General concepts for monitoring lead 212 in the SNO experiment

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The monitoring of lead 212 in the 1000 tonne $D_2O$ detector of the Sudbury Neutrino Observatory (SNO) is to serve a dual purpose: doublechecking the main method for assessing the thorium 232 levels in the water (i.e. trapping of radium 224 and subsequent measurement of the radon 220 daughter); and providing an estimate of the unsupported radon in the system, such as radon emanating from immobilized contamination on the walls of the acrylic vessel.

The level one hopes to achieve in the 1000 tonne detector is of the order 1 Pb atom/tonne. This level will be monitored by measuring the 8.8 MeV alpha emmision from the Po 212. Such extremely low levels have not been measured in the past. An essential requirement for the measurement of such low lead concentrations is the ability to concentrate lead from a large volume of water (30 tonnes corresponding to 10-30 lead atoms) and then to form a high quality alpha source in a period of time which is short compared with the half life of the lead 212 (i.e. 11 hours). During all stages one has to insure the highest possible recovery of lead from the aqueous phase. The immediate problem is that of the instability of lead in solution at neutral pH, which is the pH at which the detector is to be maintained. At such pH lead is known to form hydroxide complexes and to attach to surfaces (Gibson 1961). The common practice for circumventing this problem is by acidifying the studied aqueous phase, but this is not a desirable option in the SNO detector (mainly due to the possible ensuing corrosion/aging of stainless seel and plastic components). The process of lead monitoring in the presence of NaCl at a concentration of 0.2% and higher (following its concentration in the recirculation loop) adds further complications to most stages of the monitoring procedure. It is therefore recommended that (at least at present) the lead monitoring procedure will address the 'no salt' stage only.

The following is a suggested procedure for the concentration of lead 212 out of 30 tonnes of $D_2O$:

1) The first step is the complexing of lead in the 1000 tonnes detector (within the acrylic vessel) by the addition of a known spike of tetra sodium EDTA (sodium edetate). This is a highly soluble organic salt (103g/100cc Merck, 1976), formula weight (FW) in the unhydrous form of 380 g, stable up to $200^0$C (Dow, 1992), which forms a transparent solution in water. The lead complex formed is similarly transparent and soluble. This salt was used in radioactive separations and did not prove to introduce radioactive contamination (G. Milton, private communication). At pH range of 4-7, the acid of this salt, EDTA, is an excellent complexing agent for $Pb^{2+}$, where $K_D$, the dissociation constant, is defined as:

$$K_D = \frac{(EDTA - Pb)}{(EDTA)(Pb)}$$

where () denotes molar concentrations. $K_D$ is in the order of $10^{18}$ (Vogel, 1981).

1-2 g of this compound within the well mixed 1000 tonnes of $D_2O$ (i.e. a concentration of a few ppb's) would be sufficient to find and complex the lead ions as well as other metal ions (mainly thorium) which tend to form EDTA

complexes. This last point should be addressed if thorium activity is to be monitored separately. It should be noted that the thorium-EDTA complex (the $K_D$ for thorium-EDTA is in the order of $10^{23}$) is stable at a lower pH range as compared with lead (1-3). Furthermore, thorium forms stable nitrate complexes (at $HNO_3$ concentrations of 6M) and does not form complexes with chlorides. The opposite is true for lead (Ryan et al.). Separation of the lead and thorium after the complexation by EDTA may thus be achieved either by dropping the pH to 2 (where lead complexes are unstable and lead may be captured as the free cation) or based on the different complexing behaviour with chloride and/or nitrate ions. The efficiency of EDTA at stabilizing lead in aqueous solutions of neutral pH has been demonstrated (preliminary report to be circulated in the September water meeting at Kingston). It was further demonstrated that as such a complex, lead separation on RO membranes is highly improved (see following sections). Another consideration - that of the transparency of the EDTA and the EDTA-Pb solution will be addressed by testing the UV-Vis spectra for EDTA and EDTA-Pb solutions at the appropriate concentrations.

2) The addition of about 70 mg non radioactive lead salt (e.g. $Pb(NO_3)_2$) to the acrylic vessel (corresponding to levels of 2 mg/30 tonnes) is considered. This extra lead may serve as a carrier for lead 212 precipitation at the final stage of alpha source preparation. At levels of several mg's gravimetric/spectroscopic analysis is possible, and thus the lead recovery may be independently checked. Furthermore, the presence of an excess of nonradioactive lead will further reduce the chances for losing the lead 212 on the acrylic vessel walls/ recirculation loop pipes/ RO membrane surfaces. Preliminary measurements of low grade lead nitrate salt by alpha spectrometry did not reveal any activity above background at the 8.8 MeV region.

3) The use of reverse osmosis (RO) filtration as part of the heavy water recirculation loop had been widely discussed in the past. Two consecutive RO modules will reduce the water flow from 100 l/min. to about 1 l/hr., achieving a 1000-10000 fold concentration of the lead solution from an initial volume of 10-30 tonne down to a volume of 1-30 litres, within 3-5 hours. This efficient (more than 99%) separation of lead-EDTA on RO units was demonstrated and is included in a preliminary report to be circulated in the September water meeting at Kingston.

4) Once the volume of the water to be analyzed had been reduced to the order of 10 litres we consider two alternative paths:

a) The use of a still (possibly quartz or polysulfone) operating on line to totally evaporate the incoming heavy water, which will be subsequently recycled into the acrylic vessel. Standard commercial units are available, operating at 1-8 l/hr (higher fluxes are reported for glass units which might not be appropriate for our use). The residue will be redissolved in 100-1000 cc of diluted acid (e.g. HCl at pH of about 2), and the product will either be directly precipitated as PbS, or passed through an exchange column (either anion exchange pretreated with HCL or a cation exchange), eluted with acid and precipitated (probably as $PbCrO_4$).

Lead precipitation as the chromate salt from solutions containing 2 mg lead in 500 cc of ultra pure water (following a procedure described by D. Wiles, personal communication) has been tested and found to be quantitative and convenient to monitor. Employing nonradioactive lead salt, the procedure does not introduce any contamination above background in the 8.8 MeV alpha range.

b) The concentration of the lead solution on a cation/anion exchange. The use of a cation exchange resin depends on the preliminary dissociation of the EDTA-lead complex (which is negatively charged), probably by acidifying to pH of $\approx$2. This acidification may be performed with a deuterated acid so as not to degrade the heavy water. The lead will be subsequently trapped on a resin such as Bio Rad AG-MP 50 (Sterlow, 1985). Other resins, including $MnO_2$ are considered. The flow rates typically used for trapping lead on an ion exchange column are in the order of 1 cc/min/cm$^2$, implying that for a flux of 1 l/min. to be processed on line, a column of the order of 30 cm diameter is needed (and possibly 10x30 cm length). This process will allow separation of lead from the EDTA agent as well as its separation from thorium. The lead may then be eluted with higher acid concentrations and precipitated as its sulfide or chromate salts. Much higher flow rates may be employed on a $MnO_2$ adsorber, but lead elution from $MnO_2$ is extremely difficult and complete lead recoveries necessitate total dissolution of the $MnO_2$ exchanger (Matthews, 1983).

An anion exchange column (e.g. Dowex 1) may also be employed at this stage. The EDTA-lead complex is negatively charged and thus lead may be concentrated on the column in the complexed form, eluted and subsequently precipitated. Such a procedure will eliminate the need to acidify large volumes ($\leq$ 30 litres, depending on the efficiency of the RO process) of heavy water. The possibility of precipitating lead salt in the presence of EDTA has to be checked (e.g. at pH of 2 where the EDTA-lead complex is unstable). Alternatively, one might acidify the lead-EDTA solution and pass it on an anion exchange column pretreated with HCl (Finston and Miskel) and then follow the same elution and precipitation procedures described above for the cation exchange option. The parameters to be optimized are inflow rates, elution rates, and low background activity of the exchanging resins. As to the last of these parameters, the studied resins are routinely employed for concentrating radioactive species and are not known to contaminate the analyzed samples (G. Milton, private communication).

5. As mentioned above, the final stage will be the precipitation of a lead alpha source. Such a source should be thin and uniform, and preferably the precipitated salt should be of a strong distinct colour, to facilitate the monitoring of the precipitation procedure. Preliminary studies of the precipitation of lead chromate (2 mg lead in 500 cc solution) have been preformed. Tests of the precipitation of known spikes of lead 212 employing the same technique, and using 2 mg (or less) of nonradioactive lead as a carrier, are taking place. The final precipitation of the chromate salt is performed at neutral ($\approx$6) pH. Thus interference of EDTA in the precipitation is to be expected. Precipitation of lead in the presence of EDTA

from an acidified solution, as lead sulfide (Gibson, 1961), will be studied.

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