Adopted:
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OECD GUIDELINES FOR THE TESTING OF CHEMICALS

Determination of pH, Acidity and Alkalinity

INTRODUCTION

1. This Test Guideline 122 describes the procedure for the electrometric determination of pH of an undiluted aqueous solution or dispersion; the pH of a 1% (w/v) dilution of a solution or dispersion in distilled or deionised water; or the pH of a chemical, diluted to end-use concentration. It also describes procedures to determine acid reserve or alkali reserve for a chemical that is acidic (pH < 4) or alkaline (pH > 10) with either strong or weak acid or alkali.

2. CIPAC MT 75.3 (1) and OPPTS 830.7000 (2) describe procedures for the determination of pH of a chemical[1] or a 1% (w/v) aqueous dilution or dispersion of the chemical 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 chemicals[1] using titrimetry and electrometric fixed endpoint determination.

3. This guideline is based on CIPAC MT 75.3 "Determination of pH Values" and CIPAC MT 191 "Acidity or Alkalinity of Formulations[1]". 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 chemicals (substances and mixtures). The data will be used to assess the effects that the chemical may pose to human health and safety and the potential impact upon the environment.

SCOPE

5. The method is suitable for determining the pH of an aqueous solution or aqueous dispersion, in the range of $0 \leq pH \leq 14$. A non-aqueous solution or dispersion should be diluted in water to obtain the pH measurement.

[1] CIPAC MT publications 75.3 and 191 use the word "formulation"

6. If the pH is lower than 4, acidity is determined by titration with standardized strong base. Likewise, if the pH is higher than 10, alkalinity is determined with standardized strong acid.

DEFINITION AND UNITS

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

8. Consistent with CIPAC MT 31 and CIPAC MT 191, alkalinity is calculated as % NaOH (mass/mass) in the solution or dispersion; and, acidity is calculated as % H_2SO_4 (mass/mass) in the solution or dispersion.

Note 1: Whereas OECD governmental agencies stipulate the units of % acid or alkali per mass of chemical 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 chemical[1]) is sometimes used. 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 (milliequivalent) of either carbonate or bicarbonate.

OUTLINE OF THE METHOD

9. The pH of an aqueous solution or dispersion in water is determined with a pH meter equipped with an appropriate electrode system.

10. The acidity or alkalinity of a solution or dispersion in water is determined by titration with standard acid or alkali using electrometric endpoint detection.

DESCRIPTION OF THE METHOD

Reagents

11. The reagents used are:

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 and assign an expiration date.

Water: Distilled or deionised water:

a. With an electrical resistivity ≥ 1 MΩ.cm.

b. Freshly distilled/deionised or stored to prevent accumulation of CO_2 from the atmosphere, *e.g.* CIPAC RE 130 (6).

Sodium Hydroxide Standard Solution: NaOH 0.01 to 0.2 mol/L standardized solution. This solution may be a commercially available standard solution or prepared in the laboratory,*e.g.* CIPAC RE 25 (7).

Acid standard solution: H_2SO_4 0.01 to 0.2 mol/L standardized solution. This solution may be a commercially available standard solution or prepared in the laboratory, *e.g.* CIPAC RE 28 (8).

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

Apparatus

12. The apparatus used are:

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

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

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

Burette: 25 mL.

Beakers: 100 to 250 mL (or other suitable containers for titration).

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

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

Procedure

13. Determination of pH value of a chemical:

a. ***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.

b. ***pH Measurement of a diluted (1%) solution or dispersion***:

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

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

iii. Ensure that the temperature of the diluted solution or dispersion of the chemical does not differ from the reference solutions used for calibration. Immerse the electrode into the diluted solution or dispersion of the chemical and immediately start the stopwatch. Record the pH value after one minute and two minutes, without stirring during the measurement. If the pH values differ by more than 0.1 pH units, record and report the pH value 10 minutes after immersion of the electrode. (Note: When using an automatic pH meter, where the measurement stops when the change in measured pH is less than a pre-set drift value of 0.1 pH units/min, a measurement period of less than 10 min. is acceptable).

Note 2: 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.

c. ***pH Measurement of an undiluted aqueous solution or dispersion***: Transfer sufficient solution or dispersion to a 100-mL beaker and proceed with 13-b-iii above.

14. Determination of acidity or alkalinity of a chemical:

a. ***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.

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

i. If the pH from 13 above is < 4.0, acidity will be determined using standardized sodium hydroxide solution. If the pH from 13 above is > 10.0, alkalinity will be determined using standardized sulphuric 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 complete dissolution or dispersion (see Note 2).

Note 3: If the solution or dispersion cannot be titrated due to plugging of the electrodes, the solution or dispersion may be pre-treated with 10 mL of acetone prior to adding the deionised water. The use of acetone must be reported.

iii. Stir and titrate electrometrically with an appropriate concentration of sodium hydroxide solution or sulphuric acid solution, at ambient temperature to an endpoint of pH 7.

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

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

$$\text{Alkalinity (Calculated as NaOH)} = \frac{4.001 \times s \times c_2}{w} (\%\ m/m)$$

where:

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

c_2 = c (H_2SO_4), mol/L (normality) of the solution

t = volume (mL) NaOH solution (endpoint pH 7)

s = volume (mL) of H_2SO_4 solution (endpoint pH 7)

w = weight (g) of sample

Note 4: 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

15. 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

16. The test report should include the following information:

Chemical

i. Name, batch number (if any)

ii. Relevant physical-chemical properties or characteristics

Test conditions

i. Dates of the performance of the measurements

ii. Temperature during the experiment

iii. pH measurement time and observations , 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

Results

i. pH

ii. Temperature

iii. Acidity or alkalinity, as appropriate

iv. Measurement uncertainty

LITERATURE

(1) Collaborative International Pesticide Analytical Council, Ltd. (CIPAC) (2000), *Handbook **J*** "*MT 75.3 Determination of pH Values*" CIPAC (http://www.cipac.org) as amended by erratum http://www.cipac.org/errata.htm : Handbook J. CIPAC Publications available from: Marston Book Services Ltd.: (http://www.marston.co.uk).

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

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

(4) Collaborative International Pesticide Analytical Council, Ltd. (CIPAC) (2006), *Handbook **L*** "*MT 191 Acidity or Alkalinity of Formulations*" CIPAC (http://www.cipac.org). CIPAC Publications available from: Marston Book Services Ltd.: (http://www.marston.co.uk).

(5) ASTM International (2006), *Standard Test Methods for Acidity or Alkalinity of Water Annual* Book of ASTM Standards, ASTM D 1067-06, American Society for Testing and Materials, Philadelphia, PA.

(6) CIPAC RE 130 (Water for Laboratory Use) – Collaborative International Pesticide Analytical Council, Ltd. (CIPAC) (1993), *Handbook **E**, "Reagents, Indicators, and Solvents – RE 130 Water for Laboratory Use*" CIPAC (http://www.cipac.org). CIPAC Publications available from: Marston Book Services Ltd.: (http://www.marston.co.uk).

(7) CIPAC RE 25 (Sodium Hydroxide) – Collaborative International Pesticide Analytical Council, Ltd. (CIPAC) (1993), *Handbook **E**, "Reagents, Indicators, and Solvents – RE 25 Sodium Hydroxide*" CIPAC (http://www.cipac.org). CIPAC Publications available from: Marston Book Services Ltd.: (http://www.marston.co.uk)

(8) CIPAC RE 28 (Sulphuric Acid) – Collaborative International Pesticide Analytical Council, Ltd. (CIPAC) (1993), *Handbook **E**, "Reagents, Indicators, and Solvents – RE 28 Sulphuric Acid*" CIPAC (http://www.cipac.org). CIPAC Publications available from: Marston Book Services Ltd.: (http://www.marston.co.uk).