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A New Very Sensitive and Selective Spot Test for Mercury

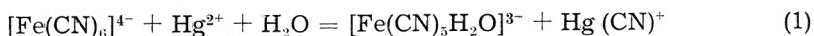
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A sensitive and selective test for the detection of mercury has been developed based on the strong catalytic action of mercuric ions on the decomposition of hexacyanoferrate (II) in the presence of nitrosobenzene. The sensitivity for the pure system expressed as limit of identification (in 0.05 ml.) is 0.002 microgram of mercury at a limiting concentration of 1 to 25,000,000. Of the cations studied only silver and gold give an analogous reaction. By following an appropriate procedure, mercury can be detected even when it is present in mixtures with cations giving coloured precipitates with the hexacyanoferrate (II).

By catalytic action of mercuric ions on the hexacyanoferrate (II) in presence of nitroso-benzene (NOPh), a violet water-soluble ion $[\text{Fe}(\text{CN})_5\text{NOPh}]^{3-}$ is formed¹.



The maximum catalytic action of mercury occurs at pH 4.1². The reaction rate is comparatively low at room temperature; by raising the temperature to 60°C the reaction is accelerated and the test becomes more sensitive. By using appropriate concentrations of the $\text{K}_4[\text{Fe}(\text{CN})_6]$ and NOPh solutions, by addition of acetate buffer (pH 4.1) and by heating, a great sensitivity of the test is obtained.

EXPERIMENTAL

1. Reagents

HgCl_2 . A 0.01 molar solution was used as stock solution. Diluted solutions were obtained by diluting the stock solution with distilled water.

$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3 \text{H}_2\text{O}$. 0.2% solution for the pure system and in the presence of small amounts of cations giving a precipitate with hexacyanoferrate (II). When such cations are present in higher concentrations, a 0.5% or 1.0% solution should be used. In order to obtain greatest sensitivity, the solution should be made up fresh each day and protected from direct sunlight.

$\text{C}_6\text{H}_5\text{NO}$. Saturated aqueous solution obtained by dissolving the substance in distilled water at 70°C, prepared fresh every week. Nitrosobenzene was prepared by oxidation of aniline with Caro's acid³.

Acetate buffer. 1-molar solution, pH 4.1.

Solution A. Mixture of acetate buffer and saturated solution of NOPh, 1 to 9, prepared fresh daily. When the solution to be tested is strongly acidic or alkaline, the concentration of the buffer must of course be increased by raising the above ratio to 1 : 4 or by adding a drop of pure acetate buffer.

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

2. Working method

All the experiments were performed on a porcelain spot plate or in micro-test tubes by using 1 drop (0.05 ml.) of diluted solution of HgCl_2 , then adding 1 drop (0.05 ml.) of solution A, and next 1 drop (0.02 ml.) of the solution of hexacyanoferrate (II).

When the spot plate is used, the warming about to 60°C can be carried out by moving the plate uniformly above a small and broad flame of a Bunsen burner. In the micro-test tubes the appropriate temperature can be obtained by dipping the test tubes into a water bath (in a beaker) heated to 60°C .

The procedure with the spot plate takes more time than with the test tubes, and as the nitrosobenzene is volatile, it is necessary to add every 2 minutes a new drop of the saturated solution of nitrosobenzene. When the concentration of mercury in the solution to be tested is very low (below $10^{-6} \text{ M}/1 \cdot \text{HgCl}_2$), a blank must be run simultaneously with the test. The blank serves also as a check on the temperature, since it gives a positive reaction when the temperature is too high (above 60°C).

In order to exclude the influence of sunlight, which has an effect similar to that of mercury, all the experiments have been conducted in the shade or in the light of an incandescent lamp. The sensitivity of the eye for faint pink or violet colour is greater in suitable artificial light than in daylight, which is important for the detection of mercury in concentrations near the concentration limit of the test.

3. Sensitivity

The sensitivity of the method has been first ascertained for the pure system, following both procedures, i. e. with the porcelain spot plate and with micro-test tubes. In both cases the same sensitivity was measured, which was, expressed as limit of identification, 0.002 microgram of mercury and, as concentration limit, 1 : 25,000.000.

TABLE I

Relation of reaction-time to concentration; micro-test-tubes procedure

Conc. HgCl_2	at 20°C	At 60°C
$1 \times 10^{-4} \text{ M}/1.$	30—40 sec.	5—10 sec.
$1 \times 10^{-5} \text{ M}/1.$	4 min.	15—20 „
$3 \times 10^{-6} \text{ M}/1.$		30 „
$1 \times 10^{-6} \text{ M}/1.$		50—60 „
$5 \times 10^{-7} \text{ M}/1.$		< 2 min.
$3 \times 10^{-7} \text{ M}/1.$		2 „
$2 \times 10^{-7} \text{ M}/1.$		2,5 „

The procedure using micro-test tubes is quicker, due to the better heat transfer through the thin glass walls: it takes not more than 2.5 to 3 minutes, as compared with up to 10 minutes for the procedure using the spot plate. By measuring the time elapsed from the moment when heat is applied to the first positive reaction, the concentration of the solution tested can be approximately estimated, as appears also from Table I, embracing a range of concentrations from 2×10^{-7} to 1×10^{-4} M/l of mercury.

4. Interferences of cations

By the procedure with the porcelain spot plate interference studies were made including cations of all six analytical groups, as well as some other cations. The solutions of the cations were prepared from c. p. grade salts: nitrates, sulphates, acetates and chlorides. The results of these studies are summarized in table II.

TABLE II
Interferences of cations
Concentration of Hg^{2+} : 0,02 $\mu g./0,05$ ml. (2×10^{-6} M/l.)

Cation	Me: Hg (by weight) ^{a)}	Remark
Ag		2×10^{-6} molar solution gives the same effect as mercury
Pb	200	
Bi	200	
Cu ²⁺	200	Cu ₂ [Fe(CN) ₆] precipitate must be destroyed after warming(with NH ₄ OH)
Cd	200	
Sn	20	
Sb	25	
As (AsO ₂ ⁻)	50	
Fe ³⁺	200	Prussian blue must be destroyed after warming (with NH ₄ OH)
Al	200	
Cr	200	
Co	50	
Ni	50	
Mn	100	
Zn	200	
Ca, Sr, Ba		0.1 molar solution is without affect
Mg	2.000	
K, Na, NH ₄		These cations show no interferences
UO ₂ ²⁺	200	(UO ₂) ₂ [Fe(CN) ₆] precipitate must be destroyed after warming (with NH ₄ OH)
Au ³⁺		1×10^{-5} molar solution gives the same effect as mercury

a) Condition at which the test is slightly influenced by the presence of these cations.

Of the cations studied only silver and gold react similarly as mercury and hence interfere with the detection of mercury when present in concentrations greater than 2×10^{-6} M/l · Ag and 1×10^{-5} M/l · Au.

Fe^{3+} , Cu^{2+} and UO_2^{2+} give coloured precipitates, but their interference is readily eliminated by making the solution alkaline with diluted NH_4OH , after it has been warmed. In the presence of greater amounts of trivalent iron it is recommended to add also a drop of a 10% solution of potassium-sodium-tartrate, and in the presence of greater amounts of copper, a diluted solution of potassium cyanide.

5. Interference of anions

Table III summarizes the results of the study of interference including some anions (as potassium or sodium salts) with the test for mercury.

TABLE III
Interferences of anions
Concentration of Hg^{2+} : 0,02 $\mu\text{g.}/0.05$ ml. (2×10^{-6} M/l.)

Anion	Concentration of anion ^{a)}	Remark
SO_4^{--} , NO_3^- , $\text{C}_2\text{H}_3\text{O}_2^-$		Without effect
Cl^-	0.01 M/l.	
Br^-	0.01 M/l.	
J^-	1×10^{-4} M/l.	2×10^{-4} M solution inhibits strongly the catalytic action
CN^-	0.01 M/l.	
CNS^-	0.01 M/l.	
SO_3^{--}	0.01 M/l.	
HPO_4^{--}	0.01 M/l.	
$\text{C}_2\text{O}_4^{--}$	0.01 M/l.	

a) Condition at which the test is slightly influenced by the presence of these anions.

The majority of the anions studied does not affect significantly the sensitivity of the test. Iodides, when present in a higher amounts, impair considerably the sensitivity of the test, and may even completely inhibit the catalytic action of mercury. Cyanides, which inhibit many reactions in which mercury takes part, affect adversely also the action of mercury in this reaction, but only in the cold⁴. On heating, the cyanides are volatilized as HCN , since the test is conducted in a feebly acidic medium; the sensitivity of the test is therefore only insignificantly affected even by larger concentrations of cyanides. The detection of mercury by this method is possible also in the presence of sulphides (H_2S), if the amounts present are not excessive. This is due to the fact that nitrosobenzene oxidizes S^{2-} to elemental sulphur, thus demasking the mercury.

6. Procedure

To 1 drop (0.05 ml.) of the solution to be tested, placed in the hollow of a spot plate or in a micro-test tube, 1 drop (0.05 ml.) of solution A is added, followed by 1 drop (0.02 ml.) of a 0.5% solution of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$. When the concentration of Hg is known to be very small, a parallel blank must be run. The reaction is accelerated by heating to 60°C . When working with micro-test tubes the heating takes not more than 2.5 to 3 minutes, with the

porcelain spot plate it may take up to 10 minutes, depending on the thickness of the porcelain wall. When the spot plate is used, a new drop of nitrosobenzene must be added every 2 minutes as long as the heating is going on. In the absence of silver ($2 \times 10^{-6} M/l.$ or more) and gold ($1 \times 10^{-5} M/l.$ or more) in the solution, a violet or pink coloration indicates the presence of mercury. If on addition of the hexacyanoferrate (II) solution a coloured precipitate is formed (owing to the presence of Fe^{3+} , Cu^{2+} , UO_2^{2+}), the precipitate must be destroyed after heating by addition of 1 drop of diluted NH_4OH ; in the presence of mercury, the violet coloration of the solution then becomes apparent. If copper is present in higher concentrations, it gives a blue coloration with the NH_4OH ; this is readily discharged by adding 1 drop of a diluted solution of KCN. In the presence of greater amounts of Fe^{3+} , the addition of 1 drop of a 10% solution of K-Na-tartrate will prove helpful.

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IZVOD

Novo, vrlo osjetljivo i selektivno dokazivanje žive u kapi*I. Kraljić i M. Mate*

Na temelju jakog katalitičkog djelovanja živinih iona na raspad heksacijanoferata (II) u prisutnosti nitrozobenzena razrađena je osjetljiva i selektivna metoda za detekciju žive reakcijom u kapi. Osjetljivost metode za čisti sistem izražena kao granica identifikacije je $0.002 \mu g Hg$ (u 0.05 ml), a kao granična koncentracija (concentration limit) 1:25,000.000. Od ispitanih kationa analognu reakciju daju još srebro i zlato. Uz odgovarajuće uvjete metoda omogućuje dokaz žive i u prisutnosti kationa, koji sa heksacijanoferatom (II) daju bojadisane taloge.

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