

DETERMINATION OF PHOSPHORUS TRACES IN PLATINUM ALLOYS BY TWO-PHASE ISOTOPE EXCHANGE

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The method of ZEMAN and KRATZER for the determination of phosphorus traces by means of two-phase isotope exchange was modified for the determination of phosphorus in pure platinum or pure platinum alloys. It was found that Pt, Rh, Ag, and As do not interfere with the determination. Among the elements usually present in platinum metal or platinum alloys, only gold interferes. It was removed by extraction from 7M HCl by MIBK and AmOAc. Hydrochloric acid also interferes but it can be removed by evaporation. The analytical procedure is given for the solution obtained by pressure decomposition of the sample (0.5 g) in a steel bomb with PTFE inlay. It is possible to determine > 2 ppm P (approximate error -10%). Using a calibration dependence instead of the well known equation for isotope exchange, the content of P in the standard solution labelled with ^{32}P need not be known.

Introduction

PEREZHOGIN and SIDOROVA¹ have found that the isotope exchange of ^{32}P between an organic phase containing the ion associate $[(\text{TPA}^+)_3, ^{32}\text{PMo}_{12}\text{O}_{40}^{3-}]$ and an aqueous phase containing phosphate occurs only in the presence of molybdate in the aqueous phase. A method of trace determination of phosphorus based on this fact was described by ZEMAN and KRATZER,² using heterogeneous isotope exchange. According to their procedure, they prepared a solution of tetraphenylarsonium (TPA) molybdophosphate in dichloroethane by extracting ammonium molybdophosphate labelled by ^{32}P with a substoichiometric amount of TPA chloride. By shaking the dichloroethane solution with the aqueous sample solution, isotope exchange occurs, resulting in the decrease of the organic phase activity. This is proportional to the phosphate content in the aqueous phase according to the well known relation

$$(\text{A}_1 - \text{A}_2)/m = \text{A}_2/s \quad (1)$$

where A_1 is the original activity of the organic phase (before isotope exchange), i.e. of the standard solution containing a mass s of phosphorus, A_2 is the activity

of the organic phase after reaching isotopic equilibrium, m is the mass of phosphorus in the aqueous phase (sample solution).

We used this principle for the determination of trace amounts of phosphorus in pure platinum metal or in pure platinum-rhodium alloys. Although the influence of 25 elements on this determination was studied by ZEMAN and KRATZER,² Pt, Rh and other elements usually present in platinum alloys were not included.

Therefore, we verified the influence of the most important factors on this determination and worked out a procedure eliminating the interference of chlorides and gold as well. According to the proposed procedure, the knowledge of the phosphorus content in the standard solution (s) is not a prerequisite.

Experimental

The stock phosphorus solution containing 3.0974 mg P per ml (0.1M) was prepared from KH_2PO_4 (reagent grade), dried 1 h at 110 °C. Its concentration was verified by measuring the pH value of the solution.³ The pH meter scale (Radeliks OP 205, Hungary) was calibrated by means of NBS buffers. The relation $\%P = (53.34 - 0.263 \text{ pH}) 0.4364$ is valid in the range $22.74 < \%P < 22.77$. The phosphorus content in the preparation used was 22.763% (theor. 22.761%). Other working solutions were prepared by diluting the stock solution. The standard phosphorus solution was prepared by extracting the mixture of 4 ml 10^{-2}M KH_2PO_4 labelled with $\text{Na}_2\text{H}^{32}\text{PO}_4$ or $\text{H}_3^{32}\text{PO}_4$, 2.5 ml 1M H_2SO_4 , 2.5 ml 0.2M ammonium molybdate and 15 ml water with 50 ml of 10^{-3}M TPACl in dichloroethane. After the phases had separated, the organic phases was filtered through Whatman 1PS filter paper. 100 μl of the standard solution soaked in a disc of filter paper gave $3.4 \cdot 10^5$ counts per min (5.7 kBq) after evaporation of the solvent.

A scintillation counter and a Tesla 54 (Czechoslovakia) counting device was used for radiometric measurements. The time for counting was chosen in such a way that the relative deviation of one measurement from the mean was $<1\%$. The counts stated here were corrected for the background.

Results

Effect of acidity and molybdate concentration in the aqueous phase

In accordance with the results of ZEMAN and KRATZER,² it was found that in the range 0.03–0.7M H_2SO_4 , the isotopic equilibrium is reached rapidly (up to 10 s) and that the same velocity of isotope exchange is attained if the molybdate concentration is 0.02M and the phosphorus concentration 0.1 μg P per ml in the aqueous phase (sample solution).

Table 1
Results of the calibration procedure

P, μg	A_2 , counts/min	A_1 , counts/min	y_{corr}
6.19	155 566	304 162	0.9520
12.39	90 569	268 158	1.9576
18.58	65 391	268 538	3.0995
24.77	61 283	304 162	3.9600
30.96	44 667	268 158	5.0003

Calibration curve

Eq. (1) was transformed to give a linear function of the phosphorus amount (or concentration) in the sample

$$(A_1 - A_2)/A_2 = s^{-1}m \quad (2)$$

[for the meaning of symbols see Eq. (1)]. The following calibration procedure was used: 0.5–2.5 ml of the working phosphorus solution was diluted to 4 ml with water in ground-glass stoppered test tubes, and 0.5 ml 1M H_2SO_4 was added, followed by 0.5 ml 0.2M molybdate solution. The aqueous phase was then shaken with 1 ml of the standard phosphorus solution for 2 min. After a short period of standing, 100 μl of the well separated organic phase was measured into a small Petri dish containing a disc of filter paper. The solvent was then evaporated, and the counts per min measured. The values found are summarized in Table 1 [$y = (A_1 - A_2)/A_2$, $y_{\text{corr}} = y - y_{\text{blank}}$]. Using the least-squares method, the equation of the regression line for calibration dependence (2) was calculated as $y = -0.01946 + 0.1604 m$ (m in μg). This relation was found to be valid up to 60 μg P in the aqueous phase (5 ml) under the conditions used.

Effect of Ag, As, Au, Pt, and Rh

The procedure given for calibration was used. The aqueous solutions (5 ml) contained the amount of phosphorus and of the elements studied as stated in Table 2, where also the results are given. Using the u_0 -test, it has been proved that the effect of As is insignificant up to 96 μg per 5 ml of the sample solution, its significance being very low at a concentration of 240 μg per 5 ml. The effect of the

Table 2
Effect of Ag, As, Au, Pt and Rh

P added, μg	Other elements, μg	y	P found, μg	Δ , %
0	0	0.033	—	—
0	240 As	0.087	—	—
15.49	192 As	2.258	14.2	-8.3
15.49	192 As	2.173	13.7	-11.7
0	1000 Rh	0.072	—	—
0	1000 Pt	0.068	—	—
0	1000 Pt + 1000 Rh	0.075	—	—
15.49	1000 Pt + 1000 Rh	2.226	14.0	-9.8
15.49	1000 Pt + 1000 Rh	2.354	14.8	-4.4
0	519 Ag ^a	0.038	—	—
0	388 Au ^b	0.377	2.5	—
15.49	519 Ag + 388 Au	3.060	19.2	+24.0

^aAs AgClO₄.

^bAs HAuCl₄.

excess of Pt, Rh, and Ag used is insignificant, but gold interferes. The error of the method described is ca. -10% with the exception of the determination in the presence of gold.

Elimination of the interference of gold

Obviously, the interference of gold is caused by competition of the chloroaurate ion for TPA ions in the organic phase, under formation of a stable ion-associate [TPA⁺, AuCl₄⁻], and under exclusion of the ion ³²PMo₁₂O₄₀³⁻ into the aqueous phase. A positive error in the phosphorus content is thus found. The interference of gold was eliminated by extracting it in the form of gold(III) chloro-complex into a mixture of methyl isobutyl ketone (MIBK) and amyl acetate (1 : 1) from 7M HCl solution ($V_{\text{aq}} : V_{\text{org}} = 1 : 2$). The aqueous phase resulting from this extraction was used for phosphorus determination either directly or after evaporation to dryness and dissolution of the residue in water. The results are shown in Table 3. It can be seen that the evaporation of the aqueous phase is necessary because either hydrochloric acid or MIBK and AmOAc dissolved in water (or both) interferes with the determination.

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Table 3
Results of the different analytical procedures
in the presence of gold

P added, μg	Au added, μg	y	P found, μg
0	0	0.040 ^a	—
0	775	0.042 ^a	—
15.49	775	0.054 ^a	—
15.49	775	0.058 ^a	—
0	0	0.038 ^b	—
0	775	0.037 ^b	—
15.49	0	2.418 ^b	15.2
15.49	775	2.258 ^b	14.2

^aWithout evaporation.

^bWith evaporation of the aqueous phase.

*Verification of the calibration dependence using the solution
after decomposition of the Pt–Rh alloy*

From the experiments described, it can be seen that neither Pt nor Rh interferes with the determination up to an excess of 60 : 1. In the alloys to be analyzed, however, a ratio of 10^5 : 1 or higher can be supposed. Therefore, the calibration procedure described was verified using standard additions of phosphorus to the sample solution. It was found that the amount of hydrochloric acid remaining in the solution after decomposition of the alloy also interferes. The removal of excess hydrochloric acid by evaporation is not suitable, because platinum precipitates from the resulting neutral solution as a hydrolytic product or reduced to the metal. It is also not suitable to convert chlorides to perchlorates by fuming with perchloric acid, as some insoluble compound is formed. If the sample solution was evaporated with sulfuric acid to remove hydrochloric acid, the extent of isotope exchange was lower. The effect of excess hydrochloric acid was thus eliminated by evaporation of the sample solution with an equivalent amount of sodium chloride to convert platinum and rhodium to chloro-complexes.

Increasing amounts of phosphorus were added to the aliquots of the solution obtained as described, and the calibration dependence was ascertained. In fact, the same slope of the calibration line (0.1593) was obtained as previously.

Recommended working procedure

Ca. 0.5 g of the alloy or platinum metal is decomposed in a steel bomb with PTFE insertion, using a mixture of 16.5 ml HCl and 1 ml HNO₃ (Ref.⁴) and keeping the bombs in an air oven at 102–105 °C for 12 h. The solution obtained is evaporated at 90 °C to dryness. Nitrates are removed by double evaporation with 5 and 3 ml HCl. The residue is dissolved in 5 ml 7M HCl, the solution transferred to a separatory funnel and the beaker washed with 3 and 2 ml of the same acid. Gold is extracted with 20 ml MIBK + AmOAc (1 : 1) for 3 min. The aqueous layer is transferred to the original beaker and the separatory funnel is washed with 2 and 1 ml of 7M HCl. The aqueous solution is evaporated to dryness with 3 ml 2% NaCl solution. The residue is dissolved in water, transferred into a 25 ml measuring flask and filled up with water. An aliquot of 4 ml is taken and the procedure described for the calibration applied. The amount of P in the sample is calculated using the equation of the regression line.

Blank: 16.5 ml HCl and 1 ml HNO₃ are evaporated to dryness and the same procedure is used, as described for the sample. The mean value of the blank found $\bar{y}_{\text{blank}} = 0.0032$ with a standard deviation of $S = 0.00126$ (from 6 measurements). From the relation $y_{\text{min}} = \bar{y}_{\text{blank}} + 3S$, the minimum value of y was calculated ($y_{\text{min}} = 0.0070$). This corresponds to the limit of determination 2 ppm P if a 0.5 g sample is used.

The method described was used for the analysis of Pt–Rh alloys and was found more advantageous than e.g. the photometric one.⁵ It is sensitive enough to allow the use of 0.5 g sample, thus lowering the amount of acids for the decomposition, which causes a low blank value and low limit of determination as well. Furthermore, platinum need not be removed by electrodeposition before phosphorus determination.

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