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Photometric Determination of Microquantities of Cyanides

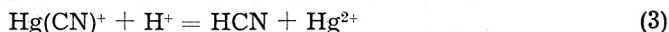
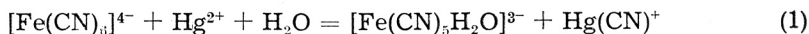
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The catalytic action of mercuric ions upon the reaction of potassium ferrocyanide and nitrosobenzene is strongly inhibited by even small concentrations of cyanide ions. The progress of the inhibitive effect may be observed by measuring the extinction of the violet reaction product $[\text{Fe}(\text{CN})_5\text{NPh}]^3$. A method for the quantitative photometric determination of microquantities of cyanides has been developed. The coefficient of variation for a concentration of 1×10^{-5} — 8×10^{-5} M/l of cyanide ion is shown to be 1.0 — 6.3%.

According to Ašperger et al.^{1,2,3}, mercuric ions exert a catalytic action on the decomposition of potassium ferrocyanide by reacting with one of the cyano-groups (reaction 1) to produce an aquo-penta-cyano-ferrate, which in its turn reacts with nitrosobenzene, giving a violet coloured product $[\text{Fe}(\text{CN})_5\text{NPh}]^3$ (reaction 2), and reproducing the mercuric ion (reaction 3).



Since the free cyanides prevent many reactions of mercury, it was legitimate to suppose that an addition of cyanide would inhibit the catalytic action of the mercuric ion, and our experiments proved this supposition to be right. An addition of as little as 1 microgram of cyanide to 25 ml. of solution brings about a measurable effect. In our endeavour to establish optimal conditions for this inhibitive effect we developed a photometric method for the determination of cyanides in microquantities.

EXPERIMENTAL

1. Apparatus

A Fisher Elektrophotometer was used with cylindrical cells of 22.6 mm. diameter, and the B525 green filter showing maximum transmission at 525 millimicrons (the absorption maximum of the reaction product¹ is at 528 millimicrons). The temperature of the water thermostat used could be controlled within $\pm 0.2^\circ\text{C}$.

2. Reagents

The *nitrosobenzene* was prepared by oxidation of aniline with Caro's acid⁴. The aqueous solution of nitrosobenzene was prepared by dissolving 0,1338 mg. of nitrosobenzene in 250 ml. at 70° on the water bath, and making up to volume with distilled water in a volumetric flask. The aqueous solution of nitrosobenzene is

stable for a few days, on prolonged standing it becomes turbid. The molar concentration of nitrosobenzene is always stated in terms of the monomeric form.

$K_4[Fe(CN)_6] \cdot 3 H_2O$. The aqueous solution was obtained by accurately weighing 0,211 g of the salt and dissolving it in 100 ml. of distilled water. Under the action of light and also if allowed to stand in the dark for a prolonged time, the solution of ferrocyanide turns yellow, and free cyanide ions are formed. Since these would have interfered with the experiments, the solution was freshly prepared every day.

$HgCl_2$. By dissolving an accurately weighed quantity of the salt in a volumetric flask, a 0,01 molar stock solution was prepared. The other concentrations were obtained by suitably diluting the stock solution with distilled water immediately before use. On prolonged standing the diluted solutions undergo a change of concentration due to adsorption on the glass.

The solution of mercuric cyanide was prepared in an analogous way.

KCN. Diluted solutions of potassium cyanide were prepared by standardizing an approximately 0.01 molar solution after Liebig-Denigès immediately before use, and diluting it with water to the selected concentration. Part of the experiments were performed with a 0.01 molar solution of KCN in 80% iso-propyl alcohol, diluted with water immediately before use.

Acetate buffer. A 1 M solution of acetic acid was mixed with a 1 M solution of sodium acetate in the suitable proportions to obtain a pH of 3.5 to 6.2. 1 ml. of buffer solution was always added to 25 ml. total volume of the sample.

Solution A. We term solution A the mixture of nitrosobenzene, $HgCl_2$ and acetate buffer solutions, freshly prepared every day by mixing the single solutions in such a proportion that 4 or 5 ml. of the resulting mixture, added to the sample solution, produce the desired concentration of nitrosobenzene, $HgCl_2$ and buffer. As a consequence, the sample and the standard always contain the same proportion of these reagents. This tends to simplify the procedure when the method is used in routine analysis.

All the reagents, with the exception of nitrosobenzene, were a. p.

Procedure

Determined amounts of distilled water (for the standard), diluted solution of KCN and solution A are added out of burettes into small Pyrex flasks. As a consequence of adding determined amounts of water, the total volume on addition of the ferrocyanide solution was always the same and equal to 25 ml. Before adding the ferrocyanide solution, the flasks were allowed to stand in a constant-temperature water bath for about 15 minutes, in order to equalize temperatures. The ferrocyanide solution was also kept in the constant-temperature bath.

Exactly 20 minutes after addition of the ferrocyanide solution the extinction was measured against water as the reference solution. For every run of measurements we determined also the extinction of a standard containing the same concentration of all reagents, except the cyanide, as the other samples.

To avoid the possible action of sunlight, which is known to exert a catalytic action upon the decomposition of the ferrocyanide, all the experiments were performed in the shade.

Effect of Acidity of Solution

The effect of the acidity of the solution on the inhibitive action of the cyanide ion was investigated first. Constancy of pH was achieved by the use of the acetate buffer. It is evident from the graph in Fig. 1 that the inhibitive action increases with the increase of pH, in keeping with the fact that HCN is a very weak acid and, consequently, is practically undissociated in acid solutions. At pH 6.2 the curve has become almost horizontal, a further increase of pH cannot be expected to lead to an increase of sensitivity.

All the ensuing experiments were performed at pH 6.2.

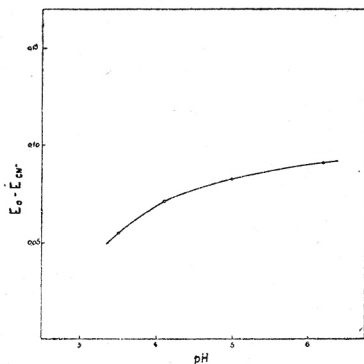


Fig. 1.

Fig. 1. Dependence of inhibition on pH in the 20 th minute. HgCl_2 : 4×10^{-6} M/l.; CN^- : 7.8 $\mu\text{g}/25$ ml.; NOPh : 6×10^{-4} M/l.; $\text{K}_4[\text{Fe}(\text{CN})_6]$: 8×10^{-4} M/l.; temp.: 20° C.

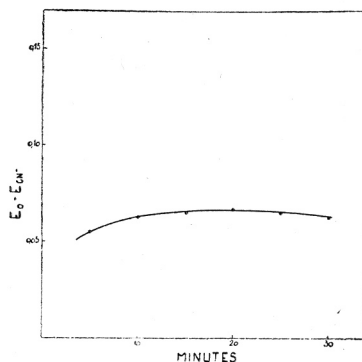


Fig. 2.

Fig. 2. Dependence of inhibition on the time of reaction. HgCl_2 : 16×10^{-6} M/l.; CN^- : 5.2 $\mu\text{g}/25$ ml.; NOPh : 6×10^{-4} M/l.; $\text{K}_4[\text{Fe}(\text{CN})_6]$: 8×10^{-4} M/l.; temp.: 20° C; pH: 6.2.

Effect of Time

At determined intervals of time beginning from the start of the reaction, the extinctions of the standard and the sample containing 5.2 micrograms in 25 ml. at pH 6.2 were measured. It is apparent from the graph in Fig. 2, where the difference between the extinctions of the standard and the sample is plotted against time, that a maximum of sensitivity is reached about the twentieth minute. The curve in the vicinity of the maximum is very flat, indicating that the time of taking readings is not critical.

For all the ensuing experiments the reaction time was fixed at 20 minutes.

Effect of the Concentration of Mercuric Ions

The effect of the concentration of mercuric ions (as HgCl_2) is apparent from the graph in Fig. 3. At lower concentrations of mercuric chloride, the inhibitive effect is less pronounced, while at higher concentrations it is virtually independent of the concentration of mercuric chloride.

A solution of mercuric cyanide also is known to have a catalytic effect

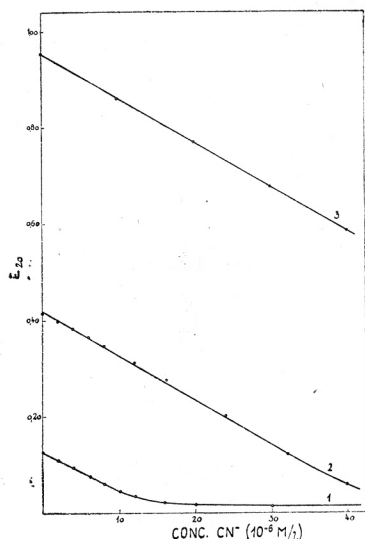


Fig. 3.

Fig. 3. Dependence of inhibition on the concentration of HgCl_2 in the 20th minute. HgCl_2 : 1.: 4×10^{-6} M/l., 2.: 16×10^{-6} M/l. 3.: 40×10^{-6} M/l. NPh 6×10^{-4} M/l.; $\text{K}_4[\text{Fe}(\text{CN})_6]$ 8×10^{-4} M/l.; temp. 20°C ; pH 6,2.

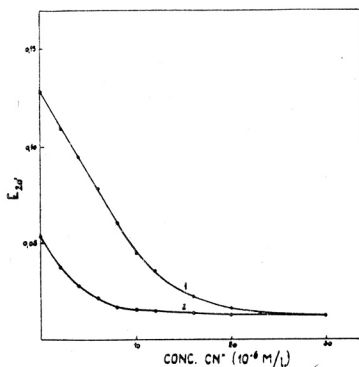


Fig. 4.

Fig. 4. Dependence of inhibition on HgCl_2 and $\text{Hg}(\text{CN})_2$ in the 20th minute. 1.: 4×10^{-6} M/l. HgCl_2 ; 2.: 4×10^{-6} M/l. $\text{Hg}(\text{CN})_2$; NPh 6×10^{-4} M/l.; $\text{K}_4[\text{Fe}(\text{CN})_6]$ 8×10^{-4} M/l.; temp. 20°C ; pH: 6,2.

TABLE I

Dependence of inhibition on the concentration of nitrosobenzene in the 20th minute. HgCl_2 : 16×10^{-6} M/l.; CN^- : $5,2 \mu\text{g}/25 \text{ ml}$.; $\text{K}_4[\text{Fe}(\text{CN})_6]$ 8×10^{-4} M/l.; pH: 6,2; temp.: 20°C

Conc. NPh ($\times 10^{-4}$ M/l.)	1	2	4	8	16
$E - E_{\text{CN}}$ ($\times 10^{-2}$)	6.4	7.3	7.4	7.6	7.4

Effect of the Concentration of Ferrocyanide

The effect of the concentration of ferrocyanide has also been examined. Table II shows the results of these experiments. With increasing concentration of ferrocyanide the inhibitive effect is slowly increasing. However, in order to increase the sensitivity to any greater extent, very concentrated solutions should have been used, which we deemed unpractical and unnecessary.

For the ensuing experiments we selected a ferrocyanide concentration of 8×10^{-4} M/l.

TABLE II

Dependence of inhibition on the concentration of $\text{K}_4[\text{Fe}(\text{CN})_6]$ in the 20th minute. HgCl_2 : 10×10^{-6} M/l.; CN^- : $5,2 \mu\text{g}/25 \text{ ml}$.; NPh: 6×10^{-4} M/l.; pH: 6,2 temp. 20°C

Konc. $\text{K}_4[\text{Fe}(\text{CN})_6]$ ($\times 10^{-4}$ M/l.)	2	4	8	16	32
$E - E_{\text{CN}}$ ($\times 10^{-2}$)	6.4	6.9	7.4	7.9	8.5

Effect of Temperature

For the determination of cyanides in an acid medium, elevated temperatures are out of the question, because of the volatility of hydrocyanic acid. The inhibitive effect has been examined at 20° and 30°C. The sensitivity increases with decreasing temperature (see graph in Fig. 5); at 20° C the reaction is about 8% more sensitive than at 30°.

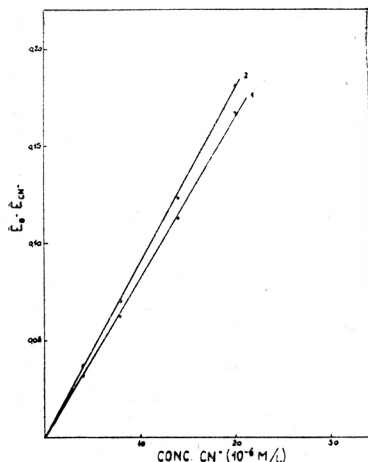


Fig. 5.

Fig. 5. Dependence of inhibition on the temperature in 20th minute. 1. : 30° C; 2. : 20° C; HgCl_2 20×10^{-6} M/l; NOPh 6×10^{-4} M/l; $\text{K}_4[\text{Fe}(\text{CN})_6]$ 8×10^{-4} M/l; pH 6.2.

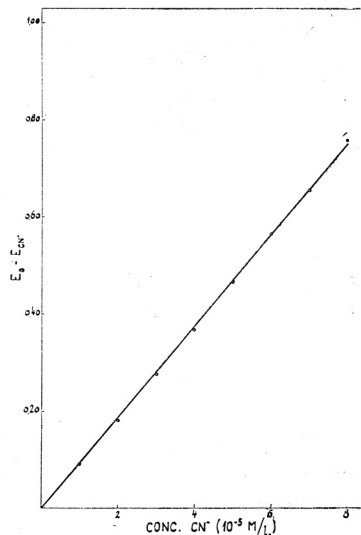


Fig. 6.

Fig. 6. Calibration curve.

Setting up of the Calibration Curve

For the calibration, the following conditions have been selected: Concentration of the reagents (in the final solution):

HgCl_2 — 40×10^{-6} M/l.
 $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ — 8×10^{-4} M/l.
 $\text{C}_6\text{H}_5\text{NO}$ — 6×10^{-4} M/l.
 Acetate buffer pH 6,2 — 4×10^{-2} M/l.
 Temperature — 20°C
 Reaction time — 20 minutes

For every cyanide concentration five independent determinations were available. The arithmetic means of these measurements were plotted as points in Fig. 6, the straight line shown is fitted to the data by the method of least squares.

In Table III the results (extinctions) are presented, as well as the standard deviation, the coefficient of variation and the corresponding values on the straight line fitted to the data.

The equation of regression, obtained by the method of least squares, is

$$C_{\text{CN}^-} = 0,0001066 E \text{ (M/l.)}$$

TABLE III

Conc. CN^- ($\times 10^{-5} \text{M/l.}$)	1	2	3	4	5	6	7	8
$E - E_{\text{CN}^-}$ ($\times 10^{-2}$)	9,5	18,5	27,6	37,1	47,3	56,2	66,0	76,1
	9,2	18,5	28,1	36,7	46,1	56,9	66,2	76,7
	8,3	18,0	26,8	37,5	47,2	55,9	64,8	75,0
	9,5	17,8	27,5	36,3	46,8	56,3	65,3	75,7
	8,7	17,8	27,4	36,6	45,9	56,9	65,9	76,0
\bar{X}	9,04	18,1	27,5	36,8	46,7	56,4	65,6	75,9
$X \text{ calc.}$	9,38	18,76	28,1	37,5	46,9	56,3	65,7	75,0
σ	0,581	0,715	0,747	0,781	0,617	0,422	0,520	1,057
$\sigma \%$	6,3	3,8	2,7	2,1	1,3	0,8	0,8	1,4

$$\sigma = \sqrt{\frac{\sum (X - X \text{ calc.})^2}{N}}$$

When applied to the determination of concentration below 0.2 p.p.m., the accuracy of the method is increased by operating with a lower concentration of the mercuric chloride, and, hence, by calibrating against a $10 \times 10^{-6} \text{M}$ solution.

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IZVOD

Fotometrijsko određivanje mikrokoličina cijanida

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Katalitičko djelovanje živina iona na reakciju između kalijeva ferocijanida i nitrozobenzena (NOPh) uvelike je inhibirano već malom koncentracijom slobodnog cijanidnog iona. Efekt inhibicije daje se pratiti fotometrijskim mjerenjem ekstinkcije ljubičastog reakcionog produkta: $[\text{Fe}(\text{CN})_5\text{NOPh}]^{3-}$. Ispitana je ovisnost inhibicionog efekta o koncentraciji Hg^{++} , $\text{K}_4[\text{Fe}(\text{CN})_6]$, NOPh, zatim o aciditetu otopine, temperaturi te o reakcionom vremenu. Izrađena je nova metoda za kvantitativno određivanje mikrokoličina cijanida u području do $8 \times 10^{-5} \text{M/l.}$

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