Research Paper

Evaluation of cadmium concentration in vapour phase by a novel approach

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ABSTRACT

An indirect way of assessing cadmium concentration in confined volume was attempted. This aim was met by measuring the oxygen concentration before and after reaction with cadmium vapour. The deduced cadmium concentration value corroborated with the data obtained from cadmium vapour pressure at different temperature.
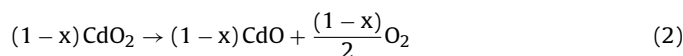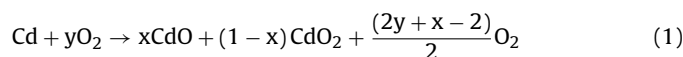
1. Introduction

Heavy metals like lead, mercury, cadmium, etc. find huge industrial applications, viz. in the manufacturing of batteries, lamps, switches, sensors, ammunition, glass, metal finishing, electronics, metal shielding, etc. These metals have been listed as the pollutants of concern due to their persistence in the environment, potential toxicity to humans and the environment. Some are even carcinogenic in nature and are known to lead to respiratory problems. There are various restrictions on the use of these heavy metals in products that have been promulgated by international, national and state agencies [1]. The vapour pressure of these elements is a strong function of temperature with little importance given on the monitoring of the processes involving them. Due to their existence in elemental form, direct sensing technique had hardly been attempted/succeeded. Different analytical methods are known [2,3], for estimation of them in environmental samples by using atomic absorption spectroscopy (AAS) [4–7], atomic emission spectroscopy (AES) [8,9], inductively coupled plasma–mass spectroscopy (ICP-MS) [10], anodic stripping voltametry (ASV) [11] and neutron activation analysis (NAA) [12,13] techniques. These analytical techniques generally involve digestion in acid, followed by pre-concentration and analysis. In case of estimation of particulates of these elements present in air, sampling is done with a pump and collected on filter paper, followed by acid extraction and analysis [14].

In the present work, we attempted an indirect on-line sensing of cadmium vapour using a potentiometric oxygen sensor. In this method, cadmium, in vapour form is allowed to react with a known oxygen partial pressure to form cadmium oxide. The reduction in oxygen pressure was measured by zirconia based oxygen sensor. From the equilibrium oxygen pressure, the activity of cadmium present in vapour form was deduced. Details of this methodology and the results obtained therein are presented in the paper.

2. Theoretical background

Cadmium in vapour form is made to react with a known amount of oxygen (in ppm levels) to form oxides of cadmium as shown below:

$$Cd + yO_2 \rightarrow xCdO + (1-x)CdO_2 + \frac{(2y+x-2)}{2}O_2 \tag{1}$$

$$(1-x)CdO_2 \rightarrow (1-x)CdO + \frac{(1-x)}{2}O_2 \tag{2}$$

Net reaction,

$$Cd + yO_2 \rightarrow CdO + \frac{(2y-1)}{2}O_2 \tag{3}$$

The first equation represents the reaction of cadmium vapour with oxygen to form cadmium monoxide [15], CdO and cadmium peroxide, CdO_2. The decomposition temperature [16,17] of cadmium peroxide is around 453 K to form CdO and O_2, Eq. (2). If cadmium source temperature is maintained above 453 K during

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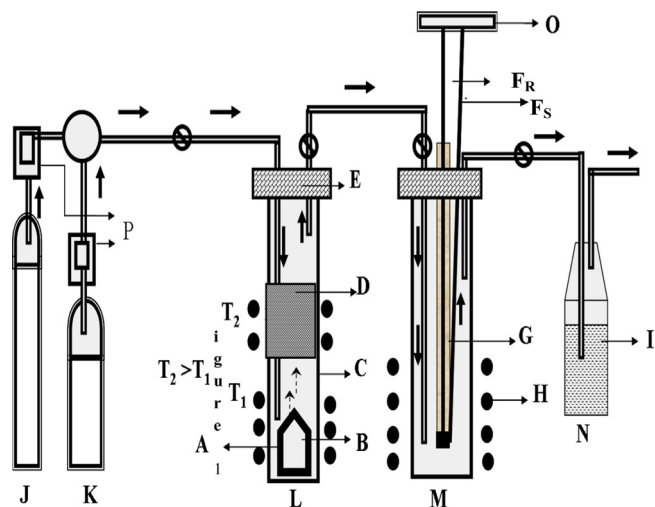
Fig. 1. Representation of the experimental set up.
(A) A Knudsen cell type crucible, (B) Cd metal (C) Quartz vessel, (D) Quartz mesh (Temp, T_2 and $T_2 > T_1$), (E) 430 ferritic steel coupling for leak tightness, [(F_R) Sample and (F_S) reference electrode], (G) Calcia stabilized zirconia tube,(H) Furnace, (I) HCl solution, (J), Argon cylinder, (K) Argon oxygen mixture, (L) Cadmium source chamber, (M) Sensor housing, (N) Scrubber chamber and (O) Instrumentation for measuring signal and (P) mass flow controllers ($T_1 = 473 - 573\,K, T_2 = T_1 + 10\,°C$) (Arrow indicates gas flow direction)

the experiments, the net oxygen consumption is through CdO formation only, as given in Eq. (3). By measuring the oxygen partial pressures, before and after the reaction with cadmium vapour, the vapour pressure/partial pressure of cadmium can be deduced (Eqs. (4) and (5)).

Amount of oxygen consumed,

$$\Delta P_{O_2} = P_{O_2}^{Initial} - P_{O_2}^{Final} \tag{4}$$

where, $P_{O_2}^{Initial}$ = oxygen partial pressure before reaction with cadmium and $P_{O_2}^{Final}$ = oxygen partial pressure after reaction with cadmium

From Eq. (3), two moles of cadmium would react with one mole of O_2, therefore, the amount of cadmium present is given by Eq. (5)

$$P_{Cd} = 2\Delta P_{O_2} \tag{5}$$

3. Experimental

3.1. Design and fabrication of apparatus

Fig. 1 shows the schematics of the experimental set up made for deriving the concentration of cadmium. It comprises of two distinct chambers and paraphernalia items. One chamber (M) houses the CSZ based oxygen sensor designed and fabricated in-house. Cadmium vapour is generated and made to react with oxygen in the other chamber (L).

Oxygen sensor was fabricated as per the details mentioned in earlier publication [18]. This sensor was made using one end closed 11 mol% calcia stabilized zirconia (CSZ) solid electrolyte tube (G) with flat bottom (typically, 13 mm outer diameter, 9 mm inner diameter and 250 mm long). The reference electrode was indium—indium oxide couple, which was mixed and melted at 1173 K in-situ in the CSZ tube itself. A molybdenum wire co-fired with the reference mixture was used as electrical lead for the reference side (F_R). The CSZ tube with the reference electrode was sealed using epoxy sealant. The sample electrode was prepared by applying platinum paste over outer bottom surface of the electrolyte tube and heating to 1123 K for 2 h in air. A platinum wire co-fired with

the platinum paste served as electrical lead for the sample side (F_S). The cell configuration is shown below:

$$Mo, In|In_2O_3||CSZ||Pt, P_{O_2} \tag{6}$$

This sensor assembly was housed in a leak tight quartz vessel (M) of volume, 120 ml with helium leak tested inlet and outlet valves. The sensor housing was placed in a furnace (H) and maintained at 873 K during the experiments.

The cadmium source chamber (L) was made of quartz tube with provision for oxygen inlet and outlet. For holding cadmium, a crucible (A) of 16 mm outer diameter, 11 mm inner diameter and 20 mm long was made using 430 ferritic steel. A small orifice was provided on the lid of the crucible for evolution of cadmium vapour. About 30 mm above the cadmium holder crucible, quartz wool mesh (D) was packed. This quartz wool provides high surface area for cadmium oxygen reaction to occur. Different partial pressures of oxygen were let into this chamber, by mixing it with argon using mass flow controllers. Oxygen inlet tubing was allowed to penetrate through the mesh and placed near the orifice of the cadmium crucible. The whole setup of source chamber was placed in a furnace such that, the quartz wool mesh was maintained at higher temperature zone than the cadmium crucible. The oxygen outlet tubing from cadmium source chamber was connected to oxygen sensor chamber. The outlet of the sensor chamber was bubbled through HCl solution (I and N).

3.2. Experimental

Prior to the experiments using cadmium, the oxygen sensor was calibrated by passing different partial pressures of oxygen (20–1000 ppm ($\pm$ 2% error)) through the sensor chamber at 1 atmosphere. For this purpose, a flow rate of 20 ml/min was maintained. The emf output dictated by Nernst equation (Eq. (7)), was measured using an electrometer (O):

$$E = \left(\frac{RT}{nF}\right) \ln \left(\frac{P_{O_2}^S}{P_{O_2}^R}\right) \tag{7}$$

Where R = Universal gas constant in Joule; T = temperature of operation of the cell (873 K, in the present studies); n = no. of electrons participate in the process (4); F = Faraday constant (96,486 C); $P_{O_2}^S$ and $P_{O_2}^R$ are partial pressure of oxygen in sample and reference sides respectively.

About 200 mg of cadmium metal was weighed in the cadmium holder crucible and placed in the cadmium source chamber. During experiments a known oxygen partial pressure (20–700 ppm) with a pre-set flow was passed through the source chamber. The oxygen let out from this was allowed to the sensor chamber. During this process, the cadmium was maintained at room temperature. The emf output of the sensor was continuously monitored during this process. When the emf output (E_1) became stable, cadmium crucible was heated to a pre-set temperature ($\geq$ 473 K). The cadmium vapours generated was made to react with the oxygen let in, to form cadmium oxide on quartz mesh. The quartz mesh was provided 3 cm above the cadmium source and was maintained about 10°C higher than the cadmium source temperature. The cadmium oxide formation reaction is a gas phase reaction between cadmium and oxygen and is exothermic [17]. The product formed is CdO. In order to dissipate the heat energy released from this reaction, a surface is required to be provided; otherwise the product formed would decompose in gas phase again, to give the elements back. Thus, quartz mesh provides the high surface area for removing the heat of the reaction. Further, the quartz mesh is always at higher temperature than the cadmium source temperature, condensation of cadmium vapour on the quartz mesh is also avoided. The unreacted oxygen was allowed to the sensor chamber. During the reaction, the