HSE
Health and Safety Executive

Hydrogen cyanide in air

Laboratory method using ion-selective electrode

MDHS56/3

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

Scope

1 This method describes a procedure for the measurement of time-weighted average concentrations of hydrogen cyanide in air. The method is suitable for both short and long-term measurements but care must be taken when carrying out personal sampling due to the potential of spillage of impinger solution. Methods more suitable for personal sampling which avoid the use of an impinger can be found elsewhere.[1, 2]

Summary

2 A measured volume of air is drawn through an impinger containing 0.1 M potassium hydroxide solution. A pre-filter, attached to the impinger inlet, reduces interference by removing cyanide and heavy metal particulates. Free cyanide ions are then determined using a cyanide ion-selective electrode.

3 The use of alternative methods not included in the MDHS series is acceptable provided they can demonstrate the accuracy and reliability appropriate to the application.

Recommended sampling

4 A minimum sample volume of 10 litres at air flow rates of 0.2–1 $l.min^{-1}$. A maximum sample volume of 40 litres is recommended. 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.[3]

5 The working range of the method is dependent on the volume of air sampled. For samples of the recommended minimum 10 litres of air the working range is approximately 0.6–70 $mg.HCN.m^{-3}$.

Prerequisites

6 Users of this method will need to be familiar with the content of MDHS14.[4]

Safety

7 Users of this method should be familiar with standard laboratory practice and carry out a suitable risk assessment. It is the user's responsibility to establish appropriate health and safety practices and to ensure compliance with regulatory requirements.

8 Cyanide salts or solutions of cyanide salts may produce hydrogen cyanide gas upon contact with acid. Ensure that disposal of cyanide containing solutions avoids the possibility of cyanide release (for example by prior treatment with sodium hypochlorite solution).

Equipment

9 Pre-filter and holder: A 25 mm filter capable of 95% filtration efficiency at 0.3 µm particle size, mounted in a suitable holder (GFA or mixed cellulose ester filter mounted in an IOM head have been found suitable). This should be connected to the inlet of the midget impinger using a short piece of flexible tubing.

10 Midget impinger with fritted tip.

11 Personal sampling pump that meets the requirements of BS EN1232.[5]

12 A portable flow meter calibrated against a primary standard, with a measurement uncertainty typically less than ±2%.

13 Flexible plastic tubing of a suitable diameter for making a leak-proof connection from the sampling head to the pump; belts or harnesses to facilitate attachment of sampling apparatus to sample subjects; small plastic or glass screw-cap bottles for transport of impinger solutions back to the laboratory.

Laboratory apparatus and reagents

14 During the analysis use only reagents of a recognised analytical grade. Use only distilled or deionised water.

15 Deionised water: Complying with the requirements of ISO 3696 grade 2 water (electrical conductivity less than 0.1 mS m^{-1} and resistivity greater than 0.01 MΩ.m at 25 °C).[6]

16 Potassium hydroxide solution (0.1 M): Dissolve 5.6 g potassium hydroxide pellets in deionised water. Cool and dilute to volume with deionised water in a 1 litre volumetric flask.

17 Silver nitrate solution (nominal concentration 0.1 M, standardise before use against sodium chloride solution using potassium chromate as indicator): Dissolve 1.699 g of silver nitrate, dried at 120 °C for 2 hours, in deionised water and make up to 100 ml in a volumetric flask. Alternatively, use commercially available silver nitrate solution diluted with deionised water if necessary to 0.1 M.

18 Cyanide stock standard solution (nominal concentration 0.1M CN^-): Dissolve 0.651 g of potassium cyanide and 0.56 g potassium hydroxide in deionised water and dilute to 100 ml in a volumetric flask. This solution has a notional concentration of 0.1 M.CN^-. In order to accurately determine the actual concentration of the stock solution, ‘y’ M.CN^-, the solution should be titrated with standardised silver nitrate solution before use (Appendix 1). Prepare a fresh cyanide solution monthly and standardise before each use.

19 Lead acetate test papers (for sulphide detection).

20 Cadmium solution (for precipitation of sulphide if required): Dissolve

21 2–3 g of cadmium nitrate ($Cd(NO_3)_2.4H_2O$) in deionised water and make up to 1 litre. Alternatively use commercially available 1000 µg.ml^{-1} solution.

22 Laboratory glassware: beakers, measuring cylinders and volumetric flasks. Glassware should be cleaned by soaking overnight in laboratory detergent or cleaned in a laboratory dishwasher followed by soaking for several hours in 0.1 M potassium hydroxide solution then finally rinsed in deionised water. For subsequent use of glassware reserved for this analysis, the overnight soaking in 0.1 M potassium hydroxide solution/dishwasher cleaning can be omitted.

23 A balance, calibrated against a primary standard, and capable of weighing to ±0.1 mg over the range 0 to 100 g.

24 Positive displacement micropipettes complying with the requirements of BS EN 8655-6:2002.[7]

25 Selective ion meter and measurement electrodes: A selective ion meter or suitable high impedance mV meter capable of ±0.1 mV resolution; an electrode system for standardisation of stock potassium cyanide solution (Appendix 1); a cyanide ion-selective electrode and reference electrode.

26 Magnetic stirrer.

Preparation and sampling

27 Select a sampling time and flow rate appropriate for the measurement, for example 10 min at 1 l.min^{-1} to assess a short-term exposure or between 1 and 3 hours at 200 ml.min^{-1} to assess a long-term exposure. Note that the maximum sampling volume is 40 litres.

28 In a clean cyanide-free area, pipette 10 ml of 0.1 M potassium hydroxide into a clean dry impinger. Attach a filter holder loaded with the pre-filter to the inlet of the impinger and connect the outlet to the pump via a trap.

29 Set up blank samplers in the same way but draw no air through them. Prepare one blank for each set of ten samples with a minimum of two blanks for ten samples or less.

30 For personal sampling, fix the sampling train on the lapel of the subject, within 200 mm of the nose and mouth. Where possible, adopt the same sampler position for each worker.

31 At the start of the sampling period, remove the protective cap from the filter holder, start the pump, set the required flow rate using the calibrated flow meter and record the time. Periodically check the flow rate during the sampling period.

32 When the sampling period is complete, note the time and flow rate. Switch off the pump and replace the protective cap on the filter holder.

33 Transport the sampling train to a hydrogen cyanide-free area and transfer the absorbing solution to a screw-cap sample bottle, washing the impinger stem with a few millilitres of 0.1 M potassium hydroxide solution, transferring the washings to the sample bottle.

34 Cap and label the samples and blank solutions and transport to the laboratory.

Calibration

35 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 samples, blanks and standard solutions is identical. The 0.1 M potassium hydroxide solution used as absorbing solution has 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.

36 Five cyanide calibration solutions (A-E) should be prepared immediately prior to use with notional concentrations of 10^{-3} M, 4 x 10^{-4} M, 10^{-4} M, 4 x 10^{-5} M, 10^{-5} M CN^- (this is equivalent to notional pCN values of 3, 3.4, 4, 4.4 and 5 respectively, where pCN is the negative logarithm of the molar cyanide concentration, ie – log10 $[CN^-]$). The actual concentration of cyanide calibration standards is dependent on the actual concentration of the standardised cyanide stock standard solution (see paragraph 47).

37 Cyanide calibration solution A (10^{-3} M CN^-.): Add 1.0 ml stock cyanide solution to a 100 ml volumetric flask and dilute to volume with 0.1 M potassium hydroxide solution. Stopper and mix.

38 Cyanide calibration solution B (4 x 10^{-4} M CN^-.): Add 1.0 ml stock cyanide solution to a 250 ml volumetric flask and dilute to volume with 0.1 M potassium hydroxide solution. Stopper and mix.

39 Cyanide calibration solutions C, D, E (10^{-4} M, 4 x 10^{-5} M and 10^{-5} M CN^- respectively): Prepared by serial dilution of cyanide calibration solution A, B and C. Pipette 5 ml of the appropriate cyanide calibration solution into a 50 ml volumetric flask and make up to volume with 0.1 M potassium hydroxide solution. Stopper and mix.

40 Equilibrate the standard solution to 25 °C ±2 °C (potential readings are a function of temperature).

41 Connect the measuring and reference electrodes to the selective ion meter or high-impedance mV meter as described in the manufacturer's operating instructions. Pre-condition the ion selective electrode by placing it in the low cyanide calibration solution E until the electrode potential becomes stable, eg when it has remained constant ±0.1 mV for 1 minute.

42 Measure the mV readings of the cyanide calibration solutions in increasing order of concentration.

43 Transfer the calibration 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. Stabilisation of the electrode potential will require a minimum of 5 minutes and very dilute solutions may require considerably longer. Record the electrode potential when stabilised at ±0.1 mV for 1 minute.

44 Rinse the electrodes thoroughly with deionised water and blot dry with tissue paper between readings.

45 Calculate the actual pCN values of the calibration standards by mulitplying the notional pCN value by 0.1/y where y is the actual molar concentration of the standardised cyanide stock standard solution (see paragraph 18), and plot a calibration graph of mV against pCN value. The slope of the graph should be –59 mV ±3 mV per decade of concentration at 25 °C if the meter and electrodes are functioning correctly.

Sample analysis

46 Transfer the sample solution to a 100 ml beaker. Rinse the sample bottle with a few millilitres of 0.1 M potassium hydroxide solution and add the washings to the sample solution.

47 Test the sample solution to determine whether any sulphide has been collected, by touching a drop onto a piece of lead acetate paper. If a positive result is given, add cadmium solution drop wise 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.

48 When the sample solution no longer discolours the lead acetate paper, filter through a suitable filter paper (eg Whatman 540), prewashed with 0.1 M potassium hydroxide solution, into a 25 ml volumetric flask. Wash the beaker with 0.1 M potassium hydroxide solution and transfer the washings to the volumetric flask through the filter paper. Finally wash the filter paper, transferring washings to the volumetric flask, make up to volume with 0.1 M potassium hydroxide solution and mix thoroughly.

49 Prepare the blank solutions in an identical manner.

50 Equilibrate the sample and blanks solutions to 25 °C ±2 °C (potential readings are a function of temperature) and analyse in an identical manner to the standards.

51 Determine the mV reading of the blank and sample solutions as for the calibration solutions to obtain the pCN values of these solutions from the calibration graph.

Calculations

Calculate the hydrogen cyanide in air results to the nearest 0.1 mg.m^{-3} from pCN values using:

$$\text{HCN in air (mg.m}^{-3}\text{)} = \frac{(10^{-\text{pCN}_S} - 10^{-\text{pCN}_b}) \times 27000 \times V_S}{V_a}$$

Where:

pCN_S = pCN of sample

pCN_b = pCN of blank

V_a = volume of air sampled (litres)

V_S = volume of analyte solution (ml)

Appendix 1: Additional information

Standardisation of the stock standard cyanide solution

Theory

1 When cyanide solutions are titrated with silver nitrate the dicyanoargenate species is formed, provided there is an excess of cyanide:

$Ag^+ + 2CN^- \leftrightarrow Ag(CN)_2^-$ (Equation 1)

2 When all the cyanide has reacted, further additions of silver nitrate result in the formation of slightly soluble silver dicyanoargenate:

$Ag^+ + Ag(CN)_2^- \leftrightarrow Ag[Ag(CN)_2]$ (Equation 2)

3 Silver dicyanoarginate imparts a turbidity to the solution, indicating the end-point of the reaction. In practice, silver cyanide is precipitated locally and redissolves very slowly, so it is more convenient to follow the course of the reaction potentiometrically.

4 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.

5 Three electrode systems are suitable for standardisation of cyanide solutions: combined silver electrode; a silver rod electrode and reference electrode; or silver/sulphide ion selective electrode and reference electrode (reference electrodes must not contain chloride since insoluble silver chloride will block the porous plug of the electrode).

6 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 two end points are approximately – 260 mV and +60 mV for $Ag(CN)_2^-$ and $Ag[Ag(CN)_2]$ respectively.

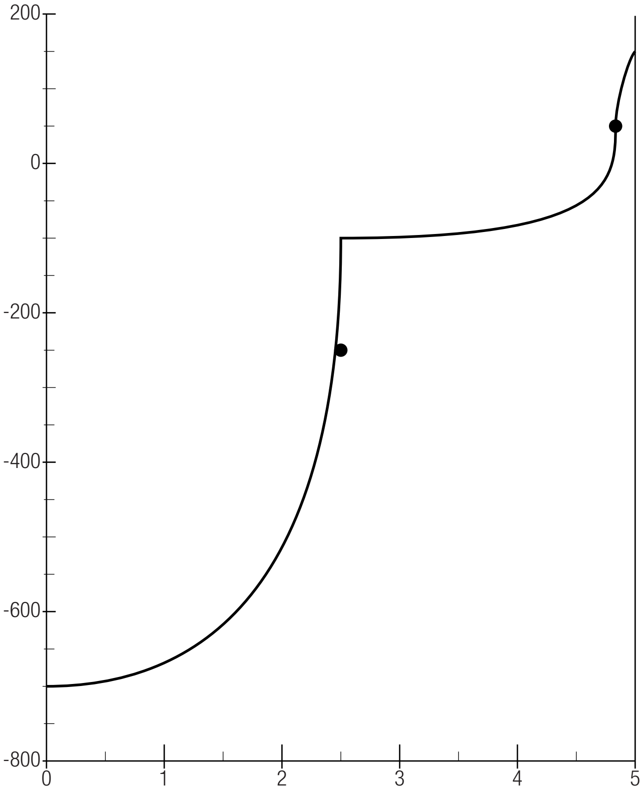

Figure 1 Titration of 5 ml of stock standard cyanide solution with 0.1 M $AgNO_3$

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

8 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. 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

9 Pipette 5 ml of the stock standard cyanide solution into a clean beaker and dilute with approximately 30 ml of deionised water. Immerse the electrode(s) in the solution and stir, either magnetically (slowly to avoid heat transfer) or mechanically. Perform the titration using an auto-titrator with 0.1 M silver nitrate solution and determine the end points. Then calculate the concentration of cyanide in the stock standard cyanide solution using Equation 3 (see paragraph 13 below).

10 Alternatively, manual titration may be used. Add 0.5 ml aliquots of 0.1 M silver nitrate solution while stirring. Record the electrode potential for each aliquot when it has become satisfactorily stable at ±0.1 mV for 1 minute. Repeat for further aliquots until one or two points have been obtained after the two very large changes in 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.

Vol of $AgNO_3$ (ml)	E (mV)
0.0	-803.7
0.5	-760.1
1.0	-727.7
1.5	-697.9
2.0	-645.5
2.5	-138.5
3.0	-136.9
3.5	-129.2
4.0	-116.7
4.5	-93.6
5.0	+171.0

Table 1 Electrode response to the addition of silver nitrate during standardisation of stock cyanide solution

11 Estimate the approximate position of the two end points, and repeat the procedure using a new aliquot of stock standard cyanide solution, but reduce the volume of the titrant added to 0.05 ml in the vicinity of the end points.

12 Calculate the first derivative, which is the rate of change of electrode potential with volume (ie ΔE/Δv) by dividing the change in 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.

Vol $AgNO_3$ (ml)	E (mV)	ΔE/Δv)	
0	-793.6		
0.50	-770.0	47	
1.00	-726.1	88	
1.50	-694.1	65	
2.00	-640.5	180	
2.05	-629.1	228	
2.10	-620.1	180	
2.15	-608.1	240	
2.20	-593.2	298	
2.25	-572.3	418	
2.30	-547.6	494	
2.35	-54.8	856	*End point 1 (2.375 ml)
2.40	-120.3	7690	
2.45	-137.0	-274	
2.50	-138.9	-38	
3.00	-134.8	8	
3.50	-127.9	14	
4.00	-115.3	25	
4.50	-91.4	48	
4.55	-87.5	78	
4.60	-82.3	104	
4.65	-76.7	112	
4.70	-69.1	152	
4.75	-57.8	226	
4.80	-40.8	340	*End point 2 (4.825 ml)
4.85	+125.9	3334	
4.90	+140.7	296	
4.95	+155.8	302	
5.00	+168.6	256	

Table 2 Precise electrode response to the addition of silver nitrate during standardisation of stock cyanide solution

13 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. Use the two end-point values to calculate separate values for the molar concentration of cyanide in the cyanide stock standard solution using Equations 3a and 3b.

Calculation of the molar concentration M_{CN} of the stock standard cyanide solution:

$$M_{CN} = \frac{2 \times M_{Ag} \times V_1}{V_{CN}} \qquad \text{(Equation 3a)}$$

or

$$M_{CN} = \frac{2 \times M_{Ag} \times V_2}{V_{CN}} \qquad \text{(Equation 3b)}$$

Where:

M_{Ag} = molar concentration of silver nitrate titrant

V_{CN} = volume of stock standard cyanide solution titrated (ml)

V_1 and V_2 = volume of titrant added at first and second end points respectively (ml).

14 Verify the results for the two end points agree to within ±5%, calculate the mean result, and use this as the value for the actual concentration of cyanide in the cyanide stock standard solution (y in paragraph 45 of the main text). In the example given in Table 2, the molar concentration of the cyanide stock standard solution as calculated from the first and second end points is 0.0950 M CN^1 and 0.0965 M CN^- respectively.

Overall uncertainty

15 The overall uncertainty for this measurement procedure as defined in BS EN 482[8] has not been determined. However, the analytical precision of the method, measured as a coefficient of variation, has been determined to be ±6.6% for samples containing 10 µg CN^-, ±5.4% for samples containing 100 µg CN^- and ±4.3% for samples containing 200 µg CN^-. For 10 litre sample volumes, these equate to air concentrations of 1, 10 and 20 $mg.m^{-3}$.[3]

16 The bias of the method has been determined to be less than ±5% for samples containing between 10 µg and 200 µg CN^-.[3]

17 Samples containing between 10 µg and 200 µg CN^- have been shown to be stable (sample loss under 10%) for up to one week at storage temperatures within the range 5 °C to 25 °C.[3]

Interferences

18 The cyanide ion-selective electrode utilises a silver iodide solid state membrane. Iodide in solution interferes with the cyanide determination as do other ions 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 which must be removed from solution as described.

References

1 ‘Hydrogen Cyanide, Methods 6010’ In NIOSH *Manual of analytical methods* (Fourth edition) Cincinnati, OHIO: US Dept of Health and Human services, Public Health Service, Centres for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering 1994

2 ‘Hydrogen Cyanide, Method 6017’ In *NIOSH Manual of analytical methods* (Fourth edition) Cincinnati, OHIO: U S Dept of Health and Human services, Public Health Service, Centres for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Physical Sciences and Engineering 1994

3 Ford J, Higgins PF and Howe AM *Evaluation and Validation of a Method for the Determination of Hydrogen Cyanide in Air by Collection in an Impinger and Analysis using a Cyanide Ion Selective Electrode* HSE Internal Report IR/L/AS/89/3 HSE 1990

4 *General methods for sampling and gravimetric analysis of respirable and inhalable dust* MDHS14/4 (Fourth edition) HSE 2014 www.hse.gov.uk/pubns/mdhs

5 BS EN 1232:1997 *Workplace atmospheres: Pumps for personal sampling of chemical agents. Requirements and test methods* British Standards Institution

6 BS EN ISO 3696:1995 *Water for analytical laboratory use. Specification and test methods* British Standards Institution

7 BS EN ISO 8655-6:2002 *Piston operated volumetric apparatus. Gravimetric methods for the determination of measurement error* British Standards Institution

8 BS EN 482 2006 *Workplace atmospheres: general requirements for the performance of procedures for the measurement of chemical agents*
British Standards Institution

You should use the most current edition of any standards listed.

Further information

For information about health and safety, or to report inconsistencies or inaccuracies in this guidance, visit www.hse.gov.uk/. You can view HSE guidance online and order priced publications from the website. HSE priced publications are also available from bookshops.

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