivalence point owing to higher solubility of $PbWO_4$ as it does in the presence of Cr and Mo. For this reason, the determination of W was limited by a minimum current of 10—12 mA. If the urotropine buffer solution or sodium acetate solution, in particular, in higher concentration was used, the results were laden with a systematic positive error because of interactions of Pb(II) with the medium.

The determination of W necessitates to hold pH exactly in the interval 7.7—8.1 because the formation of $PbWO_4$ proceeds slowly in the media with pH < 7 and, on the other hand, the competing reaction of Pb^{2+} with OH$^-$ manifests itself in the media with pH > 8.5.

Provided we used the generating electrode made of 2 % lead amalgam for generation of Pb(II) according to [9, 10] at current densities of 1—10 mA cm^{-2}, we obtained 100 % current efficiency in all above-mentioned media. In a similar way, we obtained satisfactory results with a lead electrode and, for this reason, we gave up using amalgam in further measurements.

As regards indication, we verified different kinds of electrochemical investigation of the course of determination. The biamperometric indication with a pair of polarized electrodes of Pt, Pb or Hg does not improve or make more distinct the indication as compared with amperometric indication. The potentiometric indication by means of an ion-selective lead electrode is profitable because it does not require to remove oxygen from the solution. But this indication was not reliable for some samples of ferrotungsten because a sensible response due to other present components was observed so that the potential change in the equivalence point of these samples was considerably decreased with respect to the potential change of pure solutions of Na_2WO_4. The indication with one polarized electrode (− 800 mV against SCE) represented by dropping mercury electrode, stationary mercury

Table 1

Results of the determination of Cr, Mo, and W by generated Pb(II) in standard solutions

Conditions I/mA	KNO$_3$ 5			NH$_4$ClO$_4$ 10			NH$_4$NO$_3$ 5			NH$_4$NO$_3$ 10			NH$_4$NO$_3$ + TEA (pH 8) 10			15		
Given	$\bar{X}$	s_r	e	$\bar{X}$	s_r	e	$\bar{X}$	s_r	e	$\bar{X}$	s_r	e	$\bar{X}$	s_r	e	$\bar{X}$	s_r	e
m/mg	mg	%	%	mg	%	%	mg	%	%	mg	%	%	mg	%	%	mg	%	%
Cr																		
0.520				0.527	0.9	1.3												
1.040	1.070	2.5	2.8	1.028	1.0	1.2				1.030	2.0	1.0						
1.560	1.531	1.7	−1.9				1.540	0.8	−1.3	1.600	1.0	2.6				1.601	3.1	2.6
Mo																		
0.960							0.954	0.6	−0.6									
1.919				1.891	1.2	−1.5	1.932	1.2	0.7				1.890	2.1	−1.5			
2.879							2.891	0.9	0.4	2.904	2.0	0.9.	2.822	2.4	−2.0	2.961	3.0	2.8
W																		
1.839													1.900	4.0	3.8	1.781	4.1	−3.2
3.677													3.502	2.9	−4.7	3.500	4.0	−4.9
5.516																5.40	3.0	2.2

$\bar{X}$ — Arithmetic mean of four determinations, s_r — relative standard deviation of the arithmetic mean, e — relative error of the mean.

electrode or carbon electrode necessitates removing of oxygen but gives satisfactory results. Since the indicating curves obtained with the mentioned electrodes were analogous, we chose the simplest possibility, *i.e.* the carbon electrode.

The results of the determination of Cr, Mo, and W in standard solutions (Table 1) as well as in ferroalloys (Table 2) show that the proposed method

Table 2

Results of the determination of Mo and W by generated Pb(II) in standard solutions of ferroalloys

Given m/mg	n	NH$_4$NO$_3$ $I = 8$ mA			NH$_4$NO$_3$ + TEA (pH 8) $I = 12$ mA		
		$\dfrac{\bar{X}}{\text{mg}}$	$\dfrac{s_r}{\%}$	$\dfrac{e}{\%}$	$\dfrac{\bar{X}}{\text{mg}}$	$\dfrac{s_r}{\%}$	$\dfrac{e}{\%}$
Mo							
3.02	9	3.01	1.5	−0.33			
2.47	6	2.51	2.0	1.6	2.44	0.9	−1.2
W							
4.59	7				4.68	2.1	2.0
8.20	7				7.94	4.1	−3.2
6.99	8				6.90	3.4	−1.2

n — Number of determinations, $\bar{X}$ — arithmetic mean of the results of determination (in mg).

represents a rapid and reliable determination. Provided we use milligram amounts of substance, the parameters characterizing the correctness (e) and precision (s_r) of determination in the medium of NH$_4$NO$_3$ do not exceed 3 % for Cr and Mo and 5 % for W (in the medium with an addition of TEA and pH 8).

The method does not require any extraordinary treatment of sample. This precipitating titration applied to alloys with two major elements is selective, owing to which no attention is to be paid to separation of iron, *etc.*

From the economical view-point the method is suited to industrial control. It enables us to eliminate entirely the use of mercury and 2 mg of lead are sufficient for one determination.

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