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Specific Features of the Gravimetric Determination of Palladium in Palladium-Containing Objects

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Abstract—A combined procedure for determination of macrocontents of palladium in various palladium-containing objects such as platinum metal alloys and palladium salts and complex compounds is proposed. The procedure is based on a combination of the gravimetric precipitation of palladium by dimethylglyoxime followed by determination of the residual content of palladium in the filtrates by atomic absorption spectrometry. A number of generalizations and technological conclusions are made that enable simplification of the procedure and reduction in the analysis time. On the basis of standardized test mixtures, it is shown that the relative analysis error according to the proposed procedure does not exceed 0.2%, which is practically in agreement with the error of classical gravimetric analysis.

Keywords: palladium-containing objects, palladium dimethylglyoximate, Schott glass filters, gravimetry, atomic absorption spectrometry

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The recent developments in analytical chemistry of platinum metals are associated predominantly with determination of trace contaminants of these metals by modern instrumentation methods, such as atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). As before, to determine macrocontents of platinum metals, conventional gravimetric methods of analysis are used most frequently [1]. These methods have a number of advantages, the main one of which is high accuracy and simplicity. However, the gravimetric methods have also some serious drawbacks such as long duration and laboriousness of the analysis. In some cases, the gravimetric analysis may be a multistage one, which is due to the necessity of considering the residual quantity of the analyzed element in the filters, since no absolutely complete precipitation ever occurs, and of considering the coprecipitation and sorption of the concomitant impurities by the residual that contains the element in question. This is especially important when determining the content of platinum metals because a minor error in their determination can cause significant financial losses.

In recent years, the analytic chemists engaged in analysis of platinum metals have made some attempts to simplify the gravimetric analysis by including instrumentation methods into the general scheme. These methods used to determine the residual platinum metal contents in filtrates enable a considerable reduction in the number of operations and, consequently, in the analysis time without impairing the accuracy of determination. Thus, in [2], a combined procedure for determination of macrocontents of platinum in platinum-containing products is described; the procedure is based on a combination of the gravimetric precipitation of platinum by ammonium chloride followed by determination of its residual content in the filtrate by ICP-AES. In [3], a combined method for determination of platinum and palladium is described in which the residual content of the metal in the filtrates is determined by ICP-AES after precipitating platinum by ammonium chloride and palladium by dimethylglyoxime. The authors also analyzed the derived precipitates to determine coprecipitated widespread common and platinum metal impurities by arc AES and X-ray fluorescence analysis.

In this work, a combined method for determination of the palladium content in its alloys with platinum and rhodium is studied. The method comprises the gravimetric determination of the basic palladium content and the instrumentation determination of its residual content in the filtrates. Systematic errors related, on one hand, to the coprecipitation and sorption of impurity elements by the weighed sample of palladium and, on the other hand, to partial solubility of the weighed sample, as well as their contribution to the total error balance, were studied.

There are a sufficient number of gravimetric techniques for determination of palladium [1, 4–6] using both organic and inorganic precipitants. The most selective reagent to precipitate palladium is dimethylglyoxime. The gravimetric determination of palla-

Table 1. Results of determination of palladium in standardized test solutions

Content of Pd in the standardized test sample, mass fraction, %	Finding, mass fraction, %			
	Pd in the palladium dimethylglyoximate sediment	Pd in the filtrate (on the standardized test sample basis)	Pd by the proposed method	
			without correction for the Pd content in the filtrate	with correction for the Pd content in the filtrate
16.71 ± 0.05	0.001 ± 0.0001	0.21 ± 0.02	16.48 ± 0.02	16.69 ± 0.02
33.27 ± 0.05	0.0007 ± 0.0001	0.18 ± 0.02	33.11 ± 0.03	33.29 ± 0.03
40.78 ± 0.05	0.003 ± 0.0002	0.21 ± 0.02	40.56 ± 0.03	40.77 ± 0.03
62.50 ± 0.05	0.001 ± 0.0001	0.22 ± 0.02	62.26 ± 0.04	62.48 ± 0.05

dium in jewelry alloys with dimethylglyoxime is presented in GOST (State Standard) 12564.1 [6] and ISO 11490 [7] as a standard method. In this case, metallic palladium is the weight form. Preparation of metallic palladium by calcinating dimethylglyoximate is not an easy task. Oxidization of palladium upon calcination leads to distortion of the results; therefore, according to the standard techniques, calcination should be carried out in a reducing hydrogen environment, which requires some additional equipment. Moreover, distortion of the results can occur owing to a loss of palladium in the form of volatile compounds upon calcination. It is preferable that palladium dimethylglyoximate be used as the weight form since the compound has a definite and constant composition and is sufficiently stable upon heating [4].

When precipitating palladium dimethylglyoxime, it is essential to maintain a definite acidity. Although there is no generally accepted opinion about the optimal pH value, it is known that palladium is precipitated in the most complete and selective way from almost neutral solutions (pH 5.5) [6].

Standardized test solutions that simulated solutions prepared by dissolving platinum-palladium alloys were chosen as test objects. Such solutions are widely used in engineering and also serve as objects of refining when processing platinum-containing raw materials. Four standardized test solutions were prepared. The solutions were prepared from weighed samples of pure metals. The palladium samples were 50 mg and the platinum samples were 250, 100, 73, and 30 mg. The solutions prepared in this way correspond to those prepared by dissolving alloys with 16.67, 33.33, 40.65, and 62.50 wt % of palladium. The metals were dissolved in nitrohydrochloric acid (20 mL), the nitrogen oxides were completely removed by boiling with hydrochloric acid, and afterwards the excess of hydrochloric acid was removed by a threefold addition of distilled water and evaporation of the solutions to obtain moist salts. The solutions prepared in this way were diluted to obtain a volume of ~25 mL, two drops of nitrohydrochloric acid were added to each of them to prevent the platinum recovery by dimethylglyoxime, and palladium dimethylglyoximate was precipitated by a 0.05% aqueous solution of dimethylglyoxime at room temperature. The resulting suspensions were held for half an hour and then filtered off using Schott glass filters. When the sediments were held for a longer time, they darkened owing to reduction of metallic platinum and its sedimentation together with palladium dimethylglyoximate. The filters with the sediment were dried out at a temperature of 110°C to obtain a constant weight and the content of palladium in the conditional alloy was determined.

To study the systematic errors caused by coprecipitation and sorption of impurity elements by the weight form of palladium and partial solubility of the weight form, the palladium dimethylglyoximate residuals were investigated for the impurity content and the filtrates for the palladium residual content.

The palladium dimethylglyoximate sediments were dissolved in nitrohydrochloric acid (~20 mL) and the content of the coprecipitated platinum was determined by the AAS. The same technique was applied to determine the residual content of palladium in the filtrates that had been pre-evaporated with addition of ~10 mL nitrohydrochloric acid to obtain a volume of 25 mL. The total content of palladium was determined as the sum of the palladium content established by the gravimetric method and the residual content of palladium in the filtrate with the deduction of the content of impurities sorbed by the impurity sediment. The results are presented in Table 1.

To establish the effect of impurities most common in manufacturing alloys on the total result of palladium determination, solutions that corresponded to those obtained upon dissolution of the alloy containing 50 wt % of palladium were prepared to which fixed quantities of Rh, Fe, Cu, and Ni (5, 0.1, 0.1, and 0.1 wt %, respectively) were added as impurities. Sim-

Table 2. Results of determination of the impurity contents in the palladium dimethylglyoximate sediment and in the filtrates

Object of investigation	Finding, mass fraction, %			
	Rh	Ni	Cu	Fe
Palladium dimethylglyoximate sediment	≤0.001	≤0.001	≤0.001	≤0.005
Filtrate	5.07 ± 0.05	0.0995 ± 0.0005	0.0997 ± 0.0005	0.0993 ± 0.0005

ilar to the previous case, the palladium dimethylglyoximate sediments were dissolved in nitrohydrochloric acid (~20 mL) and the contents of the coprecipitated metals were determined by AAS; in addition, the contents of the impurities in the filtrates were determined. The results are presented in Table 2.

Numerous laboratory determinations of the palladium contents in various palladium-containing products suggest the optimal conditions for conducting the analysis. Thus, it is practicable to precipitate palladium dimethylglyoximate from platinum-free samples, such as palladium acetate, palladozamine, and some dental alloys, from hot solutions, holding the sediments for 3–4 h. Under such precipitation conditions, palladium practically completely passes into the sediment and the content of the residual palladium in the filtrates can be neglected without causing detriment to the accuracy of analysis (Table 3). Consequently, the stages of evaporating the filtrates and determination of palladium in them can be excluded from the analysis procedure.

Palladium must not be precipitated from hot solution prepared by dissolving platinum-containing alloys since platinum is reduced in this case, which, undoubtedly, impairs the reliability and the accuracy of the analysis. The flowcharts of analysis for platinum-containing and platinum–free products are shown in Figs. 1 and 2.

As a result of this study, a number of generalizations and conclusions can be drawn that allow simplification of the gravimetric determination of palladium in various palladium-containing products.

1. An aqueous solution of dimethylglyoxime with a mass fraction of 0.05% rather than an alcohol solution is preferable for determination of palladium. Such a solution is stable within a wide range of temperatures [9], which enables precipitation from both a hot solution and a solution cooled to room temperature.

2. Palladium dimethylglyoximate dried at 110°C proved to be a reliable weight form. Therefore, it is not necessary to calcinate palladium dimethylglyoximate in a hydrogen flow to obtain metallic palladium. Undoubtedly, this considerably simplifies the analysis procedure in terms of both instrumentation and time consumption.

3. It is shown that the basic impurities that are most common in technological palladium alloys, such as Rh, Fe, Cu, and Ni, are sorbed by the palladium dimethylglyoximate sediment to an inconsiderable extent and do not have a significant effect on the determination of the palladium content on the object under analysis. Macroquantities of platinum behave in the same way. Platinum is coprecipitated in negligible quantities and, consequently, the resulting palladium dimethylglyoximate sediment does not need any further investigation to establish the effect of the coprecipitation on the analysis result.

4. When determining palladium in platinum-free objects, it is more practicable to precipitate palladium dimethylglyoximate from hot solutions. In this case, the precipitation is practically completely accomplished and the quantity of palladium residue in the filtrate does not have a significant effect on the analysis result, since the residual palladium content is considerably smaller than the error of the method.

Table 3. Results of determination of palladium in platinum-free samples

Subject of investigation	Finding, mass fraction, %	
	Pd according to the gravimetric analysis	Pd in the filtrate
Pd acetate	48.75 ± 0.05	0.005 ± 0.001
	48.25 ± 0.05	0.003 ± 0.001
	48.69 ± 0.06	0.005 ± 0.001
	47.58 ± 0.04	0.006 ± 0.001
Dental alloy with the 25% mass fraction of Pd	25.06 ± 0.02	0.007 ± 0.001
	25.00 ± 0.02	0.004 ± 0.001
	24.97 ± 0.02	0.004 ± 0.001
	24.98 ± 0.02	0.005 ± 0.001

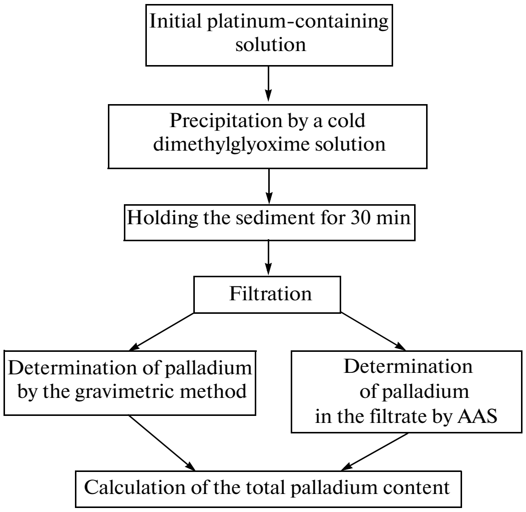

Fig. 1. Flowchart of the analysis of platinum-containing objects.

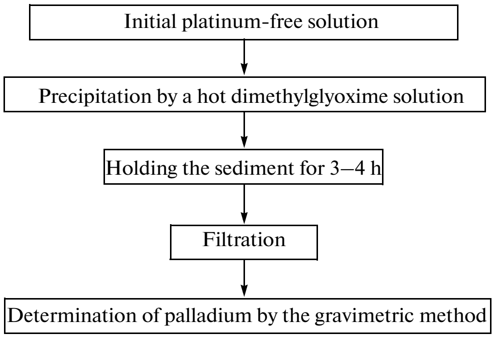

Fig. 2. Flowchart of the analysis of platinum-free objects.

5. When determining palladium in platinum-containing objects, the precipitation should be conducted at room temperature with addition of one or two drops of nitrohydrochloric acid to the solution under investigation, which prevents the reduction of platinum distorting the results of analysis.

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