Removal of the long-lived ^{222}Rn daughters from copper and steel surfaces

G. Zuzel[1]

Max Planck Institute for Nuclear Physics, P.O. Box 103 980, D-69029 Heidelberg, Germany

M. Wójcik

M. Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4,
PL-30-059 Kraków, Poland

Abstract

Removal of the long-lived ^{222}Rn daughters from copper and steel surfaces was investigated. Etching and electropolishing were applied to discs exposed earlier to a strong radon source for ^{210}Pb, ^{210}Bi and ^{210}Po deposition. Cleaning efficiency for ^{210}Pb was tested with an n-type HPGe spectrometer, for ^{210}Bi a beta spectrometer and for ^{210}Po an alpha spectrometer was used. According to the performed measurements electropolishing removes very effectively all the isotopes from copper and steel. Copper etching reduces efficiently lead and bismuth, however for polonium the effect is negligible because of its fast re-deposition. For stainless steel, etching is much more effective compared to copper and it also works for ^{210}Po.

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[1] Corresponding author. Tel.: ++48/12/6635130, fax: ++48/12/6637086
E-mail address: grzegorz.zuzel@uj.edu.pl

1. Introduction

Surface contamination with long-lived daughters of ^{222}Rn is of great interest for most of the experiments looking for rare events. These include the detection of low-energy solar neutrinos in real time (Borexino [1]), searches for neutrino-less double beta decay (Heidelberg-Moscow [2], Couricino/CUORE [3], GERDA [4]) or searches for dark matter (DAMA [5], CRESST [6]). Decays of ^{210}Pb, ^{210}Bi and ^{210}Po may contribute significantly to the experiments' background, especially when they appear close (external background coming from e.g. construction materials/shields) or directly in the active volumes (internal contamination).

A part of the ^{238}U chain starting from ^{226}Ra is shown in Fig. 1. Short-lived isotopes up to ^{210}Pb can be linked to radium. Its surface activity is measurable with high precision down to 1 µBq/m^2 level through a ^{222}Rn emanation technique [7]. If not supported (by ^{226}Ra/^{222}Rn), the short-lived daughters decay within 3 hours. Equilibrium in the uranium chain is broken very often at ^{210}Pb with the half-live of 22 years. This isotope is usually plated-out on surfaces or, due to the recoil energy (146 keV) received after ^{214}Po decay, it is implemented into a sub-surface layer of the material in question (the range of a 146 keV ^{210}Pb ion in copper is estimated to be 0.02 µm). It can remain as a main residual contamination after surface treatment (cleaning) and may appear after some time through ^{210}Bi ($T_{1/2}$ = 5.0 d, $E_{max}(\beta)$ = 1.2 MeV) or ^{210}Po ($T_{1/2}$ = 138.4 d, $E(\alpha)$ = 5.3 MeV).

Due to the broken equilibrium in the chain, one cannot conclude about the long-lived isotopes from well established high sensitivity radon emanation measurements. It is also known that the chemistry of polonium, bismuth and lead is different and in addition for ^{210}Po it is not well known. The reason is its high specific activity. The intense radiation decomposes most of the complexes and solvents very quickly. Also on some surfaces, like copper, nickel and silver, ^{210}Po plates-out very efficiently and this effect is very often used to collect it from aqueous solutions. All these reasons require that each isotope and each surface is investigated separately.

In this paper we present the test results of the two most popular surface cleaning methods, which are etching and electropolishing applied to copper and stainless steel. Because natural contamination with the long-lived ^{222}Rn daughters is usually not measurable when using standard approaches (small surface semiconductor detectors), the tested samples were artificially contaminated by exposing them to a strong radon source. Each isotope deposited on copper or stainless steel was then detected before and after cleaning. An alpha, a beta and a gamma spectrometer was used to register ^{210}Pb, ^{210}Bi and ^{210}Po decays, respectively.

2. Preparation of samples

Copper and steel samples were prepared as discs, which were 50 mm in diameter and 1 mm thick. The shape and the size were chosen in order to easily fit them into the chambers of the alpha and beta spectrometers. The fabrication material was low-radioactivity electroformed copper (OFH) and low-radioactivity stainless steel, which was used to construct the GERDA cryostat [4, 8].

30 discs were cut out of copper and steel blocks and initially cleaned according to etching procedures foreseen as those to be tested for radon daughters removal (see chapter 4, both materials were treated according to appropriate recipes). After preparation the discs were mounted vertically in a special holder (maximizing the surface available for radon daughters plate-out) and put into an exsiccator connected to a ^{222}Rn source, containing uranium salt of the activity of about 1.4 MBq. Radon

produced therein was circulated between the source container and the exsiccator by means of a small gas pump, as shown in Fig. 2. The total exposure time was 4 and 6 months for copper and stainless steel samples, respectively. During that period short- and long-lived radon daughters were accumulating on both sides of the discs. Due to the samples being investigated at least several days, up to some weeks, after being removed from the source, one could expect that ^{210}Pb and ^{210}Bi were in radioactive equilibrium (due to the short half-life time of bismuth). Deposited ^{210}Po came mostly from ^{210}Bi present in the circulated ^{222}Rn-reach gas and decaying in the exsiccator atmosphere.

3. Detection systems

To record decays of ^{210}Pb, ^{210}Bi and ^{210}Po a gamma, a beta and an alpha spectrometer was used, respectively. ^{210}Pb was identified by observing the 46.6 keV gamma line with an n-type high purity germanium detector (HPGe, 25 % relative detection efficiency, aluminum window), which was equipped with an active and a passive shield. The active guard form three multi-wire gas chambers placed on the sides and on the top of the passive shield. The last consists of a 5 cm thick paraffin layer (neutron moderator), low radioactivity lead (~ 3 Bq/kg of ^{210}Pb) in the form of a barrel with a double wall thickness of 15 cm (including the top cover) and cadmium plates placed between lead walls. The detector chamber can host a standard Marinelli baker and is permanently flushed with boil-off nitrogen coming from the crystal cooling dewar. Taking into account the 46.6 keV gamma line background of (0.020 ± 0.001) counts per minute (cpm), its detection efficiency (depending on the sample geometry, but in the range of 10

%) and a possible sample size, the sensitivity of the spectrometer for ^{210}Pb contained in high density thick samples is estimated to be ~ 20 Bq/kg.

To detect ^{210}Bi a beta spectrometer was used. It has been constructed out of two 50 mm diameter Si(Li) detectors placed in a low-activity lead shield (~ 6 Bq/kg of ^{210}Pb). The diodes can work either in 2π or in 4π geometry. Applying an energy threshold at about 300 keV the background count rate is (0.18 ± 0.02) cpm and (0.40± 0.02) cpm, respectively. For absolute activity measurements the spectrometer is calibrated using a certified, so-called thick ^{210}Bi source. With the detection efficiencies of 0.012 cpm/(Bq/kg) (2 π geometry) and 0.023 cpm/(Bq/kg) (4π) it is possible to measure ^{210}Bi bulk specific activities down to 10 Bq/kg. Samples in the form of discs with a maximum diameter of 50 mm and up to 5 mm thick can be analyzed. Measurements described in this paper were always performed in 2π geometry adopting the background value measured in presence of an unexposed and cleaned copper/steel disc ((0.20 ± 0.02) cpm as explained later).

For ^{210}Po surface activity[2] measurements an alpha spectrometer was applied. It is based on a 50 mm diameter Si detector with the background signal of about 5 counts per day (cpd) in the energy window of 1 – 10 MeV. The diode has been installed in a vacuum chamber, which also hosts samples being inserted through a special air lock. A small distance between the detector and the sample (7 mm) and low operating pressure of ~3 mbar allow for alpha spectroscopy with a good energy resolution (in case of surface activity) and high efficiency. For absolute activity measurements, the last one is determined using a certified surface alpha activity source. It applies a 50 mm disc giving about 35 %. Blank value of the system in presence of a clean disc was determined to be (0.0042 ± 0.0005) cpm.

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[2] As explained in the text in this paper we are interested only in relative changes in the signal before/after cleaning therefore the term “activity” means here rather “count rate”.

For the ^{210}Pb, ^{210}Bi and ^{210}Po removal efficiency measurements, we were interested only in the relative count rates (before/after etching or electropolishing). Therefore, none of the detectors had to be calibrated. However the same detector – sample geometry had to be assured (what concerns mainly the HPGe spectrometer).

Blank values were established in the presence of an unexposed and cleaned disc. There was essentially no difference while measuring stainless steel or copper therefore the quoted numbers are averaged over both materials and both sides of the discs. Count rates of different isotopes given in all Tables are always background corrected

Amounts of removed material have been determined by weighting the discs before and after cleaning using a precision balance. Corresponding thicknesses of detached layers were calculated adopting the densities of copper (8.9 g/cm^3) and stainless steel (8.0 g/cm^3).

The quoted results uncertainties include only statistical errors and are given always as one standard deviation. Upper limits are calculated for 90 % confidence level.

4. Cleaning of copper

4.1. Etching

The first tested technique was the etching of the copper surface. It proceeded in three steps[3]: 5 min etching in a mixture[4] of H_2SO_4 (1 %) and H_2O_2 (3 %), 5 min passivation in 1 % citric acid and finally rinsing with distilled water. This procedure was applied very often to clean copper shields for low-background germanium spectrometers [9]. All tests described below were done at room temperature (~20 ^{o}C).

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[3] Writing “etching” we always mean that three-steep procedure.

[4] Proportions are given always by mass.

Disc labeled No 2 was processed several times and each time using fresh solutions (about 250 cm^3) coming from larger batches prepared earlier. Only ^{210}Po removal was analyzed here (on both disc sides separately). The obtained activity reduction factors for individual runs and for each sample side (calculated always with respect to the previous run) are collected in Table 1. The amount (M) of removed Cu in a single cleaning step and a corresponding thickness of a removed material layer are given there as well. The data are also plotted in Fig. 3a. The cumulative (summed over all performed runs) amount of removed material M_c is calculated in the 8th column. In the 5th column an average ^{210}Po activity reduction factor R_{av} is shown (see also Fig. 3b). The cumulative reduction factor R_c reflects the overall cleaning efficiency of conducted etching steps and it is given in the 6th column. It was always calculated for each side and later averaged. R_c as a function of M_c is shown in Fig. 3c. The 7th cleaning step was performed with the ^{209}Po (activity of 1.42 Bq) added to the solution. The spectrum measured after processing the disc is shown in Fig. 4.

Another test was performed on disc No 1. Here the efficiency for ^{210}Pb, ^{210}Bi and ^{210}Po removal was questioned. Only one disc side was tested and only one complete 5 min run was done. The obtained results are collected in Table 2.

4.2. Electropolishing

The effectiveness of ^{210}Pb, ^{210}Bi and ^{210}Po removal from copper surface by electropolishing was tested using a simple setup shown in Fig. 5. It consisted of a current source, current and voltage meters and a 50 mm diameter cathode made out of copper. The applied electrolyte was a mixture of phosphoric acid (H_3PO_4, 85 %) and 1-butanol ($C_4H_{10}O$, 5 %).

Disc No 4 was the first sample taken and it was investigated only with respect to ^{210}Po. Three 35 min runs were performed where the cathode and the electrolyte were changed each time and taken from a bigger batch that was prepared earlier. The applied voltage was 1.8 V and the current was initially set to 150 mA. It decreased during electropolishing down to about 10 mA. Side “a” was facing the cathode twice and side “b” only once. The amount of removed copper was measured only at the end (for all runs together). Table 3 summarizes the obtained results (shadowed rows indicate actually polished side).

A little different procedure was applied to disc No 3. The same experimental setup with a new electrolyte was used, however the polishing was performed for 3 h without any break. During that period the disc was turned every 30 min (without switching the voltage), so that each side was exposed 3 times to the cathode. As before only ^{210}Po was investigated and the obtained results are in Table 4.

A similar test was performed on disc No 8, however the time was much shorter (1 h) and its rotation occurred every 5 min. A new electrolyte and a new cathode were used. The removal efficiency for all three isotopes was analyzed (see the results collected in Table 5), however only from one disc side.

5. Cleaning of steel

5.1. Etching

After 6 months exposure in the radon source the steel samples were treated according to the following procedure[5]: etching in a mixture of 20 % HNO_3 + 1.7 % HF, passivation in a 15 % HNO_3 and rinsing with distilled water. All the tests were performed at room

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[5] This procedure was applied to clean the inner surface of the GERDA cryostat.

temperature using aqueous solutions (it is possible to use also gels, however they may be less effective).

Disc No 1 was etched subsequently three times for 50, 90 and 120 min always using a new etchant. For all three long-lived radon daughters and for both disc sides the initial activities (before the first run) and the activities after each cleaning step were measured (for the 90 min run only ^{210}Bi on side “a” was determined). The obtained results are collected in Table 6.

Another 120 min run was performed on disc No 2. The solution was additionally stirred all the time in order to maximize the etching efficiency. The achieved reduction factors for the ^{210}Pb, ^{210}Bi and ^{210}Po count rates and the amounts of removed stainless steel are collected in Table 7.

5.2. Electropolishing

The electropolishing of disc No 3 was done in a similar way as for copper. A cathode in the form of a 50 mm diameter disc was made out of stainless steel. The applied electrolyte was a mixture of H_3PO_4 (40 %), H_2SO_4 (40 %) and CrO_3 (3 %). ^{210}Pb, ^{210}Bi and ^{210}Po were measured before and after an 18 min polishing run. Each side faced the cathode for 9 min (the disc was turned without switching off the voltage). The obtained results are collected in Table 8.

6. Results and discussion

6.1 Etching of copper

Looking at the initial ^{210}Po activities on sides “a” and “b” of the disc No 2 ((2.97 ± 0.03) cpm and (2.64 ± 0.03), respectively), one can see that they are comparable and almost three orders of magnitude above the background ((0.0042 ± 0.0005) cpm). Analyzing the results presented in Table 1 it is also clear that the polonium removal efficiency in a single 5 min etching run is very poor. Values of R agree within 1σ for both disc sides and the averages (R_{av}) change between 0.99 and 1.25. There is rather big scattering observed for the amount of removed copper, which changes from 1.77 mg/cm^2 (corresponding to a 1.99 µm thick Cu layer) up to 4.4 mg/cm^2 (4.9 µm). Both parameters are plotted as a function of the run number in Fig. 3a and 3b. From the graphs, it looks like the less Cu was removed (first runs) the better is the ^{210}Po activity reduction factor. Since the changes in R are at the level of 20 %, one could imagine that after loading in the radon source about 80 % of the polonium is sitting on the surface and the remaining 20 % is somehow distributed in a sub-surface layer of the thickness of some µm. Such a depth cannot be reached by a 146 keV ^{210}Pb atom (recoil energy received after ^{214}Po decay allows it to pass only about 0.02 µm in Cu) and may only be explained by polonium diffusion. By removing more material (thicker layer), more ^{210}Po would be released into the solution with following re-deposition on the surface (see the next paragraphs). Since the fraction of diffusing polonium should be rather small, the measured spectra will still show rather narrow peaks with small tails. This is what we observed (see Fig. 4) but to confirm this hypothesis and to give some quantitative description of the observed process, it would be necessary to perform more systematic measurements with higher ^{210}Po activities supported by a number of computer simulations.

In the 6th and 8th columns of Table 1 the cumulative reduction factors $R_{c,}$ and the cumulative amount of removed copper (M_c) is given, respectively. It is seen that after 7 etching runs (35 min all together) about 21 mg/cm^2 (corresponding to ~23 µm thick layer) of Cu has been removed. However, the ^{210}Po activity was reduced in total only by a factor of 2. R_c as a function of M_c is plotted in Fig. 3c showing almost linear and slow progression. Averaging R_{av} over 7 performed runs, gives 1.1 and doing the same for M one gets 3.0 mg/cm^2 as mean values for a single 5 min etching procedure (see the last row of Table 1).

As previously mentioned, one of the possible explanations for poor effects of ^{210}Po removal from copper is that the isotope is re-deposited on the processed surface. To test this hypothesis, the 7th etching run was performed in the solution spiked with ^{209}Po of known activity of 1.42 Bq. It was clearly visible in the spectrum registered after cleaning (see Fig. 4). The amount deposited on the disc (both sides) could be estimated assuming 35 % detection efficiency (typical in the applied geometry) and its homogeneous distribution on both disc sides. Doing so, one gets about 15 mBq, which exemplifies about 1.1 % of the initial ^{209}Po activity present in the etchant. The fraction of plated-out ^{209}Po is clearly much lower compared to re-deposited ^{210}Po (~ 100 %). This effect could be explained by the fact that ^{209}Po was homogeneously distributed in the whole etchant volume, while ^{210}Po is released from the surface into its very local vicinity and thus can be re-adsorbed very effectively (even in the short etching time period). An increase of the etching time would probably result in a higher fraction of accumulated ^{209}Po. The effect observed for ^{209}Po confirms therefore the assumption of polonium re-deposition, which makes the etching process very inefficient for this element. It shows also potential problems with industrial-scale surface treatment where the same etchant is used for several material batches (risk of polonium re-contamination).

Disc No 1 was etched only once and only one side was analyzed for ^{210}Pb, ^{210}Bi and ^{210}Po removal. As it is seen from the data collected in Table 2, the amount of material taken away (3.9 mg/cm^2) was similar to the average value obtained for the disc No 2 (3.0

mg/cm^2). The same pertains to the ^{210}Po reduction of 1.24, which is again low and comparable to the mean value of 1.1 (Table 1).

For ^{210}Pb and ^{210}Bi the situation is much better. Their activities were reduced by a factor of at least 68 (lower limit) and 41, respectively.

6.2 Electropolishing of copper

Table 3 summarizes the results obtained from electropolishing of disc No 4. Since for ^{210}Po we hardly observed a reduction after etching, it has been decided to focus first solely only on this isotope. Its initial count rates measured on side "a" and "b" equaled (9.52 ± 0.06) cpm and (1.78 ± 0.04) cpm, respectively. They are significantly different (factor ~5), which may be a result of the disc location in the exsiccator (one side was more exposed to the ^{222}Rn-rich gas stream). Since three 35 min long runs have been performed, the achieved reduction factors are given, as is the case of the disc No 2, with respect to a preceding cleaning step.

First of all it can be seen that the reduction of ^{210}Po was observed not only for the side that was actually polished (facing the cathode, shadowed rows in Table 3) but also for the opposite one (R reached here values up to 2.6, which is already remarkable). In a single step for the polished side, it varied between 8 and 44. Conservatively one could say that one 35 min electropolishing step reduced the ^{210}Po activity roughly by one order of magnitude. The overall factors obtained for side "a" (polished for 70 min) and "b" (polished for 35) are 397 and 105, respectively. This is a big improvement compared to inefficient etching. The total amount of removed material after 3 runs was 17 mg/cm^2 (19 µm thick Cu layer). Assuming that in every 35 min interval one third (5.7 mg/cm^2) has been taken away, we can compare that with the average M obtained in a single 5 min etching step (3.0 mg/cm^2, disc No 2).

On the other hand, M_c reached about 20 mg/cm^2 for the total cleaning time of 35 min. From that and from the observed current changes (drop from 150 mA down to 10 mA) one could conclude that the efficiency of the process is not constant in time and it is decreasing along the current drop. The total charge passed through the solution was at the level of 70 mAh. At the end of the electropolishing the discs were always taken out from the electrolyte with the voltage on.

Disc No 3 was processed only once but in a 3 h long run. During that period it was turned 6 times so that each side was facing the cathode 3 times for 30 min. The idea behind that was to cross-check the previous results and test if an increase in the polishing time (without changing the electrolyte) influences significantly polonium removal (only ^{210}Po was analyzed here) form the surface in question. Table 4 shows the obtained results. Starting with the total amount of removed material (20 mg/cm^2, 22.5 μm), one sees immediately that it is comparable with what has been achieved in a 1.5 h run (disc No 4). This confirms the assumption of the polishing efficiency drop in time. The ^{210}Po count rates reduction factors for both sides are in agreement. They are relatively high (R ~ 200), however almost 50 % lower compared to R measured for side “a” of disc No 4. This effect is observed although the polishing times of the single sides from the discs No 4 and No 3 are comparable. There is even some advantage for the last one (90 min for side “a” of the disc No 3 vs. 70 min for side “a” of the disc No 4). This shows again that the process is the most efficient (for ^{210}Po at least) when applying relatively short multiple cleaning steps with fresh electrolyte.

Removal efficiency of other isotopes was tested on the side “b” of disc No 8, which was again turned 6 times every 5 min during a 1 h long run. The total polishing time of the investigated side was therefore 30 min. The amount of removed material was not determined here. Observed count rates for ^{210}Po, ^{210}Bi and ^{210}Pb and calculated reduction factors are given in Table 5. For ^{210}Po, as expected from a single 35 min run (see Table 3), we obtained R ~ 30. For ^{210}Bi and ^{210}Pb the effect is one order of magnitude stronger and R reaches values of 240 and 350 (lower limit), respectively. Similar to etching, electropolishing seems to be much more efficient in removal of these two isotopes compared to polonium.

6.3 Etching of steel

Three tests were performed on disc No 3 according to the procedure described in section 5.1. ^{210}Pb, ^{210}Bi and ^{210}Po were measured on both sides however, for a second 90 min run only ^{210}Bi on side “a” was determined. In consequence reduction factors given in the last part of Table 6 (120 min etching) reflect mostly cumulative cleaning efficiencies (90 min + 120 min, except for ^{210}Bi on side “a”). As it can be seen from the data (first part of Table 6), the initial count rates from both disc sides were again significantly different. This is probably due to different exposure conditions to the ^{222}Rn-rich gas stream. The obtained reduction factors in the 50 min run for ^{210}Pb and ^{210}Bi are consistent and relatively high (in the range of 40). For ^{210}Po R is significantly different for side “a” and “b”. However, contradictory to copper, it is not negligible and it oscillates around 10 (rather conservative estimate). The amount of removed steel is comparable with that for copper after 5 min etching.

As already mentioned, after the second etching run (90 min) only ^{210}Bi on side “a” was measured. Its count rate was reduced only by a factor of 19, which is significantly lower compared to the corresponding result obtained for the 50 min run. Also the amount of removed material was considerably smaller (0.84 mg/cm^2 vs. 3.1 mg/cm^2), although the run was longer. This was somehow expected due to passivation making the surface more resistant. This effect was confirmed by the longest cleaning step showing even poorer $^{210-}$Bi removal from side “a” (factor 4.4) and comparable M (1.1 mg/cm^2). Cumulative (over last two runs) reduction factors for ^{210}Pb and ^{210}Po show a lower limit for lead and a value of 30 for polonium (see Table 6).

Disc No 2 was processed only once for 2 h with the etchant being stirred in order to maximize the process efficiency. The amount of removed material was factor 4 higher compared to the analogically long step applied to the passivated disc No 1 (see Table 7). ^{210}Pb and ^{210}Bi activity reduction factors are at the level of 170 (for lead some difference in R for both sides has been observed), while for ^{210}Po R_{av} = 31 (again a difference of about 2 between side “a” and “a” was noticed). This value is comparable with that obtained from the passivated disc No 1 processed all together for 210 min ($R_{(90+120\ min)}$ = 30, see Table 6).

6.4 Electropolishing of steel

One 18 min electropolishing run on the disc No 3 was performed. The disc was turned once, so each side was effectively processed for 9 min. The amount of removed material (16 mg/cm^2/20 µm) is comparable with that of copper after 1.5 h polishing run (see Table 3). In most cases, only lower limits for activity reduction factors for ^{210}Pb, ^{210}Bi and ^{210}Po were obtained (see Table 8). However, they are very high for all three isotopes. As adopted reduction factors (5th column of Table 8), the numbers, or better limits obtained for side “a” and “b”, have been taken. They vary from 400 for ^{210}Pb up to 800 for ^{210}Bi with ^{210}Po being between (R_a ~700). Therefore, there is also no indication that, for the polonium, the removal efficiency is somehow reduced compared to the others elements (as it was observed for etching/electropolishing of copper and for etching of stainless steel).

5. Summary and conclusions

We have performed tests of copper and stainless steel cleaning techniques using small samples artificially loaded with the long-lived ^{222}Rn daughters. High activities of collected isotopes allowed to apply standard spectrometers based on semiconductor detectors for alpha, beta and gamma radiation detection of ^{210}Po, ^{210}Bi and ^{210}Pb, respectively. The amount of removed material during etching/electropolishing processes was determined by weighting the disc before and after using a precision balance. All the samples were processed at room temperature (~20 ^{o}C). From the obtained results the following can be concluded:

- The quoted uncertainties of measured count rates (and following reduction factors) include only statistics and are small, in the range of a single percent. This is due to high activities accumulated on the samples and low background of the applied detection systems. The systematic errors were not taken into account, but as their sources one could mention here e.g. temperature variations during etching/electropolishing, inhomogeneity of the solution during etching (without mixing) or positioning of a disc with respect to the cathode during electropolishing. To determine them one needs more systematic measurements with different initial activities. Very helpful would be certainly also an analysis of the ^{210}Pb/^{210}Bi/^{210}Po content in the used etchants/electrolytes and of the activities accumulated on the used cathodes in the case of electropolishing. For rough estimates one can take into account variations of the amount of material removed from the copper disc No 2 in subsequent etching steps. As given in Table 2, the average is 3.0 mg/cm^2 and the biggest deviation 1.4 mg/cm^2, which would indicate 46 % systematic uncertainty. Unfortunately for electropolishing the mass losses in single runs were not recorded (see e.g. Table 3 for disc No 4).

- The initial activities (count rates) on different disc sides were sometimes very different for the same isotope. It was probably related to the disc position/orientation in the exsiccator and differences in exposure to the ^{222}Rn-rich gas stream. Due to unknown absolute detection efficiencies (mainly for ^{210}Pb) from the registered count rates it was also difficult to judge if there was radioactive equilibrium established between different isotopes (e.g. ^{210}Pb and ^{210}Bi).
- Obtained count rates reduction factors of a given isotope for different sides of the same disc (copper or steel) were not always consistent. This concerns mainly ^{210}Po (see e.g. Table 4, Table 6 or Table 7), but also ^{210}Pb (see Table 7). It is difficult to explain. Perhaps it is related to the handling and positioning of the discs in the etchant vessel ("access" to the fresh solution). In the case of long electropolishing runs, this effect may be related to the timely sequence of the polished sides (as shown, at the beginning the process is the most efficient).
- Tested copper etching procedure shows very minor, practically negligible, effect of ^{210}Po removal from the surface. Activity reduction factors for ^{210}Pb and ^{210}Bi were in the range of 50.
- It has been shown (with ^{209}Po added to the etchant) that polonium after being removed together with a µm-thick copper sub-surface layer is immediately re-deposited on the treated sample.
- It is possible that after plating-out ^{210}Po is partially diffusing into the sub-surface layer reaching depth of some µm. This hypothesis is supported by the observed polonium re-deposition and by the results obtained by etching several times the copper disc No 2 (see Table 1 and Fig. 3a/3b). This shows anti-correlation

between the polonium reduction factor and the thickness of the removed copper layer.

- Electropolishing removes very effectively all three long-lived radon daughters from the copper surface. The reduction factors obtained for ^{210}Pb and ^{210}Bi were in the range of 250 – 300 (1 h run) and ^{210}Po has been reduced in the best case by a factor of ~400 (2×35 min run, ^{210}Pb and ^{210}Bi were not analyzed in this test).
- For ^{210}Po removal from copper by electropolishing in a multi-stage process (using each time a new cathode and electrolyte) gives clearly better results as one long run.
- Similarly long etching and electropolishing remove similar amounts of copper. In case of a 35 min process it was about 20 mg/cm^2 corresponding to a 23 μm thick layer.
- Etching of stainless steel is as efficient as etching of copper for ^{210}Pb and ^{210}Bi (activity reduction by a factor of 40) and, however less effective, it works also for ^{210}Po (R ~ 10).
- Multi-stage etching of stainless steel become less and less effective in the following steps due to surface passivation (etching a sample several times without passivation should give better results).
- Electropolishing of steel gave the best results in terms of removal of all three long-lived ^{222}Rn isotopes in a single run. Their surface activities were reduced by almost three orders of magnitude.

Summarizing, one can state that recommended cleaning method for copper would be multi-stage electropolishing. A new electrolyte and a new cathode should be applied in each step. If possible, the entire sample surface should be exposed to the cathode. The current, the voltage and the polishing time to be applied should be determined experimentally taking into account the conditions (e.g. sample size) so that a few mg/cm^2 of the materials are being removed.

For steel electropolishing assures excellent efficiency in ^{210}Pb, ^{210}Bi and ^{210}Po removal, however multi-stage etching (which is usually easier to perform) with only one passivation step at the end could also by applied.

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Figure captions

Fig. 1. Part of the ^{238}U chain starting from ^{226}Ra with the most important decay channels. The sub-chain in the left frame contains the short-lived ^{222}Rn daughters. In the right frame long-lived isotopes are shown. The equilibrium in the chain is usually broken at the ^{222}Rn (the only one gaseous isotope in this chain) and ^{210}Pb level (22 years half-life).

Fig. 2. Schematic view of the setup used to load metal disc with long-lived ^{222}Rn daughters.

Fig. 3. Results of the etching performed on the disc No 2. Plot a) and b) show the amount of removed copper and the ^{210}Po activity reduction factors obtained for the single runs, respectively. Plot c) displays the cumulative reduction factor as a function of the cumulative amount of the removed copper.

Fig. 4. A spectrum obtained after the last etching run of the disc No 2. Peaks coming from attracted ^{209}Po and re-deposited ^{210}Po are visible. Their narrowness indicates that both isotopes were sitting on the disc surface.

Fig. 5. Schematic view of the setup used for copper/steel discs electropolishing.

Table 1. ^{210}Po count rates reduction after subsequent etching runs of the copper disc No 2. The initial ^{210}Po signal was A_{02a} = (2.97 ± 0.03) cpm and A_{02b} = (2.64 ± 0.03) cpm for side “a” and “b”, respectively. The averaged (over both sides) blank value equaled to A_{2B} = (0.0042 ± 0.0005) cpm. Averaged reduction factor R_{av} (5th column) is calculated always with respect to the previous run. The cumulative value (R_c) reflect the overall effect of the performed runs (calculated with respect to initial rates A_{02a} or A_{02b}). The same pertains to the amount (M) and cumulative amount (M_c) of removed material (summed over following runs).

Run No.	**Disc side**	**^{210}Po count rate [cpm]**	**^{210}Po reduction factor R**	**Averaged reduction factor R_{av}**	**Cumulative reduction factor R_c**	**Amount of removed copper M**	**Cumulative amount of removed copper M_c**	**Remarks**
1	a	2.36 ± 0.03	1.26 ± 0.02	1.24 ± 0.01	1.24 ± 0.01	(1.77 ± 0.02) mg/cm^2 (1.99 ± 0.02) µm	(1.77 ± 0.02) mg/cm^2 (1.99 ± 0.02) µm	Solution mixed during etching
	b	2.16 ± 0.02	1.22 ± 0.02					
2	a	1.83 ± 0.04	1.29 ± 0.03	1.25 ± 0.02	1.55 ± 0.02	(2.29 ± 0.02) mg/cm^2 (2.57 ± 0.02) µm	(4.06 ± 0.03) mg/cm^2 (4.56 ± 0.03) µm	
	b	1.79 ± 0.03	1.21 ± 0.02					
3	a	1.84 ± 0.03	0.99 ± 0.03	1.05 ± 0.02	1.63 ± 0.03	(4.40 ± 0.02) mg/cm^2 (4.91 ± 0.02) µm	(8.46 ± 0.03) mg/cm^2 (9.51 ± 0.03) µm	
	b	1.62 ± 0.03	1.10 ± 0.03					
4	a	1.65 ± 0.03	1.12 ± 0.03	1.12 ± 0.02	1.82 ± 0.03	(3.21 ± 0.02) mg/cm^2 (3.61 ± 0.02) µm	(11.70 ± 0.04) mg/cm^2 (13.15 ± 0.04) µm	
	b	1.43 ± 0.02	1.13 ± 0.03					
5	a	1.62 ± 0.03	1.02 ± 0.03	1.04 ± 0.02	1.89 ± 0.03	(3.38 ± 0.02) mg/cm^2 (3.80 ± 0.02) µm	(15.10 ± 0.04) mg/cm^2 (16.97 ± 0.04) µm	
	b	1.35 ± 0.02	1.06 ± 0.02					
6	a	1.47 ± 0.02	1.10 ± 0.03	1.09 ± 0.02	2.07 ± 0.03	(3.47 ± 0.02) mg/cm^2 (3.90 ± 0.02) µm	(18.50 ± 0.10) mg/cm^2 (20.79 ± 0.06) µm	
	b	1.25 ± 0.03	1.08 ± 0.03					
7	a	1.50 ± 0.02	0.98 ± 0.02	0.99 ± 0.02	2.04 ± 0.03	(2.37 ± 0.02) mg/cm^2 (2.66 ± 0.02) µm	(20.90 ± 0.10) mg/cm^2 (23.48 ± 0.06) µm	Solution mixed during etching, ^{209}Po added (1.42 Bq)
	b	1.26 ± 0.03	0.99 ± 0.03					
Values averaged over 7 runs				1.1		3.0 mg/cm^2 3.34 µm		

Table 2. Reduction of ^{210}Pb, ^{210}Bi and ^{210}Po count rates on the copper disc No 1 after one 5 min etching run. Only one side of the disc was investigated.

Isotope	**Initial count rate [cpm]**	**Count rate after cleaning [cpm]**	**Reduction factor R**	**Amount of removed copper M**	**Remarks**
^{210}Pb	1.49 ± 0.04	< 0.022	> 68	(3.91 ± 0.02) mg/cm^2 (4.40 ± 0.02) µm	Only one side was tested
^{210}Bi	31.2 ± 0.7	0.77 ± 0.02	40.5 ± 1.4		
^{210}Po	2.55 ± 0.01	2.06 ± 0.01	1.24 ± 0.01		

Table 3. Reduction of ^{210}Po count rates on the disc No 4 after three electropolishing runs. Initial signal on the side "a" (polished twice) and side "b" (polished once) equaled to (9.52 ± 0.06) cpm and (1.78 ± 0.04) cpm, respectively. The amount of removed copper was measured only at the end of the tests. The lower part of the table summarizes the overall activity reduction factors for both sides. Shadowed rows indicate the actually polished side in a given run.

Run No.	Disc side	^{210}Po count rate [cpm]	Reduction factor R	Amount of removed copper M (M_c)	Remarks
1	a	0.50 ± 0.03	19.0 ± 1.1	(17.0 ± 0.1) mg/cm^2 (19.1 ± 0.1) µm	Side "a" polished for 35 min. Total charge: 70 mAh
	b	1.38 ± 0.03	1.29 ± 0.04		
2	a	0.062 ± 0.003	8.06 ± 0.62		Side "a" polished for 35 min. Total charge: 70 mAh
	b	0.74 ± 0.01	1.86 ± 0.05		
3	a	0.024 ± 0.002	2.58 ± 0.25		Side "b" polished for 35 min. Total charge: 70 mAh
	b	0.017 ± 0.002	43.5 ± 5.1		

All	a	0.024 ± 0.002	397 ± 33	(17.0 ± 0.1) mg/cm^2 (19.1 ± 0.1) µm	Side "a" polished for 70 min
	b	0.017 ± 0.002	105 ± 12		Side "b" polished for 35 min.

Table 4. Reduction of ^{210}Po count rates on the copper disc No 3 after one 3 h long electropolishing run. The disc was turned 6 times so that each side was facing the cathode 3 times for 30 min.

Disc side	**Initial ^{210}Po count rate [cpm]**	**^{210}Po count rate after polishing [cpm]**	**^{210}Po reduction factor R**	**Average reduction factor R_{av}**	**Amount of removed copper M**	**Remarks**
a	2.18 ± 0.02	0.011 ± 0.001	198 ± 18	186 ± 11	(20.0 ± 0.1) mg/cm^2 (22.5 ± 0.1) µm	Facing the cathode 3 times, each time for 30 min
b	2.45 ± 0.03	0.014 ± 0.001	175 ± 13			Facing the cathode 3 times, each time for 30 min

Table 5. Reduction of ^{210}Po, ^{210}Bi and ^{210}Po count rates on the copper disc No 8 after a 1 h electropolishing run with the disc turned every 5 min.

Disc side	**^{210}Po [cpm] before/after**	**^{210}Bi [cpm] before/after**	**^{210}Pb [cpm] before/after**	**Remarks**
b	5.31 ± 0.12 0.18 ± 0.01	36.6 ± 0.5 0.15 ± 0.01	2.08 ± 0.02 < 0.006	Side “b” facing the cathode 6 times for 5 min.
	R = 29.5 ± 1.8	R = 244 ± 17	R > 346	

Table 6. Reduction of ^{210}Po, ^{210}Bi and ^{210}Po count rates on the stainless steel disc No 1 after three etching runs of different times.

Isotope	Disc side	Initial count rate [cpm]	Count rate after cleaning [cpm]	Reduction factor R	Reduction factor R_{av}/R_a	Amount of removed steel M	Remarks
^{210}Pb	a	6.87 ± 0.08	0.15 ± 0.01	45.8 ± 3.1	47.6 ± 3.9	(3.10 ± 0.02) mg/cm^2 (3.88 ± 0.02) µm	Etching for 50 min
	b	1.48 ± 0.09	0.030 ± 0.004	49.3 ± 7.2			
^{210}Bi	a	147 ± 3	4.0 ± 0.1	36.8 ± 1.2	33.9 ± 1.0		
	b	18.6 ± 0.4	0.60 ± 0.03	31.0 ± 1.7			
^{210}Po	a	16.5 ± 0.5	0.88 ± 0.07	18.8 ± 1.6	11.6 ± 0.8		
	b	1.83 ± 0.04	0.41 ± 0.02	4.5 ± 0.2			

^{210}Bi	a	4.0 ± 0.1	0.21 ± 0.02	19.0 ± 1.9	19.0 ± 1.9	(0.84 ± 0.01) mg/cm^2 (1.05 ± 0.02) µm	Etching for 90 min
	b	-	-	-			

^{210}Pb	a*	0.15 ± 0.01	< 0.0044	> 34	> 34	(1.10 ± 0.01) mg/cm^2 (1.40 ± 0.02) µm	Etching for 120 min
	b*	0.030 ± 0.004	< 0.0049	> 6			
^{210}Bi	a	0.21 ± 0.02	0.048 ± 0.019	4.4 ± 1.8	4.4 ± 1.8		
	b*	0.60 ± 0.03	< 0.047	> 13			
^{210}Po	a*	0.88 ± 0.07	0.029 ± 0.003	30.3 ± 3.9	30.0 ± 3.0		
	B*	0.41 ± 0.02	0.014 ± 0.002	29.3 ± 4.4			

*) Reduction factors obtained only after two subsequent cleaning steps. ^{210}Pb, ^{210}Bi on side “b” and ^{210}Po after 90-min run was not measured.

Table 7. Reduction of ^{210}Po, ^{210}Bi and ^{210}Po count rates on the stainless steel disc No 2 after one long etching run.

Isotope	Disc side	Initial count rate [cpm]	Count rate after cleaning [cpm]	Reduction factor R	Average reduction factor R_{av}	Amount of removed steel M	Remarks
^{210}Pb	a	6.34 ± 0.07	0.032 ± 0.003	198 ± 19	165 ± 13	(4.3 ± 0.02) mg/cm^2 (5.38 ± 0.02) μm	Etching for 120 min, solution stirred
	b	2.11 ± 0.03	0.016 ± 0.002	132 ± 17			
^{210}Bi	a	138 ± 2	0.79 ± 0.06	174 ± 14	174 ± 11		
	b	36.7 ± 0.4	0.21 ± 0.02	174 ± 17			
^{210}Po	a	24.7 ± 0.2	0.55 ± 0.02	45 ± 2	31 ± 1		
	b	5.2 ± 0.1	0.30 ± 0.01	17.3 ± 0.7			

Table 8. Reduction of ^{210}Po, ^{210}Bi and ^{210}Po count rates on the stainless steel disc No 3 after electropolishing. Due to the lower limits obtained for R adopted reduction factor (R_a) is given as the value measured for one of the disc sides or better limit.

Isotope	**Disc side**	**Initial count rate [cpm]**	**Count rate after cleaning [cpm]**	**Reduction factor R**	**Adopted reduction factor R_a**	**Amount of removed steel M**	**Remarks**
^{210}Pb	a	0.94 ± 0.02	< 0.003	> 313	432	(16.0 ± 0.1) mg/cm^2 (20.0 ± 0.1) µm	Polishing for 18 min, each disc side faced the cathode for 9 min
	b	2.16 ± 0.02	0.005 ± 0.002	432 ± 172			
^{210}Bi	a	12.4 ± 0.4	< 0.03	> 413	798		
	b	35.1 ± 0.9	0.044 ± 0.021	798 ± 381			
^{210}Po	a	2.02 ± 0.03	< 0.01	> 202	> 688		
	b	6.88 ± 0.13	< 0.01	> 688			

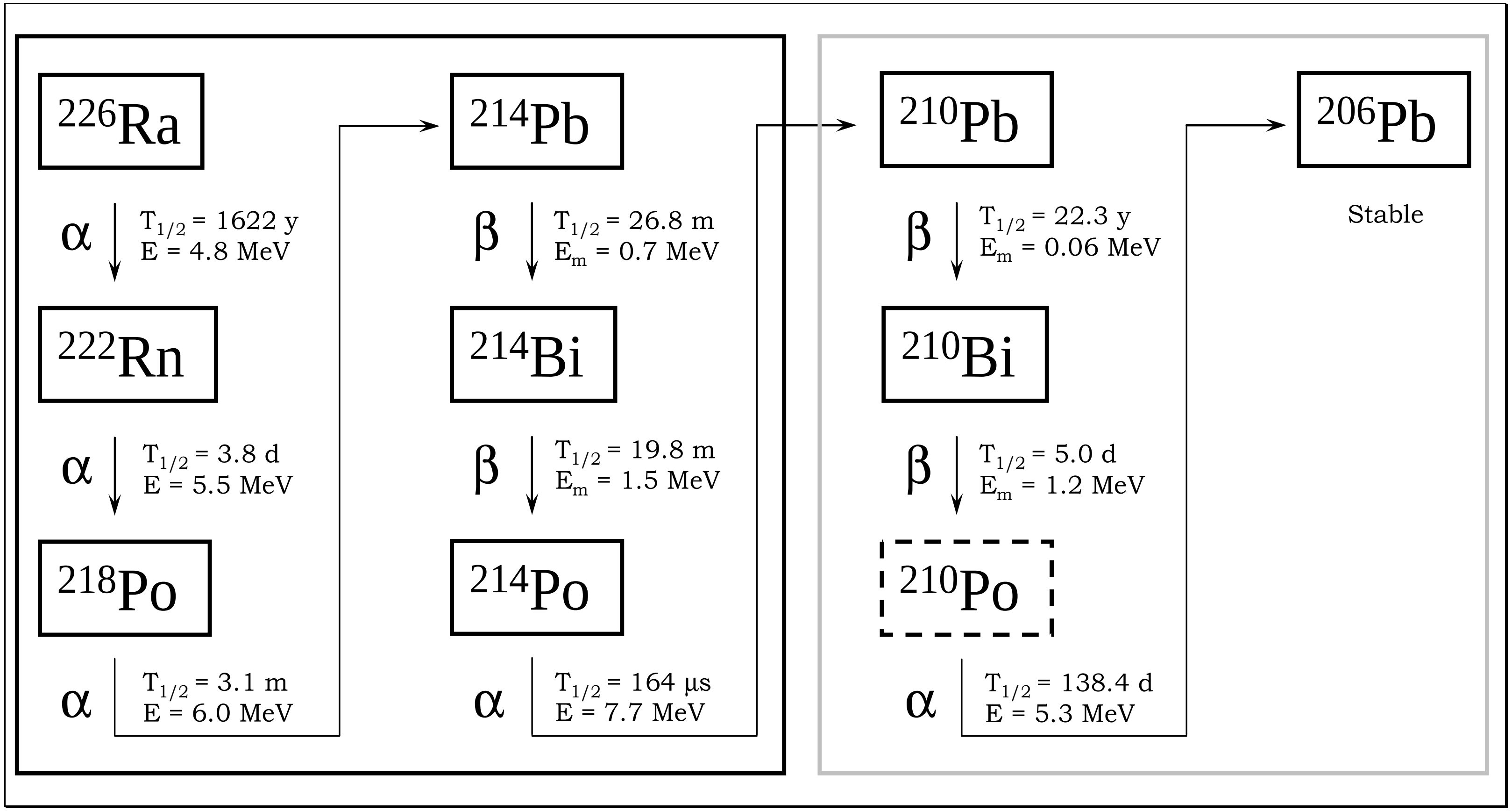

226Ra
α
T1/2 = 1622 y
E = 4.8 MeV
222Rn
α
T1/2 = 3.8 d
E = 5.5 MeV
218Po
α
T1/2 = 3.1 m
E = 6.0 MeV
214Pb
β
T1/2 = 26.8 m
Em = 0.7 MeV
214Bi
β
T1/2 = 19.8 m
Em = 1.5 MeV
214Po
α
T1/2 = 164 μs
E = 7.7 MeV
210Pb
β
T1/2 = 22.3 y
Em = 0.06 MeV
210Bi
β
T1/2 = 5.0 d
Em = 1.2 MeV
210Po
α
T1/2 = 138.4 d
E = 5.3 MeV
206Pb
Stable

Figure 1.

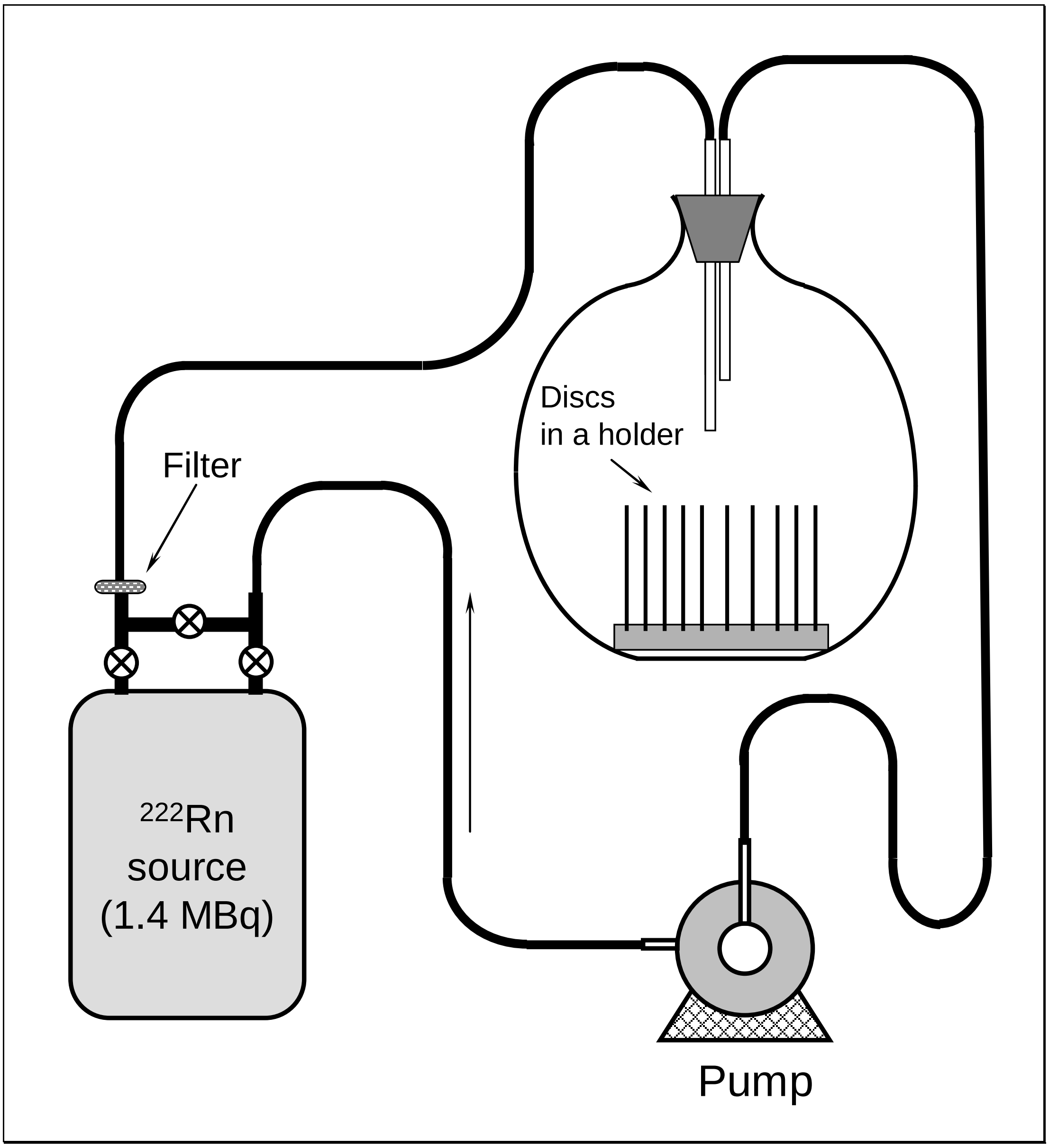


Figure 2.

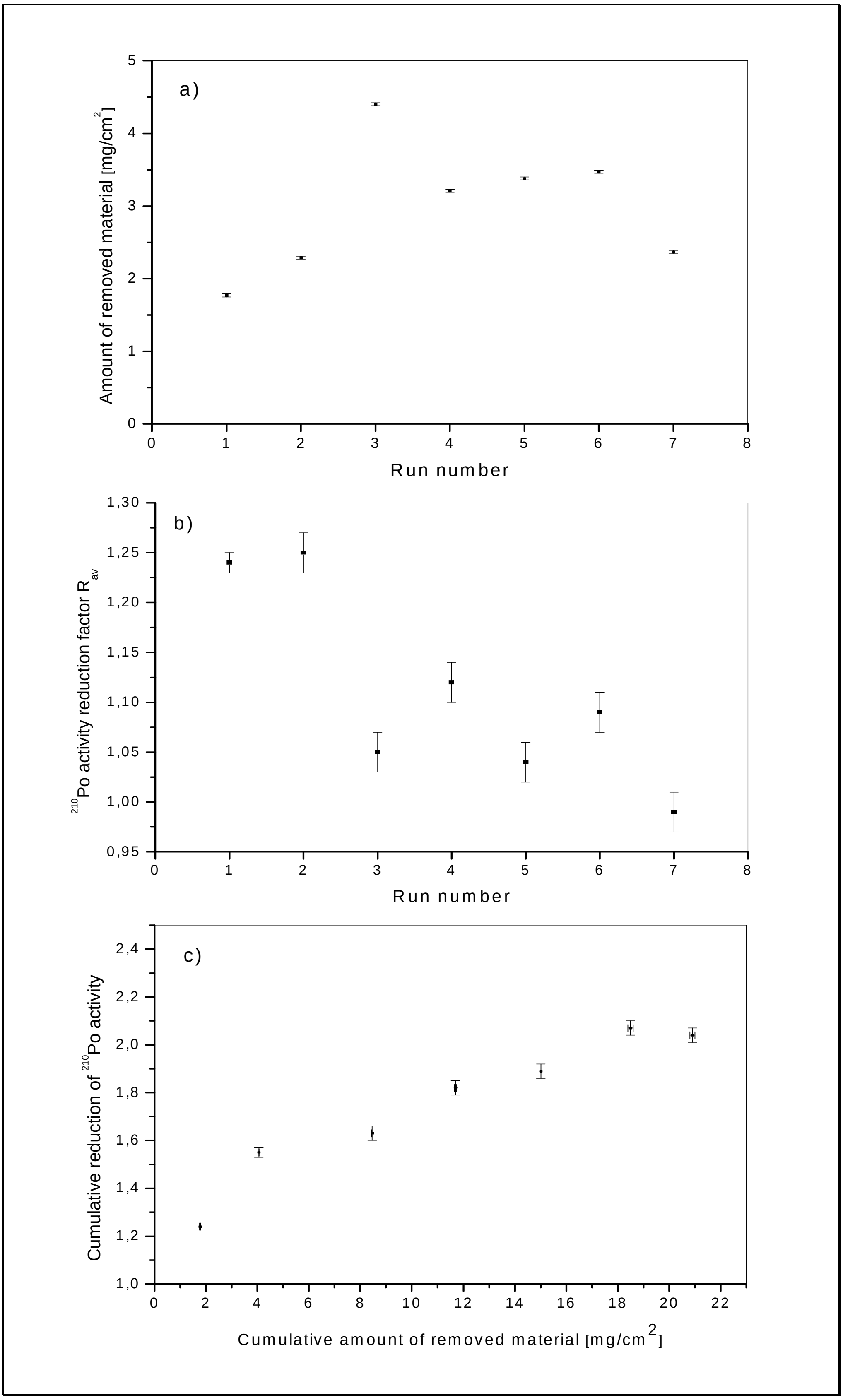
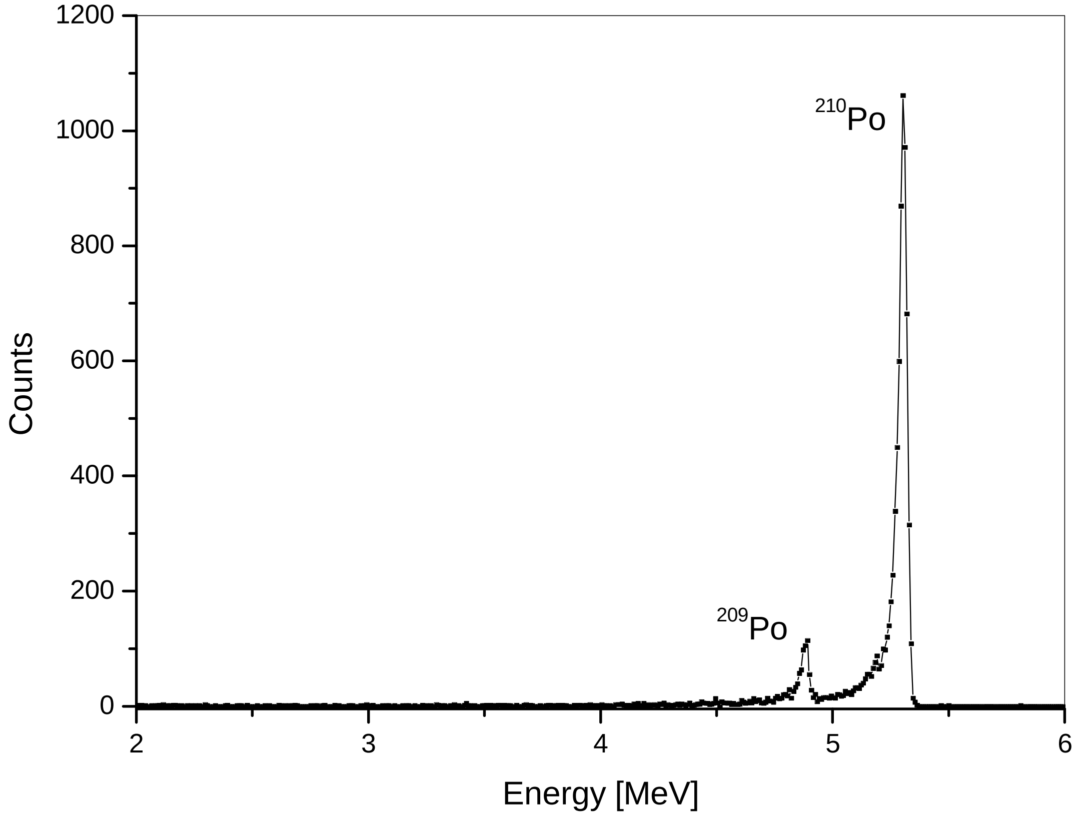
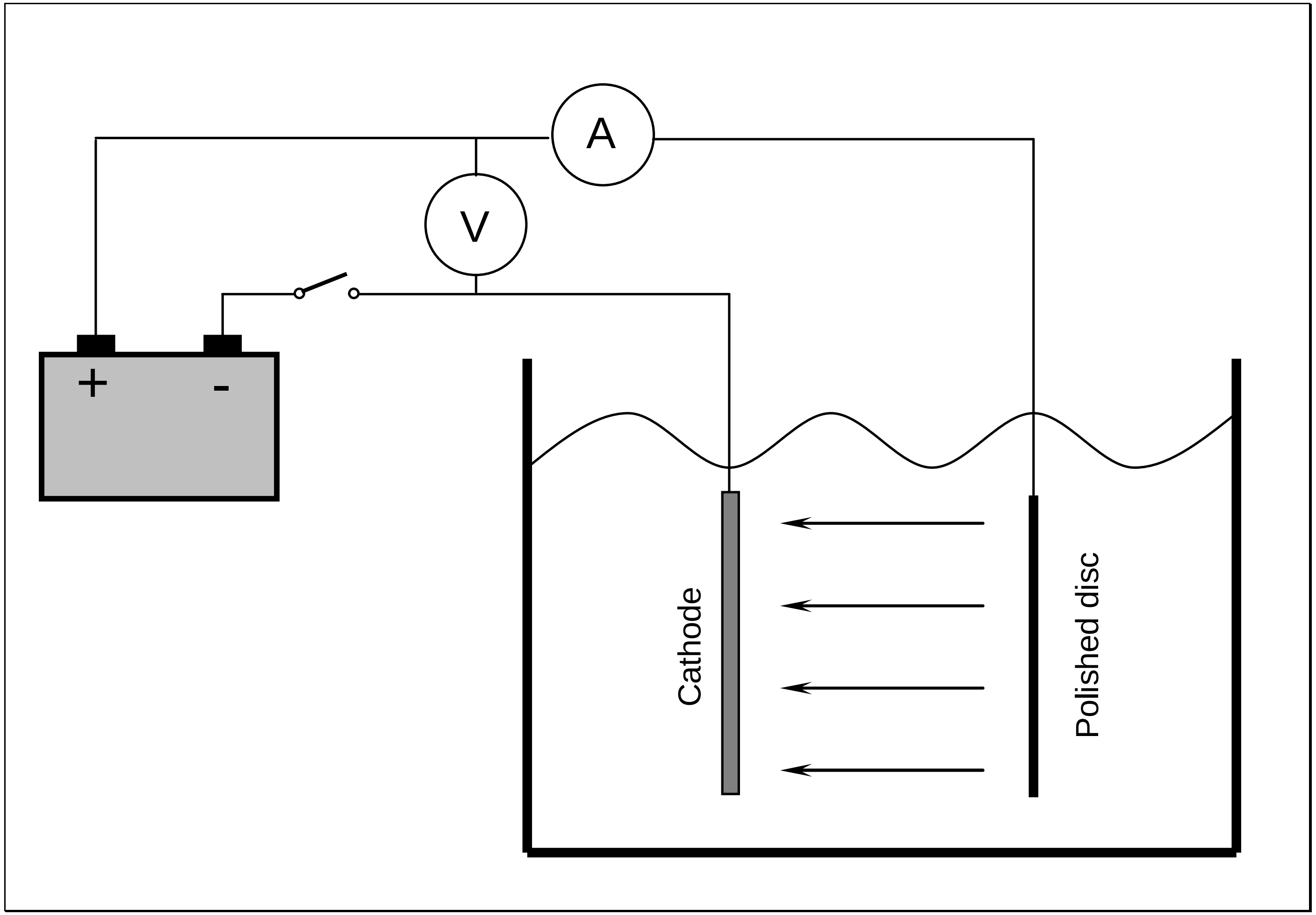

a)
Amount of removed material [mg/cm^2]
Run number
0
1
2
3
4
5
6
7
8
b)
^{210}Po activity reduction factor R_{av}
1,30
1,25
1,20
1,15
1,10
1,05
1,00
0,95
Run number
c)
Cumulative reduction of ^{210}Po activity
2,4
2,2
2,0
1,8
1,6
1,4
1,2
1,0
0
2
4
6
8
10
12
14
16
18
20
22
Cumulative amount of removed material [mg/cm^2]

Figure 3.



Counts
1200
1000
800
600
400
200
0
2
3
4
5
6
Energy [MeV]
^{210}Po
^{209}Po

Figure 4.



Figur