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A SIMPLE TITRIMETRIC METHOD FOR THE DETERMINATION OF OSMIUM(IV) IN CHLORIDE STANDARD SOLUTIONS AND INTERMETALLIC ALLOYS

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A new method for the standardization of osmium(IV) from chloride aqueous solutions by means of iodometric titration with visual (using starch as indicator) and potentiometric indicating of titration end point has been elaborated. This simple and rapid method is based on Os(IV) interaction with the excess of iodide-ions in sulphuric acid media and on the titration of liberated iodine with the standardized solution of sodium thiosulfate. The method was approved during the determination of milligram quantities of osmium(IV) in standard solution and intermetallic alloys. Relative standard deviations (RSDs) did not exceed 1.5 %.

Keywords: *osmium(IV) hexachloride, standardization, titrimetry, potentiometry, intermetallic alloy.*

Chloride complexes of platinum group elements (PGEs) are of considerable significance in the analytical and preparative chemistry of these elements. Particularly, complex chlorides of osmium(IV) are especially important for the analytical chemistry of osmium, since that very compounds are used for the preparation of standard solutions, initial for osmium determination by means of instrumental methods and for the study of osmium complexation [1, 2]. It is a known fact that in aqueous solutions osmium may exist in various anionic forms and may readily change its oxidation state depending on the acidity of the media, the nature and concentration of the metal. According to the literary data [1, 2] and to our analytical practice, when Os(IV) solutions in 1...2 mol L^{-1} HCl are kept for a long time, a number of additional processes may take place, particularly the processes of hydrolysis, aquatation or disproportionation, inherent for osmium compounds. Therefore, in Os(IV) chloride aqueous solutions particles like $Os(H_2O)Cl_5^-$, $Os(H_2O)_2Cl_4^0$ coexist next to predominant form of osmium $OsCl_6^{2-}$. Moreover, if osmium(IV) solutions from time to time are under the influence of scattered sun light, one can observe the formation of black coloured precipitate of hydrated osmium(IV) oxide $OsO_2{\cdot}2H_2O$ [3, 4]. These factors may result in the change of concentration after some period of storage in osmium(IV) hexachloride standard solutions, even purchased from reputable chemical manufacturers. At the same time, it is necessary to have osmium(IV) stock solutions with accurate concentration for the effective routine determination of osmium by means of any instrumental technique as well as for correct carrying out of scientific investigations of osmium compounds. That is why the standardization, i.e. accurately checking or confirming the concentration of osmium(IV) standard chloride solutions, is an essential part of osmium researches and it is necessary to possess a reliable technique for the standardization of such solutions. Sometimes the standard solutions of osmium(IV) hexachloride may not be

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purchased, taking into consideration high prices of specimens, but prepared from other osmium compounds, e.g. from OsO_4. In that case the procedure of standardization is especially required, since the transformation of OsO_4 into $OsCl_6^{2-}$ can be attended by osmium losses caused by the volatility of tetraoxide.

Titrimetry is the main techniques for the standardization of PGEs solutions, including Os [1, 5, 6]. The number of titrimetric methods for osmium determination is not large and all of them are based on redox reactions, since these reactions run with sufficient rate, if the conditions and reagents are correctly selected. Titrimetric methods of osmium determination are not selective and are useful for the analyses of standard solutions and the solutions, obtained after osmium separation from other PGEs, as well as for relatively simple samples of few components. The end point of titration can be rather accurately determined potentiometrically, but there are very few methods with the visual indication of the end point.

Most titrimetric methods are proposed for the determination of Os(VIII), and there are only few methods for Os(IV) [1, 7, 8]. Usually these methods are suggested for the determination of osmium, obtained after OsO_4 passing through the reductor with metallic bismuth [1]. The reduced form of osmium (Os(IV) according to [9]) is oxidized to osmium(VI) with a titrant, e.g. NH_4VO_3, an excess of which is titrated by the standardized solution of $FeSO_4$ [1, 8, 9]. However, vanadatometric titration can not be utilized for the standardization of Os(IV) chloride solutions because of few reasons. First of all, it has been established that after passing of OsO_4 sulphuric acidic solutions through the bismuth reductor, osmium is reduced to Os(III), but not to Os(IV) [10]. Os(III) is stable in air, it is oxidized to osmium(VI) in the media of 4...8 mol L^{-1} sulphuric acid with NH_4VO_3 (visual indication of the end point) or to OsO_4 with the stronger oxidants, e.g. $KMnO_4$, $Ce(SO_4)_2$ (a potentiometric determination of the end point) [1]. In addition, this technique was elaborated for osmium evaluation from sulphuric acid solutions, but not for hydrochloric acid (apparently, the nature of initial compound of Os is of consequence for the titration) and it is difficult to transform osmium(IV) chloride complexes into sulphate complexes, because they are very inactive. The matter is that $OsCl_6^{2-}$ is the most kinetically inert complex among all hexachloride complexes of PGEs [1]. To convert initial osmium(IV) hexachloride into sulphate it must be heated in the concentrated sulphuric acid at 170°C during 4...6 h [7, 11].

For the titrimetric determination of Os(IV) from acidic solutions $CrSO_4$ is proposed as the reducing agent [1, 8, 12]. But this method is very complicated, because a special apparatus is necessary to store and work with $CrSO_4$ solutions in air free media. The permanganatometric method is suggested for the determination of Os(IV) in alkaline media [1, 13]. Os(IV), which in the hydrochloric acid media exists in the H_2OsCl_6 form, by means of alkali is transferred into the suspension OsO_2, then it is dissolved in the presence of H_6TeO_2 and potentiometrically titrated with the solution of $KMnO_4$. Principal drawback of the method is the utilization of rare and highly toxic telluric acid [14]. The drawback of a recently elaborated titrimetric technique for the standardization of osmium(IV) solutions [15, 16] is the need of a reagent that is not commercially available.

Since we have carried out the investigations of osmium(IV) interaction with different azo and triphenylmethane dyes to elaborate new spectrophotometric methods for osmium determination [17–22], we faced the problem that none of known methods was suitable for standardization of Os(IV) stock solutions. Therefore, it has necessitated the development of a simple, available and effective titrimetric method for the standardization of osmium(IV) chloride solutions, and it was a purpose of our study.

For the determination of Os(IV) from chloride aqueous solutions we have adapted the iodometric method of the standardization of Ru(IV) chloride solutions [1, 23, 24]. The main point of this method for ruthenium determination consists of the reduction of Ru(IV) hydroxopentachlorides with KI in the media of 2 mol L^{-1} HCl with following titration of isolated I_2 by means of $Na_2S_2O_3$ (a visual indication of titration end point with starch), since the amount of I_2 is equal to Ru(IV) content in the sample:

$$2Ru^{4+} + 2I^{-} \rightarrow 2Ru^{3+} + I_2, \quad I_2 + 2S_2O_3^{2-} \rightarrow 2I^{-} + S_4O_6^{2-}.$$

The fact that standard redox potentials of ruthenium(IV) and osmium(IV) chloride complexes in HCl solutions are of similar values was the principal basis for the elaboration of the analogous method for Os(IV): $E^0_{Ru(IV)/Ru(III)} = E^0(RuOHCl_5^{2-}/RuH_2OCl_5^{2-}) = 0.96$ V and $E^0_{Os(IV)/Os(III)} = E^0(OsCl_6^{2-}/OsCl_6^{3-}) = 0.85$ V [1, 7, 25] (as the matter of fact, we do not compare redox potential $E^0(OsCl_6^{2-}/OsCl_6^{3-})$ with $E^0(RuCl_6^{2-}/RuCl_6^{3-}) = 1.3$ V, since Ru(IV) does not exist in the form of hexachloride, but in the form of $RuH_2OCl_5^{2-}$, when the concentration of HCI is less than 6 mol L^{-1} [7]). It should be noted, that there are examples for PGEs, when their redox potentials are not in accordance with the character of PGE complex interaction with oxidizing or reducing agent. That is why in the analytical chemistry of PGEs it is always necessary to take into account not only the values of redox potentials, but also the experimental observations, when one must choose appropriate oxidant or reductant [1].

Reagents and devices. All aqueous solutions, utilized in the research, have been prepared,using a distilled water. All chemicals were of analytical grade.

The stock solution of Os(IV) (H_2OsCl_6) was prepared by dissolving the exact mass of OsO_4 from the hermetically sealed glass ampoule (produced by the Corp. Aurat, Russia) in the concentrated HCl following the modified method [26]. The obtained osmium solution has been kept during one month, because according to [27], OsO_4 is rapidly reduced in the concentrated HCl under heating and slowly reduced in hydrochloric acid medium at room temperature. We wanted to avoid the additional reduction of OsO_4 with an alcohol as well as to exclude the heating procedure, thus preventing the possible losses of OsO_4.

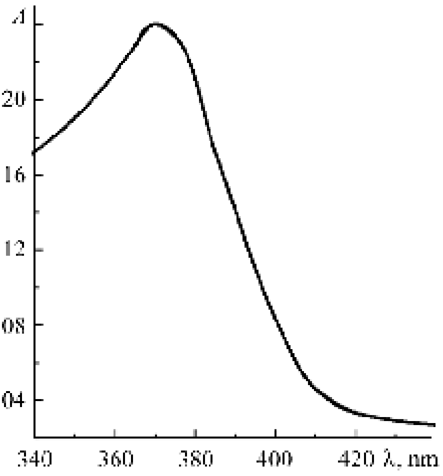

Fig. 1. Absorption spectrum of $OsCl_6^{2-}$ solution; $C_{Os(IV)} = 3.8 \cdot 10^{-3}$ mol L^{-1}, $C_{HCl} = 1.0$ mol L^{-1} (A is optical density).

The standard working Os(IV) solutions were prepared by dissolving an aliquot of osmium(IV) stock solution in *ca.* 0.5...1 mol L^{-1} HCl aqueous solution up to pH<1. According to [7], $OsCl_6^{2-}$ does not undergo the hydrolysis in these conditions ($C_{HCl}>0.5$ mol L^{-1}, room temperature), and according to [28], nearly 93% of Os(IV) exists in the form of $OsCl_6^{2-}$ in 0.1...3 mol L^{-1} hydrochloric acid solutions.

The identification of Os(IV) solutions has been carried out spectrophotometrically comparing electronic absorption spectra of obtained solutions with literature data [2, 29]. As follows from the experimentally obtained spectrum (Fig. 1), in standard stock solutions Os(IV) exists in the form of $OsCl_6^{2-}$.

Absorption spectra were recorded on UV-VIS scanning spectrophotometer SPECORD M 40 Carl Zeiss Jena (Germany) using 1 cm cuvettes. The potentiometric titration was carried out with a potentiometer pH-150 M using platinum indicator electrode ЭПЛ-02 and Ag/AgCl reference electrode ЭВЛ-1M4 (Gomel Plant of Measuring Devices, Belarus). During potentiometric titration the solutions were stirred with a magnetic stirrer.

Results and discussion. As it is generally known, the iodometric method of analysis is based on the redox properties of $I_3^-/3I^-$ system (E^0=0.545 V) [30, 31]. So the redox processes in iodometric determinations may be represented with the following half-reaction:

$$I_3^- + 2\bar{e} \leftrightarrow 3I^-.$$

In case of iodometric titration of oxidants the reaction is carried out in acidic media, at room temperature; KI is added in excess not only for a quantitative reaction yield, but also for the solubilization of liberated iodine in water and for decrease of iodine volatility due to the formation of complex ion I_3^-; a reaction mixture is kept in a dark place in order to prevent a side reaction of iodine oxidation by air oxygen ($4I^- + O_2 + 4H^+ \rightarrow 2I_2 + {} + 2H_2O$); for complete iodine liberation the interaction of I_2 with oxidant must be carried out for 10...15 min, as far as the reactions of oxidizing agents and KI are not very fast.

The end point in iodometric titration is usually determined using starch solution as a visual indicator, or potentiometrically. Since starch forms with iodine a dark blue coloured complex, so the end point is clearly defined. In case of iodine titration with a solution of $Na_2S_2O_3$ starch should be added after a moment, when main amount of I_2 is already titrated, since the adding of starch before titration leads to overestimated results.

The method elaborated for Os(IV) determination from standard chloride solutions is based of reduction Os(IV) to Os(III) with KI in sulphuric acid media. The interaction is quantitative and sufficiently fast. As it is observed, solution of osmium(IV) is pale yellow coloured due to $OsCl_6^{2-}$ [1, 32] and after adding of potassium iodide the initial solution rapidly becomes greenish, what probably corresponds to the formation of mixed chloride and iodide complexes $[OsCl_nI_{6-n}]^2$ (in [1, 33, 34] it is reported about the existence of such complexes in aqueous solutions) as well as to the simultaneous presence of yellow coloured complexes $OsCl_6^{2-}$ and $OsCl_6^{3-}$ [1, 32] with a blue complex OsI_6^{2-} [35]. After 15 min of interaction the examined solution becomes yellowish brown as a result of I_2 accumulation.

The amount of I_2, liberated after the reaction with osmium, corresponds to Os(IV) quantity in the aliquot. Therefore, in order to establish a concentration of osmium in a sample, I_2 is titrated with a standardized $Na_2S_2O_3$ solution using visual or potentiometric indication of the end point. The investigated solution again becomes yellowish as we titrate it with $Na_2S_2O_3$.

Main reactions running during the titration are described by the following equations:

$$2Os^{4+} + 2I^- \rightarrow 2Os^{3+} + I_2, \quad I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}.$$

It is possible to determine distinctly a titration end point both visually and potentiometricaly, moreover, during the potentiometric titration the potential value is stabilized rapidly enough, viz. approximately in 1 minute after a next portion of the titrant was added a sharp potential change is observed in the vicinity of the end point even as we analyze osmium(IV) solutions with C(Os)<1 mg mL^{-1}.

The results of iodometric determination of osmium(IV) from standard chloride solutions with a visual indication of the titration end point by means of starch and by potentiometric indication of the end point are presented in Table 1.

Table 1. The results of iodometric determination of osmium(IV) from standard chloride solutions with visual and potentiometric indication of titration end point; $n = 5$; $P = 0.95$

Taken, mg Os	Visual indication of end point		Potentiometric indication of end point	
	Found, $\bar{x} \pm \frac{S \times t_\alpha}{\sqrt{n}}$ mg Os	RSD, %	Found, $\bar{x} \pm \frac{S \times t_\alpha}{\sqrt{n}}$ mg Os	RSD, %
2.87	2.91 ± 0.02	0.6	2.87 ± 0.01	0.3
1.42	1.45 ± 0.02	1.0	1.43 ± 0.01	0.6
0.73	0.75 ± 0.01	1.0	0.72 ± 0.01	0.9

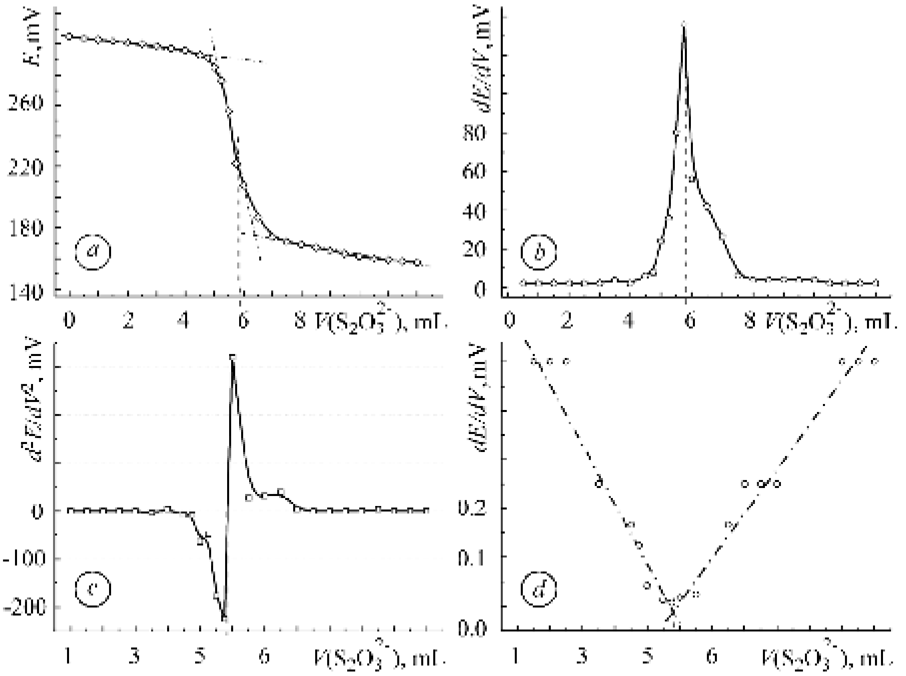

Fig. 2. Typical experimental potentiometric titration curves for iodine, liberated as a result of the reaction with $OsCl_6^{2-}$with 0.005 N $Na_2S_2O_3$ solution; *a* – normal titration curve; *b* – first derivative titration curve; *c* – second derivative titration curve; *d* – Gran plot.

Fig. 2 shows typical experimental potentiometric titration curves for iodine, liberated after the reaction with osmium, with 0.005 N $Na_2S_2O_3$ solution.

It should be mentioned that the results of Os(IV) quantification using visual indicating of titration end point appear to be somewhat overestimated relative to the results of potentiometric titration. It may be explained with insignificant over-titration of solutions, which is inherent to the techniques by a visual determination of titration end point.

As we analyzed solutions containing considerably less than 1 mg mL^{-1} of Os, the distinct inflexion points for the potentiometric titration curves were not observed, as well as clear colour change of solution from pale blue to pale yellow during a visual indicating of the end point by means of starch, thus the results obtained were insufficiently reproducible and accurate. Hence, the developed method is recommended for the standardization of Os(IV) hexachloride solutions containing milligram amounts of osmium.

We performed iodometric determination of the concentration of Os(IV) standard chloride solutions twice a year for 5 years. The results are reproducible and agree well with each other (Table 2). Therefore, we confirmed experimentally that under proper conditions of $OsCl_6^{2-}$ solutions storage the concentration of initial standard solution 0.379 mol L^{-1} changed only in the thousandth parts of concentration units, viz. no more than by *ca.* 1%.

Table 2. The results of the concentration estimation for initial standard chloride solutions of osmium(IV) in 2005–2009

Date of examination	2005	2006	2007	2008	2009
$C_{Os} \pm \Delta C$, mol L^{-1}	0.379±0.002	0.377±0.001	0.376±0.001	0.374±0.002	0.373±0.001
RSD, %	0.4	0.2	0.3	0.5	0.2

A good repeatability and reproducibility of the results of reiterated titrations suggest the accuracy of the introduced technique for the standardization of Os(IV) solution.

Also we have applied the developed titrimetric method for the estimation of osmium content in the samples of tri-component intermetallic alloys $Nd_{20}Os_{15}Si_{65}$ and $Nd_{10}Os_{30}Si_{60}$. The procedure of dissolution of intermetallide samples was as follows: 0.2...0.5 g of the intermetallic alloy was dissolved in 10...20 mL of a mixture of concentrated HCl and HNO_3 (10:1) and heated in a beaker on the sand bath for 1...2 h. Under these conditions a gray-coloured residue (elemental silicium) was formed on the bottom of the beaker. After quantitative transfer of the solution into a 100.0 mL volumetric flask the residue was washed with 1 mol L^{-1} NaOH solution for a few times. The washing liquid was placed into the same flask and distilled water was added to complete the volume to 100.0 mL. Since neodymium and silicium, present in the intermetallide samples, did not interfere in osmium(IV) interaction with KI, the alloy was analyzed directly after the dissolution. For the analytical procedure the 0.5...2.0 mL of analytes aliquots were taken. The results are presented in Table 3. The obtained findings correlate well with the nominal osmium content, i.e. calculated in the accordance with atomic per cents in the alloys. The accuracy and reproducibility of the results of Os iodometric determination in these samples are better than of the ones obtained by means of spectrophotometric methods with organic reagents [19, 20].

Table 3. The results of iodometric determination of osmium in intermetallic alloys; *n* = 5; *P* = 0.95

Intermetallide	$\omega_{Os}^{nominal}$, % w/w	Visual indication of end point		Potentiometric indication of end point	
		$\bar{\omega}_{Os}^{pr} \pm \frac{S \cdot t_\alpha}{\sqrt{n}}$, % w/w	RSD, %	$\bar{\omega}_{Os}^{pr} \pm \frac{S \cdot t_\alpha}{\sqrt{n}}$, % w/w	RSD, %
$Nd_{20}Os_{15}Si_{65}$	37.7	38.2 ± 0.7	1.4	38.0 ± 0.5	1.0
$Nd_{10}Os_{30}Si_{60}$	64.6	65.3 ± 1.0	1.2	65.1 ± 0.8	0.9

The developed method for the determination of Os(IV) from chloride aqueous solutions provides such advantages in comparison with other actual methods: the method is simple and rapid; it is suitable for the direct analysis of chloride osmium(IV) solutions; there is no necessity to use special equipments, as well as rare and toxic chemicals or organic solvents; experimentally obtained results are correct and reproducible. That is why this titrimetric method of Os(IV) solutions standardization can be useful for chemists, who deal both with the researches of osmium compounds and with osmium quantification.

Procedure of the osmium(IV) determination. An aliquot of osmium(IV) chloride standard solution (or a solution of intermetallic alloy) containing *ca.* 1 mg of osmium was placed into Erlenmeyer flask. Then 10 mL of 2 mol L^{-1} sulphuric acid and 5 mL 10% w/w KI solution, which did not contain free iodine, were added. The flask was covered with a watch glass and put into a dark place for 15 min. After that a watch glass was washed with distilled water over the flask. Isolated I_2 was then titrated with 0.005 N sodium thiosulphate, standardized after $K_2Cr_2O_7$. Titration was carried out at room temperature.

Titration end point was evaluated with a visual indicator (liberated iodine was titrated with $Na_2S_2O_3$ solution to pale yellow colour of the solution, then 1 mL of freshly prepared 0.5% w/w solution of starch was added and the titration was continued, until the colour change from blue to straw was observed after the addition of 1 drop of sodium thiosulphate solution), as well as potentiometrically (using Pt indicator electrode and Ag/AgCl reference electrode and the end point was located from the obtained potentiometric titration curves).

In order to obtain reproducible results titration procedures were repeated several times.

CONCLUSIONS

The iodometric method for the determination of milligram quantities of Os(IV) from chloride aqueous solutions has been elaborated. The method was successively approved to estimate the exact concentration of Os(IV) in standard solutions and to establish osmium content in the intermetallic alloys.

РЕЗЮМЕ. Розроблено нову методику стандартизації хлоридних водних розчинів осмію(IV) йодометричним титруванням з візуальною (за допомогою крохмалю) та потенціометричною фіксацією кінцевої точки титрування. Ця проста і експресна методика базується на взаємодії Os(IV) з надлишком йодид-іонів у сульфатнокислому середовищі та титруванні виділеного йоду стандартизованим розчином тіосульфату натрію. Методику апробовано під час визначення міліграмових кількостей осмію(IV) у стандартних розчинах та інтерметалічних сплавах. Похибка не перевищувала 1,5%.

РЕЗЮМЕ. Разработана новая методика стандартизации хлоридних водных растворов осмия(IV) иодометрическим титрованием с визуальной (с помощью крахмала) и потенциометрической фиксацией конечной точки титрования. Эта простая и экспрессная методика основана на взаимодействии Os(IV) с избытком иодид-ионов в сернокислой среде и титровании выделенного иода стандартизированным раствором тиосульфата натрия. Методику апробировано при определении миллиграммовых количеств осмия(IV) в стандартных растворах и интерметаллических сплавах. Погрешность не превышала 1,5%.

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