Foreword for the 3\textsuperscript{rd} edition

Under the academic/social needs to cope with global environmental problem such as climate changes and ocean acidification, technical innovation on ocean observations have been progressed rapidly in recent years. Progresses are also ongoing in the field of world-wide organization of ocean observation by using common observation procedures and standard/reference materials because it is obviously vital to publish data that guarantees traceability and comparability with appropriate reference materials or certified reference materials and that is clear about its uncertainties. Aiming to catch up such year-to-year progress in the ocean observations field, and to provide state-of-the-art guideline of ocean observations to the communities, the Oceanographic Society of Japan (JOS) has established the editorial committee of Guideline of Ocean Observations in 2015, and published the Guideline of Ocean Observations describing the most up-to-date oceanographic observation methods and analytical techniques. The first edition of this Guideline of Ocean Observations were published in September 2015.

In the 2\textsuperscript{nd} edition, several improvements had made in the table-of-contents page, reflecting the addition of authors and reviewers in some chapters. Some descriptions regarding sea ice observations (Vol.7, Chap.5) had updated reflecting the changes in terminology of sea ice by WMO Sea-Ice Nomenclature (2014). Also, link address of “Guide to best practice for ocean CO\textsubscript{2} measurements” in Vol.3 had changed from Carbon Dioxide Information Analysis Center (CDIAC) to the Ocean Carbon Data System located within the NOAA National Centers for Environmental Information (NOAA-OCADS). Several chapters in sediment observation (Vol.5) and natural/artificial radioactivity (Vol.9) are also added.

In this 3\textsuperscript{rd} edition, several improvements had also made in the table-of-contents page, reflecting the addition of authors and reviewers in some chapters. We hope that these guidelines will be used by many researchers worldwide and will contribute to the advance of oceanography.

Thereafter this Guideline in English version will be renewed under the review of the editorial committee, updating description corresponding to technical progresses as well as adding new observation items if necessary.

Editor in chief for 3\textsuperscript{rd} edition
Guideline of Ocean Observations
Tsuneo Ono
Foreword for the 2nd edition

Under the academic/social needs to cope with global environmental problem such as climate changes and ocean acidification, technical innovation on ocean observations have been progressed rapidly in recent years. Progresses are also ongoing in the field of world-wide organization of ocean observation by using common observation procedures and standard/reference materials because it is obviously vital to publish data that guarantees traceability and comparability with appropriate reference materials or certified reference materials and that is clear about its uncertainties. Aiming to catch up such year-to-year progress in the ocean observations field, and to provide state-of-the-art guideline of ocean observations to the communities, the Oceanographic Society of Japan (JOS) has established the editorial committee of Guideline of Ocean Observations in 2015, and published the Guideline of Ocean Observations describing the most up-to-date oceanographic observation methods and analytical techniques. The first edition of this Guideline of Ocean Observations was published in December 2016. Thereafter this Guideline is renewed every year under the review of the editorial committee, updating description corresponding to technical progresses as well as adding new observation items if necessary.

In this 2nd edition, some descriptions regarding sea ice observations (Vol.7, Chap.5) had updated reflecting the changes in terminology of sea ice by WMO Sea-Ice Nomenclature (2014). Also, link address of “Guide to best practice for ocean CO$_2$ measurements” in Vol.3 had changed from CDIAC to NOAA-OCADS.

Several chapters in Sediment Analysis (Vol.5) and Natural and artificial radioactivity (Vol.9) are added as well as other small additions.

We hope that these guidelines will be used by many researchers worldwide and will contribute to the advance of oceanography.

Editor in chief for 2nd edition
Guideline of Ocean Observations
Tsuneo Ono
Foreword

Measures to mitigate and adapt to climate change are urgently needed; the importance of understanding the state of climate change in the oceans is rising. In monitoring environmental changes at the global scale, it is obviously vital to publish data that guarantees traceability and comparability with appropriate reference materials or certified reference materials and that is clear about its uncertainties.

In recent years we have been building our knowledge of changes within the oceans through international cooperation and collaboration, for example, by re-occupation of World Ocean Circulation Experiment (WOCE); our findings were cited in the Fifth Assessment Report from the IPCC. To implement plans to make all measurement values used in climate change research completely SI-traceable, the General Conference on Weights and Measures has been providing advice to relevant institutions. Through measures such as promulgating the use of standard materials for nutrients, we are making progress in comparability of data, research that depends on this comparability, and R&D on standard materials.

However, the guidelines used for measurement and analysis do not seem to be keeping up with this progress. The Oceanographic Observation Guidelines published by the Japan Meteorological Agency in 1999 are relatively widely used in Japan, but their content is not always completely up-to-date and the Guidelines are now quite hard to obtain. In 2010, the WOCE Manual was revised and published as the GO-SHIP Oceanographic Observation Manual (IOCCP Report No.14, 2010), but this is principally for repeat hydrography in the open ocean; it was not intended to guide a wide range of users. There are a number of other manuals and guidelines available but some of them are only written in Japanese, whereas others are only written in English; moreover, they mix together up-to-date content and less up-to-date content.

In this context, the Oceanographic Society of Japan (JOS) has decided to set up an editorial committee for oceanographic observation guidelines, to review and collate the various existing guidelines, and to incorporate necessary revisions and fill in any gaps. We will publish Oceanographic Observation Guidelines describing the most up-to-date
oceanographic observation methods and analytical techniques, and we will make these new guidelines available through the JOS website.

We intend to continuously update these guidelines so that the most up-to-date methods are always accessible. We hope that these guidelines will be used by many researchers worldwide and will contribute to the advance of oceanography.

Editor in chief
Oceanographic observation guidelines

Takeshi Kawano
List of the authors at the time of writing

Michio AOYAMA  Japan Agency for Marine-Earth Science and Technology/Institute of Environmental Radioactivity, Fukushima University
Sanae CHIBA  Japan Agency for Marine-Earth Science and Technology
Fuminori HASHIHAMA  Tokyo University of Marine Science and Technology
Masao ISHII  Meteorological Research Institute, JMA
Hideki KAERIYAMA  Japan Fisheries Research and Education Agency
Kenichi KATAYAMA  Marine Works Japan Ltd.
Takeshi KAWANO  Japan Agency for Marine-earth Science and Technology
Shigeaki KOJIMA  Graduate School of Frontier Sciences / Atmosphere and Ocean Research Institute, The University of Tokyo
Naohiro KOSUGI  Meteorological Research Institute, JMA
Shinya KOUKETSU  Japan Agency for Marine-earth Science and Technology
Hiroshi MATSUNAGA  Marine Works Japan Ltd.
Yutaka MICHIDA  Atmosphere and Ocean Research Institute, the University of Tokyo
Takashi MIYAO  Japan Meteorological Agency
Toshiya NAKANO  Japan Meteorological Agency
Shinichiro NAKAOKA  National Institute for Environmental Studies
Hisashi NARITA  Tokai University
Hajime OBATA  Atmosphere and Ocean Research Institute, the University of Tokyo
Shigeyoshi OTOSAKA  Japan Atomic Energy Agency
Satoshi OZAWA  Marine Works Japan Ltd.
Hiroaki SAITO  Atmosphere and Ocean Research Institute, the University of Tokyo
Daisuke SASANO  Meteorological Research Institute
Mitsuhide SATO  Graduate School of Agricultural and Life Sciences, the University of Tokyo
Souichiro SUEYOSHI  Nippon Marine Enterprises, Ltd.
Toshio SUGA  Graduate School of Science and Faculty of Science, Tohoku University
Toru SUZUKI  Marine Information Research Center, Japan Hydrographic Association
Takenobu TOYOTA  Hokkaido University
Hiroshi UCHIDA  Japan Agency for Marine-Earth Science and Technology
Yu UMEZAWA  Graduate School of Fisheries and Environment Sciences, Nagasaki University
Taichi YOKOKAWA  Japan Agency for Marine-Earth Science and Technology
Takeshi YOSHIMURA  Central Research Institute of Electric Power Industry
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List of the reviewers at the time of review work

<table>
<thead>
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<th>Name</th>
<th>Institution</th>
</tr>
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<td>Michio AOYAMA</td>
<td>Japan Agency for Marine-Earth Science and Technology/</td>
</tr>
<tr>
<td></td>
<td>Institute of Environmental Radioactivity, Fukushima University</td>
</tr>
<tr>
<td>Ken IKEHARA</td>
<td>National Institute of Advanced Industrial Science and Technology</td>
</tr>
<tr>
<td>Tsuyoshi MATSUMOTO</td>
<td>Ryukyu University</td>
</tr>
<tr>
<td>Jun NISHIOKA</td>
<td>Hokkaido University</td>
</tr>
<tr>
<td>Stephen OBROCHTA</td>
<td>Akita University</td>
</tr>
<tr>
<td>Yugo SHIMIZU</td>
<td>Japan Fisheries Research and Education Agency</td>
</tr>
<tr>
<td>Hiroshi UCHIDA</td>
<td>Japan Agency for Marine-earth Science and Technology</td>
</tr>
<tr>
<td>Kazuyuki UEHARA</td>
<td>Tokai University</td>
</tr>
<tr>
<td>Shuki USHIO</td>
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Radiometric determination of anthropogenic radionuclides in seawater samples

Michio Aoyama (Institute of Environmental Radioactivity, Fukushima University)

Abstract

Anthropogenic radionuclides in seawater have been concerned with their ecological effects and oceanographically used as a tracer. Current concentrations of anthropogenic radionuclides in the oceanic waters are generally extremely low except areas affected by Fukushima Dai-ichi Nuclear Power plants accident in 11 March 2011. Determination of anthropogenic radionuclides in seawater has been traditionally performed with radiometric method such as $\gamma$-spectrometry, $\beta$-counting and $\alpha$-spectrometry. The radiometric method is still a useful tool to determine concentrations of anthropogenic radionuclides, although recently mass spectrometric methods have been developed extensively. In this paper, the radiometric methods to determine typical anthropogenic radionuclides, $^{137}$Cs and $^{90}$Sr in seawater, which includes recent development of the radiometric methods such as extremely low background $\gamma$-spectrometry are presented.

Keywords: Anthropogenic radionuclides; $^{137}$Cs; $^{90}$Sr, Radioanalytical method

1. Introduction

Huge amounts of anthropogenic radionuclides have been introduced in marine environments as global fallout of the large-scale atmospheric nuclear-weapon testing, discharge from nuclear facilities and ocean dumping of nuclear wastes (UNSCEAR, 2000) and Fukushima Dai-ichi Nuclear Power plants accident. The radiological and ecological effects of anthropogenic radionuclides are still world concern. To assess the marine environmental effects of anthropogenic radionuclides, it is significant to clarify their behavior and fate in the marine environments. Therefore, concentrations of anthropogenic radionuclides in seawater are an important tool to evaluate the ecological effect of anthropogenic radionuclides.

$^{137}$Cs is one of the most important anthropogenic radionuclides in the field of environmental radioactivity because of a long physical half-life of 30.2 years. It is a major fission product (fission yield: 6-7 %) from both plutonium and uranium (UNSCEAR, 2000). $^{137}$Cs in the ocean has been mainly derived from global fallout (Reiter, 1978; Bowen et al., 1980; UNSCEAR, 2000; Livingston and Povinec, 2001; Aoyama et al., 2006), together with close-in fallout from the Pacific Proving Ground nuclear explosions (Bowen et al., 1980; Livingston et al., 2001), discharge of radioactive wastes from nuclear facilities and others (Sigiura et al., 1976; Pentreath, 1988; Hirose et al., 1999). $^{137}$Cs in seawater has been determined since 1957 to elucidate radioecological effects of anthropogenic radioactivity in the marine environment (Miyake & Sugiuera, 1955; Rocco & Broecker, 1963; Shirasawa & Schuert, 1968; Bowen et al., 1980; Folsom, 1980; Nagaya & Nakamura, 1987a; 1987b; Miyake et al., 1988; Hirose et al., 1992; Aoyama & Hirose, 1995; Hirose et al., 1999; Aoyama et al.,
2000; Aoyama et al., 2001; Aoyama & Hirose, 2003; Hirose & Aoyama, 2003a; Hirose & Aoyama, 2003b; Ito et al., 2003; Povinec et al., 2003; 2004; Hirose et al., 2005, Aoyama et al., 2008a; 2009; 2012a; 2012b; 2013, 2016). Additionally, $^{137}\text{Cs}$ in seawater is a powerful chemical tracer of water mass motion at the time scale of several decades (Bowen et al., 1980; Folsom, 1980; Miyake et al., 1988; Miyao et al., 2000; Tsumune et al., 2001; Tsumune et al., 2003a; 2003b; Aoyama et al., 2008a, Tsumune et al., 2011) because most of the $^{137}\text{Cs}$ in water columns is present as a dissolved form. Another advantage of the use of $^{137}\text{Cs}$ as an oceanographic tracer is the quantity and accessibility of marine radioactivity during the past four decades in contrast with other chemical tracers such as CFCs (Warner et al., 1996).

Another important fission product is $^{90}\text{Sr}$, which is $\beta$-emitter with a half-life of 28.8 years. It has been believed that the oceanic behavior of $^{90}\text{Sr}$ is very similar to that of $^{137}\text{Cs}$ because both $^{137}\text{Cs}$ and $^{90}\text{Sr}$, a typical no particle-reactive element, exist as an ionic form in seawater. In contrast of $^{137}\text{Cs}$, measurements of $^{90}\text{Sr}$ in seawater are generally inconvenient because of complicated radioanalytical processes. For this reason, it has been performed to estimate $^{90}\text{Sr}$ activity from $^{137}\text{Cs}$ activity using a certain radioactivity ratio (eg 1.6) without measuring $^{90}\text{Sr}$. However, the behavior of $^{90}\text{Sr}$ in the ocean differs from that of $^{137}\text{Cs}$; for example, a significant amount of $^{90}\text{Sr}$ has been introduced to the ocean via river discharge in contrast of $^{137}\text{Cs}$ (Livingston, 1988), which is tightly retained in soil mineral surface. In fact, the $^{90}\text{Sr}/^{137}\text{Cs}$ ratios in oceanic waters varied spatially and temporally. $^{90}\text{Sr}$ may be considered to be a tracer of effect of river discharge to the ocean. These findings suggest that there is a need independently to determine $^{90}\text{Sr}$ in seawater.

In this paper, improved radiometric methods of $^{137}\text{Cs}$ and traditional radiometric method for $^{90}\text{Sr}$ in seawater are presented.

2. Analytical method of $^{137}\text{Cs}$ in seawater

2-1 Background

$^{137}\text{Cs}$ decays to stable $^{137}\text{Ba}$ to emit $\beta$-ray (188 keV) and $\gamma$-ray (661.7 keV). Cs, which exists ionic form in the natural water, is one of the alkali metals and chemically shows less affinity with other chemicals. The concentration of stable Cs in the ocean is only 3 nM. Known adsorbents to collect Cs in seawater are limited; ex., ammonium phosphomolybdate (AMP) and hexacyanoferrate compounds (Folsom & Sreekumaran, 1966; La Rosa, et al., 2001). The AMP has been an effective ion exchanger of alkali metals (Van R. Smit, et al., 1959). It has been known that AMP forms insoluble compound with Cs. AMP, therefore, has been used to separate other ions and concentrate Cs in environmental samples. In the late 1950s, determination of $^{137}\text{Cs}$ in seawater was carried out with $\beta$-counting because of underdevelopment of $\gamma$-spectrometry. Two to several ten mg of Cs carrier is usually added when the radiocaesium is determined by $\beta$-counting because of formation of precipitate of Cs$_2$PtCl$_4$ and calculation of chemical yields of caesium throughout the procedure (Yamagata & Yamagata, 1958; Rocco & Broecker, 1963). After the development of $\gamma$-spectrometry using Ge detectors, the AMP procedure with $\gamma$-spectrometry became a convenient concentration procedure for the determination in
the environmental samples.

Traditionally (AMP) method was believed as adsorption method (Wong et al., 1994), therefore a receipt of AMP method was very simple that pH should be adjusted between 1 and 4 by nitric acid and AMP of 0.2 g per 1 liter sample was added without stable caesium carrier. In a modified method (Baskaran et al., 2009), they recommended to add 20 mg of stable Cs carrier to the sample, however, they did not care about stoichiometry between AMP and Cs.

In Japan, the AMP method is recommended for radiocaesium measurements in seawaters, in which Cs carrier is stated to be unnecessary (Science and Technology Agency, 1982). It, however, must be noted that large volumes of seawater samples (more than 100 liters) were required to determine $^{137}$Cs because of relatively low efficiency of Ge-detectors (around 10%).

In the previous literatures, the weight yield of AMP has not been use because the chemical yield of Cs could be obtained and the loss of small amount of AMP during the treatment did not cause serious problems. Actually, the use of AMP reagent produced in the 1960s and in the mid 1980s gave the range from 70% to 90 % as weight yields of AMP without Cs carrier in the laboratory experiment in 1996. These weight yields are in good agreement with the records of weight yields of AMP in our laboratory during the 1970s and 1980s. However, the weight yield of AMP without Cs carrier had been decreasing from the end of the 1980s and it sometimes became very low, less than 10%, in the mid 1990s. To improve $^{137}$Cs determination in seawater, Aoyama et al. (2000) and Aoyama and Hirose (2008b) re-examined the ammonium phosphomolybdate (AMP) procedure. Their experiments revealed that the stable Cs carrier of the same equivalent amount as AMP, 1 mol of Cs and 1 mol of AMP, is required to form insoluble the Cs-AMP compound in an acidic solution (pH = 1.2 to 2.2). Therefore, it can be said that the AMP extraction method is by generation of insoluble compounds by chemical reaction, not adsorption method. The improved method has been achieved to have high chemical yields of more than 95% for sample volumes of less than 100 liters. Another improvement is to succeed to reduce the amount of AMP from several ten grams to 4 grams to adsorb $^{137}$Cs from seawater samples. As a result, it has been reduced the sample volume from around 100 liters to less than 20 liters to be able to use high-efficiency well-type Ge-detectors. This improvement of $^{137}$Cs is favorable to use the chemical tracer of $^{137}$Cs in the oceanographic field.

However, there was another serious problem regarding the $^{137}$Cs measurement; i.e., large-volume sampling of more than 100 liters has been required to determine $^{137}$Cs concentrations in deep waters because of very low concentrations of $^{137}$Cs (less than 0.1 Bq m$^{-3}$). A major problem not to improve sensitivity of high-efficiency well-type Ge-detectors results in higher background accompanied with $\gamma$-spectrometry in ground-level laboratories. Especially, it is difficult to determine accurate $^{137}$Cs concentrations in deep waters (>1000 m) because of the difficulty acquiring large, non-contaminated samples. However, recently, Komura (Komura, 2004; Komura & Hamajima, 2004) has established an underground facility (Ogoya Underground Laboratory: OUL) to achieve extremely low background $\gamma$-spectrometry using Ge detectors with high efficiency and low background materials.

The OUL has been constructed in the tunnel of former Ogoya copper mine (235m height from sea

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level, Ishikawa prefecture) in 1995 by Low Level Radioactivity Laboratory, Kanazawa University. Depth of the OUL is 270 meters water equivalent and contributions of muon and neutron are more than two orders of magnitude lower than those at ground level. In order to achieve extremely low background \(\gamma\)-spectrometry, high efficiency well type Ge detectors specially designed for low level counting were shielded with extremely low background lead prepared from the very old roof tile of the Kanazawa Castle. As a result, background of \(\gamma\)-ray corresponding to an energy range of \(^{137}\text{Cs}\) is two orders of magnitude lower than that in ground-level facilities. A detection limit of \(^{137}\text{Cs}\) at the OUL is 0.18 mBq for a counting time of 10000 minutes (Hirose et al., 2005). And an underground laboratory at Mol, Belgium, a detection limit of \(^{137}\text{Cs}\) is 0.1 mBq as measured for 2 weeks (Lutter et al., 2015).

There is a residual problem of underground \(\gamma\)-spectrometry for \(^{137}\text{Cs}\) measurements. AMP adsorbs trace amounts of potassium when Cs is extracted from seawater because K is a major component in seawater and radioactive potassium \(^{40}\text{K}\) contains 0.0118 % of total in the natural materials. Trace amounts of \(^{40}\text{K}\) cause elevation of background corresponding to energy range of \(^{137}\text{Cs}\) due to Compton scattering of \(^{40}\text{K}\). If \(^{40}\text{K}\) can be removed in AMP/Cs compound samples, the full performance of underground \(\gamma\)-spectrometry for \(^{137}\text{Cs}\) measurements is established. To remove \(^{40}\text{K}\) from the AMP/Cs compound, a precipitation method including insoluble platinate salt of Cs was applied for purification of Cs. This method performed to be able to trace amounts of \(^{40}\text{K}\) from the AMP/Cs compound with a chemical yield of around 90 % for \(^{137}\text{Cs}\) (Hirose et al., 2008).

2-2 Sampling and materials

Seawater samples should be collected without contamination. When using a CTD-rosette sampler, which collected seawater of each 12 liters at 24 -36 different depth layers, before sample seawater collection outside of the sampler bottles should be washed by clean water. When use a bucket, the bucket should be rinsed a few time before sample seawater collection.

In general, sample seawater should be filtered using a filter with pore size of 0.45 micrometer.

All reagents used for \(^{137}\text{Cs}\), \(^{90}\text{Sr}\) and Pu assay are special (G.R.) grade for analytical use. All experiments and sample treatments are carried out at ambient temperatures. It is very important to know background \(\gamma\) activity of reagents. For example (Aoyama and Hirose, 2008b), the \(^{137}\text{Cs}\) activity in CsCl was less than 0.03 mBq g\(^{-1}\) by using extremely low background \(\gamma\)-spectrometry and the \(^{137}\text{Cs}\) activity in AMP was less than 0.005 mBq g\(^{-1}\), respectively. There is no serious contamination of \(^{137}\text{Cs}\) from other reagents before the Fukushima accident in march 2011. It is however that in some of the commercially available AMP reagent which were produced after the Fukushima accident, a clear peak of \(^{137}\text{Cs}\) was observed which indicated contamination due to the accident. Therefore specila attention is required for use them..

2-3 Recommended AMP procedure

Proposed improved AMP procedure with the ground-level \(\gamma\)-spectrometer is as follows:

1) Measure the seawater volume (5-100 liters) and put into a tank with appropriate size.
2) pH should be adjusted to be 1.6-2.0 by adding concentrated HNO₃ (addition of 40 ml conc. HNO₃ for 20 litre seawater sample makes pH of sample seawater about 1.6).

3) Add CsCl of 0.26g and stir at a rate of 25 litre per minute or alternative method for one hour.

4) Weigh AMP of 4g and pour it into a tank to disperse the AMP with seawater.

5) 1 hour stirring at the rate of 25 litre air per minute or alternative method.

6) Settle until the supernate becomes clear. A settling time is usually 6 hours to overnight, but no longer than 24 hours.

7) Take an aliquot of 50 ml supernate to calculate the amount of the residual caesium in the supernate.

8) Loosen the AMP/Cs compound from the bottom of the tank and transfer into a 1-2 litre of beaker, if it is necessary do additional step of decantation.

9) Collect the AMP/Cs compound onto 5B filter by filtration and wash the compound with 1M HNO₃

10) Dry up the AMP/Cs compound for several days in room temperature

11) Weigh the AMP/Cs compound and determine weight yield. This weight yield should be consistent within uncertainty with a chemical yield obtained by measured stable Cs concentration in the supernat collected as step 7)

12) Transfer the AMP/Cs compound into a Teflon tube of 4ml volume and subject to γ-ray spectrometry

2-4 Underground γ-spectrometry procedure

13) the same procedure from step 1) to step 12)

14) Dissolve AMP/Cs compound by adding alkali solution, NaOH

15) Adjust the volume of solution ca. 70 ml and boiling to form Mo₂O₃ precipitate for 30 min.

16) pH should be adjusted to be ca. 8.1 by adding 2M HCl and adjust the volume of solution ca. 40 ml. Then keep room temperature 30 min. This solution should be kept one night in the refrigerator. Remove formed Mo₂O₃ precipitate by filtration using 5C

17) Adjust the volume of solution ca. 70 ml and pH should be adjusted to be ca. 8.1

18) Perform precipitation of Cs₂Pt(Cl)₄ to add chloroplatinic acid (1g/5ml D.W) at pH = 8.1 and keep in refrigerator during a half-day.

19) Collect the Cs₂Pt(Cl)₄ precipitate onto filter by filtration and wash the compound with solution (pH = 8.1)

20) Dry up the Cs₂Pt(Cl)₄ precipitate for several days in room temperature

21) Weigh the Cs₂Pt(Cl)₄ precipitate and determine weight yield

22) Transfer the Cs₂Pt(Cl)₄ precipitate into a Teflon tube of 4ml volume and subject to underground γ-spectrometry
2-5 Images of recommended AMP procedure and underground $\gamma$-spectrometry procedure at selected step

**Figure 1** Formed AMP/Cs compound at step 3

**Figure 2** Formed AMP/Cs compound at step 5
Figure 3 Formed AMP/Cs compound at step 10

Figure 4 Dissolve AMP/Cs compound by adding alkali solution at step 14

Figure 5 Formed Mo$_2$O$_3$ precipitate at step 16

Figure 6 The Cs$_2$Pt(Cl)$_4$ precipitate at step 18
3. Analytical method of $^{90}$Sr

3-1 Background

$^{90}$Sr decays to stable $^{90}$Zr via $^{90}$Y (half life: 2.67 day) with $\beta$ emitter (934 keV) to emit $\beta$-ray (196 keV). Strontium comprises about 0.025 percent of the Earth’s crust and the concentration of stable Sr in the ocean is $8.7 \times 10^{-5}$ M. It is widely distributed with calcium. The chemistry of strontium is quite similar to that of calcium, of which concentration in the ocean is $10^{-2}$ M. The biological behaviors of strontium in the ocean are also very close to those of calcium, and then the behavior of Sr in the ocean can be considered to be different from that of Cs.

The radiometric method of $^{90}$Sr is only $\beta$-counting. Therefore, radiochemical separation is required for determination of $^{90}$Sr. An essential step in $^{90}$Sr analytical methodologies is the separation and purification of the strontium, both to remove radionuclides which may interfere with subsequent $\beta$-counting and to free it from the large quantities of inactive substances typically present, i.e., calcium in seawater. In the 1950s, oxalate technique was used to separate Sr and Ca (Miyake & Sugiura, 1955). They applied the fuming HNO$_3$ method for purification of Sr. On the other hand, carbonate techniques (Sugihara et al., 1959) was used for $^{90}$Sr determination for the Atlantic sample in the 1950s. Shirasawa et al. (Shirasawa & Schuert, 1968) used similar procedures to those developed by Rocco and Broecker (1966) in which the oxalate technique was adapted. During the GEOSECS period, the oxalate technique was applied for $^{90}$Sr determination for the world ocean (Bowen et al, 1980). Classical methods for the separation of strontium from calcium rely upon the greater solubility of calcium nitrate in fuming nitric acid. Those procedures require numerous steps including repeated precipitation in strong nitric acid. Therefore, various alternative methods for separation have been proposed; precipitation methods of strontium sulfate and strontium rhodizionate (Weiss and Shipman, 1957), sorption of strontium on an ion-exchange resin from a solution of chelating agent such as CyDTA and EDTA (Noshkin & Mott, 1967). These methods, however, had not improved to shorter analytical steps because the precipitation and extraction methods yield strontium fractions containing significant amounts of calcium. In the late 1970s, Kimura et al. (1979) proposed the use of macrocyclic
polyethers for the separation of strontium and calcium. In the 1990s, extraction chromatography, using a solution of 4,4′(5′)-bis ( tert-butylcyclohexano)-18-crown-6 in 1-octanol sorbed on an inert substrate, has been developed for the separation of strontium and calcium (Horwitz et al., 1990). Recently membrane filter coating crown ether was developed for separation of strontium from others (Lee et al., 2000; Míró et al., 2002). These modern techniques have contributed for down sizing small volumes of samples. On the other hand, large volumes of seawater have been used for determination of $^{90}$Sr in seawater due to low concentrations of $^{90}$Sr. Therefore, the current practical method for separation and purification of $^{90}$Sr in seawater still contains preparing precipitation at the first step.

There are some problems in the current practical methods using the carbonate technique; one is a lower recovery of Sr with a range from 30-60% and another is along radiochemical separation. Since the radioactivity of $^{90}$Sr in seawater was lower even in the surface water in present days, improvement of the Sr recovery is one of the key issues for determination of $^{90}$Sr activity in seawater. Another key point is that Ca/Sr ratio in the carbonate precipitates is remarkably reduced from that in seawater. To improve $^{90}$Sr determination in seawater, we re-examined the Sr separation technique for seawater samples (Aoyama et al., 2006).

3-2 Method

3-2-1 Sampling and materials

Seawater samples should be collected without contamination. When using a CTD-rosette sampler, which collected seawater of each 12 liters at 24-36 different depth layers, before sample seawater collection outside of the sampler bottles should be washed by clean water. When use a bucket, the bucket should be rinsed a few time before sample seawater collection.

In general, sample seawater should be filtered using a filter with pore size of 0.45 micrometer.

$^{90}$Sr were assayed as $^{90}$Y using β-counting following radiochemical separation described in detail as follows:

3-2-2 Preconcentration of $^{90}$Sr

Coprecipitation method has been practically used for extracting Sr from large volumes of seawater. Both oxalate technique and carbonate technique has been carried out for preconcentration of Sr from large volume water samples. The preconcentration of $^{90}$Sr due to carbonate was performed 500g NH$_4$Cl and 500g Na$_2$CO$_3$ in 100 liter seawater. To improve the lower recovery of $^{90}$Sr using carbonate technique, it is essential to remove Mg as hydroxide at pH=12 from the sample seawater before performing the carbonate precipitation.

3-2-3 Radiochemical separation

At the first step of radiochemical separation of Sr from Ca, Sr is separated from calcium as oxalate precipitation at pH=4. After dissolution of oxidate precipitation, Ra and Ba are removed with Ba chromate. After Ra and Ba are removed as precipitates, Sr is recovered as carbonate precipitation. Further purification of Sr is carried out by using fuming nitric acid to remove Ca. After the $^{90}$Sr-$^{90}$Y
equilibrium has been attained, coprecipitation of $^{90}$Y with ferric hydroxide was formed and mounted on a disk for counting.

3-2-4 $\beta$-counting

$\beta$-counting of $^{90}$Y were carried out by gas proportional counters for external solid samples. A typical efficiency of $^{90}$Y counting by gas proportional counters with window is ca. 40 percent. The detection limit of $^{90}$Y is several mBq when counting time is 360 minutes.

References


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1. Introduction

In the marine environment, anthropogenic radionuclides (e.g., cesium-137) are released by atmospheric nuclear weapon tests, nuclear accident, and operation of nuclear facilities. It is known that some part of the radionuclides is accumulated in the seabed. Accurate analysis of the anthropogenic radionuclides in sediment is crucial to understand their activity concentration levels as well as deposition history to the study area. Natural radionuclides (e.g., uranium/thorium series nuclides, carbon-14) in sediment are helpful to trace the history of sedimentation in the study area and estimate sedimentation rates of the sediment. This chapter aims to provide information for successful observation of distribution of the radionuclides in seabed sediment. Procedures and important points for sediment analysis are also described in Vol. 5 of this Guideline of Ocean Observations or previous protocols (e.g., IAEA, 1993).

2. Planning for sediment collection

2-1 Selection of sampling station

In observing radionuclides in the sediments, sampling stations should be carefully selected so that the samples properly preserve the bottom environment. Especially in coastal areas, it is important to grasp approximate submarine topography and sediment characteristics in advance of the sampling, and nautical charts provide useful information for this purpose. Locations of where sediment consists of sand (symbol S) and mud (symbol M) are recommended for sediment collection, and those where the sediment consists of stone (symbol St) or rock (symbol R) should be avoided. In the case of sediments consist of gravel (symbol G) and coarse sand (symbol cS), caution is required because the sediment characteristics may change every several meters. In coastal areas, influx of material from the land should also be considered using information such as topography and land usage patterns. It is also effective to create equally spaced grids in the target area and comprehensively set sampling points along the grid. In the case of periodic surveys such as monitoring programs, even on a small scale, the use of GPS is strongly recommended from a viewpoint of continuity of the observed data.

2-2 Uncertainties due to sediment sampling

Most radionuclides in marine sediment was originally dissolved in seawater. The dissolved radionuclides adsorb onto the surface of suspended and/or settling particles and incorporated to the seabed. Unlike natural radionuclides, artificial radionuclides are supplied heterogeneously to the marine environment by nuclear incidents, nuclear weapons testing or regular operation of nuclear facilities. Considering that the removal of dissolved radionuclides associates with adsorption to suspended particles, contribution of sand/gravel and the heterogeneity of the geological characteristics affect distribution of the radionuclides in the sediment. Therefore, appropriate samplers and
procedures should carefully be selected according to the situation. Especially in coastal regions, heterogeneity of the grain size may alter the distribution of radionuclides in sediment. The state of preservation of sediment-water interface during and after the sediment coring would also affect distribution of radionuclides in the core samples. If an observation is the first trial of sample collection in the area/region or a sampling equipment, multiplicated sampling at a representative station, and assessment of the uncertainty (reproducibility) due to operation of new equipment are recommended. In order to overcome such heterogeneity problems, increasing of the sample size or use of composite samples would also be effective.

3. Sediment samplers

In this section, representative sediment samplers for measurement of radionuclides are introduced. For a monitoring of pollutants, such as artificial radionuclides, sediment samplers must collect surface sediment as well as suspended particles in the water-sediment interface without loss or disturbance. In order to assess the most recent contributions of contaminants to the surface sediment, the upper section of the sample (0–1 or 0–3 cm) should be carefully taken with the highest priority. If the primary purpose of sampling is to investigate the vertical distribution or sedimentation rates, core sampling without disturbance of the sedimentary layers must be applied. Researcher should select appropriate equipment, and combine several devices as necessary.

3-1 Grab sampler

Grab samplers are commonly used for sediment sampling in brackish and estuarine waters because of its larger sampling area and successful collection of sandy sediment that is difficult to collect by a core sampler. Although the grab sampling is not the ideal way to observe the sediment profile, it gives us some idea of distribution in the top 10 cm of sediment with careful sub-coring.

3-1-1 Ekman-Burge sampler

Ekman-Burge samplers are light weighted equipment (5–10 kg) with a sampling area of about 15 cm × 15 cm. It can collect a sample up to 3 L in volume. After arriving at the bottom, a drop messenger triggers to release shovel blades for sediment collection. It is designed to collect soft surface sediments manually in the absence of strong currents. The lack of sample disturbance, square cross section and moderate penetration make it suitable for collection of the surface sediments. Because of its lightweight and easy handling, it is well-suited for small boat operations.

3-1-2 Smith-McIntyre sampler

Smith-McIntyre sampler can collect samples of up to 20 L of fine-grained and sandy sediments. Unlike the Ekman-Burge sampler, Smith-Macintyre sampler is designed to release the shovel blades at a time when the sampler touches the seafloor.

3-2 Core sampler

Sediment cores provide helpful information for estimating the sedimentation rate, the history of
contaminant discharge to the water system, and the inventories of pollutants. In collection of a core sample, it is important to preserve the original layers of the sediment without disturbance and to avoid losing the surface layer which may hold the most recent pollutants.

The diameter of coring tube should be as large as possible to provide sufficient material for analysis. Coring tubes with a diameter of about 5–12 cm are commonly used. When the coring tube penetrates into the sediment, deformation of the sediment layers may occur by friction between the inner wall of the tube and sediment (a dome-like structure in which the sediment layer becomes convex shaped in the coring tube). Especially when the penetration speed is fast and the contact area of the inner wall of the tube per unit mass of the sediment is large, the extent of deformation becomes large. Generally, when the diameter of the coring tube is 70 mm, the extent of deformation is about 5 mm outside the sediment core, and contamination of the sample (contamination of the upper layer sediment in the lower layer) occurs in this range. In the case of sediments containing sand or larger grain sizes, or sediments with brittlestars (e.g. *Ophiura ophiura*) on the surface, they are dragged along the inner wall of the tube, and the sediment particles near the surface may move downward. Such contamination can be prevented by removing about 5 mm of the outer peripheral part of the sediment column.

3-2-1 Gravity corer

A gravity corer is an open tube fitted with a weight so that gravity can force it sufficiently deep into the sediment to isolate a sediment sample. The simplest possible corer used in shallow environments consists of a piece of plastic tubing and a weight. After this type of sampler is penetrated into the sediment, the top of the coring tube is sealed and retrieved to the boat.

3-2-2 Multiple corer

In a multiple corer, seawater in a cylinder installed at the upper center of the sampler works as a damper, and a multiple polycarbonate coring tubes attached to the lower frame are inserted into the sediment without disturbing the sediment-water interface at a very low speed (1 cm/sec or less). A guide frame surrounding coring tubes helps to maintain the tubes in a vertical position. The frame also permits installation of a mechanism that seals the bottom of the coring tube immediately after the tube is extracted from the sediment. A bottom core seal improves the success of capturing sediment in the coring tube without an internal core catcher. The core seal also enables to collect overlying water as well as sediment core.

2-3-2-3 Box corer

Box corer has a box with surface area up to 2,500 cm$^2$ (50 × 50 cm) and a maximum penetration depth of about 50 cm, and is suitable to collect large volumes of sediment. As the winch begins to retrieve the corer after the corer penetrated into the sediment, a single spade or two opposing jaws with rubber sealing surfaces are pulled through the sediment to a position in contact with the cutting edges of the box. By the larger surface area of sediment collection, compared to a tube coring, box corer is able to minimize the change in the thickness of the sediment during the coring. The box core sample is often subsampled by pushing clean coring tubes into the sediment for a further analysis. In order
to avoid shortening during the penetration of sub-coring tube, it is preferable to use a tube with a diameter at least 50 mm of which side wall is as thin as possible. When penetrating the sub-corer into the sediment, do so when overlying water is on the sediment sample in the box. Although a box corer can collect an excellent sample in muddy sediments, it is difficult to collect sandy sediment because the sealing spade is not sufficiently tight to trap water. If a box corer is retrieved with the absence of overlying water on the sediment sample, there is a possibility that the surface sediment was disturbed or partly lost. In such a case, it is recommended to collect the sample again.

3-2-4 Piston corer

In general, conventional piston cores are used when long cores (2–30 m) in fine-grained unconsolidated sediments are required for analysis of sedimentary processes in several thousands to millions of years. Ships need to be equipped with hydraulic cranes, winches and enough space for core handling. After the bottom of the piston, the barrel surrounding the piston (coring tube) penetrates into the sediment while keeping the piston on the bottom surface. When the barrel penetrates the sediment, a negative pressure occurs in a small space between the piston and the sediment, and the friction between the inner wall of the barrel and the sediment is reduced. By the negative pressure, the barrel is more likely to penetrate into the sediment. Since the piston functions as a "plug" when the barrel is pulling out, the core sample can be recovered without falling while keeping the sedimentary layers. However, for the successful sampling, the piston must be held on the seabed surface when the barrel is penetrating into the sediment.

4. Collection of sediment samples

4-1 Sampling record

As general information of sediment sampling, following items should be recorded for every collection of sediment.

- Sampling date and time
- Researcher/Operator
- Location
- Bottom depth
- Wave and heave heights
- Size classification (granule, sand, silt, clay etc.: e.g., ISO, 2002)

If available, detailed cruise data and tension record of the winch would also be helpful for replicate collection at the same location.

4-2 Subsampling from grab sampler/Box corer

After retrieving a sampler, confirm that the sediment sample was successfully collected in the bucket/box. If the sample is not sampled horizontally, if the sample overflows, or if the overlying water is not retained, it should be sampled again because a part of the sediments may be lost during the sampling.
Retrieved sampler is tightly lashed on deck to avoid slipping.
When sub-coring is performed, a sub corer with 40 ~ 80 mm in diameter is slowly penetrated into the sediment. See section 4-3 for processing after subsampling.
Drain overlying water by pumping or siphoning with silicone tube (ID: 5–10 mm). It is recommended to use a pump to prevent water from flowing back and disturb the sediment surface.
After removing the overlying water, measure the thickness of sediment and recorded. Considering the shape of the sediment box, measure the thickness at multiple points as necessary so that the approximate volume of the collected sediment can be estimated.
Place a stainless (or plastic if necessary) container (50 mm height) under the sampler. Open the jaws and scrape the sample in the bucket.
Homogenate sample with a stainless hand shovel, packed into plastic bag and sealed.
As necessary, it is possible to penetrate a clean acrylic tube into the sediment and obtain a sub-core (see section 4-3 to process the core samples). This step must be carried out before draining the overlying water.

4-3 Subsampling from core sampler

Carefully seal the bottom of coring tube with a spatula (the width of spatula must be larger than diameter of coring tube) and remove the coring tube from the corer.
Immediately seal the both ends of corer with rubber plugs, and allowed to settle suspended particles in the overlying water of the sediment surface. Care should be taken not to give shock so that sediments will not be disturbed. As necessary, the rubber plugs are sealed with plastic seal tape (c.a. 50 mm width).
Before starting the core slicing, prepare water (surface seawater or tap water will be acceptable if there is no significant contamination of target radionuclide) in a bucket. Prepare bags or bottles for storage of subsamples and note sampling date, station ID, sampling layer in advance to process samples. Plastic seal bags or plastic bottles with seal top are useful for subsampling.
After at suspended particles in the bottom water is settled, set the coring tube on a cutting piston and release the top plug. Carefully release the bottom plug, immediately slide spatula between the coring tube and bottom plug, and remove the bottom plug.
Carefully slide out the spatula and insert the core into the piston from the bottom of the coring tube.
As necessary, drain the overlying water by a pump or siphon with silicone tube (ID <5 mm). Use of a pump is recommended to prevent disturbing the surface sediment by water from flowing back to the coring tube. The piston should be kept pushing up (core is pushed down when using a fixed height) during the collection of overlying water. Weaken the flow rate of the pump at the end, fix the tip of the tube on the water surface, and suction the water and air.
When it is not necessary to sample the overlying water, push the piston up to allow the overlying water overflow. When the sediment-water interface approaches to 1~2 cm below the top end, set water absorbent material (Kimwipes are useful) on the overlying water and slowly push up the piston. The absorbent should not be contact with sediment surface as much as possible.
Push up the piston until the demanded thickness of sediment comes out. If the sediment has high water content and it is expected to overflow by the uplifting, scoop the sediment for given thickness of sediment layer and stored in a subsample bag/bottle.

Using a spatula, chip off the smearing sediment along the inner wall of coring tube. It is efficient to make a hexagon-shaped core.

Slide a spatula along the line of the top of the coring tube and cut the sediment. During this process, do not move the spatula vertically to prevent disturbing sedimentary layers in the core.

Store the cut subsample in a bag/bottle.

Before cutting the subsequent layer, spatula is washed with water and wiped.

5. Transport and storage

After the collection of the sediments using grabs or corers at the field site, the samples must be transported to the laboratory without altering properties of the original material. This involves special steps to reduce potential contamination and to minimize mixing for biological, chemical, and physical analyses.

When carrying core samples to laboratory on land, it should be secured in a vertical position so as not to disturb the sedimentary layer. For such cores, it is often advantageous to completely fill the space from the water sediment interface to the top of the coring tube with local water and to remove any air bubbles that may be trapped under the core cap.

When carrying the core by a vehicle, an enough cushioning material should be used to suppress vibration.

If the core cannot be held in a vertical position during cutting and transport, the surface of the core is covered with a Teflon sheet (about 1mm thick and cut to the interval diameter of the coring tube) followed by a PVC well plug.

Cryopreservation of core sample is not recommended. When it is necessary to store cores in a freezer, take notice of the change in core length due to expansion and the vertical movement of pore water in the sediment column. Additionally, when frozen core samples are cut, they should be processed without thawing.

6. Analysis of sediment properties

In the analysis of distribution of radionuclides in seabed sediment, the following sediment properties are especially important.

Percentage of water content (see also Vol. 5, Chap. 2 of this Guideline of Ocean Observations).
Loss on ignition, organic matter or total organic carbon (TOC) content (Vol 5, Chap. 3).
Grain size distribution (Vol. 5, Chap. 4).
Dry bulk density (Vol. 5, Chap. 2)

7. Processing sediment samples for analysis

7-1 Drying
Drying step is required because concentrations of contaminants in sediments are usually reported on a dry-weight basis. The drying step also provides an opportunity to calculate water content by simply weighing the sample before and after drying. Water content is a fundamental parameter of the sedimentary environment. The water content is also applied in calculation of the salt separated from the seawater by the drying. The drying procedures are as follows. Throughout the drying process, attention should be payed not to make cross contamination between subsamples.

Gently mix the wet sediment subsample by stainless spoon and reassemble aggregation.

Put the sample into a pre-weighed container, and measure total weight. The balance should be chosen so that the number of effective digits is 4 or more.

Place the sample in an oven at 60~105 °C (depends on element/isotope of interest).

Allow the sample at room temperature and measure the total weight.

Crush aggregates in a ceramic mortar, remove pebbles and remove stone, shell and organisms (fish, benthos, seaweeds etc.) and organisms with 2 mm sieve. In this procedure, care should be taken not to “grind” the sediment particles.

As necessary, reduce the sample size and store the dried sample in appropriate sealed vessel (see section 7-3).

7-2 Homogenization

Artificial radionuclides are often adsorbed heterogeneously onto the surface of sediment particles. In case a large amount of samples must be handled, an automatic homogenizer (mixer consists of a V- or cyrindrical-shaped rotating vessel) is helpful for homogenization. When such a homogenizer is used, all sediment samples, including fine particles and “dust” (which may have a relatively high content of radionuclides), in the vessel must be recovered.

7-3 Reduction of sample size

If large amount of sample for analysis was collected, the size of sample is reduced by the following procedures. Theoretically, it can be estimated that satisfactory homogeneity (less than 3 % of uncertainty due to processing sample) is obtained by subsample sizes larger than 100 mg with particle sizes <0.08 mm (IAEA, 1993).

Incremental method: Spread powdered sample on a clean and smooth board or sheet, let the sample square or rectangle with 15–25 mm in thickness, and divide equally into 9 blocks. Scoop samples from each block with an increment spoon, and repeat until the required amount of sample is obtained. In this method, subsamples should be taken from bottom of each block. In addition, the same number of times must be taken for all blocks.

Dividing method: Repeat dividing the sample size by a riffle sampler.

Automated method: Use a specialized device such as cascade and rotary splitter.

Detailed procedures and instruments are described in JIS (1992).

7-4 Preparation for determination of radionuclides

7-4-1 Nondestructive analysis
Gamma-ray spectrometry is the representative nondestructive technique for the determination of activity concentration of radionuclides from natural or anthropogenic origin. In the gamma-ray spectrometry, a dried and powdered sample is sealed in a pre-weighed plastic bottle for measurement. The bottles must have the same dimension of that of a certified reference material used for calibration of high-purity Germanium (HPGe) detector.

When measuring activity of radium-226 indirectly from activities of lead-214 or bismous-214, it is necessary to prevent escape of Rn-222 (a daughter nuclide of Ra-226 and a gas component). This process helps to establish the radioactive equilibrium between Ra-226 and Pb-214 or Bi-214. For this purpose, the surface of sample in the container is covered with an acrylic disk and sealed with epoxide resin.

7-4-2 Analysis that requires decomposition, separation and purification of sample

For radioanalytical techniques by alpha-/beta- counting or a high-resolution mass spectrometry, sediment samples must be decomposed by an appropriate method, followed by separation and purification of the target elements/radionuclides. When handling radionuclides as yield tracers, care must be taken so that they do not contaminate other samples by diffusing into the working environment and equipment. On the other hand, especially for mass spectrometry, it is necessary to prevent contamination of the working solution by environmental material (i.e. dust, gas etc.). When selecting the appropriate method for measurement of the target radionuclides, they also should understand correctly about the precautions for the analysis.

References

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1. Sample Collection and Storage

1-1 Plankton

Phytoplankton and zooplankton play an important role in marine ecosystems as a primary producer and secondary producer, especially zooplankton act as a vital link between primary production (phytoplankton) and higher trophic production through food webs. These organisms also play an important role in understanding the radionuclides cycling within the ocean, and the transfer of radionuclides from seawater to marine organisms. However, the activity concentration of radionuclides found within zooplankton and phytoplankton is low. In particular, the activity concentration of anthropogenic radionuclides is considerably low for long lived radionuclides in general. Analyze the activity concentration of artificial radionuclides in zooplankton and phytoplankton, it is necessary to collect a large sample volume. To collect zooplankton samples, it is recommended to use large mouth-opening plankton net (for example, an Ocean Research Institute (ORI) net or Bongo net). The oblique hauling to collect plankton several times is also recommended through the water to a depth that is approximately equivalent to the depth of the mixed layer or to the depth directly below the thermocline. Because we can expect large biomass of zooplankton existed within that layer. Furthermore, when collecting samples of large crustacean plankton such as euphausiids and micronekton, which are large and have strong swimming abilities, it is best to use larger nets or trawls allowing high speed tow such as Isaacs-Kidd Midwater Trawl Net (IKMT) or Matsuda, Oozeki and Hu Midwater Trawl (MOHT) (cf. Oozeki et al., 2004, Wiebe and Benfield, 2003). Once the net has been pulled up onto the board, the outer surface of the mesh should be thoroughly washed in seawater, and the plankton sample that has accumulated in the cod end of the net should be recovered. To aid in the data interpretation, a portion of the sample should be used to determine ecological information of zooplankton community such as the biomass, species composition, and numerical density (Kaeriyama et al., 2008, Kitamura et al., 2013, Takata et al., 2015). For this, a flow meter should be attached to the plankton net and quantify the amount of water that has been filtered. The remaining portion of the sample should be drained, placed in a Ziploc bag, frozen, and stored. Additionally, it is recommended to obtain the activity concentration of the radionuclide of interest in the seawater (dissolved matter) at the depth at which the plankton net is hauled, to calculate the concentration factor (IAEA, 2004), which is a useful value for data interpretation (Tateda, 1998; Kaeriyama et al., 2015). Furthermore, in cases when the radionuclide activity concentrations are compared among different types of zooplankton, using the concentration of stable isotopes in each type of zooplankton is an effective method for the analysis because it is difficult to collect a large quantity of a single species of plankton. When using the stable isotope concentration as an indicator of the radionuclide activity concentration, it is assumed that isotopic fractionation seen in hydrogen, carbon, nitrogen, oxygen, and sulfur does not occur (Hidaka and Akagi, 2002). The sample collected...
through the plankton net should be transferred to a large Petri dish, and individual organisms of the plankton type of interest should be selected one by one using tweezers or a pipette on the board. For large crustacean plankton such as euphausiids, and copepods, several tens of organisms should be collected. The water on the surface of the organisms should be removed, and the organisms should be frozen. The stable isotope concentration can be analyzed by drying the sample, dissolving it in acid, and analyzing the dissolved sample using ICP-AES or ICP-MS (Masuzawa et al., 1988, Marumo et al., 1998). Because exclusively collecting a large amount of phytoplankton is extremely difficult, the use of a large volume in-situ filtration system (Bishop and Edmond, 1976, Aono et al., 2008), or a cartridge filter using a seawater collection system on the board may be considered (The Oceanographic Society of Japan, the Great East Japan Earthquake WG /Analysis SWG, 2011). In such a case, the sample obtained is a suspended solid consisting mainly of phytoplankton. When using a large volume in-situ filtration system, one recommended method to collect the samples efficiently is to check the vertical profile of the chlorophyll fluorescence beforehand and perform the observation at the depth where the peak is found. The filter paper that is used for collection should be marked with its weight beforehand so that the weight of the dried sample can be calculated afterwards. The amount of filtered water measured by the flow meter should also be recorded. The filter paper with the suspension sample obtained through the cartridge filter should be frozen and carried back to the lab. When filtering the seawater, a flow meter should be installed on the outlet of the housing of the cartridge filter, and the amount of filtered water should be recorded. If it is expected that the seawater contains a high activity concentration of radionuclides, the seawater collection system, hose, and housing of cartridge should be thoroughly rinsed with field seawater, the seawater inside the system should be replaced, and the housing should be thoroughly washed with distilled water.

1-2 Benthos

Benthos collection is performed with the general collection equipment (sledge nets, dredge nets, and trawl nets. Refer to the chapter on benthos, Volume 6 Chapter 2 in this Guideline of Ocean Observations). Afterwards, the organisms should be placed in a Petri dish filled with seawater filtered on-site, and organisms were sorted as possible as in details. During this step, it is important to remove the sediment particles stuck to the benthos as much as possible, using the filtered seawater. For the radioisotopes of conservative elements, such as radiocesium, the sample should be washed with seawater containing the same level of activity concentration of radionuclides as the on-site seawater, to avoid artificial changes in the radionuclide activity concentration of the samples. After being sorted, the samples should be frozen and stored. Depending on the purpose of the investigation, the researchers should consider processing the sample, such as incubating the sample for a certain period in the filtered seawater to empty the digestive systems of the organisms, to eliminate the effect of the gastrointestinal content. For organisms such as mollusks and crustaceans for which it is possible to separate their molluscan part from the exoskeleton, it is desirable to dissect the organism and analyze these parts separately (Sohtome et al., 2014). When collecting benthos, it is recommended to also collect a sample of the sediment on the ocean floor, which is the habitat of the benthos, by using a bottom sampler and to measure the activity concentration of radionuclides in the sample of sediment.
2. Measurement Preprocessing

The best preprocessing and measurement methods depend on the radionuclide of the interest. For general preprocessing methods and radionuclide measurement methods, please refer to the radiation measurement method series published by the Ministry of Education, Culture, Sports, Science and Technology, Japan (Nos. 2, 7, 9, 12 and 16). Also, please refer to gamma ray spectral analysis techniques for emergency situations (Nos. 24 and 29). Here, we describe several points to be cautious about when preprocessing samples for measurements using germanium semiconductor detectors for gamma ray emitting isotopes including radiocesium. When the activity concentration of radionuclides is expected to be high, the raw sample of the frozen zooplankton and benthos can be directly used for the measurement. When defrosting the sample at room temperature, to prevent the loss of the cellular fluid, the sample should be divided into small portions of an amount that can fit inside the measurement container, and defrosted in a container. If the measurement container is not disposable, the sample should be placed in a plastic bag before being placed into the measurement container. To prevent contamination of the detector, the measurement container containing the sample should also be placed in a plastic bag. When the activity concentration of anthropogenic radionuclides is expected to be low, it may be difficult to conduct the measurement using the fresh sample directly. In this case, the water should be removed from the sample to reduce its volume. For this, the sample should be freeze-dried or dried using a dryer. The dried sample should be homogenized by grinding in a mortar. The sample should be filled into the container and measured using a germanium semiconductor detector. If further volume reduction is needed, the sample can be incinerated at an appropriate temperature (please refer to Volume 9 Chapter 3 in this Guideline of Ocean Observations (under review) for incineration methods). In cases where a large amount of phytoplankton suspended matter sample has been collected with a large volume in-situ filtration system, the sample can be dried, removed from the filter, ground in a mortar, placed in a pre-weighed measurement container, and measured using a germanium semiconductor detector. In cases where the sample is small, the sample can be dried, cut along with the filter, ground in a mortar, and used to fill the measurement container. The cartridge filter should be cut and should have the center part and core separated from the filter. The filter part should be incinerated to reduce its volume and used to fill the measurement container.

For samples such as radioactive strontium and plutonium isotopes that require chemical separation or extraction, procedures such as acidic cleavage and solvent extraction should be performed for the dried or incinerated sample in the same manner as for the sediment, to use it as an analysis sample (refer to Volume 9 Chapter 2: Marine sediment in this Guideline of Ocean Observations). When analyzing certain types of phytoplankton in which the cell wall contains silica, such as diatoms, it is necessary to select the appropriate method for completely dissolving the sample as per the sample characteristics, such as using hydrochloric acid for dissolving silica. When analyzing tritium, the water in the freeze dryer’s cold trap should be recovered after the sample is freeze-dried and used as the sample for analysis as free water tritium (FWT). Organically bound tritium (OBT) can be analyzed in the same manner as large organisms by freeze-drying the sample, placing the dried sample in a quartz tube, and completely burning the sample using a combustion device while running oxygen over the
sample. The generated water vapor should be collected in a cold trap and used as the sample for analysis. For both FWT and OBT, the sample should be distilled and measured using a low background liquid scintillation counter to remove the organic material. For detailed methods of analysis, please refer to No. 9 of the radiation measurement method series published by the Ministry of Education, Culture, Sports, Science and Technology (Ministry of Education, Culture, Sports, Science and Technology, 2002).

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