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Decomposition of Hexacyanoferrate(II) in Analysis. I. A New Spot Test for Silver

I. Kraljić

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

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A very sensitive and selective spot test for the detection of silver, based on the catalytic action of silver ions on the decomposition of hexacyanoferrate(II) in the presence of nitrosobenzene, has been developed. The intensely coloured violet reaction product makes possible the detection of silver in very diluted solutions. The sensitivity for the pure system, expressed as limit of identification, is 0.004 micrograms, as concentration limit, 1 : 9 275 000. Mercury and gold behave analogously. By following the described procedure, the detection of silver is possible also in the presence of cations giving coloured precipitates with the hexacyanoferrate(II).

Under the influence of ultraviolet light[1] and in the presence of some noble metals (Hg[2,3,4], Au[5,6], Pt[5], Ag[7,8], Pd[8,9]), hexacyanoferrate(II) and nitrosobenzene react to yield the intensely coloured violet pentacyanide complex[3,10,11] $[Fe(CN)_5 \cdot NOC_6H_5]^{3-}$:

$$[Fe(CN)_6]^{4-} + NOC_6H_5 \xrightarrow[Hg,Ag\ldots]{} [Fe(CN)_5 \cdot NOC_6H_5]^{3-} + CN^- \qquad (1)$$

In the absence of nitrosocompounds, that stabilize the pentacyanide complex, the decomposition of $[Fe(CN)_6]^{4-}$ proceeds to completion, *i. e.* at least part of the $[Fe(CN)_6]^{4-}$ is decomposed to yield Fe^{2+} and 6 CN^-. The demasked bivalent iron is then oxidized by oxygen present in the solution, and with the excess of $[Fe(CN)_6]^{4-}$ yields Prussian blue.

The total decomposition of hexecyanoferrate(II) was used by Feigl and Caldas for the detection of Ag, Ag halides *etc.* by a method in which the demasked iron (Fe^{2+}) is revealed by reaction with 2,2'-dipyridyl[8].

When studying the possible interference of silver in the spot test for mercury[4,7] based on the partial decomposition of $[Fe(CN)_6]^{4-}$ in presence of nitrosobenzene, it has been observed that silver reacts analogously [Reaction (1)]. If this reaction is conducted in the presence of a sufficient quantity of nitrosobenzene, the violet pentacyanide complex is formed, in the contrary case, the silver favours more the formation of Prussian blue. In that case, in the presence of Hg and Ag, and when a small quantity of nitrosobenzene is added, the appearing violet colour (caused by Hg) has a more or less blueish hue (by the influence of Ag). This may be utilized for the simultaneous detection of both those cations, — of course in the absence of Au and Pd, which behave analogously.

EXPERIMENTAL

Reagents

$AgNO_3$. A 0.01 molar solution was used as stock solution. Diluted solutions 10^{-4} molar or less were prepared fresh every day by appropriate diluting with redistilled water.

$K_4[Fe(CN)_6] + 3H_2O$. 0.25% solution, or 0.5% for the detection of silver in the presence of cations giving a precipitate with $[Fe(CN)_6]^{4-}$. For the detection of silver in very diluted solutions it is necessary to prepare the solution fresh every day. The $K_4[Fe(CN)_6]$ solution should be protected from direct sunlight and other strong light.

$C_6H_5 \cdot NO$. A saturated aqueous solution, obtained by dissolving an excess of the substance in redistilled water at 70°C (on a water bath). Fresh solutions must be prepared every 8 to 10 days. The nitrosobenzene was prepared by oxidation of aniline with Caro's acid[12].

Acetate buffer. 1-molar solution, *p*H 3.5.

Solution *A*. A 4 to 1 mixture of nitrosobenzene and acetate buffer solution.

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

Working method

A drop of the $K_4[Fe(CN)_6]$ solution is placed in the depression of a porcelain spot plate, a drop of solution *A* is added and finally a drop of the solution to be tested. A parallel blank test should be carried out with redistilled water instead of the tested solution, especially when silver in very diluted solutions is to be detected. The spot plate is warmed by moving it uniformly above a small flame of a Bunsen burner. The optimum temperature is 60°C, which can be ascertained by touching the plate with the hand. The blank test serves also as a check of the temperature, since it gives a positive reaction when the temperature is too high. When the concentration of Ag is low, it takes several minutes of warming to develop the colour, and a drop of nitrosobenzene or solution *A* must be added every 1 to 2 minutes, to make up for the nitrosobenzene lost by evaporation. At the end the blank must be colourless or faintly yellowish-green, the tested solution in the presence of Ag takes a more or less intense pink colour.

This test can be carried out also by using microtest tubes. In this case the optimum temperature is obtained simply by dipping the test tubes into a water bath (in a beaker) heated to 60°C.

Sunlight has an effect similar to that of silver *etc.* on the decomposition of hexacyanoferrate(II), so all experiments must be conducted in the shade or under the light of an incandescent lamp.

Sensitivity

In order to develop a test of maximum sensitivity, a study was made of the effects of variations in solution acidity, temperature and concentration of the reagents upon the sensitivity. By using an acetate buffer, a high sensitivity is obtained at a *p*H of 3.2 and 3.5. Since an insufficient concentration of nitrosobenzene (NOPh) gives rise to the formation of Prussian blue, the NOPh being, moreover, volatile, it is necessary to use a higher concentration of NOPh in this test. The concentration of the buffer solution is of importance for the sensitivity in as much as very acid or alcaline solutions require larger quantities of buffer. The sensitivity is also affected by the concentration of the $K_4[Fe(CN)_6]$ solution: a high sensitivity is attained by using a 0.25% solution, but for the detection of Ag in the presence of larger quantities of cations giving precipitates with hexacyanoferrate(II), it is necessary to use a 0.5% solution. In this case, the heating must be accomplished with great caution, to avoid the positive reaction occurring in the blank test. As to the effect of temperature, it has been ascertained experimentally that at low temperatures the colour is developed too slowly, while at too high temperatures also the blank test gives a positive reaction. A temperature of about 60°C gives optimum results.

For subsequent work the following conditions have been adopted:

*p*H: 3.5
Temperature: about 60°C
$K_4[Fe(CN)_6]$: 0.25% or 0.5% solution
Nitrosobenzene: saturated aqueous solution.

The study of the sensitivity of the spot test for the pure system revealed that the positive reaction still occurs on addition of one drop of a 1×10^{-6} molar $AgNO_3$ solution so that

the limit of identification is 0.004γ/0.035 ml. and
the concentration limit 1 : 9275000.

Interference of cations

Although the detection of silver with this spot test is very selective, it was necessary to investigate the effect of other cations and anions upon it. Table I summarizes the results of the interference studies with cations. Of all the cations examined, only Hg and Au (and Pd) react analogously as Ag, and hence interfere with the detection of this element. The sensitivity of the test is adversely affected by some cations, as Mn, Co, Ni, when they are present in relatively large quantities in comparison to Ag. A third kind of cation interference is that by Cu^{2+}, Fe^{3+} and UO_2^{2+}, which give with $[Fe(CN)_6]^{4-}$ intensely coloured precipitates. This interference is eliminated by using an appropriate procedure (see Table I). Cations that do not react with $[Fe(CN)_6]^{4-}$ as a rule have no influence on the sensitivity of the test.

The interference of Hg can be eliminated by evaporating the tested drop to dryness in a microcrucible and slightly igniting it to remove the mercury. In the presence of small amounts of gold, the pink colour appears at the very beginning of heating; if no colour change occurs on continued heating, only gold is present, a gradual deepening of colour indicates the presence of silver.

TABLE I

Interferences of cations

Concentration of Ag: 0.04γ/drop (10^{-5} M/l)

Cation	Concentration of cation in$M$/l or Ag:Me (by weight)	Remark
K	0.1 M	Without effect
Na	0.1 M	
Mg	0.03 M	
Ca	0.1 M	
Sr	0.1 M	
Ba	0.1 M	
Au	$2 \times 10^{-5} M$	The same effect as with Ag
Hg	$4 \times 10^{-7} M$	The same effect as with Ag
Pb	1 : 100	Considerable decrease of sensitivity
Cu	1 : 100	After warming the precipitate must be destroyed with NH_4OH or NaOH
Cd	1 : 100	Slight influence
As (AsO_2^-)	1 : 50	Considerable decrease of sens.
Fe^{3+}	1 : 25	Completely inhibits the effect
	1 : 10	Slight influence — the addition of NH_4OH after warming is necessary
Al	1 : 100	Slight influence
Cr	1 : 100	Slight influence
Co	1 : 50	Strong decrease of sensitivity
	1 : 25	Slight influence
Ni	1 : 25	Considerable decrease of sens.
	1 : 10	Without effect
Mn	1 : 50	Completely inhibits the effect
	1 : 10	Considerable decrease of sens.
Zn	1 : 100	Slight influence
U (UO_2^{2+})	1 : 100	After warming the precipitate must be destroyed with NH_4OH

Interference of anions

The results of experiments to determine the effect of anions upon the sensitivity of the test are summarized in Table II. The majority of the anions investigated have no influence on either sensitivity or uniqueness of the spot test. Free cyanides, which generally interfere with many reactions for silver, have no effect on this spot test, since they are removed as HCN by heating in acid medium. Iodides and thiosulphates were the only anions, of the ones investigated, that partly or wholly inhibit the catalytic action of silver. Some anions, on the contrary by their presence increase the velocity of the reaction.

TABLE II

Interferences of anions

Concentration of Ag: 0.04γ/drop (10^{-5} M/l)

Anion	Concentration of anion in M/1	Remark
Cl^-	0.10	Greater sensitivity
Br^-	0.10	Without effect
J^-	10^{-4}	Strong decrease of sensitivity
	2×10^{-5}	Considerable decrease of sens.
CNS^-	0.01	Greater sensitivity
	10^{-4}	Without effect
HPO_4^{2-}	0.10	” ”
$C_2O_4^{2-}$	0.10	Greater sensitivity
SO_3^{2-}	0.10	Strong decrease of sensitivity. By addition of solution *A* during warming only slight influence
CN^-	0.01	Slight influence
$B_4O_7^{2-}$	0.01	Greater sensitivity
$S_2O_3^{2-}$	0.01	Completely inhibits the effect
	1×10^{-4}	Considerable decrease of sensitivity. By addition of solution *A* during warming better results are obtained
SO_4^{2-} NO_3^- CH_3COO^-		Without effect

Procedure

In the depression of a spot plate a drop of the $K_4[Fe(CN)_6]$ solution is placed first, then a drop of solution *A*, and next a drop of the solution to be tested. When the concentration of Ag is low, the simultaneous carrying out of a blank test is indispensable. The spot plate is then uniformly moved above the flame of a small Bunsen burner to heat it to about 60°C. With low concentrations of silver the heating must be continued for several minutes, and every 1 to 2 minutes a drop of nitrosobenzene or *A* solution must be added to make up for the nitrosobenzene lost by evaporation. A pink coloration, with the blank remaining colourless or faintly yellowish-green, indicates the presence of Ag in concentrations above 10^{-6} moles/litre (in the absence of Hg above 4×10^{-7} moles/litre and Au above 2×10^{-5} moles per litre).

For the detection of Ag in the presence of Fe^{3+}, Cu^{2+} and UO_2^{2+}, the coloured precipitate must be destroyed by addition of NH_4OH or NaOH solution, in order to make the pink colouration easier visible.

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IZVOD

Dekompozicija heksacijanoferata(II) u analizi. I. Novi dokaz srebra reakcijom kapi

I. Kraljić

Na temelju djelovanja srebra na dekompoziciju heksacijanoferata(II) u prisutnosti nitrosobenzena razrađen je selektivni i vrlo osjetljivi dokaz srebra tehnikom reakcije kapi. Osjetljivost dokaza za čisti sistem iznosi 0,004γ/0,035 ml, što odgovara graničnoj koncentraciji od 1 : 9,275.000. U odsutnosti žive (iznad 4×10^{-7} *M*/l) i zlata (iznad 2×10^{-5} *M*/l) ljubičasti reakcioni produkt je dokaz za prisutnost srebra. Opisanim postupkom može se dokazati srebro i u prisutnosti većih količina (relativno prema srebru) kationa, koji s $[Fe(CN)_6]^{4-}$ daju bojadisane taloge.

ZAVOD ZA ANALITIČKU KEMIJU
TEHNOLOŠKI FAKULTET
ZAGREB

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