

**BATTERY INDUSTRY**

**STANDARD ANALYTICAL METHOD**

**For the Determination of Mercury, Cadmium and Lead  
in Alkaline Manganese Cells  
Using AAS, ICP-AES and "Cold Vapour"**

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1. **CONSTRUCTION OF AN ALKALINE MANGANESE CELL**

## 2. **DETERMINATION**

Total mercury (Hg), cadmium (Cd) and lead (Pb).

## 3. **MATERIAL**

Undischarged alkaline manganese cells.

## 4. **PRINCIPLE**

The cell is opened with cutting pliers. The opened cell, except label, is dissolved in nitric acid with dropwise addition of hydrogen peroxide. The sample is diluted to specific volume, mixed thoroughly and then filtered. An aliquot of the filtrate is taken for the determination of cadmium and lead by Atomic Absorption (AA) Spectrophotometry using air-acetylene flame or Inductive Coupled Plasma Spectrometer (ICP-AES). Another aliquot of solution is taken for determination of mercury using Cold Vapour Mercury Analyser.

Recommended wavelengths are:

Instrument	Element	Wavelength nm
AA	Pb	217
AA	Cd	228.8
ICP	Pb	220.35
ICP	Cd	228.8
Cold Vapour	Hg	253.7

Note: Wavelength selected for Pb and Cd should not interfere with elements such as Mn, Zn, Ni, Fe, Cu, Sn, Bi, In, and Ti present in the matrix.

## 5. **APPARATUS**

- i. Atomic Absorption Spectrophotometer
- ii. Inductive Coupled Plasma Spectrometer
- iii. Cold Vapour Mercury Analyser
- iv. Volumetric flasks, 2 l, 1 l, 500 ml, 250 ml, 100 ml and 5 ml
- v. Erlenmeyer flasks, 3 l, 2 l, 1 l, 500 ml and 100 ml
- vi. Buchner vacuum filter or equivalent
- vii. Filter paper, Watman No. 50 or equivalent
- viii. Volumetric pipettes, 10 ml, 20 ml, 25 ml and 50 ml
- ix. Micropipettes, 10  $\mu$ l, 50  $\mu$ l, 250  $\mu$ l, 500  $\mu$ l and 1000  $\mu$ l
- x. 300 ml BOD bottles
- xi. Closed vessel microwave
- xii. Microwave digestion vessels
- xiii. Beakers, 2 l, 1 l and 500 ml

## 6. REAGENTS

- i. Concentrated nitric acid (HNO<sub>3</sub>)
- ii. 20% nitric acid
- iii. 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)
- iv. 1000 ppm cadmium standard solution
- v. 1000 ppm lead standard solution
- vi. 1000 ppm mercury standard solution
- vii. 50% sulphuric acid (H<sub>2</sub>SO<sub>4</sub>)
- viii. 35% nitric acid (HNO<sub>3</sub>)
- ix. 10% tin chloride (SnCl<sub>2</sub>) solution
- x. 12% hydroxylamine sulphate (2NH<sub>2</sub>OH.H<sub>2</sub>SO<sub>4</sub>) solution
- xi. 5% potassium permanganate (KMnO<sub>4</sub>) solution
- xii. 1 ppm mercury working standard solution made from standard solution
- xiii. High purity zinc powder
- xiv. High purity manganese dioxide (MnO<sub>2</sub>) powder
- xv. Potassium hydroxide (KOH) pellets

## 7. STANDARDS PREPARATION

### 7.1 Matrix Preparation for Cadmium, Lead and Mercury Analysis by AA and Cold Vapour

- i. Weigh 20g of zinc powder, 40g of MnO<sub>2</sub> and 6g of KOH into 2 l beaker.  
Note: The matrix materials should be free of Hg, Cd and Pb or with known concentration of Hg, Cd and Pb to correct for the standard concentration.
- ii. Add 500 ml of DI water and 400 ml of HNO<sub>3</sub>.
- iii. Add dropwise H<sub>2</sub>O<sub>2</sub> to solution until reaction has been completed. (No bubbling upon addition of H<sub>2</sub>O<sub>2</sub>.) Heat matrix solution on hot plate to aid dissolution. Allow sufficient time for reaction/dissolution.
- iv. Transfer the cooled matrix solution to a 2 l volumetric flask and dilute to volume. Mix thoroughly.

### 7.2 Lead and Cadmium Standard Solutions for Analysis by Atomic Absorption

Into five (5) separate 100 ml volumetric flasks, add about 25 ml matrix solution. To make 0, 2.5, 5, 10 and 15 ppm Pb and 0, 0.1, 0.25, 0.5 and 1 ppm Cd standard solutions, add the following aliquots of 1000 ppm Pb and 1000 ppm Cd into each of the volumetric flasks and dilute to volume with matrix solution.

AA Standard Solution Conc.		µl 1000 ppm Pb Added in 100 ml	µl 1000 ppm Cd Added in 100 ml
Pb ppm	Cd ppm		
0	0	0	0
2.5	0.1	250	10
5	0.25	500	25
10	0.5	1000	50
15	1	1500	100

7.3 **Lead and Cadmium Standard Solutions for Analysis by Inductive Coupled Plasma Spectrometer (ICP-AES)**

- i. Matrix Preparation:
  - a. Weigh 2.3 g of zinc powder, 5.7 g of MnO<sub>2</sub>, 0.88 g of KOH, 2.6 g of can material and 0.2 g of conductor material into a 500 ml beaker.  
Note: The matrix materials should be free of Cd and Pb or with known concentration of Cd and Pb to correct for the standard concentration.
  - b. Add 50 ml of DI water and 100 ml of HNO<sub>3</sub>.
  - c. Add dropwise H<sub>2</sub>O<sub>2</sub> to solution until reaction has been completed. (No bubbling upon addition of H<sub>2</sub>O<sub>2</sub>.) Heat matrix solution on hot plate to aid dissolution. Allow sufficient time for reaction/dissolution.
  - d. Transfer the cooled matrix solution to a 500 ml volumetric flask and dilute to volume. Mix thoroughly.
  - e. Filter the thoroughly mixed matrix solution through the vacuum funnel if insolubles are present. Discard the first 25 ml of the filtrate. Filter the remaining solution into a 500 ml container for standard preparation below.
- ii. Standard Preparation:
  - a. Into four (4) separate 100 ml volumetric flasks, add about 25 ml of matrix solution from above. To make 0.1, 0.5, 2.5 and 5 ppm Pb and 0.1, 0.25 and 0.5, 1 ppm Cd standard solutions, add the following aliquots of 1000 ppm Pb and 1000 ppm Cd into each of the volumetric flasks and dilute to volume with the matrix solution.
  - b. Use the remaining matrix solution as a blank. The blank has 0 ppm of Pb and 0 ppm of Cd.

ICP Standard Solution Conc.		µl 1000 ppm Pb Added in 100 ml	µl 1000 ppm Cd Added in 100 ml
Pb ppm	Cd ppm		
0	0	0	0
0.1	0.1	10	10
0.5	0.25	50	25
2.5	0.5	250	50
5	1	500	100

7.4 **Mercury Standard Solution for Analysis by Cold Vapour Analyser**

- i. Prepare six standard solutions containing 0 to 0.7 µg mercury by placing 0, 50, 100, 250, 500 and 700 µl aliquots of the 1 ppm Hg working standard into six 300 ml BOD bottles.
- ii. Add 100 ml matrix solution from step 7.1 to each.

## 8. SAMPLE PREPARATION

Analyse cells in duplicate.

- i. Weigh the cell and record total cell weight.
- ii. Open cell with cutting pliers inside a plastic bag in case of electrolyte leakage. Remove the negative terminal with the conductor. With the help of tweezers, remove the separator paper containing the anode from the cell. Carefully and thoroughly scrape off all the anode slurry material from the separator into a centrifuge tube. Centrifuge the anode slurry to separate the gellant from the zinc. Transfer the gellant portion into microwave vessel(s)\*. Transfer the remaining components of the cell (can, cathode, electrolyte, separator, conductor including plastic grommet, etc.) and the zinc portion into a Erlenmeyer flask. (Use 3 l flask for D size cells, 2 l for C size cells, 1 l for AA cells and 500 ml for AAA and 9V cells.) Digest the gellant following step (vi). Digest the remaining cell components following steps (iii) and (v) or steps (iv) and (v).

\* Number of microwave vessels depends on cell sizes and microwave capacity.

- iii. For analysis by AA add nitric acid and water according to Table 1 below:

Table 1

Cell Size	H <sub>2</sub> O (ml)	HNO <sub>3</sub> (ml)	Final Volume (V) (ml)
D	400	400	2000
C	400	200	1000
AA	200	100	500
AAA	100	50	250
9V	200	100	500

- iv. For analysis by ICP-AES add nitric acid and water according to Table 2 below:

Table 2

Cell Size	H <sub>2</sub> O (ml)	HNO <sub>3</sub> (ml)	Final Volume (V) (ml)
D	200	200	1000
C	100	100	500
AA	40	40	200
AAA	20	20	100
9V	100	100	500

- v. Add dropwise H<sub>2</sub>O<sub>2</sub> to sample solutions until reaction has been completed. (No bubbling upon addition of H<sub>2</sub>O<sub>2</sub>) Heat sample on hot plate to aid sample dissolution. Allow sufficient time for reaction/dissolution.
- vi. Decompose the gellant obtained from step (ii) by closed vessel microwave technique using HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. (5 ml of HNO<sub>3</sub> and 2 ml H<sub>2</sub>O<sub>2</sub> for 0.5 g gellant, best consult microwave manufacturer)
- vii. Transfer the decomposed gellant solution into the same Erlenmeyer flask as in step (v) above. Mix the solution thoroughly and allow to cool.
- viii. Filter the thoroughly mixed solution and dilute to final volume according to Table 1 or Table 2.

9. **MERCURY ANALYSIS BY COLD VAPOUR ANALYSER**

- i. Set up the AAS "Cold Vapour" apparatus in accordance with manufacturer's manual.
- ii. Analyse the six standards from step 7.4 following steps iii - vii.
- iii. Add 5 ml 50% sulphuric acid. Mix.
- iv. Add 5 ml 35% nitric acid. Mix.
- v. Add 1 ml 5% potassium permanganate solution and if necessary additional portions in 1 ml increments until the purple colour persists for at least 15 minutes.
- vi. Add 2 ml of hydroxylamine sulphate to reduce excess potassium permanganate. Mix until clear.
- vii. Add 5 ml tin chloride solution and immediately attach the aeration apparatus to the BOD bottle. Allow to stand. When recorder pen has levelled off remove aeration apparatus.
- viii. Transfer a 100 ml aliquot of each sample to a 300 ml BOD bottle.
- ix. Analyse the sample in the same manner.

Note: Alternate automated continuous flow apparatus may also be used.

10. **LEAD ANALYSIS BY AA**

- i. Set-up AA with air-acetylene flame.
- ii. Set-up calibration curves by analysing 0, 2.5, 5, 10 and 15 ppm lead standard solutions.
- iii. Analyse the filtered sample solutions for lead against the calibration curve.

11. **CADMIUM ANALYSIS BY AA**

- i. Set-up AA with air-acetylene flame.
- ii. Set-up a calibration curve by analysing 0, 0.1, 0.25, 0.5 and 1 ppm cadmium standard solutions.
- iii. Analyse the filtered sample solution for cadmium against the calibration curve.

NOTE: A If Pb or Cd in the sample solutions is lower than the lowest standard, pipette a 50 ml aliquot of sample solution and concentrate to 2-3 ml on the hot plate, volumize with 20% HNO<sub>3</sub> to 5 ml in a volumetric flask and then analyse on AA.

B. If Pb or Cd in the sample solution is higher than the highest standard, take an aliquot and dilute with 20% HNO<sub>3</sub> to proper concentration range. Analyse on AA.

## 12. LEAD AND CADMIUM ANALYSIS BY ICP-AES

- i. For cell size D samples, pipette 20 ml of the filtered sample solution into a 100 ml volumetric flask. Dilute to volume with a 20% HNO<sub>3</sub> solution.  
  
For cell size C, AA and AAA, pipette 25 ml of the filtered sample solution into a 100 ml volumetric flask. Dilute to volume with a 20% HNO<sub>3</sub> solution.  
  
For 9V battery, pipette 50 ml of the filtered sample solution into a 100 ml volumetric flask. Dilute to volume with a 20% HNO<sub>3</sub> solution.
- ii. Set-up ICP according to manufacturer's instructions.
- iii. Calibrate the ICP for lead and cadmium with the ICP matrix matched standard solution.
- iv. Analyse the diluted sample from step (i) above for lead and cadmium against the standard curve without changing any parameter.

## 13. CALCULATIONS

$$\text{ppm Hg of Total Cell Weight (TCW)} = \frac{(a - b) \times V}{v \times \text{TCW (g)}}$$

$$\text{ppm Pb or Cd of TCW} = \frac{\text{ppm (Reading)} \times V \times \text{DF}}{\text{TCW (g)}}$$

Where:

- a = µg Hg in sample aliquot
- b = µg Hg in blank aliquot
- v = aliquot (in ml) taken for Hg analysis
- V = Total sample volume in ml (see Table 1 or 2)

DF = Dilution factor  
(For ICP: D size - DF= 5;  
C, AA & AAA size - DF = 4  
9V - DF = 2)

Mercury, cadmium and lead should be reported to 0.1 ppm.