

$^{76}\text{freeGeO}_2$ purification: experiment #3
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Enriched ^{76}Ge isotope for GERDA (Phase II)

Svetlana Department of the ECP (Russia):

Batch of $^{76}\text{GeO}_2$

enrichement:

Ge-76 - 87.42%

Ge-70 - 0.018%

$m = 37.5 \text{ kg}$

with purity of 99.98% (technical grade)

Goals of the experiment #3

Purification:

99.98% → 99.9999%

$$m(^{76}\text{freeGeO}_2) = m(^{76}\text{GeO}_2) = 37.5 \text{ kg}$$

Technology of production is the same as for $^{76}\text{GeO}_2$

- Yield of GeO_2/Ge metal of good quality
- Effect of isotopic dilution (^{76}Ge)/enrichment (^{70}Ge)
- Schedule of the purification : problem of activation

General scheme of Ge purification

GeO₂ (99.98% technical grade)



GeO₂ transformation to GeCl₄



Extraction*



Distillation



Rectification



**GeCl₄ conversion to GeO₂
(99.9999% & < 10 ppbw for electro-active metals)**



Reduction GeO₂ ⇒ Ge metal



**Polyzone refinement of Ge
(up to 10¹³ impurities/cm³)**

Starting material: $^{76}\text{freeGeO}_2$

Batch of $^{76}\text{freeGeO}_2$ – “waste” after $^{76}\text{GeO}_2$ production

Technology of production is the same as for $^{76}\text{GeO}_2$

$m = 54.89 \text{ kg}$ (37.667 kg of element)

Purity – 99.98%

Isotopic composition:

Ge-70 – 22.55%

Ge-72 – 30.02%

Ge-73 – 8.45%

Ge-74 – 38.45%

Ge-76 – 0.53%

Preparation to the experiment

All equipment are polluted with ^{nat}Ge!!

“Washing” procedure, example:

Chemical reactor, $V = 1 \text{ m}^3$

HCl concentr. at $t = 110 \text{ }^\circ\text{C}$, 24 hours

1st 147 mg/L

2d 35 mg/L

3d 26 mg/L

HCl conc. 1.76 mg/L

Result of the experiment

37.667 kg of $^{76\text{free}}\text{Ge}$ (in form of GeO_2)



2 batches of $^{76\text{free}}\text{GeO}_2$ purified

Yield: 72.78%

Recoverable loss

15.18%

Unrecoverable loss

12.04%

414

17.938 kg

415

22.674 kg



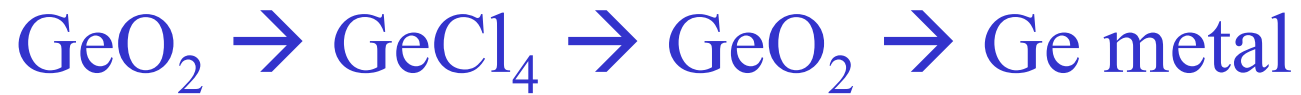
Ge metal

$m^* = 26.847$ kg

9 ingots

12 ingots

Purity: results of certification at Germany,
indirect (integral) method:



Specific resistivity at RT:

$$\rho > 30 \text{ Ohm*cm} = 80\%$$

$$\rho > 10 \text{ Ohm*cm} = 94.5\%$$

Conclusion: good quality

Experiment #3: quality control methods

Purity measurements:

- *ICP MS (ELAN 6100)* *Svetlana*
- **ICP MS X7*** **Chernogolovka**
- **ICP-EAS** Chernogolovka
- SparkSource MS (**direct!!**) Moscow
- *Measurements of $GeCl_4$ & GeO_2* *Germany plant*

Isotopic measurements:

- *TI MS & EI MS* *Svetlana*
- ICP MC NEPTUNE Moscow
- TIMS SECTOR 53 Moscow

Summary

- Yield of GeO₂ 72.78%
Recoverable loss - 15.18%
Unrecoverable loss - 12.04%
- Purity god quality:
 $\rho > 30 \text{ Ohm*cm} = 80\%$
 $\rho > 10 \text{ Ohm*cm} = 94.5\%$
- Isotopic dilution (not yet final result!) there is effect at level of 0.38% - 1.4% (^{nat}Ge)
- Duration of purification ~ 6 days (pure ⁷⁶freeGeO₂)

Results of certification: purity

- X7 – ICP MS: all of 66 elements < DL
- SS MS: all of 78 elements \leq DL,
except
 $\{C+N+O\} = 3$ ppm, Al = 0.03 ppm

Isotopic composition measurements

Product	Laboratory	Method, device	Ge76	ΔC
Natural Ge	ЦЗЛ ПО “ЕСР“	EIMS MI 1201 №15, TIMS MI 1201-AT №5	7.75	
Natural Ge	РАН ИГЕМ	ICP MS NEPTUNE	7.74	
Batch 42	ЦЗЛ ПО “ЕСР“	EIMS MI 1201 №15, TIMS MI 1201-AT №5	0.52	± 0.03
Batch 42	ВНИИНМ	TIMS SEKTOR 54	0.53	
Batch 42	РАН ИГЕМ	ICP MS NEPTUNE	0.57	
Batch 415	ЦЗЛ ПО “ЕСР“	EIMS MI 1201 №15, TIMS MI 1201-AT №5	0.69	± 0.03
Batch 415-2	РАН ИГЕМ	ICP MS NEPTUNE	0.68	
Batch 414-1	ВНИИНМ	TIMS SEKTOR 54	0.56	
Batch 414-2	РАН ИГЕМ	ICP MS NEPTUNE	0.60	

Factory/ laboratory	Deco mposi -tion	H2SO4 distilla -tion	Extrac -tion	Rectifica -tion	Total yield of pure GeCl4	Hydrolysis	Total yield of GeO2 Purified
GP, exp. #3	97.93 %	98.37%	96.7%	85.64%	79.78%	91.09%	72.78% (taking into account sampling)
Nisselson	-	-	-	92% (2 passes)	92% Recov. 3.24% Unrec. los 4.72%	-	-
GP + Nissel. - I small column	97.93 % (GP)	98.37% (GP)	96.7% (GP)	92% (Moscow)	85.703% Recov. 3.24% Unr.Los11.242%	91.09% (GP)	78.067% Recover. 9.282% Unrec. 12.836%
GP, exp #4 expected	97.93 %	98.37%	---	88%		93.26%	77.57% Recover. 13.26% Unrecov. 9.17%
GP + small column at GP	97.93 %	98.37%	96.7%	???	???	???	???
GP + Nissel. - II	97.93 % (GP)	-	-	92% (Moscow)	90% (GP + Moscow)	91.09%/ 93.26% (GP)	82%/ 83.4%

Reduction procedure ⁷⁶freeGeO₂

Boats	Batch 414 17,938 kg	Batch. 415 22,674 kg	Number of cycles
	Identification number of regulus		for boat
2-1	7	13__20	3
2-2	1__8	14__21	4
2-3	2__9	15	3
2-4	3	10__16	3
2-1-6	4	11__17	3
2-6	5	12__18	3
2-7	6	__19	3

Batch
414 – 9 regulus

Batch
415 – 12 regulus