WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 8.074
Volume 7, Issue 05, 743-754. Research Article ISSN 2277–7105

INVESTIGATION OF REFINING TECHNIQUE IN ULTRA-HIGH PURITY GE FOR PHARMACEUTICAL USE.

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Article Received on
07 Jan. 2018,
Revised on 28 Jan. 2018,
Accepted on 17 Feb. 2018
DOI: 10.20959/wjpr20185-11111

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ABSTRACT

A numerous research has been performed to optimize the parameters of zone refining process such as length, travel rate, number of passes and molten zone effect in high purification of germanium. Profiling of the impurity concentration along the zone refined germanium is established by several techniques. Due to the optimized parameters identified through the previous study, 7N (99.99999% purity) germanium is subjected to high purity zone refining for 49 passes and stirred at 30 rpm in our three-dimensional freezing system. The high purity zone refined germanium has a purity level of 8N (99.999999%) and the concentration of impurity is decreased to <1 ppb, as used by ICP- MS analysis. In this study, we proposed a new zone refining technique of 9N (99.9999999%) germanium, which is efficiency and time saving.

INTRODUCTION

A technology of zone refining developed in the early 1950s.[1] This technique leads to ultra-high purity sample of silicon and germanium with a few impurities as low as one part in ten billion.[2,3] Such zone refined samples are divided into two regions, such as n-type and p-type.[4,5] Impurities will immigrate to alternative directions in the crystal with different distribution or segregation coefficients during the refining.[6] After numerous zone refining passes, the impurities immigrate to front and end of the ingot, thus the central region of the

ingot becomes ultra-high purified.[7,8] High purity germanium (HPGe) crystal must have a impurity level under 10 ppb and Ultra-High purity germanium (UHPGe) crystal must have a impurity level under 1 ppb. Therefore, to obtain HPGe and UHPGe, it is necessary to carry out further zone refinement of the raw germanium materials.

Various studies have been carried out obtaining possible factors that affected the impurity level of the high purity germanium ingots. Researchers found that the dominant factors included composition of gas, crystallinity of ingot, type and purity of container and conditions of operation. The ratio of refined zone to the ingot length was also established.[9,10]

We have developed earlier the segregation of impurities in germanium during refining and found out suitable lengths for effective refinement. We also studied a refining process describing most optimized zone length for passes for the effective removal of impurities.

In this paper, we investigated a new technique, "perfect synthesis with nano bondage" that may refine the high quality of UHPGe. We examined by ICP-MS technique to confirm the impurities in the zone refined sample to parts per billion level.

MATERIAL AND METHOD

The modeling of impurity distribution along the germanium ingot after zone refine passes is based upon Table 1.

In the process of simulation, the germanium ingot is separated into equally spaced regions of width dx and a based concentration of impurity, C_0, is obtained for all the samples. After one single pass, the concentration of impurity for sample can be calculated using Pfann's equation. (Table 2. A).

Where $X=x/L$ is the standardized distance from the sample beginning and $Z=l/L$ is the standardized zone length of molting. The concentration of impurity distribution for the whole length of the sample except for the end of zone where natural freezing occurs. The distribution of impurity in the last region of the sample can be expressed as Table 2. B.

According to previous study, maximum removal of solute for the first refine pass can be gained when the ingot length equals the zone length. The equation for the standard freezing is given by Table 2. C.

It is necessary to perform repeated and optimized number of zone refining passes depending on the sample type, nature of impurity targets and other work conditions to gain ultra-high pure material. The concentration of impurity distribution along the sample for repeated number of zone refining passes. At $X=0$, the concentration of impurity in the beginning part of the sample is given by Table 2. D.

Where M is the number of each elements of length dx inside the molten zone volume and n is the number of zone refinement passes. At $0<X<1-Z$; the concentration of impurity is given by Table 2. E. At $1-Z<X<1$; in the last region, the distribution of impurity is given as Table 2. F.

In this part, the impurity is not taken in and the refined zone length is no longer constant. After repeated number of zone refining passes, the concentration of impurity reaches a stable state or the ultimate distribution. If the ultimate distribution of impurities reaching for $n-1$ pass be $C_S(x)$, then for the nth pass this distribution would not shift and concentration of impurity freezing out of the molten refine zone at point x will be $C_S(x)$. The solution of the ultimate distribution of impurities is given by Table 2. G. Where, A and B are constants and they can be ratiocinated by solving the equations, Table 2. H & I.

A refiner of vertical zone was built to refine germanium of 8N purity. (Fig. 1A) It is composed of alternate three heating parts and cooling parts. This alignment was made to rapid process the ingot than passing it through a single unit although the effect of final refining remains the same. Ethanol is used as the cooling agent, which is passed through the cooler and a adjustable chiller monitors the cooling agent flow. The cooling part provide to fasten the molten regions produced by the heating part and help to gain qualified crystallization from the melt quickly. Through the heating and cooling part assembly, the tube was made to pass vertically downwards by the lowering and zone travel rate of the tube was fixed at 2.5 cm/h by the drive motor controller. After passing of zone refinement, the zone refined germanium was located into three-dimensional freezing system. This three-dimensional freezing system has individual control for hot, gradient and cold zone phases, shown in Fig. 1B. The hot zone was maintained at 500℃ for 2 hours. The gradient zone temperature was controlled from 200℃ for 2 hours, 75℃ for 2 hours and after which it was fixed at 0℃. Finally, the cold zone temperature was controlled from -20℃ for 0.5 hours, 4℃ for 1 hours and -10℃ for 3 hours. This system consists of a rotation machine for rotating the tube, which acts in stirring the melted germanium enabling improved impurity. After refined,

5 g of germanium from raw and refined samples were obtained. These samples were dissolved in 10 ml of 70% HNO_3 and were imported to a flask to be diluted with 100 ml of high-purified water. The solution was used for the spectroscopy.

RESULTS AND DISCUSSION

During zone refining, the impurity segregation in the molten zone takes place due to the alternative of the concentration of the freezing phase from that of the liquid phase.[11,12] Under the same condition, the freezing rate is entirely slow enabling the processed of diffusion in the solid phase and liquid phase to counteract the gradient concentration and the solute concentration in the solid phase is always k_0 times that in the liquid phase. Under this condition, the effective distribution coefficient k, related to k_0 is given by Table 3. A. Where D is the value of the impurity in the melt zone, d is the diffusion layer and f is the zone travel rate of molted. The effective distribution coefficient k is one of the key parameters that associated the segregation of the impurity in the ingot. Under standard conditions, the thickness of diffusion layer d is 1 mm. This layer performs as a barrier for impurities to immigrate into the melt zone. However, external stirring drives the impurities to immigrate more into the melt zone from the interface, causing the barrier layer d decrease ten-fold to 0.1 mm. Stirring of the molten zone is a critical step in ultra-high purification of germanium.[13,14,15]

Increased travel rate of the molten causes irregular re-crystallization at the interface of the melt zone in which the impurities are isolated by overgrowth. For effective high purification, low travel rate is usually adopted in practice. (Fig. 2A) depicts the concentration of impurity profile along the sample reaching the state of ultimate distribution as 'f'. It is confirmed that greater reduction of impurity carries out for slower travel rate of molten zone as it attains the state of ultimate distribution. The passages of zone refining required for attaining the level of ultimate distribution, for a given alternative values of 'f', was calculated and pointed in Fig. 2B. It shows that with lower travel rate, the lower concentration at the state of ultimate distribution is attained with lesser passages. This detailed investigation provides further the basis and maintain that lower travel rate of molten zone causes significant decrement of impurity concentration as it reaches the state of ultimate distribution even with lesser passages.[16,17,18] However, lower travel rate of molten zone takes more time to pass one refining process. For a 50 cm long germanium ingot sample, if the travel rate is applied as 2.5 cm/h, it will take 25 hours to pass a refining process. However, with external stirring of the

molten, the high purification efficiency can also be reformed and if optimized stirring can be operated, the travel speed of molten zone can be adjusted by various factors. This is demonstrated in Fig. 3, indicating the simulated concentration of impurity profile along the zone-refined sample for different travel rates of molten zone, with and without external stirring. A 1000 times reduction in concentration of impurity with external stirring is gained indicating its importance in obtaining the ultra-high purity of germanium. Although it is seen that a low travel rate of molten zone influences reduction in concentration of impurity compared to that for a higher travel rate. When mechanical stirring of the melt is operated, no significant difference in the concentration of impurity profile for lower and higher rates is found. To save time, optimized stirring can be operated even with higher travel rate to gain higher purity germanium. Therefore, we optimized a 'mildly higher' travel rate of zone as 2.5 cm/h while purifying germanium in our zone refining system. The three heating parts providing three molten zones are divided. A single refining is completed as the heating part from one end reaches the position of the next heating part.[19,20]

Concentration of impurity profile attaining the state of ultimate distribution for different zone lengths is shown in Fig. 4A. It is seen that the lowest impurity concentration at the state of ultimate distribution is attained for value of '*Z*'. Fig. 4B indicates the mapping contours of the optimum passages that are required to attain the state of ultimate distribution for given values of '*Z*'. It can be suggested that by reducing the molten zone length, more refining passages can be performed to decrease the concentration of impurity to the lowest level until the state of ultimate distribution is attained finally. A shorten length of molten zone of 5 cm was chosen in our study for a 50 cm length germanium sample. In previous research, we studied the concentration of total impurity atoms distribution for two alternative types of germanium. For the first type of germanium, we regarded that all impurities in that germanium have $k<1$. For the second type of germanium, we regarded that some impurities have $k>1$ and the rest have $k<1$. Added to these observations, in this study, we have identified the number of passages required to attain the state of ultimate distribution for impurities having alternative *k* values.[21,22] (Fig. 5) It is seen that the impurities having *k* values near to unity takes passages more to attain the state of ultimate distribution, as compared to impurities having *k* values either much less than or greater than unity. The study indicates that even those impurities, having *k* values either much less or greater than unity, can reach their maximum states of immigration or states of ultimate distribution after a certain pass and cannot be decreased further. Still more zone refining passes needed to be performed to

decrease the impurity concentration, having *k* nearing unity.[23,24,25] We confirmed to perform 49 zone refining passes to enable almost impurities to attain the state of ultimate distribution.

The purified germanium, gained by zone refining and external stirring mechanism in three-dimensional freezing system was evaluated by ICP- MS technique. The result is being indicated in Table 4. We can recognize that the most impurity concentrations in germanium have blown out below the reference of ICP- MS. Such reduction in the impurity concentration distinguishes the efficiency of our refining procedure. The reduction efficiency of impurity is computed using $E_f=\{(C_0-C_f)/C_0\}$ x 100%, where C_f is the final concentration of impurity in high purified germanium. It is seen that the impurities having greatest concentration in most metals were decreased perfectly with $E_f \fallingdotseq 100\%$. Other struggle impurities, such as, Cu, Fe, Sn, Co, Na and Sn were also decreased efficiently with $E_f > 99.99\%$. The total concentration of impurity with respect to impurities in germanium was decreased to less than 0.1 ppb. We purified UHPGe in a new refinement technique. The total impurity concentration decreased under 0.1 ppb with respect to 7 struggle impurities. The overall E_f with respect to all impurities is computed to 99.999%.

Table 1.

The effective distribution coefficient *k*, defined as
C_s the concentration of the solute in the solid to
C_l the concentration of solute in the melt.
The zone length and travel rate are constant in passes.
The densities of solid and liquid are constant.
Diffusion of solute in the solid is ignorable.
The model is based upon one-dimensional analysis.

Table 2.

A: $C_s (1 , X) / C_0 = 1 - (1 - k) \exp (- k X / Z)$
B: $C_s (1 , X) / C_0 = [1 - (1 - k) \exp \{ - k (1 - Z) / Z \}] \times [1 - \{ X - (1 - Z) \} / Z]^{k-1}$
C: $C_s (1 , X) / C_0 = k (1 - X)^{k-1}$
D: $C_s (n , 0) [\sum_{i=0}^{M-1} Cs (n - 1 , i)]$
E: $C_s (n , X) = C_s (n , X - dx) + (kdx / Z) \times [C_s (n - 1 , X + Z - dx) - C_s (n , X - dx)]$
F: $C_s (n , X) = k (1 - X)^{k-1} \times (Z-k) \times [1 - dx \sum_{i=0}^{1-Z} Cs (n , i)$
G: $C_s (x) = A e^{Bx}$
H: $k = B1 / (e^{B1} - 1)$
I: $A = C_0 BL / (e^{BL} - 1)$

Table 3.

A: $k = k_0 / [k_0 + (1 - k_0) e^{-fd/D}]$

Table 4: ICP- MS purity test results of 9N germanium (in ppb).

Element	Raw germanium metal (C_0)	Refined germanium metal (C_f)	Efficiency $\{(C_0-C_f)/C_0\}x100\%$
Cu	300	<0.03	>99.99
Fe	120	<0.03	>99.975
Sn	100	<0.01	>99.99
Co	1	<0.01	>99
Na	5	<0.01	>99.999
S	1	<0.01	>99
Zn	2300	<0.02	>99.999

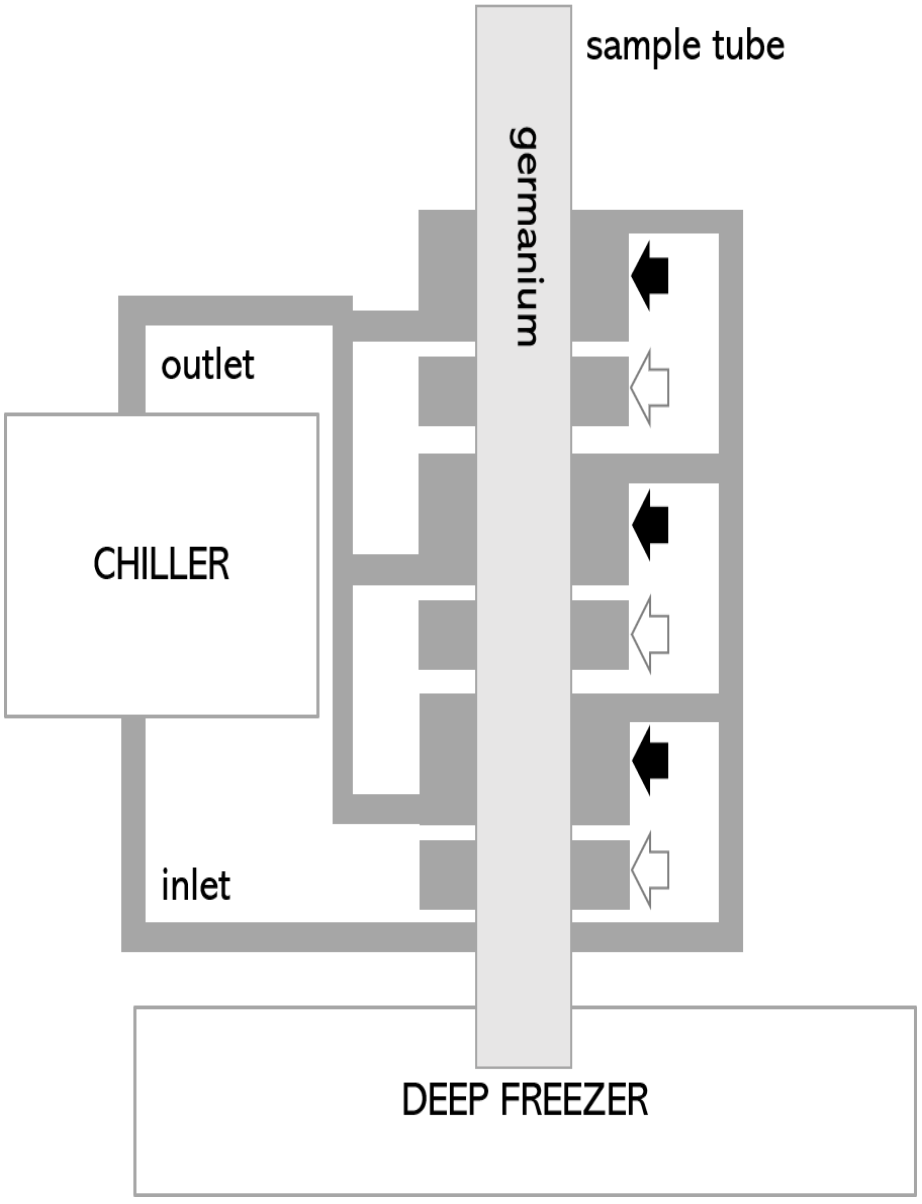


Figure 1A. Scheme of a new zone refiner. White arrows: Heating parts, Black arrows: Cooling parts.

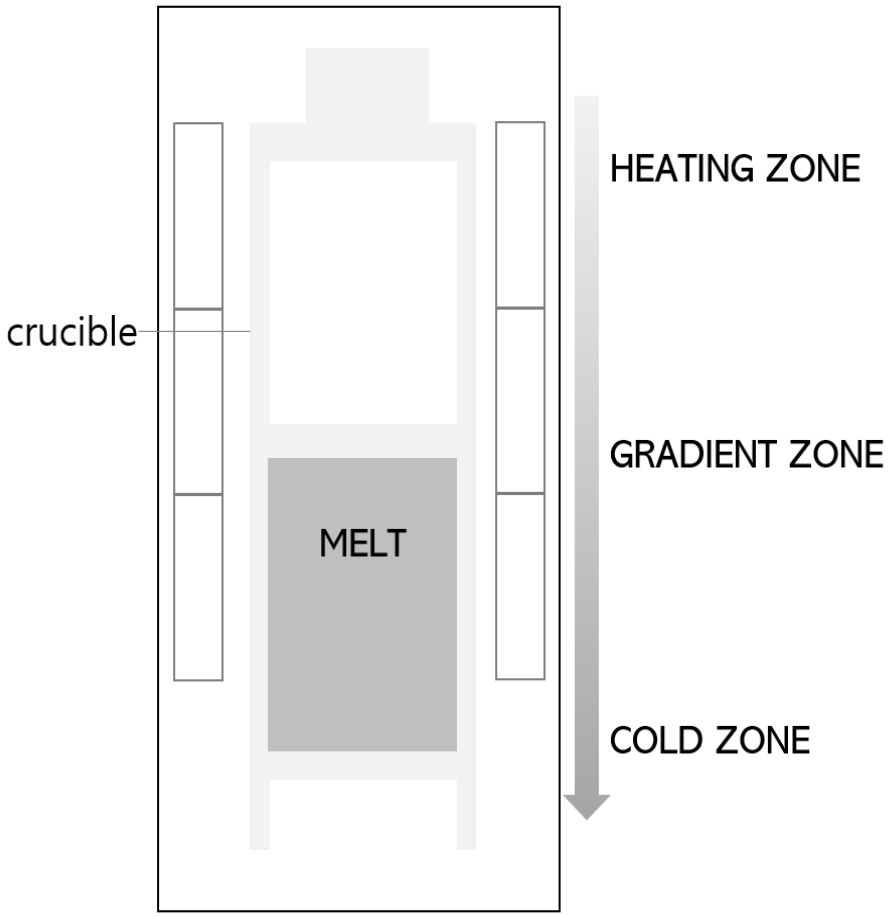
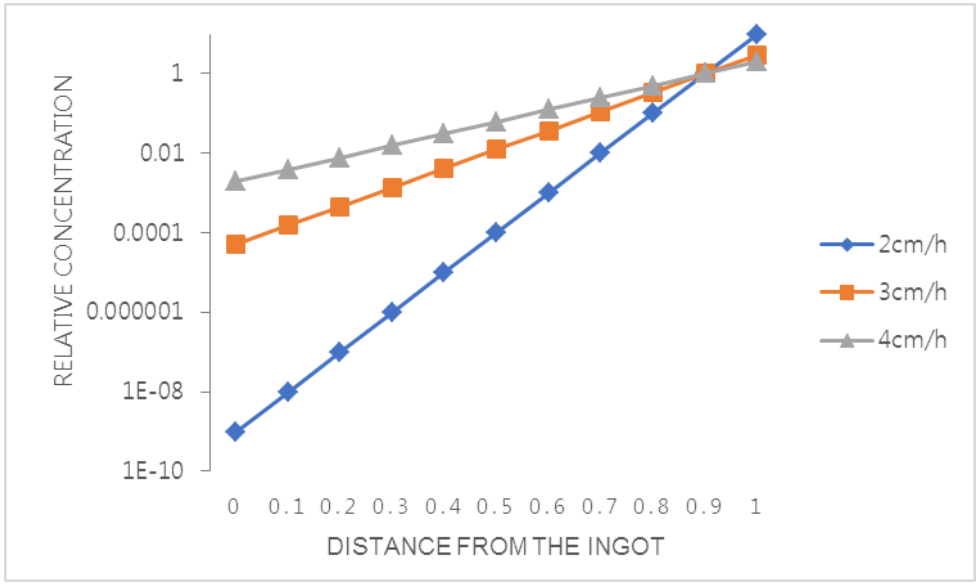
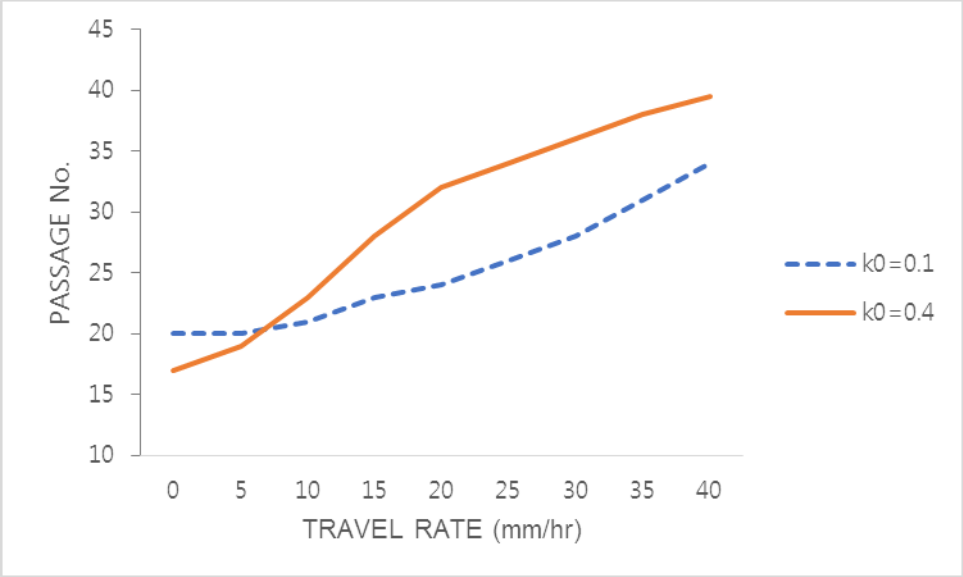


Figure 1B: Scheme of the three-dimensional freezing system.



2A.



2B)

Figure 2A. Concentration of impurity attain the state of ultimate distribution for travel rates of molten zone. Relative concentration (C_s/C_0), k_0=0.1 2B. Calculation of the passage number required for impurity having k=0.1 and 4 to attain the state of ultimate distribution as a function of travel rates of molten zone.

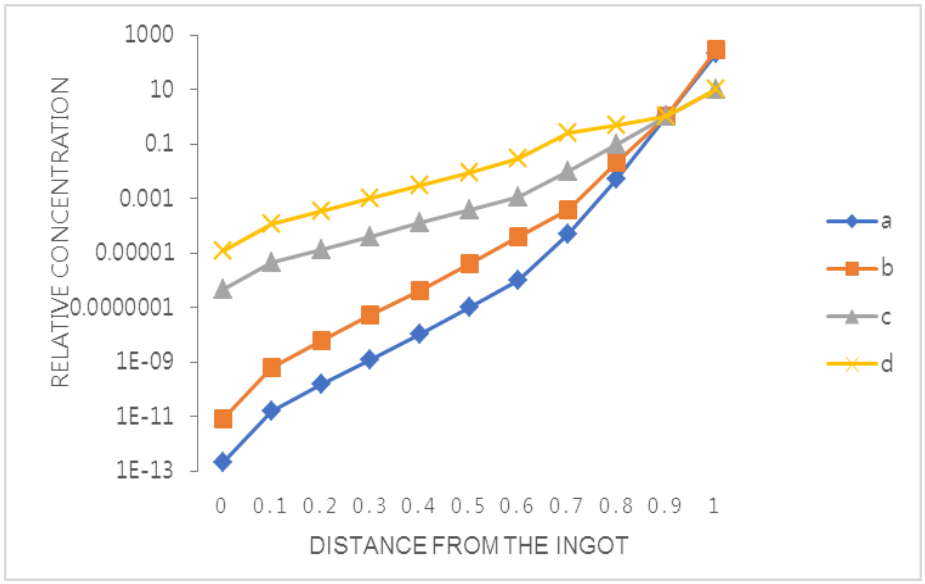
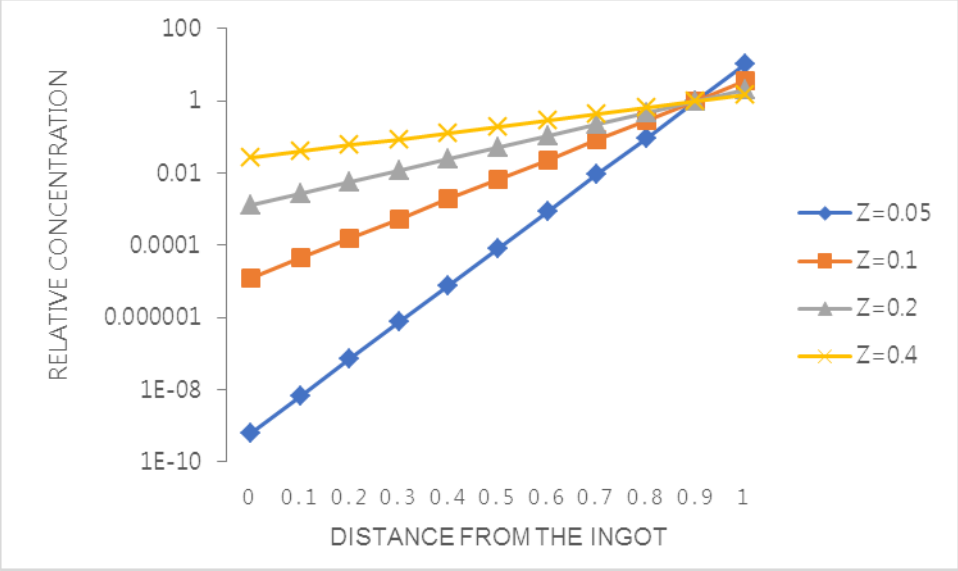


Figure 3. Comparison of the impurity concentration profile having k=0.6 after 50 passes for alternative travel rate of molten zone (f) along with stirring.

a. f=2.5cm/h w/ stirring, b. f=3.5cm/h w/ stirring, c. f=2.5cm/h, d. f=3.5cm/h

4A.



4B.

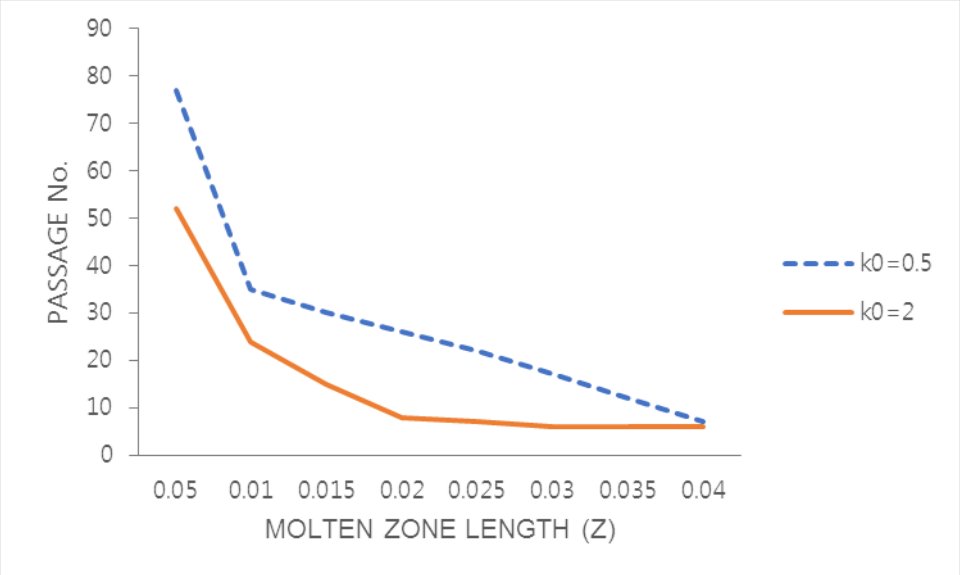


Figure 4A. Concentration of impurity profile attaining the state of ultimate distribution. 4B. calculation of the passage no. to attain the state of ultimate distribution for impurity having k=0.5 and 2.

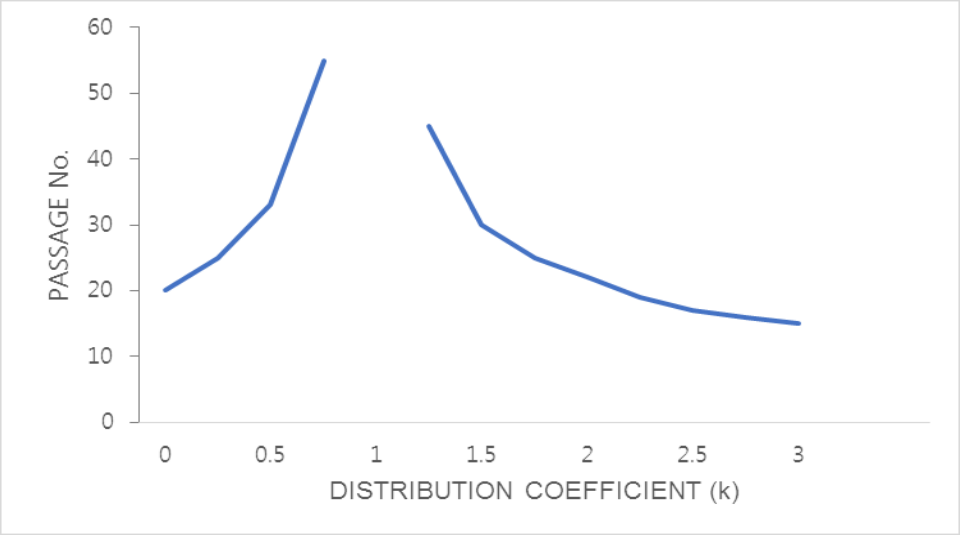


Figure 5: Passage no. to attain the state of ultimate distribution for impurities having alternative values of distribution coefficient.

CONCLUSION

In conclusion, a numerous research is presented to optimize parameters of refining process and thereby established a zone refining technique in ultra-high purifying germanium exceeding 9N purity. ICP- MS analysis data showed the presence of a few impurities and most of them have low concentration level significantly.

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