Photometric microtitrations
VIII.* Mercurimetric determination of cyanide using Naphthylazoxine 6S as indicator

V ŘÍHA, PHAM-VU QUAT**, V MACH, and S. KOTRLÝ

Department of Analytical Chemistry,
University of Chemical Technology, CS-532 10 Pardubice

Received 7 June 1985

Accepted for publication 27 February 1986

Naphthylazoxine 6S was evaluated as a suitable metal indicator for the determination of cyanide in the concentration range 5×10^{-4} to $1 \times \times 10^{-6}$ mol dm^{-3} The use of photometric indication permitted titration with a dilute standard solution of mercury(II) perchlorate ($c = 0.001$ mol dm^{-3} to 0.01 mol dm^{-3}). Under optimum conditions (pH range 5.0 to 5.5, $I \approx 0.05$ mol dm^{-3}, $c(\text{ind}) = 10^{-5}$ mol dm^{-3}; $\lambda = 530$ nm), precise results were obtained ($s_r/\% \leq 1$). A thin layer of paraffin oil on the surface prevented loss of HCN during titration so that systematic deviations, with respect to the reference Liebig—Dénigès titration with turbidimetric indication, were insignificant ($\lesssim 1$ %). Cyanide can be titrated in presence of an equal amount of chloride or thiocyanate (at pH$\approx$6); bromide interferes, while iodide is titrated with cyanide.

Нафтилазоксин 6S рекомендуется в качестве удобного индикатора металлов для определения цианид-иона в области концентраций от 5×10^{-4} до 1×10^{-6} моль дм$^{-3}$ Использование фотометрической индикации позволило провести титрацию разбавленным стандартным раствором перхлората ртути(II) ($c = 0{,}001$—$0{,}01$ моль дм$^{-3}$). При оптимальных условиях (интервал pH от 5,0 до 5,5, $I \approx 0{,}05$ моль дм$^{-3}$, $c(\text{инд}) = 10^{-5}$ моль дм$^{-3}$; $\lambda = 530$ нм) были получены точные результаты ($s_r/\% \leq 1$). Тонкий слой парафинового масла на поверхности препятствовал потере HCN в ходе титрации, так что систематические отклонения от сравнительной титрации по Либигу—Дениже с турбидиметрической индикацией были незначительны ($\lesssim 1$ %). Цианид-ион может быть титрован в присутствии равного количества хлорид- или тиоцианат-иона (при pH$\approx$6); присутствие бромид-иона мешает титрации, а иодид-ион титруется вместе с цианид-ионом.

---

* For Part *VII* see *Chem. Zvesti 33,* 499 (1979).

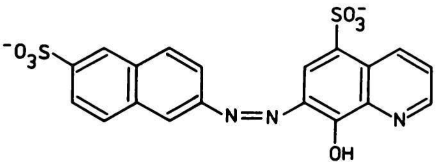
** *Present address:* Vien Bao ho lao dong, Hanoi.

Titrimetric methods for cyanide are generally based on formation of stable cyano complexes, most frequently with the Ag(I), Hg(II), and Ni(II) ions.

The Liebig—Dénigès visual argentometric titration of cyanide in ammoniacal medium is indicated by the first perceivable turbidity of silver iodide which is formed after complete conversion of cyanide into the complex $[Ag(CN)_2]^-$ For milligram amounts of cyanide, turbidimetric end-point indication [1] can be used with advantage to achieve precise results [2]. It is also possible to use *p*-(dimethylamino)benzylidenerhodanine as indicator in alkaline medium [3]: a purple complex is formed with the first excess of silver ion at the end-point (see also Ref. [4]). An indicator system of 1,10-phenanthroline and Bromopyrogallol Red was also suggested for visual and photometric end-point detection within the concentration range of cyanide 10^{-1} to 10^{-4} mol dm^{-3} and 10^{-4} to 10^{-5} mol dm^{-3}, respectively [5].

Mercurimetric titration of cyanide is based on the formation of cyano complexes which are characterized by the following overall stability constants [6]: $\log \beta_1 = 18.00$, $\log \beta_2 = 34.71$, $\log \beta_3 = 38.54$, and $\log \beta_4 = 41.5$ ($\theta = 20$ °C, $I = 0.1$ mol dm^{-3}). A review of mercurimetric (or cyanometric) methods of determination has been presented by *Magee* [7]; a more detailed procedure is described there for a visual titration of an excess of Hg(II) with a standard solution of thiocyanate which forms less stable complexes than cyanide [6]: $\log \beta_1 = 9.08$ ($I = 1.0$ mol dm^{-3}); $\log \beta_2 = 16.43$, $\log \beta_3 = 19.14$, $\log \beta_4 = 21.2$ ($\theta = 25$ °C, $I = 0.1$ mol dm^{-3}). A purple colour of the thiocyanato complex of iron(III) is formed at the end-point. A titrimetric determination can also be based on the formation of a ternary complex $[Hg(CN)(edta)]^{3-}$ [8]. A mass amount of 5 to 100 μg of cyanide is titrated with mercury(II) nitrate ($c = 5 \times 10^{-4}$ mol dm^{-3}) in presence of $H_2(edta)^{2-}$ and SCN^- using photometric indication. The end-point is marked by an increase in absorbance at $\lambda = 240$ nm, which is due to the formation of a less stable complex $[Hg(SCN)(edta)]^{3-}$

The literature indicates that mercurimetry of cyanide remains still an open problem. In a preliminary investigation of various metallochromic indicators, applicable for a mercurimetric titration of cyanide, Naphthylazoxine 6S of the chemical name 7-(6-sulfo-2-naphthylazo)-8-quinolinol-5-sulfonic acid has been selected as the most suitable indicator for photometric microtitration [9].



Naphthylazoxine 6S

A similar, nonsulfonated azo dye, has been proposed by *Cherkesov* [10] as visual indicator for mercurimetry at pH range 2 to 3. Naphthylazoxine 6S has certain advantages: it is more soluble in water and the stock solution is stable. The photometric end-point is shown by an abrupt change in absorbance and is easily evaluated by linear extrapolation of a steep linear section of the curve beyond the equivalence. In the present paper the conditions are discussed for a direct photometric microtitration of cyanide with mercury(II) perchlorate using Naphthylazoxine 6S as indicator, taking into consideration the necessary prior separation of HCN from samples of waste water and sludge.

Experimental

Reagents and solutions

Chemicals of guaranteed reagent grade (Lachema, Brno) and redistilled water were used for the preparation of all solutions and in all experiments.

A stock solution of potassium cyanide ($c = 0.1$ mol dm^{-3}) was prepared by dissolving a known mass of KCN in a dilute solution of sodium hydroxide containing a calculated amount of NaOH to achieve the concentration $c(\text{NaOH}) \approx 0.01$ mol dm^{-3} after making up to volume. Standard solution of 0.001 M-KCN was prepared by dilution and was standardized by Liebig—Dénigès argentometric microtitration with a turbidimetric indication [2].

Standard solution of mercury(II) perchlorate ($c = 0.01$ mol dm^{-3} and 0.001 mol dm^{-3}, respectively) was prepared by dissolving metallic mercury (for polarography) in a small amount of nitric acid. After addition of a double amount of perchloric acid, the solution was evaporated down to fumes of nitric acid, and then diluted with redistilled water to volume. The concentration of mercury(II) was calculated from the known mass of mercury.

Standard solution of silver nitrate ($c = 0.01$ mol dm^{-3}) was prepared from analytical-reagent grade $AgNO_3$. The solution was standardized against dried sodium chloride of primary-standard grade with the use of potentiometric titration.

Naphthylazoxine 6S solution, $c(\text{ind}) = 2 \times 10^{-4}$ mol dm^{-3}, was prepared from a purified and dried sample. Purification of the indicator, which is described elsewhere [9], was realized successfully with both a commercial reagent and a substance obtained by synthesis. It was shown by paper chromatography that no coloured and other impurities were detectable.

Buffer solutions

If found necessary, the solutions of basic components of buffers were purified by the following simple procedure.

Urotropine buffer solution ($c \approx 1$ mol dm^{-3}) was prepared by dissolving 140 g of hexamethylenetetramine in approx. 600 cm^3 of distilled water. The traces of heavy metals were then removed by extraction with a chloroform solution of dithizone. Then 120 cm^3 of

1 M-$HClO_4$ was added, and the unreacted excess of dithizone was removed from the aqueous phase by repeated extractions with pure chloroform. The solution was adjusted with 1 M-$HClO_4$ to the required pH value with the aid of a pH-meter and made up to 1 dm^3 with redistilled water.

Acetate buffer solutions (pH = 5.0, *etc.*; total concentration of acetate $c \approx 1$ mol dm^{-3}; $I \approx 1$ mol dm^{-3}) were prepared by titration of a purified solution of sodium acetate with perchloric acid under pH control.

Propionate buffer solutions were prepared by a similar procedure.

Apparatus and equipment

A Radiometer pH-meter Model PHM G4 was equipped with a glass electrode G 202 B and a reference saturated calomel electrode K 401 (Radiometer, Copenhagen). Standard buffer solutions of the operational pH-scale [11] were used for calibrations.

Absorption spectra in the visible region were registered with a Specord UV VIS (Zeiss, Jena) spectrophotometer.

Photometric titrations were performed on a Zeiss Spekol 10 spectrophotometer equipped with a microtitration attachment [12] and a micrometer syringe burette of new design. The linear 25 mm displacement of a glass piston corresponded to a delivery of 0.5 cm^3

Procedure for photometric microtitration

Transfer an aliquot of the sample solution (0.5 to 2.6 µg of cyanide) to the titration cuvette (type C, Zeiss, Jena, total volume approx. 20 cm^3, pathlength 5 cm). Add 1 cm^3 of 2×10^{-4} M-solution of Naphthylazoxine 6S and a small amount of pure paraffin oil to cover the surface of the solution. Then add a certain volume of acetate buffer to adjust the pH value to about 5, and make up the volume with redistilled water to 18—20 cm^3

Insert the cuvette into the titration attachment and adjust the position of a 500 mm^3 microburette and the stirring. The tip of a polyethylene capillary should be dipped into the titrated solution. Titrate with 0.001 M-$Hg(ClO_4)_2$ taking readings of absorbance at $\lambda = 530$ nm. When a steep decrease in absorbance is reached, limit the additions of the titrant to about 10 mm^3 Locate the end-point by linear extrapolation of the plot of the titration curve.

Results and discussion

Choice of wavelength

A family of absorbance curves in Fig. 1 illustrates the change in the absorption spectrum of Naphthylazoxine 6S in the visible region for varied mole ratio $c(Hg^{2+})/c(\text{ind})$. The free form of the indicator (*cf.* curve *1*) has a main absorption maximum at $\lambda = 507$ nm and a subsidiary maximum ($\lambda = 527$ nm) beyond a shoulder. The absorption spectra were analyzed with the aid of the programs FA 608 and FY 608 by *Kankare* [13]. The data obtained for this equilibrium system were also confirmed by the method of continuous variations. There are two consecutive indicator complexes of the type M(ind) and $M(ind)_2$ which are characterized by the following overall conditional stability constants [9]: $\log \beta_1' = 7.0$ and $\log \beta_2' = 11.6$ (pH = 5.0, acetate buffer, $I \approx 0.05$ mol dm^{-3}). The matrices of molar absorption coefficients show that the absorption maxima of the two complex species are located at the same wavelength, $\lambda = 440$ nm. The absorption maximum of the complex $M(ind)_2$ is well developed, in contrast to a much lower and flat absorption maximum of the species M(ind).

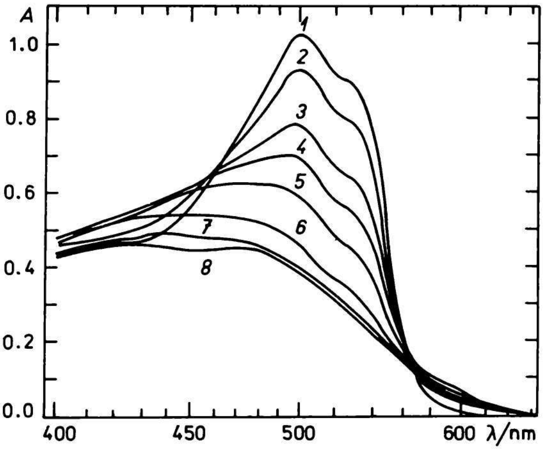


Fig. 1. Absorption spectra of the indicator Naphthylazoxine 6S for various values of the ratio $c(Hg^{2+})/c(ind)$ at constant concentration of the indicator.
Acetate buffer of pH ≈ 5, $I \approx 0.05$ mol dm^{-3} ($CH_3COONa + HClO_4$), $c(ind) = 5 \times 10^{-5}$ mol dm^{-3}, $d = 9.98$ mm, $\theta = 25$ °C.
Concentration ratios $c(Hg^{2+})/c(ind)$: *1.* (0), free form of the indicator; *2.* (0.08); *3.* (0.2); *4.* (0.28); *5.* (0.4); *6.* (0.6); *7.* (0.8); *8.* (3.0).

The titration curves for various wavelengths are shown in Fig. 2. As illustrated by curve *1*, measured at the absorption maximum of the indicator complexes, the consecutive equilibrium contributes to the formation of an extensive bend beyond the equivalence; this part of the curve makes the end-point evaluation difficult. At the wavelength $\lambda = 510$ nm (curve *3*), the titration curve corresponds to the decrease in concentration of the uncomplexed indicator: a steep fall in absorbance marks the equivalence. The titration curves for the wavelength region of the shoulder (curves *3* to *5*) have nearly the same steepness beyond the equivalence. If the wavelength is chosen from this region, the end-point change in absorbance is located within an optimum range ($A = 0.3$ to 0.6). The wavelength $\lambda = 530$ nm was taken for further experiments.

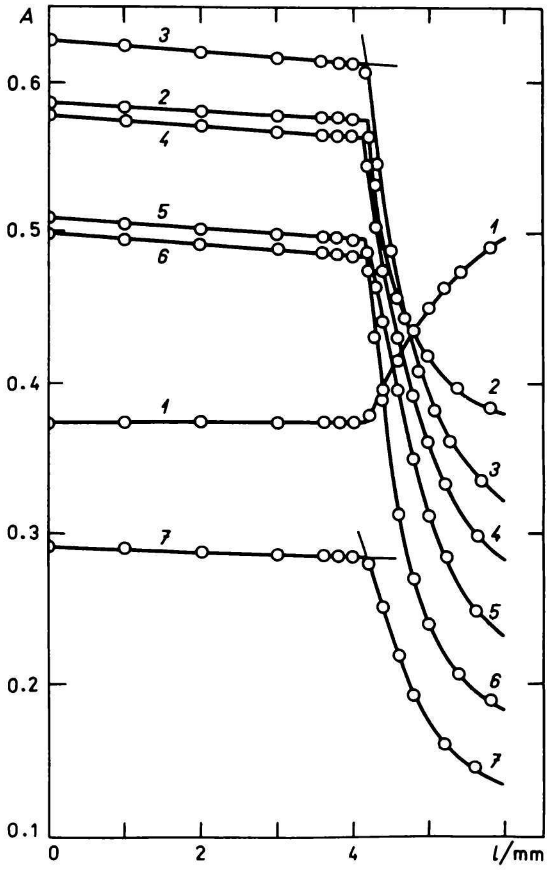


Fig. 2. Photometric titration curves of CN^- with mercury(II) perchlorate ($c = 0.01$ mol dm^{-3}) at various wavelengths.
$c(CN^-) = 8.32 \times 10^{-5}$ mol dm^{-3}, $c(ind) = 10^{-5}$ mol dm^{-3}, $pH \approx 5$, $I \approx 0.05$ mol dm^{-3} ($CH_3COONa + HClO_4$), $d = 5.0$ cm.
Wavelengths (λ/nm): *1.* (440); *2.* (490); *3.* (510); *4.* (520); *5.* (530); *6.* (540); *7.* (550).

The effect of pH and the choice of buffer

Titration curves were studied within the pH range 4 to 6 with the use of urotropine, propionate, and acetate buffers. Titrations with urotropine buffers gave distorted sigmoid bends on the curves beyond the equivalence. With propionate buffers of pH 4 and 5, a smooth bend was observed at the equivalence. At pH 6 the bend was not so extensive, but even in this case it was not possible to evaluate the end-point accurately.

As illustrated in Fig. 3, favourable shapes of titration curves were obtained with

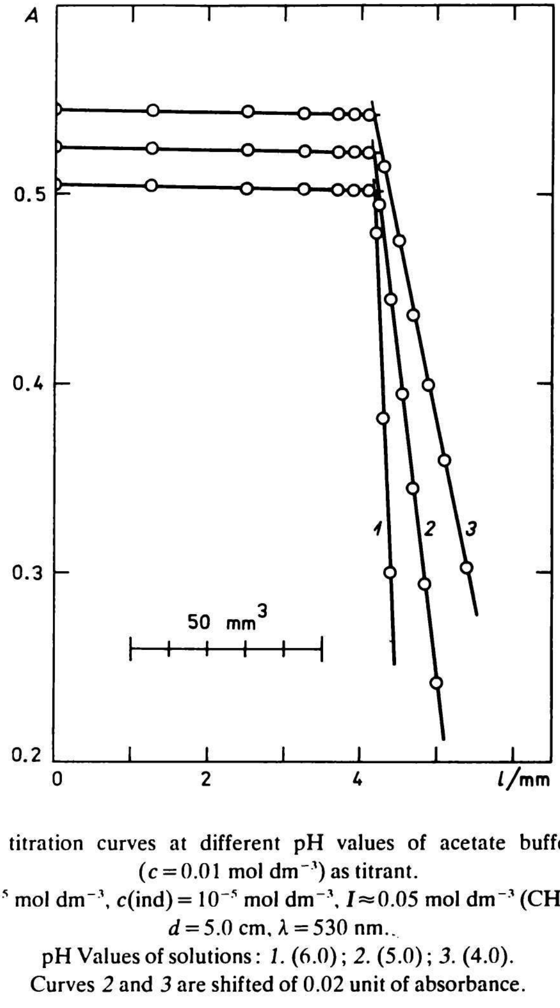


Fig. 3. Photometric titration curves at different pH values of acetate buffers using $Hg(ClO_4)_2$ ($c = 0.01$ mol dm^{-3}) as titrant.
$c(CN^-) = 8.32 \times 10^{-5}$ mol dm^{-3}, $c(\text{ind}) = 10^{-5}$ mol dm^{-3}, $I \approx 0.05$ mol dm^{-3} ($CH_3COONa + HClO_4$), $d = 5.0$ cm, $\lambda = 530$ nm..
pH Values of solutions: *1.* (6.0); *2.* (5.0); *3.* (4.0).
Curves *2* and *3* are shifted of 0.02 unit of absorbance.

the use of acetate buffers. At pH 4 the extrapolated end-point was somewhat lower (of about 10 %) than the calculated equivalence, but at pH 5 and 6 the evaluated end-points were practically identical with the theory. The buffer capacity at pH values higher than 6 was already not sufficient. In addition to that, the dissociation of the free form of the indicator begins in that region; this is accompanied with a colour change from red (corresponding to a protonated species) to yellow colour similar to that of the mercury(II) complex.

As a rule, a sample of cyanide is made alkaline prior to further treatment in order to prevent loss of HCN; therefore, the alkalinity of the sample solution has to be considered to adjust the required pH value. The addition of 1 cm^3 of an acetate buffer of pH about 5 and $I \approx 1$ mol dm^{-3} was found safe to obtain a final value of pH 5.3 to 5.5. In the course of a titration with a slightly acidic mercury(II) titrant the pH value of the solution decreases gradually, altogether of about 0.1 pH unit.

Loss of HCN *during titration*

The results of repeated series of microtitrations at pH 5 and 6 were reproducible but subject to a systematic negative error caused by the escape of HCN into the closed space of the titration attachment. In a mildly acidic solution the cyanide ion is fully protonated. A control test has revealed that the loss in HCN amounts up to 50 % during 30 min of stirring if the solution is exposed to ambient atmosphere. The extent of escape of HCN is, of course, much influenced by experimental conditions (temperature, intensity of stirring, flow of air, *etc.*). The loss in hydrogen cyanide can easily be prevented by covering the surface of the solution with a thin layer of paraffin oil which adheres to the walls and also fills the corners of the cuvette.

The effect of ionic strength

A higher amount of a salt in the titrated solution brings about decrease in the attainable change of absorbance; consequently, the steepness of the descending part of the titration curve becomes smaller. However, there is a certain practical limit for the ionic strength which cannot be further decreased, because hydrogen cyanide is transferred from a sample to the absorption solution of sodium hydroxide, $c(\text{NaOH}) = 0.025$ mol dm^{-3} The amount of salt is also increased by the addition of a buffer. If a subsequent dilution is taken into consideration, ionic strength of the solution to be titrated can reach a value of about 0.05 mol dm^{-3} This limiting value still allows to achieve a sensitive end-point location.

Choice of the indicator concentration

The attainable difference between the initial and final value of absorbance during a titration is much influenced by the concentration of the indicator. The amount of Naphthylazoxine 6S is to be chosen so that the overall change in absorbance should not be smaller than 0.3. Contrarily the end-point region should not be placed above the optimum range of absorbance. It is useful to note that a higher concentration of indicator brings about an increase in the linear section of the titration curve beyond the equivalence, which is necessary for the end-point extrapolation.

An optimum addition of the indicator is thus 1 cm^3 of a 2×10^{-4} M-solution of Naphthylazoxine 6S. The resulting concentration of the indicator is then about 10^{-5} mol dm^{-3}

Interfering effects of some anions

Photometric indication is one of the objective approaches to the study of interferences of other anions in titrations of cyanide.

The effect of chloride on the shape of the titration curve was examined for various concentration ratios and at different pH values. The competitive effect of chloro complexes becomes more evident in an acidic solution, namely at a certain value of the concentration ratio, $c(\mathrm{CN}^-)/c(\mathrm{Cl}^-) = 1/10$ to $1/50$. The sharp end-point break of the titration curve then disappears and the descending part of the curve is less steep. In presence of the same or smaller amount of chloride, the titration curve is practically unaffected (Fig. 4, curves *1* and *4*). As illustrated by the results in Table 1, the determination of cyanide is reliable under given conditions even in the presence of chloride.

The applicability of the determination of cyanide in presence of thiocyanate was also studied for similarly varied conditions. Titration curves can be evaluated safely only at a pH value about 6, and on condition that the concentration of thio-

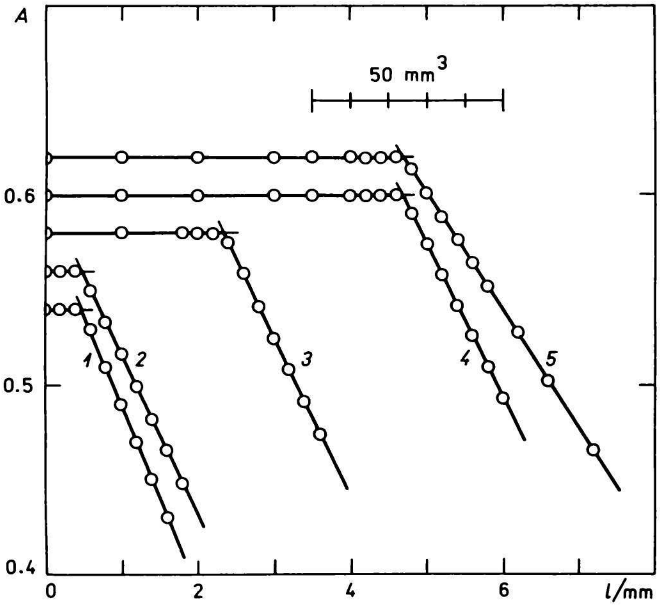


Fig. 4. Photometric titrations of micromolar solutions of cyanide with mercury(II) titrant ($c = 0.001$ mol dm^{-3}).
$c(\mathrm{ind}) = 10^{-5}$ mol dm^{-3}, pH ≈ 5.0, $I \approx 0.05$ mol dm^{-3} ($\mathrm{CH_3COONa + HClO_4}$), $d = 5.0$ cm, $\lambda = 530$ nm.
Concentrations of CN^-, c/(mol dm^{-3}): *1.* and *2.* (9.4×10^{-7}); *3.* (4.66×10^{-6}); *4.* and *5.* (9.34×10^{-6}).
Presence of the same amount of chloride has no effect on curves *1* and *4*.
Thiocyanate in admixture, $c(\mathrm{SCN}^-)$/(mol dm^{-3}): *2.* (9.4×10^{-7}); *5.* (9.34×10^{-6}).
Curves *2* to *5* are shifted successively of 0.02 unit of absorbance.

Table 1

Photometric microtitrations of cyanide

	Titrations[a] with $AgNO_3$	Titrations with $Hg(ClO_4)_2$ using Naphthylazoxine 6S as indicator				Effect of Cl^- $c(CN^-) : c(Cl^-)$ 1 1		Effect of SCN^- $c(CN^-) : c(SCN^-)$ 1 1	
c(titrant)/(mol dm^{-3})	0.1	0.01	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Titrated solution $c(CN^-)$/(µmol dm^{-3})	10^3	500	10	5	1	10	1	10	1
Found	25.16	25.35	24.86	24.81	24.61	24.92	25.65	24.97	24.63
mass of CN^- per 1 cm^3	25.22	25.41	24.60	24.92	24.08	24.71	25.39	24.86	25.65
of standard cyanide	25.16	25.24	25.12	25.02	25.13	24.97	25.12	24.66	24.08
solution, m/µg	24.63	25.23	24.81	24.60	24.87	25.02	24.34	24.81	25.39
	24.92	25.31	25.02	25.12	25.39	24.60	24.86	24.76	25.12
arithmetic mean	25.02	25.31	24.88	24.89	24.82	24.84	25.07	24.81	24.97
reliability interval	±0.30	±0.09	±0.27	±0.27	±0.67	±0.21	±0.67	±0.16	±0.80
relative width of the reliability interval, Δ/ %	2.40	0.72	2.17	2.17	5.40	1.69	5.34	1.29	6.41
Relative systematic deviation[b], δ/%	—	+1.16	−0.56	−0.52	−0.80	−0.72	+0.20	−0.84	−0.20
Lord's u-test	—	0.377	0.126	0.117	0.105	0.178	0.026	0.233	0.023

a) Turbidimetric indication of Liebig—Dénigès determination; *b*) calculated with respect to the reference argentometric method. Number of determinations in a titration series, $n=5$; significance level considered, $\alpha=0.05$; critical value of Lord's characteristic, $u_0=0.306$.

cyanate does not exceed that of cyanide. The shape of a titration curve for $c(CN^-) = 10^{-5}$ mol dm^{-3} or 10^{-6} mol dm^{-3} is then nearly the same as for the determination of cyanide alone. The competitive influence of thiocyanate becomes more evident within the pH range 5 to 4, and especially if a greater concentration of thiocyanate is present.

In presence of bromide an extensive bend at the equivalence suggests a stronger competition of the bromo complexes. When iodide is present, the titration curve has a sharp end-point break; however, this end-point corresponds to a sum of the amounts of cyanide and iodide.

The scope of applications of photometric microtitrations of cyanide

The results of several series of 5 successive titrations of cyanide within the concentration range 5×10^{-4} to 1×10^{-6} mol dm^{-3} are listed in Table 1. Two standard solutions of mercury(II) perchlorate, $c = 0.01$ and 0.001 mol dm^{-3}, were used for microtitrations at pH$\approx$5 and $I \approx 0.05$ mol dm^{-3} Absorbance was measured at $\lambda = 530$ nm and used for plotting the titration curve in dependence on the amount of the titrant read on a micrometer scale in terms of linear displacement (l/mm). The end-point was evaluated as an intersection point of the extrapolation straight lines drawn through the linear sections of the titration curve.

For an easier comparison of results of microtitrations obtained for various concentrations of cyanide, which differed within one and three orders of magnitude from the reference determination, the results were calculated in terms of the mass amount of CN$^-$ per 1 cm^3 of a standard stock solution. It can be seen that photometric indication of the mercurimetric titration using Naphthylazoxine 6S as indicator is applicable within a wide range of concentration. Precise results can be obtained in titrations with a standard solution of 0.01 M-$Hg(ClO_4)_2$ if the concentration of cyanide is about $c = 10^{-4}$ mol dm^{-3}. As illustrated by the curves in Fig. 4, the linear extrapolation can be used even for a more dilute titrant, *e.g.* $c = 0.001$ mol dm^{-3} The results are satisfactory, except for the smallest concentration of cyanide (*cf.* Table 1, $c(CN^-) = 10^{-6}$ mol dm^{-3}): twice as great value of the relative reliability interval is obtained in this case.

The accuracy attainable in mercurimetric microtitrations of cyanide was assessed with respect to the argentometric standardization. On the whole, the differences were statistically insignificant. Only in one case the u-test revealed a significant difference between the value of Lord's characteristic and the corresponding critical value.

The standard solution of 0.001 M-$Hg(ClO_4)_2$ represents evidently the greatest dilution of the titrant. The limit of determination for the given arrangement of photometric microtitration is influenced mainly by the reproducibility of the measured changes in absorbance and by the precision of the microburette. If a relative error of the determination (≈2 %) is considered as acceptable, photometric microtitration of cyanide with a dilute standard mercury(II) perchlorate can be applied even for very dilute solution containing 20 to 100 nmol, *i.e.* 0.5 to 2.6 μg of CN^- per 20 cm^3 of the solution titrated. The method represents a suitable finish of a procedure involving distillation separation of HCN from samples of waste water and sludge [14, 15].

References

1. Beerstecher, E., *Analyst* (London) *75*, 280 (1950).
2. Brandštetr, J. and Kotrlý, S., *Chem. Listy 50*, 1316 (1956).
3. Ryan, J. A. and Culshaw, G. W., *Analyst* (London) *69*, 370 (1944).
4. Hofmann, P. *et al.*, *Jednotné metody chemického rozboru vod.* (Unified Methods of Chemical Analysis of Water.) P. 339. Nakladatelství technické literatury. (Publishing House of Technical Literature.) Prague, 1965.
5. Dagnall, R. M., El-Ghamry, M. T., and West, T. S., *Talanta 13*, 1667 (1966).
6. Smith, R. M. and Martell, A. E., *Critical Stability Constants*, Vol. *4*. *Inorganic Complexes.* Plenum Press, New York, 1976.
7. Magee, R. J., *Int. Ser. Monogr. Anal. Chem. 51*, 195 (1972).
8. Toshiaki, N., *Nippon Kagaku Zasshi 89*, 580 (1968); *Chem. Abstr. 69*, 64415 (1968).
9. Pham-vu Quat, *Thesis.* University of Chemical Technology, Pardubice, 1978.
10. Cherkesov, A. I., *Zavod. Lab. 27*, 1447 (1961).
11. Definition of pH Scales, Standard Reference Values, Measurement of pH and Related Terminology. *Pure Appl. Chem. 55*, 1467 (1983).
12. Kotrlý, S. and Říha, V., *Czechoslov.* AO 169941 (1972).
13. Kankare, J., *Anal. Chem. 42*, 1322 (1970).
14. Říha, V Pham-vu Quat, and Vytřas, K., *Českoslov. Hygiena 27*, 212 (1982).
15. Říha, V Mach, V., and Chýlková, J., *Czechoslov. Appl.* PV 6566 (1984).

Translated by S. Kotrlý