A sensitive assay technique for $^{210}$Pb in water

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Abstract. SNO+ is a multipurpose neutrino physics experiment, located 2 kilometers underground in the SNOLAB facility in Sudbury, Canada. It is the successor of the SNO experiment, replacing the heavy water in the Acrylic vessel (AV) with 780 tons of liquid scintillator, Linear Alkyl Benzene (LAB). The AV is surrounded by 7000 tons of ultrapure light water, which shields the detector from naturally occurring radioactivity in the surrounding rock, PMTs, and PSUP. To achieve the radiopurity requirements, the water should be very clean and levels of U and Th contamination in the shielding water must be carefully controlled. A water assay technique, based on the capture of Ra and Th radioisotopes using Hydrous Titanium Oxide (HTiO), was developed by the SNO experiment. Ra sensitivities equivalent to $^{232}$Th: $4 \times 10^{-16}$ gTh/D$_2$O and $^{238}$U: $3 \times 10^{-16}$ gU/g D$_2$O were achieved with this technique [1]. The HTiO technique will be used in SNO+ to monitor $^{238}$U and $^{232}$Th contamination levels in the shielding water and the performance of the water purification system.

For the lower energy measurements of interest to SNO+, radon daughter radioisotopes, especially $^{210}$Po and $^{210}$Bi supported by $^{210}$Pb, are also important. Since water will be used in the purification of both the liquid scintillator and tellurium that will be chemically loaded in SNO+ to search for neutrinoless double beta decay, a technique to assay for $^{210}$Pb in water was desirable. The SNO+ collaboration has extended the HTiO assay technique to allow measurement of $^{210}$Pb in water. This technique is capable of measuring $0.4 \pm 0.13$ mBq/m$^3$ of $^{210}$Pb for a 10 tonne assay. The method developed and results of initial $^{210}$Pb measurements are presented.

1. Introduction
The SNO+ experiment [2] is the successor of the Sudbury Neutrino Observatory (SNO) experiment [3]. The SNO+ detector consists of an acrylic vessel (AV) which is surrounded by a geodesic steel structure (PSUP) of 17m diameter supporting ~9500 photomultiplier tubes (PMTs). The 12m diameter acrylic vessel holds the detector media. Different phases of SNO+ include: a water phase in which the AV will be filled with ~905 tonnes of ultra pure water (UPW), a scintillator phase in which AV will be filled with ~780 tonnes of organic liquid scintillator, linear alkyl benzene (LAB) + 2.5-
diphenyloxazole (PPO), and a tellurium loaded phase with 0.5% (3.9 tons) of Te. The primary goal of SNO+ is to search for neutrinoless double beta decay. Other physics goals of SNO+ are to study low-energy solar neutrinos (pep, spectral shape of $^8$B, and CNO neutrinos), geo and reactor antineutrinos, neutrinos and antineutrinos from core collapse supernovae, and exotics physics like invisible nucleon decay and axion-like particles. Due to lower density of the LAB, a new system of hold up ropes has been installed around the AV to counter AV buoyancy [4].

To shield against the cosmic muons (muon flux of 63 muons per day passing through 8.3 m radius detector), SNO+ detector is located 2 km (6010 m.w.e.) underground at SNOLAB. The volume between the AV and the PSUP is filled with 1700 tons of UPW and the region between the PSUP and the cavity is filled with 5300 tons of UPW. This high purity water is used to shield the detector against radioactivity coming from the rock, PMTs, hold up and hold down ropes, and PSUP. One of the main sources of backgrounds in SNO+ is that due to naturally occurring radioactivity: $^{238}$U and $^{232}$Th decay chains. To fulfill SNO+ physics requirements, extremely low radioactivity levels in water need to be achieved. A water assay technique, Hydrous Titanium Oxide (HTiO), was developed by SNO experiment to measure the amount of Ra and Th radioisotopes in the water regions [1]. HTiO is an inorganic ion exchanger that has the ability to remove heavy metal ions (Pb, Th, and Ra) from water. With this assay technique, sensitivities equivalent to $^{220}$Th: $4 \times 10^{-16}$ gTh/D$_2$O and $^{230}$U: $3 \times 10^{-16}$ gU/g D$_2$O were achieved for a 275 tonne D$_2$O assay in SNO [1]. The HTiO technique will be used in SNO+ to regularly monitor $^{238}$U and $^{232}$Th radioactivity levels in the shielding water.

During SNO construction and the transition from SNO to SNO+, $^{222}$Rn daughter radioisotopes (especially $^{210}$Pb) were embedded on the surface of detector materials. $^{210}$Pb has a relatively long half-life of 22 years (as shown in Figure 1) and it subsequently decays by beta emission to $^{210}$Bi ($T_{1/2} = 5.0$ d, $Q$-value = 1.2 MeV) and $^{210}$Po ($T_{1/2} = 138$ d, $E_\alpha = 5.3$ MeV), which are direct backgrounds for low energy solar neutrino measurement [2]. These $^{222}$Rn daughters could leach into UPW and LAB and increase the radioactivity levels. The water will also be used for purification of liquid scintillator using the water extraction technique [5, 6]. So it is very important to have $^{210}$Pb and $^{210}$Po radioactivity levels controlled in the water and hence measurement of $^{210}$Pb in water is desirable. The SNO+ collaboration has extended the HTiO technique to allow the measurement of $^{210}$Pb in water.

![Figure 1. $^{238}$U decay chain with half-life and decay modes.](image)

2. SNO+ water systems and assay technique

Before water enters the SNO+ detector, it is pretreated, purified, and degassed to levels acceptable for the SNO+ detector. It is then regassed with pure N$_2$. The water is regularly recirculated to allow
repurification and to provide cooling to the cavity region, PSUP region, and the detector volume. The pretreatment loop and the purification loop consists of following components (shown in Figure 2.): 

Pretreatment loop:
- Filter & deaerate: water arrive supersaturated with air, dissolved O$_2$ and N$_2$ comes out.
- Charcoal filter: Reduction of free chlorine to chlorides.
- Softener: Soften water removing Ca, Mg, dissolved ions.
- Primary Reverse Osmosis (RO): Removes > 99% of ionized salts, organic.

Purification loop:
- UV Lamp (185nm): Breaks large organic compounds to ionic form.
- IX columns: Remove ions.
- PDG (Process De-gasser): Remove Rn and other gases like O$_2$.
- UV Lamp (254nm): Kills biological activity.
- HX-01 (heat exchangers): cool water to improve PMT performance and inhibit biological growth.
- Polishing RO: Remove metals from recirculated water.

**Figure 2.** The SNO+ water systems underground.

The HTiO assay skid is mounted after the polishing RO to assay the water before it goes into the SNO+ region. HTiO technique is a multi-stage process. The HTiO is prepared in clean labs on surface at SNOLAB. After preparing the HTiO, it is deposited onto 10” ultra-filtration membranes, which are housed in polypropylene columns. The HTiO loaded columns are taken underground and mounted on the HTiO assay skid. Water from different regions of SNO+ (PSUP region, cavity region, AV region) or UPW plant is passed through the HTiO loaded columns for a certain period of time. During the assay, heavy metal ions (Ra, Pb, Th) get extracted onto these HTiO loaded columns. At the end of assay, columns are packed and brought to surface for further chemical processing of the columns. The chemical processing of columns takes place in the clean lab on surface. The columns are eluted with hydrochloric acid (HCl). 15L of eluate (acid + activity) from elution is collected, which is then concentrated via a secondary concentration step. The final precipitate sample is then collected in a counting pot and counted using the beta-alpha coincidence counting system. More details on HTiO assay steps can be found in [1].

It is very important to know the efficiency at each stage of the HTiO technique to see how effective is the technique. Efficiencies can be obtained by doing spike tests by introducing known amount of radioactive source. Efficiency measurements have been done on SNO (represented by * in Table 1.) and some have been repeated for SNO+ (secondary concentration) for $^{226}$Ra using $^{228}$Th radioactive source. A secondary concentration step was extended by SNO+ to measure $^{210}$Pb in water. Figure 3. show sub-steps of the secondary concentration step. The secondary concentration step separates the heavy metal ions from water.

**Table 1. Summary of efficiencies for the HTiO technique.**

| Steps                   | $^{226}$Ra Efficiency (%) | $^{224}$Ra Efficiency (%) | $^{210}$Pb |
|-------------------------|---------------------------|---------------------------|------------|
| HTiO Deposition         |                           |                           |            |
| Extraction (ext)         | $95 \pm 5^*$              | $95 \pm 5^*$              | $95.9 \pm 1.5$ |
| Elution (elu)            | $90 \pm 10^*$             | $90 \pm 10^*$             | $90 \pm 10^*$ |
| Secondary Concentration (SC) | $58 \pm 6^*$              | $37 \pm 10$               | $66 \pm 9$ |
activity from acid using ion-exchange (IX) column. The eluate is passed through an IX column containing cation exchange DOWEX resin, which traps the activity. The resin is eluted with 0.25M ethylenediaminetetraacetic acid (EDTA) and activity is collected in a Teflon beaker. The solution is then boiled with concentrated HNO3 to decompose EDTA. After decomposition, co-precipitate of activity with HTiO is formed by adding 250ml of UPW and ~2ml of 15% Ti(SO)4 to the solution. The solution is stirred and titrated to pH 9 using 10M NaOH until white precipitate is formed. The solution is centrifuged to collect the precipitate and supernate is discarded. The precipitate is dissolved in 1.5ml of concentrated HCl. The final sample is transferred into a counting pot, which is then topped up with ~42g of OptiphaseHiSafe 3 liquid scintillator for counting. The sample is counted for about two weeks using the beta-alpha coincidence counting system.

### 3. Extension of the HTiO technique for $^{210}\text{Pb}$ assay

In order to extend the HTiO assay technique to $^{210}\text{Pb}$, it was necessary to understand the behavior of Pb during the chemical processing. To see how effective the HTiO technique is in getting Pb activity, several bench scale spike tests (using $^{212}\text{Pb}$ source) were performed for the secondary concentration step. Samples were counted at different sub-steps of the secondary concentration step. The DOWEX resin was gamma counted to see how much activity it trapped and how much activity was removed from the resin after EDTA elution. The supernate sample was not discarded (as was the case for the traditional recipe on SNO) and was gamma counted to measure activity (if any). The supernate sample was evaporated to concentrate the sample. The concentrated sample was then gamma counted. The precipitate sample was counted using beta-alpha counter to measure Ra, Th and Pb.

Table 2. present all the spike tests that were done and the $^{212}\text{Pb}$ extraction efficiency from the final precipitate sample and the supernate. It can be seen from Table 2, the secondary concentration step is not very efficient in forming co-precipitate of Pb and HTiO but the supernate evaporation approach is good enough to obtain Pb activity. Based on the $^{212}\text{Pb}$ spike test results as in Table 2, it was found that most of the Pb (~75%) trapped on the resin ends up in the final supernatant solution and very little amount in the final precipitate. Many more spike tests were performed to confirm and verify the results.

### Table 2. $^{212}\text{Pb}$ spike test for the secondary concentration stage.

| Sample | $^{212}\text{Pb}$ Spike $A_0$ (Bq) | $A$ measured $A_0$ (Bq) | Pb $\epsilon$(SC) [%] | Pb $\epsilon$(SC) [%] |
|--------|---------------------------------|------------------------|-----------------------|-----------------------|
| Initial | 10.33                           | 9.75±1.86              | 6.87±0.73             | 67                   |
| Supernate | 6.87±0.73                     | 6.87±0.73             | 67                   | 67                   |

- $^a(\epsilon_{ext} \cdot \epsilon_{elu} \cdot \epsilon_{SC} \cdot \epsilon_{cnt})$
- Figure 3. Secondary Concentration Steps
Having established a method for measuring $^{210}$Pb, the efficiency with which $^{210}$Pb is collected from water by the HTiO-coated filters was determined by assaying two sets of two columns in series. The second set of columns is used to measure the amount of activity that is not collected by the first set. The collection efficiency was measured to be $\epsilon_{\text{col.}} = (95 \pm 1.5)$%.

An assay of the AV "prefill" water was performed to measure the $^{210}$Pb activity. A total water volume of 16m$^3$ was processed through the HTiO loaded columns and the supernate sample was counted using SNOLAB Canberra HPGe well detector (background of the SNOLAB well detector = 0.8 ± 0.3 mBq). The $^{210}$Pb activity was measured to be $0.23 \pm 0.04$ mBq/m$^3$. The sensitivity of $^{210}$Pb assay technique for a 10 tonnes assay was estimated to be $0.4 \pm 0.13$ mBq/m$^3$.

### 4. Conclusions

We have extended the existing secondary concentration stage of the HTiO assay technique used to determine the radioactivity in the light water. This extended HTiO technique (evaporation of supernate approach) make useful $^{210}$Pb assay technique with a sensitivity of 0.4 +/- 0.13 mBq/m$^3$. The $^{210}$Pb assays are possible by gamma counting of the supernate. The extended HTiO assay technique will allow SNO+ to measure $^{210}$Pb in the water and purify the water by trapping $^{210}$Pb with an efficiency of (95.9 ± 1.5)%.

The $^{210}$Pb assay technique is a useful technique for any large-scale water based experiment.

### References

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