# Microdetermination of *m*-Dinitro Compounds with Cyanide and Silver Electrodes

### Saad S. M. Hassan

Research Microanalytical Laboratory, Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

A new, simple, selective, and accurate method, based on a reaction with 0.2 M potassium cyanide solution followed by potentiometric titration of the excess cyanide with silver nitrate, is described for the microdetermination of *m*-dinitro compounds. Potassium cyanide, 1 mol, is quantitatively consumed per mole of *m*-dinitro compound. Compounds containing three nitro groups in meta position to each other consume 2 mol of potassium cyanide/mol. The results obtained with sample sizes in the range of 10–100  $\mu$ mol, show an average recovery of 99% and no interferences are caused by other classes of nitro and nitrogenous compounds.

Reduction of the nitro group by iron(II), vanadium(II), chromium(II), titanium(III), and tin(II) already formed the basis of several titrimetric procedures for the quantitative determination of various types of nitro compounds (1, 2). However, these methods do not differentiate between the various nitro compounds and the titrants need special precautions during preparation, storage, and use. Furthermore, the nitrate, nitramine, nitroso, azo, azoxy, and N-oxide groups have been reported to react, similarly, under the same conditions (1-3).

On the other hand, little is known about the selective determination of each class of nitro compounds because of the lack of specific reactions. However, few spectrophotometric methods have been advocated for the determination of mdinitro compounds. These are based on reactions with acetone-alkali (4), ammonia-amines (5), quaternary ammonium hydroxide-dimethyl formamide (6) and amines-dimethyl sulfoxide (7, 8). These methods suffer from the defect that the colors developed by these reactions are of limited stability, their absorption is greatly dependent on the remainder of the molecule, and a rather strict control of the reaction time and conditions is necessary (4-8).

In 1865, Pfaundler and Oppenheim (9) reported that some m-dinitro compounds react with the cyanide ion to give products whose constitution is only partly known and presumably they are substituted phenylhydroxylamine. Other workers (10-14) reported that some m-dinitro compounds react with the cyanide ion in boiling alcohol, in another fashion, to give alkoxy nitrobenzonitrile derivatives. It is quite surprising that the analytical application of this reaction has not been worked out, since the time of these publications, apart from the spot test for qualitative detection of m-dinitro compounds (15).

The present work reports a new method for quantitative microdetermination of m-dinitro compounds by reaction with potassium cyanide. Our interest in this reaction results not only from its selectivity, simplicity, and specificity, but also for its applicability with the ion-selective electrodes.

#### EXPERIMENTAL

**Reagents.** All the chemicals used were Analytical Reagent grade and double-distilled water was used throughout. Solutions of 0.2 M potassium cyanide, 0.02 M silver nitrate, and 0.05 M sodium hydroxide were used. The nitro compounds analyzed were B.D.H. laboratory reagents of purity not less than 97% and were purified by crystallization repeated several times.

Apparatus. The potentiometric measurements were read from a Pye-Unicam model 292 MK2 pH meter using either Orion cyanide ion-selective electrode (Model 94-06A) or Orion silver/sulfide ion selective electrode (Model 94-16) in conjunction with an Orion double junction reference electrode (Model 90-02) with 10% potassium nitrate in the outer compartment. "Ingold" combined glass/calomel electrode was used for pH adjustments.

The infrared spectra were recorded on Unicam SP200 G grating spectrophotometer using a potassium bromide disk technique. NMR spectra were taken with a Perkin-Elmer R12A (60 MC) spectrometer using TMS as an internal standard in deuterated acetone solution as a solvent. Spectrophotometric measurements were carried out with the aid of a Unicam SP 8000 spectrometer.

**Procedure.** Weigh accurately 2–10 mg of the ground, dried nitro sample and transfer to a Pyrex test tube  $(20 \times 2 \text{ cm})$ . Dissolve in 2 ml of methyl alcohol and compounds which are not easily soluble in methanol (e.g., 2,4-dinitrophenyl hydrazine) are dissolved in 2 ml of 1:1 mixture of methanol and dimethyl sulfoxide. Nitro compounds containing an acidic function are determined after neutralization with 0.05 M sodium hydroxide to pH 6–7.

Pipet 1.00 ml of 0.2 M potassium cyanide solution to the sample solution and mix thoroughly. Place the tube in a boiling water-bath for 10 min with occasional shaking. Cool, add 5 ml of double-distilled water. Shake and transfer the contents quantitatively to a 250-ml beaker. Wash the tube with ca. 30-40 ml of double-distilled water portion-wise. Insert either the cvanide or silver/sulfide electrode in conjunction with the double junction reference electrode and titrate with 0.02 M silver nitrate solution. As the end point is approached (indicated by increasing potential jumps), add the titrant in 0.01-ml increments. A value of twice the volume of the titrant at the first inflection point is used to calculate the cyanide concentration. Run a parallel blank in the same manner, omitting the sample. The difference between the volume of silver nitrate consumed in the blank and the experiment is equivalent to the amount of potassium cyanide reacted with the dinitro compound; (1 mol of KCN  $\equiv$  1 mol of mdinitro compound and 2 mol of KCN  $\equiv$  1 mol of symmetrical trinitro compound).

The end points are calculated, in the present work, from the maximum slope  $\Delta E/\Delta V$  vs. V using an IBM 1620 computer and checked by plotting E vs. V manually.

#### **RESULTS AND DISCUSSION**

Nature of the Reaction. The nature and products of the reaction of *m*-dinitro aromatic compounds with various nucleophiles including the cyanide ion have not been exactly known. Formation of a quinoid adduct (I and II) (6, 7, 16-18), substitution with the cyanide and replacement of one of the nitro groups by alkoxyl group to give III (10-14, 19) or reduction to give the corresponding cyano nitrohydroxylamine derivative (IV) (9) have been suggested.



 $R = -CH_2SOCH_3 (7), PO(OR)_2 (16), -CH_2COCH_3 (17), -CN (18).$ 

Due to the earlier publication of these suggestions and their contradiction, this reaction was re-investigated in the present



Figure 1. Infrared spectra of pure m-dinitrobenzene (....) and its reaction product with potassium cyanide in boiling methanol (-----)



Figure 2. NMR spectra of pure m-dinitrobenzene (...) and its reaction product with potassium cyanide in boiling methanol (-----)

work. The product of the reaction of m-dinitrobenzene with potassium cyanide in the presence of methyl alcohol was isolated by extraction with ether, crystallized, and identified.

The infrared spectrum of the product (Figure 1) shows strong peaks at 1350 and 1530 cm<sup>-1</sup> due to symmetrical and asymmetrical  $-NO_2$  stretch. The strong absorption band observed at 2215 cm<sup>-1</sup> is assigned to  $-C\equiv N$  stretch whereas the bands at 1190–1210 cm<sup>-1</sup> are referred to asymmetric stretch of etheric group (aryl-O-). At 730, 810, and 910 cm<sup>-1</sup>, there are bands due to out-of-plane wagging of three adjacent aromatic hydrogen atoms. In NMR spectrum (Figure 2), a sharp singlet at  $\delta = 4.1$  ppm due to methoxyl protons and signals for aromatic protons at  $\delta = 7.7-8.0$  ppm are observed. From the integral plot, the relative areas are 1:1. Thus, the structure of the product is 1,2,3-trisubstituted benzene containing nitro, cyano, and methoxyl groups (cf. III).

To test for the fate of the leaving nitro group, the mixture of the reaction products was acidified and potassium iodide was added followed by carbon tetrachloride. On shaking, iodine appeared in the organic layer confirming the presence of nitrite ion. Trace amounts of ammonia were also detected. Consequently, the reaction of m-dinitrobenzene with potassium cyanide in the presence of methanol may be represented by Equation 1. The reaction probably involves simultaneous reduction of some nitrite to ammonia which was detected. However, this side reaction does not affect the overall stoichiometry with potassium cyanide.

$$\underbrace{\bigcap_{NO_2}^{NO_2} \cdot cH_3OH + \kappa cN}_{NO_2} \longrightarrow \underbrace{\bigcap_{CN}^{OCH_3} \cdot \kappa NO_2 + 2H^*}_{NO_2} (1)$$

Thus, in these reactions the attack of the cyano group occurs exclusively between the two nitro groups (ortho to both). However, when this position is occupied (e.g., 2,6-dinitrophenol), the position which is ortho to one nitro group and



Figure 3. Potentiometric titration curves of (-----) potassium cyanide with silver nitrate using the silver/sulfide electrode; (- - -) potassium cyanide with silver nitrate using the cyanide electrode, and (---) excess of potassium cyanide with silver nitrate after reaction with *m*-dinitrobenzene using the cyanide electrode

para to the other is available by virtue of its electron-deficiency.

Reaction of potassium cyanide with some trinitro compounds in which the nitro groups are in meta position to each other was also investigated. These compounds consume 2 mol of potassium cyanide/mol. Attempts to isolate the reaction products were unsuccessful. However, it is possible to assume that the reaction of these compounds with 1 mol of potassium cyanide as described with m-dinitro compounds will lead to the elimination of one nitro group and the m-dinitro product upon further reaction consumes another mole of the cyanide.

**Reaction Conditions.** Preliminary experiments with some m-dinitro compounds, in which the cyanide concentration, reaction temperature, and time were varied, established that reaction with 0.2 M potassium cyanide for 10 min in boiling methanol was sufficient to effect quantitative results.

Since the reaction product of m-dinitrobenzene was found to be substituted with the O-CH<sub>3</sub> group, it was of interest to see whether methanol is necessary for this reaction. Several other water-miscible organic solvents (e.g., ethanol, propanol, dimethyl sulfoxide, acetonitrile, acetone, and dioxan) were used, but quantitative results were obtained only in the presence of methanol.

**Titration Curves.** Titration of potassium cyanide with silver nitrate using the cyanide or silver/sulfide selective electrode (Figure 3), shows two points of inflection corresponding to the reactions:

 $Ag^+ + 2 CN^- \rightleftharpoons [Ag(CN)_2]^- \qquad K = 1.3 \times 10^{-21}$  (2)

$$[Ag(CN)_2]^- + Ag^+ = 2 AgCN \qquad K = 0.7 \times 10^{-15}$$
 (3)

Although, the silver concentration at the second point of inflection is found to be twice that at the first inflection in the titration of pure potassium cyanide (20), this is not the case in the titration of excess potassium cyanide in the reaction of m-dinitro compounds. With all the compounds under investigation, the concentration of silver consumed at the first and second inflections is in the ratio of 1:2.2. Thus, the second inflection point exceeding the expected by 10%, the standard deviation being  $\pm 0.19\%$  (cf. Figure 3).

It was thought that these results might be due to the interference of potassium nitrite, which is one of the reaction products, during the titration with silver nitrate ( $K_{sp}AgNO_2$ = 10<sup>-3</sup>). However, titration of an equimolar ratio of potassium nitrite and potassium cyanide with silver nitrate shows no effect due to the nitrite and the concentration of silver at the first and second points of inflection is exactly in the ratio of 1:2. It is possible that the organic cyano compounds produced from the reaction participate in a complex reaction with silver affecting the equilibrium of reaction 3.

Since, precipitation of silver argento cyanide is not detected in these reactions and the reaction products are deeply colored (red to violet), visual detection of the end point is impossible. Moreover, the use of the conventional electrodes (e.g., silver electrode) suffer the defect of limited use in the presence of redox substances such as potassium nitrite (21). This reflects the advantages of the use of either the cyanide or silver/sulfide ion-selective electrode for the titration of the cyanide ion in this reaction.

Cyanide electrode gives end point breaks corresponding to 250 and 150 mV at the first and second inflections, respectively, whereas the silver/sulfide electrode gives breaks corresponding to 400 and 150 mV at the first and second points, respectively (Figure 3).

**Determination of** *m***-Dinitro and Symmetrical Trinitro Aromatic Compounds.** *m*-Dinitro compounds quantitatively react with potassium cyanide with the consumption of 1 mol/mol. Compounds containing three nitro groups in meta position to each other, react with 2 mol of the cyanide/mol.

Table I. Microdetermination of Some *m*-Dinitro and Symmetrical Trinitro Compounds Using the Cyanide and Silver/Sulfide Selective Electrodes

Weight, mg		$\mathbf{Std}$	Recovery	
Compound	Taken	Found	dev, %	%
<i>m</i> -Dinitro compounds				
2,4-Dinitrophenyl-	4.89	4.84		98.9
hydrazine	6.10	5.98	$\pm 0.55$	98.0
	9.70	9.60		98.9
2,4-Dinitroaniline <sup>a</sup>	5.79	5.65		97.5
	7.50	7.35	$\pm 0.37$	98.0
	9.60	9.43		98.2
2,4-Dinitrophenol	5.12	5.09		99.4
	7.85	7.69	$\pm 0.72$	97.9
	9.41	9.29		98.7
2,6-Dinitrophenol <sup>a</sup>	6.40	6.12		95.6
	8.11	7.78	$\pm 0.49$	95.9
	10.00	9.64		96.4
<i>m</i> -Dinitrobenzene	5.08	4.95		97.4
	7.01	6.92	$\pm 0.44$	98.7
	8.75	8.52		97.3
3,5-Dinitrosalicylic	5.84	5.76		98.6
acid	7.45	7.35	$\pm 0.18$	98.6
	9.20	9.11		99.0
3,5-Dinitrobenzoic	6.59	6.69		101.5
acid	7.91	8.01	$\pm 0.23$	101.2
	9.31	9.47		101.7
Symmetrical trinitro con	ipounds	5		
2,4,6-Trinitrotoluene	6.62	6.69		101.0
(TNT)	8.41	8.32	$\pm 0.76$	98.9
	9.80	9.70		98.9
2,4,6,2',4',6'-Hexanitro-	5.00	5.00		100.0
diphenylamine <sup>a</sup>	6.92	6.88	$\pm 0.31$	99.4
	8.62	8.58		99.5
2,4,6-Trinitrobenzoic	5.10	5.07		99.4
acid	7.21	7.12	$\pm 0.38$	98.7
	8.58	8.53		99.4
2,4,6-Trinitrophenol	4.85	4.80		98.9
(picric acid) <sup><math>a</math></sup>	6.82	6.72	$\pm 0.28$	98.5
	7.11	7.00		98.4

<sup>a</sup> These compounds were analyzed using the silver/sulfide ion-selective electrode.

The results obtained (Table I), show an average recovery of 99.1% and a mean relative standard deviation of  $\pm 0.4\%$  with sample sizes of  $10-100 \ \mu mol$ .

However, 3,5-dinitrobenzoic and 3,5-dinitrosalicylic acids consume 2 mol of potassium cyanide/mol, and 2,4,6-trinitrophenol and 2,4,6-trinitrobenzoic acid consume 3 mol of the cvanide/mol, since acidic groups with  $pK_a$  less than 4 were found to release 1 mol of hydrocyanic acid quantitatively per group. It was proved necessary to adjust the pH of these acidic nitro compounds to 6-7 before applying the cyanide reaction. Under these conditions, 1 and 2 mol of the cyanide are quantitatively consumed per mole of the dinitro and trinitro compounds mentioned above.

Reactions of other nitrogenous and non-nitrogenous groups with potassium cvanide under the present conditions were also tested. Mononitro, o-dinitro, and p-dinitro compounds (e.g., nitrobenzene, o-dinitrobenzene, p-dinitrobenzene) as well as azo, hydrazo, azoxy, anilide, amide, amine, nitrate, hydroxy, carbonyl, thiocarbonyl, and thiol groups (e.g., azobenzene, Table II. Spectral Data of Some *m*-Dinitro Compounds Amenable to Spectrophotometric Analysis by Reaction with Methanolic Potassium Cyanide

Compound	Wavelength of max. absorption, nm	Absorptivity, M
<i>m</i> -Dinitrobenzene	400	1470
1-Chloro-2,4-dinitroben-	340	4860
zene		
2,4-Dinitrotoluene	400	1820
2,4-Dinitroaniline	410	8240
2,4-Dinitrophenylhydrazine	375	6930
2,4-Dinitrophenol	500	2700
3,5-Dinitrosalicylic acid	480	1620
3,5-Dinitrobenzoic acid	410	2630
2,4,6-Trinitrobenzoic acid	450	3460
2,4,7-Trinitrofluorenone	400	8400

hydrazobenzene, azoxybenzene, acetanilide, acetamide, 2naphthylamine, urea nitrate, phenol, benzaldehyde, thiourea, and thiophenol) did not respond to the reaction.

To gain a further insight into the suitability of the present reaction for quantitative analysis of *m*-dinitro compounds, the procedure previously outlined was followed and the reaction products were diluted to 100 ml with 1:1 methanolwater mixture and the intensity of the colors developed by many of these compounds was measured as a function of concentration. With all the compounds examined (Table II), Beer's law is obeyed in the range of 5–100  $\mu$ g/ml of the final solution whose volume is 100 ml and the accuracy of these spectrophotometric data are within  $\pm 2\%$ .

The usefulness of the spectrophotometric procedure can be visualized by the analysis of a wide range of m-dinitro compounds particularly 3.5-dinitrobenzoic acid. 3.5-dinitrosalicylic acid, 2,4-dinitrophenol and 2,4-dinitroaniline where other spectrophotometric procedures are not applicable (7).

## LITERATURE CITED

- (1) W. I. Awad, S. S. M. Hassan, and M. T. Zaki, Anal. Chem., 44, 911 (1972).
- N. Cheronis and T. S. Ma, "Organic Functional Group Analysis by Micro (2)and Semimicro Methods", Interscience, John Wiley and Sons, New York, 1964
- (3) W. I. Awad and S. S. M. Hassan, Talanta, 16, 1383 (1969)
- F. English, Anal. Chem., 20, 745 (1948). (4)
- G. Lewis and G. Seaborg, J. Am. Chem. Soc., 62, 2122 (1940).
   C. Porter, Anal. Chem., 27, 805 (1955).
- J. Heotis and J. Cavett, Anal. Chem., 31, 1977 (1959)
- (8) D. Glover and E. Kayser, Anal. Chem., 40, 2055 (1968).
  (9) L. Pfaundler and A. Oppenheim, Z. Chem., (2) 1, 470 (1865).
  (10) C. deBruyn and V. Genus, Recl. Trav. Chim. Pays-Bas, 23, 26 (1904).
- (11) Č. deBruyn, Recl. Trav. Chim. Pay-Bas, 2, 210 (1883).
- (12) W. vanHeteren, Recl. Trav. Chim. Pays-Bas, 20, 107 (1901).
- (13) J. Blanksma, Recl. Trav. Chim. Pays-Bas, 21, 424 (1902).
- (14) R. Huisgen, Ann. 559, 101 (1948).
  (15) V. Anger, Mikrochim. Acta, 2, 3 (1937).
  (16) B. Saunders and B. Stark, Tetrahedron, 4, 197 (1958).
  (17) S. Gitis, Zh. Obshch. Khim., 27, 1894 (1957).
- (18) J. Meisenheimer, Ann., 323, 205 (1902).
- J. Bunnett, J. Cormack, and F. McKay, J. Org. Chem., 15, 481 (1950). (19)
- (20) F. J. Conrad, *Talanta*, **18**, 952 (1971).
   (21) D. Davis in "Comprehensive Analytical Chemistry", C. Wilson and D. Wilson, Ed., Vol. IIA, Elsevier, Amsterdam, 1964, p 86.

RECEIVED for review March 4, 1976. Accepted September 17, 1976.