Guide to the field sampling

Field sampling: (low tide)
Study Site: Huan Dong Romantic Line, Jimei

Field sampling session will occur in 3 rotating groups: 1. sediment sampling, 2. Submarine groundwater sampling, 3. Seawater sampling for ^{234}Th.

Students will be broken into three groups and go through training in each of sampling. We anticipate that there will be ~10 students per group.

The arrangements are as follows:

1) **Sediment sampling: Sabine Charmasson and Weifang Chen, Qikai Li**

   The Push corer and Russian Peat corer are utilized for extracting sediment cores from the beach.



   The sediment cores obtained from the Russian Peat corer will be cut *insitu* into 1 or 2 cm layers with a plastic knife.

   The sediment cores obtained from the push corer will be carefully sectioned into 1 or 2 cm layers using the Incremental Core Extruding Apparatus in the laboratory.

   Sediment sample preparation:

   The sample processing included freeze-drying, weighing, fine grinding, and sieving to a particle size of <1 mm. The moisture content of each sample was determined by the difference between its wet and dry weight. The dry bulk density values were estimated by dividing the total dry weight by the volume of each centimeter sediment layer.

   Instrumentation Analysis:

Gamma-ray energies at 46.5 keV, 351.9 keV, 661.6 keV and 59.5 keV were evaluated for the determination of ^{210}Pb, ^{214}Pb (assumed to be in secular equilibrium with its parent^{226}Ra) and ^{137}Cs for radiometric dating.

2) **Rhizon Pore Water Sampling**



Sampling: Pore water was collected from sediment cores using Rhizon soil moisture samplers (Rhizosphere Research Products, Wageningen, NL).

1. Sediment cores were first retrieved during low tide to minimize disturbance and stored vertically on ice in the dark until processing. A horizontal hole was pre-drilled into the core liner at the target depth using a sterile syringe needle or drill bit and sealed with tape before sampling.
2. Within 6 h of collection, a Rhizon SMS (0.12 µm pore size, 5 cm porous length) was carefully inserted horizontally into the sediment, taking care not to bend or kink the sampler. The Rhizon was allowed to equilibrate for 5–10 min before a sterile syringe or vacuum tube was connected to the outlet. Gentle negative pressure (approximately 0.4–0.8 bar) was applied to extract pore water; the

first 1–2 mL was discarded to purge dead volume and avoid contamination from the tubing and filter membrane.

3. Subsequent pore water was collected in acid-washed, pre-weighed vials and immediately stored on ice in the dark. Samples were processed for different analyses as required: aliquots for cation analysis were acidified to pH < 2 with ultrapure HNO_3, while those for anion or dissolved organic carbon analysis were left unacidified. All samples were frozen at –20 °C until laboratory analysis. Field blanks (ultrapure water passed through a new Rhizon) were collected periodically to monitor potential contamination.

   Instrumentation Analysis:

   $^{224}Ra/^{228}Th$ using a RaDeCC system

3) Submarine groundwater sampling (^{223}Ra, ^{224}Ra):
RaDeCC: Willard S. Moore, Guizhi Wang, Qing Li

Sampling:

1. Insert PushPoint (PP) sampler into sediments
2. Attach a large syringe and pull in a sample. If this does not work, fill the syringe with seawater and push this through the PP sampler to clear the slits.
3. Attach the PP sampler to a peristaltic pump or to a rigid carboy attached to a vacuum pump.
4. The ^{223}Ra and ^{224}Ra isotopes sample may be collected into a 5-10 L carboy or cubitainer and processed later or processed as it is collected.
5. Record the sampling date and time for each collected sample.

Short-lived Radium isotopes (^{223}Ra and ^{224}Ra) sample preparation:

1a. In the first case collect the entire sample and take aliquots for salinity, nutrients, and other measurements. Then using gravity pass it slowly (< 1 L/min) through a column filled with approximately 15 g of manganese-coated acrylic fiber (Mn-fiber) to extract radium isotopes. Carefully measure the volume processed.

1b. In the second case, attach the Mn-fiber column between the PP sampler and the carboy and slowly (< 1 L/min) collect the sample. Remove the Mn-fiber column and collect aliquots for other measurements. Measure the volume processed through the column.

Instrumentation Analysis:

As soon as possible, measure the short-lived Radium isotopes (^{223}Ra and ^{224}Ra) using a RaDeCC system.

A column filled with Mn-fiber to extract radium isotopes (^{223}Ra and ^{224}Ra). It is useful to place a small plug of raw acrylic fiber in the top of the column as a prefilter.

4) Seawater sampling for ^{234}Th： Ken O. Buesseler and Claudia Benitez-Nelson

MnO_2 precipitation

1. Four-liter seawater samples are collected, acidified with concentrated nitric acid (5 – 7 ml) to pH<2 and spiked with a known amount of ^{230}Th. Shake vigorously and allow equilibration(8h). The samples will be brought back to the lab.
2. After equilibration, raise the pH to 8.5 with concentrated ammonia (5-8 mL). The goal is to get the pH to a value of at least 8.0 but not higher than 9.0. If the pH is outside this range add a small amount of either acid or base to adjust it. Make sure to shake in between testing the pH. Record pH value on processing log
3. Using a manual 100 µL pipette or the electronic repeater pipette set to 100 µL increments add 100 µL of $KMnO_4$ (0.45 g/60 mL H_2O) to each sample
4. Make sure cap is secured and shake bottle 10 times by flipping it upside down quickly
5. Rinse the pipette tip with MQ water and then add 100 µL of $MnCl_2$ (1.2 g/60 mL H_2O) to each sample
6. Make sure cap is secured and shake bottle by flipping it upside down quickly
7. Let the sample rest for at least 8h prior to filtering.
8. Filter the precipitates and dry the filters overnight at 50°C to prepare for beta counting. Place filters in beta holders and cover with 1 layer of plastic film (can be saran wrap) and 2 layers of common aluminum foil (Reynolds regular).

Lab and instruments for practical:

1， LOW-LEVEL BETA GM Multicounter System Model RISO GM-25-5

Specifications:

4 sets for 20 samples simultaneously

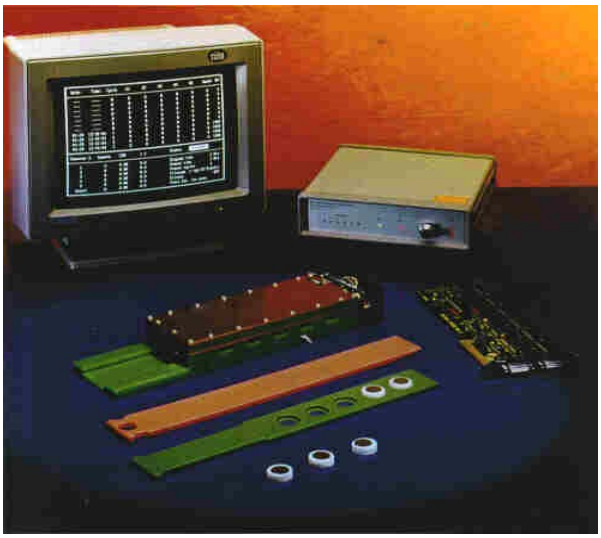
Sample size： 25mm. diameter

Background in 100mm lead shield: <0.2CPM(typically<0.15CPM)

Efficiency: 90Sr/Y: 54%
36Cl : 44%
99Tc : 42%

application: total and particulate Th-234





2，Alpha spectrometer system (Ortec OCTETE-PLUS, U.S.)

speciation:

4 sets for 16 samples simultaneously

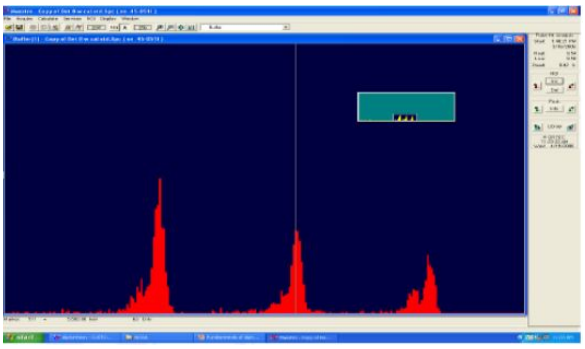
the energy resolution of the detector is <24 keV for ^{241}Am point source when the distance of detector-to-source is >detector diameter.

the detector efficiency is >25% for a distance of detector-to-source <10 mm and ^{241}Am point source.

the integrated background count is <1 h^{-1}

application: Th-228,230; Pb-210





3, High-purity Germanium (HPGe) Detectors (CANBERRA)

speciation:

4 sets: 3 for Germanium Well Detectors(GCW);

1 for Broad Energy Germanium Detectors (BEGe)

GCW: diameter-1.6cm; height-4cm

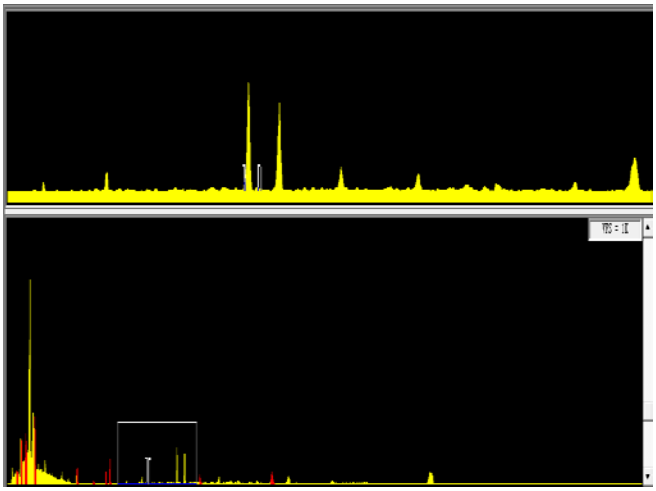
resolution: 1.4kev@122kev; 2.3kev@1332kev

BEG: area-50cm^2

resolution: 0.75kev@122kev; 2.2kev@1332kev

application: Ra-226/228; sediment dating





4,Radium delayed Coincidence Counter System

speciation:

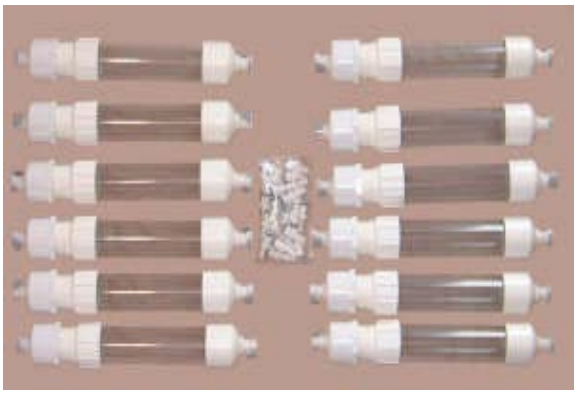
8 sets for 32 samples simultaneously

background: 0.01cpm~0.15cpm

total efficiency: 42%~47%

application: $^{223}Ra/^{224}Ra$，$^{228}Ra/^{228}Th$ in the water column\pore water\sediment





5, HR MC-ICPMS (Nu Plasma HR)

speciation:

Desolvation Nebulizer System

PFA nebulizer, ~80µL/min uptake rate

common Ni cones, glass torch

application: ^{239}/^{240}Pu,



Guide to the Lab Practical

1. Introduction

Three techniques can be applied to measure radioisotopes.

Bulk Radioactivity – measures some or all particles generated by the decaying nucleus. Examples include the geiger counter, scintillation detector, film emulsions, and track counters.

Specific Radioactivity – measure the energy or timing of particles emitted from the nucleus. For example, the energy of the alpha particle derived from ^{238}U decay is 4198 keV, slightly lower than the energy of the alpha particle that occurs from ^{234}U decay, 4774.6 keV. Variations in the energy of emission also occur with gamma-rays associated with radioactive decay. Alpha counting requires prior chemical separation of the isotopes from the matrix, while gamma counting can be conducted on bulk samples - gamma rays pass relatively easily through small amounts of matter.

Mass Spectrometer (MS) – measures the mass of the isotope. This requires extensive chemical separation prior to sample introduction into the mass spectrometer (e.g., Becker et al., 1999).

2. Lab practical

In this lab practical, three kinds of detectors will be introduced to the trainees, beta counters, radium delayed coincidence counter (RaDeCC, an alpha detector based on time rather than energy), alpha spectrometry and gamma spectrometry.

Beta counting is not isotope specific. It requires relatively simple equipment. A gas-flow anti-coincidence counter (another timing circuit) is often used and coupled with 10 cm lead shielding. This results in backgrounds of 0.15-0.20 cpm for a source of 25 mm diameter (Risø national laboratory, Roskilde, Denmark). It is the preferred method for ^{234}Th, and can be used with non-destructive techniques and onboard ship (Benitez-Nelson et al., 2011).

^{234}Th decays with relatively weak betas (maximum beta energy 0.20 MeV) to ^{234m}Pa, which is a high-energy beta emitter (maximum beta energy 2.29 MeV, half-life 1.17 min). Thus, if a filter is dried and carefully folded [possible with polycarbonate (e.g. nuclepore^{TM}) and GF/F filters, not with membrane filters, which will break] to fit the beta detector and covered with a thin foil, the beta activity measured is due mainly to ^{234m}Pa, with some contribution from ^{234}Th.

^{234}Th can be counted by non-destructive beta counting. In the open ocean, ^{234}Th activity usually overwhelms other isotopes that might contribute to the beta

signal from suspended particles, like ^{40}K or ^{210}Pb. This should be checked occasionally by following the decay over several months. If the activity does not decline with the half-life of ^{234}Th (24.1 day), this is an indication of radioactive decay contributions from other radionuclides.

The RaDeCC System: RaDeCC can be used to measure ^{223}Ra and ^{224}Ra and was developed by Moore and Arnold (1996). It is an example of a timing circuit. Briefly, the short -lived Rn daughters of ^{223}Ra and ^{224}Ra are swept into a scintillation detector where alpha decays of Rn and Po occur. Signals from the detector are sent to a delayed coincidence circuit, which discriminates decays of the ^{224}Ra daughters, ^{220}Rn and ^{216}Po, from decays of the ^{223}Ra daughters, ^{219}Rn and ^{215}Po. Because of its extremely low background, concentrations of ^{224}Ra and ^{223}Ra of a few hundred atoms per liter may be measured easily. The method may be extended to measurements of ^{227}Ac, ^{231}Pa, ^{228}Th, and ^{228}Ra.

Gamma spectrometry allows identification of a wide range of isotopes without chemical purification and is the ideal method for non-destructive techniques, e.g., ^{210}Pb in sediments (Cutshall et al., 1983) and dissolved ^{226}Ra and ^{228}Ra (Moore, 1984). Inherent (cosmic-ray and Compton) background and self-absorption by the sample, energy- and geometry-dependent detector efficiencies, coupled with low gamma branching ratios for some elements, reduces the sensitivity and accuracy of the method. These effects are evaluated using standards specific to each radionuclide and incorporated into a factor that translates cpm into dpm. The overall efficiency is generally low compared to other techniques.

Alpha spectrometry,

alpha spectrometry is characterized by good isotope separation, uniform (i.e., energy and isotope independent) detector efficiency and very low background (typically on the order of 0.001-0.003 cpm (counts per minute) for the 4-8 MeV energy range of a new surface barrier detector, increasing with time as a result of the accumulation of recoil products from measured samples). It allows precise measurements at low activities, and easy calibration with yield tracers. Alpha particles have a very short range. They are absorbed or slowed down by interaction with the sample material or by impurities on the source, the flat planchet with the purified element plated on it. The technique is therefore not practical for non-destructive measurements. Best results in terms of efficiency and energy resolution are obtained with clean sources prepared from well-purified samples.

For each instrument, detailed instructions are as below.

RaDeCC (Scientific Computer Instruments, Radium Delayed Coincidence Counter)

1) Sample processing

Groundwater samples are passed through a MnO_2-impregnated acrylic fiber (Mn-fiber) column to extract the dissolved radium at a flow rate of less than 1 L min^{-1}. The Mn-fiber is then rinsed with Ra-free water and partially dried to ~1:1 weight Mn-fiber to water with a stream of air, then ^{223}Ra and ^{224}Ra are measured .

2) Measurement protocol

2.1) Measurement of background

a. After each sample run, stop the pump, remove the sample from RaDeCC, then turn on the pump for 5-10 minutes to remove excess water from the line.

b. While the pump is running, open the program and input the recording time interval (10 minutes) in each channel. (The program remembers the last time interval selected, so this is not usually necessary.) Save data file as "bkgN_measurement_time" (N is the channel Number.). Click the "save" icon in each channel to start the test.

c. If the count rate in the "total" channel is >2 cpm after 10 minutes, turn off the pump, connect an empty column, and purge the system with He for 1 minute. Turn off the valve on the He cylinder then switch the valve on RaDeCC from "purge" to "run". Turn on the pump and reset the counter. This will determine if the excess background comes from the lab air or decay products still in the detector. If the total is still >2 cpm, wait 20 minutes, stop the count, and restart the counter with a new file name (no He purge is necessary). This should bring the total <2 cpm for a 10-minute count.

2.2) Measurement of Mn fiber samples

a. Connect the Mn-fiber column to RaDeCC. Save the data file as "station_sampling_time_measurement_time". Click the "save" icon in each channel to start the test. Turn the valve on RaDeCC to "purge". Multiple samples can be purged simultaneously. Open the He cylinder gently to keep the ball standing in the position of "6 LPM" for 1 minute. It is convenient to use the time since "save" to time the purge.

b. After 1 minute He purge, turn off the valve on the He cylinder, then switch the valve on RaDeCC from "purge" to "run". Turn on the pump.

c. After 5 minutes, reset the counter. The 5-minute delay allows the ^{220}Rn in the He stream to equilibrate with the ^{224}Ra on the fiber. Accumulate the counts (see 2.3).

d. If the flow rate increases significantly during the run, this indicates a leak. If this occurs, make a note in the program, and stop the run. Check for the source of the leak, or yell Help.

e. If there are no leaks, click the "stop" icon in each channel to stop the test. The

timing for each run is in 2.3.

2.3) Measurement duration

Because ^{224}Ra will usually be much greater than ^{223}Ra, ^{228}Th, and ^{227}Ac, we count the sample 4 times. The first count measures ^{224}Ra, the second is about 1 week later when ^{224}Ra has decreased by ~75% but ^{223}Ra has only decreased ~35%. After 4 weeks the ^{224}Ra is <1% of its original activity, so the 3rd count measures the activity of ^{224}Ra supported by its parent, ^{228}Th. Likewise, after 3 months the ^{223}Ra is <1% of its original activity, so the 4th count measures ^{227}Ac.

a. 1st run counts in 220 channel is 800.
b. 2nd run counts in 219 channel is 200; or measure for 500 min for low activity samples.
c. 3rd run counts in 220 channel is 500; or measure for 500 min for low activity samples.
d. 4th run counts in 219 channel is 200; or measure for 500 min for low activity samples.

3) Calculation

See the spreadsheet.

Alpha spectrometry

1) Preparation
   Plate
2) Sample processing

The procedure is reliable, but rather time consuming.

a) Add 228Th spike solution in MnO_2 precipitation. Remove Mn^{2+} using $Fe(OH)_3$ precipitation followed by ion-exchange chemistry.

b) Take up precipitate, $Fe(OH)_3$, in 9 mol/L HCl. The solution should be 9 mol/L HCl and have a volume of approx. 30 mL. Allow some time for complete dissolution.

c) Run a chloride column, using a wide (15 mm ø) column because a large amount of Fe has to be retained on the resin.

d) Evaporate eluate of chloride column. Dissolve in 8 mol/L HNO_3 and run a nitrate column. Collect the 8M HNO_3 eluate in a Teflon beaker. Repeat running the nitrate column if the sample is not clean enough.

e) Plate Thorium . Count 230Th/ 228Th in the alpha spectrometer.

3) Measurement protocol

a) Set on the alpha spectrometer, the vacuum pump and the computer after washing the detector chamber with water-free alcohol (Watch out for the volume of vacuum oil).

b) Put the samples in the chamber and close it.

c) Switch to "pump" and Click "acquire→ property" to input the sample information, and observe the vacuum status.

d) Click "acquire→ property→ voltage" to set up high voltage if the vacuum status is lower than 100 mT.

e) Click the "go" button to start the measurement.

f) Click the "stop" button to stop the measurement if the count number is satisfied.

g) Click the "clear" button to clear off the previous spectrogram for the next measurement.

h) Any wet experiment and usage of water be forbidden in the lab.

4) Calculation

See the spreadsheet.

Gamma-Ray Spectrometers (Canberra Industries, Inc.)

The relative humidity in the room is less than 60% and any wet experiments are forbidden. Make sure that there is always enough liquid N2 in the 30-L Dewar to keep the detector work well. Fill liquid N2 every week and keep a record each time.

1) Measurement protocol

- For ^{210}Pb a single peak at 45 keV with an intensity of 4.05% is used.
- For ^{137}Cs the energy is 661 keV (85.1% intensity).
- For ^{226}Ra, the primary energies are 295.2 (^{214}Pb), 351.99 (^{214}Pb) and 609.32 keV (^{214}Bi).
- For ^{228}Ra, the energies of 338.4 (^{228}Ac) and 911.07 keV (^{228}Ac) are used.

a. Input Detector

Open the program "Gamma Acquisition & Analysis (GAA)" in software "Genie 2000"

Click "File Open Data source"

Choose the detector connected with the computer.

b. Set up high voltage

Click "GAA→ MCA→ adjust" to input high voltage.

c. Edit sample information

Click "GAA→ Edit→ Sample Info" to edit sample title, description.

d. Open the door of the lead shield gently, put the sample vial in the middle of the detector. The vial must be dry.

e. Start analysis: Click "GAA→ Acquire→ start".

f. Stop analysis: Click “GAA→ Acquire→ stop” and “save as” to save the file.

g. Clear the finished spectroscopy to start a new test, click “GAA→ Acquire→ Clear".

2) Calculation

See the spreadsheet.

Beta RISO counter (Riso National Laboratory, Technical university of Denmark, Low-level beta multicounter system model Riso GM-25-5)

1) Measurement protocol

a. Adjust the pressure of gas cylinder (99% Argon+1% Iso-propane) to 0.02 MPa

b. Set up the computer and beta counter. Control the gas valve to purge the system for ~2 h

c. Reduce the gas speed to 60 bubbles per minute, and purge for ~6 h

d. Put the ^{99}Tc into the 5th place of the sample plate

e. Click "SETUP HV” button to set up high voltage (1100-1400 V)

f. Set up a file with 3 sub-catalogs (. data, .check, .runinfo) in order to save data

g. Put the sample into the plate, and input its measuring cycle, measuring time, and sample information

h. The character string of file name should be less than 8

2) Calculation

A=(A0-A1)/recovery/beta efficiency/b

A0: activity at sampling

A1: activity after six months, i.e., background

Recovery: derived from ^{230}Th

b: correction factor including ingrowth and decay