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**ENERGY**

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# Germanium-76 Sample Analysis

## Revision 3

RT Kouzes  
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April 2011  
Revision 1 July 2011  
Revision 3 July 2011  
Revision 3 September 2011



**Pacific Northwest**  
NATIONAL LABORATORY

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Pacific Northwest National Laboratory  
Richland, Washington 99352

## Executive Summary

The MAJORANA DEMONSTRATOR is a large array of ultra-low background high-purity germanium detectors, enriched in  $^{76}\text{Ge}$ , designed to search for zero-neutrino double-beta decay ( $0\nu\beta\beta$ ). The DEMONSTRATOR will utilize  $^{76}\text{Ge}$  from Russia.

The first one-gram sample was received from the supplier for analysis on April 24, 2011. The second one-gram sample was received from the supplier for analysis on July 12, 2011. The third sample, which came from the first large shipment of germanium from the vendor, was received from Oak Ridge National Laboratory (ORNL) on September 13, 2011.

The Environmental Molecular Sciences facility, a DOE user facility at PNNL, was used to make the required isotopic and chemical purity measurements that are essential to the quality assurance for the MAJORANA DEMONSTRATOR. The results of these analyses are reported here.

The isotopic composition of a sample of natural germanium was also measured twice. Differences in the result between these two measurements led to a re-measurement of the second  $^{76}\text{Ge}$  sample.



## Acronyms and Abbreviations

BE	Binding Energy
EMSL	Environmental Molecular Sciences Laboratory
FWHM	Full width at half maximum
ICPMS	Inductively coupled plasma mass spectroscopy
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
ppm	Part per million

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# 1 Purpose

With the results from Super-Kamiokande, SNO, KamLAND, and other neutrino experiments, it has been demonstrated that neutrinos are massive, change flavor, and play an important role in the universe. Measuring the absolute mass of neutrinos and determining their Majorana nature are two of the most important goals of the physics community today. The standard double-beta decay process results in emission of two beta particles and two neutrinos, a process that was first reliably observed in  $^{76}\text{Ge}$  by the PNNL-University of South Carolina collaboration in 1990. The much rarer, and yet unconfirmed,  $0\nu\beta\beta$  process results in emission of only the two beta particles. Observation of this process would provide direct evidence that neutrinos are Majorana particles and that lepton number is not conserved.

The MAJORANA Collaboration was initiated in 1999 in order to carry out a  $0\nu\beta\beta$  experiment in  $^{76}\text{Ge}$ . MAJORANA is a collaboration of about 100 scientists at 20 institutions worldwide supported by DOE Office of Science Office of Nuclear Physics, the National Science Foundation, and other international funding agencies. The current plan calls for the MAJORANA DEMONSTRATOR to be constructed and operated over the next several years in parallel with the European  $^{76}\text{Ge}$  experiment (GERDA). This is proposed to be followed by a single, merged, Tonne-Scale, international experiment for  $0\nu\beta\beta$  in  $^{76}\text{Ge}$ .

The MAJORANA DEMONSTRATOR experiment is now constructing an essentially background-free measurement of  $0\nu\beta\beta$  in 30 kg of natural Ge plus 30 kg of  $^{76}\text{Ge}$  with the goal of determining lepton number conservation and the neutrino mass. The MAJORANA DEMONSTRATOR requires 30 kg of isotopically enriched  $^{76}\text{Ge}$ . Currently, the only source of enriched  $^{76}\text{Ge}$  is from Russia, at a cost of  $\sim\$85/\text{g}$ . This material will be delivered to the MAJORANA DEMONSTRATOR experiment in FY11-FY12, with quality assurance (QA) samples arriving on a periodic basis during this time. These QA samples will require precision isotopic evaluation. One such measurement was performed in 2009 under an EMSL rapid proposal on a single sample using SIMS instruments [Elliott 2009]. Further measurements will take place during FY11-FY12 at EMSL.

Reported here are the results of the measurements of isotopic composition and chemical purity of samples of  $^{76}\text{Ge}$  delivered by Isoflex, the representative of ECP in Russia. The first one-gram sample of  $^{76}\text{GeO}_2$  was delivered to PNNL on April 25, 2011 for analysis, which was completed on April 27, 2011. The measurements were made in the Environmental Molecular Sciences Laboratory at PNNL under EMSL user proposal #43992. The second one-gram sample was received from the supplier for analysis on July 12, 2011, with analysis completed on July 14, 2011.

The isotopic composition of a sample of natural germanium was also measured twice. Differences in the result between these two measurements led to a re-measurement of the first  $^{76}\text{Ge}$  sample in June 2011.

## 2 Germanium Isotopic Composition

A time-of-flight secondary ion mass spectrometry (ToF-SIMS) system, of the type shown in Figure 2.1, at EMSL was used for the isotopic analysis of the germanium samples.



**Figure 2.1.** ToF-SIMS Mass Spectrometer Model Used for Isotopic Measurements

Table 2.1 provides the results of the isotopic analysis of the first Russian  $^{76}\text{Ge}$  sample, where the value in parenthesis is the uncertainty in the last digit. This analysis (1<sup>st</sup> Measurement) indicated a  $^{76}\text{Ge}$  enrichment significantly higher than the specification for MAJORANA (86% or greater with less than 0.07%  $^{70}\text{Ge}$ , and 4-nines chemical purity).

**Table 2.1.** Isotopic Composition of  $^{76}\text{Ge}$  Samples

Isotope	Fractional Composition Sample 1 (1 <sup>st</sup> Measurement)	Fractional Composition Sample 1 (2 <sup>nd</sup> Measurement)	Fractional Composition Sample 2	Fractional Composition Sample 3
$^{70}\text{Ge}$	0.00006(1)	0.00009(3)	0.00002(2)	0.00005(4)
$^{72}\text{Ge}$	0.00011(1)	0.00013(3)	0.00007(2)	0.0002(1)
$^{73}\text{Ge}$	0.00033(3)	0.00046(5)	0.0005(1)	0.0004(2)
$^{74}\text{Ge}$	0.086(5)	0.109(2)	0.122(2)	0.118(3)
$^{76}\text{Ge}$	0.914(5)	0.890(2)	0.878(2)	0.882(3)

The measurement of this first enriched sample led to the measurement of a natural germanium sample, provided by Joe Caja, to increase confidence in the measurement approach, with the result shown in Table 2.2. Since this measurement disagreed with the natural abundances of germanium, the measurement was repeated, with the results also shown in Table 2.2. The new measurement strategy used a relatively long time for cleaning and a relatively long time for measurements. Cleaning of the surface by sputtering to remove contamination for each location measured took about 10 minutes. The measurement time for each location took about 10-15 minutes, resulting in about 30 minutes per measurement. Data was obtained from 6 locations, resulting in about 3 hours per experiment. Including sample loading and data analysis, the total time was 4-5 hours.

**Table 2.2.** Isotopic Composition of a natural germanium sample

Isotope	Natural Abundance	Fractional Composition (1 <sup>st</sup> Measurement)	Fractional Composition (2 <sup>nd</sup> Measurement)
<sup>70</sup> Ge	0.2123	0.212(2)	0.217(3)
<sup>72</sup> Ge	0.2766	0.283(2)	0.278(3)
<sup>73</sup> Ge	0.0773	0.066(2)	0.079(2)
<sup>74</sup> Ge	0.3594	0.380(2)	0.354(5)
<sup>76</sup> Ge	0.0744	0.059(2)	0.071(2)

Three possible reasons were speculated for why there might be a discrepancy in the measured values: 1) Some GeH<sup>+</sup> peaks exist, which may affect the final result, though the system was calibrated for this issue; 2) A powder sample was used, whereas a wafer sample gives more accuracy because the wafer sample is flat; 3) Signal saturation may happen for ToF-SIMS detector if the Ge<sup>+</sup> signal is too strong, even though the software has a function to calibrate this issue. The improved, longer measurement method should help reduce these effects.

The second, repeat measurement of the first enriched sample (2<sup>nd</sup> Measurement), also shown in Table 2.1, showed a somewhat lower <sup>76</sup>Ge value of 89%. It appears that this longer measurement process is needed to obtain accurate results.

The results from measurement of the second sample of <sup>76</sup>Ge that was received in July 2011, listed in Table 2.1 (Sample 2), show an enrichment of 88%.

The results from measurement of the third sample of <sup>76</sup>Ge that was received in September 2011, listed in Table 2.1 (Sample 2), show an enrichment of 88%. Labs at ORNL also measured samples from this shipment, giving results reasonably consistent with the PNNL measurement.

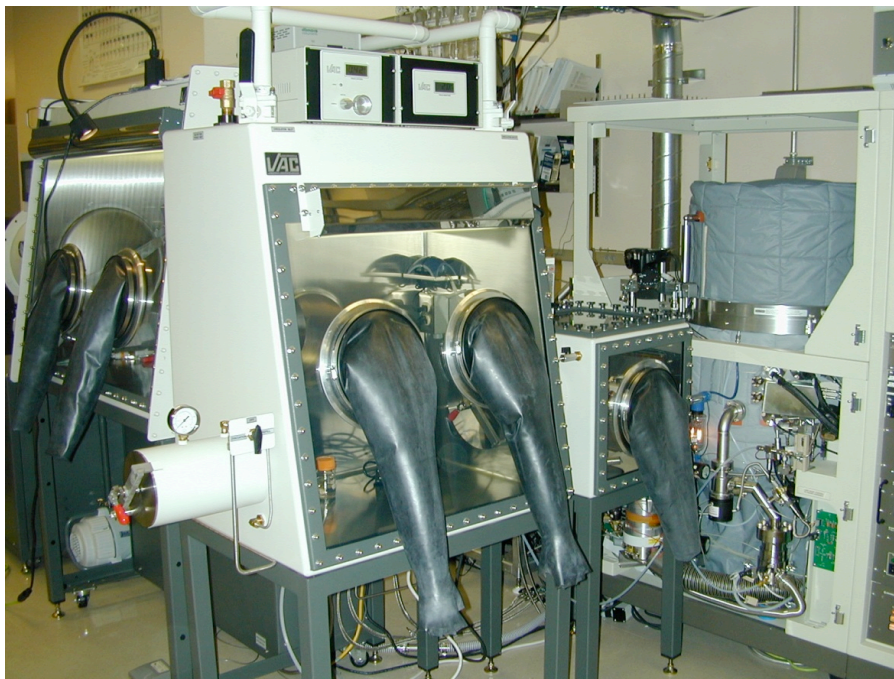
Since we only have at most two measurements from one sample, it is difficult to know the systematic errors in the measurements. We can speculate at this point that they are on the order of 1%, so the <sup>76</sup>Ge material appears to be about 88(1)% pure.

### 3 <sup>76</sup>Ge Chemical Analysis

X-ray photoelectron spectroscopy (XPS) was used to perform the chemical purity analysis only for the first <sup>76</sup>Ge sample in April 2011. XPS is more surface sensitive and provides relative concentration and chemical state information. Further samples were not analyzed with this method since it only provides limited chemical purity information.

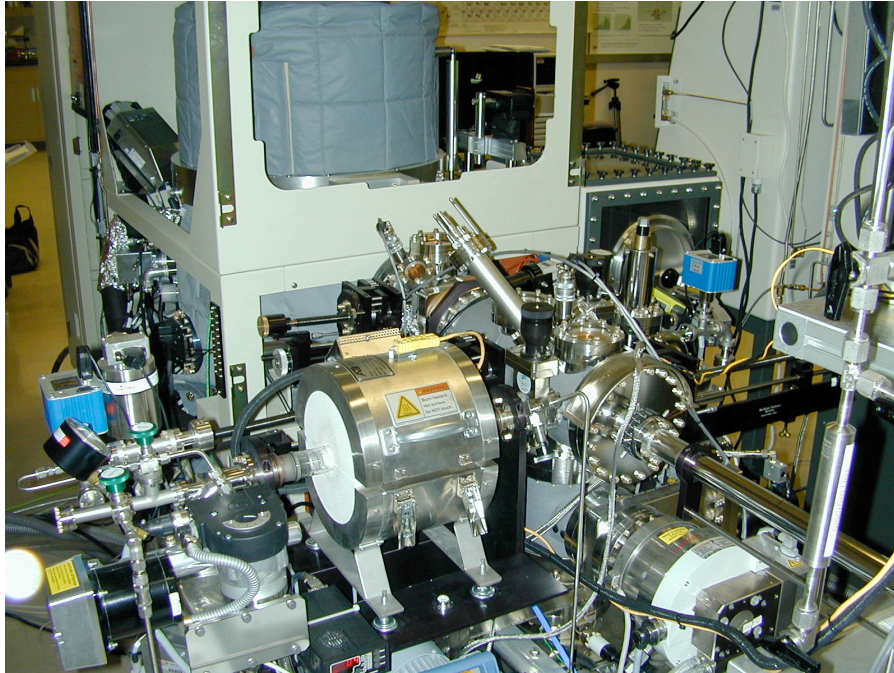
XPS measurements were performed with a Physical Electronics Quantera Scanning X-ray Microprobe. This system uses a focused monochromatic Al K $\alpha$  X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 32-element multichannel detection system. A 100 W X-ray beam focused to 100  $\mu$ m diameter was rastered over a 1.4 mm x 0.1 mm rectangle on the sample. The X-ray beam is incident normal to the sample and the photoelectron detector is at 45° off normal. High energy resolution spectra were collected using a pass-energy of 69.0 eV with a step size of 0.125 eV. For the Ag 3d<sub>5/2</sub> line, these conditions produced a full width at half maximum (FWHM) of 0.91 eV. The sample experienced variable degrees of charging. Low energy electrons at ~1 eV, 20  $\mu$ A and low energy Ar<sup>+</sup> ions were used to minimize this charging. The binding energy (BE) of adventitious carbon line was set at 284.8 eV to compensate for any surface-charging effects.

The GeO<sub>2</sub> powder samples were pressed onto clean double sided Nichiban tape supported by 1 cm x 3 cm flat Si wafers. The sample holder was then placed into the XPS vacuum introduction system and pumped to less than 1x10<sup>-6</sup> Torr using a turbomolecular pumping system prior to introduction into the main ultra high vacuum system. The main vacuum system pressure is maintained at less than 5x10<sup>-9</sup> Torr during analysis and pumped using a series of sputter ion pumps.



**Figure 3.1.** PHI Quantera XPS with inert atmosphere glove box for inert sample transfer. XPS is on the right wrapped in the blue blanket.





**Figure 3.2.** PHI Quantera XPS and connecting catalytic side chamber for in-situ controlled pressure and temperature sample processing.

Figures 3.1 and 3.2 show two views of the XPS system in EMSL.

### XPS Results

Calculated atomic concentrations for sample number 1-A  $^{76}\text{GeO}_2$  from the high-energy resolution narrow scan (spectral output file 02261.103). Figure 3.3 shows the broad energy range spectrum obtained. Figures 3.4 – 3.7 show high resolution scans of specific peaks.

Table 3.1 shows the measurement results for the three observed elements: Ge, O, and C. The Relative sensitivity factor (RSF) is corrected for specific instrument effects and is used to derive the atomic percentages shown. From these values, the XPS quantified ratio of Ge/O is 0.52, compared to the expected Ge/O ratio of 0.50.

**Table 3.1.** Elemental Composition of Sample

Element:	C1s	O1s	Ge3d
Relative sensitivity factor (RSF)	0.314	0.733	0.535
RSF corrected for specific instrument	21.075	49.679	41.210
Atomic Percent	5.4	62.3	32.3

### Contamination

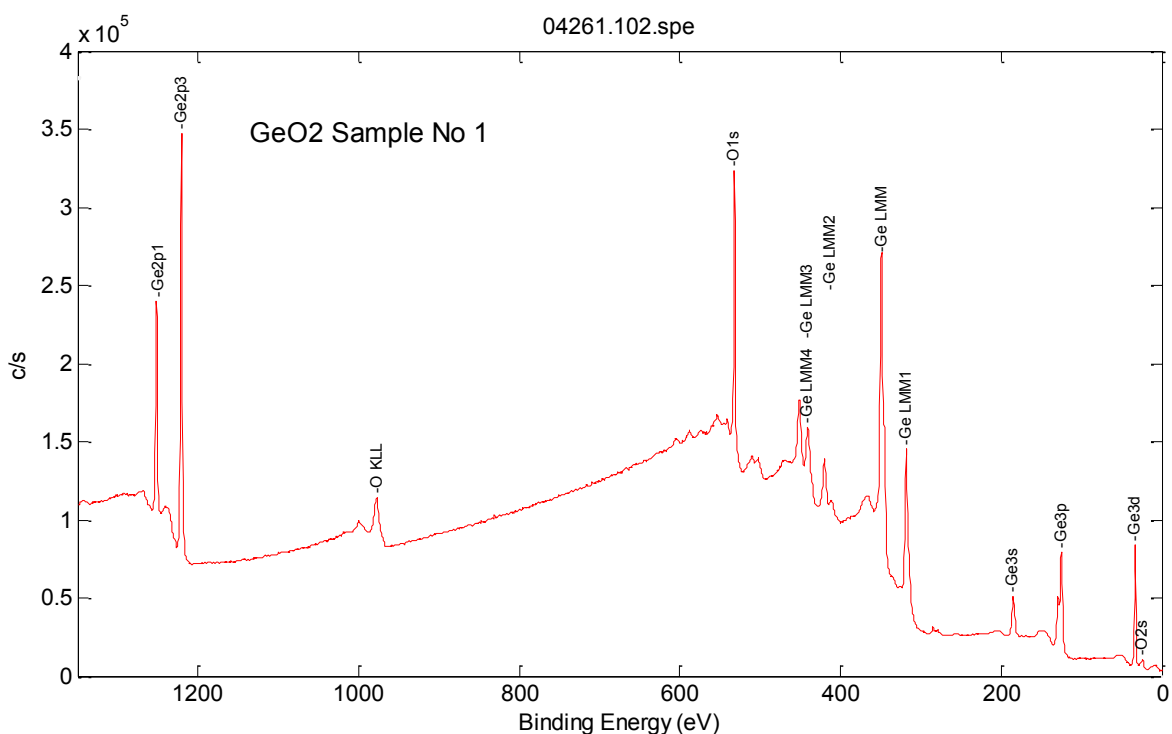
Approximately 5.4 atomic percent carbon was detected on the surface of the sample, which is consistent with adventitious hydrocarbons typically detected on surfaces exposed to atmosphere. No other contaminants were observed above the background level of 0.5 atomic percent.



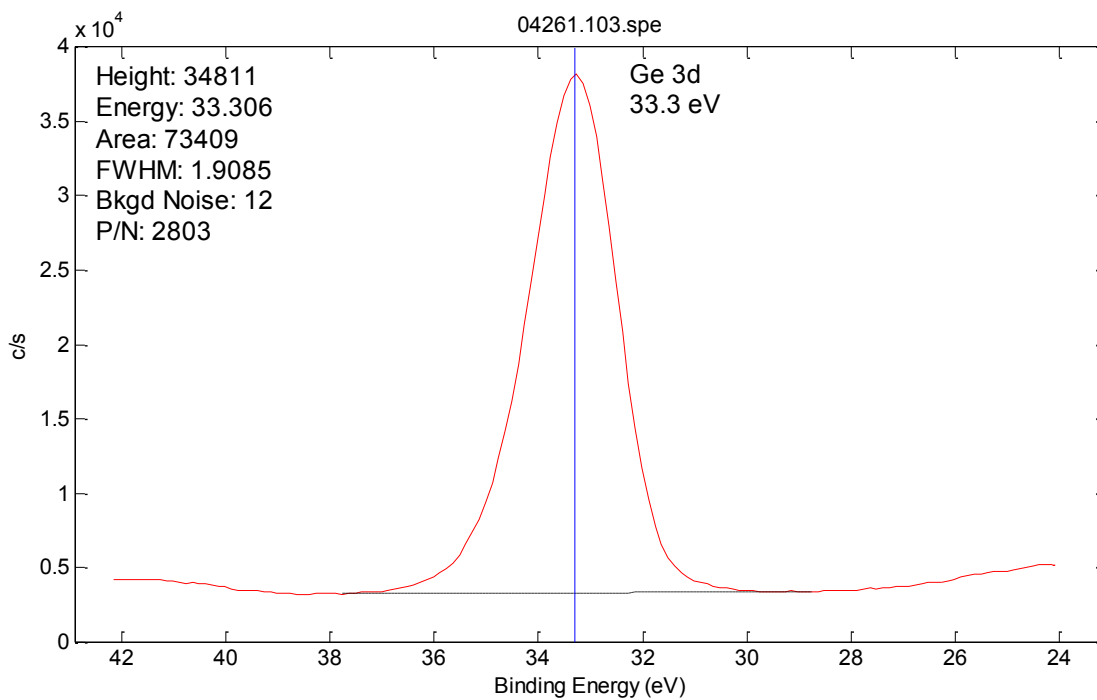
### Chemical States (Measured Binding Energies And Reference Energies)

Both the Ge 2p3 and O 1s photoemission line energies of 1220.8 and 532.1 eV, respectively, are consistent within  $\pm 0.2$  eV of reference line energies published in the NIST Standard Reference Database 20, Version 3.5. The Ge 2p3 reference line energy for GeO ( $\text{Ge}^{+2}$ ) is 1221.5 eV, whereas it would be 1217.4 eV for Ge metal ( $\text{Ge}^0$ ), verifying that the observed material is  $\text{GeO}_2$ .

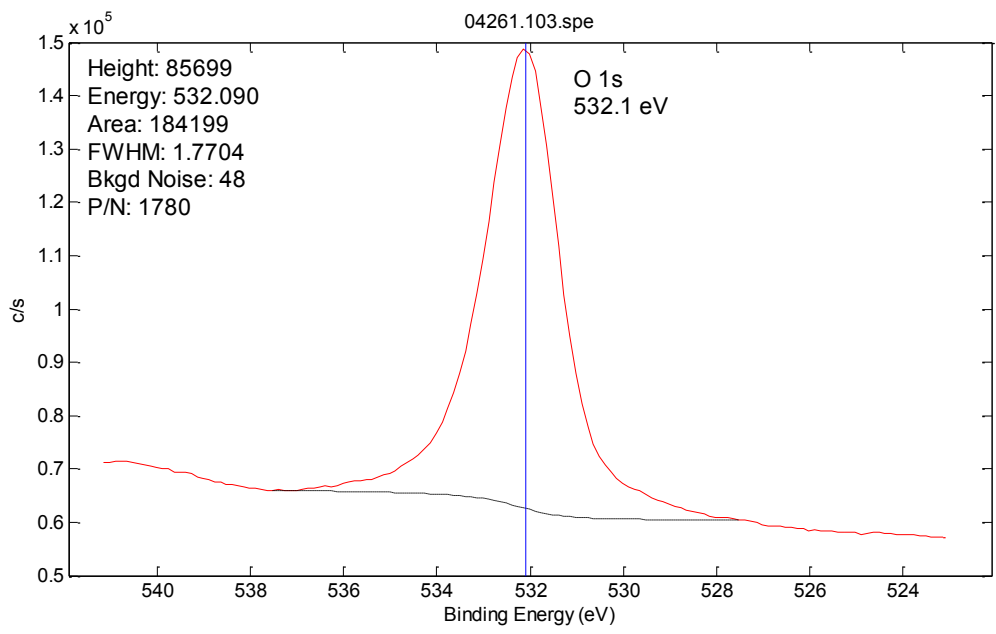
The germanium (IV) dioxide ( $\text{GeO}_2$ ) XPS binding energy references are: Wagner [1975] for Ge2p3 (1220.6 eV), Wagner et al. [1980] for O 1s (531.9 eV), and Nefedov et al. [1975] for O1s (532.2 eV).



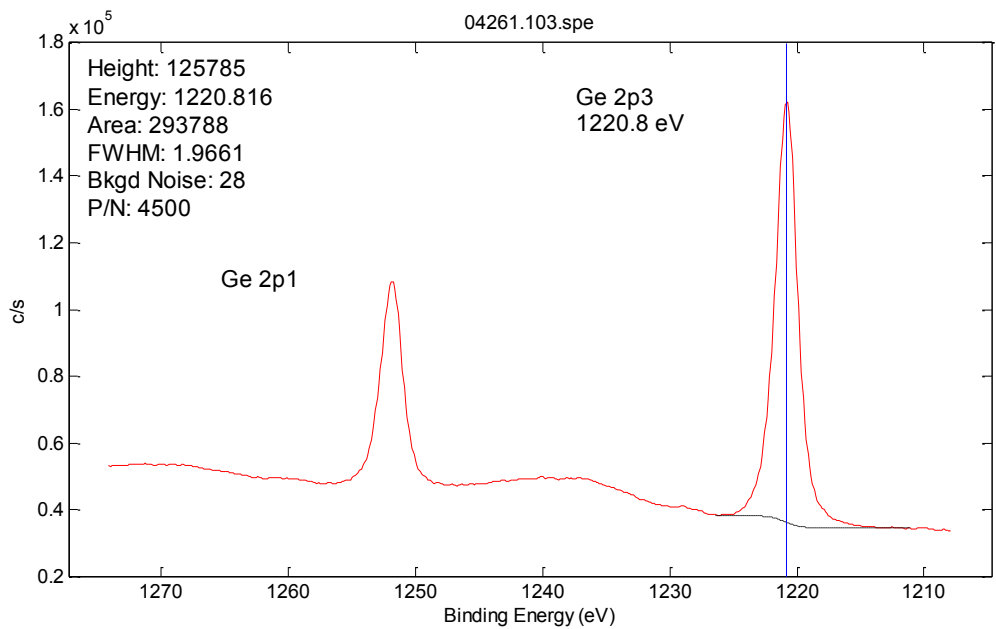
**Figure 3.3.** XPS wide scan spectrum (low energy resolution).



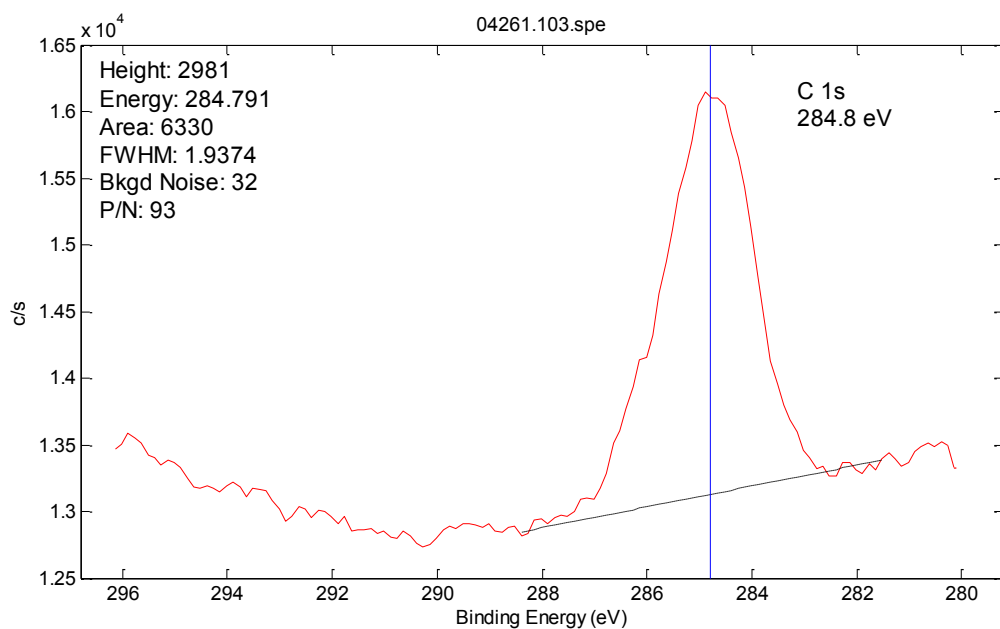
**Figure 3.4.** XPS narrow scan spectra (high energy resolution) for Ge 3d region.



**Figure 3.5.** XPS narrow scan spectra (high energy resolution) for O 1s region.



**Figure 3.6.** XPS narrow scan spectra (high energy resolution) for Ge 2p region.



**Figure 3.7.** XPS narrow scan spectra (high energy resolution) for C 1s region.

## 4 ISOFLEX Analysis

Isoflex used Maxxam Analytics (Barnaby, BC, Canada) to perform isotopic and chemical analysis of the  $^{76}\text{Ge}$  samples. Analysis was made using inductively coupled plasma mass spectroscopy (ICPMS). Maxxam utilized the entire sample and so their results should be more accurate than those from PNNL, which only sampled the material.

Maxxam states that their analysis was as follows:

“The entire sample was weighed into a 15 ml polypropylene tube and reacted with a mixture of nitric acid and hydrofluoric acid. The digested solution was then made to a final volume of 10 mL with distilled/de-ionized water.

The sample was analyzed by conventional ICP-MS, at a dilution of x5 for the full scan and x500 for isotopic ratio. Each element was fully quantified against a certified standard using single point calibration. Sample analysis and operation of the ICP-MS was done according to in-house SOPs.

Please note silicon data was not given because hydrofluoric acid was used in the digestion. Arsenic and niobium's detection limits were changed due to molecular interference.

Table 4.1 shows a comparison of the Maxxam and PNNL results for isotopics. The measurement results are very similar. Table 4.2 provides the results from Maxxam for chemical purity. The largest impurity is at the ppm level, with most contaminants being much smaller.

**Table 4.1.** Maxxam results compared to PNNL results for isotopics

<b>Isotope</b>	<b>Fractional Composition Sample 1 PNNL</b>	<b>Fractional Composition Sample 1 Maxxam</b>
$^{70}\text{Ge}$	0.00009(3)	0.0001
$^{72}\text{Ge}$	0.00013(3)	0.0002
$^{73}\text{Ge}$	0.00046(5)	0.0005
$^{74}\text{Ge}$	0.109(2)	0.104
$^{76}\text{Ge}$	0.890(2)	0.895

**Table 4.2.** Maxxam results for chemical purity of <sup>76</sup>Ge sample 1

		Attn:	Patrick Hardy
			<u>Isoflex USA</u>
		Material:	Ge-76 (Oxide)
		Client ref:	
		Maxxam ref:	CN56
Attn:	Patrick Hardy	Units:	ug/g
	<u>Isoflex USA</u>		
Material:	Ge-76 (Oxide)	Maxxam ID	CN5601
Client ref:		Sample ID	110422-01
Maxxam ref:	CN56		
Units:	ug/g		
Maxxam ID	CN5601	Lithium	0.2
Sample ID	110422-01	Beryllium	<0.01
		Boron	<1
		Sodium	<10
		Magnesium	1.0
		Aluminium	<1
Antimony	<0.01	Phosphorus	<10
Tellurium	1.5	Potassium	<10
Caesium	0.05	Calcium	20
Barium	0.06	Scandium	1.5
Lanthanum	<0.01	Titanium	9.5
Cerium	<0.01	Vanadium	<1
Praseodymium	<0.01	Chromium	0.9
Neodymium	0.01	Manganese	0.2
Samarium	<0.01	Iron	<10
Europium	<0.01	Nickel	0.6
Gadolinium	<0.01	Cobalt	0.09
Terbium	<0.01	Copper	0.4
Dysprosium	<0.01	Zinc	4
Holmium	<0.01	Gallium	<0.1
Erbium	0.03	Arsenic	<100
Thulium	<0.01	Selenium	<1
Ytterbium	1.66	Rubidium	<0.01
Lutetium	<0.01	Strontium	0.08
Hafnium	<0.05	Yttrium	0.03
Tantalum	<0.05	Zirconium	10.1
Tungsten	0.14	Niobium	<50
Rhenium	<0.05	Molybdenum	1.41
Iridium	<0.05	Ruthenium	<0.01
Platinum	0.41	Rhodium	<0.01
Gold	<0.07	Palladium	<0.01
Mercury	<0.05	Silver	0.04
Thallium	<0.01	Cadmium	0.04
Lead	0.03	Indium	<0.05
Bismuth	0.02	Tin	0.03
Thorium	<0.01		
Uranium	<0.01		

## 5 Conclusions

The results of the isotopic composition of  $^{76}\text{GeO}_2$  samples from Russia showed somewhat higher than expected enrichment in the measurements performed than the specified enrichment. With the longer measurement time, the agreement for the natural germanium sample was improved, and confidence in the enriched values should be higher.

The chemical purity of the first sample is consistent with a  $\text{GeO}_2$  sample and shows no contamination above background at 0.5 atomic percent.



## 6 References

- Elliott S.R., V.E. Guiseppe, B.H. LaRoque, R.A. Johnson, S.G. Mashnik, *Fast-Neutron Activation of Long-Lived Isotopes in Enriched Ge*, submitted for publication December 2009.
- Nefedov V.I., Gati D., Dzhurinskii, B.F., Sergushin N.P., Salyn Y.V. *Zh. Neorg. Khimii* 20, 2307 (1975)
- Wagner C.D., *Discuss. Faraday Soc.* 60, 291 (1975)
- Wagner C.D., Zatzko D.A., Raymond R.H. *Anal. Chem.* 52, 1445 (1980)

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