# Rapid method for determination of Po isotopes in biological matter

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A short review of the existing analytical procedures for determination of Po-210, showing their advantages and disadvantages, is presented.

The criteria for selecting the proper method, according to the scope and type of matrix in study are summarised.

The rapid method which is described here consists of total digestion, auto deposition and measurement by means of alpha spectrometry. The classical method in this very simple form as presented here is result of studying the possible interferences and validating the method.

The application of this method in analyzing the Po-210 concentration in fresh water wild fish caught in some lakes in Austria is discussed.

The corresponding ingestion dose to the public, due to Po-210 intake through consumption of these kinds of fish is estimated.

Keywords:

Polonium, Auto deposition, Alpha-spectrometry, Fish, Ingestion-Dose

## Introduction

The work described in this paper was part of the Project "Radioactivity of the wild living fish" during the year 2010 and 2011. This project was funded from the Austrian Ministry of Health.

The motivation for this project was the European Commission Recommendation of 14 April 2003 on the protection and information of the public with regard to exposure resulting from the continued radioactive caesium contamination of certain wild food products as a consequence of the accident at the Chernobyl nuclear power station.

The following lakes were selected for fish sampling; Grundlsee (surface 4km², depth 64m coordinates 47° 38′ 2″ N, 13° 51′ 53″ E), Zellersee (4,4km², 68m, 47° 19′ 30″ N, 12° 48′ 30″ E), Toplitzsee (0,5km²,103m, 47° 38′ 30″ N, 13° 55′ 40″ E) and Neusiedlersee (157 km², 2m, 47° 49′ 4″ N, 16° 44′ 55″ E). The fish was collected during the period April-September 2010.

The predatory carnivorous fish as end link of the food chain as burbot (Lota Lota), europian perch (Perca fluviatilis), northern pike (Esox lucius), wels catfish (Silurus glanis) and Zander (Stizostedion lucioperca) were collected and analysed.

The edible part of the fish, flesh was analysed for radioactive isotopes of Kalium, $^{40}$K, Strontium $^{90}$Sr, Cesium $^{134}$Cs, $^{137}$Cs, Lead $^{210}$Pb, Polonium $^{210}$Po, Uranium $^{234}$U, $^{235}$U, $^{238}$U and Plutonium $^{238}$Pu, $^{239/240}$Pu, $^{241}$Pu.

This paper describes the results and analysis of $^{210}$Po in the wild living fish in above mentioned lakes.

## Polonium isotopes and their origin

Polonium has 25 known radioactive isotopes with mass numbers of 192 to 218, of which $^{211}$Po, $^{215}$Po belongs to $^{235}$U natural decay chain, $^{210}$Po, $^{214}$Po, $^{218}$Po isotopes to $^{238}$U natural decay chain and $^{212}$Po, $^{216}$Po to $^{232}$Th natural decay chain. Among them $^{210}$Po, with about 100 µg per ton uranium ore, is the most interesting isotope from the radiation protection point of view, as well as studying transfer mechanisms in the environment. Other known radionuclides with considerable half-life are $^{208}$Po and $^{209}$Po artificial isotopes which are commonly used as tracer in radiochemical analysis of polonium in environmental samples. All known isotopes of Polonium are pure alpha emitting radionuclides with well resolved energies between each other.

The discussion in this paper will be concentrated on almost pure alpha emitting radionuclide $^{210}$Po with half-life 138,4 d. This isotope emits also weak gamma photons with energy 803,1 keV and an intensity of 0,001%. Gamma radiation is not relevant for analyzing $^{210}$Po in environmental samples. Gamma spectrometry becomes interesting only for high activity samples about and above 1 MBq.

$^{210}$Po like other already mentioned radionuclides $^{208}$Po, $^{209}$Po can be produced in the nuclear reactor for industrial and research purposes.

## Preparation analysis

In order to be able to analyse numerous fish samples we first started to optimise the methods for each radionuclide. Where it was possible we combined the analyses of several radionuclides in one sample. This part is not described here.

In this project different kind of fish with different length and weight had to be analysed. In sum there were more than 50 fish samples, beginning from several grams to few kilograms. The aim was to obtain as much information as possible for all samples. Radionuclides like $^{238}$U, $^{234}$U, $^{238}$Pu, $^{239}$Pu, $^{240}$Pu, $^{241}$Pu, $^{90}$Sr could not be quantitatively measured for all kind of fish samples because the fish flesh weight in most of the samples was some decagrams and it was not enough to be detectable.

The only nuclide which could be quantitatively measured even for very small fish like 10-20 gram was Polonium, by alpha spectrometry, which did not need more than 2-3 grams sample and could be directly considered after gamma spectrometric measurements without undergoing special and tedious sample preparation procedures like drying or ashing, needed to preconcentrate the radionuclides to a measurable amount.

Analysis of $^{210}$Po is related to the determination of $^{210}$Pb in the sample, if the concentration of this last one and if the time between collection and analysis is considerable. In the case of the fish the $^{210}$Pb is located in the skeleton (Watson 1983) and not in the edible part, flesh which was analysed here. $^{210}$Pb is approximately 100 times less in activity than $^{210}$Po, as it was estimated in further analysis for samples with weight more than 200 g.

In the literature there are two main methods for analysing $^{210}$Po that of organic extraction and measuring of beta and alpha particles by a certain alpha beta counting technique like liquid scintillation counting, LSC and the other method is spontaneous deposition of Polonium and measuring by alpha spectrometry.

The Polex (organic material) extraction and LSC for analyzing $^{210}$Po, as described in (Katzlberger 2001, Wallner 1997, Vajda 1995) are also the basis for the standard procedure for measuring $^{210}$Po and $^{210}$Pb in water in our laboratory but due to the limits of this method could not be applied here.

The advantages and disadvantages of these methods are summarised in the tables (table 1, table 2) below.

| **Organic extraction and LSC method** | |
|---|---|
| **Advantages** | **Disadvantages** |
| Easy to perform | Chemical recovery is assumed |
| High counting efficiency | Chemical extraction yield is assumed |
| $^{210}$Pb can be simultaneously measured with $^{210}$Bi and $^{210}$Po | Not appropriate for high organic content material |
| | Not easy to account for the interferences in the environmental samples |
| | Often the equilibrium is assumed or a certain time is needed to reach the equilibrium |

Table 1. Organic extraction method

| **Auto deposition and alpha spectrometry** | |
|---|---|
| **Advantages** | **Disadvantages** |
| Easy to perform | $^{210}$Pb and $^{210}$Bi can not be simultaneously measured with $^{210}$Po |
| No interferences of beta radionuclides due to selectivity of alpha detectors | |
| Counting right after the source preparation | |
| Where necessary the lead fraction can be separated before spontaneous deposition of Polonium | |

Table 2. Alpha spectrometry

The organic matter in fish and the volatility of Polonium are the biggest problem in analysing this radionuclide for this reason the radiochemical recovery must be evaluated. Unfortunately by Liquid Scintillation Counting it is not yet possible to resolve the tracer $^{208}$Po or $^{209}$Po from $^{210}$Po. Another reason for selecting this method was the lower minimum detectable activity using alpha spectrometry. The alpha spectrometry demanding less amount of sample is time efficient for the analysis. $^{209}$Po was used as tracer to determine the chemical recovery of $^{210}$Po.

In order to optimise the method we decided to compare the procedures in the literature with the results we found in our laboratory.

Recent work in our laboratory has shown that Polonium in fish can efficiently and easily spontaneously deposited in silver plates and accurately measured by alpha spectrometry without any radiochemical separation of Polonium allowing several samples to be analysed at a time.

## Sample dissolution

First of all the digestion procedure was tested using a fresh flesh sample of ca. 2-4 grams.

Three digestion procedures were analysed first with Nitric acid 65% and $H_2O_2$ 27%, the second with HCl 35% and the third one the aqua regia as reported in literature.

After 2 hours heating and stirring the first sample was completely digested and ended up into a clear solution which means the most of the organic matter was destroyed.

Both other media did not have the same effect in such a short time. So it was decided to follow the first method.

After total digestion the $^{209}$Po spiked samples were evaporated and the rest of organic matter was destroyed by addition of few millilitres of nitric acid 65% and $H_2O_2$ 27% several times, until the total organic matter was destroyed than the precipitate was treated with HCl 35% to transfer the media into chloride form.

## Spontaneous deposition of Polonium

Also here there are several procedures reported in the literature among them (Hamilton and Smith 1984, Smith and Hamilton 1986, Johansson 2008) which are based on the same principle that of spontaneous deposition of metalized Polonium into the surface of a certain metal. The deposition of polonium as well as the interfering elements depends on the material plate, for e.g. Silver or Nickel. It is already known that Polonium has higher deposition efficiency in silver plates, 99% (Johansson 2008) and in a shorter time than nickel plates with 75% deposition efficiency.

The deposition time of 5 hours or more is also reported. By heating at 300°C, 25 % of Polonium is lost from Nickel plates and 4 % from Silver plates (Johansson 2008). Which means that polonium is implanted better in the surface structure of Silver. Addition of ascorbic acid was seen that is more efficient than the other reducing agents (Smith Hamilton 1886). The pH of the media in which the deposition takes place is also some times reported from some authors (IAEA/AQ/12) and from other ones not.

In order to distinguish among the most important factors that influence the spontaneous, simulated matrixes containing $^{210}$Po, $^{210}$Pb and $^{210}$Bi were prepared and auto deposited in silver plates. The results are presented graphically in the figure 1. The spontaneous deposition was performed in 0,5M HCl with and without ascorbic, with adjusted and not adjusted pH depending on the time. The yellow line shows

the auto deposition without ascorbic acid and no pH adjustment of the solution. The upper lines show the recovery of Polonium at pH=2 with and without ascorbic acid. Adding the ascorbic acid the recovery becomes from 90% to 95%. As we can see the most important factor affecting the recovery of Polonium on the plate was the pH of the solution. Ascorbic acid is not really the most important factor, at least for the biological materials. So the procedure was finalised with the deposition on silver plates for 90 minutes in pH=2 in chloride form. The spontaneous deposition of interfering elements like Bi and Pb was not dependent on both pH and reducing agent only on the deposition time (see figure 1). If the deposition lasts longer time like 150 minutes the probability of codeposition of other cations is higher.

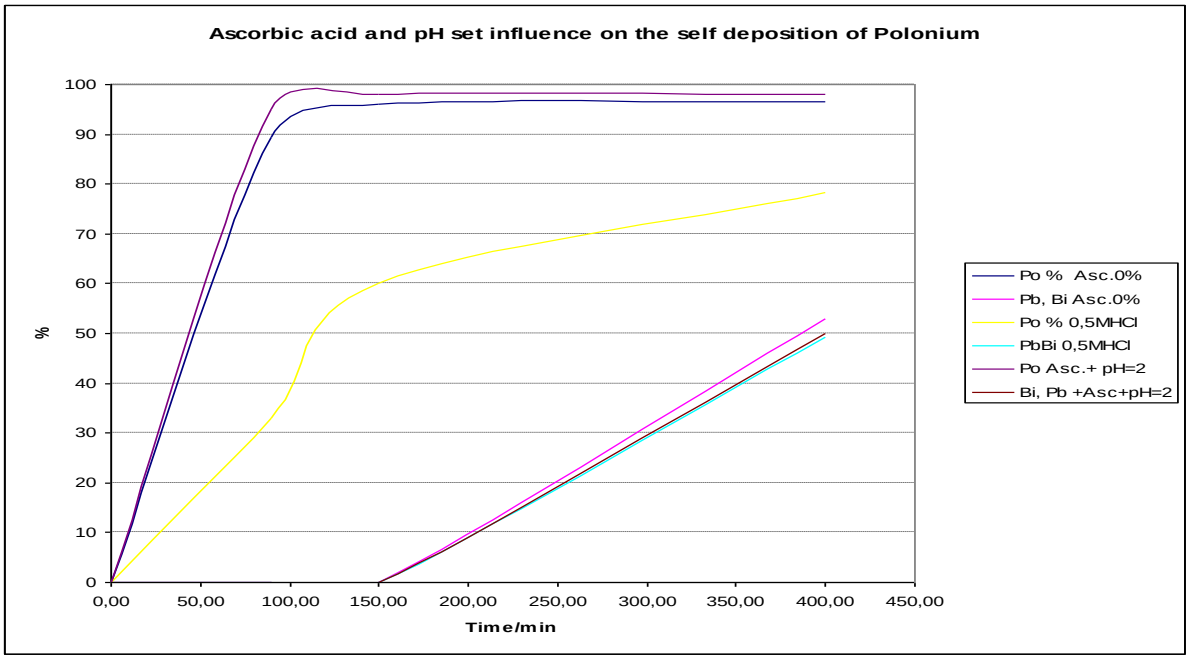

Fig.1. Influence of ascorbic acid and pH set in the self-deposition of Polonium

Maximal content of Pb stable in fish muscle was determined as 0,04 mg $kg^{-1}$ (ppm) which means that stable lead was less than several µg per gram sample.

The sample was transferred in a glass beaker where Teflon mounting with magnetic stirrer containing the prepared silver plate was placed. The temperature was controlled at 85° to 95 °C via an infrared thermometer.

The silver plate was rinsed with alcohol and acetone and after 10 minutes was able to be measured by alpha spectrometry using PIPS Canberra detectors with recoil protection.

The sample preparation time before measurement is ca. 8 hours. The organic matter destruction is the most time consuming part, the less the sample the shorter the preparation time. The microwave digestion with nitric acid and peroxide (5:1) can be successfully used.

## Interferences and method validation

Polonium is separated from Pb and Bi during spontaneous deposition as shown in previous paragraph using higher concentrations of these interference elements. In the alpha detector the beta particles do not interact and pass through it, without interfering alpha spectrum.

For the method validation, reference materials for $^{210}$Po in biological tissue were investigated.

It is necessary to notice that is not easy to find such reference materials. In the following reference materials which are chosen for evaluation of the procedure the values of $^{210}$Po are only information values not certified.

Reference materials which were analysed were IAEA414 and IAEA385. The second one was selected because of its high concentration of $^{210}$Pb ($^{210}$Po). In both cases these two radionuclides were considered in equilibrium. The mean values of samples analysed were; 1,9 ± 0,2 (5) for IAEA-414 and 32,4 ± 1,9 (2) for IAEA-385.

The samples were measured by possibility right after the auto deposition. The samples with higher $^{210}$Po concentration were measured again in order to see the purity of Po and check the repeatability of the measurement. In all these samples the $^{210}$Po concentration was the same inside the measurement uncertainty. The mean chemical recovery in the fish samples was 75%.

## Results and discussion

This method was applied in measuring the concentration of the Polonium isotopes in fish. In principle with this method it is possible to identify all the Polonium isotopes available in the sample. Here the only isotope identified quantitatively was $^{210}$Po.

As already known $^{210}$Po concentration in biological material depend on the local natural radioactivity, seasonal variations and on the type of biological species.

Figure 2 shows the variation of concentration of $^{210}$Po with fish type in Grundl lake.

The maximal value was found to be 6,2 Bq kg$^{-1}$ fresh weight in northern pike in Grundl lake.

Selecting the same type of fish in a certain lake, a negative correlation was seen between the activity concentration and the weight (or length). In the figure 3 the variation of $^{210}$Po activity concentration in northern pike in Grundl Lake with the fish weight is as an example presented.

The results show a negative trend with a correlation factor $R^2$ between 0,3 and 0,7. Even not very plausible this trend can be interpreted if we assume that the weight is an age indicator. The smaller the weight means the younger the fish the higher the intake from the body for the same concentration of $^{210}$Po in the water. For the very small fish between 10 and 20 g, $^{210}$Po concentration is higher, this might happen also because it is difficult to separate the organs from the fish flesh. It is well known that Polonium is even more concentrated in the organs (Jahresbericht 2010, Kanton Basel-Stadt).

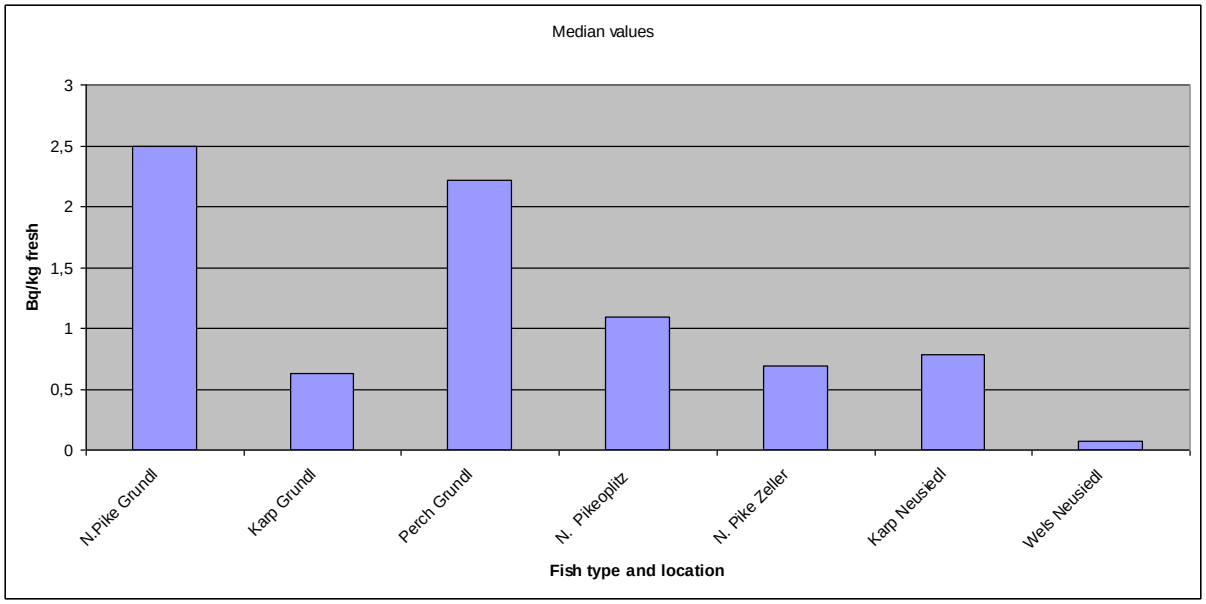


Fig. 2 Median values of the concentration of $^{210}$Po in different type of fish in the Grundl, Zeller, Toplitz and Neusiedl lakes in Austria

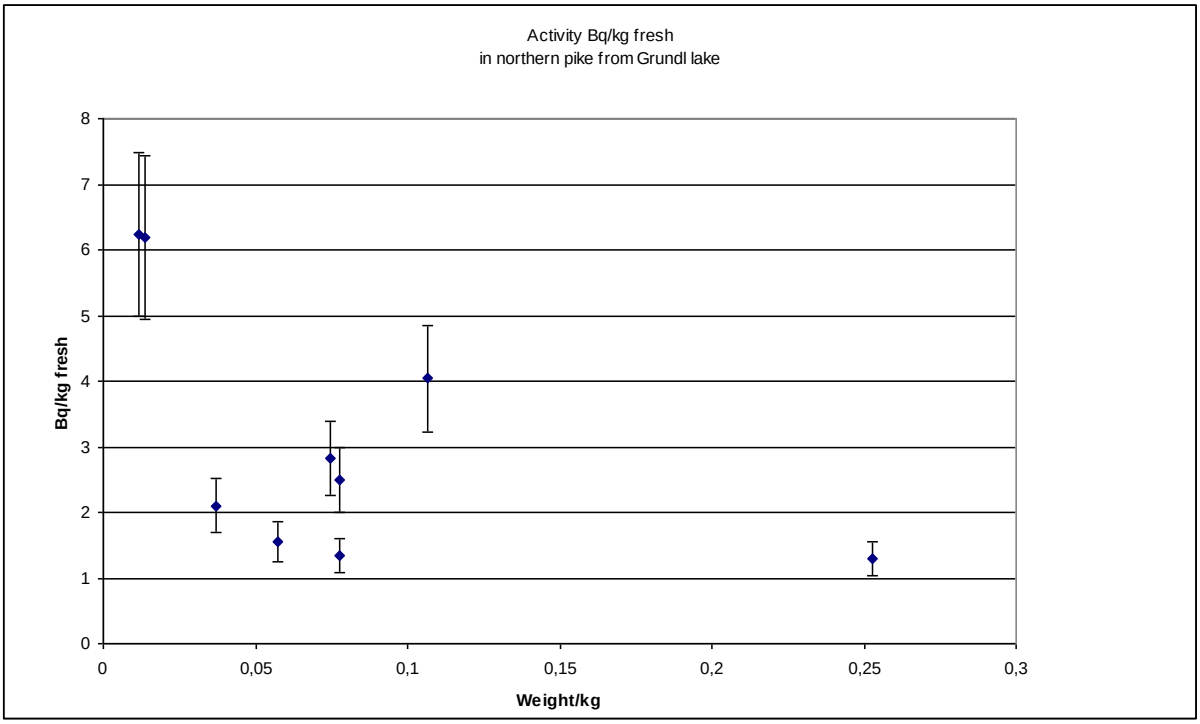


Fig. 3 210 Po Activity concentration in Northern pike in Grundl Lake variation with fish weight

Last but not least the ingestion dose by consuming these kinds of fish was calculated. Comparing with the results in the literature the above mentioned results are lower than the see water fish concentrations (Jahresbericht 2010, Kanton Basel-Stadt). According (Lebensmittelbericht Österreich 2010) the fresh water fish consume is only 5% of the fish consumed in Austria, which is up to 7,5 kg. Considering the ingestion dose conversion factor for $^{210}$Po 1,2 µSvBq$^{-1}$ (EU Directive 96/29/EURATOM) for adults (>17 years old) the ingestion dose is calculated 2,7 µSvyear$^{-1}$, while for children under 1 year the

ingestion dose conversion factor for $^{210}$Po is 26 µSvBq$^{-1}$. Considering the maximal fish consume for children the same as the adults we come up with a dose contribution of 58 µSv year$^{-1}$ for wild living fish.

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