DRAFT OECD GUIDELINE FOR THE TESTING OF CHEMICALS

DETERMINATION OF PH, ACIDITY AND ALKALINITY

INTRODUCTION

1. This guideline describes the procedure for the electrometric determination of pH of an undiluted aqueous formulation; or, the pH of an aliquot of formulation mixed with distilled or deionized water. This guideline also describes procedures to determine acidity or alkalinity for a formulation that is acidic (pH < 4) or alkaline (pH > 10).

2. CIPAC MT 75.3 (1) and OPPTS 830.7000 (2) describe procedures for the determination of pH of a formulation or a 1% (w/v) aqueous dilution or dispersion of the formulation using a pH meter, electrode and calibration solutions. ASTM D1193 (3) and CIPAC MT 191 (4) provide guidance on the reagent water used for dilution. CIPAC MT 191 and ASTM D1067 (5) describe the procedures to determine acidity or alkalinity of formulations using titrimetry and electrometric fixed end-point determination.

3. This guideline is based on CIPAC MT 75.3 "Determination of pH Values" and CIPAC MT 191 "Acidity or Alkalinity of Formulations." CIPAC MT 191 was adopted from CIPAC MT 31 "Free Acidity or Alkalinity."

SIGNIFICANCE

4. This test guideline provides procedures to obtain data on pH, acidity and alkalinity of aqueous solutions or aqueous dispersions of formulations. The data will be used to assess the effects that the formulation may pose to human health and safety and the potential impact upon the environment.

SCOPE

5. This method is suitable for determining the pH of an aqueous formulation, in the range of $4 \leq pH \leq 10$. A non-aqueous formulation is dispersed in water to obtain the pH measurement.

6. If the formulation has a pH < 4, acidity is determined by titration with standardized strong base. Likewise, if the formulation has a pH > 10, alkalinity is determined with standardized strong acid.

OUTLINE OF THE METHOD

7. The pH of an aqueous formulation or a mixture of a formulation with water is determined with a pH meter equipped with an appropriate electrode system.

8. The acidity or alkalinity of a formulation in water is determined by titration with standard acid or alkali using electrometric end-point detection.

DEFINITION AND UNITS

9. Electrometric determination of pH measures the negative $\log_{10}$ aqueous hydronium ion concentration $[H_3O^+]$ of ideal solutions.

10. Consistent with CIPAC MT 31 and CIPAC MT 191, alkalinity is calculated as % NaOH (mass/mass) in the formulation; and, acidity is calculated as % HCl (mass/mass) in the formulation.

Note: Whereas OECD governmental agencies stipulate the units of % acid or alkali per mass of formulation as per CIPAC MT 191, there are other units encountered to express acidity and alkalinity. For example, g/kg (g acid or alkali per kg formulation) is sometimes used as a formulation specification. As carbonate and bicarbonate are naturally occurring buffers in the environment, alkalinity and acidity of a test substance may sometimes be reported as the meq/L of either carbonate or bicarbonate.

DESCRIPTION OF THE METHOD

Reagents

11. ***Buffer Solutions:*** pH 7, pH 4 and pH 10. These may be commercially available reference solutions or solutions prepared in the laboratory. If the solutions are prepared in the laboratory, document the preparation of the buffer solutions.

12. ***Water:*** Distilled or deionized water:

    a. With an electrical resistivity ≥ 1 mΩ-cm.

    b. Freshly distilled/deionized or stored to prevent accumulation of CO2 from the atmosphere (*e.g.* CIPAC RE 130).

13. ***Sodium Hydroxide Standard Solution:*** NaOH 0.01 to 0.02 mol/L standardized solution. This solution may be a commercially available standard solution or prepared in the laboratory (*e.g.* CIPAC RE 25).

14. ***Hydrochloric Acid Standard Solution:*** HCl 0.01 to 0.02 mol/L standardized solution. This solution may be a commercially available standard solution or prepared in the laboratory (*e.g.* CIPAC RE 14).

15. ***Acetone:*** An appropriate grade of acetone that reports acidity and alkalinity <0.01%.

Apparatus

16. ***pH Meter:*** Capable of at least a two-point calibration.

17. ***pH Electrode System:*** *e.g.* a single or dual glass electrode system conditioned and maintained according to the manufacturer's instructions.

18. ***Graduated Mixing Cylinders:*** 50 mL and 100 mL with stoppers.

19. ***Burette***: 25 mL.

20. ***Beakers:*** 200 to 250 mL (or other suitable containers for titration).

21. ***Magnetic Stirrer:*** Magnetic stirrer and stir bars suitable for titration.

22. ***Automatic Titrator:*** as alternative to the pH meter, pH electrode system, burette and stirrer.

Procedure

23. Determination of pH Value of a Formulation

c. ***Calibration:*** Operate the pH meter and the pH electrode system according to the manufacturer's operating instructions. Calibrate the measurement system (i.e. pH meter and pH electrode system) according to the manufacturer's operating instructions using at least two appropriate buffer solutions.

d. ***pH Measurement of a Diluted (1%) Formulation:***

i. Weigh 1.0 g of sample into a mixing cylinder containing ~50 mL reagent water. Add reagent water to 100 mL, stopper and shake vigorously until the formulation is completely mixed or dispersed.

ii. Transfer the solution or dispersion to a 200-mL beaker and allow any suspended material to settle for 1 minute.

iii. Ensure that the temperature of the formulation/water mixture does not differ from the reference solutions used for calibration. Immerse the electrode into the formulation/water mixture and measure the pH without stirring. Record the pH value after 1 minute. If the pH value changes more than 0.1 pH unit during this equilibration time, record the pH 10 minutes after immersion of the electrode.

Note: Fluctuation of the pH reading may be observed. This may be the result of insufficient ion concentration. The ion concentration can be increased, and pH reading stabilized, with the addition of some drops of a concentrated sodium chloride solution.

e. ***pH Measurement of an Undiluted Aqueous Formulation:*** Transfer sufficient formulation to a 100-mL beaker and proceed with 23-b-*iii* above

24. Determination of Acidity or Alkalinity of a Formulation

f. ***Calibration:*** Operate the pH meter and the pH electrode system according to the manufacturer's operating instructions. Calibrate the pH meter and pH electrode system according to the manufacturer's operating instructions using at least two appropriate buffer solutions.

g. ***Titration of Acidity or Alkalinity:***

i. If the pH from 23 above is < 4.0, acidity shall be determined using standardized sodium hydroxide solution. If the pH from 22 above is > 10.0 alkalinity, shall be determined using standardized hydrochloric acid solution.

ii. Weigh 10.0 g (record mass to the nearest mg) of sample into a 200-mL beaker. Add 100 mL reagent water and stir until the formulation is completely mixed or dispersed (see note at the end of 23-b-*iv*).

Note: If the formulation/water mixture cannot be titrated due to plugging of the electrodes, the formulation may be pre-treated with 10 mL of acetone prior to adding the deionized water. The use of acetone must be reported.

iii. Stir and titrate electrometrically to pH 7 at ambient temperature with an appropriate concentration of sodium hydroxide solution or hydrochloric acid solution depending on the pH of the solution.

iv. Calculate acidity or alkalinity using the appropriate equation below:

$$\%\ \text{Acidity (calculated as } H_2SO_4) = \frac{4.904 \times t \times c_1}{w}$$

$$\%\text{Alkalinity (calculated as NaOH)} = \frac{4.000 \times s \times c_2}{w}$$

where:

c_1 = c(NaOH), mol/L (normality) of the sodium hydroxide solution.

c_2 = c(HCl), mol/L (normality) of the hydrochloric acid solution.

t = volume (mL) of sodium hydroxide solution.

s = volume (mL) of hydrochloric acid solution.

w = weight (g) of sample.

Note: The sample weight (w) may be reduced if high acidity or alkalinity (*i.e.* exceeding 25 mL titrant) is anticipated.

DATA AND REPORTING

Raw Data

25. All raw data related to pH, alkalinity and acidity should be retained. This includes test facility worksheets, original observations, printouts from automated equipment, *etc.*

Test Report

26. The test report should include the following information:

h. Test substance or test item:

i. Formulation name, batch number (if any).

ii. Relevant physical-chemical properties or characteristics.

i. Test conditions:

i. Dates of the performance of the studies.

ii. Temperature during the experiment.

iii. pH observations and time, if necessary.

iv. Weights of samples.

v. Volume and titer of titrant used.

vi. Dilution of test substance.

vii. Use of acetone, if necessary.

viii. Description or identification of apparatus used.

j. Results:

i. pH.

ii. Temperature.

iii. Acidity or alkalinity, as appropriate.

LITERATURE

1. *Collaborative International Pesticide Analytical Council, Ltd. (CIPAC) Handbook*, "MT 75.3 Determination of pH Values," CIPAC, Hatching Green, Harpenden, Hertfordshire, England (1999).

2. United States Environmental Protection Agency, Product Properties Test Guidelines OPPTS 830.7000 "pH" EPA 712-C-96-030 (1996).

3. *Annual Book of ASTM Standards,* ASTM D 1193-06, "Standard Specification for Reagent Water," American Society for Testing and Materials, Philadelphia, PA (2006).

4. *Collaborative International Pesticide Analytical Council, Ltd. (CIPAC) Handbook*, "MT 191 Acidity or Alkalinity of Formulations" CIPAC, Hatching Green, Harpenden, Hertfordshire, England (2005).