

CCA-211

542.984.2:546.726:544.83:546.98

Decomposition of Hexacyanoferrate(II) in Analysis. VII.* New Spot Test for Palladium

I. Kraljić

*Institute of Analytical Chemistry, Faculty of Technology, University of Zagreb,
Zagreb, Croatia, Yugoslavia*

Received January 12, 1961

A new spot test, based on the action of Pd^{2+} on the decomposition of hexacyanoferrate(II) in the presence of nitrosobenzene, was developed for the detection of palladium. The sensitivity for the pure system under optimum conditions is $0,02 \mu\text{g Pd}$ expressed as limit of identification, at the concentration limit 1:2,000,000. Hg, Ag and Au react analogously. Iodides, even in rather high concentrations, do not impair the sensitivity, whereas cyanides interfere strongly with the test.

The decomposition of hexacyanoferrate(II) for the detection of traces of metals (mercury) has been used by Pinter¹. In the method proposed by him in 1940, in the presence of traces of mercury in an acid solution and at elevated temperature, the product of decomposition of the hexacyanoferrate(II) is Prussian blue. This is because the Hg ions catalyze the total decomposition of $[\text{Fe}(\text{CN})_6]^{4-}$ into Fe^{2+} and 6 CN^- , whereupon the demasked Fe^{2+} is oxidized by oxygen from the air and the solution to yield Fe^{3+} , which by reaction with surplus $[\text{Fe}(\text{CN})_6]^{4-}$ produces a colloidal solution of Prussian blue. The same effect was used also for the photometric determination of mercury².

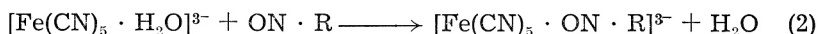
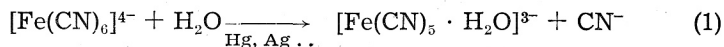
Feigl and Caldas³ have also used the total decomposition of hexacyanoferrate(II) for analytical purposes, namely for the detection of Hg, Ag and Ag-halides, Pd, and $[\text{Fe}(\text{CN})_6]^{4-}$. In these methods the demasked Fe^{2+} is revealed by means of 2,2'-dipyridyl or *o,o'*-phenanthroline. Some photometric methods for the determination of mercury⁴ and silver⁵ are also based on the same reaction with the addition of these reagents. The sensitivity of the method for silver is $0.01 \mu\text{g}/5 \text{ ml}$.

A spot test for silver⁶ based likewise on the total decomposition of hexacyanoferrate(II) (Reaction product: Prussian blue) is extraordinarily sensitive, its limit of identification being $0.00075 \mu\text{g}/0.035 \text{ ml}$. This spot test can be used also in the presence of a large excess — in relation to the silver present — of chlorides, bromides, and even iodides.

While in all these methods total decomposition of the hexacyanoferrate(II) occurs, and the product of the decomposition is the demasked Fe^{2+} , in another type of decomposition reactions the decomposition proceeds only as far as the pentacyanide complexes, which can be readily detected by the addition of appropriate aromatic nitroso-compounds (Baudisch⁷, Feigl *et al.*⁸, Ašperger *et al.*⁹, Kraljić *et al.*¹⁰). Besides a number of quantitative photometric methods

* VI. Z. anal. Chem. (in press)

for the determination of mercury⁹, cyanides¹¹, gold¹², mercury and gold in mixtures¹³, palladium¹³, pyridine¹³ and some nitroso-compounds¹³, several methods for the detection of traces of mercury¹⁴, silver¹⁵, gold¹⁶ and some nitroso-compounds¹⁰ have been based upon this reaction. All these methods are based on the following reactions^{9,10,17}:



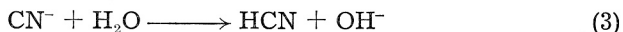
The arising pentacyanide complexes are intensely coloured, which allows an easy detection of the incomplete decomposition.

The detection of the individual cations by the method using nitrosobenzene has the following sensitivities, expressed as limit of identification per drop:

Hg: 0.002 μg ; Ag: 0.004 μg ; Au: 0.05 μg ;

while a method for the detection of mercury in the presence of some other nitroso-compounds¹⁸ has a sensitivity of 0.004 μg Hg. The application of this type of decomposition to a spot test for some aromatic nitroso-compounds gave a sensitivity of 0.02-1 $\mu\text{g}/\text{drop}$ ¹⁰.

In the first stage of the decomposition of $[\text{Fe}(\text{CN})_6]^{4-}$, cyanide ions are liberated⁹ according to equation (1). These ions are hydrolyzed:



resulting in a decrease of the acidity of the solution. Such a change of *pH* in the system $[\text{Fe}(\text{CN})_6]^{4-} - \text{Hg}^{2+} - \text{methylorange}$ can also be used for the detection of mercury¹⁹, and probably likewise for the detection of gold, silver and palladium.

The present paper deals with a spot test for the detection of Pd, developed on the base of the partial decomposition of hexacyanoferrate (II) in the presence of nitrosobenzene. This test, besides being selective, has a fairly good sensitivity. The well known and very sensitive spot test using *p*-nitrosodimethylaniline or *p*-nitrosodiphenylamine²⁰ is only 4 to 5 times as sensitive.

EXPERIMENTAL

Reagents

PdCl_2 . A 0.01 molar solution was prepared as stock solution. Solutions of lower concentrations were prepared fresh every day by aliquot dilution of the stock solution in Pyrex or Jena glassware.

Na_2HPO_4 . A 0.5 molar solution.

$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ (Merck's grade). A 0.5% solution freshly prepared every day and kept away from direct sunlight and other stronglight.

$\text{C}_6\text{H}_5 \cdot \text{NO}$. A 0.05% solution, prepared by dissolving an appropriate quantity of substance in redistilled water at 70°C. The solution must be prepared fresh every 8 to 10 days.

All the reagents used, except the nitrosobenzene, were *c. p.* grade.

Sensitivity

The effect of temperature, acidity of the solution, concentration of the reagents and the presence of some ions on the sensitivity of the test has been studied. It has been found that at too high a temperature (70 to 80°C) the blank gives a positive reaction. The temperature of 60°C has been adopted as giving a negative blank test and a sufficiently fast reaction (2 minutes at the most). The acidity of the

solution also affects the sensitivity of the test. While the spot tests developed for mercury, silver and gold on the base of analogous reactions have a maximum sensitivity in slightly acid solutions (acetate buffer), the test for Pd is most sensitive when the reaction is alkaline. The affect of the pH on the sensitivity has been investigated by means of acetate and phosphate buffers, and also by means of Na_2HPO_4 , NH_4OH , and NaOH solutions. High sensitivity was attained by using a 0.5 molar solution of Na_2HPO_4 , corresponding to a pH of approximately 9. Less concentrated solutions gave a lower sensitivity. The concentration of the $\text{K}_4[\text{Fe}(\text{CN})_6]$ test solution also affects the sensitivity: a higher concentration (above 1%) gives a somewhat higher sensitivity, but may cause the blank to be positive. Therefore the concentration of 0.5% has been adopted for further work. As to the concentration of the nitrosobenzene solution, 0.02 to 0.05% gave high sensitivities.

In studying the effect of the time of heating, it has been found that within 2 minutes the positive reaction appears under optimum conditions and with the Pd concentration at the lower limit of sensitivity.

With optimum conditions prevailing, the sensitivity of the spot test has been found to be the following:

| | |
|-------------------------|-----------------------------|
| limit of identification | 0.02 $\mu\text{g}/0.04$ ml. |
| concentration limit | 1 : 2,000,000. |

Interferences

Since it was known that mercury, silver and gold give an effect analogous to the one produced by palladium (the effect showing a maximum in a slightly acid medium), these cations have been investigated for interferences with the test for palladium under its optimum conditions (alkaline reaction). The results of these investigations, as well as the effect of some other cations and anions are shown in Table I. It is interesting to note that a pretty large excess of iodides does not interfere with this spot test for Pd, while even an equivalent amount of I^- interferes with the detection of Pd by the test based on the principle of induced reduction of Ni^{2+} with NaH_2PO_2 .²¹

TABLE I

Interferences

| Concn. of Pd: 0.1 $\mu\text{g}/\text{drop}$ (2×10^{-5} M/l) | | |
|---|--------------------|--------------------------------------|
| Ion | Concn. in M/l | Remark |
| K^+ | 1×10^{-1} | Without effect |
| Na^+ | 1×10^{-1} | " " |
| Hg^{2+} | 1×10^{-6} | The same effect as with Pd |
| Au^{3+} | 1×10^{-5} | " " " |
| Ag^+ | 1×10^{-5} | " " " |
| PtCl_6^{2-} | 1×10^{-3} | Considerable decrease of sensitivity |
| Fe^{3+} | 1×10^{-3} | Slight influence |
| Cu^{2+} | 1×10^{-3} | Strong interference ^{a)} |
| Cl^- | 1×10^{-2} | No influence |
| SO_4^{2-} | 1×10^{-2} | " " |
| NO_3^- | 1×10^{-2} | " " |
| HPO_4^{2-} | 5×10^{-1} | " " |
| I^- | 1×10^{-3} | " " |
| | 1×10^{-1} | Considerable decrease of sensitivity |
| CN^- | 1×10^{-4} | The effect is strongly inhibited |

a) Even by decolorizing the $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ (after warming) with 0.01 M KCN, the sensitivity is greatly reduced.

Procedure

In the bottom of a dry test-tube or micro test-tube is placed first a drop of a 0.5 molar solution of Na_2HPO_4 , then a drop of a freshly prepared 0.5% solution of $\text{K}_4[\text{Fe}(\text{CN})_6]$, next a drop of a 0.05% aqueous solution of nitrosobenzene, and at last a drop of the solution to be tested. A blank is run with a drop of distilled water instead

of the tested solution. The test-tubes are immersed into a water bath at $60 \pm 2^\circ\text{C}$ for two minutes at the most. A pink or violet coloration reveals the presence of palladium above 2×10^{-6} moles/liter in the absence of mercury (above 1×10^{-6} M/l), silver (above 1×10^{-5} M/l), and gold (above 1×10^{-5} M/l).

REFERENCES

1. T. Pinter, *Farm. Glasnik* **3** (1940) 932.
2. T. Pintar and H. Dresner, *Mikrochim. Acta* **4** (1955) 803.
3. F. Feigl and A. Caldas, *Anal. Chim. Acta* **13** (1955) 526.
4. V. Karas and T. Pinter, *Croat. Chem. Acta* **30** (1958) 141.
5. I. Kraljić, *Mikrochim. Acta* **9** (1960) 586.
6. I. Kraljić, *Z. anal. Chem.* in press. See also: M. N. Orlova and K. B. Yatsimirskii, *Izvest. Vysshikh Ucheb. zavedenii, Khim. i Khim. Tekhnol.* **3** (1960) 630.
7. O. Baudisch, *Ber.* **54** (1921) 413.
8. F. Feigl, V. Anger, and O. Frehden, *Mikrochemie* **15** (1934) 183.
9. S. Ašperger, I. Murati, and O. Čupahin, *J. Chem. Soc.* **1953** 1041.
10. I. Kraljić, M. Kopriva, and M. Pungaršek, *Bull. sci. Conseil acad. RPF Yougoslavie* **3** (1957) 104.
I. Kraljić, *Mém. XVI. Congrès Intern. de Chimie Pure et Appliquée*, Paris 1957., p. 823.
11. I. Kraljić and M. Mate, *Croat. Chem. Acta* **28** (1956) 249.
12. I. Kraljić, *Bull. sci. Conseil acad. RPF Yougoslavie* **3** (1957) 103.
13. To be published.
14. I. Kraljić and M. Mate, *Bull. sci. Conseil acad. RPF Yougoslavie* **3** (1956) 5;
Croat. Chem. Acta **28** (1956) 273.
15. I. Kraljić, *Croat. Chem. Acta* **32** (1960) 43.
16. I. Kraljić, *Anal. Chim. Acta* **23** (1960) 514.
17. G. Emschwiller, *Contributi teorici e sperimentali di polarografia*, vol. 3^o, Supplemento a *La Ricerca Scientifica*, Anno 27^o — 1957, p. 3—22.
18. I. Kraljić, *Croat. Chem. Acta* **32** (1960) 103.
19. Unpublished studies.
20. J. H. Yoe and L. G. Overholser, *J. Am. Chem. Soc.* **61** (1939) 2058; **63** (1941) 3224.
21. F. Feigl and E. Fränkel, *Ber.* **65** (1932) 340.

IZVOD

**Dekompozicija heksacijanoferata(II) u analizi. VII.
Novi dokaz paladija reakcijom kapi**

I. Kraljić

Na temelju djelovanja Pd^{2+} -iona na dekompoziciju heksacijanoferata(II) u prisutnosti nitrozobenzena razrađen je dokaz paladija reakcijom kapi. Pod optimalnim uvjetima postignuta osjetljivost ovog dokaza za čisti sistem izražena kao granična količina je $0,02 \mu\text{g Pd}$, kod granične koncentracije $1:2,000.000$. Živa, srebro i zlato daju analogni efekt. Jodidi i u velikom suvišku ne smanjuju osjetljivost, dok cijanidi jako smetaju.

ZAVOD ZA ANALITIČKU KEMIJU
TEHNOLOŠKI FAKULTET
ZAGREB

Primljeno 12. siječnja 1961.