Environmental Security of the Coastal Sea Floor

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Abstract. The activities related to the development of capabilities for the evaluation of environmental security of the coastal sea floor are summarized. Several hundred coastal sea sediment samples have been collected and analyzed for 18 chemical elements by using EDXRF as an analytical tool. Contour maps of antifouling biocide elements (Cu, Zn, As and Pb) have been generated for the entire eastern coast of Adriatic Sea indicating the locations of "hot spots" in the distribution of chemical elements used as biocides. In order to be able to establish if objects found on the sea floor contain some sort of threat material (explosives, chemical warfare) a system using neutron sensor installed within an unmanned underwater vessel has been developed and tested. The results from the laboratory tests for the detection of the presence of (C, H, N, O - explosives) and (P, S, Cl, F, As or Br – chemical warfare) are presented. Tests with neutron probe submerged in the pool filled with sea water with targets being: 10 litters of diesel fuel, 5 kg of explosive and different chemicals placed behind 16 mm steel plate and behind sandwich 18 mm steel plate – 10 cm air bag – 16 mm steel plate were also performed.

1. Introduction

Environmental security of ports and waterways depends on number and type of materials and objects dumped into the coastal seas or oceans. The dumping of material in the sea waters has a long history. The easiest and 'cheapest' way to 'eliminate' chemical weapons and munitions following World War II was to dump them into the sea. As environmental awareness has increased the ecological repercussions of such actions have made them unacceptable. Among the military ordnance dumped at sea, chemical weapons (CWs) and riot control agents represent a not negligible percentage. The actual amount of dumped war material, subject to the corrosive action of sea water which causes the release of chemical products, has to be considered as a relevant source of persistent pollutants in need of in-depth scientific investigations. Some areas in Europe are of special concern because of large ammouts of dumped ammunitions. These include Baltic Sea, Atlatic Ocean, North Sea and Mediterranean[1-4]. Many of the sites are rather close to the shore. Dumped munitions, and in particular the disturbance of dumped munitions by seabed activities, e.g. fishing, sand and gravel extraction, dredging and dumping operations and the placement of cables and pipelines, is an important issue and should be addressed. It is essential that details of the locations of all munitions dumpsite and areas where munitions are detected on the seabed be maintained. Any seabed activities to be undertaken within or close to these locations should be subject to a full assessment of the potential risk prior to the approval of these activities by national authorities.

Many of the materials on the bottom of the seas are due to numerous shipwrecks. The recent efforts include so called SREP and AMIO databases of WWII shipwrecks[5,6]. Although work on the Pacific SPREP database is relatively complete, work on shipwrecks in the other oceans has only recently commenced. The Atlantic, Mediterranean and Indian Ocean (AMIO) database of WWII shipwrecks is in its initial stages. Currently, the AMIO database contains over 3953 WWII vessels over 1000 gross tons equating to over 20 million tons of shipping lying on the bottom of the ocean.

In adition, inspection of the cargo area within the ship's body below water surface for the presence of the threat materials is required in the fight against terrorism activities. In such a scenario a detection systems needs to approach ship's underwater hull and analyze the material present from the other side of ship's hull, i.e. in ships cargo area. Even though boat and ship construction dates back to ancient times, some production technologies have been slow to change, illustrated by an only recent shift in technology at a major shipyard[7]. Modern commercial ship hulls continue to be built with 14- to 19-millimeter-thick (0.5- to 0.75-inch) carbon steel plate. Tanker hulls must be made with double construction, while other transport vessels, such as those for containers and bulk dry cargo, must have double-hull construction only in their fuel tank areas. While the outer hull is 14 to 19 mm thick, the inner hull may be 12 to 14 mm thick.

In this report our activities related to the development of capabilities for the evaluation of environmental security of the coastal sea floor are summarized. The background in the measured gamma ray spectra is generated, among other, by sediment on the sea floor on which the investigated object is laying. Therefore, the knowledge of the sediment chemical composition is mandatory.

2. Experimental

The experimental work has been performed both in the laboratory and in the field. For the work in the laboratory the prototype of the underwater system «Surveyor» containing neutron generator, shielding and gamma ray detector has been used[9]. The neutron generator used by the "Surveyor" can be rotated by two step motors so that different volume elements chosen by the relative position of the neutron generator and gamma ray detector could be inspected. In such a way a profile of concentrations could also be measured. Gamma detector is placed inside aluminum made holder, thickness 5 mm. The detector is shielded on one side by lead shield thickness 5 cm. The submarine body is made of polyester and Kevlar with the wall thickness of 1.5 cm. Below the detector there is a window (variable materials are being tested) of dimensions (46 x 26 x 0.5) cm.

Several sets of measurements have been done: different materials in different geometries have been placed into the tank filled with water and resulting gamma ray spectra measured (see FIG. 1.). In such a way the capability of the system to confirm the presence of threat materials in the objects placed in the water has been tested. Data for TNT, SAMTEX and some other explosives (bare or within grenades) have been accumulated.

In order to demonstrate the possibility of identifying the material within sunken ships and other objects on the sea floor, the tests were performed with the 14 MeV sealed tube neutron generator incorporated inside a small submarine submerged in the test basin filled with salt water[10]. Investigated targets were 10 litters of diesel fuel, 5 kg of explosive and different chemicals (expected components of chemical warfare agents) placed behind 16 mm steel plate in the first measurement and behind sandwich 18 mm steel plate – 10 cm air bag – 16 mm steel plate in the second measurement, respectively. Using window on the measured alpha- gamma time spectrum, gamma rays originating from the investigated volume were separated from the background radiation. From the inspection of the measured gamma spectra it was possible to identify all of the investigated materials in both measurement geometries.

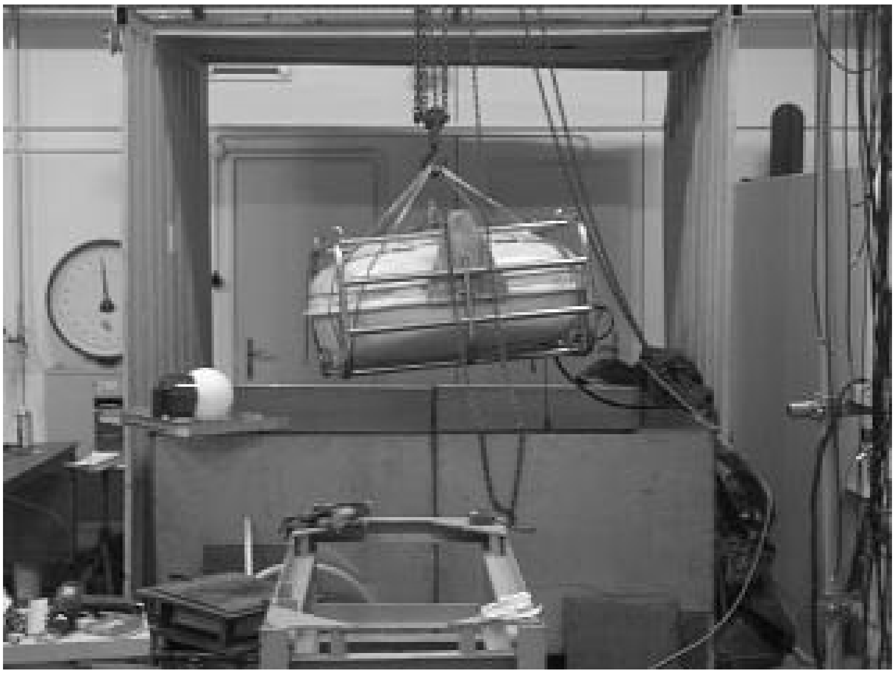

FIG.1. Underwater system "Surveyor" being lowered towards object to be interrogated placed in the test pool filled with water.

In order to obtain information about coastal sea sediments of Croatian coast some seven hundred coastal sea sediment samples have been collected and analyzed for 16 chemical elements by using EDXRF as an analytical tool. This corresponds to approximately one sediment sample per 12.5 km of the coastal line. For each sample following information has been recorded: exact GPS coordinates, their local name, site description, depth and category. Sediment samples were grouped in 7 categories: bays, beaches, villages, ports, marinas – pier area, marina – service areas and others (sea mud, river inflows and similar). The data obtained were used to produce the contour maps of concentrations[10,11] indicating the locations of "hot spots".

3. Results and Discussion

3.1. Costal sea sediment contamination with biocide elements

In this work, special attention has been paid to investigation of the coastal sea sediments at the locations were human activities are most intensive – ports and harbors. At these locations the great increase in concentration of the antifouling biocide elements (Cu, Zn, As and Pb) have been noticed. Contour maps of antifouling biocide elements have been generated for the entire eastern coast of Adriatic Sea indicating the locations of "hot spots" in the distribution of chemical elements used as biocides. FIG. 2. shows contour maps for As concentration values in surface layer of the costal sea sediments presented for one of the seven administrative units (counties) in Croatia. From this figure the presence of «hot spots» is evident. These are locations with concentration values significantly increased relatively to the background indicating the anthropogenic influence. These "hot spots" for Cu and As, as well as for Zn and Pb, are invariably connected to ports, harbors (civilian and military) and marinas, where ships repairs and antifouling coating are performed. It must be noted[10] that contour maps presented in FIG. 2. do not have physical meaning, since the samples evaluated are not distributed properly. In this case contour maps have only the purpose of the visualization and fast screening of "hot spots". Concentrations of antifouling elements in sediments at these locations are several orders of magnitude greater than background, strongly impacting marine environment diversity, health and vitality of its ecosystem and its productive capacity. Besides, those are the locations where matrix effects have to be carefully examined before application of neutron methods for threat material inspection. The background values for the costal sea sediments in Adriatic Sea were obtained by analyzing sediment samples collected in bays free of anthropogenic influence[11].

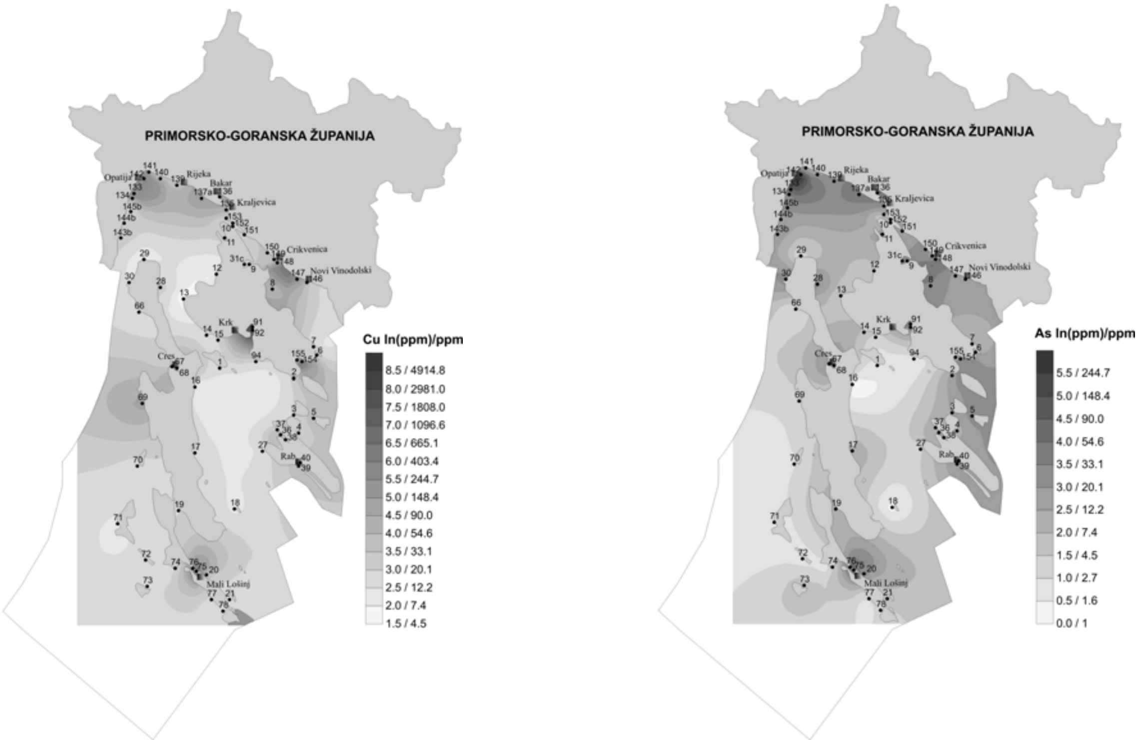

FIG.2. Distribution maps for the logarithm of Cu and As concentrations in the coastal sea sediment.

3.2. Coastal sea sediment contamination with explosive devices

The primary task of SURVEYOR is to detect the presence of explosive inside different objects, to evaluate the size of explosive load and the type of explosive used. In order to be able to establish if an object on the sea floor contains some sort of threat material (explosives, chemical warfare) a system using neutron sensor should be placed at the distance of 10 cm or less from the object. The presence of explosive is established from the C and O gamma ray intensities and ratios. FIG. 3. shows one such example.

The ammunition left on the sea floor after WWII is slowly disintegrating after so many years. In order to evaluate the effects on the environment sediments samples in the vicinity of torpedo that was dumped during the WWII on the bottom of the sea were collected[12], as shown in FIG. 4a.-c. presenting the measured contour maps for Cr and Ni concentrations respectively. From FIG. 4. one can see that dumped ammunition besides the security threat by means of uncontrolled explosion also present the threat of the heavy metal pollution from ammunition casing.

Grenade above the rock

Gamma ray spectra from 60 mm grenade (red) and background (grenade removed, black). TOTN = 18 x 107. Measurement time ~3975 s.

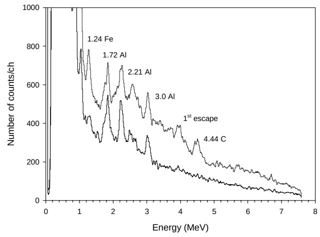

FIG. 3. The active grenade was measured in variety of geometries, here is shown above a rock. Results of the measurement, target in – target out under the same experimental conditions.

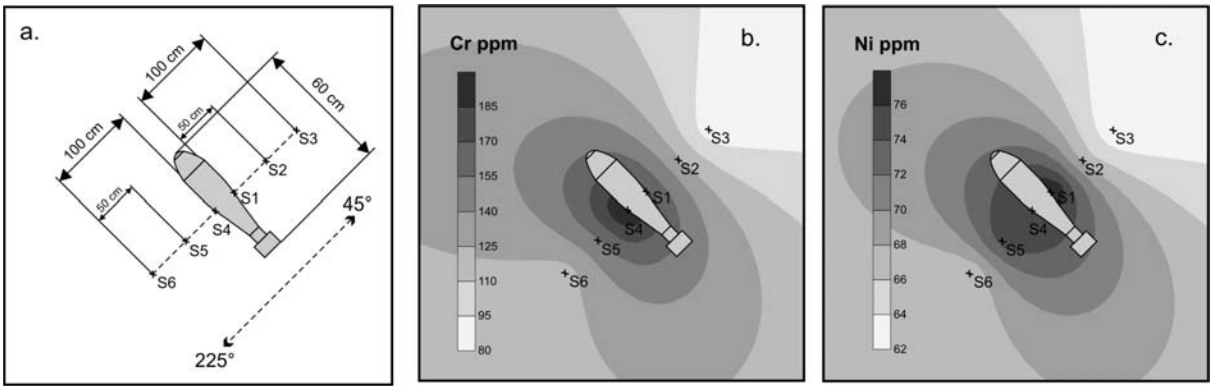

FIG. 4. Cr and Ni concentrations in the surface sediments in the vicinity of the dumped torpedo, a. - sampling scheme, b. – Cr contour map and c. - Ni contour map.

3.3. Coastal sea sediment contamination with CW devices

The contamination of sea floor by ordinance containing some sort of CW agents is serious problem in several regions[13]. In order to identify the CW agent one needs information about its chemical composition. While the commonly used military explosives are characterized by the presence of only four chemical elements carbon (C), hydrogen (H), nitrogen (N) and oxygen (O), the presence of chemical elements phosphorus (P), sulphur (S), chlorine (Cl), fluorine (F), arsenic (As) and bromine (Br) inside the investigated object (mine, shell, grenade and similar) can be related to the presence of CW agents. The gamma ray spectra of the irradiation of sulphur, chlorine, arsenic and fluorine targets (as simulates for CW) behind the 10 cm thick water layer are shown in FIG. 5.

In our previous experiments we have shown that the gamma ray spectra obtained from the measurements of the sea floor sediments are dominated by lines of silicon or calcium, oxygen and carbon. Sediments of volkanic origin (magmatic rocks) in Adriatic Sea do not contain calcium as a dominated element. If silicon lines are absent, the sediments are of biologic origin (limestones and dolomites, recent sedimentation) and the spectra are then characterized by the presence of calcium, oxygen and carbon lines. The Nitrogen, which is a major component of explosives, was not detected in any type of rocks. Hence, the sediments should be easily distinguished from the threat materials such are explosives and CW if they do not contain unusually high concentrations of elements which can interfere with the threat material inspection as a consequence of pollution or natural variability of the sediment chemical composition.

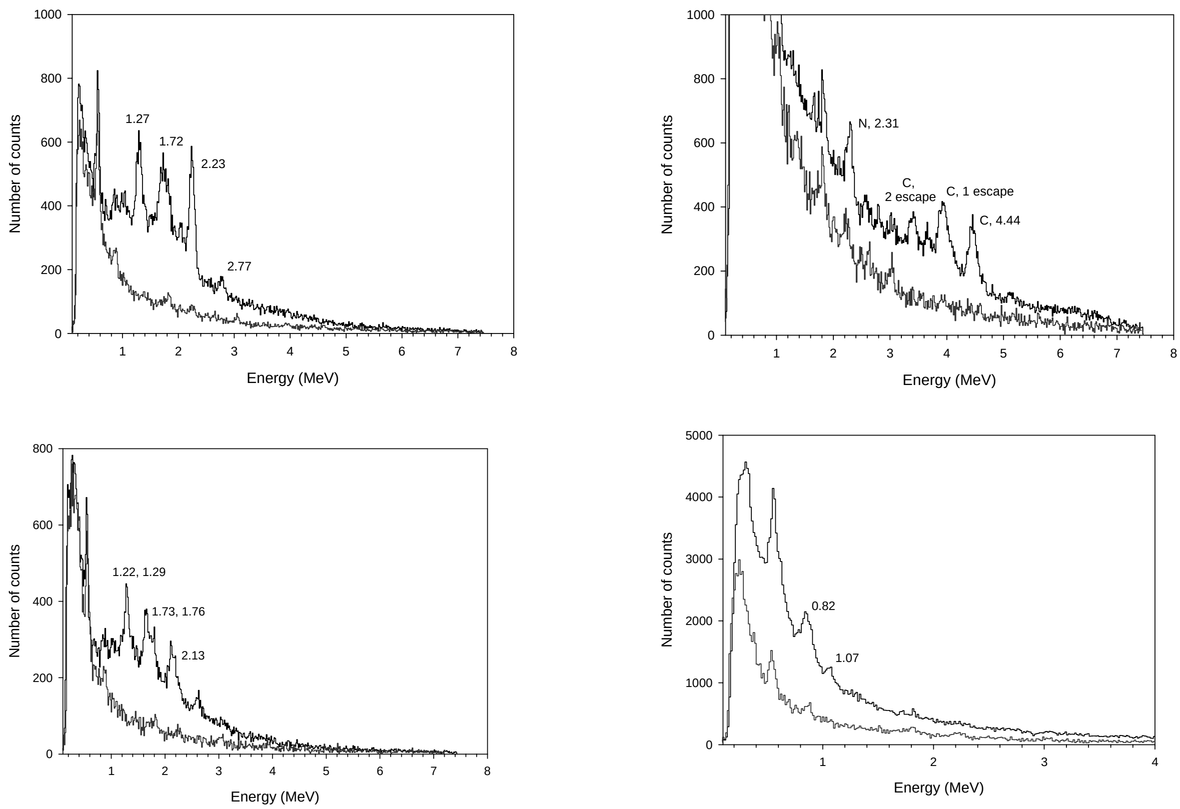

FIG. 5. The measured gamma ray spectra (upper) are obtained with the following experimental conditions: Top-left: sulphur mass 1 kg, measurement time 6,351 s, 24 x 10^7 emitted tagged neutrons; Top – right: melamine mass 1 kg, measurement time 8979 s, 36x10^7 emitted tagged neutrons; Bottom-left: sodium-chloride mass 1 kg, measurement time 10,969 s, 36 x 10^7 emitted tagged neutrons; Bottom-right: arsenic trioxide mass 2 kg, measurement time 7,000 s, 24 x 10^7 emitted tagged neutrons. The background spectra (lower) are obtained for the same experimental conditions with the target out.

3.4 Inspecting underwater hulls and sunken ships

It is often required to inspect ship hulls, either to detect potential anomalies attached to the hull, or to determine the nature of materials within hull, especially of sunken ships. We have performed tests with our system submerged in the test basin filled with sea water with targets being: 10 litters of diesel fuel, 5 kg of explosive and different chemicals (expected components of chemical warfare agents) placed behind 16 mm steel plate in the first measurement and behind sandwich 18 mm steel plate – 10 cm air bag – 16 mm steel plate in the second measurement, respectively. The thickness of the iron plate positioned between the submarine and explosive (mass 5 kg) has been varied. Submarine to explosive (mass 5 kg) distance was 11 cm. Using window on the measured alpha- gamma time spectrum gamma rays originating from the investigated volume were separated from the background radiation. From the inspection of the measured gamma spectra we were able to identify all of the investigated materials in both measurement geometries.

The graph in FIG. 6. shows the number of counts in carbon 4.44 MeV peak (black) and oxygen 5.62 MeV peak – first escape peak of oxygen 6.13 MeV line (red) as a function of iron plate thickness. Solid lines correspond to the exponential fit (a $e^{-b\,x}$). The total number of tagged neutrons in each measurement was 3.6 x 10^8, with neutron beam of ~10^7 n/s corresponding to the measurement time of ~176 min. The measurements have been done for a long time period in order to obtain better statistics. Conclusions on the existence of peaks can be reached in much shorter time.

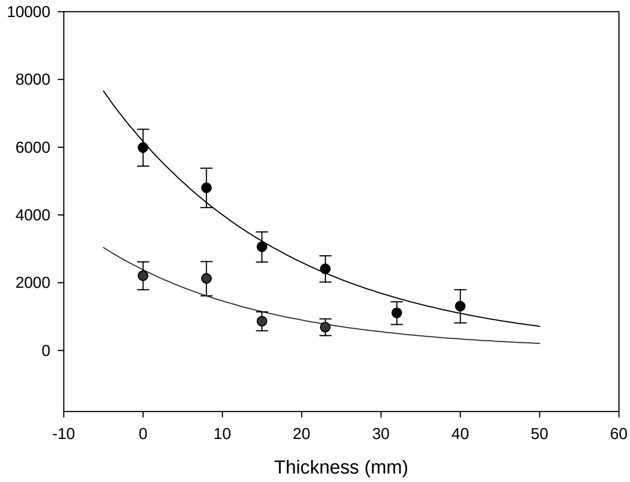

FIG. 6. The number of counts in carbon 4.44 MeV peak (upper) and oxygen 5.62 MeV peak – first escape peak of oxygen 6.13 MeV line (lower) as a function of iron plate thickness.

In comparison with the benign materials TNT explosive is characterized with a big C/O ratio. However, in the case of thicker iron plates conclusions can be drown in some situations from the presence of carbon peak only.

4. Conclusions

The results of irradiation of elements present in explosives (carbon, nitrogen, oxygen) and chemical warfare agents (sulphur, chlorine, arsenic) behind 10 cm thick water layer show that the presence of these elements can be easily determined by a sealed tube neutron generator placed inside an underwater vehicle. The source of background in all cases is sediment. Their gamma ray spectra of different types of sediments are dominated by lines of silicon or calcium, oxygen and carbon. Anyhow, the sediments can contain increased concentrations of other elements because of natural geological background or anthropogenic pollution of other source types which can interfere with the threat material inspection. In order to examine the concentration variations in sediments of Adriatic Sea geochemical contour maps were produced. These geochemical maps can be used for evaluating background for neutron sensor applications. Typically, increased values of Zn, Cu, As and Pb in sediments can be found in ports and harbors, close to the service area where the antifouling paints are applied to the boats. Therefore, in addition to the use of chemical analysis of explosives, CW and their “containers” by means of determination of presence or absence of particular elements of interest or determination of their ratios, the matrix that produces background has to be well studied in order to not be misinterpreted.

In addition, the system described here is capable to inspect ship hulls, either to detect potential anomalies attached to the hull, or to determine the nature of materials within hull, especially of sunken ships. This has been confirmed for the following targets: 10 litters of diesel fuel, 5 kg of explosive and different chemicals (expected components of chemical warfare agents) placed behind 16 mm steel plate, and behind sandwich 18 mm steel plate – 10 cm air bag – 16 mm steel plate.

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