



Health and Safety Executive  
Occupational Medicine and  
Hygiene Laboratory

## MDHS 56/2

Methods for the  
Determination of  
Hazardous Substances

April 1990



# Hydrogen cyanide in air

Laboratory method using an ion-selective  
electrode

## INTRODUCTION

### Properties<sup>1-5</sup>

1 Hydrogen cyanide is a colourless gas or a bluish white liquid at room temperature, its boiling point being 26°C. It has a characteristic odour of bitter almonds for those individuals able to perceive its presence by smell.

2 Hydrogen cyanide burns in air with a blue flame. It is miscible with water and alcohol, and is slightly soluble in ether. It is a very weak acid, having a pKa of 9.31.<sup>5</sup> It is highly flammable, with a flash point of -18°C. Its flammable limits in air are 6% to 40%, and it has a high potential for explosions in confined spaces.

### Toxicity<sup>1-4</sup>

3 Hydrogen cyanide is an extremely toxic industrial chemical. It is primarily an acute poison and its toxicity is a function of dose, ie the product of concentration and exposure time, rather than just a function of concentration alone.

4 Hydrogen cyanide is a mild upper respiratory irritant and skin or eye contact with the liquid also leads to irritation. Hydrogen cyanide acts as an asphyxiant, inactivating certain enzyme systems including cytochrome oxidase which occupies a fundamental position in the respiratory process. Inhalation of hydrogen cyanide vapour may be rapidly fatal. Exposure to low levels of hydrogen cyanide may cause weakness, headache, nausea and vomiting while exposure to higher levels of hydrogen cyanide may cause loss of consciousness, cessation of respiration and ultimately death.

5 A chronic form of hydrogen cyanide poisoning may occur. Medical studies have indicated an increase in subjective symptoms such as headache, nervous instability and abdominal colic. Enlargement of the thyroid gland has also been reported. This may be attributed to the effects of thiocyanate, the chief metabolite of cyanide, as thiocyanate impedes the uptake of iodide by the thyroid gland.

6 There is no evidence to suggest that hydrogen cyanide should be considered carcinogenic, mutagenic

or teratogenic, though it seems probable that it depresses the activity of all cells, both normal and transformed.

### Precautions and first aid<sup>6,7</sup>

7 Precautions and first aid are fully covered in an HSE leaflet on cyanide poisoning,<sup>6</sup> and an HSE pocket card<sup>7</sup> is available as an aide-memoire.

8 In connection with laboratory work it should particularly be noted that hydrogen cyanide may be produced inadvertently if cyanide salts or solutions containing cyanide salts are accidentally allowed to come into contact with acid. It is therefore very important that cyanide standard solutions and sample solutions are disposed of in an appropriate manner (see para 70).

### Requirements of the COSHH Regulations<sup>8</sup>

9 The Control of Substances Hazardous to Health (COSHH) Regulations require that persons who may be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. The COSHH Regulations also include a requirement to assess the health risk created by work involving substances hazardous to health, and to prevent or control exposure to such substances. Employers must therefore ensure that the requirements of the COSHH regulations are fully satisfied before allowing employees to undertake any procedure described in this method.

### Analytical methods

10 This is not a 'reference' method in the strict analytical sense of the word. There are frequently several alternative methods available for the determination of a particular analyte (eg other methods in the MDHS series). With the exception of a few cases, where an exposure limit is linked to a specific method (eg rubber fume or asbestos), the use of methods not included in the MDHS series is acceptable provided they have the accuracy and reliability appropriate to the application.

## PRINCIPLE

11 Hydrogen cyanide is collected by drawing the test atmosphere through 10 ml 0.1M potassium hydroxide

absorbing solution contained in a midget impinger. A filter holder loaded with a pre-filter is attached to the inlet tube of the midget impinger to remove heavy metal particulates before entrapment of the hydrogen cyanide, since heavy metals interfere with the measurement of free cyanide in solution by forming cyanide complexes. Interference from particulate cyanides will also be reduced by use of a pre-filter, although it may not be eliminated because under conditions of high humidity hydrogen cyanide is liberated from the collected particulate cyanides.

12 The resulting sample solution is quantitatively transferred to a 25 ml volumetric flask and made to volume with absorbing solution. Free cyanide ions are determined using a cyanide ion-selective electrode.

13 The method described is similar in many respects to that published by NIOSH.<sup>9</sup> However, a significantly lower maximum sample volume is recommended than in the NIOSH method (see para 14), in accordance with results obtained from method validation work carried out by HSE.<sup>10</sup> (After about 40 litres of air have been sampled, absorbed carbon dioxide begins to severely impair sampling efficiency for the more weakly acidic hydrogen cyanide. Eventually, further carbon dioxide absorption actually results in displacement of collected hydrogen cyanide.)

## SCOPE

### Applicability

14 The method described is suitable for the determination of time weighted average concentrations of hydrogen cyanide in workplace atmospheres, and may be used, for example, in assessing compliance with statutory requirements.<sup>8</sup> The method is suitable for air sample volumes within the range 10 litres to 40 litres, and may be used to measure both short-term and long-term exposure (see para 44).

15 The method described is not suitable for immediate personal protection against an acute hazard, for which purpose a direct reading instrument or meter should be used.

### Working range

16 The working range of the method is dependent upon the volume of air sampled. For samples of the recommended minimum 10 litres of air, the lower limit of the working range is approximately 0.6 mg HCN/m<sup>3</sup> and the upper limit of the working range is approximately 70 mg HCN/m<sup>3</sup>.

### Precision and bias

17 On the basis of laboratory experiments,<sup>10</sup> the analytical precision of the method, measured as a coefficient of variation (CV<sub>A</sub>), has been determined to be

± 6.6% for samples containing 10 µg CN<sup>-</sup>, ± 5.4% for samples containing 100 µg CN<sup>-</sup>, and ± 4.3% for samples containing 200 µg CN<sup>-</sup>. These amounts of cyanide are approximately equivalent to those which would be collected at 1 mg HCN/m<sup>3</sup>, 10 mg HCN/m<sup>3</sup>, and 20 mg HCN/m<sup>3</sup> respectively, for samples of the recommended minimum 10 litres of air.

18 Assuming a sampling pump error (CV<sub>P</sub>) of ± 5% (see para 33), the overall precision of the method (CV<sub>T</sub>) for samples of the minimum 10 litres of air in the range 1 mg HCN/m<sup>3</sup> to 20 mg HCN/m<sup>3</sup> is expected to be generally better than ± 10%.

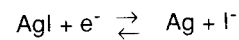
19 The bias of the method has been determined<sup>10</sup> to be less than ± 5% for samples containing between 10 µg CN<sup>-</sup> and 200 µg CN<sup>-</sup>.

### Sample stability

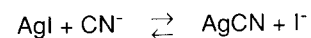
20 Samples containing between 10 µg CN<sup>-</sup> and 200 µg CN<sup>-</sup> have been shown to be stable for up to one week<sup>10</sup> at storage temperatures within the range 5°C to 25°C (ie sample loss is less than 10% under these conditions).

### Interferences

21 The cyanide ion-selective electrode utilises a silver iodide solid state membrane. Its electrode potential is governed by



The electrode also measures the activity (which is proportional to concentration under the experimental conditions described) of free cyanide ions in solution through the reaction



Iodide necessarily interferes with cyanide determination, as do certain chemical agents which form insoluble salts or complexes with silver, iodide or cyanide. In particular the cyanide ion-selective electrode is subject to severe interference from sulphide, but this is removed by quantitative addition of a cadmium salt solution before determining cyanide (see para 61).

### REAGENTS

22 During the analysis use only reagents of recognised analytical reagent grade. Use only distilled water or de-ionized water, or water of equal purity (para 23). DO NOT PIPETTE BY MOUTH.

### Water

23 Distilled or de-ionized water. The electrical resistance should be greater than 0.5 Megohm x cm or

the electrical conductance less than 2 µmho/cm.

### 0.1 M potassium hydroxide solution

24 Dissolve 5.6 g of potassium hydroxide pellets in de-ionized water (para 23). Cool, and dilute to volume with de-ionized water in a 1 litre volumetric flask. Mix thoroughly.

### 0.1 M silver nitrate solution

25 Either : Dissolve 1.699 g of silver nitrate, dried at 120°C for 2 hr, in de-ionized water (para 23), and make to volume with de-ionized water in a 100 ml volumetric flask.

or : Dilute commercially available ampoules of concentrated silver nitrate solution to volume with de-ionized water (para 23) in an appropriate size of volumetric flask.

or : Use commercially available 0.1 M silver nitrate solution.

NOTE : Protect the silver nitrate solution from the light (eg store it in an amber container), and freshly prepare/replace this reagent regularly. For complete accuracy standardise it before use with sodium chloride, using potassium chromate/potassium dichromate as an indicator.<sup>11</sup>

### Stock standard cyanide solution

26 Dissolve 0.651 g of potassium cyanide and 0.56 g potassium hydroxide in de-ionized water (para 23), and dilute to volume with de-ionized water in a 100 ml volumetric flask. Mix thoroughly. This solution has a notional concentration of 0.1 M CN<sup>-</sup>. In order to accurately determine the actual concentration of the stock standard cyanide solution, 'y' M CN<sup>-</sup>, the solution should be titrated with standardised silver nitrate (see Appendix 1).

NOTE 1: Prepare this reagent freshly each month. Re-determine the actual molar cyanide concentration of the solution on every occasion that the solution is to be used to prepare fresh cyanide calibration solutions (paras 55-59).

NOTE 2: Dispose of unused stock standard cyanide solution in an appropriate manner (see para 70) when fresh reagent is prepared.

### Lead acetate test papers

27 Commercially available lead acetate test papers.

### Cadmium solution

28 A suitable solution for precipitation of sulphide may be prepared by dissolving between 2 g and 3 g of cadmium nitrate (Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O) in 1 litre of de-ionized

water (para 23). Alternatively use commercially available 1000 µg/ml cadmium solution, as supplied for atomic absorption spectrometry.

## SAMPLING EQUIPMENT

### Pre-filter for hydrogen cyanide

29 A 25 mm diameter filter that will give more than 95% filtration efficiency at 0.3 µm at a flow rate between 200 ml/min and 1 litre/min. Filters that meet this specification include Millipore mixed cellulose ester, 0.8 µm pore size, type AA, and Gelman glass fibre, type A/E. Similar filters are made by Balston Ltd, Glasrock Inc, Sartorius Instruments Ltd, Whatman Laboratory Products Ltd, etc. Filters made from other materials may also be suitable.

### Filter holder

30 A filter holder designed to take a 25 mm diameter filter is required. A protective cap is required to cover the loaded filter holder while not sampling. The filter and filter holder must not permit leakage of dust or vapour.

### Midget impinger

31 A suitable midget impinger is required. A number of designs of impinger are available, some of which are described in references 12 and 13. The design is not critical, but it is suggested that a 'fritted tip' midget impinger is used. The two parts should be matched so that the distance between the inlet tube and the receiver bottom is between 1 mm and 2 mm.

32 A holder for the midget impinger is required for personal sampling. This will also need to accommodate a trap, if used (see para 34).

### Pump

33 A pump is required that is capable of maintaining the recommended flowrates of either 200 ml/min or 1 litre/min (see para 44) through the loaded filter holder and midget impinger throughout the sampling period. The total volume of air sampled by the pump over the sampling period should be within ± 5% of the calculated volume. A flow-stabilised pump may be necessary to achieve this. For personal sampling, the pump should be light and portable, such that it is capable of being worn by employees while carrying out their normal work. Reference 14 gives useful information on portable pumps.

34 A suitable trap may be connected between the midget impinger and the pump to prevent any splashover of impinger liquid resulting from accidental tipping from being drawn into the pump.

### Flowmeter

35 A portable flowmeter, previously calibrated against a primary standard (see Appendix 2), is required. This

should have enough sensitivity to permit the flow to be read to within  $\pm 5\%$  (para 33). If it meets this requirement, the flowmeter incorporated into the pump can be used, but it should be calibrated with a loaded filter holder and midjet impinger in line, and read with the flowmeter vertical if of the supported float type. A flowmeter in the pump or elsewhere in-line will also be misleading if there are leaks in the sampling train between sampling head and flowmeter.

#### **Ancillary equipment**

36 Flexible plastic tubing is required to connect the filter holder to the midjet impinger (this should be kept to the minimum possible length), and the midjet impinger to the pump; for personal sampling a belt or harness to which the pump can conveniently be fixed is required unless the pump is sufficiently small to fit in the worker's pocket; and leakproof narrow-mouthed plastic bottles with screwcap closures, or similar, are required to transport sample solutions.

### **ANALYTICAL APPARATUS**

#### **Labware**

37 A selection of standard laboratory glassware or plastic ware is required, for example beakers, volumetric flasks, measuring cylinders etc. These should be specially cleaned (para 54) and kept specifically for use in cyanide determination.

#### **Piston Operated Volumetric Apparatus (POVA)**

38 An adjustable microlitre pipette, suitable for use over the range 20  $\mu\text{l}$  to 200  $\mu\text{l}$ , is recommended for preparation of standard solutions; and an additional adjustable microlitre pipette, multi-dispensing pipettes, or bottletop dispensers are recommended for reagent addition and for dilution of the sample solution (if necessary).

39 POVA should be regularly maintained according to the manufacturer's or supplier's instructions, and should be checked prior to use to verify accuracy.

#### **Selective ion meter and measuring electrodes**

40 A selective ion meter or suitable high-impedance mV meter, capable of reading to  $\pm 0.1$  mV, is required.

41 An electrode system is required (see para (v) of Appendix 1) for use in standardisation of the stock standard potassium cyanide solution (para 26).

42 A cyanide ion-selective electrode, and suitable reference electrode, as recommended by the manufacturer of the cyanide ion-selective electrode, are required for cyanide determination.

#### **Stirrer**

43 A magnetic stirrer and small magnetic follower, or a mechanical stirrer is required.

### **TAKING THE SAMPLE**

#### **Selection of sampling time and flowrate**

44 Select the sampling time and flowrate with due regard to the purpose of measurement. Measurement of short-term exposure is necessary to check that statutory requirements are being met, since hydrogen cyanide is listed in Schedule 1 of the COSHH Regulations<sup>8</sup> with a short-term maximum exposure limit. This measurement is achieved through sampling for 10 minutes at a flowrate of 1 litre/min. Measurement of long-term exposure is achieved through sampling for between 1 hour and 3 hours at a flowrate of 200 ml/min. Note that the maximum sample volume is 40 litres (see para 14).

#### **Preparation of the sampling equipment**

45 Pipette 10 ml of 0.1 M potassium hydroxide solution (para 24) into a clean dry midjet impinger (para 31). Attach a filter holder (para 30) loaded with a pre-filter (para 29) to the inlet tube of the midjet impinger, and connect the outlet tube to the suction side of the pump (para 33) via a trap (para 34). To minimise contamination, carry out this preparation in a cyanide-free environment.

46 Prepare sample blanks by setting up filter holder/midjet impinger assemblies, as described in para 45, and subjecting them to the same handling procedure as that used for sampling, except that no air is drawn through them. Prepare one blank for each batch of ten samples, with a minimum of two blanks for ten samples or less.

#### **Preparation for sampling**

47 To allow the pump to warm up, connect it to a loaded filter holder/midjet impinger assembly using flexible tubing, set the required flowrate of either 200 ml/min or 1 litre/min using the calibrated flowmeter (para 35), and allow it to run for 15 minutes so that the flowrate can steady (experience may show warm-up to be unnecessary with some types of stabilised flow pumps, although the precision requirements in para 33 should be met). Then replace the midjet impinger used to set up the flowrate with one through which no air has been drawn, for collection of the sample. Finally, re-adjust the flowrate to 200 ml/min or 1 litre/min using the calibrated flowmeter (para 35).

#### **Positioning the sampler**

48 For measurement of personal exposure, fix the filter holder/midjet impinger assembly to the upper lapel or shoulder of the worker's clothing, as close to the mouth and nose as practical, but in any case within 200 mm of them. Wherever possible adopt the same sampler position for each worker. In some circumstances a higher concentration may be expected on one side of the worker than the other; in such cases position the sampler on the side expected to give the higher result.

## Collection of samples

49 At the start of the sampling time remove the protective cap from the filter holder, start the pump, and note the time.

50 If long-term exposure is being measured, check the flowrate periodically (eg hourly) during the sampling period, using the calibrated flowmeter (para 35). Re-adjust to 200 ml/min as appropriate. (Operating experience may show this to be unnecessary with some types of pump, but it is still advisable in order to check that the equipment is functioning correctly.)

51 When the required sample volume (see para 44) has been drawn through the filter, note the time, check the flowrate, switch off the pump, replace the protective cap on the filter holder, and remove the sampling equipment from the worker or sampling position.

52 Transport the filter holder/midget impinger assembly intact to a hydrogen cyanide-free area, and transfer the absorbing solution to a leakproof narrow-mouthed plastic bottle with screwcap closure, or other suitable container. Wash the impinger and stem with a few millilitres of 0.1 M potassium hydroxide solution (para 24), and add the washings to the bottle. Label the bottle, and seal tightly to prevent leakage during transportation to the laboratory. Discard the pre-filter.

53 Proceed with analysis as soon as possible after sampling.

## ANALYSIS

### Cleaning of glassware

54 Before use, clean all glassware. Firstly soak overnight in detergent solution to remove residual grease or chemicals; then soak in 0.1 M potassium hydroxide solution (para 24) for several hours to remove any leachable contaminants; and finally rinse thoroughly with de-ionized water (para 23). Glassware which has previously been subjected to this cleaning procedure, and which has been reserved for analysis of cyanide, is adequately cleaned by rinsing thoroughly with 0.1 M potassium hydroxide solution and then with de-ionized water.

### Preparation of standard solutions for calibration of selective ion meter

55 The ion-selective electrode determination of cyanide is affected by pH and ionic strength, so it is important that the concentration of potassium hydroxide in sample, blank and standard solutions is identical.

NOTE: The 0.1 M potassium hydroxide (para 24) used as absorbing solution has a sufficiently high ionic strength and pH to ensure that any changes that occur as a result of air sampling are not large enough to impair accurate quantitative determination of cyanide.

56 Five cyanide calibration solutions (A-E) are prepared (paras 57-59) at notional concentrations of  $10^{-3}$  M  $\text{CN}^-$ ,  $4 \times 10^{-4}$  M  $\text{CN}^-$ ,  $10^{-4}$  M  $\text{CN}^-$ ,  $4 \times 10^{-5}$  M  $\text{CN}^-$ , and  $10^{-5}$  M  $\text{CN}^-$  (notional pCN values of 3, 3.4, 4, 4.4, and 5 respectively). The actual concentration of the cyanide calibration solutions (see para 65) is dependent upon the actual concentration of the stock standard cyanide solution (see para 26 and Appendix 1). Prepare the calibration solutions immediately before use.

57 Cyanide calibration solution A ( $10^{-3}$  M  $\text{CN}^-$ ). Add 1.00 ml of stock standard cyanide solution to a 100 ml volumetric flask, and dilute to volume with 0.1 M potassium hydroxide solution (para 24). Stopper, and shake to mix thoroughly.

58 Cyanide calibration solution B ( $4 \times 10^{-4}$  M  $\text{CN}^-$ ). Add 1.00 ml of stock standard cyanide solution to a 250 ml volumetric flask, and dilute to volume with 0.1 M potassium hydroxide solution (para 24). Stopper, and shake to mix thoroughly.

59 Cyanide calibration solutions C, D, and E ( $10^{-4}$  M  $\text{CN}^-$ ,  $4 \times 10^{-5}$  M  $\text{CN}^-$ , and  $10^{-5}$  M  $\text{CN}^-$  respectively) are prepared by serial dilution of cyanide calibration solution A (para 57), cyanide calibration solution B (para 58), and cyanide calibration solution C (para 59), respectively. Pipette 5 ml of the appropriate ten strength cyanide calibration solution into a 50 ml volumetric flask, and make up to volume with 0.1 M potassium hydroxide solution (para 24). Stopper, and shake to mix thoroughly.

### Preparation of sample solutions

60 Transfer the sample and blank solutions from the bottles used for transportation to separate 100 ml beakers. Rinse each bottle with a few millilitres of unused 0.1 M potassium hydroxide solution (para 24), and combine the washings with the original solution.

61 Test each sample solution to determine whether any sulphide has been collected, by touching a drop of sample solution to a piece of lead acetate paper (para 27). If a positive identification of sulphide is given, add cadmium solution (para 28) dropwise until no further precipitation of yellow cadmium sulphide is apparent. Recheck the solution with lead acetate paper, and if sulphide has not been completely removed repeat the process.

62 When a drop of solution no longer discolours lead acetate paper, filter through a suitable paper filter (eg Whatman 540), pre-washed with 0.1 M potassium hydroxide (para 24), into a 25 ml volumetric flask. Wash the beaker with 0.1 M potassium hydroxide, and transfer the washings to the volumetric flask contents through the filter paper. Ensure that the filter paper is also subsequently adequately washed with 0.1 M potassium hydroxide, then make up to volume with 0.1 M potassium hydroxide and stopper and mix thoroughly.

### Preparation for analysis

63 Adjust the standard, blank, and sample solutions to

the same temperature eg  $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . (Potential readings are a function of temperature.)

64 Connect the measuring and reference electrodes to the selective ion meter or high-impedance mV meter (para 40) as described in the manufacturer's handbook. Pre-condition the ion-selective electrode by placing it in the low cyanide calibration solution E (para 59) until the electrode potential becomes satisfactorily stable, eg when it has remained constant to  $\pm 0.1$  mV for 1 minute.

#### Calibration

65 Measure the mV readings of the cyanide calibration solutions in increasing order of concentration, following the instructions in paras 68/69. Calculate the actual molar cyanide concentration of the calibration solutions by multiplying the notional molar concentration (see para 56) by the factor 'x', where  $x = 0.1/y$  and y is defined in para 26. Then calculate the actual pCN value of the calibration solutions (pCN is the negative logarithm of the molar cyanide concentration, ie  $-\log_{10}[\text{CN}^-]$ ), and plot a calibration graph of mV against pCN value. The slope of the calibration graph should be  $-59 \text{ mV} \pm 3 \text{ mV}$  per decade of concentration at  $25^{\circ}\text{C}$  if the meter and the electrodes are functioning correctly.

#### Determination of cyanide concentration

66 Determine the mV reading of the blank and sample solutions, following the instructions in paras 68/69. Obtain the pCN values of these solutions from the calibration graph (para 65).

67 Calculate hydrogen cyanide-in-air results from pCN values using the formula given in para 71.

#### Potential measurements

68 Transfer the solution to be measured to a small beaker, immerse the cyanide ion-selective electrode and the reference electrode in the solution, and stir, either magnetically or mechanically (if magnetic stirring is used, care should be taken to ensure that there is no heat transfer from the stirrer to the sample). Record the electrode potential when it has become satisfactorily stable, eg when it has remained constant to  $\pm 0.1$  mV for 1 minute.

NOTE: A minimum of 5 minutes is needed for the electrode potential to stabilise, and with very dilute solutions this time becomes considerably longer. Therefore, measure standards and samples in order of increasing concentration to minimise this response time.

69 Rinse the electrodes thoroughly with water between readings, and blot dry with tissue paper. This prevents any cyanide carry over to the next solution measured.

#### Disposal of solutions containing cyanide

70 Dispose of cyanide standard solutions and sample solutions containing cyanide in an appropriate manner,

with due consideration to the fact that hydrogen cyanide will be liberated if such solutions are allowed to come into contact with acid. For example, treat such solutions with sodium hypochlorite solution to destroy the cyanide prior to discharge into drains.<sup>15</sup>

#### CALCULATIONS

71 Let  $\text{pCN}_s =$  pCN of sample  
 $\text{pCN}_b =$  pCN of blank  
 $V_a =$  volume of air sampled (litres)  
 $V_s =$  volume of analyte solution (ml)

Then

$$\text{Concentration of hydrogen cyanide in air (mg HCN/m}^3) = \frac{(10^{-\text{pCN}_s} - 10^{-\text{pCN}_b}) \times 27\,000 \times V_s}{V_a}$$

#### REPORT

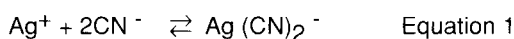
72 Report the hydrogen cyanide-in-air concentration to the nearest  $0.1 \text{ mg HCN/m}^3$ .

#### APPENDIX 1

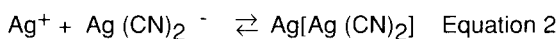
##### Standardisation of stock standard cyanide solution

##### Theory

(i) When cyanide solutions are titrated with silver nitrate the dicyanoargentate species is formed, provided there is an excess of cyanide:



(ii) When all the cyanide has reacted, further additions of silver nitrate result in the formation of slightly soluble silver dicyanoargentate:



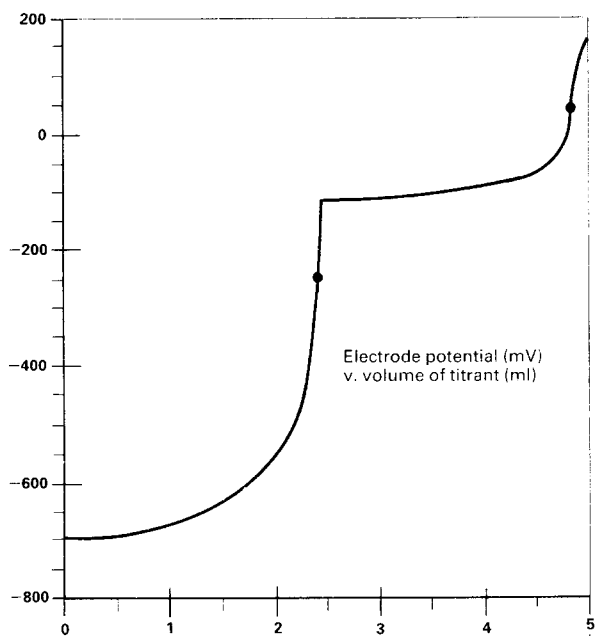
Silver dicyanoargentate imparts a turbidity to the solution, indicating the end-point of the reaction. The occurrence of this turbidity is the basis of the method for standardisation of cyanide solutions proposed by Liebig, which was later modified by Deniges to produce the Liebig-Deniges method.<sup>16</sup>

(iii) However, in practice silver cyanide is precipitated locally and redissolves very slowly, so it is more convenient to follow the course of the reaction potentiometrically.

(iv) Potentiometric titration involves addition of aliquots of standardised silver nitrate solution to the cyanide solution to be standardised, and measurement of the

electrode potential after each addition. Near the equivalence points smaller aliquots are added.

(v) There are three possible electrode systems which are equally suitable for the standardisation of cyanide solutions by potentiometric titration. These are a 'combined' silver electrode, a silver rod electrode and reference electrode, or a silver/sulphide ion selective electrode and reference electrode. (Reference electrodes used must not contain chloride, since insoluble silver chloride will block the porous plug of the electrode.)



**Fig 1** Titration of 5ml of stock standard cyanide solution (para 26) with 0.1 M  $\text{AgNO}_3$  (para 25)

(vi) When the electrode potential is plotted against the volume of titrant added, the end points of the titration can be estimated from the graph by inspection. Figure 1 illustrates the general appearance of the plot obtained when using a 'combined' silver electrode, and it can be seen that the two end points are approximately -260 mV and +60 mV for  $\text{Ag}(\text{CN})_2^-$  and  $\text{Ag}[\text{Ag}(\text{CN})_2]$  respectively.

(vii) However, the end points are more accurately determined by calculating the first derivative, plotting this against the volume of titrant added, and determining the position of the peaks.

(viii) The molar concentration of cyanide in the stock standard cyanide solution is calculated from the titre of 0.1 M silver nitrate solution added at the end points. From equation 1, the number of moles of cyanide in the aliquot of cyanide solution titrated is equal to twice the number of moles of silver in the titre of silver nitrate added at the first end point; and from equations 1 and 2, the number of moles of cyanide in the aliquot of cyanide solution titrated is equal to the number of moles of silver in the titre of silver nitrate added at the second end point. Each of the two end points yields a separate result for

the molar concentration of cyanide in the stock standard cyanide solution. These can be used to cross-check one another.

#### Method

(ix) Pipette 5 ml of the stock standard cyanide solution (para 26) into a clean beaker or conical flask, and dilute with approximately 30 ml of de-ionized water (para 23). Immerse the electrode(s) in the solution, and stir, either magnetically or mechanically (if magnetic stirring is used, care should be taken to ensure that there is no heat transfer from the stirrer to the sample).

Either:

(x) Carry out the titration using an autotitrator to automatically titrate the solution with 0.1 M silver nitrate solution (para 25) and determine the end points. Then proceed to para (xvi) of this appendix to calculate the concentration of cyanide in the stock standard cyanide solution.

Or:

(xi) Position a 5 ml burette containing the titrant, 0.1 M silver nitrate solution (para 25), over the beaker, in such a way that the solution can be added to the beaker while stirring. Record the electrode potential when it has become satisfactorily stable, eg when it has remained constant to  $\pm 0.1$  mV for 1 minute.

(xii) Add 0.5 ml of titrant to the solution being titrated using the burette, and record the electrode potential when it has become satisfactorily stable, eg when it has remained constant to  $\pm 0.1$  mV for 1 minute. Continue to add 0.5 ml aliquots of titrant, and record the stable electrode potentials until one or two points have been obtained after the two very large jumps in the potential (of the order of 500 mV and 250 mV respectively) which correspond to the two end points. Typical results are shown below in Table 1.

**Table 1**

Vol of $\text{AgNO}_3$ (ml)	$E$ (mV)
0	-803.7
0.50	-760.1
1.00	-729.7
1.50	-697.9
2.00	-645.5
2.50	-138.5
3.00	-136.9
3.50	-129.2
4.00	-116.7
4.50	-93.6
5.00	+171.0

(xiii) Estimate the approximate position of the two end points by inspection, and repeat the procedure given in paras (xi) and (xii) using a new aliquot of stock standard cyanide solution, but reduce the volume of the aliquot of titrant added to 0.05 ml in the vicinity of the end points.

### Determination of end points

(xiv) Calculate the first derivative, which is the rate of change of electrode potential with volume (ie  $\Delta E/\Delta v$ ), by dividing the change in the electrode potential by the volume of titrant added. (Note that the value of the first derivative obtained relates to the mean volume of titrant added for the range over which the derivative was calculated.) Typical results are shown below in Table 2.

**Table 2**

Vol of AgNO <sub>3</sub> (ml)	E (mV)	$\Delta E/\Delta v$
0	-793.6	47
0.50	-770.0	88
1.00	-726.1	64
1.50	-694.1	180
2.00	-640.5	228
2.05	-629.1	180
2.10	-620.1	240
2.15	-608.1	298
2.20	-593.2	418
2.25	-572.3	494
2.30	-547.6	856
2.35	-504.8	7690
2.40	-120.3	-274
2.45	-137.0	-38
2.50	-138.9	8
3.00	-134.8	14
3.50	-127.9	25
4.00	-115.3	48
4.50	-91.4	78
4.55	-87.5	104
4.60	-82.3	112
4.65	-76.7	152
4.70	-69.1	226
4.75	-57.8	340
4.80	-40.8	3334
4.85	+125.9	296
4.90	+140.7	302
4.95	+155.8	256
5.00	+168.6	

\*End point 1 (2.375 ml)

\*End point 2 (4.825 ml)

(xv) Determine the end points accurately by inspection, or plot the first derivative against the volume of titrant added and locate the end points accurately by the position of the peaks. Calculate the molar concentration of cyanide in the stock standard cyanide solution using the formulae given in para (xvi).

### Calculation

(xvi)

- Let  $M_{Ag}$  = molar concentration of the silver nitrate titrant  
 $V_{CN}$  = volume of stock standard cyanide solution titrated (ml)  
 $V_1$  = volume of titrant added at 1st end point (ml)  
 $V_2$  = volume of titrant added at 2nd end point (ml)

Then the molar concentration of the stock standard cyanide solution,  $M_{CN}$  is given by either:

$$M_{CN} = \frac{2 \times M_{Ag} \times V_1}{V_{CN}}$$

or by

$$M_{CN} = \frac{M_{Ag} \times V_2}{V_{CN}}$$

(xvii) Verify that the results obtained from the two end points agree to within  $\pm 5\%$ , calculate the mean result, and use this value as the actual concentration of cyanide in the stock standard cyanide solution ('y'  $\mu\text{g CN}^-/\text{ml}$  in para 26). In the example given in Table 2, the molar concentration of the stock standard cyanide solution as calculated from the first and second end points is 0.0950 M  $\text{CN}^-$  and 0.0965 M  $\text{CN}^-$  respectively, and the mean result is 0.0957 M  $\text{CN}^-$ .

## APPENDIX 2

### Primary standard for calibration of portable flowmeter

The primary standard should preferably be a flowmeter whose accuracy is traceable to national standards, used with careful attention to the conditions of the calibration certificate. A bubble flowmeter may be used. This is an arrangement whereby the pump under test draws a soap film up a calibrated tube. The passage of the film is accurately timed between two marks whose separation defines a known volume. A 1 litre burette can form a suitable tube. The volume between the marks can be checked by filling the burette with de-ionized water (para 23), allowing temperatures to stabilise, drawing off a known volume, and weighing the water, making allowance for the dependence of volume on temperature. A suitable bubble solution can be made by mixing one part of concentrated washing-up liquid, two parts glycerol, and four parts water. The burette must be thoroughly wetted with the solution, and several attempts at drawing the film up the tube may be necessary before the tube is wet enough for this to be achieved consistently. (Traceability of the calibration will require checking of the clocks, and use of certificated weights.)

### ADVICE

Advice on this method and the equipment used may be obtained from the Health and Safety Executive, Occupational Medicine and Hygiene Laboratory, 403 Edgware Road, London NW2 6LN (Tel 081-450 8911).

The Health and Safety Executive wishes, wherever possible, to improve the methods described in this series. If users have any comments which they feel could be so used, they are invited to send them to the above address.

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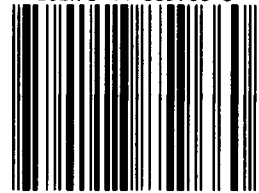
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