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Seabed sediments collection for physicochemical analyses – a review

Pobieranie morskich osadów dennych do badań fizykochemicznych

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Abstract: A description of equipment and tools relative to the sampling of seabed sediments for physicochemical analyses is presented in accordance with the Polish Standard PN-EN ISO 5667-19:2006. The paper reports sampling procedures for various purposes, instructions regarding samples handling, with emphasis on hazardous substances, chemical warfare agents (BST). It also includes information and instructions concerning a high level of safety while working at sea, in accordance with international conventions SCTW and SOLAS.

Keywords: bottom sediments, sampling, safety, chemical weapon, sampling equipment

Streszczenie: W artykule opisano proces pobierania prób morskich osadów dennych przeznaczonych do badań fizykochemicznych zgodnie z polską normą PN-EN ISO 5667-19:2006 Opis ten zwraca uwagę na zachowanie wysokiego stopnia bezpieczeństwa podczas wykonywania prac oraz przestrzegania zasad bezpiecznej pracy na morzu w myśl międzynarodowych konwencji SCTW i SOLAS. Przedstawiona została instrukcja na wypadek kontaktu i wyłowienia ładunku zawierającego Bojowe Środki Trujące (BST). Przedstawiony został sprzęt oraz narzędzia służące do pobierania morskich osadów dennych z uwzględnienie specyfiki osadu. Opisano w jaki sposób postępować, konserwować i zabezpieczyć pobrane próby w zależności od badanego analitu.

Słowa kluczowe: osady denne, morskie osady denne, pobieranie prób, bezpieczeństwo, bojowe środki trujące, broń chemiczna, sprzęt do pobierania osadów dennych

INTRODUCTION

Seabed sediment is defined as matter deposited on the bottom of a water body as a result of the sedimentation of suspended particulate matter, such as eroded particles from watersheds and seston. Sediment consists of both mineral fraction, such as clays, silts, sands, rubble, and fine to coarser organic constituents. The amount, accretion rate, composition, and structure of sediments in a water body depend mainly on its atrophy, type and nature of the water catchment area. Materials may be temporarily or permanently removed from the water column. Return to water circulation is achievable through disturbance of sediment surface, such as resuspension in response to changes on the current field and bioturbation. A large amount of biogenic material is stored at sediments of water bodies with high trophic level indexes. Water catchment areas with a large urbanized surface may generate large quantities of anthropogenic contaminants, i.e., oils, heavy metals, post-industrial pollutants [17]. In order to determine the concentration and hazardousness of these contaminants, bottom sediments are collected using appropriate tools. Sampling should be performed by qualified and trained staff who observe all regulations regarding safety. This paper compiles information relative to the collection of seabed sediments regarding commonly used techniques and equipment. Potential hazards and risk during sediment collection were also referred, including handling chemical warfare agents (BST) at the Baltic Sea.

TOOLS AND TECHNIQUES OF SEABED SEDIMENT COLLECTION

Equipment commonly used for the collection of seabed sediments are grab samplers, gravity corers, and box-corers [2]. A grab sampler, also called a grab, is a tool for scooping (grab-

Tab. I. Exemplary technical data of the Van Veen grab [22].

PARAMETER	VERSION XL	VERSION L	VERSION M	VERSION S
mass of grab	125 kg	65 kg	25 kg	5 kg
dimensions of device	238 x 54 x 60 cm	42 x 62 x 85 cm	136 x 36 x 35 cm	20 x 20 x 70 cm
sample area	2500 cm^2	1250 cm^2	1000 cm^2	250 cm^2

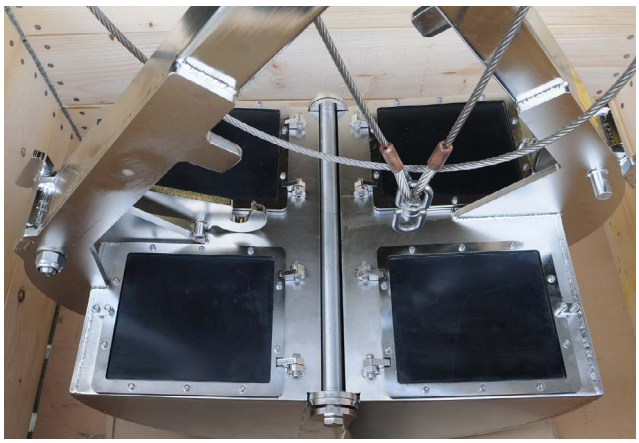

Fig. 1. The Van Veen grab [photo http://www.kc-denmark.dk/products/sediment-samplers/van-veen-grab/van-veen-grab-2500-cm^2.aspx].

bing) liquids or loose materials from the bottom of a water body. Types of different size and producers can be found. The first example of a grab sampler is the Van Veen sampler, designed to obtain samples of seabed sediment together with benthic organisms. It was made of stainless steel in accordance with the regulations of the Baltic Marine Biologists. It has been used as a mandatory instrument in international monitoring research related to surveys of macrobenthos, benthos and sediment geochemistry of the Baltic Sea, carried out according to the regulations of the Helsinki Convention.

When the instrument is lowered, a special hook keeps the jaws in an open position. Windows enabling a free flow of water and removing air from the jaws are placed in both parts of the jaws. This procedure prevents the shock wave effect while reaching the bottom. The windows are covered with a stainless net with a mesh size of 1 mm^2. When the grab touches the bottom, the hook automatically releases a safety device. When the jaws of the grab close, they delve into the bottom down to the depth depending on the bottom's hardness. After taking a sample, the jaws tighten with a great strength thanks to levers on which a rope is hooked.

The quantity of collected sample depends on the hardness and structure of the upper sediment and the volume and weight of the instrument. Smaller models may be equipped with additional weights in order to facilitate the penetration into sediment, and help to keep the rope in a vertical position during lowering and hoisting of the grab. A portable version has been designed for surveys in shallow zones with the use of small vessels.

Another popular grab is the Ekman's grab made of corrosion-proof stainless steel with a sampling area of 225 cm^2, with extra weights. The equipment is lowered open into the water column; after touching the bottom, its jaws stay raised under the pressure of the grab and close automatically. In fine sediments, the most reliable method of closing it is the use of a messenger weight that is lowered down on a rope; a closing mechanism is triggered when it reaches the dipper or bathometer. In shallow waters, the trigger mechanism may be lashed on a telescope rod. This grab sampler is intended for fine to medium-grained sediments, the jaws can get blocked in coarse-grained sediments. Gravity corers are considered to be the best tools for collecting sediments with undisturbed structure, sediment layering can be observed and thin slices collected. The internal part of the sampler is made of a pipe made of a transparent high-quality PVC, impact-resistant, and the external one is made of stainless steel. Other materials that do not react with the sample are alternatives. It is closed from the top with a valve. It has a special ending at the bottom, which keeps sediment inside, and serves as a sample container. Collection is activated by the gravitation force. During free falling, the sampler gains kinetic energy necessary to thrust itself into the sediment. In the manual method, the sampler should be pressed into the sediment manually, with the use of force directed inwards, thus increasing the length of the collected core.

Box corers are designed to collect cores with a shape of paralepidids with intact structure. During lowering, inserting and collecting samples, the upper part of the test-tube on the sampler stays open, enabling the water to flow freely. This prevents the increase of pressure and consequent disturbance of the sediment surface. When the probe reaches the bottom or the maximum depth, an automatic mechanism releases the closing scoop. The scoop is pulled to a vertical position in such a way that the bottom of the drawer is closed and the sample stays inside. After pulling the sampler out of the seabed, its upper part is closed and sealed with the use of a hinged flat made of soft rubber material.

The flaws of this device include large dimensions and mass, as well as the necessity to use a special crane on a vessel. Vibrocorers also called vibratory corers are the most complex devices used to collect sediment cores. They are used to survey coarse-grained ground and compact clays. They are fitted with special internal combustion, hydraulic or electric engines enabling to penetrate until deep sediment layers. Vibratory corers used with diving bells can collect continuous ground cores down to a depth of 20 m [1, 3]. For maintaining high quality during sediment sampling, procedures and standards regarding handling sediment samples should be followed [PN-EN ISO 5667-19:2006, PN-EN ISO 5667-15:2009]. Instruments of sediment sampling should be selected in accordance with the objective of the survey.

Tab. II. Exemplary technical data of the Ekman grab sampler [21].

PARAMETER	STANDARD VERSION	LEIGH VERSION
mass of grab	18.0 kg	5.8 kg
dimensions of device	360 x 280 x 650 mm	270 x 215 x 425 mm
sample area	400 cm²	225 cm²

Tab. III. Exemplary technical data of gravity corers [20].

PARAMETER	HYDROBIOS TYPE CORER	KAJAK TYPE KC-DENMARK	KAJAK CORER
mass of grab	6 kg	4 kg	9.1 kg
core diameter	70 mm	60/52 mm	80/72 mm
core length	600 mm	500 mm	500–1000 mm
material	Stainless steel, PVC (core)	PVC (core), acrylic	Stainless steel, PVC

Tab. IV. Exemplary technical data of gravity corers [20].

PARAMETER	KC BOX CORER 600 CM²	KC BOX CORER 1,000 CM²	KC BOX CORER 2,500 CM²
mass of device	200 kg	220 kg	1,050 kg
dimensions of device	110 x 80 x 110 cm	110 x 80 x 110 cm	255 x 178 x 220 cm
sample area	600 cm²	1,000 cm²	2,500 cm²

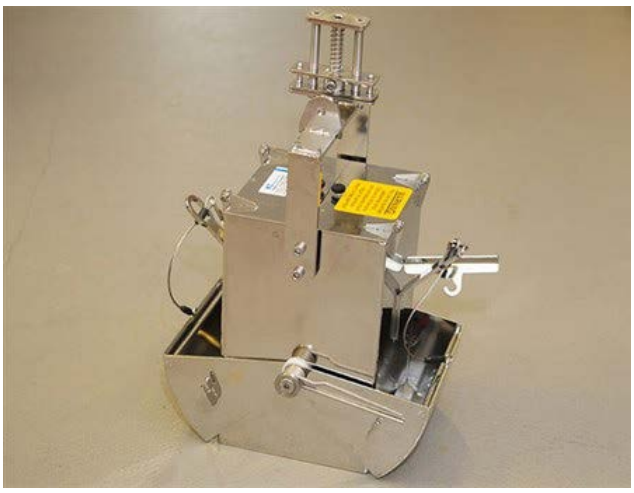

Fig. 2. Ekman's grab [photo http://www.biomm.pl/oferta/czerpacze-dna-ekman-i-lenz#&gid=1&pid=1].

Summary

The table below summarizes information on equipment for collecting bottom sediments and their destination for specific type of sediments.

HAZARDS DURING SEDIMENT COLLECTION

Operating instruments and tools to collect sediment sampling at sea are activities of high risk. Risks are dependent on natural conditions, such as weather and sea conditions during the campaign. Hazards include: falling of a crew member overboard, damages of sampling and measuring equipment, loss of equipment in sea, foundering of a vessel. In order to prevent these potential threats, measurements and sampling should be done by trained and qualified staff. The International Convention on Standards of Training, Certification and Watch-keeping (STCW) and International Convention for the Safety of Life at Sea (SOLAS) describe rules, regulations, and the best procedures. Each person should undertake a short training regarding the procedures and regulations on board provided by the captain or a designated officer aboard.

An additional factor allowing potentially hazardous incidents is using the staff's personal safety measures, consisting of a four-point helmet, safety goggles, protective clothing fitted with reflective elements, appropriate shoes, and a life jacket. While lowering the measuring equipment or sampling, the sampler should be equipped with a safety set consisting of a harness and be fastened with safety ropes to permanent elements of the deck [6, 7, 10].

POTENTIALLY HAZARDOUS INCIDENTS DURING SAMPLING

Chemical weapons

Potential risks during the collection of sediment samples may include hazardous substances, such as chemical warfare agents (BST). This risk may be encountered in the Baltic Sea; after the World War II, it was decided to sink chemical weapons. In years 1946–1948, the German Military Authorities sunk chemical munition and containers with chemical warfare agents (BST), such as sulphur mustard, organic and inorganic arsenic compounds in selected regions of the Baltic Sea (Deeps: Gotland and Bornholm, The Little Belt Strait, and – as it was revealed later – the Gdańsk Deep) [11, 23]. Due to the risk of accidental collection of sediments containing the BST, procedures were defined to be implemented in these cases.

Tab. V. Exemplary technical data of vibrocorers [18, 19] .

PARAMETER	HIGH POWER VC10000	STANDARD POWER VC4000	HYDRAULIC VIBROCORER HC6000
mass of device	2350–4075 kg	1450–2500 kg	2350–3500 kg
height of tower/width of support base	1.2 m / 5m	1.2 m / 5m	1.2 m / 5m
vibration power	89 kN	44 kN	125 bar

Tab. VI. Summary of information regarding bottom samplers [4].

SAMPLING DEVICE	TYPE OF SAMPLES	TYPE OF SAMPLERS	TYPE OF SEDIMENTS	DESCRIPTION
Grab	Surface sediments	Van Veen grab sampler Ekman grab sampler	Clay, sludge, sands Sludge, peat	One of the most frequently used devices for collecting seabed sediment samples. Collecting a sample from the surface of the bottom involves cutting it out with the use of two steel buckets placed on a single axis. The buckets are usually tightened with the use of a spring or hydraulically.
Gravity cores	Bottom sediment cores	KAJAK sampler	Clay, sludge, sand	It allows sediment cores to be collected at any depth of water. It has a very wide use, from small cores of bottom sediments for biological and chemical surveys, to respectively larger cores for surveys preceding dredging works – carried out as part of reconnaissance of the bottom for coastal and marine construction projects – or laying pipelines and cables on the seabed.
Box corers	Bottom sediment cores	Box corer	Clay, sludge, sand	A sample is collected into a box with a round or square base, penetrating the ground under its own weight, which is then cut off and closed tightly from the bottom, which prevents its damage during pulling out of the sampler. The standard box corer has a steel frame, with a box ballasted with a weight from 200 to 300 kg inside, enabling it to be inserted into the seabed. The system of cutting off and closing the sample works on the basic of a self-timer, when the whole box penetrates the ground.
Vibrocorer	Surface sediments	Hydraulic Vibrocorer HC6000	Clay, sludge, rubble, till, sand	It is used when the ground conditions are not suitable for gravity corers or when the length of the core obtained as the result of a free fall is too small. Ground cores collected with the use of a vibrocorer provide valuable information regarding the layering of seabed sediments and samples for laboratory analyses.

When sediment contains a suspicious substance indicating hazardous or military origin, the captain is obliged to undertake all measures to remove such a material from the ship as soon as possible. The dumping place should be marked with a buoy painted yellow, and the position of the incident should be recorded and reported at the nearest alarm point. In the case of taking chemical warfare agents aboard, the vessel should be kept upwind, so that all potentially toxic gases escape towards the sea. All openings in the wheelhouse and other rooms should also be closed.

At this time, the captain proceeds to the bridge and instructs the inspection of the suspicious substance. The person appointed by the captain puts on a special impermeable garment equipped with a mask with special filters.

If the suspicious cargo is classified as BST, the vessel informs the nearest alarm point of this fact. Then, the crew takes all precautions until a representative of a Maritime Office arrives, e.g., the Harbor Master's Office. After making arrangements, the vessel proceeds safely to the nearest harbor, where the cargo is secured and forwarded for utilization, and the vessel with its crew is quarantined of any residue [5, 23].

Oil spills and secondary water pollution

Oil spills and the possibility of secondary pollution of the demersal waters with material trapped by sediments constitute another hazard. It can happen through surface sediments' disturbance by the ship's propeller, sampler's jaws not closing properly, or defected sample collection equipment. An accidental collision with a pipeline, a fuel line, a wreck, unidentified cargo lying on the bottom is another risk. This may lead to a leakage within the walls and fuel and oils leaking into the water column. Disturbing the seabed structure is also possible, as a result of which a layer of crude-oil derivative hydrocarbons (mineral oils) or other contaminants trapped under a thin layer of seabed sediments may be released into the water column causing its contamination. Such a degradation of the environment is a risk to the ecosystem in its component of biology, chemistry and economy (ecosystem service).

In order to prevent such phenomena, the MARPOL convention – International Convention for the Prevention of Pollution from Ships 1973 as modified by the Protocol of 1978 was introduced. The Maritime Office in the Polish coastal zone and the Polish economic water zone keeps record of all sunk ships and cargoes and designates closed zones. Each newly discovered wreck and cargo is positioned and placed on maps with sea areas [8].

OPERATING PROCEDURE - TOOLS, MAINTENANCE, AND STORING SAMPLES

Seabed sampling should be carried out in accordance with the Standard PN – EN ISO 5667–19. The first stage consists in preparing a plan, a strategy and a program for taking samples that

Fig. 3. Gravity corer [photo http://www.kc-denmark.dk/products/sediment-samplers/kajak-corer/kajak-corer.aspx].

Fig. 4. Gravity corer [photo http://www.kc-denmark.dk/products/sediment-samplers/kajak-corer/kajak-corer.aspx].

Fig. 5. Vibrocorer [photo IMG].

correspond to the purposes of the research and enable data of a specific quality to be obtained. It is important to incorporate the required precision of results, local changes to sediment components, topographic and hydrological conditions of the survey area into the strategy of sampling. Potential sources of contamination should also be identified, and when possible, historic data regarding the sampling location should be found.

Choice of sampling equipment

The selection of an appropriate sampler depends on the type of sediment, its granulometry and cohesiveness, as well as the research purpose. During surveys involving organic contaminants, it is recommended to use corer sampler pipes made of high-strength plastic (it is usually a polymethyl methacrylate (PMMA)), or stainless steel, and in the case of metal contamination – samplers made of both stainless steel and plastic, i.e., polyvinyl chloride (PVC), and polymethyl methacrylate (PMMA) are used. Plastic used should be very hard and friction resistant. In accordance with the Standard PN-EN ISO 5667-19:2006, the equipment should be cleaned of sample residue after each change of the sampling location. Additionally, its technical condition should be checked, and in the case of any unconformity, it should be subjected to maintenance or a new one should be used. The equipment and the sampler that had contact with oil contaminants should be washed with sea or salty water with addition of soap numerous times in order to remove oil contaminants. To collect very soft material (liquid), such as sludge, the equipment should be constructed in such a way to allow the water to flow through freely during its lowering. Its purpose is to prevent the generation of a wave of pressure in front of, e.g., a grab, which could sweep fine-grained material before its activation.

Handling samples

After collecting the sample, the technician or scientist assesses it visually, describing its smell, appearance, and records the pre-

Fig. 6. Four-point helmet and pneumatic life jacket (Photo MJG).

Tab. VII. Guidelines for samplers regarding the choice of sampling device [13].

MAIN PURPOSE	REQUIREMENTS	FINE-GRAINED SEDIMENT	COARSE-GRAINED SEDIMENT
Pilot research	Intact surface sediment	Grab sampler, single corer, box corer	Grab sampler, piston corer, box corer
Basic survey	Intact surface sediment	Grab sampler, single corer, piston corer, box corer	Grab sampler, piston corer, box-corer
Surveys of changes in time	Intact surface sediment or vertical sediment layers (continual sedimentation)	Single corer, piston corer, multiple corer, box corer	Not used

NOTE: a single corer sampler is usually of a gravity type

sence of organisms. During vertical penetration of the seabed, a device should drill to an intended depth in such way allowing the sediment surface to stay similar to the actual layering. Water under the sediment should stay intact in order to maintain the sample in a condition similar to the original.

The collected sediment should be handled in such a way that it does not affect the results of analyses. When the sample is prepared for packaging, it should be averaged in an appropriate manner with the use of proper equipment, such as a spoon made of polytetrafluoroethylene (PTFE) or another material that will not react with the sample. During averaging and packaging into an appropriate container, one should remember about personal protection in the form of gloves (e.g., nitrile, neoprene), mask, and protective goggles. In order to maintain high quality of sampling, it is recommended to collect at least one additional sample at the same site. According to the analytical requirements, the samples should be kept in an appropriate container at specific conditions as listed in the table below [16].

Maintenance and storing samples

Recording sample collections

For each sampling, appropriate records describing the process of sediment collection need to be prepared. Such a record should contain identification of the site of collection, the exact geographical coordinates of each of the collected samples, sampling method, tools used for samples collection. It should contain personal data of the person responsible for collection, length of the core, macroscopic description of the sample, depth of water at the collection site, meteorological data [13].

SUMMARY

The paper compiles the current knowledge on seabed sediment sampling. It contains a detailed description of procedures and standards concerning sediment samples' handling and

Tab. VIII. Conditions of storing and maintaining samples depending on the analysis type [15].

ANALYTE	CONTAINER TYPE	MINIMUM SAMPLE AMOUNT [G]	MAXIMUM STORAGE TIME	STORAGE CONDITIONS	SPECIAL COMMENTS
Benzene	PTFE glass	50	4 days	1–5°C in dark place	-
AOX	Plastic and glass	50	7 days	1–5°C in dark place	-
Anions (Cl, Br, F, SO_4)	Plastic and glass	50	1 month	1–5°C in dark place	-
metals (except for Hg i Cr^{6+})	Plastic and glass	50	1 month	1–5°C in dark place	-
Nitrates	Plastic and glass	50	7 days	1–5°C in dark place	-
Kjeldahl nitrogen	Plastic and glass	50	7 days	1–5°C in dark place	-
Nitrites	Plastic and glass	50	7 days	1–5°C in dark place	-
Volatile organic compounds (VOC)	PTFE glass	50	4 days	1–5°C in dark place	Collect sediment possibly up to the cork, after collection put the jar upside down
Mineral oils (C10–C40)	Glass	100	1 month	1–5°C in dark place	-
Oils and greases	Glass	100	1 month	1–5°C in dark place	–
Non-volatile Hg	Plastic and glass	50	1 month	1–5°C in dark place	–
Volatile Hg	Plastic and glass	50	4 days	1–5°C in dark place	–
Cr^{6+}	Plastic and glass	50	2 days	1–5°C in dark place	–
Cyanides	Plastic	50	1 month	< -18°C	–
	Glass	50	4 days	1–5°C in dark place	–
Orthophosphates	Plastic and glass	50	2 days	1–5°C in dark place	–
Total phosphorus	Plastic and glass	50	1 month	1–5°C in dark place	–
PCB, PAH, Organochlorine (OC) pesticides	PTFE glass	50 (in a group of compounds)	1 month	1–5°C in dark place	–
pH	Plastic and glass	50	24 h	1–5°C in dark place	–
TOC and TIC	PTFE glass	25	1 month	1–5°C in dark place	–

the necessity of using appropriate equipment that does not affect the analytical results. It draws attention to the necessity of complying with international recommendations in terms of safety of on board operations and handling hazardous substances. It contains ready recommendations and instructions to be followed in the case of the extraction of suspicious cargoes and the potential positive identification of hazardous substances, such as BST.

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