

## High purity tellurium production using dry refining processes

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**Abstract.** Tellurium (99.95 at.% purity) is purified using dry processes such as selective vapourization and zone melting in a thoroughly etched and cleaned quartz boat, under continuous flow of hydrogen (H<sub>2</sub>) gas. The tellurium ingot was quadruple zone refined (QZR) under continuous flow of H<sub>2</sub> gas. Thus, the purified tellurium of ultra high purity (UHP) grade is analysed for 60 impurity elements in the periodic table using glow discharge mass spectrometer (GDMS). The sum of all elemental impurities indicate that the purity of tellurium as 7N (99.99999 at.%). The total content of gas and gas forming impurities like O, N and C are found to be within acceptable limits for opto-electronic applications.

**Keywords.** 7N (99.99999 at.%) tellurium; ultra-purification; horizontal-zone melting; quadruple zone refining; trace analysis.

### 1. Introduction

The high purity materials are mainly associated with their applications in microelectronics, space engineering, atomic energy, medicine and basic science research. High purity materials purification by vacuum and solid–liquid interface techniques is usually termed as dry processes. Most radical ways of enhancing the efficiency of materials purification is to employ refinement techniques with different mechanisms of impurity separation. Many of the processes begin with chemical, physico-chemical and end up with dry processes like vacuum distillation (selective vapourization), and zone refining. The final purity is invariably achieved by growing single crystals with perfect lattice structures. We reported previously that UHP tellurium up to 6N+ purity can be obtained in a clean room environment (Munirathnam *et al* 2003). Most of the UHP materials required for opto-electronic applications demand 7N (99.99999 at.%) purity with minimum gaseous and gas-forming impurities. The purpose of the present work is to report the methodology to purify 3N+ purity tellurium by dry processes and analyse the purity by glow discharge mass spectrometry (GDMS).

### 2. Experimental

#### 2.1 Vacuum distillation

The basis of separation of impurities from the base metal is by evaporation and condensation due to difference in

the vapour pressure (Fricke Jr. and Riechard 1978; Varavi 2003). The separation coefficient 'a' is defined as

$$a = (P_i/P_m) * (N_i/N_m) * (g_i/g_m) * (\sqrt{M_m/M_i}),$$

where  $P$  is the vapour pressure,  $N$  the mole fraction,  $g$  the activity coefficient and  $M$  the molecular weight of impurity (i) and base metal (m). This technique was employed to prepare high pure tellurium by distilling under a dynamic vacuum of nearly  $1 \times 10^{-5}$  torr. The raw tellurium (3N pure) was kept in a graphite crucible and distilled at about 525°C under dynamic vacuum. The material deposited over the water cooled SS fingers was then subjected to ICP–OES analysis. The overall purity of trace impurity elements was more than 99.995% except selenium which is around 115 ppm. The gaseous impurities like oxygen and nitrogen in vacuum distilled tellurium was analysed on LECO make (model TC-236) nitrogen/oxygen determinator and observed both as < 1 ppm.

#### 2.2 Zone refining

The chunks of vacuum distilled tellurium (5N pure except selenium) of nearly 1000 g weight was taken in a thoroughly cleaned and etched quartz (GE214 grade) boat container of dimensions  $34 \times 38 \times 560$  mm (ID  $\times$  OD  $\times$  L) and melted at a temperature,  $T_m$ , nearly 13 to 15% more than the melting point of tellurium in a uniform temperature gradient furnace under a constant flow of hydrogen gas (IOLAR I grade). After completely melting, the H<sub>2</sub> gas flow continued till the tellurium bar temperature was cooled down to room temperature (RT) to avoid any possible oxidation. After taking out the tellurium bar, a small portion of the tellurium material at one end was cut and analysed to check for any added impurities during

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melting. It was observed from the analysis that the selenium impurity content was 115 ppm and the sum of the amounts of the remaining elemental impurities content indicated the purity of tellurium bar remaining nearly as 99.999 at.%.

The tellurium bar which was in the shape of a uniform semi-circular of 560 mm long was placed in a thoroughly etched and cleaned quartz boat and inserted into a 44 mm dia and 1600 mm long quartz tube and evacuated for at least 4 to 5 h under dry hydrogen gas flow of ~ 80 CCM. Microprocessor controlled stepper motor driven quadruple zone refiner (QZR) with the heater zone width of ~ 30 mm and controlled by 'MAXTHERMO' make PID temperature controllers with an accuracy of  $\pm 1^\circ\text{C}$  was used to purify tellurium in a clean room environment of class 10000. The hydrogen gas generated from "Dominick Hunter" make hydrogen generator of capacity ~ 160 CCM was used for maintaining continuous ambient flow. The cleaning procedures of quartz ware (GE 214 grade) and experimental procedure to purify tellurium were same as described elsewhere (Munirathnam *et al* 2003). The final refined material was packed in polypropylene (PP) coated aluminum covers and stored in vacuum glove box.

### 2.3 Analysis

The samples for analysis were cut from the melted tellurium bar using a stainless steel (SS) cutter. The metallic impurities during the process were analysed on ICPOES and oxygen and nitrogen were analysed by nitrogen/oxygen analyser. The samples for ICPOES are prepared by dissolving cut portion of the tellurium (2 to 3 g) in 50% suprapure  $\text{HNO}_3$  in a teflon beaker. The final purified material by zone refining was analysed for 60 trace impurity elements on glow discharge mass spectrometer (GDMS) at the National Research Council (NRC), Canada.

### 3. Results and discussion

The results of zone refined tellurium analysed by GDMS is given in table 1. The analytical data show 90 ppb of carbon, 8 ppb of nitrogen and 110 ppb of oxygen (total content, 208 ppb). However, we are aware of the commercial samples where sum of the contents of all the above three impurities viz. carbon, oxygen and nitrogen, is much less than 250 ppb, which would be supplied at an extra cost. Therefore, this batch can be named as the best batch for opto-electronic applications. In our case, except silicon impurity content which is 50 ppb, all other elemental impurities have been shown as below detection limits of GDMS. The segregation coefficient of selenium in tellurium is around 0.44–0.5 (Kuchar *et al* 1996). Therefore, it is normally difficult to separate selenium impurity in tellurium matrix by conventional zone refining. Normally selenium is removed by passing hydrogen

**Table 1.** GDMS analysis of zone-refined tellurium (values in ppb).

Sl. no.	Element	CMET 'Te'
1	Li	< 0.8
2	Be	< 1.0
3	B	< 2
4	C	90
5	N	8
6	O	110
7	F	< 3
8	Na	< 0.9
9	Mg	< 1
10	Al	< 0.4
11	Si	50
12	P	< 0.9
13	S	< 1
14	Cl	< 0.8
15	K	< 3
16	Ca	< 13
17	Sc	< 0.6
18	Ti	< 0.2
19	V	< 0.2
20	Cr	< 0.7
21	Mn	< 0.5
22	Fe	0.8
23	Co	< 0.3
24	Ni	< 0.7
25	Cu	< 2
26	Zn	< 4
27	Ga	< 1
28	Ge	< 3
29	As	< 0.8
30	Se	< 10
31	Br	–
32	Rb	< 0.5
33	Sr	< 0.3
34	Y	< 0.2
35	Zr	< 0.2
36	Nb	< 0.2
37	Mo	< 0.4
38	Pd	NA
39	Ag	< 1
40	Cd	< 3
41	In	< 0.4
42	Sn	< 3
43	Sb	< 35
44	Te	matrix
45	I	< 610
46	Cs	< 4
47	Ba	< 5
48	La	< 0.5
49	Ce	< 4
50	Hf	< 0.3
51	Ta	NA
52	W	< 0.4
53	Pt	< 0.9
54	Au	< 10
55	Hg	< 2
56	Tl	< 0.5
57	Pb	< 0.7
58	Bi	< 0.4
59	Th	< 0.06
60	U	< 0.07

NA = not analysed.

gas on the molten tellurium (Jennings 1971; Munirathnam *et al* 2002).

The selenium is expected to react with hydrogen at the molten surface and get converted into hydrogen selenide, which would be carried away by hydrogen gas flow. This of course, would be neutralized by passing the outgoing gas into sodium hydroxide solution before letting it out into atmosphere. The content of selenium in the neutralized sodium hydroxide is analysed to ensure the removal of selenium. After the analysis of this solution on ICPOES, it was observed that during the first 8 h of zone melting experiment of tellurium, ~ 4 ppm of selenium was collected indicating the removal of selenium. Thus, the selenium impurity in the tellurium ingot was reduced from 115 ppm to 5.6 ppm after 20 days of continuous quadruple zone melting, which is much higher than the allowable quantity of selenium in 7N purity tellurium. Therefore, it is necessary to reduce selenium up to ~ 1 ppm before initiating zone refining. In view of this, at the stage of initial tellurium bar preparation for zone refining, the hydrogen gas flow at the rate of ~ 100 CCM is continued onto the molten tellurium for 60 h at around 500°C and the samples for analysis were collected at the intervals of 8, 24, 46, and 60 h and analysed for selenium content using ICPOES. It was observed that after a period of 60 h selenium decreased to < 1 ppm. This material when zone refined has given a selenium content of < 10 ppb.

#### 4. Conclusions

The following conclusions were drawn in the purification of 3N pure tellurium.

(I) Ultrapure tellurium (7N) was prepared using selective vapourization and zone refining techniques. The tellurium was purified, using simple and indigenously developed horizontal zone refiner, to 7N grade with respect to 60 elements and analysed by GDMS.

(II) The selenium content, by passing hydrogen gas at the rate of ~ 100 CCM on a completely molten tellurium at 500°C for 60 h, has reduced to < 1 ppm.

(III) The tellurium bar with < 1 ppm of selenium has further reduced to < 10 ppb during quadruple zone refining operation.

(IV) The total amount of impurity contents of gas and gas forming impurities like carbon, nitrogen and oxygen is 208 ppb.

The tellurium thus purified can be used for the preparation of substrates for opto-electronic applications.

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