

Preparation of electronics grade bismuth, antimony, tellurium, cadmium and zinc by vacuum distillation and zone refining

A. J. SINGH, B. S. MATHUR, P. SURYANARAYANA and
S. N. TRIPATHI

A PART from the usual importance of bismuth, antimony, tellurium, cadmium and zinc in the chemical, metallurgical, cosmetic, pharmaceutical and paint industries, these materials in their high purity forms (99.99 to 99.999 +%) have recently acquired special significance in the electronics industry for semi-conductor and various other applications. The major applications of these electronics grade materials in the electronic industry are:

Bismuth: solders and thermo-electric devices,

Antimony: semi-conductor devices (for crystal doping), photocell cathodes,

Tellurium: Compound semi-conductors,

Cadmium: Solders mostly for semi-conductor processing and for compound semi-conductors, such as CdS,

Zinc: dopant and diffusant in semi-conductors.

Apart from these, antimony (99.9%) is required for the fabrication of (Sb-Be) neutrons sources.

To fulfil the need of high purity and electronics grade materials, methods such as precipitation, crystallization, electrolysis distillation, ion-exchange, solvent extraction, zone melting, etc. have been investigated and developed by various workers in different laboratories. The methods of purification for a particular material are worked out in accordance with the type and extent of impurities present in the starting material. Usually a combination of purification methods is required to achieve the desired ultra-purity. A literature survey of the methods to produce electronics grade materials reveals that vacuum distillation and

SYNOPSIS

Several electronics grade metals are now required in the electronics industry. The initial steps in the methods of purification vary from material to material. Vacuum distillation and zone refining are, perhaps, the most important ones to achieve the final purity of 99.999% or better. These two techniques have been developed in the Chemistry Division, BARC, to produce electronics grade bismuth, antimony, tellurium, cadmium and zinc using resistance heating furnaces fabricated in the Divisional Workshop.

Starting with the best commercially available materials (purity 98 to 99.95%), the methods were, in the initial stage, worked out for 250 g to 1 kg scale operations and were subsequently stepped up to 3 kg to 10 kg scale operations. Although other steps in the operations can be scaled up by using bigger sized equipments, zone melting seems to be a bottleneck in the production. Zone melting can be scaled up only by having larger number of zone melting units.

Vacuum distillation units have been designed and fabricated to produce 99.99% pure antimony, cadmium and zinc. Zone melting studies have been carried out to optimize experimental conditions to get 99.999%, or better bismuth, antimony, tellurium and cadmium. A vacuum distillation assembly, taking 5 kg charge of either antimony, cadmium or zinc, and an automatic zone refining unit taking up to 6 kg charge of any of these metals, are described. The know-how developed will be utilized to produce the metals in the required quantities at the Special Materials Plant in Hyderabad.

zone refining are, perhaps, the most important techniques to produce electronics grade materials.

The estimated annual requirements for the high purity and electronics grade materials in India by 1975 have been envisaged in the Electronics Committee Report, Government of India, February, 1966.¹ Some

Messrs A. J. Singh, B. S. Mathur, P. Suryanarayana and S. N. Tripathi, Bhabha Atomic Research Centre, Bombay.

of these materials are required in small quantities and the laboratory size equipment will be adequate to produce the requisite amounts. A few of the materials which fall into this category are the following :

Bismuth	...	9 tonnes/year
Antimony	...	20 kg/year
Tellurium	...	9 tonnes/year
Cadmium	...	200 kg/year
Zinc	...	a few kg/year

Except bismuth and tellurium the other metals in commercial grade are now indigenously available.

Foreseeing the annual requirements of pure and electronics grade materials in India by 1975, vacuum distillation and zone melting techniques have been developed to prepare bismuth, antimony, tellurium, cadmium and zinc of the appropriate grades and to establish the maximum convenient amounts of each which can be handled in a laboratory scale operation. Starting with the best commercially available materials (purity 98 to 99.95%), the methods were, in the initial stage, worked out for 250 g to 1 kg per batch scale operations and were subsequently stepped up to 3 kg to 10 kg scale. A purity 99.999% and better has been achieved for these materials, as far as we know, for the first time in the country. Plans are already underway to prepare these materials in quantities shown above and for this purpose a Special Material Plant is being set up at Hyderabad.

Vacuum distillation

During the distillation of metals, the equilibrium conditions are rarely attained because the evaporating metal atoms from the surface of the melt condense on the substrate and are prevented from returning. The non-attainment of the equilibrium leads to a continuous evaporation of the metal at a rate dependent on vapour pressure, residual gas pressure and the pressure gradient of the metal atoms between the metal surface and the condensate, which in turn depends on the temperature of the condenser and distillant. Distillation under vacuum has the following advantages over atmospheric distillation :

- (i) the rate of evaporation increases with decrease in residual gas pressure,
- (ii) better separation of volatile constituents may be achieved at a lower pressure,
- (iii) the possibility of interaction of metal atoms with a gas is eliminated, and
- (iv) working at a lower temperature is an asset because of negligible changes of metal to container interaction and the low running cost of the process.

A general equation for the rate of evaporation is :

$$W = 0.05833 P \sqrt{M/T} \text{ g/cm}^2/\text{sec.}$$

where P is the pressure in torr, M is the molecular weight and T the temperature on the absolute scale. However, the rate of condensation is actually lower than W because of inter-atomic collisions and return of atoms to the surface of the melt. This is the case when we deal with pure metals only, but in our case the distillation is intended for the purification of the metals. The purification will be governed not only by the vapour pressure of each constituent, but also by their mole fraction in the melt, e. g. assuming Raoult's law holding good, the fraction of the less volatile constituent in the vapour for a binary alloy is given by :

$$C_2 = \frac{M_2 P_2}{M_2 P_2 + M_1 P_1}$$

where M_1 and M_2 are the respective mole fractions and P_1 and P_2 are the vapour pressures of the pure metals.

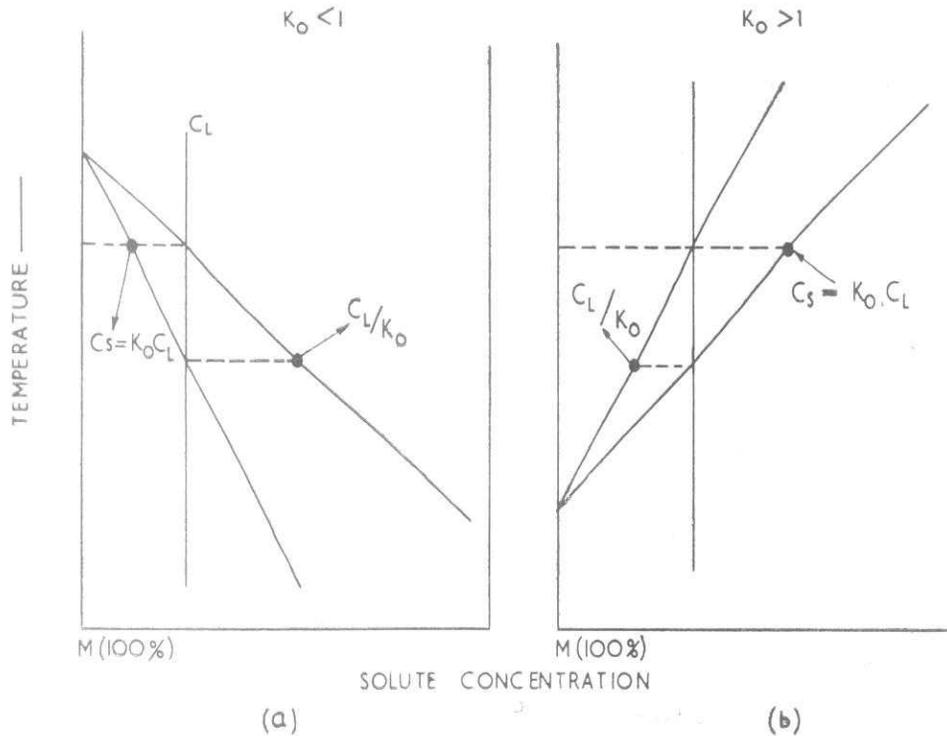
While designing an apparatus for distillation of metal it should be borne in mind that high rate of evaporation will not necessarily give a high rate of distillation since this depends also on the rate of removal of vapour from the surface towards the condenser. The rate of removal of vapour is dependent on the size of the still and the residual gas pressure. In a case where an impurity is present in small quantities and is more volatile, the diffusion rate of the more volatile constituent in the liquid limits its evaporation rate. Under such circumstances it is this that governs the separation obtainable and not the mole fraction in the melt. Rate of evaporation can also be inhibited by the presence of a film on the evaporating surface.

In the case of distillation of antimony, cadmium and zinc, problems such as construction of the furnace and choice of the container material did not pose any particular difficulties ; graphite was found to be an ideal container for these metals and the working temperature was established to be 400°-900°C.

Zone refining

The technique of zone melting was introduced by W. G. Pfann² for the purification of materials employed as semi-conductors. Subsequently the technique was extended for the purification of metals and inorganic and organic compounds.

Purification of a substance by zone melting depends on the difference in solubility of an impurity in the molten and the frozen phase in equilibrium. In practice, liquid-solid interfaces are obtained by causing a narrow molten zone to traverse the length of an ingot of the charge. Depending on whether an impurity lowers or raises the melting point of a material, passage of a molten zone through the charge will concentrate the impurity in the molten or frozen phase respectively. We can show it by considering a simple binary phase diagram given in Fig. 1. The ratio C_s/C_L is known as segregation or distribution co-efficient (k_0) of the impurity. Fig. 1 (a) shows a diagram where the impurity lowers the melting point of substance M and $k_0 < 1$, while in the case of Fig. 1(b) the addition



1 Portions of phase diagrams for binary systems where the solute (a) lowers ($K_0 < 1$) and (b) raises ($K_0 > 1$) melting point of the pure metal (M)

of impurity in M raises the melting point and $k_0 > 1$. In the former case the impurity will be carried forward along with the molten zone while in the latter case this will be depleted in the molten zone.

Conditions such as narrow molten zone length, low rate of zone traverse and more number of zone passes, make the separation efficient in cases where k_0 is not equal to unity. However, considerations are made to make the process economical timewise. Fig. 2 shows the impurity distribution in an ingot during zone refining where k for the impurity is < 1 .

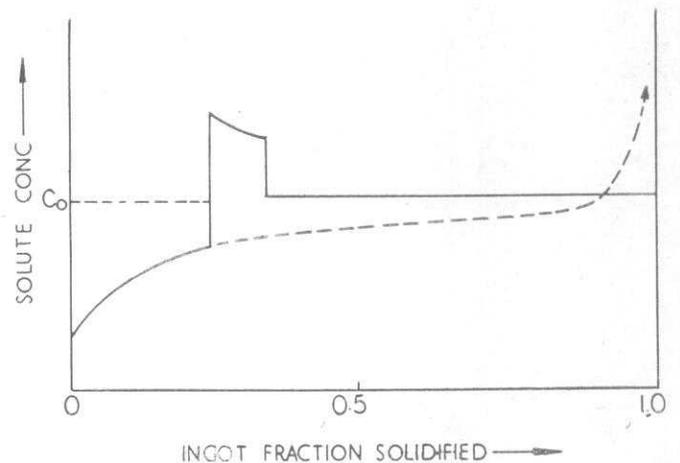
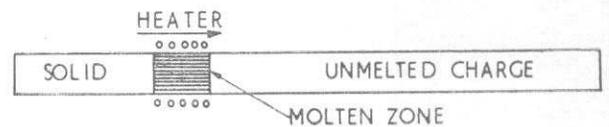
Zone refining of bismuth, antimony, tellurium and cadmium was carried out using boats made of pyrex glass for bismuth, quartz for tellurium and graphite for antimony and cadmium. Small ring resistance heaters, made out of sillimanite tube, were employed to produce narrow molten zones.

System description

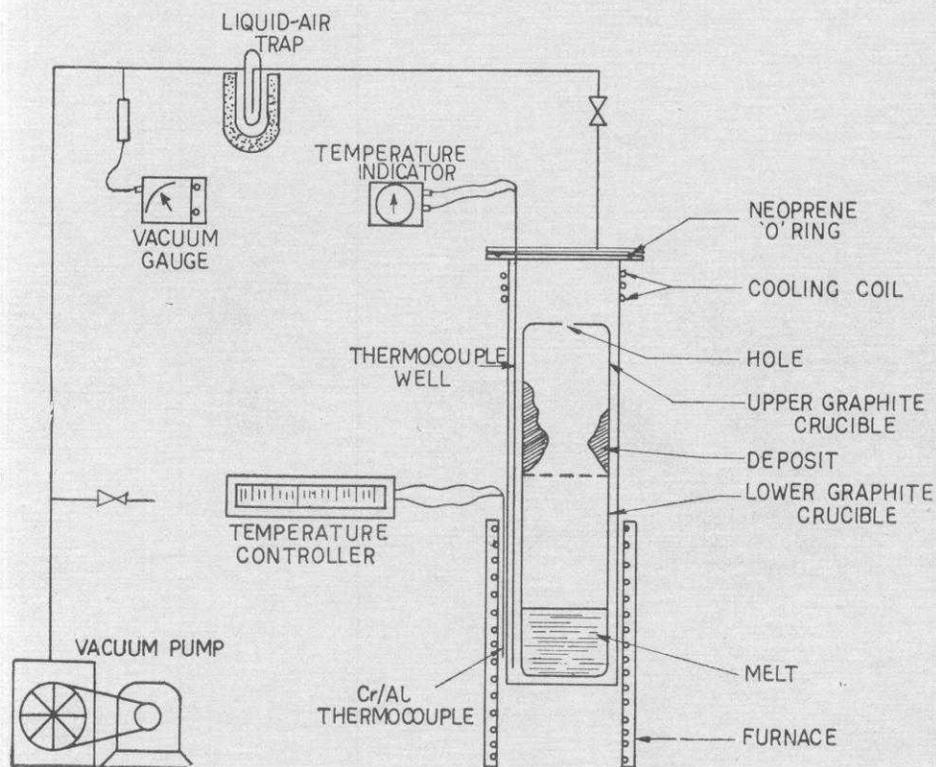
Vacuum distillation

A schematic drawing for the distillation assembly used for antimony, cadmium and zinc metals, is shown in Fig. 3; the vessel is made by welding a stainless steel flange to a stainless steel pipe. The flange is provided with a groove for neoprene O-ring, thermocouple well and fittings for evacuating the vessel. The neck of the vessel is cooled by water circulation through a copper coil wound round the neck. The inside temperature gradient of the vessel is determined with the help of a sliding chromel-alumel thermo-couple. Another chromel-alumel thermo-couple is placed just outside the

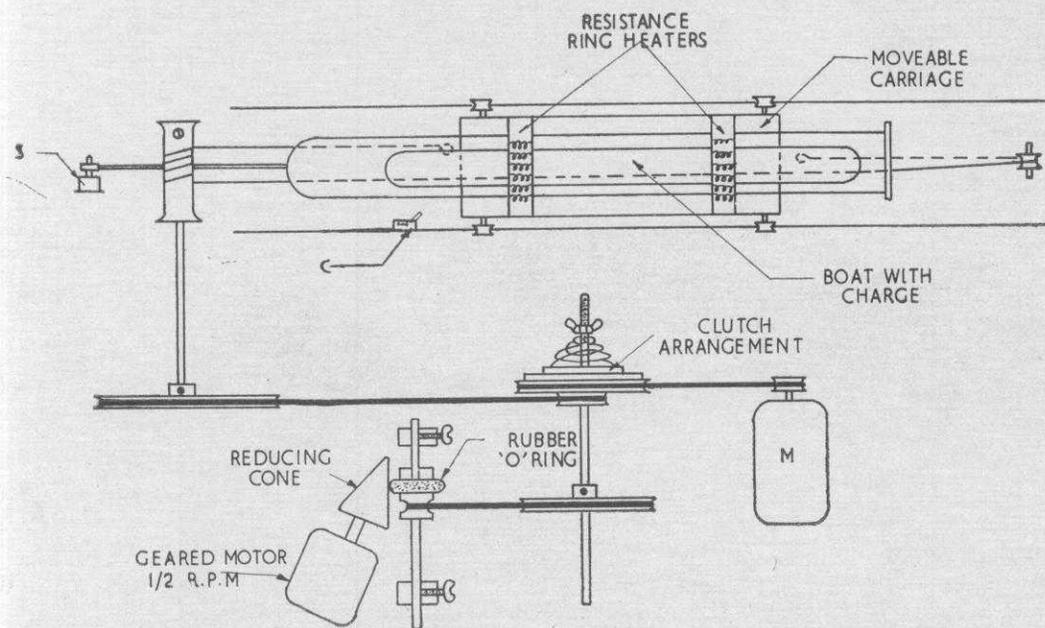
vessel and nearest the melt to control the temperature of the melt. A graphite crucible placed inside the vessel acts as container and an identical one, but with a hole, inverted over the former through collars



2 Distribution of an impurity during zone refining for an ingot with initial concentration C_0 and $K < 1$



Apparatus for vacuum distillation (schematic)



4 Automatic zone refining apparatus

serves as a substrate. The vessel is placed in a resistance furnace. A vacuum rotary pump and liquid air trap are employed to produce a pressure of the order of 300 to 30 μ . A thermo-couple gauge measures the pressure.

Zone refining

An automatic zone refining unit, fabricated in the Chemistry Division Workshop, is shown schematically in Fig. 4. It comprises:

- a slow drive mechanism consisting of a series of reduction gears and pulleys and a cone speed reducing arrangement to achieve a final steady molten zone speed, varying from 0.5 cm/hour to 20 cm/hour,
- a reversing motor and a clutch arrangement to facilitate quick reversal of the heaters to their starting positions, while the main slow drive mechanism is on, and
- a movable carriage for resistance heaters.

The tube containing the charge is fixed horizontally and the resistance heaters move slowly from one end to the other thus enabling narrow molten zones to move. At the end of each pass the toggle switch (S) is actuated and the reversing motor (M) brings back the heaters to their respective original starting positions. A mechanical stroke counter (C) is positioned in such a way that it counts one just before the reversing toggle switch (S) is actuated. Once the experimental conditions, such as, voltage of the heaters, traverse rate and ambient are set, experiments are allowed to run continuously till the requisite number of passes are over.

The melting points of the metals under consideration are: Bi-271°C; Sb-630.5°C; Te-449.5°C; Cd-319.6°C and Zn-419.5°C.

Bismuth

The best commercially available bismuth metal is 99.95% pure with Fe, Pb, Cu, Sb, Ni, Ag as the main impurities. Although purification by simple recrystallization or precipitation of Bi(NO₃)₃ · 5 H₂O or bi-oxalate³ respectively gives a fairly pure product, those methods involve increased use of reagents, great number of separation steps and handling of more apparatus. Electrolytic method³ has the disadvantage of low-current efficiency and Ag is not removed. Vacuum distillation^{4,5,9} involves working around 1000°C to have an appreciable vapour pressure of the metal. Zone refining technique^{7-14,15,16,8,17} has been found to be the most effective and suitable for purification of bismuth metal. Yashiya,⁸ Wormick,¹² and Worner¹³ have claimed a purity of 99.999% by this technique.

In our laboratory the work was initiated with a view to achieving the final purity of 99.999% by directly zone refining the commercially available bismuth metal. Experiments were initially conducted with a charge of 250-500g of the metal and after optimi-

zing the experimental conditions, preparation of 3.5 kg of the metal was handled in a single lot.

Bismuth is a relatively low melting (m. pt. 271°C) metal, and pyrex glass capsules 60 mm O. D. and 45 cm long could be conveniently employed to hold a charge of 3.5 kg of the metal. Two resistance heaters of 90 mm I. D. and 11 cm length produced narrow molten zones of length 4.5 cm. The temperature of the heaters was controlled by means of variacs.

Two horizontal capsules (total charge 7 kg) were fixed parallel on the zone melting unit. 15 passes were made at 4 cm/hour under a pressure of 30 μ . The samples removed from different lengths of the ingot were analysed spectrographically. Table I shows the analysis of such an ingot and of the starting material. About 80% of the zone refined ingot length was found to be 99.999% pure. The purity of the product was also established by comparing our sample with an imported 99.999% pure sample of bismuth metal by the Electronics Division.

TABLE I Spectrographic analysis of bismuth metal (in p.p.m. by weight)

Impurity	Starting material	Zone entry end	Middle fraction	Last frozen end	Detection limit
Pb	5	n.d.	n.d.	10	2
Sn	n.d.	n.d.	n.d.	2	2
Ni	5	n.d.	n.d.	10	2
In	5	n.d.	n.d.	n.d.	2
Cu	n.d.	n.d.	n.d.	10	5
Sb	5	5	n.d.	n.d.	5
Cd	n.d.	n.d.	n.d.	n.d.	10
As	n.d.	n.d.	n.d.	n.d.	10
Si	12	>250	n.d.	n.d.	10
Fe	20	20	n.d.	n.d.	10
Al	10	25	n.d.	n.d.	10
Zn	n.d.	n.d.	n.d.	n.d.	20

n.d.=not detected.

Antimony

As, Si, Fe, Sn, Ni, Bi, Cu and Pb are the main impurities present in the commercial grade antimony metal. Arsenic and some heavy metals are difficult to remove by zone melting methods,¹⁸ and their removal can only be effected by chemical treatment or vacuum distillation. Vacuum distillation of antimony with 1 kg

TABLE II Spectrographic* analysis of antimony metal (in p. p. m. by weight)

	As	Pb	Si	B	Fe	Sn	Ni	Bi	Cu
Fraction I	> 250	65	n.d.	n.d.	n.d.	15	n.d.	n.d.	n.d.
Fraction II	> 250	10	n.d.	n.d.	n.d.	5	n.d.	n.d.	n.d.
Fraction III	100	250	n.d.	5	n.d.	14	2	40	n.d.
Residue †	—	250	—	—	>250	—	—	—	>250
Starting material	1500‡	500‡	25	4	200	25	200	12	>250

*Detection limits are Si, 10; B, 2; Fe, 10; Ni, 2; Bi, 5 and Cu, 5 ppm.

†Containing high amounts of Fe, Cu and Pb; therefore other elements are not reported.

‡Values from chemical analysis.

n.d. not detected.

of metal charge has already been studied by the present authors,¹⁸ where it was shown that about 60% of the condensate is free from Si, B, Fe, Ni and Cu, with slight traces of Sn, Bi and Pb and about 100 p. p. m. as could be obtained by vacuum distillation of commercial grade antimony. Although vacuum distillation of the commercial grade antimony metal does not yield a product suitable for the electronics industry, the need for antimony metal as per the specification ASTM, B 237-52, Grade A for the fabrication in B. A. R. C. of Sb-124 source (for Sb-Be) can be met.

In the present work, distillation was carried out with 6-7 kg of the charge, temperature 900°C and pressure 3×10^{-1} torr. A graphite crucible of 12.5 cm I. D and 30 cm high was employed for this purpose. The analysis of the sample removed from the starting material, pure condensate and residue are shown in Table II.

Zone refining of antimony metal has been reported by several workers.¹⁹⁻²⁶ Miura²¹, Vigdorovich²³⁻²⁵ and Ivelva²⁴ have reported that almost all the impurities

are more or less segregated except arsenic which has a segregation co-efficient equal to unity. It is because of the arsenic impurity that chemical purification steps are considered essential while aiming at the final purity of 99.999%.

The starting material for zone refining in our case was chemically purified antimony metal.²⁷ Graphite boats 30 cm \times 3 cm \times 2 cm were employed, each holding 650-700 g of the metal. 20 passes of molten zone of length 5 cm were made to traverse through the ingot at 3.5 cm/hour rate. The experiments were conducted in an atmosphere of purified nitrogen. Spectrographic analysis of different samples is given in Table III. Sn, Ni and Fe which were present in quantities less than their respective spectrographic detection limits, are shown up in the last frozen end of the zone refined ingot. The final purity check up was done by resistivity measurement by the Electronics Division of B.A.R.C. About 75% of the ingot is found to have the requisite purity 99.999+%.

TABLE III Spectrographic analysis of antimony metal (in p.p.m. by weight)

	Pb	Sn	Ni	Bi	Ga	In	B	Si	Zn	Cu	Cd	Ag	Al	Fe
Starting material	nd													
Zone refined	nd													
Last frozen end of ingot	2	2	2	nd	60									
Detection limit	2	2	2	5	2	2	2	10	20	5	10	10	10	10

nd=not detected.

Tellurium

The major impurities which are frequently present in commercial grade tellurium (95–98%) are Pb, Cu, As, Bi, Zn, Fe, Se, S, Ag and Au. Preparation of tellurium of high purity is usually carried out by ion exchange, distillation or zone refining or a combination of those techniques. Distillation and zone refining of tellurium has been described by many workers.^{28–38} Preparation of electronics grade tellurium by a combination of chemical and vacuum distillation techniques in this laboratory has already been reported.³⁹ The present work was intended to produce electronics grade tellurium from the chemically treated tellurium powder, with zone refining technique as an alternative for the more tedious vacuum distillation methods.

250 g. of chemically purified powder was taken in a 25 cm × 3 cm × 1.5 cm quartz boat. A step involving the hydrogen treatment of the precipitated tellurium at 500°C prior to zone refining, was found essential. Hydrogen treatment reduces any TeO₂ present to the element.

20 molten zones were made at a rate of 7.5 cm/hour in an atmosphere of hydrogen gas. Analysis of the samples by spectrographic methods could not be done. Atomic absorption spectral analysis of the different samples for the impurities reported in Table IV were

TABLE IV Atomic absorption spectrophotometric analysis of tellurium (in p.p.m. by weight)

Impurity	Starting material (chemically purified Te)	Zone refined Te	Last frozen end of zone refined ingot
Fe	6.5	1	10
Cu	3	1.5	6
Sb	<10	<10	<10
Bi	<10	<10	<10

TABLE V Spectrographic analysis of cadmium metal (in p.p.m. by weight)

	As	Co	Sb	Fe	Cr	Sn	Al	Bi	Cu	Zn	Pb	Mg
Starting material	nd	nd	nd	10	nd	nd	10	nd	20	nd	>100	10
I fraction (~5%)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	20
Middle fraction (~80%)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Residue (~10–15%)	>250	nd	nd	50	nd	nd	40	nd	25	nd	>250	nd
Detection limits	100	10	10	10	10	5	10	5	10	50	5	10

nd = not detected.

therefore carried out. Here too, the final check to ascertain the purity was made in the Electronics Division, wherein the tellurium supplied by us was converted to Bi₂Te₃ and compared with Bi₂Te₃ made from imported standard materials.

Cadmium

The best quality commercially available cadmium metal has a purity of about 99.95% with Fe, Cu, Pb, Zn, Al, Mg and Bi as the main polluting elements. Distillation of cadmium metal under vacuum has been described by many workers.^{40–45} Vacuum distillation^{42,43} has been reported using a pressure of 10⁻⁴ torr, the melt at 450–500°C and the substrate at 250–300°C. Most of the impurities are removed by distillation; even arsenic which has a high vapour pressure does not come with the condensate as a result of the formation of Cd₃As₂.⁴⁵ Starting with 99.98% pure cadmium metal, by distillation alone a purity of 99.99995% has been claimed by Alexandrov.⁴⁶ This suggests that direct distillation of commercially available cadmium metal 99.95% may yield a product of the requisite purity, i.e. 99.999%. Aleksandrov⁴³ has employed a tantalum foil as the substrate for the deposit. In our work, we employed an apparatus described above using graphite both for container of the melt and the substrate.

A charge of 5 kg metal was kept in the graphite crucible 40 cm × 9 cm O. D. and slid in the stainless steel distillation vessel. The experimental conditions were, temperature 450°C and pressure 7 × 10⁻² torr. The deposit was found on the inner walls of the upper graphite crucible at temperatures less than 300°C. About 5% of the charge collected as first fractions and another 10 to 15% of the charge remaining as residue were discarded, being impure. About 80% of the charge collected as distillate was found to be 99.999% pure. The final check on this purity 99.999% was made by the Electronics Division by comparing this material with an imported standard sample. The results of spectrographic analyses of the different samples are given in Table V.

Zone refining of cadmium metal has been described

TABLE VI Spectrographic analysis of cadmium metal (in p.p.m. by weight)

	Sb	Fe	Pb	Sn	Bi	Al	Cu	As	Zn	Co	Mg	Ni
Starting material	nd	10	>25	nd	nd	nd	nd	nd	nd	nd	nd	nd
Zone refined	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Detection limits	10	10	5	5	5	10	10	100	50	10	10	5

nd=Not detected

TABLE VII Spectrographic analysis of zinc metal (in p.p.m. by weight)

	Sn	Bi	Sb	Ni	Cu	Cr	Pb	Co	Fe	Al*	As*	Cd*
Starting material	20	nd	nd	nd	nd	nd	25	nd	nd	100	nd	nd
I fractions	9	nd	nd	nd	nd	nd	20	nd	nd	100	nd	nd
Pure fractions	nd	nd	nd	50	nd	nd						
Residue	8	nd	nd	nd	nd	nd	115	nd	35	500	nd	nd
Detection limits	5	5	5	5	5	5	5	10	10	50	100	100

* Values are semiquantitative
nd=Not detected.

by various workers.^{40, 42, 46, 47} Zone refining removal of Si, Pb, Fe, Cu, Zn, Al and Ni from cadmium has been reported by Medcalf⁴⁰ and Alexandrov.⁴⁶ Zone melting alone of cadmium of 99.98% purity results in 99.9995% pure metal.⁴⁷ In the present studies, cadmium metal 99.95% pure was subjected to zone refining by making 20 passes at 7.5 cm/hour in graphite boats of 60 cm × 3 cm × 2 cm (charge each boat 2.50 kg metal) in an atmosphere of nitrogen or hydrogen. Spectrographic analysis results of the samples are given in Table VI. About 80% of the charge is found to be 99.999% pure.

Zinc

The major impurities in commercial grade zinc metal are Pb, Cd, Cu and Fe. A purity of 99.999% by distillation at 400°C has been claimed by Bregman⁴⁸, Desalov⁴⁹ and Erwin.⁵⁰ A survey⁵¹ of the methods of preparation of ultrapure zinc metal shows that distillation is the best method for achieving the high purity. Electrolysis to prepare electronics grade zinc has been recommended by Nizhnik⁵² and Steintviet.⁵³ In the present studies, we have employed the

apparatus and experimental conditions similar to those for the case of distillation of cadmium metal, except that the working temperature was 500°C. The condensate was found deposited on graphite substrate at temperatures less than 395°C. The spectrographic analysis of the different samples is shown in Table VII. Here too, about 75% of the charge was found to be 99.999% pure. The final check of purity was ascertained by the Electronics Division.

Acknowledgement

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Discussions

Mr Narinder singh (N M L) : 1. Is any work being done at Bhabha Atomic Research Centre to recover tellurium from indigenous sources like copper slimes or lead zinc ores?

2. Are there studies on hand at the B. A. R. C. on recovery of other metals used in electronics industry such as germanium, gallium and selenium from indigenous sources ?

Mr A. J. Singh (Author) : 1. Yes, some work of exploratory nature has been done in the Metallurgy Division (Bhabha Atomic Research Centre) for the recovery of tellurium from copper slimes.

2. Some preliminary work has also been done for the recovery of selenium from copper slimes by the Metallurgy Division. Sometime back, work on recovery of germanium from different samples of fly ash by

chlorination was done in the Chemistry Division (Bhabha Atomic Research Centre). The maximum germanium content is about 150 ppm in some samples of the fly ash. A recovery of about 90% was achieved.

As regards the gallium recovery, an electrolytic method to recover gallium from Bayer's liquor was developed in the Chemistry Division, and based on this method large cells for recovery of gallium from the Bayer's liquor have been set up at HINDALCO, Renukut, in U. P.

Mr L. Wallace Coffey (Operation Hardrock, New Delhi) : Germanium monoxide (GeO) and germanium sulphide (GeS) are volatile at high temperature while germanium dioxide (GeO_2) is quite stable. We were able to drive germanium monoxide and sulphide out of

a fluidized bed of zinc sulphide concentrate using a stream of nitrogen to fluidize the bed at about 1600°F. Germanium is recovered in the dust collected from the bed.

Another method we used for germanium extraction was a sodium hydroxide bake followed by leaching with water. This takes germanium into solution as sodium germanate. It can be precipitated from this solution at the iso-electric point (as I recall, about pH6) provided germanium has been oxidized to the quadra-valent state by the use of sodium or hydrogen peroxide.

This work was done at the Battelle Memorial Institute about 1958 and I am giving the results only from memory because I do not believe that they were published. I hope this information can be of some assistance in your work on germanium.