Investigation of the Interaction of Palladium with Potassium Tetrafluorobromate

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Abstract. In this investigation, the interaction of metallic palladium with potassium tetrafluorobromate was examined in open system, the reaction products were identified using X-ray phase analysis. A thermogram of the interaction of Pd with KBrF$_4$ was obtained, the temperature range of the reaction (187.9-328°C) and the thermal effect (431.31 J/g) were determined. It was found that the fluorination process is a multi-stage process. The solubility of the obtained K$_2$PdF$_6$ compound in nitric and hydrochloric acids was investigated. The process of extraction of palladium from nitric acid solutions with tributyl phosphate was carried out and the influence of the concentration of palladium and the acidity of the initial solution on the distribution coefficient was investigated.

1. Introduction

At present, the problem of processing technology-related waste is becoming more urgent than ever in the context of rational nature management. Natural ore reserves are depleting, and the level of pollution with technology-related waste is growing. According to experts, in 2014 41.8 million tons of electronic equipment wastes were accumulated in the world [1]. Given the rising prices for raw materials and energy, the processing of household, industrial and other equipment is becoming increasingly important, as technology-related waste contains valuable components such as noble metals and other rare elements [2].

There exist various methods for waste processing in order to extract valuable components. The most popular are pyrometallurgical and hydrometallurgical technologies [3,4]. But both of these methods have their drawbacks. For example, pyrometallurgical processing of electronic scrap is attended with toxic emissions into the environment, and high temperatures. During the processing of technology-related waste with nitric acid, meta-tin acid is formed, which makes it difficult to isolate valuable components. Processing of secondary waste with the aqua regia is attended by the release of toxic gaseous waste - nitrogen oxides ("red smoke"). But the main drawback of all these methods is the duration of the main stages and the low yield of noble metals, associated with the difficulty of their quantitative oxidation.

However, there are compounds that can replace conventional reagents used to recover the noble metals. Such substances are halogen fluorides or their modern forms of coordination compounds with alkali and alkaline earth metals: the most popular and currently studied compounds are based on bromine trifluoride - fluorobromates (III) of alkali and alkaline earth metals [5]. They are very effective in the processing of materials containing noble metals, as they allow for high speed and efficiency of opening...
with a minimum number of stages. One of the most widely used reagents is potassium tetrafluorobromate (III) KBrF₄, which is a solid at room temperature, and is a powdery compound and exhibits excellent oxidative abilities when heated.

In earlier papers [6, 7], the authors investigated the interaction of potassium tetrafluorobromate with palladium and other noble metals in closed systems. They determined the phases of resulting products and the mechanism of chemical interaction. The reaction with palladium is described by reaction (1) [7]:

\[
2 \text{KBrF}_4 + \text{Pd} \rightarrow \text{K}_2\text{PdF}_6 + 2 \text{BrF}.
\]  

(1)

In this work, we investigated the interaction of potassium tetrafluorobromate (III) with palladium in open system. The temperature ranges of the interaction and the thermal effects of its main stages were determined by the thermogravimetric method with combined calorimetry. For further study of methods for extraction and separation of foreign noble metals present in technology-related waste, the solubility of K₂PdF₆ in nitric and hydrochloric acids was investigated. Also the effect of the concentration of palladium and the acidity of the initial solution on the distribution coefficient in the extraction system of nitric acid solution with tributyl phosphate was explored.

2. Analysis procedure

To investigate the reaction of interaction of Pd with KBrF₄, the thermogravimetric method with combined differential scanning calorimetry was used on an SDT Q600 analyzer (TA Instruments, USA).

Sample preparation was carried out in a dry sealed stainless steel box in an atmosphere of dried argon. Palladium powder was used to investigate the reaction; potassium tetrafluorobromate was synthesized by the reaction of interaction of bromine trifluoride and with potassium fluoride according to the procedure described in [8]. Glassy carbon crucibles (HTW Hochtemperatur Werkstoffe GmbH, Germany), resistant to the oxidative effects of the fluoride systems under study, were used for analysis. The ratio of source materials was chosen according to the stoichiometry of reaction 1 (Me:2KBrF₄ mol.), which amounted to 0.1286 g and 0.4714 g, respectively. The mixture of reagents was heated from 20 to 500°C with a heating rate of 10 degrees per minute. The reaction proceeded in an argon stream.

Quantitative oxidation for subsequent investigation was carried out in a 50 ml glassy carbon beaker. The initial amount of reagents was chosen with a 6-fold excess from stoichiometry (Me:12KBrF₄ mol.), which amounted to 0.045 g and 1 g, respectively, according to the procedure [9]. The crucible with the sample was heated in a muffle furnace to 400°C for 120 minutes, kept at this temperature for 150 minutes and then slowly cooled to room temperature for 240 minutes. The reaction products were ground and sent for X-ray phase analysis to confirm the formation of K₂PdF₆.

Samples of the obtained K₂PdF₆ product weighing 0.05 g each were dissolved in 50 ml of hydrochloric and nitric acids with a concentration of 35 and 65%, respectively. As a result of the interaction, the following complexes are presumably formed [10]:

\[
\text{K}_2\text{PdF}_6 + \text{HCl} \rightarrow \text{K}_2\text{PdCl}_6 + \text{HF},
\]

(2)

\[
\text{K}_2\text{PdF}_6 + \text{HNO}_3 \rightarrow \text{K}_2\text{Pd(NO}_3)_6 + \text{HF}.
\]

(3)

The time of K₂PdF₆ dissolution in nitric acid at room temperature was 3.5 minutes.

The K₂PdF₆ sample was left to dissolve in hydrochloric acid for 45 minutes at room temperature; under these conditions, the complete dissolution of the sample was not achieved. The hydrochloric acid solution with the sample was brought to boil, K₂PdF₆ completely dissolved within 5 minutes.

To study the process of extraction of palladium from nitric acid solutions, tributyl phosphate was used as an extraction agent. Extraction was carried out in a separation funnel with a volume ratio of 1:1 of the organic and aqueous phases. To calculate the distribution coefficient, 5 ml of the initial solution and raffinate were taken. The concentration of palladium in the extract was determined as the difference in the quantitative content of palladium between the initial solution and the raffinate. The organic phase was re-extracted with water in 3 stages with an organic/aqueous phases ratio of 1:1 by volume. X-ray
fluorescence analysis showed that no traces of palladium were found in the regenerated tributyl phosphate.

3. Results and discussion
The results of thermogravimetric analysis of the mixture of palladium and potassium tetrafluorobromate are presented in Figure 1.

![Thermogram of the interaction of Pd with KBrF₄ (1:2 M ratio): mass change curve (green solid line), heat flux curve (blue solid line) and thermal effects determination interval (red solid line).](image)

When interpreting the results, the data on the thermal decomposition of pure potassium tetrafluorobromate [10] was used. Three endothermic and two exothermic effects are reflected on the heat flux change curve.

The first two endothermic effects, observed at temperatures of 62.8 and 101°C, can be attributed to the process of removing gaseous products from the pores of fluorine bromate, including bromine, which boiling point is 58.2°C, bromine trifluoride and hydrogen fluoride and freon.

According to [11], palladium exhibits the most characteristic oxidation states of 2+, 4+, less commonly – 1+, 3+, and 5+. The exothermic effects observed at 201.5 and 314°C (peak maximum) indicate a multi-stage process of fluorination, the formation of palladium with intermediate oxidation states.

The main exothermic effect is observed at a temperature of 201.5°C (peak maximum); this effect corresponds to the beginning of the process of palladium fluorination, which is confirmed by a decrease in the mass of the sample.

The last endothermic effect with a temperature of 410.2°C is believed to relate to the decomposition of residual potassium tetrafluorobromate.

On the mass change curve, inflections are marked with points A, B, C, D, E, F, G, and I. In sections AB and BC, residual gaseous products are removed from the pores of the sample.

Point D at a temperature of 187.9°C corresponds to the beginning of the process of palladium fluorination, and DE curve, accompanied by a significant loss of mass (23% of the sample initial mass), characterizes the process of palladium oxidation to an oxidation state of 2+ and the emission of gaseous reaction products in accordance with the reaction (1).
The next EF section corresponds to the second stage of palladium fluorination, and FG section corresponds to the formation of the final product K₃PdF₆, which is accompanied by the exothermic effect with a peak at 314°C. At GH section, the residues of potassium tetrafluorobromate are decomposed with the release of bromine trifluoride into the gas phase. At 425°C, the mass change curve reaches a plateau; accordingly, the processes of chemical transformation end. The mass of the obtained product according to the thermogram is 20.11 mg, which corresponds to the stoichiometric calculated mass of K₃PdF₆ (20.21 mg). The total thermal effect of fluorination reactions was 433.31 J/g.

It is also illustrative that the onset of palladium fluorination occurs at a temperature below the melting and decomposition temperatures of potassium tetrafluorobromate, i.e. KBrF₄ has sufficient oxidizing ability to transfer metallic palladium to the oxidized state at a temperature below the point of melting and decomposition of potassium tetrafluorobromate (III) [12].

The results of X-ray phase analysis obtained by quantitative oxidation of palladium in an open system are shown in Figure 2.

![Figure 2](image.png)

**Figure 2.** X-ray diffraction pattern of the reaction product of Pd with KBrF₄ (1:12 M ratio). Triangles indicate peaks corresponding to K₃PdF₆, circles – to KBrF₄.

The diffraction product pattern of the reaction of palladium with KBrF₄ was obtained on an XRD-7000 diffractometer (Shimadzu, Japan) and decoded using the PDF-2 database. To obtain clear diffraction patterns, the sample was preliminary ground into a fine powder and pressed into a tablet. Analysis showed that the main reaction product is K₃PdF₆. The presence of a certain amount of KBrF₄ was also detected. A number of undecrypted peaks can be attributed to the hydrolysis products of KBrF₄ (KBrO₃, KHF₂). X-ray phase analysis confirmed the 4+ oxidation state of palladium, which corresponds to earlier studies of the authors [7], and is described by the reaction (1).

To determine the palladium concentration in solutions, iCAP 6300 Duo atomic emission spectrometer (Thermo Scientific, Great Britain) was used. A high-temperature source of excitation was an inductively coupled plasma with a power of 750–1350 W. All samples were diluted and brought to a volume of 10 ml.

The obtained data on the palladium concentration in the initial solution and in the raffinate, and the calculated values of the palladium concentration in the organic phase, and the palladium distribution
coefficient are presented in Table 1. The table also shows the concentration of nitric acid in the initial solution.

**Table 1.** Palladium distribution coefficients in the nitric acid - tributyl phosphate extraction system.

| C (HNO₃), mol/l | C(Pd) in init., mg/l | C(Pd) in raff., mg/l | C(Pd) in org., mg/l | D[Pd] |
|----------------|-----------------------|----------------------|---------------------|-------|
| 1              | 14.44                 | 43.8                 | 7.46                | 36.34 | 4.87 |
| 2              | 11.02                 | 30.3                 | 5.66                | 24.64 | 4.35 |
| 3              | 7.22                  | 14.82                | 2.42                | 7.8   | 3.22 |
| 4              | 3.61                  | 7.86                 | 1.84                | 6.02  | 2.27 |
| 5              | 2.7                   | 5.1                  | 2.52                | 2.58  | 1.02 |
| 6              | 1.8                   | 5.44                 | 4.96                | 0.48  | 0.002 |

According to the data obtained, the influence of the palladium concentration in the initial solution and the initial solution acidity on the palladium distribution coefficient was determined (Figure 3).

![Figure 3](image-url)  
*Figure 3.* The effect of palladium concentration (orange curve) and the acidity of the initial solution (green curve) on the palladium distribution coefficient.

This dependence shows that the palladium distribution coefficient increases with an increase in the palladium concentration in the initial solution and the solution acidity. To carry out extraction from solutions with a palladium concentration of less than 5.83 mg/l and a concentration of free nitric acid of 2.59 mol/l, the raffinate is enriched with palladium. To transfer palladium to the organic phase, it is necessary to use more concentrated and acidic solutions.

**4. Conclusion**

In the course of the investigation, the interaction of palladium with KBrF₄ heated to 500°C was studied. The reaction product was identified as KBrF₆. Palladium is oxidized to a tetravalent state. The fluorination process is a multi-stage process and in the intermediate products palladium demonstrates a degree of oxidation of 2+ and 3+. The total thermal effect of the reaction was 433.31 J/g. The fluorination process begins at a temperature of 187.9°C, and ends at 335°C. It is proved that KBrF₆...
possesses sufficient oxidizing ability to transfer metal palladium to the tetravalent state at a temperature below the point of decomposition and formation of bromine trifluoride.

The solubility of K₂PdF₆ in hydrochloric and nitric acids was investigated, as well as the process of extraction of the palladium nitrate solution - tributyl phosphate system. The influence of the palladium concentration and the initial solution acidity on the distribution coefficient in the extraction system was determined. With an increase in the palladium concentration and the solution acidity, the separation coefficient also increases. It was found that in the process of extraction from solutions with a palladium content of more than 5.83 mg/l and 2.59 mol/l of nitric acid, the organic phase is enriched with palladium.

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