

## Purification of cadmium up to 5N+ by vacuum distillation

S T ALI\*, J V RAO, K S VARMA and T L PRAKASH

Centre for Materials for Electronics Technology (C-MET), IDA Phase II, Cherlapally, HCL PO, Hyderabad 500 051, India

**Abstract.** Cadmium was refined by vacuum distillation, a technique suitable for low boiling and melting point materials, to remove the heavy and low vapour pressure impurities at ppm level. The detailed analysis of the purified Cd as well as raw Cd was done by ICP–OES techniques for 27 impurity elements. Purification was carried out in an efficient high-yield vacuum distillation system designed and fabricated for purifying 3N+ purity indigenous cadmium to 5N+ (99.999%). Analysis confirmed the reduction of total impurity content from 134 ppm (3N7) for raw Cd to 3 ppm (5N7) upon vacuum distilled Cd. The present study shows that the analysis of impurities such as Fe, Mg and Ca are contributed from environmental effect, whereas impurities such as Pb, Bi, Ag, Ni, Cu, Zn and Tl require adaptation of elemental analysing technique to counter dilution effect. The Hg trace analysis can however be carried out by hydride generation techniques.

**Keywords.** Vacuum distillation; high pure cadmium.

### 1. Introduction

The device applications in electronic field demand the materials of high purity. Presence of trace amount of impurities affects the device performance because carrier life-time and its mobility are strongly dependent on the impurity concentration. Therefore, high pure (HP) material in the range of 5N, ultra pure (UP) in the range of 6N and supra pure (SP) in the range of 7N have become very important.

High purity cadmium is a strategic electronic material used for preparation of compound semiconductors such as CdTe, HgCdTe, CdZnTe, CdS, CdSe etc. The Cd based semiconductor devices are primarily used as solar cells, IR detectors, imaging devices, electro-optic modulators, fluorescence, and thermoelectric coolers in the areas of defence, military and aero-space (Lejbov *et al* 1989). Other areas of applications include telecommunications, electric vehicle and remote area storage systems.

The problem connected with profound purification and characterization of the materials that are used for the synthesis of electronic materials remains critical. The advantage of methods providing efficient purification using rather simple and cheap equipment is evident. As far as the characterization of ultra-pure material is concerned, the effect of every impurity on the target properties of the material often remains unknown. Therefore, multi-element methods remain preferable because they provide the lowest possible detection limits for several tens of impurities simultaneously.

In this study, vacuum distillation of cadmium, a by-product of zinc extraction at HZL, Udaipur, were carried

out by an indigenously built system and the characterization of the purified Cd using ICP–OES is reported.

### 2. Experimental

#### 2.1 Vacuum distillation

Vacuum distillation is one of the techniques used for removal of major impurities at ppm level in cadmium from 3N+ to 5N+. Although the zone refining and allied techniques are used to remove the impurities from 5N and above, the vacuum distillation is used (Kovelevski *et al* 1996) as a preceding supportive to remove the high melting point impurities.

A self-explanatory schematic diagram of vacuum distillation is shown in figure 1. A suitable amount of material is taken in a crucible, kept at the bottom of the retort under vacuum. As the inside temperature of the crucible surpasses the melting point and the vapour pressure of a particular element in the melt is higher than the partial pressure of the element in the gaseous phase, the material starts evaporating and condenses at the bottom of the cooled collectors placed on top leaving heavy melting point and low vapour pressure impurities at the bottom of the crucible. The critical process parameters such as vacuum level, temperature are to be optimized to get the desired evaporation rate and subsequent condensation rate (VCRL Transactions 10036). The condensed material thus distilled is then removed from the collectors and re-distilled till desired purity is obtained.

The distillation experiments of 5 kg batch-size were conducted on Cd in a clean environment. A dynamic vacuum level of  $5 \times 10^{-4}$  torr were maintained using high density graphite crucible and water cooled SS U-tube collectors. Each experiment was conducted in two

\*Author for correspondence

temperature phases. The 1st phase at 350°C was carried out to remove high vapour pressure and lesser boiling point (than Cd) light impurities. Then the SS collectors were cleaned off this '1st fraction' material. A soaking temperature of 450°C was maintained for 2nd phase i.e. main distillation. The yield of purification was found to be 80–90%. The material collected on the SS U-tubes at this stage is taken as 'middle fraction' (highest purity) and the impurities left at the bottom of the graphite crucible is the '3rd fraction' for analysis. The middle fraction material is shown in figure 2.

## 2.2 Chemical analysis

Various chemical analyses techniques such as atomic absorption spectroscopy (AAS), spark source mass spectroscopy (SSMS), laser scan mass spectroscopy (LSMS), glow discharge mass spectroscopy (GDMS), inductively coupled plasma mass spectroscopy (ICPMS) and inductively coupled plasma optical emission spectroscopy (ICPOES) have been used to assess the trace impurity of the material. In ICP–OES technique, the material is

dissolved in a suitable solvent and then injected into an argon plasma at about 8000 K. Free atoms and ions are electronically excited to higher energy states. When they return to a more stable state within nsec, the ultraviolet radiation emitted is measured in terms of both wavelength and intensity by a suitable spectrometer.

In this study, ICP–OES (Jobin Yvon, model JY-24) was used to determine the purity of the starting and purified cadmium used for vacuum distillation. The cadmium samples from 'first fraction', 'middle part' and 'bottom residue' were collected (5 g each) and powdered, dissolved in 50% suprapure HNO<sub>3</sub> solution in a Teflon beaker. The supernatant liquid was transferred to volumetric flask after thorough washing with the same solution. The solution was then used for analysis using ICP–OES.

## 3. Results and discussion

The vacuum distillation results have been studied for 27 most prominent impurities in cadmium. Table 1 shows the typical results of the ICP–OES analysis of cadmium before and after vacuum distillation. The figures are given in ppm and show low levels of most impurities except for Ni, Cu, Se, Sb and Pb. It is observed that most of the impurities had gone below the detection limit including Fe, Mg and Ca when the distillation and the sample preparation for analysis were done inside clean room. In experiments conducted in a normal laboratory (non-clean) environment, the presence of 1.78, 0.51, 2.83 ppm, respectively of Fe, Mg and Ca in vacuum distilled Cd were recorded. The reason of higher levels of Fe, Mg and Ca is attributed to the environmental effect.

The residues at the bottom of crucible contained major impurities such as Fe, Ni, Cu, Zn, Ag, Sb, Bi etc. High volatile impurities such as Cs, Rb, S, Na, K, Cl had been removed by the vacuum pump and these were not detected in the distilled Cd. There are inherent difficulties to analyse C, O and Hg directly using ICP–OES. The combustion technique is commonly used for determining the carbon and sulfide contents (Murray and Lograsso 1990). The sample is combusted with oxygen and the resulting CO<sub>2</sub> or SO<sub>2</sub> are measured by IR absorption. The absorption of the IR signal is proportional to the CO<sub>2</sub> concentration. O and Hg can respectively be analysed by vacuum fusion and hydride formation techniques.

The efficiency of purification of a material using vacuum distillation depends on evaporation rate of substance, transportation of vapour for condensation and removal of distillate. Vacuum pump capacity, crucible materials, methods of heating and cooling of distilled material play major role in deciding the optimum distillation process parameters.

The key aspect leading to the high degree of purification obtained is the use of proper amount of heat removal through collectors. The material should be solidified at a

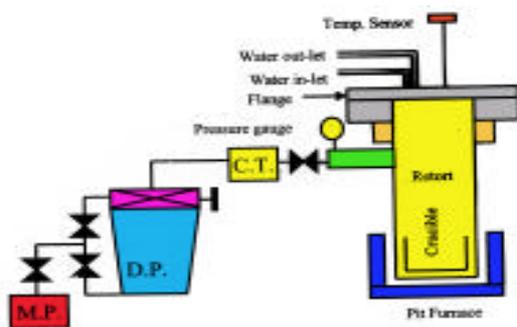


Figure 1. Vacuum distillation system.

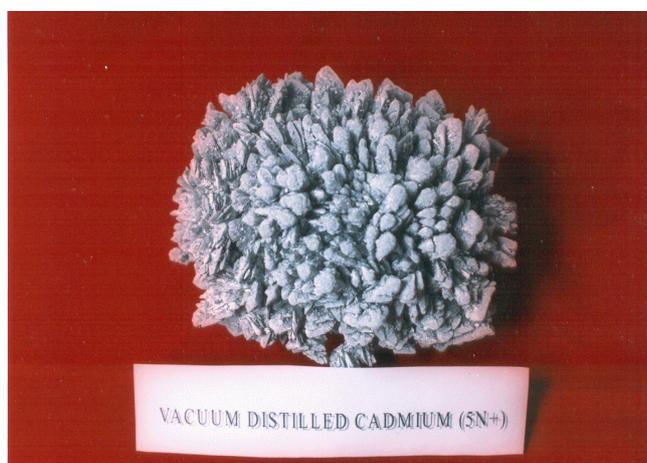


Figure 2. Vacuum distilled Cd.

**Table 1.** ICP-OES analysis of cadmium.

Element	HZL raw Cd (ppm)	Vacuum distilled Cd (ppm)	Element	HZL raw Cd (ppm)	Vacuum distilled Cd (ppm)
(1) B	0.1	0.07	(15) Zn	1.16 (0.05–10.3)	< 0.1
(2) Mg	0.1	0.08	(16) Ga	< 0.1	< 0.1
(3) Al	< 0.1	< 0.1	(17) As	< 0.1 (< 0.1–3.0)	< 0.1
(4) Si	< 0.1	< 0.1	(18) Se	0.73	0.52
(5) P	< 0.1	< 0.1	(19) Ag	39.84	< 0.1
(6) Ca	3	0.09	(20) Cd major	99.00–99.95%	99.9997%
(7) Ti	0.1	0.07	(21) In	< 0.1	< 0.1
(8) V	0.1	0.07	(22) Sn	0.12	< 0.1
(9) Cr	< 0.1	< 0.1	(23) Sb	0.4 (< 0.1–2.0)	0.38
(10) Mn	0.1	0.08	(24) Te	< 0.1	< 0.1
(11) Fe	0.38 (1.8–6.1)	< 0.1	(25) Tl	< 0.1 (< 0.1–11.7)	< 0.1
(12) Co	< 0.1	< 0.1	(26) Pb	32.68 (68–122)	< 1.5
(13) Ni	41.8 (7.7–72)	0.20	(27) Bi	3.9	< 0.1
(14) Cu	8.7 (37–145)	< 0.40			

substantially lesser rate than the rate of condensation of said material. In general, the solidification rate should be about 0.5 to about 10%, preferably about 1 to about 5%, of the condensation rate (Lawrence 1988). Thus as the solid material is formed, a pendulous drop forms thereon. Periodically, a drop of this liquid falls from the solid back into the evaporation zone of the melt. This continuous washing of the solid surface removes any impurities rejected during the solidification providing a highly purified product.

#### 4. Conclusion

99.9997% purity (5N7) cadmium is obtainable from vacuum distillation of 3N5 raw Cd. Environment plays a dominant

role in controlling impurity levels of Fe, Mg and Ca in the vacuum distilled Cd. The rate of evaporation and heat transfer during condensation is mainly responsible for improving purification efficiency.

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