MODERN APPROACHES TO MONITORING THE CONTENT OF HEAVY METALS IN MARINE WATERS

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The article describes the sources of pollution of sea water with heavy metal compounds, including copper, chromium, tin, nickel and cobalt ions, their impact on the ecosystem, as well as possible methods of detecting these pollutants. In Ukraine, before the start of hostilities, were river runoff and the discharge of insufficiently treated industrial wastewater were the main sources of heavy metal compounds entering the Black Sea and the Sea of Azov. After the start of the war, industry in the southern regions experienced a reduction in volumes, but a new source of pollution appeared, namely sunken military equipment, shells, mines, cartridges, etc. Alloys with a high content of various heavy metals are widely used in military equipment and weapons to give the alloys corrosion resistance and the necessary mechanical characteristics. With prolonged exposure to water, as a result of interaction with both the water itself and with impurities dissolved in it or existing microorganisms, metal ions are gradually leached into the water. Heavy metals not only harm marine biota, but also have the properties of bioaccumulation and biomagnification. As a result, the content of heavy metals in predatory fish and marine mammals increases significantly, and commercial fishing is threatened due to the possible non-compliance of the caught fish with sanitary and hygienic requirements. In order to timely detect and eliminate sources of pollution of marine waters with heavy metals, constant monitoring of the quality of marine waters is necessary. There are a large number of monitoring tools, including electrochemical sensors, but one of the fastest, cheapest and most convenient approaches is the use of indicator systems based on chromogenic compounds that change their color upon contact with a certain pollutant. The article considers examples of such compounds for the detection of copper, chromium, tin and nickel ions.

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1. Introduction

Heavy metals naturally occur in the Earth's crust at very low concentrations. However, human activities such as industrial waste discharge, mining, coastal construction, and dredging have significantly increased their levels in marine environments (Shah, 2021). In Ukraine, before the start of hostilities, were river runoff and the discharge of insufficiently treated industrial wastewater were the main sources of heavy metal compounds entering the Black Sea and the Sea of Azov. After the start of the war, industry in the southern regions experienced a reduction in volumes, but a new source of pollution appeared, namely sunken military equipment, shells, mines, cartridges, etc. (Litynska & Pelekhata, 2024). Alloys with a high content of various heavy metals are widely used in military equipment and weapons to give the alloys corrosion resistance and the necessary mechanical characteristics (Kyrii et al., 2024). With prolonged exposure to water, as a result of interaction with both the water itself and with impurities dissolved in it or existing microorganisms, metal ions are gradually leached into the water. Marine waters are significantly affected by heavy metal pollution, with copper, chromium, tin and nickel compounds being among the most prominent contaminants. Heavy metals are divided into essential and non-essential types. Essential heavy metals have biological functions and become toxic only above certain thresholds, while non-essential heavy metals have no known biological role in marine invertebrates and are highly toxic when they accumulate in metabolically active sites (Shah, 2021).

Heavy metals are persistent, non-biodegradable, and toxic, posing serious ecotoxicological risks. They tend to bioaccumulate, with accumulation depending on the metal's total amount, bioavailability, uptake routes, storage, and excretion mechanisms (Shah, 2021). Metal speciation strongly affects its bioavailability, toxicity, movement, and interactions. Factors such as pH, and the presence and concentration of inorganic and organic ligands and colloidal species influence metal speciation, thereby affecting its environmental impact (Shah, 2021). For example, heavy metals toxicity to marine organisms, including Mytilus, was significantly related to dissolved organic carbon (DOC) concentrations (DeForest & Schlekat, 2013).

The high toxicity, environmental persistence, and bioaccumulation potential of these elements result in serious ecological and public health concerns. The European Union's Existing Substances Regulation EEC 793/93, the REACH Regulation and Water Framework Directive all share common guidance for conducting environmental effects assessments, which can be further used to derive predicted no effect concentrations and environmental quality standards for chemical substances (DeForest & Schlekat, 2013).

2. Tin Contamination in Marine Waters: Risks and Detection Methods

Tin in the marine environment exists in both inorganic and organic forms. Inorganic tin has low toxicity due to its limited solubility and weak absorption, whereas organic compounds such as tributyltin (TBT) are highly toxic and can disrupt the endocrine systems of marine organisms (Ostrakhovitch, 2022; Niloy et al., 2024).

One of the primary sources of organic tin is the shipbuilding industry. The use of TBT in marine paints was a common practice for many years, leading to significant accumulation of this metal in bottom sediments. Despite the ban on TBT in 2008, its concentrations in marine waters remain high due to re-release from contaminated sediments (Ostrakhovitch, 2022; Saidon et al., 2023).

Another source of pollution is plastics containing organotin stabilizers. As plastics degrade in water, they release organic tin compounds, which enter the trophic chains of marine ecosystems. This leads to the bioaccumulation of tin in top predators and increases the health risks for humans (Ostrakhovitch, 2022; Niloy et al., 2024; Omdehghiasi et al., 2024).

Detection methods for tin in the marine environment have been significantly advanced. The most effective approaches include a combination of gas chromatography-mass spectrometry (GC-MS) and inductively coupled plasma mass spectrometry (ICP-MS). Graphite furnace atomic absorption spectrometry (GF-AAS) achieves high sensitivity, particularly for trace concentrations of tin in seawater and sediments (Ostrakhovitch, 2022; Omdehghiasi et al., 2024). Modern adsorbents, such as polymers with specific sorption capabilities, substantially enhance the accuracy of organotin compound analysis (Ostrakhovitch, 2022; Ray & Vashishth, 2024).

Colorimetric analysis using acrylic polymers with terpyridine motifs is one of the contemporary approaches. These polymers chelate Sn(II), resulting in a color change (yellow for Sn(II)) in aqueous solutions at controlled pH levels. This method detects Sn(II) at concentrations as low as 1.4×10^{-5}M. Key reagents include $SnCl_2$, hydrophobic and hydrophilic monomers, and terpyridine polymers, with the sensory monomer constituting 1% of the molar composition (Trigo-López et al., 2015).

Another method, electrothermal atomic absorption spectrometry (ETAAS) with magnetic ionic liquids, involves pre-concentration of Sn(IV) by forming a complex with diethyldithiophosphate (DDTP), followed by extraction into a magnetic ionic liquid ($[P_{66614}][FeCl_4]$) and quantification via ETAAS. The detection limit is 72 ng/L. Reagents include $SnCl_4$, DDTP, magnetic ionic liquids, and acetonitrile, with 50 μL of ionic liquid used for a 10 mL sample (Muñoz-Sandoval et al., 2024).

Spectrophotometric detection using pyrocatechol violet (PCV) is based on the different reaction rates of Sn(II) and Sn(IV) with the dye at pH 4.0. Sn(II) oxidizes to Sn(IV), which forms complexes with PCV. The reaction of Sn(IV) is faster, allowing component separation through kinetic profile analysis. The reaction mixture includes PCV, a buffer (acetic acid/sodium acetate), $SnCl_2$, and $SnCl_4$. The optimal ratio is 1.68 mL of PCV (1.0×10^{-3}M) per 25 mL of solution. This method enables simultaneous detection of Sn(II) and Sn(IV) without prior separation (Madrakian et al., 2007).

The chemical foundations of these methods involve chelation of tin to form stable complexes and the use of reaction kinetics to enhance sensitivity. Innovative approaches, such as magnetic ionic liquids, improve metal pre-concentration, while spectrophotometry provides simple and rapid analysis.

3. Copper Contamination in Marine Waters: Risks and Detection Methods

Copper is an essential element for the functioning of biological systems, but its excessive concentrations in marine waters have toxic effects. Major sources of copper contamination include industrial and agricultural discharges, corrosion of metal structures, and the use of pesticides and fungicides (Ray & Vashishth, 2024; Niloy et al., 2024; Omdehghiasi et al., 2024).Elevated copper concentrations in the marine environment disrupt cellular processes in marine organisms. Copper inhibits enzymatic activity, induces oxidative stress, and damages cell membranes. In mollusks and crustaceans, it causes reproductive impairments and growth retardation, leading to long-term consequences for populations and marine ecosystems as a whole (Ray & Vashishth, 2024; Niloy et al., 2024; Omdehghiasi et al., 2024).

Both classical and innovative methods are widely used for detecting copper in marine waters. Spectrometric techniques, such as ICP-MS and GF-AAS, provide high precision even at trace metal concentrations (Omdehghiasi et al., 2024; Aguiar et al., 2024). Novel graphene-based adsorbents demonstrate high efficiency in copper removal, eliminating up to 99% of the metal under optimal conditions. These materials are environmentally safe and have potential for large-scale applications (Niloy et al., 2024; Omdehghiasi et al., 2024).

One approach involves colorimetric analysis using sensory polymers with terpyridine motifs. These polymers interact with Cu(II), forming stable complexes that result in a green color change. The polymers contain 1% sensory monomer, enabling detection sensitivity at 9×10^{-5}M. This method is simple and accessible for visual detection of Cu(II) in aqueous environments (Trigo-López et al., 2015).

Another effective approach is fluorometric analysis with a thiazoline-amidoquinoline-based probe (QT2). The probe forms a 1:1 complex with Cu(II), causing fluorescence quenching. This method provides high sensitivity with a detection limit of 4.84 ppb and can be used to detect Cu(II) in food and water samples. Reagents include QT2 and standard solutions of Cu(II) (Paisuwan et al., 2024).

Additionally, microfluidic sensors based on chemical chelators enable rapid and precise analysis of copper concentrations under real-world conditions. These devices open possibilities for on-site monitoring of marine waters, particularly in high-risk zones (Aguiar et al., 2024; Saidon et al., 2023; Ray & Vashishth, 2024).

Microfluidic paper-based analytical devices (mPADs) combined with PVC membranes allow reagent fixation, such as pyrocatechol violet and chrome azurol S, on paper surfaces, preventing reagent diffusion. This method provides stable color responses and enables Cu(II) detection with a limit of 1.7 mg/L. These devices are convenient for field analysis due to their portability and ease of use (Sharifi et al., 2020).

The basis of these processes involves the formation of chelate complexes, which alter the spectral properties of solutions, and the use of specialized materials to fix reagents and enhance sensitivity. Together, these methods make detection techniques versatile for a wide range of applications, including environmental monitoring.

4. Chromium Contamination in Marine Waters: Risks and Detection Methods

Chromium is a heavy metal that usually enters aquatic ecosystems through industrial discharges from the metallurgical, chemical, textile, leather industries, etc. It can be found in water in various forms, most commonly as Cr(III) and Cr(VI). Trivalent chromium is an essential component of some enzymes, is non-corrosive and has poor membrane permeability and low biomagnification capacity in the food chain. Cr(VI) is the more toxic form and is dangerous for fish, as it has an intense oxidising potential and can penetrate biological membranes (Yadav et al., 2023; Halysh et al., 2020).

Military operations increase the amount of chromium significantly due to its possible ingress with gunpowder gases, remnants of weapons, maintenance of military infrastructure, use of shells, bombs, shipwrecks, etc. (Shukla et al., 2023).

The presence of Cr(VI) in marine waters has a negative impact on the marine ecosystem, as this pollutant often bioaccumulates and causes toxic effects on its biological systems (Speer et al., 2019). Thus, bioaccumulation of Cr (VI) in fish occurs in vital organs and causes changes in organ-somatic parameters and histoarchitectonics, and often leads to cell death (Kamila et al., 2023). Chromium is also toxic to marine animals and can cause damage to many organs, including the liver. Scientists have found that the presence of Cr(VI) in seawater can cause a wide range of toxic effects, including various inflammations, oxidative stress, energy metabolism, protein synthesis and metabolism, cell morphology, cell cycle regulation, cell death and cancer cell development, etc. (Ni et al., 2020). Other scientists have found that prolonged exposure to heavy metals, especially high concentrations of Cr(VI), combined with high temperatures, causes significant changes in fish histology and tissue damage (Hu et al., 2024). Awasthi et al. in their article (Awasthi et al., 2018) concluded that chromium, being mutagenic and carcinogenic, affects the physiology, behaviour, histology, biochemistry, genetics and immune system of fish.

The authors' research (Prasad et al., 2021) demonstrates that the uptake of chromium by organisms in water is influenced by species type, size, salinity, developmental stage, pH, other pollutants, temperature and alkalinity. In addition, the authors found that the toxic effect of Cr(VI) on algae is relatively low, but at the same time, it reduces the growth and photosynthesis of other aquatic plants.

Thus, the release of chromium into water, including during military operations, poses a significant environmental threat, especially given the high level of chromium toxicity to aquatic organisms and its ability to accumulate. This requires finding ways to monitor it operationally, especially in regions with high industrial activity or military operations, to respond quickly to pollution and take possible measures.

The recognised standard methods for detecting chromium are spectroscopic methods using diphenylcarbazide, atomic absorption spectroscopy, and ion chromatography. However, these techniques have several drawbacks, including high costs, the need for qualified personnel, complex materials, and multiple steps required for analysis. Therefore, atomic absorption spectroscopy and ion chromatography should be discussed further.

The colorimetric method for determining Cr(VI) relies on its complexation with diphenylcarbazide in an acidic medium for 10 minutes, producing a red-violet complex that can be measured spectroscopically at 540 nm (Standard Methods, 1915; Hilali et al., 2020). This technique is limited to clear, colorless samples. The range of chromium content for this method is 30-20000 μg/l (Biswas et al., 2017).

Wiryawan et al. studied the determination of chromium by diphenylcarbazide at a pH of 1 and found that Cr(VI) can be analysed using diphenylcarbazide at a concentration of 0.0015% and a solution of H_3PO_4 as an acid at a concentration of 0.03 mol/L with a reaction time of 5 min (Wiryawan et al., 2018). According to the authors, this method's detection limit is 0.1959 ppm. Other researchers have used the colourimetric method with diphenylcarbazide for incorporation into micro-scale detection systems (Lace et al., 2018). The Cr(VI) sample (2 mL) was transferred to a glass test tube. Sulfuric acid (0.2 M, 1 mL) and 1,5-diphenylcarbazide (0.5% w/v, 1 mL) were added, and the mixture was gently shaken and left for five minutes. The absorbance was measured at 543 nm against a blank reagent. The pH of the water samples was adjusted to 2.2. The detection limit and quantitation limit were found to be 0.023 and 0.076 mg/L, respectively.

The unique properties of diphenylcarbazide have been used to fabricate a carbon paste electrode to improve the analytical determination of Cr(VI) and Cr(III) using voltammetric methods (Paniagua et al., 1993).

Thus, the method with diphenylcarbazide is promising and can be widely used for the determination of chromium in water.

Standard methods for determining chromium in water require labour-intensive sample preparation, transport to the laboratory and long processing times. This is why various chemical sensors are becoming increasingly popular. In addition, chemical sensors offer numerous advantages, such as fast response, simple instrumentation, excellent selectivity, easy sample preparation, wide dynamic range, non-destructive analysis, etc. (Gupta et al., 2005).

Electrochemical sensors are the most widely used today. The basic principle of operation of such sensors is based on an electrocatalytic reaction between the electrodes and the analyte present in the sample under test. For example, to detect chromium, an electrochemically purified gold electrode immobilised with methylene blue was used (Biswas et al., 2017). Methylene blue was reduced on the electrode to form leucomethylene blue, which reacted with Cr(VI) to form Cr(III) and was recovered to methylene blue (Korshoj et al., 2015). Salimi et al. have prepared a novel electrochemical sensor for the detection of Cr(III) using a nanocomposite containing chitosan and multi-walled carbon nanotubes as a platform for immobilising electrodeposited nanostructured manganese oxide. The obtained modified electrode showed excellent electrocatalytic activity for the oxidation of Cr(III) in solutions with natural pH. The detection limit, sensitivity and linear range of the sensor concentrations were 0.3 μM, 18.7 nA/μM and 3-200 μM, respectively (Salimi et al., 2014).

In addition to electrochemical sensors, optical sensors are increasingly being used today. For example, Raquel et al. have shown the selective and sensitive detection of Cr(VI) using an optical membrane sensor (Güell et al., 2007). The proposed sensor showed an optical response in the range of 1.1×10^{-5} – 1.0×10^{-3} M.

Zamani and Sahebnasagh developed a novel poly(vinyl chloride) membrane sensor with high selectivity for Cr(III) ions, utilizing diethyl 2-phthalimidomalonate as the ionophore. The sensor demonstrated Nernstian behaviour, characterized by a slope of 20.6 ± 0.2 mV per decade, across a concentration range of 1.0×10^{-7} to 1.0×10^{-2} mol/L, with a detection limit of 8.6×10^{-8} mol/L. The sensor exhibited a rapid response time (~5 seconds) over the entire concentration range and was operational within a pH range of 2.9 to 6.1 (Zamani & Sahebnasagh, 2013). Heryanto et al. proposed ion-selective electrodes for determining chromium(VI) based on PVC membranes modified with 1,5-diphenylcarbazide and natural zeolite. The performance of the proposed ion-selective electrode was evaluated in terms of Nernstian response, concentration range, detection limit, response time, and selectivity coefficient. The electrode exhibited a linear potential response within the concentration range of 10^{-1} to 10^{-6} M $K_2Cr_2O_7$, with a Nernstian slope of mV/decade, a detection limit of 2.14×10^{-6} M, and a response time of approximately 250 seconds (Heryanto et al., 2022).

Mohamed et al. developed a selective and cost-effective modified carbon paste electrode based on a simple ionophore, benaze. The sensor exhibited a Nernstian slope of 19.20 ± 0.39 mV per decade over a concentration range of 8.0×10^{-6} to 1.0×10^{-1} mol/L, with a rapid response time of 10 seconds. The device remained functional for at least 54 days with minimal changes in performance. The proposed electrode demonstrated a stable potentiometric response within a pH range of 2.5–6.5 and high selectivity toward Cr(III) ions compared to various inorganic cations (Mohamed et al., 2021).

Although sensors are designed with a focus on cost reduction and adaptation for real-time applications, the concentration of heavy metals in a sample does not always accurately correlate with their toxicity. Toxicity is determined by the ionic form of the metal, its physiological state, and its bioavailability. Consequently, biosensors are increasingly being developed to enhance selectivity, sensitivity, and specificity by incorporating biological recognition elements, such as enzymes, microorganisms, or other biocomponents. This enables rapid and precise on-site analysis through specific interactions with the target analyte. Biosensors provide sensitivity and accuracy comparable to traditional sensors but with a higher detection threshold.

A biosensor is an analytical device that uses surface biomolecular interactions to detect biochemical changes and rejects unintended nonspecific signals (Mohanty & Kougianos, 2006).

Depending on the type of biological signalling mechanism and signal transmission mechanism, there are four different categories of biosensors: potentiometric biosensors, amperometric biosensors, conductometric biosensors, and impedimetric biosensors.

A potentiometric biosensor measures the potential difference between an indicator electrode and a reference electrode in a system, with the potential being directly related to the concentration of the target analyte. These sensors are based on the selective recognition of specific molecules by a biological component and the transduction of this recognition event into an electrical signalIn the study by Çevik et al., a $PdRuO_2$/PVP nanomaterial was synthesized and used as an ionophore in potentiometric sensor electrodes for detecting Cr(III) ions. The potentiometric characteristics of the sensor were investigated within the concentration range of $1 \times 10^{-6} – 1.0 \times 10^{-1}$ M. The detection limit of this sensor was exceptionally low, at 8.6×10^{-8} M. The potentiometric measurements demonstrated the high efficiency of the $PdRuO_2$/PVP ionophore for Cr^{3+} detection across a wide pH range (2.0–8.0) and confirmed its stability, which remained effective for over one year Çevik et al., 2024).

An amperometric biosensor operates by measuring the current generated by the oxidation or reduction of an electroactive species at an electrode surface. The current produced is directly proportional to the concentration of the target analyte in the sample. Caroline et al. demonstrated the quantification of chromium in groundwater using an enzymatic amperometric biosensor, where cytochrome c3 (Mr 13,000) from D. norvegicum (DSM 1741) was evaluated for pH, temperature and ionic strength (Caroline et al., 2006). Nepomuscene et al. (Nepomuscene et al., 2007) developed a sol-gel immobilization sensor for detecting chromium in water, utilizing enzyme inhibition activity, and assessed the effects of both free and immobilized enzymes on biosensor performance. For chromium concentrations up to 50 mg/L, a current change of approximately 200 μA was observed. The activity of immobilized urease, inhibited by chromium ions, was restored by soaking the sensor chip in a buffer solution containing ethylenediaminetetraacetic acid. Additionally, kinetic parameters were evaluated, demonstrating that the biosensor's activity and stability remained consistent after six uses over four days (Nepomuscene et al., 2007).

A conductometric biosensor operates by measuring changes in the electrical conductivity of a solution due to a biochemical reaction. These changes occur as a result of the production or consumption of ions during the interaction of the analyte with the biological recognition element. A conductometric biosensor uses two noble metal electrodes immersed in a solution to measure its conductivity. Enzymatic reactions serve as a mechanism for converting neutral substrates into charged products that change the conductivity of the medium. Despite the limited distribution of such sensors, this method is widely used to determine the salinity of marine ecosystems (Biswas et al., 2017). For example, a study (Qambrani et al., 2013) examined the impact of Cr(VI) pollution by inhibiting thiosulfate-oxidising bacteria. The analysis was carried out by measuring electrical conductivity, pH and sulphate formation due to thiosulphate oxidation. These bacteria use thiosulfate as an electron donor, forming sulfate, which is accompanied by a decrease in pH and an increase in electrical conductivity. This makes it possible to determine Cr(VI) concentrations in dissolved water of less than 100 μg/l. In addition, Qambrani et al. also used thiosulfate-oxidising bacteria to detect Cr(VI) with a detection limit of 100 μg/L, and also used sulfur-oxidising bacteria to determine both Cr(III) and Cr(VI) (Qambrani et al., 2013).

Due to their sensitivity, speed, and environmental friendliness, biosensors show significant potential for monitoring chromium in water. Further innovations in materials science, biotechnology, and electronics can help facilitate their widespread adoption in environmental monitoring and water treatment.

5. Nickel Contamination in Marine Waters: Risks and Detection Methods

Nickel is a widely distributed metal found in animals, plants, soil, and various water bodies (Begum et al, 2022). Leaching from rocks and soils is the main natural route of nickel entering natural waters. It also exists in adsorbed form on clay particles or associated with organic matter of detritus, algae, and bacteria or as soluble salts of humic and fulvic acids (Begum et al, 2022).

Industrial activities like mining, processing, and smelting are main anthropogenic sources of nickel (Begum et al, 2022). Also nickel is associated with the manufacture of computer components and other metal-plating activities (Hunt et al., 2002). As one of the most abundant metals found in heavy oils, nickel has experienced significant increases in concentration due to industrial and traffic sources. These anthropogenic nickel pollutions have disrupted natural geochemical cycles (Wu et al., 2021). In the Baltic Sea the average value of anthropogenic nickel input is about 57% (Cempel & Nikel, 2006). In the case of oil spills, the ratio Ni/Ca significantly increases in corals due to bioaccumulation (Wu et al., 2021). Industrial wastewaters, tailing pile runoff, landfill leachate and stormwater runoff often have significant level of nickel compounds. Urban stormwater runoff samples have been found to contain nickel levels ranging from 1 g/L to 87 g/L (Begum et al, 2022). Nickel can also enter seawater as a result of corrosion of various steels and alloys (Ni-Mo steel, B10 copper-nickel alloy, nickel aluminium bronze alloy, etc.) that are components of ships and other vehicles, reinforcement in concrete structures, pipes, etc. (Dong et al., 2022; Sun et al., 2015; Arcos et al., 2023).

Seawater typically contains about 0.5–2 ppb of nickel, while river waters have lower levels, around 0.3 ppb (Begum et al, 2022). This is explained by the accumulation of nickel in the seas and oceans as a result of many years of input with river runoff and pollution from industry and ships.

Many harmful effects arise from nickel disruption of the metabolism of essential metals like Fe(II), Mn(II), Ca(II), Zn(II), Cu(II), and Mg(II), which can alter or reduce its toxic and carcinogenic impact. Toxicity of nickel primarily stems from its capacity to replace other metal ions in enzymes and proteins or to bind with cellular molecules containing oxygen, sulfur, and nitrogen atoms (enzymes, nucleic acids, etc.) leading to their inhibition and impaired biological functions (Cempel & Nikel, 2006). Echinoderms, molluscs and crustacea are the most sensitive marine taxa, when they are exposed to nickel through waterborne and/or dietary routes (Wang et al., 2020).

There are many methods for detecting nickel ions in water, but some of the most popular are various spectrophotometric techniques due to the relatively low cost of the equipment and the visually noticeable result.

Usage of dimethylglyoxime reagent is the most popular method of Ni determination, but a significant disadvantage is the formation of colored compounds with some other heavy metal ions under the same conditions (Ubaydullayeva et al., 2022). Pyridylazo compounds are more sensitive and selective. The reaction of nickel ions with 1-(2-pyridylazo)-2-hydroxy-4-mercaptofenol in the presence of aminofenols can be used for the nickel concentration in water from 0.5 mg/L to 18 mg/L at wavelength about 550 nm and pH 10.7-12.8 (Zalov et al., 2021). But photometric detection with 1-(5-iodo-2-pyridylazo)-2-hydroxy-4-mercaptophenol in the presence of 2,6-bis(N,N-dimethylaminomethyl)-4-methylphenol is significantly more sensitive. The limit of photometric detection is about 0.009 mg/L (Askerova et al., 2022). But these compounds are very expensive, so dimethylglyoxime is most widely used for field detection methods.

Kamnoet et al. have designed paper-based analytical device fabricated by a wax printing method for simultaneous determination of Cu(II), Co(II), Ni(II), Hg(II), and Mn(II). Dimethylglyoxime was used for nickel detection. The analytical results were achieved with the lowest detectable concentration of 0.59 mg/L and the linear range of 5.87–352.16 mg/L (Kamnoet et al., 2021).

In addition to paper-based analytical device, there are other approaches to determining the nickel content in water in field conditions.

Optical sensing membrane can be used for detecting of nickel ions, utilizing the entrapment of 5-(2-benzothiazolylazo)-8-hydroxy-quinoline within a matrix of polyvinyl chloride combined with dioctyl adipate. This sensor has a broad linear span range from 0.0025 to 0.110 mg/L (Alluhayb et al., 2025). Fluorescent chemosensor based on 4-[4,5-di(pyridin-2-yl)-1H-imidazol-2-yl]benzoic acid has the limit of quantification lower than 0.006 mg/L (Robert-Peillard et al., 2022).

Among the considered methods of determination, the cheapest and most accurate is paper-based analytical device with dimethylglyoxime.

6. Conclusions

In the study the primary pathways of copper, chromium, tin and nickel ions entry into the marine environment, their impact on ecosystems, and modern detection methods are discussed.

Heavy metals cause different negative health effects and also have the properties of bioaccumulation and biomagnification. As a result, the content of heavy metals in predatory fish and marine mammals increases significantly, and commercial fishing is threatened due to the possible non-compliance of the caught fish with sanitary and hygienic requirements. In order to timely detect and eliminate sources of pollution of marine waters with heavy metals, constant monitoring of the quality of marine waters is necessary. There are a large number of monitoring tools, including electrochemical sensors, but one of the fastest, cheapest and most convenient approaches is the use of indicator systems based on chromogenic compounds that change their color upon contact with a certain pollutant.

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СУЧАСНІ ПІДХОДИ ДО МОНІТОРИНГУ ВМІСТУ ВАЖКИХ МЕТАЛІВ У МОРСЬКИХ ВОДАХ

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В статті розглянуто джерела забруднення морських вод сполуками важких металів, включаючи іони купруму, хрому, стануму, нікелю та кобальту, їх вплив на екосистему, а також можливі способи виявлення цих полютантів. В Україні до початку воєнних дій основними джерелами надходження сполук важких металів у Чорне та Азовське моря були річковий стік та скидання недостатньо очищених промислових стічних вод. Після початку війни промисловість у південних областях зазнала скорочення обсягів, але з'явилось нове джерело забруднення, а саме затонувша військова техніка, снаряди, міни, гільзи тощо. У військовій техніці та озброєнні широко використовуються сплави з високим вмістом різних важких металів для надання сплавам корозійностійкості та необхідних механічних характеристик. При тривалому знаходженні у воді внаслідок взаємодії як з самою водою, так і з розчиненими в ній домішками чи наявними мікроорганізмами, поступово відбувається вимивання іонів металів у воду. Важкі метали не лише завдають шкоди морській біоті, а й мають властивості до біоакумуляції та біомагніфікації. В результаті суттєво підвищується вміст важких металів у хижих рибах та морських ссавцях, а промисловий вилов риби стає під загрозою, внаслідок можливої невідповідності виловленої риби санітарно-гігієнічним вимогам. Для вчасного виявлення та ліквідування джерел забруднення морських вод важкими металами необхідний постійний моніторинг якості морських вод. Існує велика кількість засобів моніторингу, включаючи електрохімічні сенсори, але одним з найбільш швидких, дешевих та зручних підходів є використання індикаторних систем на базі хромогенних сполук, які змінюють своє забарвлення при контакті з певним полютантом. У статті розглянуто приклади таких сполук для виявлення іонів купруму, хрому, стануму та нікелю.

Ключові слова: *важкі метали, виявлення забруднювачів, водне середовище, забруднення води, якість води*