
ARTICLES

Determination of Platinum by Atomic Absorption Spectrometry with Chromatographic Preconcentration from Aqueous Solutions

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Abstract—The conditions for determining platinum by electrothermal atomic absorption spectrometry after its extraction–chromatographic preconcentration and separation from iron(III) and copper(II) were selected. A procedure was developed that allows 0.01–0.1 mg/L platinum to be determined with a relative standard deviation of 5–7 % in the presence of 1000-fold amounts of Fe(III) and Cu(II).

The determination of platinum-group metals in complex samples, including platinum-containing ores, products of their processing, catalysts, biologically active samples, and medicines, has always been a complex analytical task for any analytical method. The main difficulties are related to the low concentrations of platinum-group metals in test objects and to the effect of sample matrix on the analytical signal.

Electrothermal atomic absorption spectrometry (ETAAS) is one of the most widely used methods for determining platinum-group metals. It is characterized by high selectivity and the lowest detection limits for platinum-group methods (≤ 10 for Pt) at the introduction of minor volumes of test solutions into the atomizer.

However, in the majority of papers on the determination of platinum-group metals by atomic absorption spectrometry, e.g., in [1–3], it was noted that matrix components significantly affect the analytical signal, especially when the concentration of matrix components is several orders of magnitude higher than that of the analyte. This effect must be studied and taken into account in each particular case. Different methods for correcting for nonselective absorption can eliminate so-called spectral interferences but do not solve the problem of matrix effects due to chemical interactions of platinum-group metals with concomitant impurities in the test solution and solid and gas phases in the atomizer. In the last case, the general solution is to preliminarily separate the analytes from the concomitant impurities. The rapid direct analysis of samples of complex composition by EYAAS is possible only after the thorough optimization of the parameters of the atomic absorption spectrometer, including the knowledge of the behavior of sample vapors in the atomizer. Note that no systematic data were found on the effect of matrix components, such as Fe, Cu, Ni, Co, and others in determining platinum by ETAAS with a

Massmann graphite furnace. The use of modifiers cannot fully eliminate the inhomogeneity of sample vapors in the atomizer. In addition, the separation of analytes from the matrix significantly simplifies the calibration of the atomic absorption spectrometer.

Although methods for the separation of platinum and platinum-group metals have long been sought, the number of methodological solutions suitable for ETAAS is limited [2]. The majority of procedures for the extraction and adsorption preconcentration of platinum-group metals is based on the use of extractants and adsorbents bearing nitrogen- and sulfur-containing functional groups; these reagents cannot extract analytes from aqueous solutions of the composition acceptable for ETAAS [3]. Another important requirement for the method for platinum preconcentration and extraction, irrespective on the method for its subsequent determination, is the composition of the initial solution. Methods for transferring platinum to solutions are based mainly on the formation of chloride complexes. Therefore, extraction, adsorption, and chromatographic methods for the separation of platinum were developed mainly for solutions of its chloride complexes or involve preliminary conversion of platinum compounds to chlorides. In addition, most procedures for determining platinum were developed for hydrochloric acid and chloride solutions. Electrothermal atomic absorption spectrometry is no exception [2]. For this method, extraction chromatography using oxygen-containing extractants as the stationary phase offers most promise as the preconcentration method. Among the extractants is tributyl phosphate (TBP), which allows the reversible extraction of platinum(IV) as chloride complexes and, correspondingly, makes possible the preconcentration of platinum under conditions of a chromatographic experiment [4, 5].

The aim of this work was to select the conditions for the extraction–chromatographic preconcentration of

platinum with its simultaneous separation from iron(III) and copper(II) and extraction as a dilute hydrochloric acid solution for the subsequent determination of platinum by ETAAS with background correction based on the principles of Zeeman polarization spectroscopy with high-frequency modulation [6].

EXPERIMENTAL

Platinum solutions. A stock solution of platinum(IV) (20 mg/L) was prepared by dissolving a calculated portion of metallic platinum in a 3 : 1 mixture of HCl and HNO₃ (both of high-purity grade) using heating. After the complete dissolution of the metal, the solution was evaporated to wet salts while adding new portions of conc. HCl to remove nitrogen oxides. The dry residue was dissolved in 5 mL of conc. HCl, the solution was transferred to a 100-mL volumetric flask and diluted to the mark with deionized water. Platinum solutions of lower concentrations were prepared by diluting the stock solution.

Extraction–chromatography column. The stationary phase in the extraction–chromatography column was supported on a pellet of porous polytetrafluoroethylene F-4M 12 mm in diameter and 60 mm in length, which was made by caking porous powder with a particle size of 0.25–0.50 mm. The porous powder was obtained by caking the starting material, grinding, and the extraction of a corresponding fraction. To apply the stationary phase, the fluoroplastic pellet was impregnated with tributyl phosphate; its excess was washed with a mixture of 0.1 M HCl and 4 M H₂SO₄. Elution rate was 0.5–1.0 mL cm⁻² min⁻¹.

Instruments. Measurements were conducted on an MGA-915 atomic absorption spectrometer with Zeeman correction for nonselective absorption (Lumex, St. Petersburg). The spectrometer operates based on the principles of Zeeman polarization spectroscopy with high-frequency modulation. A standard Massmann graphite furnace was used as an atomizer.

RESULTS AND DISCUSSION

When selecting atomization conditions in determining platinum by atomic absorption spectrometry, we assumed that the dissolved extractant may occur in the test solution.

The atomizer of the MGA-915 atomic absorption spectrometer is a Massmann graphite furnace with or without a L'vov platform. We did not use the L'vov platform in determining platinum. Water was evaporated at 130°C (drying step). A pyrolysis step at 600°C was introduced to remove organic substances. In our experiments, organic components were removed completely, which was evident from the reproducible value of the maximum analytical signal for platinum corresponding to the signal obtained upon the introduction of a hydrochloric acid solution bearing equal amount of platinum

Table 1. Conditions for determining platinum by atomic absorption spectrometry

Analysis step	Time, s	Temperature, °C	Flow rate of argon, L/min
Drying	30	130	0.5
Pyrolysis	5	600	0.2
Atomization	1	2290	0
Cleaning	1.5	2300	0.5
Pause	50		

into the atomizer. When selecting the optimum atomization temperature, we searched for conditions under which the analytical signal for a given element attained a maximum at the lowest atomization temperature. The optimum temperature was 2290°C. The selected atomization conditions are listed in Table 1. We registered the ratio between the integral signals of overall and nonselective absorption.

To construct a calibration graph, different volumes of a 0.25 mg/L platinum in 0.1 M HCl were introduced into the atomizer.

Taking into account the lack of quantitative data on the interference of Fe(III) and Cu(II) with the determination of Pt(IV), before selecting the conditions for the preconcentration of platinum with its simultaneous separation from concomitant impurities, we studied the effects of Fe(III) and Cu(II) on the analytical signal from platinum in electrothermal atomization.

To study the effect of Fe(III) ions on the analytical signal from platinum in electrothermal atomization, we prepared a series of solutions containing 0.25 mg/L platinum in 0.1 M HCl and 2.5, 25, 250, and 2500 mg/L Fe(III). Equal volumes of these solutions were successively introduced into the atomizer of the MGA-915 atomic absorption spectrometer. The results obtained are presented in Fig. 1 (curve 1). The analytical signal from platinum upon the introduction of an equal volume of a solution containing 0.25 mg/L platinum in 0.1 M HCl was 0.5 arb. units. As can be seen in Fig. 1, the analytical signal from platinum significantly decreased when the amount of Fe(III) in the solution was higher than 20-fold. The dependence of the analytical signal from platinum on the concentration of copper(II) was studied similarly. It is also shown in Fig. 1 (curve 2). One can see that, in the presence of 20-fold and higher amounts of copper, the analytical signal from platinum(IV) significantly increases. Thus, the results obtained indicate that platinum must be separated from concomitant iron and copper in its determination by ETAAS.

According to the results of our previous investigations [4], the maximum distribution coefficient for platinum(IV) and the maximum selectivity coefficients for Fe(III) and Cu(II) are attained when platinum is extracted with TBP from solutions in a mixture of

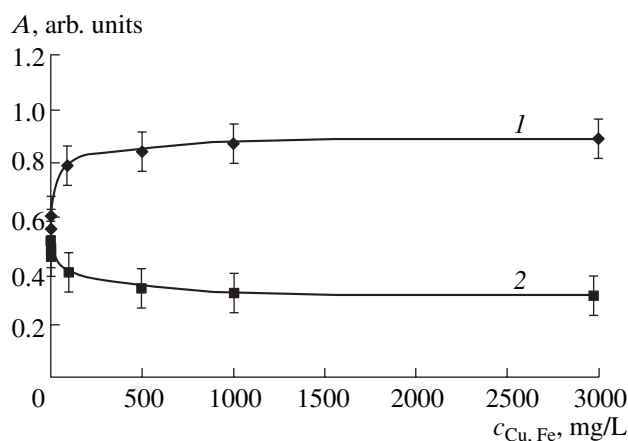


Fig. 1. Analytical signal from platinum as a function of the concentration of (1) Fe(III) and (2) Cu(II).

hydrochloric and sulfuric acids with the lowest concentration of HCl (0.01–0.1 M HCl and 4–6 M H₂SO₄). The back extraction of platinum(IV) can be performed with hydrochloric acid solutions of the same concentration (0.01–0.1 M HCl) containing no H₂SO₄; these conditions best correspond to the conditions of sample introduction into the atomizer in determining platinum [5]. Based on these data, we selected the conditions for the extraction–chromatographic separation of Pt(IV) with the simultaneous removal of Fe(III) and Cu(II).

Taking into account the difficulties with the preparation of mixtures of hydrochloric and sulfuric acids of the required composition for the extraction–chromatographic separation of Pt(IV), the test sample or a sample of a standard hydrochloric acid solution were preliminarily evaporated to wet salts under an IR lamp. The salts were then dissolved in an aliquot portion of a mixture of 0.1 M HCl + 4 M H₂SO₄; this mixture was then passed through an extraction–chromatography column. The column was washed with a solution of the same composition. The eluant was 0.01 or 0.1 M HCl. Figure 2 presents elution curves for Pt(IV) that were obtained after the absorption of 100 mL of a solution containing 0.025 mg/L Pt(IV) in 0.1 M HCl + 4 M H₂SO₄ on an extraction–chromatography column followed by elution with 0.01 M HCl (curve 1) and 0.1 M (curve 2) HCl.

Because the elution peak shapes differed insignificantly, the subsequent experiments were performed with 0.1 M HCl, which best corresponds to the found conditions of sample introduction into the atomizer.

To check the efficiency of the selected scenario for Pt(IV) extraction with its separation from the interferents, after passing 100 mL of a hydrochloric acid–sulfuric acid solution containing 0.05 mg/L platinum(IV) and 1000-fold amounts of Fe(III) and Cu(II), the column was additionally washed with 5 mL (fivefold free column volume) of 0.1 M HCl + 4 M H₂SO₄ and platinum was eluted with 0.1 M HCl. In these experiments,

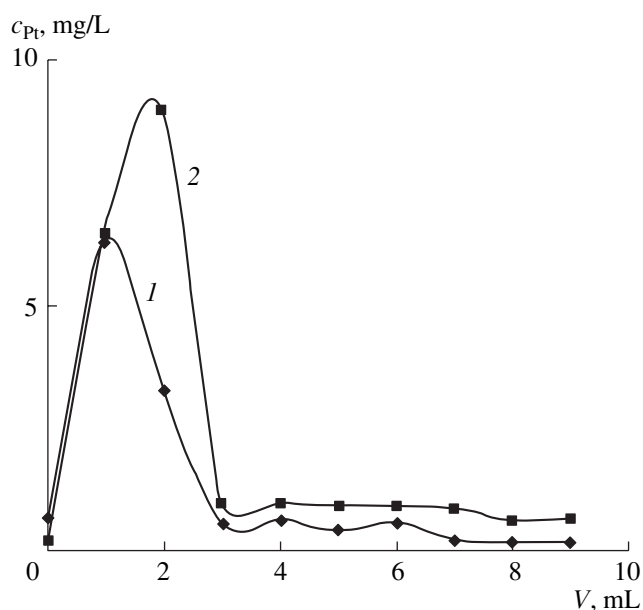


Fig. 2. Curves of elution of platinum(IV) with (1) 0.01 M HCl and (2) 0.1 M HCl.

the recovery of platinum in the first four milliliters of the eluate approached 100% of its total amount in the test solution. The concentration factor was 25. The factors of platinum purification of copper and iron were no less than 10⁴.

Based on the results of the above study, we selected the following procedure for determining platinum by atomic absorption spectrometry after its separation from Fe(III) and Cu(II) by extraction–chromatography. A test sample of a hydrochloric acid solution of platinum(IV) was evaporated to wet salts. Their solution in a mixture of 0.1 M HCl and 4 M H₂SO₄ was passed through an extraction–chromatography column containing TBP as the stationary phase. The allowable sample volume was up to a 100-fold free column volume. The column was washed with a mixture of hydrochloric and sulfuric acids (0.1 M HCl + 4 M H₂SO₄; fivefold free column volume). Platinum(IV) was eluted by 0.1 M HCl (a fourfold free column volume). The conditions of sample atomization are presented in Table 1.

The results of procedure verification using hydrochloric acid solutions with the known concentrations of platinum, Fe(III), and Cu(II) are presented in Table 2.

The third, fourth, and fifth rows in Table 2 present the results of platinum determination in the presence of 10³-fold amounts of Fe(III) and Cu(II). The last three rows present the results of determining platinum in the presence of 10⁵-fold amounts of Fe(III) and Cu(II).

The accuracy of the results was estimated using the *t*-test. The last column in Table 2 presents tabulated values of Student's test and *t*_{exp} calculated using the conventional equation. A comparison of their values for five replicate measurements at a confidence level of

Table 2. Determination of platinum by atomic absorption spectrometry in hydrochloric acid solutions containing 10^3 - and 10^5 -fold amounts of iron(III) and copper(II) after the extraction–chromatographic separation using the proposed procedure ($n = 5$; $P = 0.95$; $t_{\text{table}} = 2.78$)

Added Pt, mg/L	Found Pt, mg/L	s , mg/L	RSD, %	t_{exp}
10 ³ -fold amount of Fe(III) and Cu(II)				
0.015	0.014 ± 0.001	0.001	7	2.23
0.05	0.049 ± 0.004	0.003	7	0.74
0.1	0.096 ± 0.006	0.005	5	1.78
10 ⁵ -fold amount of Fe(III) and Cu(II)				
0.015	0.031 ± 0.005	0.005	15	7.13
0.05	0.08 ± 0.01	0.01	12	6.69
0.1	0.18 ± 0.03	0.03	8	5.95

0.95 indicates that, in the presence of 10^3 -fold amounts of Fe(III) and Cu(II), $t_{\text{exp}} < t_{\text{table}}$. This suggests that the difference between the found and added platinum concentrations is insignificant.

In the presence of 10^5 -fold amounts of Fe(III) and Cu(II), the experimentally found values of Student's test were greater than the tabulated values. This suggests the significant deviation of the results obtained from the true values.

The matrix components also affect the reproducibility of the results of analysis. The relative standard deviations presented in Table 2 for the analytical range were

5–7% in the presence of 10^3 -fold amounts of Fe(III) and Cu(II) and 8–15% in the presence of their 10^5 -fold amounts.

Thus, under the selected conditions for the AAS determination of platinum after its extraction–chromatographic separation from 1000-fold amounts of Fe(III) and Cu(II), platinum can be determined at a level of 0.01–0.1 mg/L with a relative standard deviation of 5–7%.

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