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**Khatsevych O.M., Mykytyn I.M., Fedorchenko S.V., Kurta S.A.**

# WATER QUALITY ANALYSIS: EUROPEAN EXPERIENCE

## MANUAL

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**Authors:**

**Khatsevych O.M.** – PhD., Associate Professor of the Department of Chemistry, Faculty of Natural Sciences, Vasyl Stefanyk Carpathian National University (Ivano-Frankivsk); learned secretary State institution «State Scientific Research and Design Institute of Basic Chemistry»;

**Mykytyn I.M.** – PhD., Head of the Department of Chemistry, Faculty of Natural Sciences, Vasyl Stefanyk Carpathian National University, (Ivano-Frankivsk);

**Fedorchenko S.V.** – PhD., Associate Professor of the Department of Chemistry, Faculty of Natural Sciences, Vasyl Stefanyk Carpathian National University, (Ivano-Frankivsk);

**Kurta S.A.** – Doctor of Technical Sciences, Professor of the Department of Chemistry, Faculty of Natural Sciences, Vasyl Stefanyk Carpathian National University, (Ivano-Frankivsk).

**Reviewers:**

**Myronyuk Ivan Fedorovych -** Professor of the Department of Chemistry, Faculty of Natural Sciences, Vasyl Stefanyk Carpathian National University, Doctor of Chemical Sciences, Professor;

**Maria Semenovna Zasidko -** Head of the Water Monitoring Laboratory of the Western Region of the Dniester Basin Water Resources Department.

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The manual is intended for students of the speciality E3 «Chemistry» and natural sciences who are studying the courses «Monitoring of environmental objects», «Water analysis», «Environmental chemistry», «Ecology», and «Water chemistry». It can be used by students of full-time and part-time forms of study to perform research work, solve scientific and practical tasks related to the study of the ecological status of surface and underground species and the possibilities of their monitoring. The textbook contains theoretical material and presents key methods of analysing the chemical composition of water that are proven and available for use under laboratory conditions. It highlights the approaches of the European Union countries to monitoring environmental objects, particularly water bodies, and the processes of harmonising Ukrainian environmental monitoring with European requirements. Studying the material of the textbook will contribute to the promotion of European environmental principles and the right to safe living, as well as to providing course participants and the public with accurate and up-to-date information about the state and methods of monitoring water quality.

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# CONTENTS

# INTRODUCTION

## The importance of surface waters in the ecosystem of Ukraine

Surface waters, including rivers, lakes and reservoirs, are integral to maintaining ecological balance and supporting human and animal life. These water bodies provide essential resources for drinking water supply, agriculture, industry and energy production. Surface water quality reflects the interaction between natural processes and anthropogenic activities. Factors such as geological conditions, soil properties, vegetation and hydrological processes affect the composition of surface waters. For example, natural factors such as the dissolution of minerals and the decomposition of organic matter affect nutrient levels and water pH. Conversely, human activities (agriculture, urbanisation, industrial processes) often lead to the introduction of pollutants that degrade water quality and disrupt aquatic ecosystems. Surface waters are also a critically important habitat for a variety of aquatic organisms, whose vital activities depend on water quality. Parameters such as dissolved oxygen, temperature, nutrients, and contaminant concentrations affect the natural condition of aquatic ecosystems. Moreover, surface waters play a vital role in mitigating climate change, acting as carbon sinks, and regulating regional climate.

Surface water quality management faces significant challenges due to increasing anthropogenic pressure. These challenges include pollution by extraneous substances, the impact of climate change, toxic substances and anthropogenic alterations, each of which poses a particular threat to aquatic ecosystems and human water resources.

**Pollution from point and diffuse sources.** Point sources, such as industrial discharges and wastewater treatment plants, release concentrated pollutants directly into water bodies. These pollutants often contain heavy metals, nutrients and organic matter, which can seriously affect water quality. In contrast, diffuse pollution is caused by sources such as agricultural wastewater and urban sewage. It contributes to the enrichment of aquatic environments with nutrients, which is the cause of eutrophication. Furthemore, the input of pesticide residues and pharmaceuticals contributes to an increase in the load on sediments and, as a result, disrupts the ecological balance of aquatic systems.

**Climate change impacts.** Climate change exacerbates water quality problems in many ways. Rising temperatures reduce the solubility of oxygen in water, leading to lower levels of dissolved oxygen, which is critical for aquatic life. In addition, warmer conditions can increase thermal stratification in lakes, which further affects oxygen distribution. Increased frequency and intensity of floods and droughts disrupt natural water cycles, altering pollutant transport and dilution processes, which can exacerbate water quality deterioration.

**Toxic substances.** The presence of toxic substances in surface waters is a growing concern. Heavy metals, persistent organic pollutants, and emerging pollutants such as pharmaceuticals and microplastics pose significant risks to aquatic ecosystems and human health. These substances often bioaccumulate within the food chains, leading to long-term impacts on biodiversity and ecosystem stability. In addition, these pollutants pose challenges to water treatment systems, often making it more difficult to provide a clean water supply.

**Anthropogenic alterations.** Human activities, such as dam construction, river channelization, and urbanization, are significantly altering natural aquatic systems. These changes disrupt natural flow regimes, sediment transport processes, and habitat availability for aquatic organisms. For example, channelization of a river can lead to habitat loss of species that depend on the natural dynamics of the river, while dam construction can block migration routes for fish and other aquatic organisms. Addressing these issues through effective monitoring, regulation, and the implementation of sustainable practices can preserve surface water quality, supporting both ecological integrity and human needs.

**The impact of war on Ukraine's aquatic ecosystems.** Russia's full-scale invasion of Ukraine has caused unprecedented damage to the country's aquatic ecosystems, with far-reaching consequences for biodiversity, human livelihoods, and water security. Since 2022, Ukraine has lost more than a third of its freshwater reserves, and reservoirs and water infrastructure have been destroyed as a result of military actions. This includes the catastrophic destruction of the Kakhovka Dam in June 2023, which released an estimated 14 km$^3$ of water and drained almost 90% of the reservoir, exposing about 1,870 km$^2$ of the lakebed and radically changing the hydrology and ecology of the lower Dnipro River [1, 2]. The destruction has led to the loss of key ecosystem services, such as drinking water supply, irrigation, fisheries, and flood regulation. It is estimated that about 5 million people have lost access to clean water, and fishing volumes have decreased by more than 50% in inland waters and by more than 80% in marine areas [1]. In addition to economic losses, this collapse of ecosystem services threatens regional food security, especially for communities that depend on fish protein and agricultural productivity supported by irrigation. Studies conducted in Zaporizhia and Kherson regions reveal alarming levels of contamination of sedimentary rocks and soils. Elevated concentrations of heavy metals (e.g., cadmium, mercury, lead), persistent organic pollutants (such as PCBs, PAHs), and synthetic chemicals such as PFAS have been found [1]. These pollutants pose risks to aquatic ecosystems and human health, particularly through biomagnification within the food chains and the use of contaminated water for irrigation. Climate change exacerbates these problems. For example, in Mykolaiv, where Russian troops destroyed the main drinking water supply system, alternative sources such as the Southern Bug River are currently under evaluation. However, hydrological models predict that climate change will cause both seasonal and annual variability in river flow, which will exacerbate water shortages in the summer months [3]. These combined stresses caused by war and climate require adaptive management strategies that take into account both immediate infrastructure restoration as well as the long-term ecosystem sustainability. Additional hydromorphological alterations caused by the war, particularly in the Irpin River basin, lead to floodplain degradation and changes in sediment transport. These changes increase the content of organic matter and nutrients downstream, leading to algal blooms, hypoxia, and the loss of spawning grounds. Therefore , the restoration of Ukraine’s water sector will require coordinated efforts from different sectors. A comprehensive strategy should combine ecosystem-based restoration, resilient infrastructure design, sustainable irrigation processes, and long-term environmental monitoring [1]. This approach prioritizes ecosystem services in post-conflict reconstruction planning and establishes reliable monitoring systems to restore and prevent future degradation of water bodies. Therefore, the environmental impact of the war on Ukraine’s aquatic bodies is profound and threatens both natural ecosystems and human well-being. [4] Without urgent, science-based interventions, the complex consequences of infrastructure destruction, pollution and climate change could leave lasting negative consequences on Ukraine’s water landscapes.

Consireding the destruction of aquatic environments by war, the EU Nature Restoration Act (European Parliament and Council of the European Union, 2024) [5] offers a relevant model for Ukraine’s ecological restoration. This legislation establishes legally binding targets for the restoration of degraded ecosystems, including rivers, floodplains, and wetlands. By focusing on natural solutions and restoring ecological connectivity, the law provides a blueprint for post-war restoration efforts that combine biodiversity restoration with climate resilience and water security. While the principles of this provision are not directly binding for Ukraine, they are highly applicable in the context of the restoration of rivers, the rewetting of drained peatlands, and the removal of artificial obstacles to free-flowing rivers.

## Analysis of the state of water resources in Europe

Water, from melting glaciers to groundwater, lakes, rivers and seas, is an interconnected and vital resource. Pollution, overexploitation, physical alterations of aquatic environments and climate change continue to affect Europe's water bodies and the life that depends on them. Freshwater resources are limited. Europeans use billions of cubic metres of water every year for drinking, agriculture, manufacturing, heating, cooling, energy production, tourism and other sectors of the economy. Population growth, urbanisation, pollution and the effects of climate change, such as persistent droughts and extreme temperatures, are putting increasing pressure on Europe's freshwater reserves and deteriorating their quality. European seas cover over 11 million km², ranging from shallow, semi-enclosed seas to vast expanses of the deep ocean. They form a very diverse range of coastal and marine ecosystems. Despite the fact that EU countries have managed to reduce some of the pressure, the state of conservation of marine ecosystems also remains critical.

In recent years, the European Union and its Member States have been intensively implementing measures to improve water quality, reduce pollution and enhance the state of aquatic ecosystems. In particular, in areas such as the quality of bathing water , drinking water and urban wastewater treatment , impressive progress has been made. However, challenges remain, in particular regarding the conservation of wetlands, the increase in plastic waste in the seas and other hazardous chemical components in water bodies , which is also a cause for concern.

Pollution, habitat degradation of aquatic biota, climate change impacts, and overexploitation of freshwater resources are placing European lakes, rivers, coastal waters, and groundwater under unprecedented pressure. According to the latest report on the assessment of the state of European water bodies [6], the established targets for improving the water status in line with EU requirements are also not being met. Improving water management is key to increasing water resilience, reducing pressure on water resources, and ensuring sufficient quantities of high-quality water for European citizens, nature, and industry. According to the report [6], agriculture is the biggest pressure on both surface and groundwater. According to Member States' own monitoring, this is due to water pollution resulting from the intensive use of nutrients, fertilizers, and pesticides. Agriculture is the largest water consumer in Europe, and without changes in practice, the demand from irrigated agriculture is likely to increase further under climate change. The EU can achieve significant water savings by improving water efficiency, particularly in agriculture, energy production and water supply systems.

In recent years, water withdrawals have increased in almost all sectors except electricity and cooling, contributing to increasing water scarcity. Climate change is exacerbating the effect, making water availability more unpredictable. Efficient water use is an important step to ensure resilience to growing demand and seasonal shortages.

With growing evidence of the harmful effedcts of microplastics and micropollutants to the environment and human health, this problem is increasingly recognized by scientists, policymakers and society [https://wasserdreinull.de/en/technology]. However, water quality is still rarely a priority in policy, and effective measures to limit these pollutants are implemented slowly or not at all. The requirement to upgrade wastewater treatment plants and introduce standardised monitoring is a step forward, but the new directive underestimates the role of treatment plants as a major source of microplastics. It provides only minimal and ineffective controls, which do not incentivise targeted removal of microplastics during upgrades. This makes the process longer and more costly than it could be with a comprehensive approach. Moreover, many EU countries still do not meet the previous requirements for wastewater treatment, and EU controls are insufficient. This could further slow down modernization and reduce its real impact.

There is also growing concern in many European countries about contamination by perfluorocarbon acetates, but comprehensive monitoring data are often limited. Most monitored rivers, transitional and coastal waters, as well as a significant proportion of lakes in Europe, are contaminated with at least one of a numerous highly persistent chemical compounds that are harmful to humans and the environment. It is difficult to draw conclusions about the extent of the problem in Europe due to uncertainties and a lack of data. However, there are challenges in achieving zero pollution targets for the environment and in attaining good chemical status (as required by the Water Framework Directive).

Compared to other parts of the world, Europe still has relatively large freshwater reserves. However, these resources are unevenly distributed. According to the report [6], Europe already experiences water stress, where demand exceeds available supplies over a period of time. Water stress affects approximately 20% of Europe’s territory and 30% of its population annually [6], and these figures are likely to increase due to climate change.

- ✓ According to data provided by EU Member States, only 37% of Europe's **surface water bodies** achieved “good” or “high” ecological status, which is a key indicator of an aquatic ecosystem health, while only 29% achieved “good” chemical status over the period 2015-2021 according to the EU Water Framework Directive, [6].
- ✓ **Groundwater resources** are in better condition than its surface waters: 77% of it is in good chemical status, and in terms of supply, 91% of groundwater is reported to be in good quantitative status [6]. However, problems related to pesticide and nutrient pollution remain.
- ✓ **Agriculture** remains an important consumer and source of pollution. In 2017, it accounted for 59% of total freshwater consumption in Europe. Recent data

indicate that 22% of Europe's surface water bodies and 28% of groundwater areas are subject to diffuse pollution from agriculture, nutrients and pesticides.

- ✓ **Groundwater** supplies 65% of drinking water and 25% of water for agricultural irrigation in most EU Member States.
- ✓ **Ocean acidity** has increased by 30% since the 1980s due to climate change, and research suggests further acidification is on the way. Average sea surface temperatures have increased by 0.2° C to 0.5° C per decade [6].

Climate change is predicted to reduce water availability in Europe, creating additional challenges for southern regions that are already facing water scarcity. Much of Europe is expected to experience more frequent flooding, while low-lying regions are threatened by sea-level rise and more frequent storms. EU cities and regions are on alert and are implementing measures ranging from reducing leakage and water reuse to incorporating blue and green zones in urban areas aming to minimise the risks of flooding and water-related hazards.

However, it is worth noting that over the past four decades, Europe has made significant progress in regulating water quality, wastewater treatment, and protecting marine and freshwater habitats. EU policies cover drinking water, urban wastewater, marine environment protection, and bathing water quality. Improved legislation on single-use plastics, industrial emissions, and restrictions on the use of hazardous chemicals also contribute to ensuring clean water. European water legislation has recently been revised to take into account the current situation. The Water Framework Directive (WFD) is the main legislative framework for protecting and monitoring water quality in the EU. One of the WFD’s key objectives is to ensure that all water bodies are in “good status”, in order to prevent further deterioration of aquatic ecosystems and their water-related needs, and to protect and improve their status. Other regulatory documents have also been adopted, including: the Floods Directive, which encourages the development of flood risk management plans; the Urban Wastewater Directive; the Nitrates Directive, the Drinking Water Directive, the Groundwater Directive, The Marine Strategy Framework Directive, the Bathing Water Directive. All of these will be discussed in greater detail within this textbook.

As most of water-related issues are linked to economic activity, other EU initiatives, including those on the circular economy, clean energy and safe chemicals under the European Green Deal, also play an important role in ensuring the sustainable use of marine and freshwater resources.

# CHAPTER 1

# Regulatory documents for water quality assessment in Ukraine

In the current conditions, it is very important to systematize practical tools for the proper application of current regulatory standards for assessing water quality for various purposes: environmental, hygienic, fisheries, and drinking water quality control. Below are key definitions [7] for a clear understanding and accurate application:

- ✓ **Water quality regulation** is the establishment in a directive manner, of regulated permissible values or limits of a particular indicator.
- ✓ **A water body** is a natural or artificially created element of the environment in which water is concentrated (sea, river, lake, reservoir, pond, canal, aquifer). Surface water bodies are divided into watercourses (water flowing in a channel, example - a river) and reservoirs (slow water exchange, or drainless, example - a lake).
- ✓ **Water quality of a water body** is a consideration of the physical properties of water, its chemical and biological composition, which determines its suitability for specific types of water use.
- ✓ **Drinking water** - water intended for human consumption (tap water, bottled water, water from public fountains, wells), the composition of which, according to organoleptic, microbiological, chemical, physical and radiation indicators, meets hygienic requirements.

## 1.1 Transformation of the regulatory framework: from old standards to European approaches

The signing of the Association Agreement between Ukraine and the EU in 2014 was a turning point for the national water resources management system. This strategic step launched a process of fundamental reform aimed at implementing the provisions of the EU Water Framework Directive. The transition from the outdated Soviet system to modern European approaches required a comprehensive revision, not only of the monitoring methodologies, but also of the entire regulatory architecture of this area.

Table 1.1 below provides a chronology of the main changes to water quality assessment documents that occurred in Ukraine during 2014–2019 and formed the modern architecture of water monitoring.

These changes have created a new, more complex, but more integrated and potentially effective monitoring system. It requires specialists to have a deep understanding of new methodologies, especially in the area of environmental assessment, where fundamental changes have been introduced.

Table 1.1

Chronology of major changes in water quality assessment documents in Ukraine

| Year/Date | Regulatory change and its consequences |
|---|---|
| 2014 | Signing of the Association Agreement between Ukraine and the EU. The process of harmonizing Ukrainian legislation, in particular in the field of water policy, with EU norms, has been initiated. |
| 01.02.2015 | Entry into force of DSTU 7525:2014 "Drinking Water". New requirements and methods for controlling the quality of drinking water have been established, which is an important step in modernizing standards for the end-users. |
| 2016 | Adoption of the Law on the implementation of the basin principle of water resources management. Amendments were made to the Water Code of Ukraine, which implemented the provisions of the EU WFD on hydrographic zoning and water monitoring. |
| 01.01.2017 | Cancellation of sanitary legislation. Cabinet of Ministers' Order No. 94-r canceled the validity of outdated sanitary regulations (including SanPiN 4630-88), which created a "regulatory vacuum". Also in 2017, the State Sanitary and Epidemiological Service was liquidated, and its functions were redistributed between the Ministry of Health, the State Labor Service, and the State Service of Ukraine on Food and Consumer Protection, which deepened regulatory uncertainty. |
| 09.19.2018 | Approval of the "Procedure for State Water Monitoring". Resolution of the Cabinet of Ministers No. 758 defines a new structure and types of monitoring (diagnostic, operational, research) in accordance with European requirements. |
| 14.01.2019 | Approval of the new "Methodology for classifying surface water bodies...". Order No. 5 of the Ministry of Environment and Natural Resources introduced a revolutionary approach to environmental assessment, based on classes of ecological and chemical status, which replaced the outdated concept of classification by maximum permissible concentrations (MPC). |

## 1.2. Ecological assessment of water quality: a new methodology under the EU Water Framework Directive

The most revolutionary shift in the national practice of water monitoring has occurred in the field of environmental assessment. The new methodology, harmonized with the EU Water Framework Directive, abandons the outdated approach based on the concept of maximum permissible concentrations (MPC).

Instead, a comprehensive system of classification **of the ecological** and **chemical status of surface water bodies** (SWBs) was introduced. This approach is more holistic, as it assesses not only the presence of pollutants, but also the general state of the aquatic ecosystem. The water quality of a water body determines its suitability for specific types of water use: domestic and drinking purposes, cultural and household (recreational), and fisheries (Fig. 1). The overall assessment of the state of a water body is provided by the ecological water quality assessment.

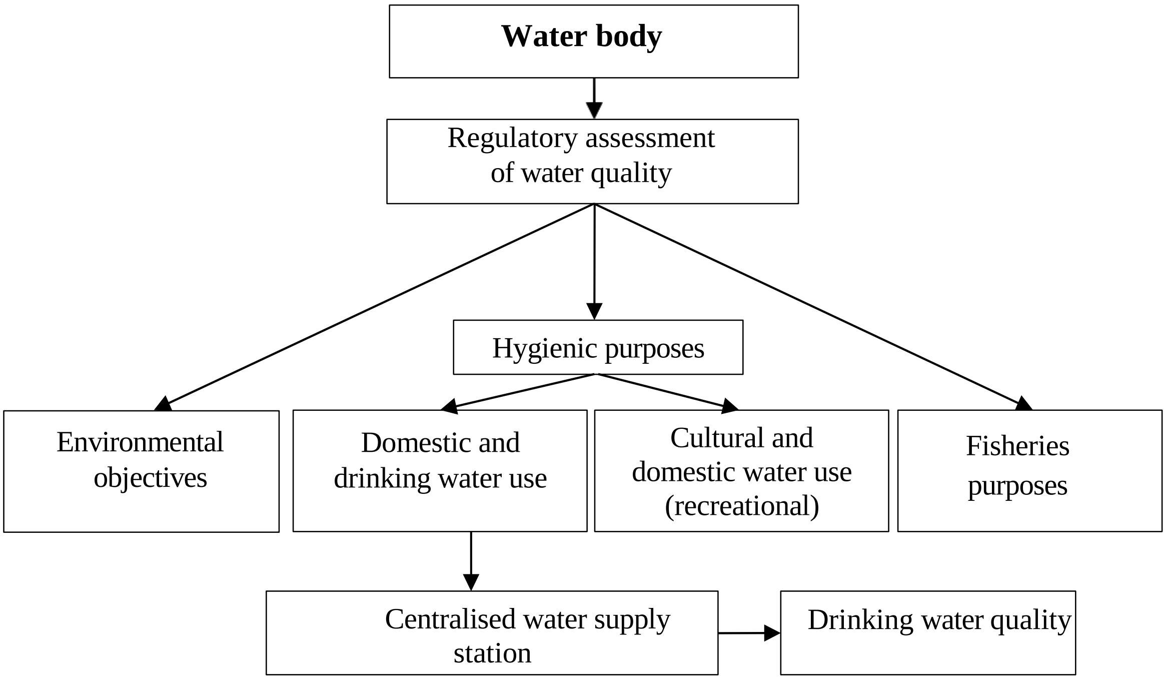


Fig. 1.1. Scheme of water quality assessment of a water body for various purposes. (source [7])

The quality of drinking water intended for human consumption is considered separately. In centralized water supply, drinking water is the product of special preparation at the water supply station.

The key object of the new state monitoring system is the surface water body (SWB) — a specifically defined, separate and significant part of a water body (for example, a river section). A SWB can belong to one of five categories:

1. Rivers
2. Lakes
3. Transitional waters
4. Coastal waters
5. Artificial or significantly modified surface water bodies

The State Water Monitoring (SWM) Program provides comprehensive control over four groups of indicators, enabling a thorough assessment of the condition of a water body:

1. Biological (state of flora and fauna);
2. Physico-chemical (temperature, pH, dissolved oxygen, etc.);
3. Chemical (priority pollutants);
4. Hydromorphological (channel structure, flow regime).

The key principle of the new methodology (approved by the Order of the Ministry of Environmental Protection nad of Natural Resources No. 5 of 14.01.2019) is to compare actual indicators not with abstract MPCs, but with "reference conditions". This concept describes the state of the aquatic environment in the absence or under minimal anthropogenic impact, which allows us to assess the degree of deviation of the ecosystem from its natural, pristine state. For hydrochemists, this approach is close to the concept of "relative hydrochemical background", which has long been used to determine the anthropogenic impact on ion flow. Based on this comparison, the ecological state of the SWB is classified into five classes, each of which has its own color designation for visualization on maps.

The practical significance of this classification is that it provides the basis for the development of river basin management plans. The ultimate goal of these plans is to achieve at least "good" ecological status for all surface water bodies.

Table 1.2

Classification of the ecological status of surface water bodies (SWBs)

| Class | Status name | Color coding | Evaluation criteria |
|---|---|---|---|
| **I** | High | Blue | The values of biological indicators correspond to reference conditions. Anthropogenic alterations in hydromorphological, chemical and physicochemical indicators are absent or very insignificant. |
| **II** | Good | Green | The values of biological indicators show a low level of anthropogenic impact and slightly deviate from reference conditions. The concentrations of chemical and physico-chemical indicators do not exceed the ecological quality standards corresponding to the "good" status. |
| **III** | Modirate | Yellow | The values of biological indicators deviate moderately from reference conditions. Concentrations of chemical and physico-chemical indicators exceed the ecological quality standards established for the ecological status of "good". |

|  |  |  |  |
|---|---|---|---|
| **IV** | Poor | Orange | Significant changes in biological indicators are observed and substantional deviations from the norms of biological populations characteristic of reference conditions. |
| **V** | Bad | Red | Very strong changes in biological indicators are observed, including the absence of a large part of the corresponding biological coenoses, characteristic of reference conditions |

## 1.3. Hygienic assessment of water quality: current standards

In contrast to the revolutionary changes in environmental assessment, in the field of hygienic regulation, the approach based on maximum permissible concentrations (MPC) remains relevant. This is due to its strategic importance for the direct protection of public health when using water for drinking, domestic and recreational needs. MPC is the maximum permissible concentration level of a substance in water, above which the water is considered unsuitable for drinking or other water use. [8] In the context of drinking water, this means that the content of a harmful substances must not exceed the established maximum permissible concentrations in order to ensure safety for human health during daily consumption.

### 1.3.1. Selection of sources of centralized water supply (DSTU 4808:2007)

DSTU 4808:2007 "Sources of centralized drinking water supply. Hygienic and environmental requirements..." is used to select and assess water bodies as potential sources for centralized water supply. The suitability of a source is determined based on comprehensive classifications for surface and groundwater, covering a wide range of indicators.

The classifications include assessment across seven groups of indicators:

- Organoleptic
- General sanitary
- Hydrobiological
- Microbiological
- Parasitological
- Radiation safety
- Priority toxicological

Overall, the classification for surface waters covers 80 indicators, and for groundwater - 71 indicators. Within the framework of this standard, the quality of water source is divided into four classes: **excellent, good, satisfactory** and **mediocre.**

### 1.3.2. Water use in settlements (DSP 173-96)

The regulation of water quality in water bodies used for domestic drinking purposes and cultural, domestic (recreational) water use is regulated by Annex 11 to the "State Sanitary Rules for Planning and Development of Settlements" (DSP 173-96). This document establishes requirements for the composition and properties of water at water intake points and recreation areas.

Key indicators standardized according to DSP 173-96:

- ✓ Suspended matter
- ✓ Odors, colors, floating impurities
- ✓ Temperature and pH value
- ✓ Biochemical oxygen demand (BOD) and chemical oxygen demand (COD)
- ✓ Mineralization
- ✓ Microbiological indicators (lactose-positive E. coli, coliphages) and parasitological indicators (helminth eggs, protozoan cysts).

Following the repeal to the former SanPiN 4630-88 in 2017, which contained a comprehensive list of MPCs for hundreds of chemical substances, a “normative and regulatory vacuum” was formed. To address this gap, the Ministry of Health of Ukraine in 2017 developed a draft document entitled “Hygienic standards for water quality of water bodies to meet drinking, domestic and other needs of the population”. This draft practically duplicates the indicators from DSP 173-96 in its structure, while significantly expanding the list of regulated chemical substances, by establishing MPCs for 1,346 compounds. The Order of the Ministry of Health of Ukraine No. 721 dated 02.05.2022 approved the Hygienic Standards for Water Quality in Water Bodies with requirements for the composition and properties of water bodies used for public needs (drinking, domestic, etc.) as a valid regulatory act. [10] In 2023, amendments to this Order (Order of the Ministry of Health of Ukraine dated January 13, 2023 No. 77) were also made. Such a regulatory document contributes to the protection of human health, while the regulatory instruments discussed below are primarily aimed at the protection of aquatic ecosystems.

## 1.4. Water quality assessment for fisheries purposes

Water quality assessment for the needs of fisheries has its own specifics, as it is aimed at the formation and maintenance of conditions favorable for the life, growth, and reproduction of fish and other aquatic biological resources. This area is regulated by highly specialized standards that differ from hygienic or general environmetal standards.

The main regulatory document in this area is the Order of the Ministry of Agrarian Policy and Food of Ukraine No. 471 dated July 30, 2012, which approved the "Standards for Environmental Safety for Water Bodies Used For Fisheries Purposes...". This document establishes standards for five key indicators that directly affect the state of aquatic ecosystems:

- ✓ $BOD_5$
- ✓ COD
- ✓ Suspended matter
- ✓ Ammonium nitrogen ($NH_4^+$)
- ✓ Mineral phosphorus ($PO_4^{3-}$)

The standards are established differently for three types of water bodies, taking into account their natural characteristics:

1. Marine waters
2. Natural freshwater bodies
3. Fish ponds

While these specialized regulations protect aquatic biological resources, the final stage of water use for human needs—drinking water—is regulated by an even more stringent and separate set of standards.

## 1. 5. Drinking water quality regulation: requirements for the final product

It is important to clearly distinguish between the concepts of "water quality in a water body " and "drinking water quality". The first concept characterizes the state of the natural environment, whereas the second refers to the final product that has undergone purification at a water treatment plant (in the case of centralized water supply) and is intended for direct human consumption. Separate, most stringent hygiene requirements apply to drinking water, since the health of the population directly depends on its quality.

In Ukraine, drinking water quality is regulated by two main regulatory documents that are mandatory for compliance. These two documents (Table 1.3) form the basis for state control over the safety of drinking water in Ukraine. They establish a comprehensive list of quality indicators and their limit values, which guarantee the safety of water for consumers.

An analysis of the regulatory framework shows that the correct choice of water quality assessment methodology is determined by the goal. Using an inappropriate regulatory document is a serious methodological error that can lead to incorrect conclusions.

DSTU 7525:2014 "Drinking water. Requirements and methods for quality control" provides standards for two types of drinking water:

1) water from centralized drinking water supply systems;
2) water from non-centralized drinking water supply (non-bottled and bottled).

Standards are established for the following groups of drinking water safety and quality indicators:

- ✓ microbiological, virological, parasitological and mycological – 12 indicators;
- ✓ toxicity level indicators – 4;
- ✓ radiological safety indicators – 2;
- ✓ organoleptic indicators – 4;
- ✓ chemical indicators affecting organoleptic properties – 17;
- ✓ toxicological indicators of the harmlessness of the chemical composition – 50.

Table 1.3

Regulatory documents governing drinking water quality

| Regulatory document | Regulatory objects | Main groups of indicators |
|---|---|---|
| DSanPiN 2.2.4-171-10 (2010) | 1. Tap water.<br>2. Water from wells and spring catchments.<br>3. Bottled water, water from filling points and buvets | ✓ epidemic safety (11 indicators)<br>✓ sanitary and chemical (66 indicators)<br>✓ radiological (8 indicators) |
| DSTU 7525:2014 | 1. Water from centralized drinking water supply systems.<br>2. Water from non-centralized water supply (non-bottled and bottled). | ✓ microbiological, virological, parasitological and mycological – 12<br>✓ toxicity level indicators – 4<br>✓ radiological safety – 2<br>✓ organoleptic – 4<br>✓ chemical, affecting organoleptic properties – 17<br>✓ toxicological indicators of harmlessness of the chemical composition – 50 |

For convenience, a summary reference table is provided below to facilitate the rapid identification of the appropriate regulatory document for a specific task.

Table 1.4

Summary table of regulatory documents for determining water quality for various purposes

| Purpose of water quality assessment | Applicable regulatory document(s) | Key assessment principle |
|---|---|---|
| **Ecological** | "Methodology for classifying a surface water body into one of the classes of ecological and chemical states..." (Order of the Ministry of Environmental Protection and Natural Resources No. 5 dated January 14, 2019)<br>https://zakon.rada.gov.ua/laws/card/z0127-19/conv?utm_source=chatgpt.com | Classification of the condition (5 classes) based on comparison with "reference conditions", without using MPC |
| **Hygienic** (sources of centralized water supply) | DSTU 4808:2007 "Sources of centralized drinking water supply..."<br>https://ukrmts.com/docsdb/6642.html?utm_source=chatgpt.com | Classification of spring water quality (4 classes) based on comparison with hygienic and environmental criteria (MPC) |
| **Hygienic** (domestic, drinking and cultural and household water use) | DSP 173-96 "State Sanitary Rules for Planning and Development of Settlements" (Appendix 11)<br>https://zakon.rada.gov.ua/go/z0379-96 | Assessment of compliance of water composition and properties with established hygienic requirements (MPC) |
| **Fisheries** | Order of the Ministry of Agrarian Policy of Ukraine No. 471 of July 30, 2012 ("Environmental Safety Standards...")<br>https://zakon.rada.gov.ua/go/z1369-12?utm_source=chatgpt.com | Assessment of compliance of 5 key indicators ($BOD_5$, COD, etc.) with established standards for the needs of fisheries |
| **Drinking water** (final product) | DSanPiN 2.2.4-171-10 (2010) and DSTU 7525:2014 "Drinking water..."<br>https://zakon.rada.gov.ua/go/z1369-12?utm_source | Assessment of water compliance with strict hygienic safety requirements based on a wide list of indicators |

# CHAPTER 2

# Water legislation of Ukraine and its harmonization with European Union practices

Ukraine's status as a candidate country for EU membership requires the implementation of the requirements of EU law. The acquis communautaire consists of 6 clusters and 35 chapters. The "Water quality" sector is included in Chapter 27 "Environment and climate change", which belongs to Cluster 4 "Green Agenda and Sustainable Connectivity" [11]. Ukraine has already made significant progress in implementing and transposing EU directives [12], especially those relating to the environment. A significant level of implementation has been assessed for the EU Water Framework and Floods Directives.

The Government of Ukraine has adopted Flood Risk Management Plans (in 2022) and River Basin Management Plans (in 2024). This document has been prepared in order to identify the main gaps in the regulatory and legal framework and to support the continuation of European integration reforms in the field of water policy, in particular the EU Water Framework Directive. One of the challenges for the implementation of River Basin Management Plans (RBMPs) is the execution of measures aimed at reducing hydromorphological alterations and their impacts. This type of measures requires the accumulation of project-based and practical experience, as well as the consideration of nature-based solutions. Below is a list of regulatory acts (current and draft) that require amendment and/or the development of new ones within the framework of European integration commitments. The materials were prepared based on the analysis and use of the following sources: the Action Plan for the Implementation of the Association Agreement between Ukraine, on the one hand, and the European Union, the European Atomic Energy Community and their Member States, on the other hand (CMU Resolution No. 1106 of 25 October, 2017); data from the information and analytical system for monitoring the implementation of the Association Agreement “Pulse of the Agreement” [13]; the EU questionnaire and the Ukraine’s responses in connection with its acqusition of EU candidate country status (2022) [14]; progress reports within the framework of the European Union Enlargement Package 2024 (Ukraine 2023 Report, Ukraine 2024 Report) [15-17]; the Action Plan for the Implementation of the European Commission’s Recommendations presented in the Report on Ukraine’s Progress within the framework of the European Union Enlargement Package 2024 (CMU Resolution No. 300-r of 28 March, 2025) [18]; documents prepared as part of the official screening of Chapter 27 "Environment and Climate Change".

Key Stages of the Negotiation Process for Ukraine's Accession to the European Union

**23 June 2022**

Ukraine was granted the status of a candidate country for membership in the European Union.

**14 December 2023**

The European Council decided to open accession negotiations with Ukraine.

**3 January 2024**

Preparations for accession negotiations with Ukraine began. The European Commission launched the screening process of Ukrainian legislation and initiated the development of the negotiation framework.

**25 June 2024**

The first Intergovernmental Conference between Ukraine and the European Union was held in Luxembourg.

This conference officially launched accession negotiations between Ukraine and the European Union.

During the event, the EU presented the negotiation framework defining the structure of the negotiation process.

**16–20 June 2025**

Bilateral meetings between Ukraine and the European Commission took place as part of the official screening of Ukraine's compliance with EU law under Negotiation Chapter 27, "Environment and Climate Change", including the sub-sector "Water Quality".

Fig. 2.1 Infographics of the preparation of Ukrainian legislation for accession to the EU

National water legislation includes a set of regulatory legal acts that regulate the use, protection and reproduction of water resources, as well as relations arising in the field of water management. The main codified act in the field of water policy in Ukraine is the Water Code of Ukraine. The main principles (strategy) of the state environmental policy of Ukraine for the period up to 2030 are determined by the Law of Ukraine No. 2697-VIII of 28 February, 2019. The Water Strategy of Ukraine up to 2050 was approved by the Cabinet of Ministers of Ukraine Resolution No. 1134-r of 9 December, 2022. Liability for violation of the requirements of the legislation in the field of water resources management is provided, in particular, by the Code of Ukraine on Administrative Offenses and the Criminal Code of Ukraine. Sectoral regulatory legal acts that contain provisions on water resources management also apply for sectoral integration. Examples of such acts are given in Table 2.1.

Table 2.1

Sectoral regulatory legal acts containing provisions on water resource management

| | |
|---|---|
| Natural resources | Law of Ukraine "On Environmental Protection";<br>Land Code of Ukraine;<br>Forest Code of Ukraine;<br>Law of Ukraine "On the National Geospatial Data Infrastructure";<br>Subsoil Code of Ukraine;<br>Strategy on Environmental Security and Adaptation to Climate Change for the Period up to 2030 (CMU Resolution No. 1363-r of 20 October, 2021);<br>Law of Ukraine "On Drinking Water and Drinking Water Supply". |
| Industry | Law of Ukraine "On Integrated Prevention and Control of Industrial Pollution";<br>Energy Strategy of Ukraine for the period up to 2050 (CMU Resolution No. 373-r dated 21 April, 2023). |
| Agriculture | Law of Ukraine "On Fisheries, Industrial Fishing and Protection of Aquatic Biological Resources";<br>Strategy for the Development of Agriculture and Rural Areas in Ukraine for the Period up to 2030 and the Operational Plan of Measures for its Implementation in 2025-2027 (CMU Resolution No. 1163-r of November 15, 2024);<br>Long-term Plan for the Development of Ukraine’s Irrigation System up to 2050 (CMU resolution of 25 March, 2025 No.280-r); |
| Housing and communal services | Law of Ukraine “On Wastewater Disposal and Treatment”; |
| Regional development | Law of Ukraine "On the Principles of State Regional Policy";<br>Law of Ukraine "On Regulation of Urban Planning Activities";<br>State Strategy for Regional Development for 2021-2027 (CMU Resolution No. 695 of 5 July, 2020). |

## 2.1. Harmonization of Ukrainian legislation with EU standards

The harmonization of Ukraine’s national legislation with the requirements of the legal acts of the European Union is carried out within the framework of the Association Agreement between Ukraine, on the one hand, and the European Union, the European Atomic Energy Community and their Member States, on the other hand. Annex XXX to Chapter 6 “Environment” of Section V “Economic and Sectoral Cooperation” of the Association Agreement with the EU determines the list of European Union directives and regulations that are subject to implementation into Ukraine’s national legislation [19, 20]. For the sector “Water quality and management of water resources, including the marine environment”, the implementation of six key EU directives is envisaged, namely:

- ✓ Water Framework Directive [21] – Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy;
- ✓ Floods Directive [22] – Directive 2007/60/EC of the European Parliament and of the Council of 23 October 2007 on the assessment and management of flood risks;
- ✓ Marine Strategy Framework Directive [30] – Directive 2008/56/EC establishing a framework for Community action in the field of marine environmental policy;
- ✓ Urban Wastewater Treatment Directives [23] – Council Directive 91/271/EEC of 21 May 1991 concerning urban wastewater treatment, as amended by Directive 98/15/EC and Regulations (EC) 1882/2003 and (EC) 1137/2008;
- ✓ Drinking Water Directives [24] – Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption;
- ✓ Nitrates Directive [25] – Council Directive of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC).

As part of the implementation of these European integration commitments, new regulatory legal acts were adopted or amendments were made to a number of existing regulatory legal acts [18] regarding:

- ✓ definition of river basin districts, sub-basins and water management areas, as well as their boundaries;
- ✓ definition of surface water bodies and groundwater bodies;
- ✓ development of water management balances;
- ✓ establishment of basin councils;

- ✓ water monitoring, environmental quality standards, condition assessment classification;
- ✓ flood risk management plans;
- ✓ river basin management plans [20].

Some regulatory legal acts intended to implement European integration requirements were adopted with a postponement of entry into force or the start of application due to the full-scale invasion of Ukraine by the Russian Federation. The 2024 report on the implementation of the EU-Ukrainet Association Agreement confirms the progress of implementation in the area of "Environment and Civil Protection" at approximately 83 % [17], and 3% of progress over the last year.

Also in 2024, important processes were implemented, including:

- ✓ Management plans for nine river basins were approved: the Danube, Dniester, Dnipro, Don, Southern Bug, Vistula, rivers of the Azov region, rivers of the Black Sea region, and rivers of Crimea.
- ✓ Amendments have been made to some resolutions of the Cabinet of Ministers of Ukraine (CMU) concerning water monitoring (CMU Resolution No. 1071 of 6 September, 2024), which will contribute to the implementation of the provisions of Directive 2009/90/EC and the Water Framework Directive.
- ✓ Environmental standards for the quality of surface water bodies were approved (by order of the Ministry of Environmental Protection and Natural Resources of Ukraine dated 01.04.2024 No. 332, registered with the Ministry of Justice of Ukraine on 29.05.2024 under No. 789/42134).

The European Commission published (08.11.2023) the first Report [15] on Ukraine's progress within the framework of the European Union Enlargement Package, which includes recommendations for advancing reforms. The Report [15] notes that Ukraine has achieved some progress in the field of environment and climate change, despite the difficult conditions caused by war. In particular, legislative acts aimed at approximation to EU law in the fields of horizontal environmental legislation, water quality, waste management, and regulation of chemical substances were adopted. The European Commission Report also outlines the main tasks for Ukraine for the next year (2024), [16] in particular:

- ensuring cross-sectoral integration of environmental and climate measures in the process of the country's recovery, including the development of a "green recovery" strategy for priority sectors, prioritizing relevant EU legislation and standards within the National Programme for the Adaptation of Legislation to EU Law;

– adoption of primary and secondary legislation to continue reforms in the areas of water resources management and waste management, including the adoption of the law on environmental control, as well as regulatory acts ensuring harmonization with the EU acquis in the field of industrial emissions;

– adoption of the climate law and launching the update of the Long-term Low-Carbon Development Strategy in accordance with the EU framework until 2030.

The European Union’s Long-Term Low Greenhouse Gas Emissions Development Strategy submitted by the European Union to the UNFCCC platform in accordance with the requirements of Article 4(19) of the Paris Agreement on mid-century strategies [26] defines the path towards climate neutrality, in particular through the systematic integration of climate objectives into all sectors of the economy. Regarding water resources, the strategy emphasizes the need to increase the resilience of aquatic ecosystems to the effects of climate change (droughts, floods, deterioration of water quality). Particular attention is given to the effecient of water resource management, reducing energy consumption in water treatment and supply, and using nature-based solutions. Water is a key element for adaptation to climate change and for achieving the EU's long-term climate and environmental goals.

As already noted, Ukraine is currently developing river basin management plans [20] and standards for assessing the ecological status of rivers, lakes, transitional and coastal waters using four of the five Biological Quality Elements, (BQEs) provided for under the Water Framework Directive (2000/60/ EC (WFD). These four biological elements include:

- ✓ **Phytoplankton –** assessment of species composition and biomass of algae as an indicator of nutrients and eutrophication.
- ✓ **Benthic invertebrates** – assessment of benthic organisms (macroinvertebrates) that are sensitive to organic pollution and environmental alteration.
- ✓ **Aquatic flora (macrophytes) –** assessment of the status of higher aquatic plants, reflecting the overall ecological balance.
- ✓ **Fish** – assessment of the structures and indicators of fish populations as an indicator of ecosystem stability

The fifth biological element according to the Water Framework Directive — **phytobenthos** — is used very rarely in water monitoring practice in Ukraine due to limitations in methods and data. As a result, water assessment focuses on the first four biological quality elements.

Significant progress in changing the approach and improving water monitoring has been facilitated by legislative initiatives by Ukraine, including:

- ✓ In October 2022, the Government of Ukraine approved Flood Risk Management Plans within the framework of the implementation of the transposed Floods Directive.

- ✓ In December 2022, the Water Strategy of Ukraine until 2050 was approved. Its action plan provides the identification of nitrate-vulnerable areas by December 2023, as well as the establishment of a number of indicators for wastewater discharges, in accordance with the requirements of the Urban Wastewater Treatment Directive.
- ✓ At the end of 2022, the next national annual report on the quality of drinking water and the state of drinking water supply for 2021 was published. Drinking water quality problems are taken into account in the current Ukrainian legislation and in the Water Strategy, however, alignment with European Union requirements remains relevant.
- ✓ In January 2023, the Law of Ukraine "On Water Disposal and Wastewater Treatment" entered into force, regulating certain provisions of the directive.

On October 30, 2024, the European Commission presented the Report [16] within the framework of the EU Enlargement Package for 2024, which made an annual assessment of Ukraine's progress in reforms and transformation towards membership in the European Union across all negotiation chapters. Progress was recorded in the development of national legislation for Chapter 27 "Environment and Climate Change", namely water quality, which has been partially aligned with the EU acquis. The implementation of the Water Framework Directive has been most evident through the preparation and implementation of draft River Basin Management Plans covering the entire territory of Ukraine. In August 2023, amendments were made to the Marine Environmental Protection Strategy of Ukraine for the further development of action plans. And relevant regulatory legal acts were adopted to assess the quality of surface waters. In addition, in August 2023, the Law of Ukraine "On Water Disposal and Wastewater Treatment" entered into force. Laws have been adopted regulating maximum permissible discharges of pollutants into centralized wastewater systems and preliminary treatment of wastewater before discharge. The issue of ensuring cost recovery for the provision of water supply services in accordance with the economic principles of the EU water policy remains relevant and unresolved. Moreover, the implementation of many measures and procedures continues to be constrained by insufficient financial resources.

The European Union has proposed a financial assistance programme for Ukraine for 2024–2027 — the Ukraine Facility aimed to support financial stability, economic recovery, and structural reforms. The Ukraine Facility is one of the main instruments for the country’s recovery, reconstruction, and modernization, which should contribute to accelerating the process of gaining membership in the European Union. The Ukraine Facility Plan, which lists all the measures that Ukraine must implement, was approved by the order of the Cabinet of Ministers of Ukraine No.

244-р (18.03.2024). The priority of the Plan remains the further alignment of Ukraine’s water legislation with the EU law and ensuring the effective implementation of already adopted regulatory legal acts. The document provides for the implementation of the first cycle of river basin management planning, systematic collection and use of water quality monitoring data and other indicators, as well as the application of economic instruments for investing in the development of water infrastructure.

The implementation of the Directive on technical aspects of chemical analysis and monitoring of water status is currently ongoing. Due to a lack of funding, administrative capacity in the water sector is still insufficient.

## 2.2. Ukraine's European integration commitment regarding water legislation

EU water legislation should provide a unified approach to water management, guaranteeing its quality and availability, through the establishment of a legislative and policy framework. Its scope covers issues ranging from the protection of public health and ensuring access to clean drinking water, to the implementation of sustainable wastewater treatment practices, their reuse. Water legislation is the basis of the EU's commitments to environmental protection and sustainable development. EU Water Legislation is a set of regulatory and legal acts addressing various aspects of water resources management and use [19]. The main acts of the EU Water Legislation include:

- ✓ Water Framework Directive [21]
- ✓ Floods Directive [22]
- ✓ Urban WasteWater Treatment Directive [23]
- ✓ Drinking Water Directive [24]
- ✓ Nitrates Directive [25]
- ✓ Groundwater Directive [27]
- ✓ Sewage Sludge Directive [28]
- ✓ Bathing Water Directive [29]
- ✓ Marine Strategy Framework Directive [30]
- ✓ Water Reuse Regulation [31]

Each of the above-mentioned acts serves a specific purpose within the overall EU water management system. These documents are part of a holistic framework that should ensure integrated water management. Related EU regulations, strategies, plans and priorities include:

- ✓ Industrial Emissions Directive (Integrated Approach to Pollution Prevention and Control) [32];
- ✓ Directive on Environmental Quality Standards in the Field of Water Policy [33];

- ✓ Nature Restoration Regulation [34];
- ✓ Biodiversity Conservation Strategy to 2030 [35];
- ✓ Taxonomy Regulation and related Delegated Acts [36];
- ✓ Circular Economy Action Plan [37];
- ✓ Zero Pollution Action Plan [38];
- ✓ European Green Deal [39];
- ✓ European Water Resilience Strategy [40].

Table 2.2

Challenges, gaps and next steps for WFD implementation [11]

| Challenges, gaps | Next steps | Deadline |
|---|---|---|
| Shortage of qualified personnel | Capacity development and staff training | ongoing, until 2030 |
| Shortage of funding for RBMP implementation | To approve and implement the State Target Environmental Programme for the technical modernization of water disposal and wastewater treatment enterprises owned by the state or municipal government for the period until 2034.<br>To amend the Budget Code of Ukraine and the Tax Code of Ukraine, establishing that rent and tax payments related to the use of water resources are directed to the implementation of the RBMP. | 2025 - 2034<br>2028 |
| Groundwater monitoring is not carried out | Ensure groundwater monitoring | 2026 |
| Surface water monitoring needs further development (staff, network, parameters) | Development of surface water monitoring capacity (expansion of monitoring network, database, laboratory, assessment) | ongoing, until 2030 |
| The principle of cost recovery for water supply is not implemented | Develop a comprehensive strategy and methodology to address cost recovery issues for water services, including financial, environmental and resource costs | 2026 |
| Combined approach for point and diffuse sources is partially implemented | Develop methodologies to establish appropriate emission limits for activities not covered by BAT conclusions | 2026 |
|  | Promote the application of best environmental practices of EU Member States to control emissions from diffuse sources | 2027 |
| Sanctions applied to violations of water legislation are not effective,proportionate and dissuasive | Review the sanctions applicable to violations of water legislation to make them more effective, proportionate and dissuasive | 2026 |

Screening is the first step on the EU membership negotiation process and involves an analysis of the candidate country's national legislation for compliance with the relevant EU acquis. Based on the results of the screening carried out for each cluster, priority actions for accelerated integration and key reforms are agreed between the EU and the candidate country. Once the priorities are implemented, the cluster (and its associated chapters) is opened without further conditions. Each chapter has its own benchmarks for completion. Chapters within a given cluster are assessed and closed separately. The key task of screening is to identify the main gaps.

Table 2.2 below provides information on the gaps in the transposition of EU legislation in the context of selected directives included in the agenda of the European Commission's bilateral screening meeting under Chapter 27 "Environment and Climate Change" of the "Water Quality" sector. A detailed analysis of the challenges, gaps and next steps required for full implementation of the Water Framework Directive is also presented.

To implement the Water Framework Directive in Ukraine, it is necessary to continue developing and adopting legislation in the relevant areas. The implementation of the adopted legislation requires material and financial resources and the development of institutional and administrative capacity. The next steps for the implementation of the Water Framework Directive should be planned and coordinated in accordance with the implementation periods of the RBMPs (2025-2030) and their updates (2026-2031). This process equires effective coordination among all involved stakeholders at both the national and regional levels.

## 2.3. Implementation of River Basin Management Plans (RBMPs)

The Government of Ukraine has approved the following River Basin Management Plans (RBMPs) for 2025-2030 [41]:

- ✓ The Dnipro and Don river basins (order of the Cabinet of Ministers of Ukraine No. 1077-r dated 01.11.2024);
- ✓ The rivers of the Black Sea, Azov Sea and the Crimea (order of the Cabinet of Ministers of Ukraine No. 1079-r dated 01.11.2024);
- ✓ The Vistula, Dniester and Southern Bug river basins (order of the Cabinet of Ministers of Ukraine No. 1078-r dated 01.11.2024);
- ✓ The Danube river basin (order of the Cabinet of Ministers of Ukraine No. 1347-r dated 31.12.2024).

The above-mentioned documents stipulate that ministries, central executive bodies, regional and municipal state administrations should take into account the measures specified in the RBMPs in their own short-term and medium-term planning documents, targeted programs, and other important documents. Local self-government bodies are recommended to take into account the RBMP measures into their own short-term and medium-term planning documents, targeted programs. National legislation stipulates the development of plans (strategies) at the national, regional, and local levels. While the development of strategies and plans for their implementation in Ukraine is carried out according to the administrative-territorial principle, and the RBMPs provide for the application of an integrated approach based on the basin principle, which must be taken into account while budget planning processes, both at the local and state levels.

Currently, there are such challenges for the RBMP [11]:

✓ insufficient funding for RBMP measures;
✓ misuse of rental payments and environmental taxes for water resources;
✓ low level of intersectoral integration of strategies and plans.

To address these challenges, the following implementation mechanisms may be applied [11]:

✓ improving planning through coordination and communication at both the national and river basin district levels, continuous dialogue among Basin Department of Water Resources, local authorities and local self-government bodies;

✓ establishing inter-institutional working groups for RBMP implementation at the national level (chaired by ministries) and at the river basin district level (chaired by the BDWR);

✓ legislative consolidation of responsibility for achieving environmental goals;

✓ amendments to the Budget Code of Ukraine and the Tax Code of Ukraine regarding the allocation of rent and tax payments to achieving good status of surface water bodies and groundwater bodies;

✓ strengthening the role of basin councils and expanding their mandates.

There are issues regarding the coordination of River Basin Management Plans (RBMPs) and Flood Risk Management Plans (FRMPs). The timing of the first cycle of the FRMPs implementation (2023-2030) and the RBMPs (2025-2030) in Ukraine has been agreed. However, the content and objectives of the Water Framework Directive and the Floods Directive are different and sometimes contradictory. Achieving the FRMPs objectives is linked to hydromorphological changes and poses risks to attaining the environmental objectives set in the RBMPs. Therefore, RBMPs should include mitigation measures to reduce the impact of the FRMP measures, in particular through the implementation of best international practices and nature-based solutions.

For example, investments in green infrastructure, such as the conservation and restoration of floodplains and wetlands located upstream, are more cost-effective and provide improved infrastructure solutions. Aligning measures aimed at achieving good ecological status (defined in the RBMPs) with measures to protect against flood risks and hazards (defined in the FRMPs) requires coordination and joint efforts at all levels. The following key challenges can be summarized [11]:

- ✓ lack of mitigation measures to reduce the impact of Flood Risk Management Plan (FRMP) implementation;
- ✓ lack of green infrastructure practices and nature-based solutions in flood risk management.

These challenges can be overcome by introducing the following implementation mechanisms:

- ✓ integration of nature-oriented solutions into regulatory legal acts;
- ✓ improving coordination in updating RBMPs and FRMPs;
- ✓ implementation of green infrastructure practices in flood risk management, including amendments to the requirements for the preparation of project documentation.

It is also important to ensure alignment of river basin management plans with climate strategies and action plans. In accordance with the Law of Ukraine "On the Basic Principles of State Climate Policy", the Government of Ukraine has approved the National Energy and Climate Plan up to 2030, and also provides for the development and adoption of the Climate Change Adaptation Strategy. In order to achieve medium- and long-term goals of state policy in this direction and to fulfill international commitments, central executive authorities and local self-government bodies are preparing sectoral programme documents aimed at reducing anthropogenic greenhouse gas emissions and increasing their absorption. The following challenges may be identified [11]:

- ✓ lack of legislation on drought management;
- ✓ insufficient intergation of the climate component into water resources management;
- ✓ the need to adapt water management to climate change.

Mechanisms for implementing the above challenges [11]:

- ✓ implementation of drought management plans;
- ✓ development of a strategy for adapting water management to climate change;
- ✓ planning of sectoral programme documents taking into account the RBMPs;
- ✓ integration of climate change considerations into the updating of the RBMPs.

### 2.4. Implementation of pollution reduction measures

Pollution reduction measures account for more than 70% of the RBMPs Programme of Measures and require 96% of the investment. Pollution reduction can be achieved by implementing the requirements of the Urban Waste Water Treatment Directive and the Water Framework Directive (hereinafter referred to as the WFD), in particular through the application of the following provisions [11]:

- ✓ Article 9 – recovery of costs for water services, including environmental and resource costs,
- ✓ Article 10 – application of the mixed approach to point and diffuse sources,
- ✓ Article 23 – penalties.

Water pricing policy (under Article 9 of the WFD) has to encourage water users to make efficient and sustainable use of water resources and to contribute to the achievement of the WFD environmental objectives. Different types of water use (industry, households, agriculture) should bear appropriate compensation for the costs of water services, based on an economic analysis, taking into account the "polluter pays" principle. At the same time, the WFD establishes a framework for achieving the objectives of Article 10 in terms of controlling all discharges, taking into account the following requirements:

- ✓ Water Directives [21]
- ✓ Birds Directive
- ✓ Drinking Water Directives [24]
- ✓ Industrial Accidents Directives (SEVESO)
- ✓ Environmental Impact Assessment Directives
- ✓ Sewage Sludge Directives [28]
- ✓ Urban Wastewater Treatment Directives [23]
- ✓ Plant Protection Products Directives
- ✓ Nitrates Directive [25]
- ✓ Habitats Directive (Directive 92/43/EEC)
- ✓ Industrial Emissions Directives [32].

However, there are the following challenges [11]

- ✓ low cost recovery for water use services (according to the latest data, the level of cost recovery for water services is approximately 20%);
- ✓ the entry of pollutants with wastewater due to the poor technical condition of treatment facilities and sewerage networks;
- ✓ contamination of water bodies with hazardous substances (pesticides, pharmaceuticals, industrial pollutants);
- ✓ regulation of pollutant discharges does not ensure achievement of the environmental quality standard of the surface water body;
- ✓ lack of control over pollution from diffuse sources.

To address the challenges, the following implementation mechanism has been proposed: [11]:

✓ seeking sponsors and implementation of an investment programme for the modernization of wastewater treatment plants;

✓ review of water service tariffs, taking into account the costs of achieving the environmental goals of the RBMPs;

✓ aligning the system of pollutant discharge standards into water bodies with the requirements of Article 10 of the Water Framework Directive;

✓ development, adoption, and implementation of an inventory of emissions, discharges and losses.

## 2.5. Updating river basin management plans

According to the Water Framework Directive, RBMPs are approved and updated every 6 years. Three years after the update (publication) of the RBMP, an interim review is submitted in accordance with Article 13 of the Water Framework Directive, noting the progress in implementing the planned programme of measures. The content of the updated RBMP should include [11]:

- ✓ comparison of changes in the updated river basin management plan with the previous plan;
- ✓ assessment of progress towards the ecological status of surface waters, groundwater and protected areas, and in case of non-achievement, an explanation of the reasons;
- ✓ list and analysis of measures that have not been implemented.

The main challenges include:

- ✓ lack of legal regulation of the preparation of the interim review;
- ✓ insufficient regulatory framework for updating RBMP data for groundwater bodies; the need to define reference conditions for all types of groundwater bodies;
- ✓ the need to take into account the impact of military operations in updating the RBMPs;
- ✓ weak institutional interaction among surface water monitoring authorities on issues of assessing the status of surface water bodies.

The following mechanisms are proposed to implement the challenges:

✓ updating methodological recommendations for the analysis of anthropogenic loads and their impacts on the status of surface and groundwater;

✓ updating the classifications for assessing the ecological state of the surface water bodies, approved by the Methodology for assigning surface water bodies to specific ecological and chemical status classes of water bodies;

✓ adoption of the Methodology for assigning groundwater bodies to quantitative and chemical status classes of surface water bodies;

- ✓ updating the Procedure for developing the RBMPs and developing methodological recommendations for the interim review and updating of the RBMP;
- ✓ development and adoption of Regulations (Procedures) for information exchange to assess the ecological status/potential of the surface water bodies;
- ✓ development of guidelines for creating data for reporting to the EC.

It is worth mentioning that the Ministry of Environmental Protection was liquidated by Resolution of the Cabinet of Ministers of Ukraine No. 903 dated July 21, 2025. The successor of the assets, rights and obligations of the Ministry of Environmental Protection and Natural Resources is the Ministry of Economy, Environment and Agriculture.

The start of negotiations on Ukraine's accession to the European Union and the conduct of bilateral screening under Chapter 27 "Environment and Climate Change" necessitate the formation of clear negotiation positions and the acceleration of the implementation of European integration commitments. Preparation for the screening confirmed the importance of the correct application of EU law to ensure proper implementation and avoidance of discrepancies between Ukrainian and European legislation. The implementation of EU legal acts in the water sector requires a systematic dialogue with key water-dependent sectors of the economy, in particular municipal services, agriculture, industry, and energy. It is important to take into account new challenges, in particular the increasing relevance of the problem of water scarcity, which is caused by climate change and the consequences of military operations.

A current challenge remains the achievement of the environmental objectives set out in the river basin management plans. The implementation of measures related to hydromorphological changes requires closer integration with biodiversity conservation and restoration policies, as well as the systematization and dissemination of implementation experience. It is essential to consider the impact of military operations and the formulation of post-war recovery objectives in achieving environmental objectives based on clear legislative criteria.

Reducing water pollution is directly related to the modernization of water management infrastructure, which requires significant investments, primarily in water drainage and wastewater treatment. For successful adaptation to EU standards, the decisive factor is the presence of effective state institutions capable of ensuring the implementation of reforms and monitoring compliance with legislation. The success of European integration will depend on Ukraine's ability to adapt state policies and the institutional system to EU standards, provided that actions are coordinated at all levels.

# CHAPTER 3
# Modern approaches and methods of water quality monitoring

## 3.1. Water monitoring indicators

The EU Water Framework Directive (2000/60/EC): provides for the assessment of the ecological and chemical status of surface and groundwater based on a system of monitoring indicators.

1. **Biological indicators -** reflect the state of aquatic ecosystems and are key to determining ecological status. They include:

- ✓ phytoplankton,
- ✓ phytobenthos,
- ✓ macrophytes (aquatic vegetation),
- ✓ benthic invertebrates,
- ✓ fish.

2. **Hydromorphological indicators -** characterize the physical conditions of water bodies:

- ✓ hydrological regime (water flow, levels),
- ✓ morphology of the riverbed, banks and bottom,
- ✓ the connection of the river with the floodplains.

3. **Physico-chemical indicators -** show the conditions necessary to maintain biological elements:

- ✓ temperature,
- ✓ oxygen content,
- ✓ nutrients (nitrogen, phosphorus),
- ✓ acidity, salinity, transparency.

4. **Chemical indicators.** They are used to assess chemical status of water: concentrations priority and hazardous substances (heavy metals, pesticides, organic pollutants) and comparing them with EU environmental quality standards.

Together, all these indicators allow us to classify water bodies into five classes of ecological status — from "excellent" to "poor" — and determine the necessary measures to achieve good water status.

Water quality monitoring relies on a combination of physical, chemical, and biological parameters to assess the condition of a water body and identify potential sources of pollution. Physical parameters include parameters such as temperature, turbidity, and electrical conductivity. Temperature affects dissolved oxygen levels and biological activity; turbidity indicates the presence of suspended particles that reduce light penetration; and conductivity reflects the concentrations of dissolved ions, often associated with sources of pollution [42].

Chemical indicators provide information on the presence of pollutants and the overall chemical composition of water. Key chemical parameters include pH, dissolved oxygen (DO), biochemical oxygen demand ($BOD_5$), chemical oxygen demand (COD), nutrients such as nitrates and phosphates, as well as hazardous substances such as heavy metals (Pb, Cd, Hg) and persistent organic pollutants [42, 43].

Biological indicators assess the presence and abundance of living organisms, such as macroinvertebrates, fish, or algae, that reflect long-term environmental conditions and the cumulative impact of pollution [42]. Fish and benthic invertebrates are most commonly used in water monitoring due to their sensitivity and ecological significance.

Table 3.1

Overview of key water quality indicators and methods for their assessment

| Indicator type | Examples | Purpose | Method |
|---|---|---|---|
| Physical | Temperature, turbidity, conductivity | Affects oxygen solubility and light penetration | Field sensors |
| Chemical | pH value, dissolved oxygen, BOD, COD, nutrients, heavy metals | Indicates pollution levels and ecosystem balance | Professional spectrophotometry, ICP-MS |
| Biological | Macroinvertebrates, fish, algae | Reflects long-term ecological health | Sampling, identification, biotic indices |
| Microbia | Escherichia coli, coliform bacteria | Indicates fecal contamination and health risk (especially in drinking water) | Membrane filtration, PCR |

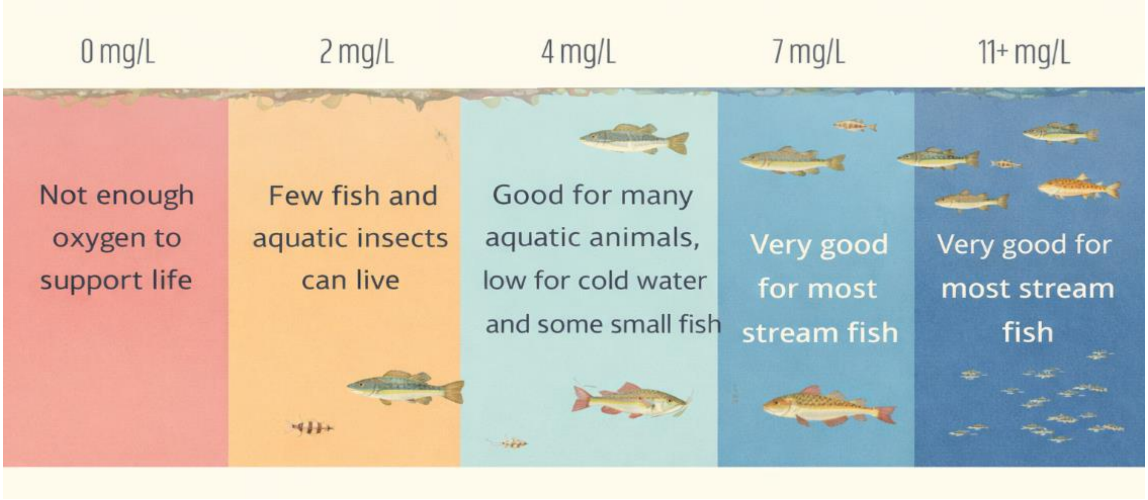


Fig. 3.1. Relationship between dissolved oxygen levels and fish survival in water

Figure 3.1 shows how oxygen concentrations can be determined using fish. Low oxygen concentrations can be fatal to aquatic organisms, while higher levels support healthy ecosystems.

## 3.2. Sampling methods: sampling, composite, and sediment

The accuracy of water quality monitoring depends on effective sampling methods. Sampling, as well as their preservation and handling is regulated by ISO 5667 Water Quality Sampling, an international series of standards that establishes principles, methods and guidelines for sampling water and related environments (wastewater, groundwater, bottom sediments, etc.).

The main objective of the series is to ensure the representativeness, reproducibility and reliability of samples used for water quality assessment in environmental monitoring programs, water supply control and scientific research. The series consists of multiple parts, each addressing specific sampling methods or environments:

- ✓ ISO 5667-1 - General principles of sampling;
- ✓ ISO 5667-3 - Preservation and handling of samples;
- ✓ ISO 5667-4 - Sampling from lakes;
- ✓ ISO 5667-5 - Sampling of drinking water;
- ✓ ISO 5667-6 - Sampling from rivers and streams;
- ✓ ISO 5667-10 - Wastewater sampling;
- ✓ ISO 5667-12 - Sampling of bottom sediments;
- ✓ ISO 5667-14 - Quality assurance and quality control of sampling;
- ✓ ISO 5667-23 - Methods for passive sampling in surface waters;
- ✓ ISO 5667-27:2025 - Sampling guidelines for microplastics.

Common sampling methods include grab sampling, composite sampling, and sediment core sampling. Table 3.2 provides a comparative characterization of water and sediment sampling methods along with references to the relevant standards.

Table 3.2

Comparative characteristics of water sampling methods

| Selection method | ISO definition | ISO standards | Characteristic | Advantages | Limitations |
|---|---|---|---|---|---|
| Grab sample | Simple sample, specific time and place | ISO 5667-1, ISO 5667-6, ISO 5667-10 | Instant "snapshot" of water status | Simplicity efficiency, minimal costs | Does not account for temporal variability |
| Composite sample | A sample formed by mixing several individual samples | ISO 5667-1, ISO 5667-10 | Time or space – averaged measurement | Representativeness for long-term analysis | Loss of peak concentration values |
| Sediment sample | A sample of bottom material taken from the surface or by core | ISO 5667-12 | Reflects accumulated contamination | Analysis of long-term impacts | More complex interpretation |

Table 3.3

Comparison of grab and composite samples (ISO 5667-1)

| Criterion | Grab sample | Composite sample |
|---|---|---|
| Sampling time | Single point in time | During a certain period |
| Spatial representativeness | Low | Medium–high |
| Peak concentration display | ✓ Yes | ✗ No |
| Opeartional complexity | Low | Medium |
| Typical application | Control, emergencies | Regular monitoring |
| ISO regulations | ISO 5667-1, 6, 10 | ISO 5667-1, 10 |

According to the ISO 5667 series of standards, the choice of water sampling method (grab, composite or sediment sampling) should be based on the monitoring objectives, the spatial and temporal variability of the parameters, and the required level of representativeness. Grab samples provide an assessment of water state at a specific moment, composite - average values over a certain period, while bottom sediment samples allow for the analysis of long-term accumulation of pollutants.

Table 3.4

Sampling of bottom sediments (ISO 5667-12)

| Parameter | ISO requirements |
|---|---|
| Sample type | Surface or core sample |
| Tools | Grapples (Van Veen, Ekman), core samplers |
| Target substances | Heavy metals, organic pollutants, nutrients |
| Representativeness | Displays contamination history |
| Special requirements | Minimizing sediment re-disturbance |
| Standard | ISO 5667-12 |

Table 3.5

Sample preservation and quality control (ISO 5667-3, ISO 5667-14)

| Parameter | ISO requirements |
|---|---|
| Container material | Glass or inert polymer |
| Storage temperature | ≤ 4 °C (typically) |
| Time between sampling and analysis | Minimized |
| QA/QC | Field forms, duplicates, calibration |
| Traceability | Documentation of all stages |

Practical experience is given on the example of the Czech Republic. Water sampling procedures are carried out in accordance with the requirements of ISO 5667-3:2024 and national methodological recommendations [43]. Point (grab) sampling provides information on the state of the aquatic environment at a specific point in time, while composite sampling allows for the collection of time-integrated data, which is especially informative in conditions of significant variability of pollution levels. To assess historical pollution loads, bottom sediment sampling is used, while avoiding excessively detailed stratification of the core with intervals of 2–5 cm. Samples containing organic pollutants (pesticides, hydrocarbons, industrial chemical compounds) require storage at a temperature of about 4 ° C and extraction within 24 hours in order to prevent degradation or transformation of substances. At the same time, some sensitive inorganic components require chemical preservation to maintain their original state during transportation and storage.

For long-term monitoring of pollution, automated samplers are widely used, which perform regular sampling (e.g. hourly or daily). The composite samples collected in this way provide an integrated assessment of pollution levels over time and allow recording short-term or episodic emissions that may remain unnoticed during a single sampling. In terms of monitoring bottom sediments, the Czech technical standard ČSN 75 7221 (*Water quality – Classification of surface water quality*) [44] recommends the use of core sampling with a vertical resolution of 2–5 cm. Analysis of individual sediment layers enables the reconstruction of pollution chronology, the assessment of the long-term accumulation of pollutants, and the evaluation of the effectiveness of previously implemented management measures. Bottom sediments act both as accumulators and as potential secondary sources of pollution, in particular hydrophobic organic compounds and trace amounts of metals, highlighting their critical role in comprehensive water quality assessment [11].

## 3.3. Chemical and physico-chemical analytical methods in the context of the EU Water Framework Directive (WFD)

In accordance with the requirements of the EU Water Framework Directive (2000/60/ EC) and the related Directives 2008/105/ EC and (EU) 2013/39, the assessment of the chemical status of surface waters is based on the reliable determination of concentrations of priority and priority hazardous substances in water, bottom sediments and biota. Modern chemical and physico-chemical methods of analysis are used to assess the quality of surface waters, ensuring sensitivity, selectivity and reproducibility of results at levels that meet environmental quality standards (EQS).

The determination of trace and ultra-trace concentrations of metals (including mercury, cadmium, lead, nickel, arsenic), which are included in the list of priority substances of the WFD, are most commonly carried out using inductively coupled plasma mass spectrometry (ICP - MS) and atomic absorption spectroscopy (AAS) in accordance with the ISO 17294-1:2024 standard. The ICP - MS method provides detection limits sufficient to control the compliance of concentrations with the EQS requirements and enables multi-element analysis, which is important for an integrated assessment of the chemical status of water bodies. At the same time, AAS remains an effective and reliable tool for the ongoing control of individual metals during operational and surveillance monitoring.

For the identification or quantative determination of organic priority pollutants (pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), persistent organic compounds), gas chromatography with mass spectrometric detection (GC - MS) and liquid chromatography coupled with mass spectrometric detection (LC - MS / MS) are applied. These methods meet the requirements of the WFD for reliable identification of substances, low limits of quantification, and the ability to analyze complex matrices.

Laboratory analyses also include physico-chemical parameters, in particular: pH, electrical conductivity, dissolved oxygen, biochemical and chemical oxygen demand, nutrient concentrations (nitrogen, phosphorus). Such parameters are determined by standardized methods and are used as supporting indicators for assessing the ecological status of surface waters, in accordance with the WFD. These parameters enable the interpretation of biological and chemical results and allow assessing anthropogenic impact on aquatic ecosystems.

Microbiological analyses are based on membrane filtration, most probable number (MPN) or polymerase chain reaction (PCR) to identify indicator organisms such as coliform bacteria and Escherichia coli. Such studies are crucial in assessing water-related health risks [46]. In addition to traditional indicators, molecular methods are used to detect genes associated with antimicrobial resistance, which informs about the prevalence of resistant pathogens in the aquatic environment. These research methods, combined with appropriate sampling methods, allow a reliable assessment of water quality.

The combination of chemical, physico-chemical, and biological analytical methods forms an integrated monitoring approach, as envisaged by the EU WFD, contributing to an objective assessment of the chemical status of waters, identification of pollution trends, and monitoring the effectiveness of water resources management measures within the framework of River Basin Management Plans (RBMPs).

### 3.4. The role of bioindicators in water quality monitoring

Biological assessment plays a crucial role in water quality monitoring, assessing the state of aquatic ecosystems based on the presence and abundance of certain organisms. Unlike physical and chemical indicators, which reflect short-term conditions, bioindicators integrate the cumulative impact of pollution and environmental stress over time [45, 46].

Bioindicators are organisms that are sensitive to changes in the environment and can be used as reliable markers of water quality. Bioindicators include fish, macroinvertebrates, microbes, and algae, each of which responds differently to pollutants and environmental changes (Rosenberg & Resh, 1993) [47]. Fish and benthic macroinvertebrates remain key biological indicators for assessing freshwater quality due to their ecological importance, well-documented sensitivity to pollution, and established use in standardized monitoring frameworks (e.g., WFD, IBI) [45].

Currently, despite traditional morphological identification, DNA-based methods are increasingly being used to improve resolution and efficiency.

Table 3.6

Biological indicators and their sensitivity to pollution

| Group | Representative species | Sensitivity to pollution | Use in monitoring |
|---|---|---|---|
| Macroinvertebrate test | Mayflies, stoneflies | High | Benthic sampling, IBI |
| Fish | Salmonids, cyprinids | Moderately high | Electrofishing, species richness |
| Algae | Diatoms, cyanobacteria | Medium | Chlorophyll-a, biomass indices |
| Microorganisms | Escherichia coli, coliform bacteria | Indicator of faecal inputs | Membrane filtration, qPCR |

Key bioindicators used for assessing water quality include:

**Macroinvertebrates**, such as insect larvae, molluscs, and crustaceans, are widely used as bioindicators due to their varying levels of tolerance to pollution [48]. For example, species such as mayflies and stoneflies thrive in clean water and are very sensitive to pollution, while leeches and some worms can survive in polluted water conditions. Analysis of the diversity and composition of macroinvertebrate communities allows scientists to assess the biological integrity of aquatic ecosystems.

**Fish populations.** Fish are important indicators of water quality because of their place within the aquatic food chain, their sensitivity to changes in oxygen levels, temperature, and chemical pollutants. A balanced fish population with a variety of species indicates a healthy ecosystem, while the dominance of pollution-resistant species or a decline in sensitive species indicates deterioration in water quality. Fish-based Indices of Biotic Integrity (IBI) are widely used in monitoring programmes.

**Algae and phytoplankton** play a fundamental role in aquatic ecosystems, producing oxygen through photosynthesis. However, excessive growth of cyanobacteria (blue-green algae) indicates excessive nutrient pollution, leading to harmful algal blooms (HABs) [49]. The bloom process contributes to the reduction of oxygen levels and the release of substances that are harmful to aquatic organisms and human health. Monitoring the diversity and density of algal blooms helps to assess nutrient loads and ecosystem balance. Chlorophyll-a concentration is used in water quality assessment as an indicator of algal biomass [45].

**Microbial indicators.** Bacterial species such as Escherichia coli (E. coli) and coliform bacteria are commonly used to assess microbial contamination of water sources. The presence of these bacteria in water indicates fecal contamination, which poses a risk to human health. Microbial indicators are particularly important for monitoring drinking water sources and recreational waters. Membrane filtration and PCR-based methods are used for their detection and quantification [46].

### 3.4.1. Biological monitoring methods

Biological monitoring applies standardized field and laboratory methods to assess the presence, abundance, diversity, and structure of aquatic organisms that serve as bioindicators. The main methods include:

- ✓ **Benthic macroinvertebrate sampling** from riverbeds using standardized protocols (e.g., net sampling, Surber sampler method) that are effective in detecting chronic pollution or habitat disturbance.
- ✓ **Electrofishing** to assess the composition and abundance of fish communities, especially in streams and rivers with accessible water movement conditions.
- ✓ **Phytoplankton monitoring**, with algal biomass assessed by chlorophyll-a concentration as an indicator, providing insight into nutrient loading and eutrophication risk.
- ✓ **Microbial assessments** using culture-based methods (e.g., *E. coli detection*).
- ✓ **Molecular methods** such as PCR, qPCR, for the detection of microbial contaminants and community composition. DNA barcoding and metabarcoding may be applied for high-resolution taxonomic identification, particularly for plankton and microbial communities.

These methods are described in the WHO Guidelines for Drinking-Water Quality (WHO, 2017, chapters 7 and 11) [46], which recommend to integrate biological data with physical and chemical indicators for achieving a comprehensive understanding of water quality and health risks.

## 3.5. Major pollutants of surface waters

Monitoring of chemical and toxicological parameters is essential for assessing water quality and identifying potential risks to human health and the environment. Surface water pollution can be caused by a variety of pollutants, including heavy metals, pesticides, nutrients, as well as pollutants such as pharmaceuticals and microplastics.

### 3.5.1. Classification of major pollutants

- ✓ Heavy metals: lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), are considered among the most hazardous pollutants of surface waters. As a rule, heavy metals enter water through industrial discharges, urban wastewater and as a result of mining activities [46]. They are persistent in the environment, bioaccumulate in aquatic organisms, and pose a significant risk to human health and wildlife. The detection of heavy metals is usually carried out using AAS (atomic absorption spectroscopy) or inductively coupled plasma mass spectrometry (ICP - MS), a highly sensitive analytical method that allows quantitative determination of trace metal concentrations (ISO, 2016).

✓ Pesticides, including herbicides, insecticides, and fungicides, are widely used in modern agriculture and urban landscapes. These chemicals can enter water bodies through waste water, leaching, and atmospheric precipitation. Persistent organic pollutants (such as DDT organophosphates) are of particular concern due to their persistence in the environment and toxic effects on the aquatic environment. Pesticide residues are analyzed using gas chromatography-mass spectrometry (GC-MS) [46].

✓ Nutrients (nitrogen (N), phosphorus (P)). Excessive inputs of nutrients, primarily nitrogen and phosphorus, cause algal blooms, oxygen depletion, and irreversible changes in aquatic ecosystems. Sources of nutrient pollution include agricultural fertilizers, or more precisely, their excess, as well as wastewater. Standard monitoring includes measurements of nitrates ($NO_3^-$, nitrites ($NO_2^-$), ammonium ($NH_4^+$) and phosphates ($PO_4^{3-}$) using spectrophotometric or ion chromatography methods [46].

✓ Emerging pollutants such as pharmaceutical compounds, microplastics, and substances derived from personal care products are becoming a growing concern in water quality monitoring [11]. The pollutants enter surface waters through wastewater treatment plants, industrial processes, the unsustainable disposal of goods.

Table 3.7

Priority pollutants in surface waters: analytical methods, health risks

| Substance group | Example | Analytical method | Health/ environmental issues |
|---|---|---|---|
| Heavy metals | Lead ( Pb, Cadmium (Cd),  Mercury ( Hg) | ISP-MS | Neurotoxicity - bioaccumulation |
| Pesticides/POPs | DDT, PCBs, PAHs | GC-MS | Carcinogenicity, endocrine disruption |
| Pharmaceuticals and endocrinological hygiene products | BPA, EE2 (17a-ethynylestradiol) | LC-MS,<br>in vitro assays | Hormonal effects, chronic toxicity |
| Microplastics | PET, PE, PP | Filtration, FTIR/SEM spectroscopy | Physical obstruction, pollutants vector |

For example, in the Czech Republic, microplastics have been detected in both raw and treated drinking water, with polyethylene, polypropylene, and polyethylene terephthalate being the most common [50]. Advanced analytical methods such as LC-MS and HPLC are used to detect these substances at trace levels [51, 52].

### 3.5.2. Determination of microplastics in drinking water

Article 13(6) of Directive EU 2020/2184 on the quality of water intended for human consumption (recycled) requires the European Commission to adopt a methodology for measuring microplastics in drinking water within 3 years of entry into force of the Directive (12 January 2021). To support the development and implementation of such a methodology, the Joint Research Centre has conducted a review of the scientific knowledge base regarding the nature, distribution and quantity of microplastics in drinking water. Based on a literature review and practical scientific studies, potential instrumental methods have been identified and documented in order to summarise their technical capabilities, limitations, sample throughput, as well as operational and investment costs.

The activities and progress of standardization bodies related to microplastic analytical methods were also assessed. In order to define the scope of the monitoring methodologies, possible descriptors of microplastics were considered, including: particle size, particle shape, polymer type, measurement parameters (mass/quantity). The information summarized in the EU report forms the basis for developing evidence-based recommendations on key parameters to be measured, the selection of the most effective analytical methods that can be used to develop the methodology. The official document Delegated Decision (EU) 2024/1441establishes a methodology for the measurement of microplastics in drinking water [52]. This is the most important contemporary EU standard on microplastics in drinking water, with legal force for all Member States. This Decision supplements Directive (EU) 2020/2184 and establishes the official methodology to be used by Member States for the measurement of microplastics in water intended for human consumption. This document includes:

- ✓ determining the parameters of microplastics (size, shape, measurement units),
- ✓ methodological requirements for monitoring,
- ✓ administrative provisions for reporting and subsequent inclusion of microplastics in the “watch list” - a monitoring list that identifies priority pollutants.

Analytical methods for measuring microplastics are compiled in a technical publication of the European Commission (Joint Research Centre): Analytical Methods to Measure Microplastics in Drinking Water [51], the main content of which includes:

- ✓ review of existing analytical methods for measuring microplastics (IR spectroscopy, microscopy, etc.),
- ✓ justification of the technical basis for the choice of methods,
- ✓ recommendations on metrology (particle sizes, fractions, measurement units).

This report is a detailed technical guide that supports the implementation of Delegated Decision 2024/1441 and is essential for laboratories and national monitoring programmes. According to the Joint Research Center (JRC), the EU has developed a practical methodology for collecting, filtering and analysing microplastic samples in water (e.g. with 100 μm and 20 μm filters, analysis using infrared or Raman microscopy).

The main provisions of the practical methodology determine:

- ✓ minimum sample volume for evaluation (typically ≥1000 l),
- ✓ types of polymers, size fractions and forms (particles/fibers),
- ✓ standardized procedures for sample preparation and analysis.

The main framework Directive (EU) 2020/2184 obliges Member States to establish monitoring methods for emerging pollutants, including microplastics. According to the “watch list” policy under WFD (“watch list” for surface water contaminants), EU countries may add microplastics as priority pollutants for monitoring surface waters (relevant documents are currently under development). [51-52].

### 3.5.3. Toxicological aspects of water quality assessment

The toxicological assessment of surface waters is based on the potential health effects of chemical pollutants on aquatic organisms and humans. The main factors that influence the toxicity of pollutants are: bioavailability, persistence, interaction with other substances. The most critical health risks associated with surface water pollution include neurological effects of heavy metals [46], endocrine disruption from pesticides [50], plastic additives, as well as carcinogenic risks of polycyclic aromatic hydrocarbons such as benzo[a]pyrene (Petrlik and al., 2024) [55].

The introduction of regular screening for toxic substances in drinking water sources has a decisive impact on the protection of public health. Many pollutants, in particular heavy metals and persistent organic substances, have the ability to accumulate in the tissues of aquatic organisms. The process of bioaccumulation leads to higher concentrations of these substances in organisms located higher in the food chain (a phenomenon called biomagnification). International organizations (UNEP, WHO) emphasize the importance of monitoring such substances for assessing long-term environmental and human health risks.

Water quality assessments often include laboratory toxicity tests using indicator species such as algae, Daphnia (water fleas), and fish larvae. Standardized biological assays, such as the Microtox test (using bioluminescent bacteria), as well as other toxicity tests, help to determine the harmful effects of specific contaminants. These tests provide insight into both lethal and sublethal effects, guiding regulatory limits and pollution control measures.

Some synthetic and naturally occuring chemicals found in surface waters can affect the endocrine system of aquatic organisms and humans (European Chemicals Agency, ECHA, 2021) [54]. These endocrine-disrupting chemicals (EDCs) include pharmaceuticals, plasticizers (e.g. bisphenol A) and industrial by-products. EDCs can cause reproductive impairments and developmental problems even at low concentrations of the toxicants. Similarly, internationally recognised organizations such as WHO and ECHA report that EDCs affect multiple hormonal pathways, and early detection using in vitro assays represents a promising prospect. ECHA works closely with the European Integrated Pollution Prevention and Control Bureau (EIPPCB), providing data and advice on chemicals management to improve the implementation of the Industrial Emissions Directive. ECHA has also initiated the development pan-European positive lists of chemicals that can be safely used in materials in contact with drinking water, in accordance with the relevant Directive. The objective is to protect people from contaminated drinking water, improve access to safe drinking water, and ensure harmonised safety and hygiene standards across all EU Member States.

Integrating chemical and toxicological indicators into water quality monitoring contributes to a better understanding of pollution sources by environmental authorities, enables a comprehensive assessment of risks to ecosystems and human health, as well as the implementation of appropriate mitigation strategies in order to protect water resources [52- 54].

### 3.6. Implementation of long-term monitoring systems

Effective long-term water quality monitoring requires a structured and scientifically sound approach. A well-designed monitoring system provides reliable data in order to assess environmental trends, identify sources of pollution and ensure compliance with water quality standards. Clear objectives, representative site selection, appropriate monitoring frequency and quality assurance are essential elements. The first step in establishing a monitoring system is to define its objectives. General objectives include tracking seasonal variations in water quality, detecting pollution incidents, assessing the effectiveness of pollution control measures and supporting regulatory compliance. The selection of monitoring sites should be based on three key factors: proximity to pollution sources, hydrological characteristics, and ecological significance.

The frequency of monitoring depends on the parameters being measured and the specific objectives of the programme. For example, physical and chemical parameters such as temperature, dissolved oxygen may require continuous or frequent monitoring, while biological assessments may be carried out quarterly or annually. The Water Framework Directive recommends a three-year cycle for biological elements and more frequent intervals for physicochemical parameters (European Parliament and Council, 2000).

Automated monitoring stations equipped with sensors can provide data on critical water quality parameters in real time, improving the detection of sudden changes or pollution incidents [45]. Sampling protocols should follow standardised methodologies to ensure consistency and comparability of data across EU Member States. This includes appropriate procedures for sample collection, storage and transport, as well as the use of accredited laboratory analytical methods. ISO 5667-3 provides guidance on sample handling, while ISO/IEC 17025 defines general requirements for laboratory competence.

Community and stakeholder engagement is another important aspect of long-term water quality monitoring programmes. Collaboration with governmental authorities, research institutions, local communities, and environmental organizations improves data sharing and promotes effective decision-making. For example, long-term water quality monitoring programmes in the Czech Republic integrate automated sensor networks with traditional laboratory analyses. Stationary sensor stations for real-time monitoring of dissolved oxygen, conductivity, and pH in large river basins are key components. Another key component is citizen science initiatives. Involving the public in water sampling has expanded data sets, especially for monitoring nutrient pollution in agricultural regions. Integration with hydrological models is also essential, as predictive tools help assess pollution risks from extreme weather events such as floods and droughts. These methods are compatible with EU approaches and can be used as models to strengthen monitoring capacity in Ukraine.

The implementation of long-term environmental monitoring systems in Ukraine is one of the key objectives in the process of European integration and the fulfillment of commitments under the EU Association Agreement. Establishing such a system involves the transition from short-term observations to continuous, scientifically based and institutionally established monitoring, which corresponds to the approaches and principles applied in the EU Member States. This is particularly important for the water resources sector, which is managed in the EU on the basis of an integrated river basin approach.

In the context of alignment with European standards, Ukraine is gradually harmonizing its national legislation and monitoring practices with the requirements of key EU directives, in particular the Water Framework Directive. This means the introduction of systematic long-term observations of the ecological and chemical status of surface and groundwater, a combination of physicochemical, biological, hydromorphological indicators. It is also envisaged to use standardized sampling and analytical methodologies compatible with European ISO and EN standards. It is important to develop biological monitoring as a tool for integrated assessment of aquatic ecosystem status, which allows detecting long-term changes associated with anthropogenic load and climate-related factors.

Table 3.8

Recommended monitoring frequency by parameter type

| Parameter type | Recommended frequency | Notes |
|---|---|---|
| Physical/chemical | Monthly or permanent | Continuous monitoring for real-time sensors |
| Biological | 1-4 times a year | Depends on seasonality and sample size |
| Sediment sampling | Every 3-5 years or after an incident | To assess pollution of residual contamination |
| Microbial (e.g. E. coli) | Monthly or after heavy rainfall | Especially important for drinking/recreational water |

The institutional transformation of the monitoring system in Ukraine involves a clear division of responsibilities among central executive authorities, river basin administrations, research institutions and accredited laboratories, as well as the establishment of an effective mechanism for coordination and data exchange. In this context, it is especially relevant to strengthen the role of scientific and research institutions of the National Academy of Sciences of Ukraine and sectoral institutes for providing methodological support, interpreting results and forming scientifically grounded recommendations for management bodies. This approach aligns with European practices of involving scientific expertise into the implementation of national environmental policy.

The long-term nature of monitoring is of fundamental importance for Ukraine, as it enables the development of time-series data necessary for assessing the effectiveness of environmental protection measures, implementing waterbody restoration programmes, and preparing river basin management plans. Aligning monitoring cycles with European planning periods creates the prerequisites for comparability of results and integration of Ukrainian data into European environmental monitoring information systems.

Financial support for long-term monitoring in Ukraine, within the context of European integration should be based on a combination of state funding, environmental funds, and international technical assistance, including EU programmes. Stable financing is a key condition for ensuring the continuity of observations and preventing data loss, which is critical for assessing long-term environmental trends.

Therefore, the implementation of long-term environmental monitoring systems in Ukraine according to the European model is not only a formal fulfillment of EU obligations, but also a necessary condition for the formation of an effective natural resource management system and increasing environmental safety based on scientifically proven data.

## 3.7. River basin management plans

A River Basin Management Plan (RBMP) is a strategic document that helps achieve “good” water status. It is based on data collection and results in a strategy for environmental improvement.

**The characteristics of the water basin** are the first stage on which the RBMP is based. This is the foundation of the pyramid (Fig. 3.2). At this stage, the boundaries of the river basin are determined, along with hydrographic and water management zoning, climate, topography, geology, hydrogeology, soils, vegetation, fauna, hydrological regime, specifics of the river basin, and the typology of surface water bodies. An analysis of different water bodies types (rivers, lakes, groundwater) is also conducted.

**Analysis of anthropogenic load.** At this level, anthropogenic impacts on the quantitative and qualitative status of surface and groundwater are assessed, including both point and diffuse sources: wastewater discharges, water abstraction for irrigation, the presence of dams and pollution from agriculture, accidental pollution, and the impact of contaminated areas. Also, potential hydromorphological alterations are determined:

- disruption of the free flow of rivers;
- disruption of the hydraulic connection of the riverbed and the adjacent part of the floodplain;
- hydrologic alterations;
- modification of river morphology.

At this stage, the risk that the water body will not achieve good status is assessed.

**Monitoring and assessment of water status.** At this stage, chemical and ecological studies are conducted, which determine:

Ecological status (for surface waters) is the main indicator that demonstrates the health of a river as a living system. It is assessed according to three groups of criteria:

- ✓ **Biological indicators:** the condition of fish, macroinvertebrates (e.g. insects, bottom snails), and phytoplankton (algae) is studied. If the species composition corresponds to the natural one, the ecological status is considered good.
- ✓ **Hydromorphological indicators:** assess whether the river's flow is not disturbed by dams, whether it has natural banks, and what its depth is.
- ✓ **Chemical and physico-chemical indicators:** parameters such as water temperature, oxygen level, nitrogen and phosphorus content (nutrients that in large quantities cause water "blooming") are evaluated.

The chemical status of surface waters is a test of water for the presence of "high risk" pollutants. Water is analyzed for the content of **priority substances** defined by EU standards:

- ✓ Heavy metals (cadmium, mercury, lead, nickel).
- ✓ Pesticides and herbicides.
- ✓ Persistent organic pollutants.
- ✓ Oil refining products.

There can be only two types of condition: **"good"** (if the concentration of any substance does not exceed the norm) or **"not good enough"**.

After collecting all the data, each water body is assigned a certain status. For surface waters, a five-level scale is used (Fig. 3.1):

- ✓ High (blue color on the maps);
- ✓ Good (green) is the target status that all countries should strive for;
- ✓ Moderate (yellow);
- ✓ Poor (orange);
- ✓ Bad (red).

**Economic analysis of water use.** This level estimates the cost of water supply and wastewater services, and also estimates the funds required for resource restoration. It is important to understand who should pay for water use and in what amount. The analysis considers anticipated economic development within the river basin, the current patterns of water use (municipal, industrial, agricultural, transport, and other sectors). It provides a forecast of water demand for key economic sectors and determines economic control tools for maximum cost recovery the use of water resources.

**Programme of measures.** This is the practical part of the plan. It includes a list of programmes (plans) for the river basin district (sub-basin), their scope and the problems that are intended to be solved:

**for surface waters, measuresfocus on:**

- ✓ reducing pollution from organic substances;
- ✓ reducing pollution from biogenic substances;
- ✓ reducing pollution from hazardous substances;
- ✓ improvement/restoration of the hydrological regime, morphological indicators in case of disruption of the free flow of rivers, hydraulic connection between river channels and their floodplains, hydrological alterations, modification of river morphology;
- ✓ infrastructure projects and measures aimed at reducing their impact on the status of surface waters;

**for groundwater, measures aimed at:**

- ✓ pollution reduction;
- ✓ preventing groundwater depletion;
- ✓ planned infrastructure projects and measures that involve reducing their impact on the status of groundwater.

Examples of measures may include the construction of wastewater treatment plants, coastal restoration, and the prohibition of certain pesticides. Each measure has a deadline and a responsible person (if necessary, justifications for setting less stringent goals or postponing the deadlines for their achievement are used).

**Environmental objectives and strategic outcome.** This stage reflects the summary of all previous steps and determines the target water status to be achieved within 6 years (the standard RBMP cycle). This is an outcome that guarantees clean water for both people and the ecosystem.

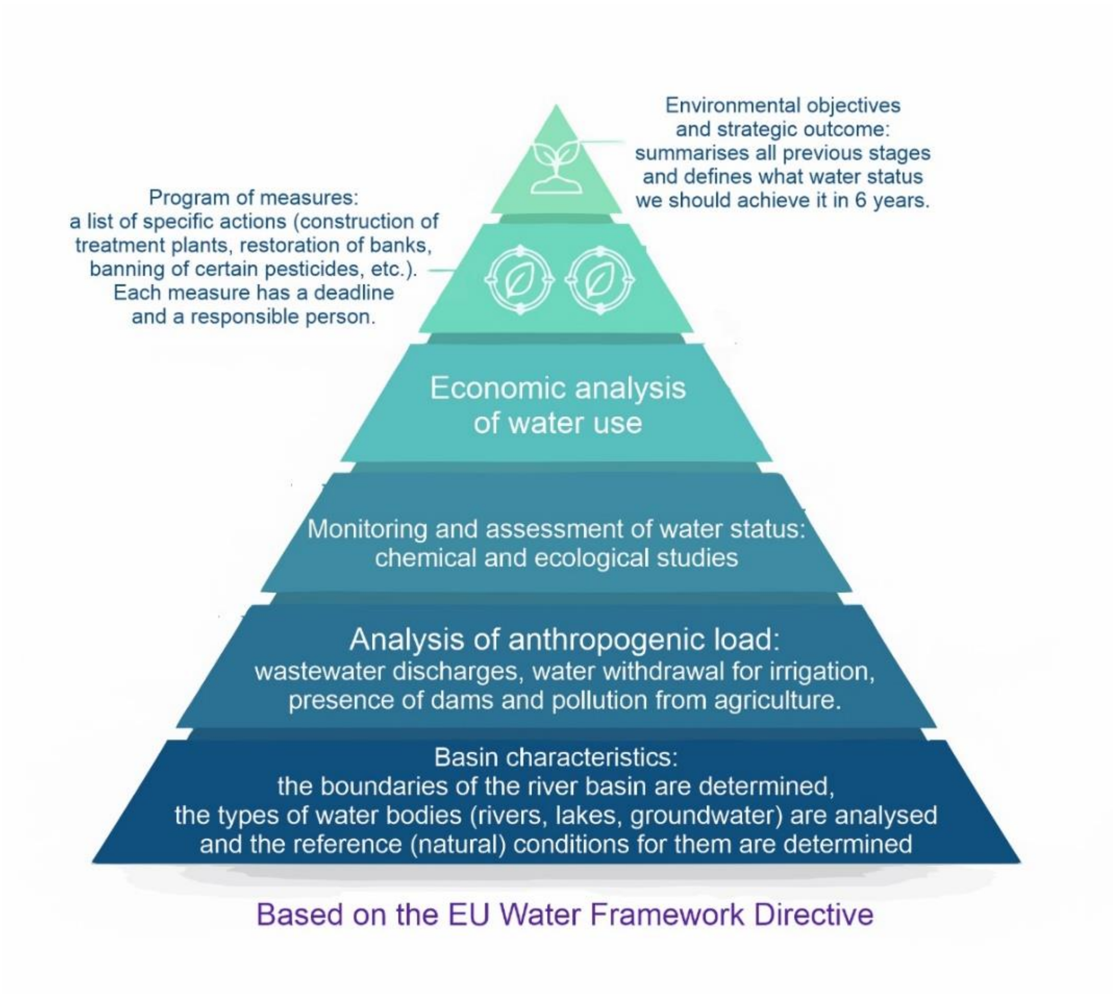


Fig. 3.2 River Basin Management Plan (RBMP).

# CHAPTER 4

# Global experience in water resources management practices

The European water resources monitoring system is being established in accordance with the requirements of the European Union Water Framework Directive (Water Framework Directive, 2000/60/ EC), which lays the foudation for an integrated approach to assessing the status of surface, groundwater, transitional, coastal and marine waters. The key principle of this system is river basin management**,** which involves considering the river basin as a single hydrological unit regardless of administrative or national borders (European Commission, 2000). The spatial distribution and density of monitoring sites in EU countries are reflected in the **WISE SoE (Water Information System for Europe – State of the Environment)** [69-70], administered by the European Environment Agency (EEA). The interactive WISE SoE maps cover all water quality monitoring stations reported by EU Member States since 1992, including rivers, lakes, reservoirs, groundwater, transitional, coastal and marine waters. The system includes both active and historical monitoring points, allowing the analysis of long-term trends in water quality. An important element of European monitoring is the international coordination of transboundary river basin management**.** Most of the major European river basins have specialised international commissions, responsible for coordinating monitoring, exchanging data, developing joint programmes of measures and preventing transboundary pollution. Key institutions include the International Commission for the Protection of the Danube River (ICPDR) [71], the Rhine (ICPR) [72], the Elbe Commision (IKSE), the Oder Commision (ICPOAP) and the Scheldt Commision (ISC). Of particular importance is the activity of the ICPDR, which involves both EU Member States and non-EU countries, including Ukraine, creating a unique example of integrated water resources management at the international level (ICPDR).

European experience demonstrates a variety of approaches to the spatial division of territories into river basins, depending on the hydrographic structure of the country. For example, the Czech Republic has three basins (Danube, Elbe and Oder), France has eight, Germany has six, while Poland and the United Kingdom each have ten. At the same time, the areas of the basins differ significantly: more than 90% of the territory of Poland is covered by only two basins – the Vistula and Oder, while in Lithuania about 74% of the territory falls on the Niemen River basin. Such differentiation is taken into account when planning monitoring programmes and developing River Basin Management Plans (RBMPs).

The water monitoring system in the EU countries includes **surveillance, operational** and **investigative monitoring. Surveillance** monitoring ensures regular collection of open data on hydromorphological, physico-chemical, and biological indicators of water quality. These data are published through national and European information portals, in particular the EEA and specialized basin platforms (e.g., the Elbe River data portals). Investigate monitoring is aimed at in-depth study of processes affecting the state of aquatic ecosystem, in particular in areas of intensive anthropogenic load. The key objects of such monitoring are urban, industrial, agricultural and drainage water discharge points, river estuaries, transboundary reservoirs and the final sections of basins, along which the water management balance is carried out. In some countries, in particular Germany, mobile operational monitoring stations are actively used**,** which allow to record the dynamics of key indicators in close to real time and transmit data to centralized management systems. Special attention within the framework of investigate monitoring is paid to small rivers**,** which are the most vulnerable to land use changes and local pollution. They largely determine the hydrochemical and hydrological regimes of medium and large watercourses. European practice shows that systematic monitoring of small rivers is critically important for assessing self-purification processes, accumulation of pollutants in bottom sediments and forecasting alterations in water quality across entire river basin.

Below is data on water resources management in France, Poland, Germany, Spain, as well as notable projects in other countirs worldwide.

### 4.1. France: Basin Management Model and Financial Sustainability

France is considered one of the pioneers of decentralized water resources management, having introduced the river basin approach by law back in 1964.

French water policy is based on four main legislative acts and is shaped by the adoption of the European Water Framework Directive in 2000. This Directive defines the concept of "good water status", which all EU Member States must strive to achieve. The territory of France is divided into 12 river basins. [58]

The 2004 Water law transposed the WFD, which directs entire water policy towards achieving efficiency objectives and achieving good water status by 2015. It sets ambitious targets for the conservation and restoration of water resources and the aquatic environment through the SDAGE (Master Plan for the Development and Management of Water Resources). The aim was to achieve good general status for both groundwater and surface water by 2015. In accordance with the WFD, an initial list of 33 substances was adopted in 2011. It includes metals, pesticides, hydrocarbons ( Decision No. 2455/2001/EC of 20 November 2001 ) , supplemented by a Directive ( D 2008/105/EC) setting environmental quality standards applicable to eight other products.

The 2006 act revises the principles of water pricing, in particular to ensure greater transparency for consumers. It introduces the principle of the "right to water" and the obligation to take climate change into account in all decisions concerning water resources management. The 2006 Act modernised the tools used by water police to better respond to changes in water resources. It provided additional tools to address new challenges and extended the scope of local water management plans (SAGE). Furhtermore, this law established the National Directorate for Water and the Aquatic Environment in France.

Currently, France has a water monitoring system based on the basin principle, which allows obtaining up-to-date information on the chemical and ecological status of water bodies. There are 12 River Basin Management Plans (RBMPs) in France, the documents for which are developed on the basis of a six-year cycle: 2010-2015, 2016-2021, 2022-2027. Dynamic monitoring is carried out, which allows making adjustments to the next cycle based on the observed results. Water resources management itself is an integral part of dynamic monitoring process. For each river basin, the basin committee establishes the main guiding principles within the framework of national and European water policies. The assembly is composed of a broad representation of all categories of stakeholders in the field of water resources: 40% elected local authorities; 40% representatives of water users (industrial operators, farmers, environmental associations, fishing associations, consumer associations); 20% representatives of the state. In France, the Water Resources Management and Development Plan (SAGE) is implemented as a territorial project based on a voluntary, consultative approach involving local stakeholders. Its task is to adapt the Master Plan for the Development and Management of Water Resources (SDAGE) to a more local scale. That is, taking into account the specific characteristics of a given territory, it aims to reconcile the needs and development of the different uses of water (drinking water, industry, agriculture ) and the protection of the aquatic environment . It is an important tool for the implementation of the Water Framework Directive (WFD).

In addition, the system is continuously developing from both a technical and scientific perspective, with new methods and tools being introduced. This is why technical and scientific institutions are closely involved in this monitoring. Coordinated by the French Water Partnership, the Water Expertise France platform is the first platform to reference French water know-how at international level. It is part of the Water Expertise France toolkit, an initiative implemented by the FWP in cooperation with ASTEE - the Association of Water and Wastewater Experts aimed at promoting French water know-how https://www.partenariat-francais-eau.fr/en/water-expertise-france/.

The financial component of the system is based on the “polluter/user pays” principle. The agencies have seven types of fees, including fees for pollution, irretrievable water use and deterioration of the aquatic environment. Approximately 90% of the agencies’ budget is allocated to financial assistance for water users for the implementation of environmental measures. Each basin has a water police that monitors the compliance of treatment facilities with established regulatory requirements.

## 4.2. Poland: legislative framework and unique funding system

The Polish model of water resources management combines European requirements with national specifics, including the country's administrative structure [56, 57].

Water policy in Poland is regulated by national legislation. The main act is the law “Prawo wodne” (2001), which establishes the principles of rational use, cooperation between authorities and the public, as well as the priority of the ecological function of water. The management system is self-sufficient due to funds for water supply services.

Public funding is crucial for water resources management. A key element is the National Fund for Environmental Protection and Water Management, established in 1989. The Fund accumulates resources from environmental fines, budgets, and EU financial assistance, allocating them towards the construction of wastewater treatment facilities and the modernization of hydrotechnical facilities.

The distinctive feature of water monitoring lies in its innovative approach. Polish experts apply biomonitoring using mussels. These organisms are very sensitive to pollution: in case of danger, they close their shells, which allows them to instantly respond to changes in water quality.

There are 9 river basin districts in Poland. Water management plans were first developed in 2011. They were updated for the second time in 2016 and then again in 2022. Water management plans show how public funds will be allocated. Priorities are established for 6 years and it is decided where the greatest investment should be made. In the middle of each cycle, the European Commission must submit a report on the implementation of measures aimed at achieving good water status. For the Commission, this is a tool to check how funds have been spent and to assess the effectiveness of their use.

This approach to water resources management has had a positive impact on the quality of drinking water in Poland. Tap water in this country has not always been of high quality. Even 15-20 years ago, it was not recommended to drink it without prior treatment, however following Poland's accession to the European Union, everything has changed dramatically. In recent years, the water purification system has been completely modernized, and in all cities across the country, drinking tap water is even safer than bottled water. The quality of water supplied centrally to residential buildings and apartments is constantly monitored. There are many private companies in Poland that monitor the quality of drinking water, purify rivers, and fish stocking. For example, the company "Prote" carries out biomonitoring by tracking the quality of drinking water using mussels. These organisms are very sensitive to water pollution. They have a protective effect and close their shells when they are exposed to contaminants. The average daily water consumption rate in Poland is about 160 liters. Thus, in Poland, water consumption per capita is about 20% higher than in Germany (120 litres per day). In general, the largest amount of water consumption is for hygiene purposes.

### 4.3. Germany: technological excellence and resource conservation

Germany is one of the EU countries that demonstrates high efficiency in the field of water treatment and rational urban planning [59].

The official strategy of the German Federal Government**,** adopted on March 15, 2023 by the Ministry of the Environment (BMUV/BMUKN), is a key document that defines approaches to sustainable water resources management, ensuring a high-quality water supply, and adaptation to climate change**.** The strategy is a framework and describes a long-term (up to 2050) vision for the water sector, in particular water treatment, water protection, and integrated planning in both urban and rural areas.

In Germany, up to 70% of drinking water is obtained from underground sources. For disinfection, chlorine (IV) oxide ($ClO_2$) is used instead of chlorine ($Cl_2$), which is safer. Water treatment plants operate on the principle of flocculation filtration, using ferrum salts to precipitate micro-impurities.

A rainwater collection and storage project has been implemented in Berlin (Potsdamer Platz area). Rainwater is collected in underground tanks and covers up to 80% of the domestic needs of nearby buildings (toilets, air conditioning), while the surplus supplies an artificial lake.

In addition, Germany applies the practice of using mobile monitoring stations for small rivers. They automatically measure water quality parameters every few hours and transmit the data to the network.

For the first time, the National Water Strategy brings together water-related measures in all relevant sectors: agriculture and nature conservation, administration and transport, urban development and industry. It is also the first time that all stakeholders are involved: the federal government, the federal states and municipalities, as well as all economic sectors and groups that depend on water resources. The Strategy plays a key role in implementing the #WaterInAllPolicies approach. This means that water is placed at the centre of attention in a number of policy areas that have a direct or indirect impact on water management. This is the only way to achieve the water transition that is necessary for water sustainability in the context of the climate and other challenges, as well as to meet the demand for a reliable water supply.

The scientific basis for the draft National Water Strategy was established by the German Environmental Protection Agency within the framework of a research and development project. The key objectives of the National Water Strategy are: high-quality and affordable drinking water in Germany even after 30 years; water quality is guaranteed – groundwater and surface water bodies (lakes, streams, rivers, oceans) are cleaner; the "polluter pays" principle and efficient use of resources; the restored semi-natural water regime has become more sustainable; the water supply and wastewater infrastructure is adapted to the effects of the climate crisis.

The first program of measures will be gradually implemented by 2030. The first steps have already been taken, including:

- ✓ Development of national guidelines for addressing water scarcity. In cooperation with the federal states and through dialogue with stakeholders, a unified system will be established to ensure that sufficient drinking water resources are always available nearby.
- ✓ Alignment with Federal Action Plan funds on Nature-Based Solutions for Climate and Biodiversity.
- ✓ The transition to water-smart cities is already underway, and the Federal Government is currently supporting municipalities that promote water-smart urban development. The Federal Government and the federal states are working intensively on the implementation of the "White Paper" on Urban Greening.
- ✓ The Federal Institute for Hydrology (BfG) is developing a national, user-oriented low water information system (Niedrigwasser-Informationssystem, NIWIS).
- ✓ The Federal Ministry for the Environment has launched a water communication strategy aimed at raising public awareness about the use of water as a resource.
- ✓ Engagement of other relevant stakeholders in the water sector, including federal states and professional associations, which have already joined efforts to promote the National Water Strategy by initiating their own projects.

### 4.4. Water resources management system in Spain

In Spain, the water resources management system is based on integrated river basin management, as required by the EU WFD. That is, water resources are assessed and planned not according to administrative borders, but within river basin districts, through the development of River Basin Management Plans and sets of measures aimed at achieving "good status" of water bodies.

In Spain, the Hydrographic Confederations (Confederaciones Hydrographicas) play a key role in basin management, which operate under the Ministry of Ecological Transition and Demographic Challenges (MITECO) https://www.miteco.gob.es/es/ministerio.html. Hydrographic Confederations implement water resources management at the level of large river basins. Their main responsibilities include:

- ✓ development and implementation of River Basin Management Plans;
- ✓ monitoring water quantity and quality;
- ✓ management of large water infrastructure (reservoirs, canals);
- ✓ water use control and permit issuance;
- ✓ participation in public consultation processes.

The Ministry develops national water policy, sets general priorities, and ensures coordination between confederations and other relevant bodies. Basin councils and governing bodies of confederations include representatives of state bodies, local governments, industry, agriculture, and civil society organizations, ensuring the principle of integrated management, taking into account the interests of different stakeholder groups.

Monitoring of water quality and quantity in Spain is carried out primarily by River Basin Authorities (Confederaciones Hidrográficas) within the framework of the implementation of the requirements of the EU Water Framework Directive. Based on monitoring results, status maps of water bodies and databases are compiled and incorporated into the River Basin Management Plans. In addition to public institutions, there are also independent research organizations in Spain that conduct additional research on water resources, in particular: The Catalan Institute for Water Research (ICRA) — studies water cycles, water quality and use, and the effects of climate change.

The state budget is the main funding source for the activities of the confederations and management bodies through the Ministry for Ecological Transition and the respective budgets of the confederations themselves. A significant part of the funding for projects related to the modernization of the water sector (e.g. wastewater treatment plants, monitoring tools, water quality management programmes) is provided through EU funds. The River Basin Authorities have the right to charge fees for the use of water resources and wastewater, which are partly used to cover their administrative and monitoring costs.

Summarizing the experience of these countries, it can be argued that the success of water resources management in the EU is ensured by a combination of strict legislative control, economic incentives to reduce pollution, and active public involvement in decision-making at the local level.

### 4.5. Experience of water resources management in Japan

Japan's experience in rational use of water resources is noteworthy. This country has experienced severe water shortages in recent years. In particular, during the 1994 water shortage affected almost all of Japan, approximately 16 million people were impacted. Therefore, the water management plan for the 21st century established three main objectives: 1) the development of a sustainable water use system; 2) protection and improvement of the aquatic environment; 3) restoration of water management culture and promotion of water-use culture. In Japan, in addition to the main water supply system, auxiliary water use is applied. Auxiliary water use is a general term referrring to water used for flushing toilets, cooling, air conditioning, and water used in sprinkler systems, which is obtained from the circulation of wastewater, industrial wastewater, rainwater, etc. Auxiliary water is primarily used in the municipal and domestic sector, but its quality is lower than that of tap water. The use of auxiliary water leads to a reduction in overall water consumption, increasing awareness of water conservation and the perception of the rational use of limited water resources. The effect of using such water is expressed in a reduction in sewage discharges and the improvement in the state of the environment. The use of auxiliary water can be divided into two types: wastewater recycling and the use of precipitation. Rainwater is used as auxiliary water, sometimes in combination with wastewater recirculation systems. Both large-scale systems and individual barrels for collecting rainwater, which are installed in private household, are used. It is not surprising that the invention of rain chains belongs to the Japanese. In their culture, the contemplation of water is considered one of the most calming factors. The Japanese came up with rain chains instead of the traditional drain, in which the flowing jets are not visible at all. These are open-type structures along which water moves in a cascade, flowing from one container to another. There are about 2,500 large-scale auxiliary water use systems in Japan. To encourage the use of auxiliary water, wastewater recycling projects are being developed and measures are being taken, including reduction of taxes, low-interest loans, subsidies, etc. for the installation of such facilities [60, 73].

### 4.6. Danube River Basin Monitoring Programme

The Danube River Basin Monitoring Programme, coordinated by the International Commission for the Protection of the Danube River (ICPDR) [61], is one of the largest transboundary water-monitoring programmes in Europe. The programme's institutional structure is based on intergovernmental cooperation among the 14 Danube basin countries and the European Union.

The ICPDR plays a coordinating and methodological role, while national water authorities and environmental agencies are responsible for the direct collection and initial processing of data. The programme is financed by contributions from the participating countries, European Union funds (in particular through the LIFE and INTERREG programmes), and support from international financial institutions.

Monitoring is implemented within the framework of the Joint Monitoring Programme (JMP/Joint Danube Survey), which provides unified sampling and analytical methods. Water quality monitoring covers physico-chemical parameters (temperature, pH, dissolved oxygen, nutrients, heavy metals), biological quality elements (phytoplankton, macrozoobenthos, ichthyofauna), as well as analysis of hazardous and priority substances in accordance with the requirements of the EU Water Framework Directive. A new phase of monitoring (JDS 5) started in mid-2025 at sampling sites in 14 countries of the Danube River Basin. JDS 5 builds on the successes of previous surveys (JDS 1-4) by integrating innovative technologies such as environmental DNA (eDNA) analysis, microplastic assessment and advanced monitoring methods. The focus on public engagement is an effort to bridge the gap between science and communities by involving stakeholders in monitoring activities. Particular attention is paid to identifying diffuse sources of pollution, in particular agricultural runoff, as well as the impact of industrial and municipal discharges.

The data obtained serve as a basis for the development and adjustment of the Danube River Basin Management Plans. Monitoring data are used to inform the River Basin Management Plans, the assessment of transboundary pollution transfers and the development of joint environmental protection measures.

### 4.7. Water quality monitoring in the Czech Republic

In the Czech Republic, the key institution in the field of water quality monitoring is the Czech Hydrometeorological Institute (CHMI), which is subordinate to the Ministry of the Environment [62]. The institute is responsible for the organization and operation of a national network of monitoring stations on rivers, lakes, reservoirs, groundwater, as well as for the standardization of observation methods. The institute's activities are financed from the state budget, supplemented by European Union funds and grant programs (INTERREG, Horizon, LIFE) aimed at implementing EU environmental legislation.

The national water monitoring system of the Czech Republic operates in accordance with the legislation (Act No. 254/2001 Sb., «Water Act»), which establishes requirements for determining the status of water resources [62]. Monitoring uses both classical laboratory analyses and automated continuous monitoring stations. Water quality assessment methods include the determination of physical parameters (temperature, turbidity), chemical parameters (nutrients, organic pollutants, metals) and biological indicators of ecological status.

The results are evaluated in accordance with the national Water Protection Act and WFD requirements, ensuring data comparability at the European level and enabling their use in regulatory and management decisions [62-64].

### 4.8. Water quality monitoring in the UK

The Catchment Based Approach (CaBA) in the UK is based on a decentralised model of water resources management, combining the activities of governmental authorities, local communities, non-governmental organisations, academic institutions and businesses. Institutionally, the initiative is coordinated by the Environment Agency of England, while specific projects are implemented at the level of individual catchment basins.

CaBA is financed through public environmental programmes, local budgets, charitable foundations, and private contributions. Water quality monitoring often combines professional measurements with citizen science, thereby expanding the spatial coverage of observations.

Water quality monitoring includes basic physico-chemical parameters, bioindication methods, and visual assessments of the state of watercourses. This approach contributes to increasing environmental awareness among the population and forming shared responsibility for the state of water resources.

CaBA has proven the effectiveness of combining scientific methods with public participation, which has contributed to improving the ecological condition of rivers and raising environmental awareness among the population [65].

### 4.9. Great Lakes Water Quality Agreement (USA – Canada)

The institutional framework for monitoring under the Great Lakes Water Quality Agreement (GLWQA) is based on bilateral cooperation between the governments of the United States and Canada. The United States Environmental Protection Agency (EPA) and Environment and Climate Change Canada play a leading role, along with regional and scientific institutions [66].

Funding is provided through the federal budgets of both countries and special Great Lakes restoration programmes.

Monitoring methods include field measurements, laboratory analyses, remote sensing and automated real-time observation systems. Water quality monitoring includes assessment of nutrients, toxic pollutants, biological status of ecosystems and spread of invasive species. The data obtained have enabled significant reduction in industrial loading, decreased phosphorus pollution and respond in a timely manner to harmful algal blooms.

### 4.10. Namami Ganga Program (India)

The Namami Gange Programme is implemented by the National Mission for Clean Ganga (National Mission for Clean Ganga (NMCG) under the supervision of the Government of India. Its institutional structure includes central and regional governments, scientific institutes and municipalities [67].

Funding is provided through the Indian state budget and international financial and technical assistance.

Monitoring is based on a network of automated stations transmitting data in real time. Control methods include measuring biochemical oxygen demand, coliform bacteria, heavy metals and other indicators critical to public health. The data is used for operational management of wastewater treatment plants and for strengthening control over industrial discharges.

### 4.11. Murray–Darling Basin (Australia)

The Murray-Darling Basin Authority coordinates a comprehensive monitoring programme spanning several Australian states. The institutional model combines federal and regional water management agencies.

Funding is provided through the state budget and special environmental funds.

Monitoring actively uses satellite remote sensing, automated sensors and biological assessments. Water quality monitoring focuses on salinity, turbidity, nutrients and the state of aquatic ecosystems, enabling adaptive management in response to climate variability and water management pressures.

Optimizing water distribution, reducing salinity, and adapting to climate change.

The case studies examined demonstrate that effective water quality monitoring is based on three key components:

- ✓ clear institutional roles and coordination;
- ✓ stable, multi-channel funding;
- ✓ combination of traditional and innovative monitoring methods.

Using such experience is extremely valuable for improving national water monitoring systems, particularly in countries aligning their legislation with EU requirements [68].

## 4.12. Comparison of global monitoring practices

An analysis of real water monitoring practices in the world shows that the most systematic and environmentally friendly approaches are taken by the countries of the European Union. The progressive aspects of the EU countries lies in the following:

- ✓ They are distinguished by a unified legal framework. The Water Framework Directive (WFD) establishes a mandatory, harmonised system across all 27 EU Member States and candidate countries.
- ✓ An important feature is the assessment of ecological status, not just concentrations. In particular, the EU is a global leader in the use of: bioindicators, hydromorphological criteria, and integrated ecological indices.
- ✓ Basin management principle. Managing water resources beyond administrative boundaries is a key advantage.
- ✓ Scientific support (JRC, EEA). Decisions are based on systematic reviews, not fragmented data.

The weaknesses include:

- ➢ Slow implementation of innovations;
- ➢ Bureaucracy;
- ➢ The complexity of unifying data among countries.

Thus, the EU demonstrates the most progressive approach to water monitoring in terms of conceptual framework, ecological philosophy, and long-term sustainability.

The water monitoring systems of the USA and Canada are characterized by technological and analytical advantages, in particular, the following strengths can be noted:

- ✓ Rapid implementation of new technologies: real-time monitoring, sensor networks, big data and AI analytics.
- ✓ Strong laboratory base (EPA): development of new methods for microplastics, toxicology, emerging screening contaminants.
- ✓ Flexible governance: states/provinces can be innovative “testing grounds” for new practices.

However, the weaknesses of water monitoring in these countries can be considered:

- ➢ Less unification across regions;
- ➢ A focus on chemical standards rather than holistic ecosystem assessment.

North America has the most technologically advanced environmental monitoring systems, including water monitoring, but is characterized by less systematicity at the national level.

The monitoring system in Australia is the most innovative in the context of climate challenges, and demonstrates a high capacity for rapid adaptation. Key strengths include:

- ✓ Leadership in remote sensing, hydrological modelling, and water scarcity management.
- ✓ Availability of flexible climate change adaptation tools.

The weaknesses include:

- ➢ Less attention is paid to bioindicators compared to the EU;
- ➢ Greater focus on the quantity of water rather than its quality.

Australia is among the global leaders in climate-adaptive monitoring, and such experience can be valuable given current trends toward abrupt climate change.

The water monitoring system of Asian countries (India, China, South Korea) is characterized by speed and large-scale implementation. The strengths of the monitoring systems in these countries include:

- ✓ Mass implementation of automated stations;
- ✓ Centralized data platforms;
- ✓ High frequency of measurements.

Weaknesses in water monitoring Asian countries include:

- ➢ Limited transparency;
- ➢ Fewer ecosystem indicators;
- ➢ Political, not ecological, motivation.

Table 4.1

Comparative table of world practices of water quality monitoring (summary)

| Criterion | EU | USA/Canada | Australia | Asia |
|---|---|---|---|---|
| Legal unity | ☆ ☆ ☆ ☆ ☆ | ☆ ☆ ☆ | ☆ ☆ ☆ ☆ | ☆ ☆ ☆ |
| Ecosystem-based approach | ☆ ☆ ☆ ☆ ☆ | ☆ ☆ ☆ | ☆ ☆ ☆ | ☆ ☆ |
| Innovation | ☆ ☆ ☆ ☆ | ☆ ☆ ☆ ☆ ☆ | ☆ ☆ ☆ ☆ | ☆ ☆ ☆ ☆ |
| Real-time monitoring | ☆ ☆ ☆ | ☆ ☆ ☆ ☆ ☆ | ☆ ☆ ☆ ☆ | ☆ ☆ ☆ ☆ ☆ |
| Transparency | ☆ ☆ ☆ ☆ ☆ | ☆ ☆ ☆ ☆ | ☆ ☆ ☆ ☆ | ☆ ☆ |
| Flexibility | ☆ ☆ ☆ | ☆ ☆ ☆ ☆ ☆ | ☆ ☆ ☆ ☆ | ☆ ☆ ☆ |

Water monitoring in Asian countries is a global leader in terms of scale and speed, but not in quality of data integration. Table 4.1 below provides a comparative overview of water quality monitoring practices across countries.

Thus, the most progressive in a conceptual and ecosystem-based terms is the European Union model, which provides long-term sustainability, legal certainty and integration of monitoring with water resources management. At the same time, North American countries and Australia are ahead of the EU in the rapid implementation of technological innovations, while some Asian countries demonstrate unprecedented scale and efficiency of monitoring, but with less emphasis on ecological integration.

### 4.13. Current EU water monitoring policy

The current water policy of the European Union is based on the provisions of the Water Framework Directive, the key implementation tool of which is the River Basin Management Plans. At the same time, the results of their implementation indicate the presence of significant problems: a significant proportion of surface and groundwater in the EU Member States still does not achieve good chemical status, and there are noticeable differences between countries in the level of achievement of environmental objectives. An evaluation conducted in 2019 on the suitability of the WFD highlighted the need to update the lists of priority pollutants, as the existing lists do not fully account for emerging chemical substances, the combined effects of chemical mixtures, and cumulative impacts. The assessment also revealed shortcomings in the field of monitoring, data management and reporting procedures.

In response to these challenges, the European Commission has initiated a revision of a number of water directives, including the Water Framework Directive [21], the Groundwater Directive [27] and the Environmental Quality Standards Directive for Water [33]. The proposed changes are aimed at achieving the EU’s strategic objective of zero pollution of the environment by 2050, which is part of the European Green Deal. Chemical contamination of water resources is considered a serious threat to aquatic ecosystems and human health, due to toxic effects, accumulation of pollutants in food chains and loss of biodiversity.

The European Union has a legal obligation to regularly review the lists of substances that pose a risk to surface and groundwater and to establish appropriate environmental quality standards. The updated approaches focus on per- and polyfluoroalkyl substances (PFAS), pharmaceuticals and pesticides, for which new or stricter standards are defined. PFAS, known as “persistent chemicals”, are widely used in everyday life and industry, which means they are widespread in the aquatic environment. EU Member States have agreed to establish environmental quality standards for these substances in surface waters.

Separate provisions concern the improvement of monitoring and reporting approaches. Interim reports are being introduced, along with new observation methods, including remote sensing, and the possibility of establishing a pan-European monitoring centre is being considered. At the same time, the concept of deterioration of the status of a water body is being clarified, taking into account case law and scientific approaches, which allows for a more flexible assessment of short-term and local impacts without increasing the overall pollution load.

Regarding groundwater, the updated policy envisages the establishment of pan-European standards for the most hazardous synthetic substances, aligned with the requirements of the Drinking Water Directive. In addition, a mandatory "watch list" mechanism for groundwater is being introduced, which will allow for a timely responses to the emergence of new pollutants. Member States are given a lengthy transitional period to comply with the new standards, taking into account the complexity and resource intensity of the measures required.

The preliminary political agreement reached in 2025 between the Council of the EU and the European Parliament on the update of the lists of pollutants and the corresponding quality standards was an important step in the modernisation of EU water policy. It ensures that regulatory requirements are aligned with current scientific knowledge, strengthens the protection of aquatic ecosystems and lays the foundation for more effective and transparent water resource management in Europe.

### 4.13.1. Ukrainian perspectives in water policy on the path to European integration

Despite significant achievements in aligning Ukraine's water legislation with the requirements of the EU Water Framework Directive, the implementation process is accompanied by several scientific, institutional, and practical problems. In particular, these include: incomplete harmonization of the lists of priority pollutants and environmental quality standards with the provisions of European Union directives; an insufficient number of accredited laboratories for determining compliance with environmental quality standards ( EQS ); the absence or limited availability of reference conditions for certain types of water bodies; the fragmented and uneven state water monitoring data; as well as a shortage of financial and human resources for the effective implementation of river basin management plans. A special emphasis is required on the deeper integration of scientific research into the decision-making processes for water management.

Overcoming these challenges requires a consistent state policy, strengthening scientific and methodological support, and deepening cooperation with European Union institutions. The introduction of approaches to water resources management harmonized with EU standards opens up a number of advantages for Ukraine, including access to modern methods, expanding opportunities for financing environmental projects, and strengthening transboundary cooperation.

At the same time, such approaches contribute to protecting public health, preserving biodiversity, and laying the foundations for sustainable economic development related to the use of water resources. Although Ukraine is not an EU Member State, the application of European water legislation provides a clear roadmap for improving the national water resources management system, addressing current water quality problems, and progressing toward a sustainable future.

# CHAPTER 5

# Water analysis methods: adaptation to international requirements

Ukraine has adopted the first European standards for the analysis of water and water bodies. In the process of European integration, Ukraine must establish an effective state system for environmental monitoring and oversight of compliance with environmental legislation, in line with the European Union's requirements and practices. An essential component of this process is instrumental and laboratory control, which is carried out by the units of the State Ecological Inspectorate and its territorial bodies.

Ukraine's acquisition of the status of an affiliated member of CEN - CENELEC implies obligations to implement European standards (EN, EN ISO) and to eliminate discrepancies between the national standardisation system and EU standards. For this reason, as well as to document the damage caused to the environment, determine the extent of losses, in particular as a result of military aggression, the bodies of the State Ecological Inspectorate must ensure the examination of selected samples of atmospheric air, surface water and soil on the territory of Ukraine in accordance with European and international standards adopted in the national standardisation system.

The OSCE Support Program for Ukraine, to assist our state in fulfilling these obligations, has ensured the development of 18 national standards of Ukraine aimed at implementing laboratory and instrumental control of surface water quality.

The national standards were developed by a team of experts from the OSCE Support Programme for Ukraine together with the national technical standardisation committees TSC 82 "Environmental Protection" and TSC 147 "Drinking Water Quality".

National regulatory documents were developed by the translation method in accordance with the requirements of DSTU 1.7:2015 “National standardisation. Rules and methods for adopting international and regional regulatory documents” and DSTU 1.2:2024 “National standardisation. Rules for conducting national standardisation work”. In accordance with the rules and procedures of national standardisation, the following were adopted by the order of the State Enterprise UkrNDNC dated 16.07.2025, No. 131:

**DSTU EN ISO 5667-1:2025** Water quality - Sampling - Part 1: Guidance on the development of sampling programmes and methods (EN ISO 5667-1:2023, IDT; ISO 5667-1:2023, IDT) — to replace DSTU EN ISO 5667-1:2022 (EN ISO 5667-1:2022, IDT; ISO 5667-1:2020, IDT);

**DSTU EN ISO 5667-3:2025** Water quality - Sampling - Part 3: Guidelines for the storage and handling of samples (EN ISO 5667-3:2024, IDT; ISO 5667-3:2024, IDT) — to replace DSTU EN ISO 5667-3:2022 (EN ISO 5667-3:2018, IDT; ISO 5667-3:2018, IDT);

**DSTU EN ISO 5814:2025** Water quality - Determination of dissolved oxygen - Electrochemical method using a probe (EN ISO 5814:2012, IDT; ISO 5814:2012, IDT) — to replace DSTU EN ISO 5814:2022 (EN ISO 5814:2012, IDT; ISO 5814:2012, IDT);

**DSTU EN ISO 5815-1:2025** Water quality - Determination of biochemical oxygen demand after n days (BOD n). Part 1: Dilution and plating method with addition of allylthiourea (EN ISO 5815-1:2019, IDT; ISO 5815-1:2019, IDT) — to replace DSTU EN ISO 5815-1:2022 (EN ISO 5815-1:2019, IDT; ISO 5815-1:2019, IDT);

**DSTU EN ISO 7393-2:2025** Water quality - Determination of free and total chlorine - Part 2: Colourimetric method using N, N-dialkyl-1,4-phenylenediamine for routine monitoring (EN ISO 7393-2:2018, IDT; ISO 7393-2:2017, IDT) — to replace DSTU EN ISO 7393-2:2022 (EN ISO 7393-2:2018, IDT; ISO 7393-2:2017, IDT);

**DSTU EN ISO 7887:2025** Water quality - Examination and determination of colour (EN ISO 7887:2011, IDT; ISO 7887:2011, IDT) — to replace DSTU EN ISO 7887:2022 (EN ISO 7887:2011, IDT; ISO 7887:2011, IDT);

**DSTU EN ISO 8467:2025** Water quality - Determination of permanganate oxidation (EN ISO 8467:1995, IDT; ISO 8467:1993, IDT) — to replace DSTU EN ISO 8467:2022 (EN ISO 8467:1995, IDT; ISO 8467:1993, IDT);

**DSTU EN ISO 10304-1:2025** Water quality - Determination of dissolved anions by liquid ion chromatography - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate (EN ISO 10304-1:2009, IDT; ISO 10304-1:2007, IDT) — to replace DSTU EN ISO 10304-1:2022 (EN ISO 10304-1:2009, IDT; ISO 10304-1:2007, IDT), DSTU EN ISO 10304-1:2022 (EN ISO 10304-1:2009, IDT; ISO 10304-1:2007, IDT)/Amendment No. 1:2022 (EN ISO 10304-1:2009/AC:2012, IDT; ISO 10304-1:2007/ Cor 1:2010, IDT);

**DSTU EN ISO 10304-4:2025** Water quality - Determination of dissolved anions by liquid ion chromatography - Part 4: Determination of chlorate, chloride and chlorite in water with low levels of contamination (EN ISO 10304-4:2022, IDT; ISO 10304-4:2022, IDT) — to replace DSTU EN ISO 10304-4:2022 (EN ISO 10304-4:2022, IDT; ISO 10304-4:2022, IDT);

**DSTU EN ISO 10703:2025** Water quality - Gamma-emitting radionuclides - Test method using high-resolution gamma spectrometry (EN ISO 10703:2021, IDT;

ISO 10703:2021, IDT) — to replace DSTU EN ISO 10703:2022 (EN ISO 10703:2021, IDT; ISO 10703:2021, IDT);

**DSTU EN ISO 15061:2025** Water quality - Determination of dissolved bromate - Liquid ion chromatography method (EN ISO 15061:2001, IDT; ISO 15061:2001, IDT) — to replace DSTU EN ISO 15061:2022 (EN ISO 15061:2001, IDT; ISO 15061:2001, IDT);

**DSTU EN ISO 17495:2025** Water quality - Determination of selected nitrophenols - Method using solid-phase extraction and gas chromatography with mass spectrometry (EN ISO 17495:2003, IDT; ISO 17495:2001, IDT) - replacing DSTU EN ISO 17495:2022 (EN ISO 17495:2003, IDT; ISO 17495:2001, IDT);

**DSTU EN ISO 18412:2025** Water quality - Determination of chromium (VI) - Photometric method for slightly polluted waters (EN ISO 18412:2006, IDT; ISO 18412:2005, IDT) - to replace DSTU EN ISO 18412:2022 (EN ISO 18412:2006, IDT; ISO 18412:2005, IDT);

Also, by order of the State Scientific and Technological Research Council of Ukraine dated July 29, 2025, No. 141, the following were adopted:

**DSTU EN ISO 5667-6:2025** Water quality - Sampling - Part 6: Guidance on sampling from rivers and streams (EN ISO 5667-6:2016, IDT; ISO 5667-6:2014, IDT) - Replaces DSTU EN ISO 5667-6:2022 (EN ISO 5667-6:2016, IDT; ISO 5667-6:2014, IDT);

**DSTU EN ISO 5667-14:2025** Water quality - Sampling - Part 14: Guidelines for quality assurance and control of sampling and processing of natural water samples (EN ISO 5667-14:2016, IDT; ISO 5667-14:2014, IDT) - Replaces DSTU EN ISO 5667-14:2022 (EN ISO 5667-14:2016, IDT; ISO 5667-14:2014, IDT);

**DSTU EN ISO 9377-2:2025** Water quality - Determination of petroleum products - Part 2: Liquid extraction and gas chromatography method (EN ISO 9377-2:2000, IDT; ISO 9377-2:2000, IDT) - To replace DSTU EN ISO 9377-2:2022 (EN ISO 9377-2:2000, IDT; ISO 9377-2:2000, IDT);

**DSTU EN ISO 17294-1:2025** Water quality - Application of inductively coupled plasma mass spectrometry (ICP - MS). Part 1: General guidelines (EN ISO 17294-1:2024, IDT; ISO 17294-1:2024, IDT) - To replace DSTU EN ISO 17294-1:2022 (EN ISO 17294-1:2006, IDT; ISO 17294-1:2004, IDT);

**DSTU EN ISO 18857-2:2025** Water quality - Determination of selected alkylphenols - Part 2: Gas chromatography-mass spectrometry determination of alkylphenols, their ethoxylates and bisphenol A in unfiltered samples after solid-phase extraction and derivatisation (EN ISO 18857-2:2011, IDT; ISO 18857-2:2009, IDT) — To replace DSTU EN ISO 18857-2:2022 (EN ISO 18857-2:2011, IDT; ISO 18857-2:2009, IDT).

The development of new state standards was carried out within the framework of the project "Ecological Monitoring of the Consequences of War and Recovery Strategy". The Ministry of Environment explains that at the beginning of 2024, national standards that did not comply with international and European standards were cancelled in Ukraine. Some of them were replaced with European standards in the original language (English, French) without taking into account national application conditions. But since the need for adequate water quality control has not disappeared, the national standards have been restored for the period of implementation of European standards, until May 1, 2025. It is worth noting that integration with the EU in the field of surface water quality monitoring requires approval of more than 600 standards and the modernisation of laboratory equipment (https://ecopolitic.com.ua/ua/news/mindovkillya-predstavilo-proiekti-dstu-shhodo-monitoringu-yakosti-vodi-za-ievropejskimi-normami).

According to the orders of the State Enterprise "Ukrainian Research and Training Center for Standardization, Certification and Quality", the standards will come into effect from November 1, 2025. Instead, their adoption serves as the basis for modernising the laboratory infrastructure and improving the qualifications of laboratory personnel, as a prerequisite for implementing European methods for controlling wastewater, surface water, and water resources. You can order official copies of standards through official partners: https://uas.gov.ua/poslugi/official-copies-of-regulatory-documents.

Below are detailed analytical research methods that take into account international standards and the real practical capabilities of training laboratories.

# WATER ANALYSIS METHODS

(used in the educational process)

## 5.1. Methodology for measuring mass concentrations of calcium and magnesium in surface and treated wastewater by the titrimetric method

*The method of titrimetric determination of mass concentrations of calcium and magnesium meets the requirements of ISO6059:2003, ISO6059:1984, ISO6058:1984 (EN ISO*), as well as *MVV No. 081/12-0006-01.*

### 1. Scope of application

This document establishes a methodology for measuring mass concentrations of calcium and magnesium in surface and treated wastewater by the titrimetric method.

The measurement range for calcium mass concentration in surface and treated wastewater is 10 to 150 mg/dm$^3$, inclusive.

The measurement range for the mass concentration of magnesium in surface and treated wastewater is 10 to 150 mg/dm$^3$, inclusive.

The determination is interfered with by metals, which also form complex compounds with Trilon B. This is manifested in an unclear colour change at the equivalence point. The determination is affected by the sample's high alkalinity, which is neutralised with hydrochloric acid and then boiled to remove carbon dioxide completely. The determination is interfered with by suspended solids. With an iron content exceeding 50 mg/dm$^3$, this method is not suitable for the determination of calcium and magnesium without prior iron removal. The determination of calcium is interfered with by magnesium if its concentration in the water being analysed is more than 50 mg/dm$^3$, because it adsorbs murexide and interferes with the apparent fixation of the end of the calcium titration.

### 2. Norms and characteristics of measurement errors

Error rates for measurements of calcium and magnesium mass concentration in surface and wastewater are given in Table 1.

Table 1

Measurement error rates

| Indicator | Surface water | | Wastewater | |
|---|---|---|---|---|
| | Measurement range, mg/dm$^3$ | Norm errors, % | Measurement range, mg/dm$^3$ | Norm errors, % |
| Calcium | from 0.5 to 50 inclusive<br>over 50 | 10<br>5 | from 5 to 100 inclusive<br>over 100 | 10<br>5 |
| Magnesium | from 1.0 to 4.0 inclusive<br>over 4.0 up to and including 10<br>over 10 | 25<br>10<br>5 | from 3.0 to 10 inclusive<br>over 10 | 10<br>5 |

MVV provides measurements of mass concentrations of calcium and magnesium in surface and treated wastewater, with limits of total relative error. The values, at a confidence probability of *P* = 0.95 for the result, the average of two parallel measurements (*n* = 2), are given in Table 2.

Table 2

Bounds of the total relative error of measurements of mass concentrations of calcium and magnesium at a confidence probability of *P* = 0.95 for the result, the average of two parallel measurements, *n* = 2

| Indicator | Surface and treated wastewater | |
|---|---|---|
| | Mass concentration measurement range, mg/dm$^3$ | Boundaries of the total relative errors ± $\delta$, % |
| Calcium | from 10 to 50 inclusive<br>over 50 up to and including 150 | 10<br>5 |
| Magnesium | from 10 to 150 inclusive | 5 |

**3. Measuring instruments, auxiliary equipment, reagents, materials**

3.1 Measuring instruments

3.1.1 General-purpose laboratory scales, class 3, with a maximum weighing limit of 200 g

3.1.2 Volumetric flasks 2-100-2, 2-250-2, 2-1000-2

3.1.3 Single Mark Pipettes 1-2-5, 1-2-10, 1-2-20, 1-2-50, 1-2-100

3.1.4 Graduated pipettes 1-2-2-2, 1-2-2-5

3.1.5 Burettes 1-1-2-5-0.02; 1-1-2-25-0.05

3.1.6 Measuring cylinders 1-50, 1-100, 1-200, 1-500

3.1.7 State standard sample of calcium ion solution composition (SSS 022.41-96) with certified mass concentration of calcium ions 1 mg/cm$^3$.

3.1.8 State standard sample of the composition of a solution of magnesium ions (SSS 022.80-98) with a certified mass concentration of magnesium ions of 1 mg/cm$^3$.

3.2 Reagents

3.2.1 Methyl red

3.2.2 Distilled water

3.2.3 Trilon B

3.2.4 Magnesium sulfate

3.2.5 Ammonium chloride

3.2.6 Murexide

3.2.7 Eriochrome black T

3.2.8 Sodium chloride

3.2.9 Aqueous ammonia

3.2.10 Hydrochloric acid

3.2.11 Sodium hydroxide

3.2.12 Sodium sulfide

3.2.13 Hydroxylamine hydrochloride

3.2.14 Calcium carbonate

3.3 Chemical glassware and materials

3.3.1 Ashless filters "blue ribbon"

3.3.2 Conical flasks, graduated cylinders, calcium chloride tube

The qualification of reagents must be no worse than “p.d.a.” unless otherwise specified.

## 4. Principle

The method for measuring the mass concentration of calcium and magnesium in surface and treated wastewater is based on the formation of calcium and magnesium complexes with Trilon B. The complex of calcium ion with the anion of ethylenediaminetetraacetic acid is stable in a very alkaline environment at pH 12-13, and the complex of magnesium ion in this environment is destroyed. Magnesium is in the form of hydroxide. Calcium is titrated with Trilon B with the indicator murexide. Calcium with murexide forms a pink complex. After binding all calcium into a complex with Trilon B, the colour of the free indicator appears - lilac-violet. After decomposition of murexide with bromine water or boiling, a pH 10 environment is created, and magnesium is titrated with Trilon B using the indicator eriochrome black T (chromogen black). Magnesium with the indicator eriochrome black T forms a lilac-violet complex. After binding all the magnesium to a Trilon B complex, the free indicator appears blue.

The volumes of Trilon B solution used for calcium titration with the indicator murexide and magnesium titration with the indicator eriochrome black T are measured by the titrometric method. The mass concentration of calcium and magnesium is determined by the calculation method.

## 5. Preparing to take measurements

In preparation for measurements of the mass concentration of calcium and magnesium in water, solutions are prepared; the exact concentration of the titrant is determined; samples are selected and preserved; and sample preparation is performed.

5.1 Preparation of a solution of Trilon B with a molar concentration of 0.025 mol/dm$^3$.

A portion of Trilon B weighing (9.31±0.01) g is dissolved in bidistilled water. The volume of the solution is brought to the mark with bidistilled water in a volumetric flask with a capacity of 1 dm$^{3,}$ according to item 3.1.2, and mixed thoroughly. If the solution is cloudy, it is filtered.

The solution is suitable for use when stored in a corked glass under laboratory conditions for two months.

Note: Trilon B solution can be prepared from standard titers.

5.2 Preparation of a calcium chloride solution with a molar concentration of 0.025 mol/dm$^3$ to determine the exact concentration of the Trilon B solution

A portion of freshly precipitated, dried at 105 °C to constant mass, calcium carbonate weighing (2.5023±0.0008) g is dissolved in hydrochloric acid (1:1). The dissolution is carried out in a conical flask with a capacity of 500 cm$^3$. After complete dissolution of calcium carbonate with a cylinder according to p. 3.1.6, 200 cm$^3$ of double-distilled water is added, heated, and boiled for 20 minutes. After cooling and adding three drops of methyl red, ammonia or hydrochloric acid is added dropwise until the indicator colour changes. The resulting solution is quantitatively transferred into a volumetric flask according to p.3.1.2 with a capacity of 1 dm$^3$. The solution volume is brought to the mark with double-distilled water, then mixed thoroughly.

The solution is suitable for use when stored in a corked glass under laboratory conditions for three months.

5.3 Preparation of a magnesium sulfate solution with a molar concentration of 0.025 mol/dm$^3$ to determine the exact concentration of the Trilon B solution.

5.3.1 Option A. A portion of magnesium sulfate heptahydrate weighing (6.1625±0.0008) g is dissolved in water to which 0.5 cm$^3$ of sulfuric acid (1:10) has been added. The volume of the solution in a volumetric flask, according to item 3.1.2, with a capacity of 1 dm$^3$, is brought to the mark with bidistilled water and mixed thoroughly.

5.3.2 Option B. The contents of the standard titer ampoule are brought to the mark in a volumetric flask of 1 dm$^3$ capacity, filled with bidistilled water, and mixed thoroughly. The molar concentration of the resulting magnesium sulfate solution is 0.05 mol/dm$^3$.

To prepare a magnesium sulfate solution with a molar concentration of 0.025 mol/dm$^3$, use a pipette according to item 3.1.3 to take 50.0 cm$^3$ of a magnesium sulfate solution with a molar concentration of 0.05 mol/dm$^3$, transfer it to a volumetric flask according to item 3.1.2 with a capacity of 100 cm$^3$, bring the volume of the solution to the mark with bidistilled water and mix thoroughly.

The solution is suitable for use when stored in a corked glass under laboratory conditions for six months.

5.4 Preparation of a solution of magnesium sulfate with a molar concentration of 0.05 mol/dm$^3$ for the preparation of a buffer solution

A portion of magnesium sulfate heptahydrate weighing (1.232±0.001)g is dissolved in bidistilled water, and the solution is brought to the mark with bidistilled water in a volumetric flask of 100 $cm^3$ capacity, according to item 3.1.2. The solution is suitable for use when stored in a corked glass under laboratory conditions for one year.

5.5 Preparation of a sodium hydroxide solution with a molar concentration of 1 $mol/dm^3$

A portion of sodium hydroxide weighing (40±1) g is dissolved with stirring in a heat-resistant beaker in approximately 500 $cm^3$ of freshly boiled bidistilled water. After cooling, the solution is quantitatively transferred into a volumetric flask according to item 3.1.2 with a capacity of 1 $dm^3$. Bring the solution volume to the mark with bidistilled water, then mix thoroughly. The solution is suitable for use when stored in a corked polyethene container protected from air by a calcium chloride tube with soda lime in laboratory conditions for one month.

5.6 Preparation of ammonia buffer solution

A portion of ammonium chloride weighing (26.8±0.1)g is placed in a conical flask with a capacity of 1 $dm^3$, 100 $cm^3$ of bidistilled water is added using a cylinder according to p.3.1.6, dissolved with stirring, 300 $cm^3$ of concentrated ammonia solution is added using a cylinder according to p.3.1.6 and mixed thoroughly. To the resulting solution, 50 $cm^3$ of magnesium sulfate solution prepared according to p.5.4 and an equivalent amount of Trilon B solution with a molar concentration of 0.05 $mol/dm^3$ are added using a cylinder according to p.3.1.6, as determined by a preliminary titration of 10 $cm^3$ of magnesium sulfate solution. The solution is thoroughly mixed.

The suitability of the buffer solution is checked as follows: 5 $cm^3$ of the buffer solution is added to 100 $cm^3$ of bidistilled water, mixed thoroughly, and the pH is measured electrometrically, the value of which should be within (10 ±1). Titration of this control solution with ammonia solution ($pH < 9.9$) or hydrochloric acid ($pH > 10.1$) and subsequent conversion to the available amount of buffer solution establishes the volume of ammonia or hydrochloric acid solution required to adjust the pH of the buffer solution.

The solution is suitable for use when stored in a corked glass under laboratory conditions for one year.

5.7 Preparation of a hydrochloric acid solution with a molar concentration of 1 $mol/dm^3$

Using a cylinder according to item 3.1.6, 88 $cm^3$ of concentrated hydrochloric acid ($d=1.18\ g/cm^3$) is placed in a volumetric flask according to item 3.1.2 with a capacity of 1 $dm^3$, the volume of the solution is brought to the mark with bidistilled water and mixed thoroughly. The solution is suitable for use when stored in a corked glass under laboratory conditions for one year.

5.8 Preparation of a dry mixture of murexide indicator

A portion of murexide weighing (0.2±0.1) g is mixed with (100±1) g of sodium chloride. The mixture is thoroughly ground to a fine powder. The mixture is stored in a dark place. The shelf life of the mix is limited by that of murexide.

5.9 Preparation of a dry mixture of Eriochrome Black T indicator

A portion of eriochrome black T weighing (0.5±0.1) g is mixed with (100±1) g of sodium chloride. The mixture is thoroughly ground to a fine powder. The mixture is stored in a dark place. That of eriochrome black T limits the shelf life of the mix.

5.10 Establishing the exact concentration of Trilon B solution and correction factor

To establish the precise concentration of the Trilon B solution, using pipettes according to item 3.1.3, three aliquots of different volumes (e.g., 10, 15, 20 cm$^3$) of calcium chloride solution according to item 5.2 or magnesium sulfate solution according to item 5.3 are taken.

When using a calcium chloride solution, each aliquot is placed in a 250 cm$^3$ conical flask, using a cylinder as described on p. 3.1.6, add bidistilled water to 100 cm$^3$, using a pipette according to p. 3.1.3, add 2 cm$^3$ of sodium hydroxide solution according to p. 5.5 (to pH 12-13) and 15 mg of a dry mixture of murexide indicator according to p. 5.8, titrate with Trilon B solution according to p. 5.1 with stirring until the colour changes from pink to lilac-violet, note the volume of Trilon B solution used for titration. Separately, perform a blank titration with 100 cm$^3$ of bidistilled water.

When using a magnesium sulfate solution, each aliquot is placed in a 250 cm$^3$ conical flask, using a cylinder as described on p. 3.1.6, double-distilled water is added to 100 cm$^3$, using a pipette according to p. 3.1.3, 5 cm$^3$ of ammonia buffer solution according to p. 5.6, 15 mg of a dry mixture of eriochrome black T indicator, according to p. 5.9, are added, and the mixture is titrated with a Trilon B solution until the colour changes from lilac-violet to blue; the volume of Trilon B solution used for titration is noted. Separately, perform a blank titration with 100 cm$^3$ of bidistilled water.

5.11 The exact concentration of the Trilon B, C and solution, mol/dm$^3$, is calculated using the formula:

$$C_i = \frac{C' \cdot V'}{V_i - V_x}, \tag{1}$$

where: $C'$ - concentration of calcium chloride solution according to item 5.2 or magnesium sulfate solution according to item 5.3 (0.025 mol/dm$^3$);

$V'$ - volume of calcium chloride solution or magnesium sulfate solution taken for titration, cm$^3$;

$V_i$ - volume of Trilon B solution used for titration of the $i$-th solution, cm$^3$;

$V_x$ - volume of Trilon B solution used for blank titration, cm$^3$.

5.12 The correction factor, $k$, to the concentration of the Trilon B solution is calculated by the formula:

$$k = \frac{1}{I}\sum_{i=1}^{I} k_i = \frac{1}{I}\sum_{i=1}^{I} \frac{C_i}{C^*}, \tag{2}$$

where: $C_i$ - the exact concentration of the Trilon B solution, mol/dm$^3$, established in accordance with clause 5.11;

$C^*$ - the specified concentration of the Trilon B solution (0.025 mol/dm$^3$).

The difference between the coefficients $k_i$, established by parallel titrations, should not exceed 0.001. The value of the correction factor should not exceed the limits (1 ±0.03). If the correction factor exceeds the specified limits, the solution is diluted accordingly, or Trilon B is added, and the correction factor is established again.

The correction factor is usually set at 20 °C. The titrated solution is used at the same temperature. If these operations are carried out at different temperatures, a temperature correction is introduced in accordance with Appendix A.

The titrated Trilon B solution is stored in a glass tube indoors at room temperature, in a place protected from direct sunlight. The glass with a tube indicates the given molar concentration, the correction factor, the temperature, and the date the correction factor was set. The correction factor is checked weekly.

5.13. Sampling and preservation of samples

Samples are taken in glass or polyethene containers. The volume of the sample intended for measuring the mass concentration of calcium and magnesium according to this MVV must be at least 300 cm$^3$. Samples are not preserved. They can be stored at room temperature for 1 month, filtered through a "blue ribbon" paper filter immediately after sampling and acidified to 2 pH units.

5.14 Sample preparation

If calcium carbonate precipitates in the filtered sample during storage, dissolve it with the smallest possible volume of hydrochloric acid before analysis. If the sample is colored, pass it through a column of activated carbon BAU (d = 1.5 - 2 cm, h = 25 - 30 cm) at a speed of 2 cm/min.

For titration with pipettes according to item 3.1.3, a volume of 100 cm$^3$ or less is taken, placed in a 250 cm$^3$ conical flask, and distilled water is added to 100 cm$^3$ using a cylinder according to item 3.1.6. In the titration volume, the calcium content should not exceed 7 mg, and the magnesium content should not exceed 3 mg.

If the mass concentration of phosphates in the sample exceeds 75 mg/dm$^3$ and/or magnesium - 50 mg/dm$^3$, then the smallest possible volume of the sample is taken for analysis and brought to 100 $cm^3$ in a conical flask or an accurate dilution of the sample is carried out beforehand and 100 $cm^3$ is taken for titration with a pipette according to p.3.1.3 . Before carrying out the analysis, the alkalinity of the sample is determined. If the alkalinity of the sample exceeds 6 $mmol/dm^3$, an equivalent amount of hydrochloric acid (0.1 $mol/dm^3$) is added to the aliquot selected for titration, the mixture is heated to boiling for 1 minute to remove carbon dioxide, and then cooled.

5.15 If the sample contains more than 2 $mg/dm^3$ of copper, more than 20 $mg/dm^3$ of iron (II) and (III), more than 10 $mg/dm^3$ of manganese, more than 5 $mg/dm^3$ of zinc, lead, aluminum, tin, then 2 $cm^3$ of a 10% sodium sulfide solution and 5 drops of an alcoholic solution of hydroxylamine hydrochloride with a 4.5% alcohol content are added to the previously neutralised sample before creating the required pH for calcium titration using a pipette according to item 3.1.3.

## 6. Measurement procedure

6.1 To the sample treated according to p.5.2, add 2 $cm^3$ of sodium hydroxide solution, 15 mg of dry mixture of murexide indicator according to p. 5.8 with a pipette according to p.3.1.3 and using a burette according to p.3.1.5 with a volume of 25 $cm^3$, titrate calcium with Trilon B solution according to p.5.1 until the color changes from pink to lilac-violet, note the volume of Trilon B solution used for calcium titration. Then add 1.5 $cm^3$ of hydrochloric acid (p. 5.7) to the sample and boil until the colour disappears. After cooling, 5 $cm^3$ of buffer solution is added to the sample using a pipette, as described on p. 3.1.3, 15 mg of eriochrome black T indicator according to p. 5.9 and after checking the volume on the burette or bringing it to the zero mark, titrate the magnesium with a solution of Trilon B according to p. 5.1 until the colour changes from lilac-violet to blue, note the volume of Trilon B used for the magnesium titration. If the titration volume contains more calcium and magnesium than required, the titration is repeated with a smaller volume of the sample, diluted to 100 $cm^3$ with distilled water. If the magnesium content is less than 30 $mg/dm^3$, a burette of the type described in item 3.1.5 with a capacity of 5 $cm^3$ is used for magnesium titration. The volume used for titration is noted with an accuracy of 0.02 $cm^3$.

6.2 Perform two parallel titrations.

6.3 For each series of samples, perform a blank titration of 100 $cm^3$ of distilled water.

6.4 Titration results are recorded to the third significant figure.

## 7. Processing the results

7.1 The result of a single measurement of the mass concentration of calcium in the initial sample $\rho_{\mathrm{Ca}\,i}$, $mg/dm^3$, is calculated by the formula:

$$\rho_{\mathrm{Ca}i} = \frac{(V_{\mathrm{Ca}i} - V_{\mathrm{х}}) \cdot 0{,}025 \cdot k \cdot 40{,}08 \cdot 1000}{V_{\mathrm{пр}}} = \frac{(V_{\mathrm{Ca}i} - V_{\mathrm{х}}) \cdot k \cdot 1002}{V_{\mathrm{пр}}}, \tag{3}$$

where: $V_{\mathrm{Ca}\,i}$ -volume of Trilon B solution used for the *i*-th titration of $Ca^{2+}$, $cm^3$;

$V_{\mathrm{x}}$ - volume of Trilon B solution used for blank titration, $cm^3$;

0.025 - exact concentration of Trilon B solution, $mg/dm^3$;

*k* - correction factor for bringing the concentration of the Trilon B solution to a concentration of 0.025 $mol/dm^3$;

40.08 molar mass of $Ca^{2+}$ equivalent in complexometric titration;

1000 - conversion factor for calcium concentration in $mg/dm^3$;

$V_{\mathrm{pr}}$ - volume of the initial sample taken for titration, $cm^3$;

*and* - number of the single mass concentration measurement, $i = 1, 2$.

The result of a single measurement of the mass concentration of magnesium in the initial sample $\rho_{\mathrm{Mg}\,i}$, $mg/dm^3$, is calculated by the formula:

$$\rho_{\mathrm{Mg}i} = \frac{(V_{\mathrm{Mg}i} - V_{\mathrm{х}}) \cdot 0{,}025 \cdot k \cdot 24{,}32 \cdot 1000}{V_{\mathrm{пр}}} = \frac{(V_{\mathrm{Mg}i} - V_{\mathrm{х}}) \cdot 607{,}8}{V_{\mathrm{пр}}}, \tag{4}$$

where: $V_{\mathrm{Mg}\,i}$ - volume of Trilon B solution used for the *i -th* $Mg^{2+}$ titration, $cm^3$;

$V_{\mathrm{x}}$ - volume of Trilon B used for blank titration, $cm^3$;

0.025 - exact concentration of Trilon B solution, $mol/dm^3$;

*k* - correction factor for bringing the concentration of the Trilon B solution to a concentration of 0.025 $mol/dm^3$;

24.32- molar mass of the equivalent of $Mg^{2+}$ in complexometric titration;

1000 - conversion factor for magnesium concentration in $mg/dm^3$;

$V_{\mathrm{pr}}$ - volume of the initial sample taken for titration, $cm^3$;

*i is* the number of single measurements of mass concentration; $i = 1, 2$.

The results of calculations using formulas (3, 4) are rounded and recorded to the third significant figure. The result of measurements of the mass concentration of calcium (magnesium) is calculated by formula (5) as the arithmetic mean of the results of two parallel single measurements $\rho_{\mathrm{Ca(Mg)1}}$, $\rho_{\mathrm{Ca(Mg)2}}$ :

$$\rho_{\mathrm{Ca(Mg)}} = \frac{\rho_{\mathrm{Ca(Mg)1}} + \rho_{\mathrm{Ca(Mg)2}}}{2}, \tag{5}$$

The relative discrepancy between which, at a confidence probability of 0.95, does not exceed the value of the operational control convergence standard, $d_{sb}$, %:

$$\frac{2\left|\rho_{Ca(Mg)1} - \rho_{Ca(Mg)2}\right|}{\rho_{Ca(Mg)1} + \rho_{Ca(Mg)2}} \leq 0{,}01 \cdot d_{зб} \tag{6}$$

For surface and treated wastewater, the values of the operational control convergence standard (confidence probability $P = 0.95$) are:

- for calcium in the range from 10 to 50 $mg/dm^3$ inclusive – 15%; in the range from over 50 to 150 $mg/dm^3$ inclusive – 5%;

- for magnesium in the range from 10 to 150 mg/dm$^3$ inclusive – 10%.

The result of calculations (5) is rounded to the second significant figure.

7.2 The result of measuring the mass concentration of calcium (magnesium) in surface and treated wastewater is taken to be the arithmetic mean of the results of two parallel single measurements of the mass concentration of calcium (magnesium) in the prepared sample. The result of measuring the mass concentration of calcium (magnesium) in surface and treated wastewater is presented in the form:

$(\rho_{\text{Ca(Mg)}} \pm \Delta_{\text{Ca(Mg)}})$, mg/dm$^3$; $P = 0.95$; $n = 2$,

where: $\pm\Delta_{\text{Ca (Mg)}}$ - limits of absolute error of the result of measurement of the mass concentration of calcium (magnesium) for the confidence probability $P = 0.95$, mg/dm$^3$;

$n$ – number of parallel measurements, $n = 2$; or

The result of measuring the mass concentration of calcium (magnesium) in surface and treated wastewater ($\rho_{\text{Ca( Mg )}}$), mg/dm$^3$, limits of total relative error ( $\pm\delta$) Ca (Mg), %; $P = 0.95$; $n = 2$.

7.3 The limits of absolute error of the measurement result of the mass concentration of calcium (magnesium) in surface and treated wastewater are calculated by the formula:

$$\Delta_{\text{Ca(Mg)}} = \frac{\delta_{\text{Ca(Mg)}} \cdot \rho_{\text{Ca(Mg)}}}{100} \tag{7}$$

The results of the calculations are rounded to the second significant figure and recorded.

7.4 The measurement results are recorded in the protocol.

## 5.2 Methodology for measuring the mass concentration of sulfates in surface and treated wastewater by the gravimetric method

*The procedure for measuring the mass concentration of sulfates in surface and treated wastewater by the gravimetric method complies with ISO 9280:1990 (EN ISO 9280), DSTU ISO 15923-1:2018 (ISO 15923-1:2013, IDT)*

### 1. Scope of application

This document establishes a methodology for measuring the mass concentration of sulfates in surface and treated wastewater using the gravimetric method (hereinafter, the gravimetric measurement).

The measurement range of mass concentrations of sulfates is:

- in surface waters from 15 to 2000 mg/dm$^3$ inclusive;
- in treated wastewater from 50 to 5000 mg/dm$^3$ inclusive.

The determination of sulfates is interfered with by suspended matter, humic substances, silicates if their presence in the sample volume taken for precipitation is more than 2.5 mg (7.5 mg/dm$^3$ in the precipitation solution), iron in an amount of more than 20 mg (100 mg/dm$^3$ in the precipitation solution), calcium in an amount of more than 100 mg (500 mg/dm$^3$ in the precipitation solution), phosphates and chromates in an amount of more than 10 mg (50 mg/dm$^3$ in the precipitation solution). Sulphites are determined simultaneously with sulfates.

### 2. Norms and characteristics of measurement errors

Error rates for measurements of sulfate mass concentration in surface and wastewater are given in Table 1.

Table 1

Measurement error rates

| Natural waters | | Wastewater | |
|---|---|---|---|
| Measurement range of mass concentration of sulfates, mg/dm$^3$ | Relative error rates, $\pm\delta$, % | Measurement range of mass concentration of sulfates, mg/dm$^3$ | Relative error rates, $\pm\delta$, % |
| from 1 to 10 inclusive | 25 | over 50 | 10 |
| over 10 up to and including 100 | 20 | | |
| over 100 | 15 | | |

The MVV ensures measurements of the mass concentration of sulfates in surface and treated wastewater with limits of total relative error ($\pm\delta$), %, the values of which at a confidence probability *of* $P = 0.95$ for the result, the average of two parallel measurements, $n = 2$, are given in Table 2.

Table 2

Bounds of the total relative error of measurements of the mass concentration of sulfates at a confidence probability of *P* = 0.95 for the result, the average of two parallel measurements, *n* = 2

| Natural waters | | Wastewater | |
|---|---|---|---|
| Measurement range of mass concentration of sulfates, mg/dm$^3$ | Boundaries of the total relative errors, ± $\delta$, % | Measurement range of mass concentration of sulfates, mg/dm$^3$ | Boundaries of the total relative errors, ± $\delta$, % |
| from 15 to 2000 inclusive | 10 | from 50 to 5000 inclusive | 10 |

## 3. Measuring instruments, auxiliary equipment, reagents and materials

3.1 Measuring instruments

3.1.1 General-purpose laboratory scales of classes 2 and 3 with a maximum weighing limit of 200 g

3.1.2 Measuring pipettes with one mark 2-2-0.5, 2-2-5

3.1.3 Measuring pipette graduated 1-2-2-5

3.1.4 Measuring cylinders 1-5, 1-100, 1-200, 1-1000

3.1.5 State standard sample of the composition of the sulfate ion solution DSZU 022.88-98 with a certified value of the mass concentration of $SO_4^{2-}$ 10 mg/cm$^3$.

3.2 Reagents

3.2.1 Distilled Water

3.2.2 Barium chloride

3.2.3 Hydrochloric acid

3.2.4 Silver nitrate

3.2.5 Calcium chloride h.

3.2.6 Ammonium molybdate

3.2.7 Potassium rhodium

3.2.8 Hydrogen peroxide

3.2.9 Methyl orange

3.2.10 Sodium hydroxide

3.3 Chemical glassware and materials

3.3.1 Heat-resistant beakers with a capacity of 500 and 1000 cm$^3$, filter funnels, glass rods, desiccators, and washing flasks.

3.3.2 Porcelain crucibles according to GOST 29225

3.3.3 Water bath of any design

3.3.4 Sand bath of any design

3.3.5 Muffle furnace of any design

3.3.6 Drying cabinet of any design

3.3.7 Ashless filters “blue ribbon”, “white ribbon” according to TC 6-09-1678.

The qualification of reagents must be no worse than “p.d.a.”, unless otherwise specified.

## 4. Principle.

The measurement of the mass concentration of sulfates is based on the formation of a sparingly soluble precipitate of barium sulfate when a solution of barium chloride is added to the sample being analysed. The precipitate of barium sulfate is separated by filtration, washed, dried and calcined at 800°C to constant mass. The mass of the precipitate of barium sulfate is measured gravimetrically.
The mass concentration of sulfates is calculated.

## 5. Preparing to take measurements

In Preparation for measuring sulfate mass concentration, the following steps are performed: preparing the muffle furnace and crucibles for operation; preparing solutions; selecting and preserving samples; selecting the volume of the aliquot for precipitation; and preparing samples.

5.1 Preparation for the operation of the muffle furnace is carried out in accordance with the requirements of the operational documentation for the stove.

5.2 Preparation of porcelain crucibles for work is carried out by calcining them to a constant mass at 750 - 800 °C.

5.3 Preparation of solutions

5.3.1 Preparation of barium chloride solution (concentration 100 g/dm$^3$)

A portion of barium chloride 2-hydrate weighing (100±1) g is dissolved in a heat-resistant beaker in 800 cm $^3$ of bidistilled Water, heated to 40 °C to facilitate dissolution. After cooling, the solution is quantitatively transferred to a measuring cylinder with a capacity of 1000 cm $^3$ according to p. 3.1.4, and the volume of the solution is brought to the mark with bidistilled Water. If turbidity appears, the solution is filtered through a "blue ribbon" filter.
The solution is suitable for use when stored in a corked glass under laboratory conditions for one year.

5.3.2 Preparation of hydrochloric acid solution (1:1)

Pour 500 cm$^3$ of concentrated hydrochloric acid (d = 1.18 g/cm$^3$) into the measuring cylinder according to item 3.1.4 and carefully add 500 cm$^3$ of bidistilled Water. Transfer the solution to a glass or polyethene container and mix. The solution is suitable for use when stored in a corked glass under laboratory conditions for one year.

5.3.3 Preparation of a 10% by mass sodium hydroxide solution

A portion of sodium hydroxide weighing (10.0±0.1) g is placed in a heat-resistant beaker, 100 $cm^3$ of bidistilled Water is added using a measuring cylinder according to item 3.1.4, and the mixture is dissolved by stirring. The solution is suitable for use when stored in a corked polyethene container under laboratory conditions for one month.

5.3.4 Preparation of a silver nitrate solution with a mass fraction of 1.7% for conducting a qualitative reaction on the chlorine ion

A portion of silver nitrate weighing (1.7±0.1) g is placed in a conical flask, 100 $cm^3$ of bidistilled Water is added using a measuring cylinder according to item 3.1.4, and the mixture is dissolved by stirring. The solution is suitable for use when stored in a corked dark glass bottle under laboratory conditions for one year.

5.3.5 Preparation of a solution of ammonium molybdate with a mass fraction of 5% for a qualitative reaction on the silicon ion

A portion of ammonium molybdate weighing (5.0±0.1) g is placed in a conical flask, 100 $cm^3$ of bidistilled Water is added using a measuring cylinder according to item 3.1.4, and the mixture is dissolved by stirring. The solution is suitable for use when stored in a corked glass under laboratory conditions for six months.

5.3.6 Preparation of a solution of potassium rhodium with a mass fraction of 20% for conducting a qualitative reaction for iron

A portion of potassium rhodium weighing (20.0±0.1) g is placed in a conical flask, 100 $cm^3$ of bidistilled Water is added using a measuring cylinder according to item 3.1.4, and the mixture is dissolved by stirring. The solution is suitable for use when stored in a corked glass container under laboratory conditions for 6 months.

5.4 Sample collection and preservation

Samples are taken in glass or polyethene containers. The volume of the water sample for determining the mass concentration of sulfates for a given MVA must be at least 2 $dm^3$. Samples are not preserved. They may be stored at room temperature. If unstable sulfur compounds are present in the Water being analysed, they are removed by boiling, or the analysis is performed immediately after sampling.

5.5 Selecting the volume of the aliquot for precipitation

The aliquot of the sample, used for precipitation, should contain no more than 50 mg of sulfates. The volume of the aliquot is chosen based on the previously determined sulfate concentration. To do this, measure 5 $cm^3$ of the water sample using a measuring cylinder, as described on p. 3.1.4, add 5 drops of hydrochloric acid according to p. 5.3.2 and with a pipette according to p. 3.1.2 0.5 $cm^3$ of the barium chloride solution according to p. 5.3.1. The nature of the turbidity or sediment approximately indicates the level of sulfate concentration in the sample. The approximate sulfate concentration, depending on the nature of the turbidity or sediment, and the recommended volumes of the sample aliquot for precipitation are given in Table 3.

Table 3

Approximate sulfate content depending on the nature of the turbidity or sediment, and recommended aliquot volumes for precipitation

| Turbidity and sediment characteristics | Mass concentration of sulfates, mg/dm$^3$ | Sample volume for analysis, cm$^3$ |
|---|---|---|
| Slight turbidity appears after 2 minutes | 15 – 25 | 1000-500 |
| Weak haze appears immediately | 25 - 100 | 500-200 |
| Strong turbidity, settles quickly | 200 - 5000 | 100-10 |

If during the qualitative reaction the barium sulfate precipitates quickly, the Water is diluted at least 5 times, and the qualitative response is repeated to clarify the sulfate content. Based on the results of this reaction, the volume of barium sulfate required for precipitation is calculated so that it contains no more than 50 mg and no less than 15 mg of sulfate.

5.6 Sample preparation

5.6.1 Water taken for analysis is filtered through a “blue ribbon” filter. Surface water samples are passed through a column filled with activated carbon at a rate of 2 cm3/min to remove humic substances, and an aliquot of the filtrate is collected for precipitation.

5.6.2 The filtrate is checked for the presence of silicic acid by means of a qualitative reaction with a solution of ammonium molybdenum oxide according to p.5.3.5. To do this, 5 cm$^3$ of a sample of Water or filtrate obtained according to p. 5.6.1 is measured with a measuring cylinder according to p.3.1.4, 5 drops of hydrochloric acid according to p. 5.3.2 are added and 3 cm$^3$ of ammonium molybdenum oxide solution according to p. 5.3.4 are added with a pipette according to p.3.1.3. The appearance of a yellow color indicates that silicon is present in the sample at a concentration of more than 7.5 mg/dm$^3$.

5.6.3 The presence of iron in the filtrate in a concentration that interferes with measurement is detected by reaction with the rhodanide ion. To do this, measure 10 cm$^3$ of the water sample with a measuring cylinder according to p.3.1.4, add 2 drops of concentrated nitric acid, 2 drops of concentrated hydrogen peroxide and then add with a pipette according to p.3.1.2 0.5 cm$^3$ of the potassium rhodanide solution according to p. 5.3.6. The appearance of a pink colour indicates that the sample contains iron at a concentration of no more than 2 mg/dm$^3$. The appearance of an orange colour suggests that the sample includes iron at a concentration of 2 mg/dm$^3$ to 10 mg/dm$^3$. The presence of red colour indicates that the sample contains iron at a concentration above 10 mg/dm$^3$. In this case, for a more accurate determination of the iron concentration, the qualitative reaction is repeated after diluting the Water a fixed number of times to obtain a pink or orange solution. The iron concentration is estimated based on the degree of dilution.

5.6.4 In the presence of only silicic acid, at a concentration exceeding 2.5 mg in the aliquot selected for precipitation, this volume of Water is evaporated to dryness in a porcelain cup at a temperature not exceeding 95 °C, having previously acidified the sample by adding 5 cm$^3$ of hydrochloric acid solution according to p.5.3.2. The dry residue is heated for 1 hour at a temperature of 105 $^0$C in a drying oven, moistened with 5 cm$^3$ of hydrochloric acid solution (1:1), heated and diluted to 50 cm$^3$ with bidistilled Water. The hot solution is filtered through a "white ribbon" filter and washed with a diluted HCl solution (1:50). If only iron is present, with a concentration exceeding 20 mg in the aliquot selected for precipitation, 1 cm$^3$ of nitric acid solution (1:1) is added to the aliquot, boiled for 10 minutes on low heat. After that, ammonia solution (1:1) is added to the alkaline reaction and the mixture is heated on a water bath for 30 minutes. The precipitated hydroxides are filtered through a “white ribbon" filter and washed with hot bidistilled Water. The filtrates are used for precipitating sulfates. In the case of the simultaneous presence of silicic acid and iron, when their content exceeds 2.5 mg and 20 mg, respectively, in the aliquot taken for precipitation, the silicic acid is first removed as indicated above. Then the iron is precipitated in the filtrate remaining after the removal of the silicic acid.

## 6. Measurement procedure

6.1 The aliquot taken from the filtrate according to p.5.6.1 and treated, if necessary, according to p.5.6.4, is transferred to a heat-resistant beaker, and the volume of the solution is brought to 200 cm$^3$ by evaporating it on a water bath or adding bidistilled Water to the solution. The solution is neutralised with hydrochloric acid (HCl) solution according to p.5.3.2 or sodium hydroxide solution according to p.5.3.3, after which 2 cm$^3$ of HCl solution according to p.3.1.2 is added with a pipette according to p.3.1.2 to bring the solution to pH 2-3.

The solution is heated to 90 $^0$C. 5 cm$^3$ of the barium chloride solution, according to p. 5.3.1, is added dropwise from a pipette according to p. 3.1.2, continuously stirring the solution with a glass rod (slow precipitation from a hot dilute acidified solution leads to the formation of larger crystals and reduces the coprecipitation of accompanying ions). The mixtures are allowed to stand until a transparent layer forms above the precipitate, then 5 drops of barium chloride solution, according to p.5.3.1, are added along the wall of the beaker. Turbidity indicates incomplete precipitation of barium sulfate. In this case, another 1 cm$^3$ of barium chloride solution, according to p.5.3.1, is added with a pipette, according to p.3.1.2, to create an excess, which decreases the solubility of the barium sulfate precipitate and contributes to the complete precipitation of sulfates.

The mixture is stirred with a stick for 1 minute, without touching the walls of the beaker, heated for 2 hours in a water or sand bath at 90 - 95 ºC, the tub is turned off, and the beaker is left on it for 8 - 10 hours for the sediment to mature. The sediment is first washed by decantation, filtering the washing liquid through a "blue ribbon" filter, quantitatively transferring the sediment to this filter, washing away the remains of the sediment from the walls of the beaker with Water and a piece of "blue ribbon" filter, which is added to the sediment on the filter. The sediment on the filter is washed with small portions of bidistilled Water at 25-40 °C, and the upper edge of the filter is washed after each portion. The filter is allowed to wait for complete liberation from the previous portion. Washing is continued until the wash water is free of chloride ions, as indicated by a qualitative reaction with silver nitrate solution (the filtrate is checked for chloride ions after 3-4 washes).

The filter with the precipitate is carefully folded so that the precipitate remains in the lower part of the filter, and the filter is then placed in a crucible that has been brought to a constant mass and dried under low heat. The temperature is slowly increased, and the filter is charred without igniting the paper, with sufficient air access (in conditions of oxygen deficiency, carbon monoxide can form, which reduces barium sulfate). After charring the filter, the crucible is calcined at 750 – 800 °C (at a higher temperature, partial thermal dissociation of barium sulfate is possible). Calcination is carried out for at least one hour until the ash turns white. The crucible is cooled in a desiccator over calcium chloride and weighed. Calcination is repeated for 20 min., the crucible is cooled in a desiccator over $CaCl_2$ and weighed again.

6.2 Weighing results are recorded to the fourth significant figure.

6.3 Calcination is considered complete when the difference between two repeated weighings is no more than 0.0008 g.

6.4 Perform two parallel measurements from two identical aliquots.

### 7. Processing the results

7.1 The result of a single measurement of the mass concentration of sulfates, $\rho$i, mg/dm$^3$, is found by the formula:

$$\rho_i = \frac{0{,}4115 \cdot m \cdot 1000}{V}, \tag{1}$$

where: 0.4115 is the coefficient for conversion from barium sulfate to sulfates;

*m* - mass of barium sulfate precipitate, mg;

1000 - conversion factor in mg/dm$^3$ ;

$V$ - volume of the initial sample taken for sulfate precipitation, $cm^3$;

$i$ - unit measurement number, $i = 1, 2$.

The results of calculations according to formula (1) are rounded to the third significant figure. The result of measurements of the mass concentration of sulfates is calculated according to formula (2) as the arithmetic mean of the results of two parallel single measurements $\rho_1$, $\rho_2$:

$$\rho = \frac{\rho_1 + \rho_2}{2}, \qquad (2)$$

The relative discrepancy between which, at a confidence probability of 0.95, does not exceed the value of the operational control convergence standard, $d_{sb}$, %.

$$\frac{2|\rho_1 - \rho_2|}{\rho_1 + \rho_2} \leq 0{,}01 \cdot d_{зб} \qquad (3)$$

For surface waters in the range from 15 to 2000 $mg/dm^3$ inclusive, the value of the operational control standard for convergence at a confidence probability *of* $P = 0.95$ is 15%. For treated wastewater in the range of 50 to 5000 $mg/dm^3$ inclusive, the standard for operational control of convergence at a confidence probability *of* $P = 0.95$ is 15%. The results of calculations according to formula (2) are rounded to the second significant figure and recorded.

7.2 The result of measuring the mass concentration of sulfates in surface and treated wastewater is taken to be the arithmetic mean of the results of two parallel single measurements, $\rho_1$ and $\rho_2$, of the mass concentration of sulfates in the prepared sample. The measurement result is presented in the form: $(\rho \pm \Delta)$, $mg/dm^3$; $P = 0.95$; $n = 2$,

where: $\pm\Delta$- limits of absolute error of the result of measurement of mass concentration of sulfates for confidence probability $P = 0.95$, $mg/dm^3$; $n$ is the number of parallel measurements, $n = 2$; or result of measurement of mass concentration of sulfates in surface and treated wastewater ($\rho$), $mg/dm^3$, limits of total relative error ( $\pm\delta$), %; $P = 0.95$; $n = 2$.

7.3 The limits of absolute error of the measurement result of the mass concentration of sulfates in surface and treated wastewater are calculated by the formula:

$$\Delta = \frac{\delta \cdot \rho}{100} \qquad (4)$$

7.4 The measurement results are recorded in the protocol.

## 5.3 Methodology for measuring the mass concentration of chlorides in surface and treated wastewater by the titrimetric method

*Methodology for measuring the mass concentration of chlorides in surface and treated wastewater - Water quality. Determination of chloride. Silver nitrate titration with chromate indicator (Mohr's method) ISO 9297:1989*

### 1. Scope of application

This document establishes a methodology for measuring the mass concentration of chlorides in surface and treated wastewater by the titrimetric method (MWT).

The measurement range of chloride mass concentrations is:

- in surface waters – from 10 to 500 mg/dm$^3$ inclusive;
- in treated wastewater - from 10 to 1500 mg/dm$^3$ inclusive.

According to this MVV, neither acidic nor alkaline solutions can be titrated. In an acidic medium, chromate is reduced to dichromate, which forms a red precipitate with silver ions, which are soluble in acids. In an alkaline solution, silver oxide and hydroxide are formed. When titrating, the solution pH should be not less than 5.0 and not more than 9.5. In the presence of ammonium salts, the solution pH should be 5.5-7.5.

Titration is hindered by ions that form precipitates with chromate ions, namely: mercury, lead, barium, and others. Phosphates hinder Titration at concentrations above 25 mg/dm$^3$, as do bromides, iodides, cyanides, sulfides, and ammonium ions, which form precipitates or complexes with silver ions. Iron interferes with Titration if its content exceeds 2.5 mg in the titration volume, because it makes it difficult to determine the endpoint due to the formation of brownish-brown iron oxides and hydroxides. Titration is hindered by high concentrations of iron(II) and sulfite ions, as they reduce chromate ions. Titration is hindered by colour and suspended substances. If there is reason to believe that sulfites, sulfides, or thiosulfates are present in the water being analysed, their interfering effect is eliminated by adding a few drops of a 30% hydrogen peroxide solution to a neutral or alkaline sample.

### 2. Norms and characteristics of measurement error

The error rates for measurements of the mass concentration of chlorides in surface and wastewater are given in Table 1.

The MVV ensures measurements of the mass concentration of chlorides in surface and treated wastewater with limits of total relative error ( $\pm\delta$), %, the value at a confidence probability *of* $P$ = 0.95 for the result, the average of two parallel measurements, $n$ = 2, is given in Table 2.

Table 1

Error rates for measurements of the mass concentration of chlorides in natural and wastewater

| Natural waters | | Wastewater | |
|---|---|---|---|
| Measurement range of mass concentration of chlorides, mg/dm$^3$ | Relative error rates, ±$\delta$, % | Measurement range of mass concentration of chlorides, mg/dm$^3$ | Relative error rates, ±$\delta$, % |
| from 1 to 10 inclusive | 25 | from 10 to 50,000 inclusive | 10 |
| over 10 up to and including 500 | 10 | over 50,000 | 5 |
| over 500 | 5 | | |

Table 2

Bounds of the total relative error of measurements of the mass concentration of chlorides in surface and treated wastewater at a confidence probability of $P$ = 0.95 for the result, $n$ =2

| Surface waters | | Treated wastewater | |
|---|---|---|---|
| Measurement range of chloride mass concentration, mg/dm$^3$ | Boundaries of the total relative errors, ± $\delta$, % | Measurement range of chloride mass concentration, mg/dm$^3$ | Bounds of the total relative error, ± $\delta$, % |
| from 10 to 500 inclusive | 10 | from 10 to 1500 inclusive | 10 |

## 3. Measuring instruments, auxiliary equipment, reagents, materials

3.1 Measuring instruments

3.1.1 General-purpose laboratory scales of class 3 with the largest weighing limit 200 g

3.1.2 Ionometer or pH meter of any modification

3.1.3 Volumetric flasks 2-500-2, 2-1000-2

3.1.4 Single-mark pipettes 2-2-10, 2-2-20, 2-2-100

3.1.5 Measuring cylinders 1-500, 1-1000

3.1.6 Burettes with a capacity of 25 cm3 with a graduation value of 0.05 cm$^3$

3.1.7 State standard sample of chloride ion solution SSS 022.8-86 with a certified mass concentration of chloride ions of 10 mg/cm$^3$.

3.2 Reagents

3.2.1 Distilled water

3.2.2 Silver nitrate

3.2.3 Potassium chromate

3.2.4 Sodium chloride, chemical grade or sodium chloride standard titer

3.2.5 Nitric acid
3.2.6 Sodium hydroxide
3.2.7 Aqueous ammonia
3.2.8 Potassium aluminium sulfate, 12-hydrate
3.2.9 Ammonium aluminium sulfate, 12-hydrate
3.3 Chemical glassware and materials
3.3.1 Conical flasks, beakers
3.3.2 Ashless filters "white ribbon", "blue ribbon" (TU 6-09-1678).

## 4. Principle

Measurements of the mass concentration of chlorides are based on the precipitation of chloride ions with a solution of silver nitrate in the form of sparingly soluble silver chloride. The solubility product of silver chloride at a temperature of 25 °C is $1.56 \cdot 10^{-10}$. A solution of potassium chromate is used as an indicator, which reacts with an excess of silver ions, forming a precipitate of silver chromate of orange-brick colour. For the formation of a precipitate of silver chromate at the equivalence point, it is necessary that the concentration of chromate in the solution be at least 0.02 mol/dm$^3$. The volume of silver nitrate used to precipitate chlorides is measured by Titration. The mass concentration of chlorides is determined by the calculation method.

## 5. Preparing to take measurements

In preparation for measurements of chloride mass concentration, the following steps are performed: preparation of solutions; determination of the exact concentration of the titrant; selection and preservation of samples; and sample preparation.

5.1 Preparation of solutions

To prepare the solutions, use double-distilled water, which is checked for the absence of chloride ions by a qualitative reaction with silver ions.

5.1.1 Preparation of a silver nitrate solution with a molar concentration of 0.02 mol/dm $^3$

A portion of silver nitrate, previously dried at 105 °C, weighing (8.4837±0.0008) g, is quantitatively transferred into a volumetric flask according to item 3.1.3 with a capacity of 1 dm $^3$, dissolved in bidistilled water, and the volume of the solution is brought to the mark with bidistilled water. The solution is suitable for use when stored in a corked glass or dark glass container with a ground stopper under laboratory conditions for 1 month.

5.1.2 Preparation of a sodium chloride solution with a molar concentration of 0.02 mol/dm$^3$.

This solution can be prepared in two ways: from a sodium chloride sample or from a standard titer.

5.1.2.1 A portion of sodium chloride, previously calcined to constant mass at 500 °C, weighing (1.1689±0.0008) g, is quantitatively transferred into a volumetric flask according to item 3.1.3 with a capacity of 1 dm$^3$, dissolved in bidistilled water and the volume of the solution is brought to the mark with bidistilled water.

5.1.2.2 The contents of the ampoule of standard titer of sodium chloride are diluted in a volumetric flask according to p.3.1.3 with a capacity of 1 dm$^3$ with bidistilled water according to the instructions, thereby obtaining a solution with a molar concentration of 0.1 mol/dm$^3$.

Using a pipette according to item 3.1.4, take 10 cm $^3$ of 0.1 mol/dm$^3$ sodium chloride solution, place it in a volumetric flask according to item 3.1.3 with a capacity of 500 cm$^{3,}$ and bring the solution to the mark with bidistilled water. The solution is suitable for use when stored in a corked glass under laboratory conditions for six months.

5.1.3 Preparation of a 10% potassium chromic acid solution

A portion of potassium chromic acid weighing (50±1) g is dissolved in a small amount of double-distilled water in a beaker, a solution of silver nitrate according to p.5.1.1 is added dropwise until a red precipitate begins to form, and left for 2 hours. After settling, the solution is filtered, transferred to a measuring cylinder with a capacity of 500 cm$^3$ according to p. 3.1.5, and the volume of the solution is brought to the mark with double-distilled water. The solution is suitable for use when stored in a dark glass container with a cork for 6 months.

5.1.4 Preparation of a nitric acid solution with a molar concentration of 0.5 mol/dm $^3$

Using a pipette according to item 3.1.4, 25 cm$^3$ of concentrated nitric acid (d=1.50 g/cm$^3$) is taken, transferred to a volumetric flask with a capacity of 1 dm$^{3,}$ and the volume of the solution is brought to the mark with bidistilled water. The solution is suitable for use when stored in a corked glass container under laboratory conditions for 6 months.

5.1.5 Preparation of sodium hydroxide solution with a molar concentration of 0.5 mol/dm$^3$

A portion of sodium hydroxide weighing (20±1) g is dissolved with stirring in a heat-resistant beaker in approximately 500 cm$^3$ of boiled, double-distilled water. After cooling, the solution is quantitatively transferred into a volumetric flask with a capacity of 1 dm$^3$ according to item 3.1.3. The solution is made up to volume with bidistilled water and mixed thoroughly. The solution is suitable for use when stored in a corked polyethene container protected from air by a calcium chloride tube in the laboratory for one month.

5.1.6 Preparation of aluminium hydroxide suspension for decolourisation of water sample

A portion of potassium aluminium sulfate dodecahydrate or ammonium aluminium sulfate dodecahydrate weighing (125±1) g is placed in a chemical beaker, 1 $dm^3$ of bidistilled water is added using a measuring cylinder according to p.3.1.5, dissolved by heating to 60 °X °C, and gradually 55 $cm^3$ of concentrated ammonia solution is added with constant stirring. After settling for 1 hour, the precipitate is transferred to a 500 $cm^3$ beaker and washed by decantation with bidistilled water until chlorides, nitrates, and nitrites are no longer detected in the washing water. The suspension is suitable for use when stored in a corked glass in the laboratory for six months.

5.2 Determining the exact concentration of silver nitrate solution according to p.5.1.1

The precise concentration of the silver nitrate solution is determined by individual portions of sodium chloride or individual aliquots of sodium chloride solution according to clause 5.1.2.

5.2.1 To determine the exact concentration of the silver nitrate solution by the method of separate portions, take at least three portions of sodium chloride, previously calcined to a constant mass at 500 °C, of different masses from 0.05 to 0,15 г. The portion of sodium chloride, weighed to the nearest 0,0008 г, is quantitatively transferred to a conical flask, washed with bidistilled water, the beaker in which it was weighed, the volume of the solution is brought to 100 $cm^3$, 1.5 $cm^3$ of potassium chromic acid solution is added according to p.5.1.3 and titrated with a solution of silver nitrate with vigorous continuous stirring until a permanent orange-brick color appears. The Titration is carried out on a white background.

Separately, perform a blank titration with 100 $cm^3$ of bidistilled water.

The exact concentration of silver nitrate solution, $C_i$, mol/$dm^3$, is calculated using the formula:

$$C_i = \frac{m_i \cdot 1000}{58{,}4 \cdot (V_i - V_x)}, \qquad (1)$$

where: $m_i$ - mass *of the i*-th portion of sodium chloride, g;

*and* - sample number, *and* = 1,..., *And* , *And* ≥3;

1000 - coefficient for conversion to mol/$dm^3$;

58.4 is the molar mass of sodium chloride.

$V_i$ - volume of silver nitrate solution used for the Titration of the *i*-th sample solution, $cm^3$;

$V_x$ - volume of silver nitrate solution used for blank Titration, $cm^3$.

5.2.2 To establish the exact concentration of the silver nitrate solution by the method of separate aliquots for Titration using pipettes according to p.3.1.4, three different aliquots of sodium chloride solution according to p.5.1.2 are taken, for example, 10, 15, and 20 $cm^3$. Each aliquot is placed in a 250 $cm^3$ conical flask, using a cylinder according to p. 3.1.5. Double-distilled water is added to 100 $cm^3$, using a pipette according to p. 3.1.4, 1.5 $cm^3$ of potassium chromic acid solution according to p. 5.1.3 is added and titrated as indicated in p.5.2.1.

The exact concentration of silver nitrate solution, $C_i$, mol/$dm^3$, is calculated using the formula:

$$C_i = \frac{C' \cdot V'}{V_i - V_x}, \qquad (2)$$

where: $C'$ - concentration of sodium chloride solution, mol/$dm^3$;

$V'$ - volume of sodium chloride solution taken for Titration, $cm^3$;

$V_{and}$ - the volume of silver nitrate solution used to titrate *the i*-th aliquot of sodium chloride solution, $cm^3$;

$V_x$ - volume of silver nitrate solution used for blank Titration, $cm^3$.

5.2.3 The correction factor, *k*, for the concentration of the silver nitrate solution is calculated by the formula:

$$k = \frac{1}{I}\sum_{i=1}^{I} k_i = \frac{1}{I}\sum_{i=1}^{I}\frac{C_i}{C^*}, \qquad (3)$$

where: $C_i$ - the exact concentration of the silver nitrate solution, mol/$dm^3$, established according to p.5.2.1 or p.5.2.2;

$C^*$ is the molar concentration of the silver nitrate solution (0.02 mol/$dm^3$).

The difference between the coefficients determined by parallel titrations should not exceed 0.001. The value of the correction factor, *k*, should not exceed the limits (1 ±0.03). If the correction factor exceeds the specified limits, the solution is diluted accordingly, or silver nitrate is added, and the correction factor is determined again. The correction factor is determined at 20 °C.

5.2.4 The titrated silver nitrate solution is stored in a dark glass beaker with a ground stopper in a dark place. Under such storage conditions, the solution is stable for a month, after which the correction factor is checked. The given molar concentration, correction factor, date, and temperature at which the correction factor was set are indicated on the beaker.

5.3 Sample collection and preservation

Samples are taken in glass containers. The volume of the sample must be at least 300 $cm^3$. Samples are not preserved. They can be stored at room temperature. If other chlorine compounds, for example, active chlorine, are present in the water being analysed, the analysis is performed immediately after sampling.

5.4 Sample preparation

5.4.1 If the water sample taken for analysis is clear but has a colour, it is removed by shaking with activated carbon, which is added at the rate of 0,5 гevery 100 cm$^3$ of the sample. The activated carbon is preliminarily checked for the absence of chlorides with bidistilled water. After decolourisation, the water sample is filtered through a "blue ribbon" filter.

If the coloured sample is cloudy, it is clarified with a suspension of aluminium hydroxide. To do this, for every 100 cm$^3$ of water, add 3 cm$^3$ of aluminium hydroxide suspension according to p., then shake the mixture until the liquid is discoloured, then filter through a "white ribbon" filter.

5.4.2 If the water sample prepared for Titration according to p.5.4.1 is alkaline or acidic, it is neutralised to pH from 5.0 to 9.5 by adding dropwise nitric acid solution according to p.5.1.4 or sodium hydroxide solution according to p.5.1.5. If ammonium ions are present in the sample in a concentration above 10 mg/dm$^3$, set the pH from 5.5 to 7.5. The pH is controlled with a pH meter.

5.4.3 Using a pipette according to p.3.1.4, take an aliquot of the sample prepared according to p.5.4.1 or p.5.4.2 with a volume of 5 to 100 cm$^3$. The chloride content in the aliquot should be in the range of 1 to 8 mg. The aliquot is placed in a conical flask and, if necessary, add bidistilled water to 100 cm$^3$ using a measuring cylinder according to p.3.1.5. At the same time, prepare a blank sample, for which 100 cm$^3$ of bidistilled water is taken using a pipette according to p.3.1.4 and placed in a conical flask.

### 6. Measurement procedure

6.1 To the sample prepared according to p.5.4.3, add 1.5 cm$^3$ of potassium chromate solution according to p.5.1.3 and titrate with silver nitrate solution according to p.5.1.1. Titration is carried out on a white background, adding the titrant in portions not exceeding 0.5 cm$^3$, and at the end of the titration, drops by constantly and thoroughly mixing the solution being titrated. Titration is complete when the colour changes from greenish-yellow to orange-brick.

6.2 Perform two parallel titrations.

6.3 Simultaneously titrate a blank sample.

6.4 Titration results are recorded to the third significant figure.

### 7. Processing the results

7.1 The result of a single measurement of the mass concentration of chlorides in the initial sample $\rho_i$, mg/dm$^3$, is calculated by the formula:

$$\rho_i = \frac{(V - V_X) \cdot 0{,}02 \cdot k \cdot 35{,}453 \cdot 1000}{V_{пр}}, \quad (4)$$

where: V- the volume of silver nitrate solution used for the Titration of the sample, cm$^3$;

$V_x$ - volume of silver nitrate solution used for blank Titration, cm$^3$;

0.02 - the specified concentration of silver nitrate, mol/dm$^3$;

k- correction factor for reducing the concentration of silver nitrate to a concentration of 0.02 mol/dm$^3$;

35.453 is the molar mass of the chloride ion.

1000 - coefficient for converting concentration into mg/dm$^3$;

$V_{pr}$ - volume of the initial sample taken for Titration, cm$^3$;

i – number of the unit measurement, i = 1, 2.

The results of calculations according to formula (4) are rounded and recorded to the third significant figure.

The result of measurements of the mass concentration of chlorides, $\rho$, is calculated by formula (5) as the arithmetic mean of the results of two parallel single measurements $\rho_1$, $\rho_2$ :

$$\rho = \frac{\rho_1 + \rho_2}{2}, \tag{5}$$

The relative discrepancy between which, at a confidence probability of 0.95, does not exceed the value of the operational control convergence standard, $d_{sb}$, %.

$$\frac{2|\rho_1 - \rho_2|}{\rho_1 + \rho_2} \le 0{,}01 \cdot d_{зб} \tag{6}$$

The results of calculations using formula (5) are rounded to the second significant figure and recorded.

7.2 The result of measuring the mass concentration of chlorides in surface and treated wastewater is taken as the arithmetic mean of the results of two parallel single measurements of the mass concentration of chlorides in the prepared sample. The measurement result is presented in the form: $(\rho \pm \Delta)$, mg/dm$^3$; $P$ = 0.95; $n$ = 2,

where: $\pm\Delta$- limits of absolute error of the measurement result for the confidence probability $P$ = 0.95, mg/dm$^3$; $n$ - number of parallel measurements, $n$ = 2;
or the result of measuring the mass concentration of chlorides in surface and treated wastewater ($\rho$), mg/dm$^3$, the limit of the total relative error:

$(\pm\delta)$ , %; $P$ = 0.95; $n$ = 2.

7.3 The limits of absolute error of the measurement result of the mass concentration of chlorides in surface and treated wastewater are calculated by the formula:

$$\Delta = \frac{\delta \cdot \rho}{100} \tag{7}$$

The results of the calculations are rounded to the second significant figure and recorded.

7.4 The measurement results are recorded in the protocol.

## 5.4 Methodology for measuring the mass concentration of total chromium, chromium (VI), chromium (III) in surface, groundwater and return waters

*The methodology is based on the international standard ISO 18412:2005 Water quality — Determination of chromium ( VI ) — Photometric method for weakly contaminated water (Water quality - determination of chromium ( VI ) - photometric method for slightly polluted waters) MVV No. 081/12-0114-03, p. 8.6.2.*

### 1. Scope of application

The methodology for measuring (hereinafter referred to as MVM) mass concentrations of total chromium, chromium (VI), and chromium (III) in surface, groundwater, and return waters uses the extraction-photocolorimetric method.

The measurement range of the mass concentration of total chromium, chromium (VI), chromium (III) in water is from 0.010 mg/dm$^3$ to 0.200 mg/dm$^3$ inclusive when measured without prior dilution. or concentration of the initial sample. When measuring using the dilution operation, the upper limit of the measurement range of mass concentrations of total chromium, chromium (VI), and chromium (III) is 2.0 mg/dm$^3$. When measuring using the extraction concentration operation, the lower limit of the mass concentration measurement range for total chromium, chromium (VI), and chromium (III) is 0.001 mg/dm$^3$.

The determination of the mass concentration of chromium (VI) is interfered with by iron (III). To eliminate this interference, orthophosphoric acid and a sodium fluoride solution are added to the sample.

### 2. Norms and characteristics of measurement error

Error rates for measurements of the mass concentrations of chromium (VI) and chromium (III) in natural and wastewater samples are presented in Tables 1 and 2, respectively.

Table 1

Error rates for chromium (VI) measurements

| Natural waters | | Wastewater | |
|---|---|---|---|
| Measurement range of mass concentration of chromium (VI), mg/dm$^3$ | Relative error rates, $\pm\delta$, % | Measurement range of mass concentration of chromium (VI), mg/dm$^3$ | Relative error rates, $\pm\delta$, % |
| from 0.0005 to 0.005 inclusive | -65 +100 | from 0.005 to 0.01 inclusive | -65 +100 |
| over 0.005 to 0.1 inclusive | 50 | over 0.01 to 1.0 inclusive | 50 |
| more than 0.1 | 25 | over 1.0 | 25 |

MVV provides measurements of the mass concentration of total chromium, chromium (VI), chromium (III) in surface, groundwater and return waters with limits of total relative error, ( $\pm\delta$)%, the values of which, at a confidence probability of P = 0.95 for the result, the average of two parallel measurements, n = 2, do not exceed:

- for the range from 0.001 to 0.010 mg/dm $^3$ inclusive – 35%;
- for the range from 0.010 to 2.0 mg/dm $^3$ inclusive – 23%.

Table 2

Error rates for chromium (III) measurements

| Natural waters | | Wastewater | |
|---|---|---|---|
| Measurement range of mass concentration of chromium (III), mg/dm$^3$ | Relative error rates, $\pm\delta$, % | Measurement range of mass concentration of chromium (III), mg/dm$^3$ | Relative error rates, $\pm\delta$, % |
| from 0.0005 to 0.005 inclusive<br>over 0.005 to 0.01 inclusive<br>over 0.01 | -65, +100<br>50<br>25 | — | — |

## 3. Measuring instruments, auxiliary equipment, reagents and materials

3.1 Measuring instruments

3.1.1 Photoelectrocolorimeter equipped with cuvettes

3.1.2 General laboratory scales, class 2, with a weighing limit of 200 g

3.1.3 Volumetric flasks 2-50-2, 2-100-2, 2-200-2, 2-1000-2

3.1.4 Single Mark Pipettes 2-2-1, 2-2-2, 2-2-5, 2-2-10, 2-2-20, 2-2-25

3.1.5 Graduated pipettes 3-2-2-1, 3-2-2-5, 3-2-2-10

3.1.6 Cylinders 1-25, 1-50, 1-100, 1-250, 1-500

3.1.7 State standard sample of the composition of the solution of chromium (VI) ions DSZU 022.84-98 with a certified concentration value of 1.0mg/cm$^3$.

3.2 Reagents

3.2.1 Diphenylcarbazide

3.2.2 Trichloroacetic acid "h"

3.2.3 Sodium fluoride

3.2.4 Isoamyl alcohol

3.2.5 Distilled water

3.2.6 Ethyl alcohol

3.2.7 Sulfuric acid

3.2.8 Orthophosphoric acid

3.2.9 Ammonium persulfuric acid

3.2.10 Concentrated nitric acid ( d = 1.39-1.40 g/cm$^3$ )

3.2.11 Acetic acid

3.3 Materials and equipment

3.3.1 Electric hob with closed spiral

3.3.2 Filter paper “white tape”

3.4 Laboratory glassware

3.4.1 Funnels

3.4.2 Flasks Kn-2-100-34, Kn-2-250-34, Kn-2-500-34, Kn-2-1000-42

3.4.3 Funnels B-36-80

The purity of the reagents must be no worse than “p.d.a."

## 4. Principle

The measurement of the mass concentration of chromium (VI) above 0.01 mg/dm$^3$ is based on the formation of a colored compound during the reaction of chromium (VI) with diphenylcarbazide in an acidic medium. The mass concentration of total chromium is determined after oxidation of chromium (III) with ammonium persulfuric acid in an acidic medium to chromium (VI). The mass concentration of chromium (III) is determined by the difference between the found mass concentrations of total chromium and chromium (VI).

The method for measuring the mass concentration of chromium (VI) below 0.010 mg/dm$^3$ is based on the formation of a coloured compound during the reaction of chromium (VI) with diphenylcarbazide, followed by extraction of the complex with trichloroacetic acid in isoamyl alcohol.

The optical density of the coloured solution is measured by photometric colourimetry. The optimal wavelength for measuring optical density is 540 nm. The mass concentration of chromium (VI) in an aliquot of the sample is determined by the calibration characteristic.

The mass concentration of chromium (VI) in the initial sample before oxidation and the mass concentration of total chromium in the initial sample after oxidation are determined by the calculation method.

## 5. Preparing to take measurements

When preparing to measure the mass concentration of chromium, the following steps are performed: preparing the photoelectrocolorimeter for operation; preparing solutions; preparing calibration solutions; constructing a calibration characteristic; sampling; and sample preparation.

5.1 Preparation of the photoelectrocolorimeter for measurements is carried out in accordance with the requirements of the operational documentation for the device.

5.2 Preparation of solutions

5.2.1 Preparation of a 3% by mass sodium fluoride solution

A sample of sodium fluoride weighing (3.0 ± 0.1) g is added to a volumetric flask of 100 cm3 capacity as described in 3.1.3. The volume is made up to the mark with distilled water and immediately transferred to a polyethene bottle.

The solution is suitable for use when stored in a corked polyethene bottle in the laborastory for 1 month.

5.2.2 Preparation of a 20% trichloroacetic acid solution

A portion of trichloroacetic acid weighing (20.0 ± 0.1) g is placed ±in a conical flask with a capacity of 250 cm$^3$, and 80 cm$^3$ of distilled water is added, and the mixture is mixed thoroughly until complete dissolution. The solution is suitable for use when stored in a corked glass in the laboratory for 1 month.

5.2.3 Preparation of a 1% mass fraction of diphenylcarbazide solution

In a volumetric flask according to 3.1.3 with a capacity of 50 $cm^3$, a portion of diphenylcarbazide weighing (0.50 ±± 0.01) g is added, 5 $cm^3$ of acetic acid is added in the cold, and, after dissolution, the volume is brought to the mark with ethyl alcohol.

The solution is suitable for use when stored in a corked dark glass bottle in a cool place for 1 month. If a reddish colour appears, the solution must be replaced with a freshly prepared one.

5.2.4 Preparation of a 1.0% by mass ammonium persulfate solution

Into a volumetric flask of 100 $cm^3$ capacity according to 3.1.3, a portion of ammonium persulphate weighing (1.0 ± 0.1) g is added, and the volume is made up to the mark with distilled water. The solution cannot be stored and must be used immediately after preparation.

5.2.5 Preparation of sulfuric acid solution (1:1).

Using the cylinder according to 3.1.6, 100 $cm^3$ of distilled water is added to a conical flask made of heat-resistant glass with a capacity of 500 $cm^3$, then 100 $cm^3$ of concentrated sulfuric acid (d) is added using the same cylinder (d = 1.96 $g/cm^3$). The solution is stirred and cooled to room temperature.

The solution is suitable for use when stored in a corked glass in the laboratory for 1 year.

5.2.6 Preparation of a sulfuric acid solution with a molar concentration *of* ($H_2SO_4$) = 0.5 $mol/dm^3$.

Into a volumetric flask of 1000 $cm^3$ capacity according to 3.1.3, 500 $cm^3$ of distilled water are introduced using a cylinder according to 3.1.6 28 $cm^3$ of concentrated sulfuric acid (d = 1.96 $g/cm^3$) are added using a cylinder according to 3.1.6, and the volume is made up to the mark with distilled water. The solution is suitable for use when stored in a corked glass in the laboratory for 1 month.

5 .2.7 Preparation of a nitric acid solution with a mass fraction of 50 %

Using the cylinder according to 3.1.6, 500 $cm^3$ of distilled water are added to a conical flask made of heat-resistant glass with a capacity of 1000 $cm^3$, then 350 $cm^3$ of concentrated nitric acid are added using the same cylinder. The solution is stirred and cooled to room temperature. The solution is suitable for use when stored in a corked glass in the laboratory for 1 year.

5.3 Preparation of solutions for constructing a calibration curve

5.3.1 Preparation of the initial solution with a mass concentration of chromium (VI) 100 $mg/dm^3$

Using a pipette, according to 3.1.4, take 5 $cm^3$ of SSS 022. 84 -98, transfer it to a volumetric flask with a capacity of 50 $cm^3$ according to 3.1.3, and bring the volume to the mark with distilled water. The solution is suitable for use when stored in a corked glass container under laboratory conditions for 3 months.

5.3.2 Preparation of the initial solution with a mass concentration of chromium (VI) 10 $mg/dm^3$

Using a pipette according to 3.1.4, take 10 $cm^3$ of the solution with a chromium (VI) mass concentration of 100 $mg/dm^3$ according to 5.3.1, transfer it to a volumetric flask according to 3.1.3 with a capacity of 100 $cm^3$, and bring the volume to the mark with distilled water. The solution is suitable for use when stored in a corked glass for 1 week.

5.3.3 Preparation of a working solution with a mass concentration of chromium (VI) of 1.0 $mg/dm^3$

Using a pipette according to 3.1.4, take 10 $cm^3$ of the original solution according to 5.3.2, transfer it to a volumetric flask of capacity 100 $cm^3$ according to 3.1.3, and bring the volume to the mark with distilled water. The solution is suitable for use when stored in a corked glass under laboratory conditions for 12 hours.

5 .3.4 Preparation of a working solution with a mass concentration of chromium (VI) of 0.10 $mg/dm^3$

Using a pipette according to 3.1.4, take 1 $cm^3$ of the original solution according to 8.3.2, transfer it to a volumetric flask of capacity 100 $cm^3$ according to 3.1.3, and make up to the mark with distilled water. The solution is suitable for use when stored in a stoppered glass under laboratory conditions for twelve hours.

5 .3.5 Preparation of solutions for constructing a calibration characteristic in the range of mass concentration of chromium (VI) from 0.01 to 0.20 $mg/dm^3$ inclusive.

Into a volumetric flask according to 3.1.3 with a capacity of 100 $cm^3$, pipette the required volume of the working solution with a mass concentration of chromium (VI) ions of 1.0 $mg/dm^3$ according to 5.3.3, add 1 $cm^3$ of sulfuric acid solution according to 5.2.5, 0.3 $cm^3$ of concentrated orthophosphoric acid, bring the volume to the mark with distilled water, mix thoroughly. Then add 2 $cm^3$ of diphenylcarbazide solution as described in 5.2.3 and mix thoroughly again.

Information on the required pipettes, volumes of working solution according to 5.3.3 for preparing solutions for constructing the calibration curve, and the corresponding mass concentrations of chromium (VI) in the solutions are given in Table 3.

For each mass concentration, a series of at least 5 calibration solutions is prepared. Calibration solutions are ready on the day of use. At the same time, a blank sample is prepared in distilled water, with all reagents added.

5.3.6 Preparation of solutions for constructing a calibration characteristic in the range of mass concentration of chromium (VI) from 0.001 to 0.010 mg/dm$^3$ inclusive.

Into a volumetric flask according to 3.1.3 with a capacity of 200 cm$^3$, use a pipette to measure the required volume of the working solution with a mass concentration of chromium (VI) ions of 0.10 mg/dm$^3$ according to 5.3.4. Make up the volume to the mark with distilled water and mix.

Table 3

Information on solutions for constructing a calibration characteristic in the range of mass concentration of chromium (VI) from 0.01 to 0.20 mg/dm$^3$ inclusive

| Solution No. for constructing the calibration characteristic | Nominal capacity of the pipette according to 3.1.4, cm$^3$ | Volume of working solution according to 8.3.3, cm$^3$ | Mass concentration of chromium (VI) in the solution for constructing the calibration characteristic, mg/dm$^3$ |
|---|---|---|---|
| 1 | 1 | 1.0 | 0.01 |
| 2 | 2 | 2.0 | 0.02 |
| 3 | 5 | 5.0 | 0.05 |
| 4 | 10 | 10.0 | 0.10 |
| 5 | 20 | 20.0 | 0.20 |

The contents of the volumetric flasks are successively transferred into 500 cm$^3$ separating funnels, a portion of sodium chloride weighing (10.0 ± 0.5) g is added. After its dissolution with a pipette according to 3.1.5, 4 cm$^3$ of sodium fluoride solution according to 5.2.1, 10 cm$^3$ of trichloroacetic acid solution according to 5.2.2, 2 cm$^3$ of diphenylcarbazide solution according to 5.2.3 are added, and the mixture is thoroughly mixed. After 15 minutes, 25 cm$^3$ of isoamyl alcohol is added, and the mixture is shaken for 1 minute. After the mixture has separated, the lower layer is decanted and discarded. Then the organic phase is decanted into a cuvette and filtered through a “white ribbon” filter moistened with isoamyl alcohol.

Information on the required pipettes, volumes of working solution according to 5.3.4 for preparing solutions for constructing the calibration curve, and the corresponding mass concentrations of chromium (VI) in the solutions are given in Table 4.

For each mass concentration value, a series of five calibration solutions is prepared. The calibration solutions are ready on the day of use.

At the same time, a blank sample is prepared: 200 cm$^3$ of distilled water is added to a separating funnel with a capacity of 500 cm$^3$ using a cylinder with a capacity of 200 cm$^3$, according to 3.1.6, and all the operations provided for in this paragraph are then performed.

Table 4

Information on solutions for constructing a calibration characteristic in the range of mass concentration of chromium (VI) from 0.001 to 0.010 mg/dm $^3$ inclusive

| Solution No. for constructing the calibration characteristic | Nominal capacity of the pipette according to 3.1.4, 3.1.5, cm$^3$ | The volume of the working solution according to 8.3.4, cm$^3$ | Mass concentration of chromium (VI) in the solution for constructing the calibration characteristic, mg/dm$^3$ |
|---|---|---|---|
| 1 | 2 | 2.0 | 0.0010 |
| 2 | 5 | 4.0 | 0.0020 |
| 3 | 10 | 7.0 | 0.0035 |
| 4 | 10 | 10.0 | 0.0050 |
| 5 | 20 | 20.0 | 0.0100 |

### 5.4 Construction of the calibration characteristic

5.4.1 To establish the calibration characteristic in the range of mass concentration of chromium (VI) from 0.01 to 0.20 mg/dm$^3$ inclusive, measure the optical density of the solutions according to 5.3.5 (reference solution - distilled water) using a photoelectrocolorimeter according to 3.1.1, prepared according to 5.1. Measurements are performed at 540 nm using a cuvette with a 50 mm working length. The optical density of the blank sample is subtracted from that of the solutions.

The parameters of the linear calibration characteristic are calculated using the least-squares method: optical density, D, and A are the mass concentration of chromium (VI) and the calibration solution density, respectively.

5.4.2 To establish the calibration characteristic in the range of mass concentration of chromium (VI) from 0.001 to 0.010 mg/dm$^3$ inclusive, measure the optical density of the extracts according to 5.3.6 (reference solution - isoamyl alcohol) using a photoelectrocolorimeter.

Measurements are performed at 540 nm using a cuvette with a 50 mm working length. The optical density of the blank sample is subtracted from that of the extracts.

The parameters of the linear calibration characteristic are calculated using the least squares method: optical density, $D_\lambda$, B – mass concentration of chromium (VI), $\rho_{\text{grB}}$, in the calibration solution.

### 5.5 Sample collection and preservation

Surface water sampling is carried out in accordance with DSTU ISO 5667-6; sample storage – according to DSTU ISO 5667-3.

The determination is carried out no later than 2 hours after sampling. The water sample is filtered through a “white tape” filter. The volume of the water sample for measuring the mass concentration of chromium must be at least 2000 cm$^3$.

5.6 Sample preparation

5.6.1 The water sample is filtered through a “white ribbon” filter.

5.6.2 Sample preparation for the determination of chromium in the concentration range from 0.01 to 0.20 mg/dm$^3$ inclusive.

5.6.2.1 Sample preparation for the determination of total chromium.

To 100 cm$^3$ of the filtered sample, add 0.3 cm$^3$ of the sulfuric acid solution according to 5.2.6, 10 cm$^3$ of the ammonium persulfuric acid solution according to 5.2.1 using appropriate pipettes according to 3.1.4 or 3.1.5 and boil for 30 minutes. The solution is cooled, quantitatively transferred to a 100 cm$^3$ volumetric flask, and 1 cm$^3$ of the sulfuric acid solution is added according to 5.2.5, 0.3 cm$^3$ of concentrated orthophosphoric acid, and the volume is made up to the mark with distilled water. Mix thoroughly. Add 2 cm$^3$ of the diphenylcarbazide solution according to 5.2.3 and mix thoroughly again. At the same time, a colour sample is prepared, performing all operations with a filtered sample without adding diphenylcarbazide solution and a blank sample in distilled water with the addition of all reagents.

5.6.2.2 Sample preparation for chromium ( VI ) determination.

In a volumetric flask with a capacity of 100 cm$^3$, 30 cm$^3$ of the filtered sample are introduced with a cylinder, 1 cm$^3$ of the sulfuric acid solution according to 5.2.5, 0.3 cm$^3$ of concentrated orthophosphoric acid are added using appropriate pipettes according to 3.1.4 or 3.1.5, and the volume is brought to the mark with the filtered sample, mixed thoroughly. Then 2 cm$^3$ of the diphenylcarbazide solution according to 5.2.3 is added and mixed thoroughly again.

At the same time, a sample is prepared to take into account colour, performing all operations with a filtered sample without adding diphenylcarbazide solution, and a blank sample in distilled water with the addition of all reagents.

5.6.3 Sample preparation for the determination of chromium in the concentration range from 0.001 to 0.010 mg/dm$^3$ inclusive.

5.6.3.1 Sample preparation for the determination of total chromium.

To 200 cm$^3$ of the filtered sample, add 0.6 cm$^3$ of the sulfuric acid solution according to 5.2.6, 10 cm$^3$ of the ammonium persulfuric acid solution according to 5.2.1 and boil for 30 minutes. The solution is cooled and transferred to a 200 cm$^3$ volumetric flask, then made up to the mark with distilled water.

Transfer the contents of the volumetric flask into a 500 cm$^3$ separating funnel, add a portion of sodium chloride weighing (10.0 ± 0.5) g, and after dissolving it, add

4 cm$^3$ of sodium fluoride solution according to 5.2.1, 10 cm$^3$ of trichloroacetic acid solution according to 5.2.2, 2 cm$^3$ of diphenylcarbazide solution according to 5.2.3, using appropriate pipettes according to 3.1.4 or 3.1.5, and mix thoroughly. After 15 minutes, add 25 cm$^3$ of isoamyl alcohol using a cylinder according to 3.1.6, and shake for 1 minute.

After the mixture has separated, the lower layer is decanted and discarded. The organic phase is then decanted into a cuvette and filtered through a "white ribbon" filter moistened with isoamyl alcohol.

At the same time, a sample is prepared to account for colour, performing all operations with a filtered sample without adding diphenylcarbazide solution, and a blank sample in distilled water with all reagents added.

5.6.3.2 Sample preparation for chromium ( VI ) determination.

In a separating funnel with a capacity of 500 cm$^3$, add 200 cm$^3$ of the filtered sample using a volumetric flask according to 3.1.3, add a portion of sodium chloride weighing (10.0 ± 0.5) g and after dissolving it with appropriate pipettes according to 3.1.4 or 3.1.5, add 4 cm$^3$ of sodium fluoride solution according to 5.2.1, 10 cm$^3$ of trichloroacetic acid solution according to 5.2.2, 2 cm$^3$ of diphenylcarbazide solution according to 5.2.3, mix thoroughly. After 15 minutes, add 25 cm$^3$ of isoamyl alcohol using a cylinder according to 3.1.6 and shake for 1 minute.

After the mixture has separated, the lower layer is drained and discarded first. Then the organic phase is drained into a cuvette and filtered through funnels with pre-wetted "white ribbon" filters.

At the same time, a sample is prepared to account for colour, performing all operations with a filtered sample without adding diphenylcarbazide solution, and a blank sample with distilled water and the addition of all reagents.

5.6.4 Sample preparation for the determination of chromium in the concentration range of over 0.2 to 2.0 mg/dm$^3$ inclusive.

An aliquot of the filtered sample with a volume of 20 cm$^3$ is taken with a pipette according to 3.1.4 into a volumetric flask with a capacity of 200 cm$^3$ according to 3.1.3, and the volume is brought to the mark with distilled water. Then, the sample preparation is carried out according to 5.6.2.1 (5.6.2.2).

## 6. Measurement procedure

6.1 To determine chromium in the concentration range from 0.01 to 0.20 mg/dm$^3$ inclusive, measure the optical density of the solutions obtained in 5.6.2 using a photoelectrocolorimeter prepared in 5.1 at a wavelength of 540 nm. The reference solution is distilled water. Use cells with a working length of 50 mm. From the obtained optical density value, subtract the optical density of the blank sample and the optical density of the sample to account for colour.

6.2 To determine chromium in the concentration range from 0.001 to 0.010 mg/dm $^3$ inclusive, measure the optical density of the extracts obtained in 5.6.3 using a photoelectrocolorimeter prepared in 5.1 at a wavelength of 540 nm. The reference solution is isoamyl alcohol. Use cells with a working length of 50 mm. From the obtained optical density, subtract the optical density of the blank sample and the optical density of the sample to account for colour.

6.3 The results of optical density measurements are recorded to the third significant figure.

**7. Processing the results**

Measurement results are processed as follows.

7.1 The result of a single measurement of the mass concentration of total chromium and chromium (VI) in the initial sample in the range of mass concentrations from 0.010 to 0.200 mg/dm$^3$ inclusive, $\rho_,$ is found by the formula:

$$\rho_\text{i} = \rho_\text{грA} \qquad (1)$$

where: $\rho_{gr\ \text{A}}$ – mass concentration of chromium, found based on the optical density value using the calibration characteristic parameters previously calculated in accordance with 5.4.1, mg/dm$^3$; i – number of the unit measurement, i = 1, 2.

The results of calculations according to formula (1) are rounded to the third significant figure and recorded.

The result of measurements of the mass concentration of total chromium and chromium (VI) is calculated by formula (2) as the arithmetic mean of the results of two parallel single measurements $\rho_1$, $\rho_2$

$$\rho = \frac{\rho_1 + \rho_2}{2} \qquad (2)$$

The relative discrepancy between which, at a confidence probability of P = 0.95, does not exceed the value of the operational control standard of convergence, $d_\text{sb}$, %:

$$\frac{2\left|\rho_1 - \rho_2\right|}{\rho_1 + \rho_2} \le 0{,}01 \cdot d_\text{зб} \qquad (3)$$

For mass concentrations of total chromium and chromium (VI) from 0.010 to 0.200 mg/dm$^3$ inclusive, the value of the standard for operational control of convergence at a confidence probability of P = 0.95 is 40%. The results of calculations according to formula (2) are rounded to the second significant figure and recorded.

The mass concentration of chromium (III) is determined by the difference between the found mass concentrations of total chromium and chromium (VI).

7.2 The result of a single measurement of the mass concentration of total chromium and chromium (VI) in the initial sample in the range of mass concentrations from 0.20 to 2.00 mg/dm$^3$ inclusive, $\rho$, is found by the formula:

$$\rho_\text{i} = \frac{\rho_\text{грА} \cdot 200}{V} \qquad (4)$$

where: $\rho$ $_\text{grA}$ – mass concentration of chromium, found based on the optical density value using the calibration characteristic parameters previously calculated in accordance with 5.4.1, mg/dm$^3$;

200 – volume of the volumetric flask used to prepare an aliquot of the sample during its dilution, cm$^3$;

$V$ – volume of the sample aliquot taken for dilution, cm$^3$; and – number of the single measurement, i = 1, 2.

The results of calculations using formula (4) are rounded to the third significant figure and recorded.

The result of measurements of the mass concentration of total chromium and chromium (VI) is calculated by formula (2) as the arithmetic mean of the results of two parallel single measurements $\rho$ $_1$, $\rho$ $_2$, the relative difference between which, calculated by formula (3), with a confidence probability of P = 0.95 does not exceed the value of the operational control convergence standard, $d$ $_\text{sb}$, %.

For mass concentrations of total chromium and chromium (VI) from 0.10 to 2.00 mg/dm$^3$ inclusive, the value of the standard for operational control of convergence at a confidence probability of P = 0.95 is 40%.

The result of the calculations using formula (2) is rounded to the second significant figure and recorded. The mass concentration of chromium (III) is determined by the difference between the found mass concentrations of total chromium and chromium (VI).

The result of a single measurement of the mass concentration of total chromium and chromium ( VI ) in the initial sample in the range of mass concentrations from 0.001 to 0.010 mg/dm$^3$ inclusive, $\rho$ and, is found by the formula:

$$\rho_\text{i} = \rho_\text{грБ} \qquad (5)$$

where: $\rho_\text{grB}$ – mass concentration of chromium, found based on the optical density value using the calibration characteristic parameters previously calculated in 5.4.2, mg/dm$^3$; i – number of single measurement 1, 2.

The result of calculations according to formula (5) is rounded to the third significant figure. The result of measurements of the mass concentration of total chromium and chromium (VI) is calculated according to formula (2) as the arithmetic mean of the results of two parallel measurements $\rho_1$, $\rho_2$, the relative discrepancy calculated according to formula (3), with a confidence probability of P=0.95, does not exceed the convergence $d_\text{sb}$, %.

### 5.5 Methodology for measuring the mass concentration of manganese in Surface, groundwater, and return waters by the photocolorimetric method

*Methodology for measuring the mass concentration of manganese, the photocolorimetric method with ammonium persulfate (MBB No. 081/12-0107-03 Surface, groundwater and return waters) complies with ISO / TS 15923-2:2017 (automatic photometric analysis) or ISO 6333:1986 (classical photometric determination method)*

#### 1. Scope of application

This document establishes a methodology for measuring the mass concentration of manganese in Surface, groundwater and return waters by the photocolorimetric method (hereinafter referred to as the photocolorimetric method).

The range of measured mass concentrations of manganese in Surface, groundwater, and return waters is 0.05 to 1.0 mg/dm$^3$, inclusive, when measured without prior dilution or concentration of the initial sample. When measured using dilution and concentration operations, the range of measured mass concentrations of manganese is 0.005-20 mg/dm$^3$. When concentrated, it can be used for waters with a chloride content of no more than 500 mg/dm$^3$ and a total salt content of no more than 1000 mg/dm$^3$.

The measurement of manganese is interfered with by molybdenum, tungsten, and titanium. Chromium (VI) interferes with its colour; in its presence, the measurement of the optical density for manganese is carried out at a wavelength of $\lambda = 535$ nm.

The interfering effect of iron (III) colour is eliminated by adding orthophosphoric acid. The interfering effect of other ions can be eliminated by reducing permanganate ions with a solution of sodium nitrite. The measurement of manganese is interfered with by chlorides, which are removed by evaporation with sulfuric acid. The interfering effect of organic substances is eliminated by boiling the sample with nitric acid.

#### 2. Norms and characteristics of measurement error

The error rates for measurements of the mass concentration of manganese in natural and return waters are given in Table 1.

The MVV ensures measurements of the mass concentration of manganese in Surface, groundwater and return waters with limits of total relative error ( $\pm\delta$)%, the values of which, at a confidence probability of $P = 0.95$ for the result, the average of two parallel measurements, $n = 2$, do not exceed:

for the range from 0.005 to 0.05 mg/dm$^3$ inclusive – 50%;

for the range of over 0.05 to 0.5 mg/dm$^3$ inclusive – 25%;

for the range from 0.5 to 20 mg/dm$^3$ inclusive – 10%.

Table 1

Measurement error rates

| Natural | | Return waters | |
|---|---|---|---|
| Measurement range of manganese mass concentration, mg/dm$^3$ | Relative error rates, ±δ, % | Measurement range of mass concentration of manganese, mg/dm$^3$ | Relative error rates, ±δ, % |
| from 0.005 to 0.05 inclusive | 50 | from 0.01 to 0.1 inclusive | 50 |
| more than 0.05 | 25 | more than 0.1 | 25 |

## 3. Measuring instruments, reagents and materials

3.1 Measuring instruments

3.1.1 Photoelectrocolorimeter equipped with cuvettes with a working length of 50 and 100 mm.

3.1.2 General-purpose laboratory scales, class 2, with a maximum weighing limit of 200 g

3.1.3 Volumetric flasks 2-50-2, 2-100-2, 2-250-2, 2-500-2

3.1.4 Single-mark pipettes 2-2-0.5, 2-2-1, 2-2-5, 2-2-10, 2-2-25

3.1.5 Pipettes graduated 1-2-2-2, 1-2-2-5, 1-2-2-10

3.1.6 Cylinders 1-50, 1-100, 1-250, 1-1000

3.1.7 State standard sample of manganese solution composition SSS 022.46-96, certified value of manganese mass concentration 10 mg/cm$^3$.

3.2 Reagents

3.2.1 Ammonium persulfuric acid

3.2.2 Orthophosphoric acid 85%

3.2.3 Distilled water

3.2.4 Silver nitrate

3.2.5 Sodium nitrite

3.2.6 Nitric acid

3.2.7 Sulfuric acid

3.3 Laboratory glassware and materials

3.3.1 Electric hob with closed spiral

3.3.2 “Blue Ribbon” Ashless Filters

3.3.3 Glasses B-1-100, B-1-1000

3.3.4 Flask K-1-2000-29/32

3.3.5 Laboratory funnels

3.3.6 Watch glass

The purity of the reagents should be no worse than “p.a.”, unless otherwise specified.

## 4. Principle

The measurement method is based on the oxidation of manganese ( II) to the permanganate ion. Oxidation is carried out in a nitric acid medium using ammonium persulfate as the oxidant, with silver ions as a catalyst. The solution acquires a pink colour.

The photocolorimetric method measures the optical density of a colored solution. The optimal wavelength for measuring optical density is λ. = 540 nm.

The calibration characteristic determines the mass concentration of manganese in an aliquot of the sample. The mass concentration of manganese in the original sample is determined by the calculation method.

## 5. Preparing to take measurements

When preparing to measure the mass concentration of manganese in water, the following steps are performed: preparing the photoelectrocolorimeter for operation; preparing solutions; preparing calibration solutions; constructing a calibration characteristic; selecting and preserving samples; and preparing samples.

5.1 Preparing the photoelectrocolorimeter for measurements

Preparation of the photoelectrocolorimeter for measurements is carried out in accordance with the device's operating documentation.

5.2 Preparation of solutions

5.2.1 Preparation of a silver nitrate solution with a molar concentration of 0.1 mol/d $m^3$

A portion of silver nitrate weighing (17.0±0.1) g is dissolved in 1 $dm^3$ of water. distilled. The solution is suitable for use when stored in a corked dark glass bottle under laboratory conditions for 1 month.

5.2.2 Preparation of distilled water that does not contain organic substances

3 of distilled water in a round-bottomed flask, add 20 $cm^3$ of concentrated nitric acid using a cylinder according to 3.1.6, a portion of ammonium persulphate weighing (2.0 ± 0.1) g, and 4 $cm^3$ of silver nitrate solution according to 5.2.1 using a pipette according to 3.1.5. Boil for 10 minutes. Cool the solution. The solution is suitable for use when stored in a corked glass container under laboratory conditions for 5 days.

5.2.3 Preparation of sodium nitrite solution, mass fraction - 5 %

A portion of sodium nitrite weighing (5.0 ±± 0.1) g is dissolved in distilled water according to 5.2.2 in a volumetric flask of capacity 100 $cm^3$, and the volume of the solution is brought to the mark with the same water. The solution is suitable for use when stored in a corked glass in the laboratory for fifteen days.

5.2.4 Preparation of the initial manganese solution with a mass concentration of 200 $mg/dm^3$

Using a pipette according to 3.1.4, take 5 $cm^3$ of SSS 022.46-96 according to 3.1.7, transfer it to a volumetric flask of capacity 250 $cm^3$ according to 3.1.3, and bring the solution to the mark with distilled water prepared according to 5.2.2. The solution is suitable for use when stored in a corked glass in the laboratory for six months.

5.2.5 Preparation of a standard solution with a mass concentration of manganese of 10 $mg/dm^3$

Using a pipette according to 3.1.4, take 25 $cm^3$ of the stock solution 5.2.5, transfer it to a volumetric flask according to 3.1.3 with a capacity of 500 $cm^3$ and bring the volume of the solution to the mark with distilled water prepared according to 5.2.2. The solution is suitable for use when stored in a corked glass in the laboratory for one month.

5.3. Preparation of solutions for constructing a calibration curve

Into a volumetric flask according to 3.1.3 with a capacity of 100 $cm^3$, use a pipette to measure the required volume of a standard solution with a mass concentration of manganese of 10 $mg/dm^3$ according to 5.2.5, and bring the volume of the solution to the mark with distilled water prepared according to 5.2.2.

The solution is quantitatively transferred into a heat-resistant beaker according to 3.3.3, covered with a watch glass and evaporated to dryness on an electric hotplate. The dry residue is moistened successively with 5 $cm^3$ of sulfuric acid and 5 $cm^3$ of concentrated nitric acid and evaporated to dryness again. The beaker is cooled. 10 $cm^3$ of hot distilled water is added with a pipette according to 3.1.4. The solution is acidified with concentrated nitric acid to pH 2–3, and filtered into a beaker according to 3.3.3 through a "blue ribbon" filter. The filter with the precipitate is washed with distilled water according to 5.2.2 until the volume of the filtrate is approximately 40 $cm^3$ . Using a pipette according to 3.1.4, add 1 $cm^3$ of concentrated orthophosphoric acid to the filtrate, heat to boiling, add a portion of ammonium persulfuric acid weighing about 0.1 g and cook evenly, preventing the solution from splashing, for 10 minutes.

After that, add 2-3 drops of silver nitrate solution according to 5.2.1, a portion of ammonium persulphate weighing about 0.1 g and boil for another 2 minutes until a pink colour appears. The solution is forcibly cooled, transferred to a volumetric flask with a capacity of 50 $cm^3$ according to 3.1.3, and the volume is brought to the mark with distilled water prepared according to 5.2.2. In this way, all calibration solutions are ready.

A blank sample is prepared in the same way, but without adding the standard manganese solution.

Information on the required pipettes, volumes of standard solution according to 5.2.5 for preparing solutions for constructing the calibration characteristic, and the corresponding mass concentrations of manganese in these solutions are given in Table 2. For each mass concentration value, a series of five calibration solutions is prepared.

The optical density of the calibration solutions is measured in accordance with 8.4 immediately after the preparation procedure is completed.

**Note**. Due to the reduced stability over time of weakly colored solutions and the sensitivity of the manganese oxidation reaction to changes in the volume of the solution, obtaining measurement results with satisfactory reproducibility in the range of mass concentrations from 0.05 to 0.25 mg/dm$^3$ is possible under the following conditions:

- maintaining the volume of the solution at the stage of colour formation within 35 - 40 cm$^3$;
- forced cooling of colored solutions, bringing to the final volume and measuring the optical density separately for each solution without delay, which is ensured by alternate treatment of calibration solutions at the stage of colour formation (oxidation with ammonium persulfate) with an interval of at least 5 minutes.

Table 2

Information about solutions for constructing the calibration curve

| Solution No. for constructing the calibration characteristic | Nominal pipette capacity, cm$^3$ | | Volume of standard solution according to 8.2.5, cm$^3$ | Mass concentration of manganese in the solution for constructing the calibration characteristic, $\rho_{gr}$, mg/dm$^3$ |
|---|---|---|---|---|
| | for 3.1.4 | for 3.1.5 | | |
| 1 | 0.5 | – | 0.5 | 0.05 |
| 2 | 1 .0 | – | 1.0 | 0.10 |
| 3 | – | 2.0 | 1.5 | 0.15 |
| 4 | 2.0 | – | 2.0 | 0.20 |
| 5 | – | 5.0 | 2.5 | 0.25 |
| 6 | – | 5.0 | 4.0 | 0.40 |
| 7 | – | 10.0 | 6.0 | 0.60 |
| 8 | – | 10.0 | 8.0 | 0.80 |
| 9 | – | 10.0 | 10.0 | 1.00 |

5.4 Construction of the calibration characteristic

5.4.1 Measure the optical density of the calibration solutions and the blank sample according to 5.3 using a photoelectrocolorimeter prepared according to 5.1, using a wavelength of 540 nm (reference solution - distilled water according to 5.2.2). To measure the optical density of calibration solutions No. 1 - No. 5 (0.05 - 0.25 mg/dm$^3$), use cuvettes with an optical path length of 100 mm. To measure the optical density of calibration solutions No. 5-9 (0.25-1.0 mg/dm$^3$), use cuvettes with a working length of 50 mm. For each mass concentration value, five parallel measurements of optical density are performed according to the number of calibration solutions in the series.

The optical density of the blank sample is subtracted from that of the calibration solutions.

The parameters of linear calibration characteristics are calculated by the least squares method: optical density, $D_{\lambda, B}$ and mass concentration of manganese, $\rho$, mg/dm$^3$ for the calibration ranges:

from 0.05 to 0.25 mg/dm$^3$ inclusive, from 0.25 to 1.0 mg/dm$^3$ inclusive and corresponding calibration errors.

### 5.5 Sample collection and preservation

Surface water sampling is performed according to DSTU ISO 5667-6; storage and handling of samples is according to DSTU ISO 5667-3.

Samples are taken in polyethene containers. If the manganese concentration is not measured immediately, the samples are preserved by adding 5 cm$^3$ of concentrated nitric acid to 1 dm$^3$ of the sample. The volume of the water sample for measuring the mass concentration of manganese is not less than 1.5 dm$^3$.

### 5.6 Sample preparation

5.6.1 To determine the gross manganese content, the sample is not filtered. To determine the dissolved forms of manganese, the sample is filtered at the sampling site through a 45 μm filter before preservation.

5.6.2 To determine the volume required for measurements, take 50 cm$^3$ of the sample, add a few drops of nitric acid, then add silver nitrate dropwise until the turbidity disappears at the point of application of the drop. Then add 0.5 g of ammonium persulfate and heat to boiling. In the presence of manganese (about 0.1 mg/dm$^3$), the solution turns pale pink. The presence of a clear pink colour indicates manganese in excess of 0.2 mg/dm$^3$.

5.6.3 An aliquot of the sample prepared according to 5.6.1, with a volume of 1000 cm$^3$ to 5 cm$^3$, with a manganese content of 0.005 to 0.1 mg, is placed in a heat-resistant beaker according to 3.3.3, covered with a watch glass and evaporated to dryness on an electric hotplate. The beaker is cooled, and the dry residue, the walls of the beaker, and the watch glass are moistened sequentially with 5 cm$^3$ of sulfuric acid and 5 cm$^3$ of concentrated nitric acid, then evaporated to dryness again. The beaker is cooled, 10 cm$^3$ of hot distilled water is added with a pipette according to 3.1.4, the solution is acidified with concentrated nitric acid to pH 2–3, and filtered into a beaker through a "blue ribbon" filter. The filter with the precipitate is washed with distilled water until the volume of the filtrate is approximately 40 cm$^3$ . Using a pipette according to 3.1.4, add 1 cm$^3$ of concentrated orthophosphoric acid to the filtrate, heat to boiling, add a portion of ammonium persulfuric acid weighing about 0.1 g and cook evenly, without splashing the solution, for 10 minutes.

After that, add 2-3 drops of silver nitrate solution according to 5.2.1, a portion of ammonium persulphate weighing about 0.1 g, and boil for another 2 minutes until a pink colour appears. The solution is forced to cool, transferred to a volumetric flask with a capacity of 50 cm$^3$ according to 3.1.3, and the volume is brought to the mark with distilled water prepared according to 5.2.2.

**Note**. Due to the reduced stability over time of weakly colored solutions and the sensitivity of the manganese oxidation reaction to volume changes, obtaining measurement results with satisfactory reproducibility in the mass concentration range from 0.05 to 0.25 mg/dm$^3$ is possible under the following conditions:

– maintaining the volume of the solution at the stage of colour formation within 35 - 40 cm$^3$;

– forced cooling of coloured solutions to the final volume, measuring the optical density of each sample without delay, and ensuring alternate treatment of samples at the stage of colour formation (oxidation with ammonium persulfate) with an interval of at least 5 minutes.

5.6.4 At the same time, prepare a blank sample in the same way, using 100 cm$^3$ of distilled water prepared according to 5.2.2.

5.6.5 If necessary, prepare a sample to take into account the colour. To do this, add the sodium nitrite solution (5.2.3) dropwise to an aliquot of the solution obtained according to 5.6.3 until the colour disappears. Measurements are performed immediately after the sample preparation is complete.

## 6. Measurement procedure

6.1 The optical density of the sample prepared according to 5.6.3 is measured using a photoelectrocolorimeter prepared according to 5.1, using a wavelength of 540 nm and a cuvette with an optical path length of 50 mm or 100 mm, depending on the mass concentration of manganese (reference solution - distilled water, prepared according to 5.2.2).

At the same time, measure the optical density of the blank sample according to 5.6.4 and, if necessary, of the sample, taking into account colour according to 5.6.5 (reference solution: distilled water, prepared according to 5.2).

The optical density of the blank sample according to 5.6.4 and, if necessary, the optical density of the sample to account for colour according to 5.6.5 are subtracted from the optical density of the sample prepared according to 5.6.3.

6.2 The results of optical density measurements are recorded to the third significant figure.

## 7. Processing the results

Measurement results are processed as follows.

7.1 The mass concentration of manganese in the aliquot of the sample prepared in 5.6.3, $\rho_{gr(i)}$, mg/dm$^{3,}$ is found using the parameters of the appropriate calibration characteristic previously set in 5.4. The result is recorded to the third significant figure.

The result of a single measurement of the mass concentration of manganese in the initial sample, $\rho$i, mg/dm$^3$, is found by formula (1):

$$\rho_{\mathrm{i}} = \frac{\rho_{\text{гр(i)}} \cdot 100}{V} \tag{1}$$

where: $\rho_{\text{gr(i)}}$ - mass concentration of manganese in the solution according to 5.6.3, found using the previously calculated parameters of the calibration characteristic, mg/dm$^3$;

$V_0$ – volume of the sample aliquot taken for analysis, cm$^3$;

100 – volume of the volumetric flask used to set the calibration characteristic parameters, cm$^3$;

The results of calculations using formula (1) are rounded to the second significant figure and recorded accordingly.

7.2 The results of measuring the mass concentration of manganese in the initial sample are calculated by formula (2) as the arithmetic mean of the results of two parallel single measurements, r1, $\rho_2$

$$\rho = \frac{\rho_1 + \rho_2}{2} \tag{2}$$

The relative discrepancy between which, at a confidence probability of 0.95, does not exceed the value of the operational control convergence standard, $d_{\text{sb}}$, %:

$$\frac{2\left|\rho_1 - \rho_2\right|}{\rho_1 + \rho_2} \le 0{,}01 \cdot d_{\text{зб}} \tag{3}$$

The values of the operational control convergence standard for the confidence probability P = 0.95 are:

for the range of mass concentrations of manganese from 0.005 to 0.05 mg/dm$^3$ inclusive, 80%;

for the range of mass concentrations of manganese from 0.05 to 0.5 mg/dm$^3$ inclusive, 35%;

for the range of mass concentrations of manganese 0.5 - 20 mg/dm$^3$, inclusive of 5%.

## 5.6 Method for measuring the mass concentration of potassium and sodium ions in natural surface, groundwater, return waters, and salt solutions

*ISO 9964-3:1993 — Water quality — Determination of sodium and potassium — Part 3: Determination of sodium and potassium by flame emission spectrometry*.

### 1. Areas of application

This document establishes a methodology for measuring the mass concentration of potassium and sodium ions in natural surface, groundwater, and return waters, and in salt solutions, by the flame-photometric Method (hereinafter referred to as the FPM).

The Method is intended for determining the mass concentration of potassium and sodium ions in natural surface, groundwater, return waters and solutions of potassium salts in the range:

for potassium from 0 to 0.7820 %

for sodium from 0 to 0.4598%.

The measurement range for the mass concentration of sodium and potassium ions is 1 to 100 mg/dm $^{3,}$ inclusive.

The influence of the accompanying elements $Mg^{2+}$, $Ca^{2+}$, and $SO_4^{2-}$ was not detected.

### 2. Norms and characteristics of measurement error

The relative error rates for measuring the mass concentrations of sodium and potassium ions in natural surface water, groundwater, return waters, and solutions of potassium salts are specified in DSTU 27384:2005. They are ±10% with a confidence probability of P = 0.95.

### 3. Measuring instruments, reagents and materials

3.1 Measuring instruments

3.1.1 flame-photometric analyser with technical and metrological characteristics that provide measurements in a given range;

3.1.2 general-purpose laboratory balance, 2 class accuracy with the largest weighing limit 200 г;

3.1.3 chemical beakers;

3.1.4 Measuring laboratory glassware, 2-class accuracy;

3.1.5 burette with a capacity of 1-1-2-25-0.05;

3.1.6 volumetric flasks with capacities 2-100-2, 2-250-2, 2-1000-2;

3.1.7 pipettes with capacities 1-2-2-1, 1-2-2-5, 1-2-2-10.

3.2 Reagents

3.2.1 Sodium chloride of chemical grade;

3.2.2 Potassium chloride of chemical grade;

3.2.3 lithium chloride 1-hydrogen, chemical grade;

3.2.4 distilled water;

3.2.5 air for supplying pneumatic devices and automation equipment;

3.2.6 Propane gas.

3.3. Auxiliary equipment, chemical vessels and materials

3.3.1 drying cabinet with a thermostat with automatic adjustment accuracy at an operating temperature of ±2 °C;

3.3.2 glass SV 14/8;

3.3.3 volumetric flasks with a capacity of 2-1000-2 for storing calibration solutions;

3.3.4 Polyethene cups for sampling.

## 4. Principle

The measurement of the mass concentration of ions of the substance being determined in water is carried out by the flame-photometric Method, which is based on measuring the intensity of radiation of sodium and potassium atoms, which, when excited in the gas flame of the flame-photometric analyser burner under the influence of high temperature, emit light of a specific wavelength. Using a photocell, a spectral line is isolated from the entire spectrum of light, corresponding to the wavelengths of radiation emitted by sodium and potassium atoms.

The sample is sucked in, atomised, and fed into the burner's gas flame as an aerosol. When the aerosol-gas mixture is burned, a cone-shaped yellow flame forms. The intensity of the flame colour depends on the number of ions in the sample.

The intensity of the flame colour depends on the radiation intensity of the atoms of the substance being determined. It is a quantitative characteristic of the process occurring in the gas burner flame of the flame-photometric analyser.

## 5. Preparing to take measurements

When performing measurements, it is necessary to comply with the requirements applicable to this MVV, as well as those of the operational documentation for measuring instruments and auxiliary devices. For selecting a series of samples from surface/groundwater, the international standard for water sampling, ISO 5667, is used. Before performing measurements of the mass concentration of sodium and potassium ions, the flame photometric analyser is prepared for operation, calibration solutions are ready, and the analyser is calibrated.

5.1. Preparation for the operation of the flame photometric analyser is carried out in accordance with the operating instructions.

5.2. Preparation of solutions.

5.2.1. Preparation of lithium chloride solution.

18.105 g of rsalts are dissolved in distilled water, transferred quantitatively into a 2-1000-2 flask, made up to the mark with distilled water and mixed. Then 50 cm$^3$ of the prepared solution is transferred into a 2-1-50 flask with a 2-1000-2 pipette and dissolved to the mark. The final concentration of LiCl is 15 mg ·equiv/l.

5.2.2. Preparation of calibration solutions.

Sodium and potassium chlorides are calcined at a temperature of 500 °C for 40 minutes. Cool in a desiccator to 30 °C, then use to prepare calibration solutions.

Table 1

| | Ratio C NaCl / $C_{KCl}$* | Required amount of NaCl, cm$^3$ | Dilution volume , cm$^3$ | Required amount of KCl, cm$^3$ | Dilution volume, cm$^3$ | Total volume of calibration solution, cm$^3$ |
|---|---|---|---|---|---|---|
| 1 | 5/20 | 1.0 | 200.0 | 1.0 | 50.0 | 250.0 |
| 2 | 10/20 | 1.0 | 100.0 | 1.0 | 50.0 | 150.0 |
| 3 | 10/40 | 1.0 | 100.0 | 1.0 | 25.0 | 125.0 |
| 4 | 10/80 | 2.0 | 200.0 | 2.0 | 25.0 | 225.0 |
| 5 | 10/100 | 1.0 | 100.0 | 1.0 | 10.0 | 110.0 |
| 6 | 10/120 | 3.0 | 300.0 | 3.0 | 25.0 | 325.0 |
| 7 | 20/10 | 1.0 | 50.0 | 1.0 | 100.0 | 150.0 |
| 8 | 20/50 | 1.0 | 50.0 | 1.0 | 20.0 | 70.0 |
| 9 | 30/20 | 3.0 | 100.0 | 3.0 | 150.0 | 250.0 |
| 10 | 40/10 | 1.0 | 25.0 | 1.0 | 100.0 | 125.0 |
| 11 | 50/20 | 1.0 | 20.0 | 1.0 | 50.0 | 70.0 |
| 12 | 60/40 | 3.0 | 50.0 | 3.0 | 75.0 | 125.0 |
| 13 | 80/10 | 2.0 | 25.0 | 2.0 | 200.0 | 225.0 |
| 14 | 90/30 | 3.0 | 33.33 | 3.0 | 100.0 | 133.33 |
| 15 | 100/10 | 1.0 | 10.0 | 1.0 | 100.0 | 110.0 |
| 16 | 120/20 | 3.0 | 25.0 | 3.0 | 150.0 | 175.0 |
| 17 | 160/8 | 2.0 | 12.5 | 2.0 | 250.0 | 262.5 |

$C_{NaCl}$ / $C_{KCl}$ * – the ratio of the concentration of sodium chloride $C_{NaCl}$ (mol/l) to the concentration of potassium chloride $C_{KCl}$ (mol/l).

A series of calibration solutions used to calibrate the flame photometric analyser (Table 1) on the working ranges can be prepared in two ways:

*Method 1.* Calibration solutions are prepared according to Table 1, by diluting and mixing pre-prepared solutions of sodium chloride and potassium chloride with a concentration of 1 mol/dm $^3$.

To prepare a 1 mol/dm$^3$ sodium chloride solution, weigh a portion of NaCl (58.4428 g) on an analytical balance and place it in a 1000 cm$^3$ volumetric flask. Dissolve in distilled water, then bring the solution in the flask to the mark.

To prepare a 1 mol/dm$^3$ sodium chloride solution, weigh a portion of KCl (74.555 g) on an analytical balance and place it in a 1000 cm$^3$ volumetric flask. Dissolve in distilled water, then bring the solution in the flask to the mark.

*Method 2.* Prepare calibration solutions of the concentrations given in Table 1.

The mass of the sample for preparing calibration solutions with a volume of 100 cm$^3$ of the required molar concentration is calculated using the formulas

for sodium $$NaCl = \frac{C\left(Na^{+}\right) * 58.4428}{10000}(г) \qquad (1)$$

for potassium $$KCl = \frac{C\left(K^{+}\right) * 74.555}{10000}(г) \qquad (2)$$

where $C\left(Na^{+}\right), C\left(K^{+}\right)$ is the molar concentration of sodium and potassium (mmol/l);

or by the formula

$$m_{р.р.} = \frac{C * V_{р-ну} * MM}{1000} \qquad (3)$$

$m_{р.р.}$ – mass of dissolved substance (NaCl or KCl), *g*;

*C* is the concentration of the solution, mol/l.

Measure the required amount of the starting solution with a burette, transfer it to a volumetric flask, bring the flask to the mark with distilled water, and mix.

5.2.3. Calibration of the flame photometric analyser.

The working concentration range of calibration solutions should be selected based on the expected analyte concentrations in the samples. The highest concentration of the calibration solution at which the scale of the selected range is extended should not be less than the concentration of the analyte in the samples. If, within the range of concentrations of sodium and potassium present in the samples, there are samples that differ by more than an order of magnitude, they are divided into groups, and a working range is established for each group.

## 6. Measurement procedure

6.1 . Measurement conditions.

- compressed air pressure – 276 KPa,
- fuel gas pressure from 552 to 827 KPa.

6.2. Conducting measurements.

The flame photometric analyser is turned on according to the device's instructions. Then the beakers are filled with the following solutions in the following order: distilled water, calibration solution, and test samples. Then, according to the device's operating instructions, the concentrations of the standard (calibration solution) and the test solutions are measured.

During operation, calibrate the device every 20 samples.

## 7. Processing the results

The mass fraction (in %) of sodium and potassium is calculated by converting the instrument readings in m*eq/l to % (mass) using the formulas:

$$\%Na_i = \frac{n*22.9898*V}{10000*m_{NaCl}} \qquad \%K_i = \frac{n*39/102*V}{10000*m_{KCl}} \tag{4}$$

where $n$ – instrument readings, m*eq/dm$^3$;

$V$ – volume in which the sample is dissolved, dm$^3$;

$t$ – weight, g;

22.9898 and 39.102 are the molecular weights of sodium and potassium, respectively.

The results of calculations according to formulas (1) and (2) are rounded and recorded to the second decimal place.

7.1. The result of measurements of the mass concentration of sodium and potassium ions is calculated according to formulas (5) as the arithmetic mean of the results of two parallel single measurements $\%Na_i$ $\%K_i$:

$$\%Na = \frac{\%Na_1 + \%Na_2}{2} \qquad \%K = \frac{\%K_1 + \%K_2}{2} \tag{5}$$

The result of measurements of the mass concentration of sodium and potassium ions in natural surface, groundwater, return waters and salt solutions is taken to be the arithmetic mean of the results of two parallel single measurements ( $\%Na_1$ and $\%Na_2$ or $\%K_1$ $\%K_2$) of the mass concentration of sodium and potassium ions in the prepared sample.

The measurement result is presented in the form:

$(\%Na \pm \Delta)$, *mg/dm*$^3$*; P = 0.95; n = 2,*

where: $\pm\Delta$ – limits of absolute error of the result of measurement of the mass concentration of sodium and potassium ions for the confidence probability P = 0.95, mg/dm $^3$; $n$ – number of parallel measurements, $n = 2$; or

The result of measurements of the mass concentration of sodium and potassium ions in natural surface, groundwater, return waters and salt solutions of potash enrichment plants $(\%Na)$ and $(\%K)$ *mg/dm* $^3$, relative error limits $(\pm\delta)$, *%; P=0.95; n=2.*

7.2 The limits of absolute error of the result of measuring the mass concentration of sodium and potassium ions in natural surface, groundwater, return waters and salt solutions of potassium enrichment plants are calculated by formulas (6) and:

$$\Delta = \frac{\delta*\%Na}{100} \qquad \Delta = \frac{\delta*\%K}{100} \tag{6}$$

The results of the calculations are rounded to the second significant figure and recorded. The measurement result must end with the same number of decimal places as the absolute measurement error.

7.3 The measurement results are recorded in the protocol.

## 5.7 Methodology for measuring mass concentrations of calcium by the titrimetric method using ethylenediaminetetraacetic acid

*The method for titrimetric determination of calcium mass concentrations complies with the requirements of ISO 6058:1984 (IDT)* (Water quality – Determination of calcium content – EDTA tetrametric method*) and DSTU ISO 6058:2003.*

### 1. Scope of application

This standard specifies a titration method using ethylenediaminetetraacetic acid (hereinafter referred to as EDTA) for the determination of calcium in ground and surface waters and in drinking water. It may also be applied to raw water for municipal and industrial use, provided it does not contain heavy metals at levels likely to cause interference. The method does not apply to seawater or other similar waters with high salt concentrations. It applies to waters with a calcium content of 2 mg/dm$^3$ to 100 mg/dm$^3$ (0.05-2.5 mmol/dm$^3$). For waters containing more than 100 mg/dm$^3$ of calcium, a diluted sample should be used.

### 2. Normative references

ISO 385/1 Laboratory glassware – Burettes – Part 1: General requirements
ISO 5667 Water quality – Sampling
Part 1: Guidance on the design of sampling programs
Part 2: Guidance on sampling techniques
Part 3: Guidance on the preservation and handling of samples.

### 3. Principle

Calcium ions are titrated complexometrically with an aqueous solution of the disodium salt of ethylenediaminetetraacetic acid EDTA at a pH of 12-13. Calconcarboxylic acid, which forms a red complex with calcium ions, is used as an indicator. Magnesium precipitates in the form of hydroxide and does not affect the course of the reaction.

During the titration, ethylenediaminetetraacetic acid first reacts with unbound calcium ions, which form a complex with the indicator. The indicator changes colour from red to bright blue.

### 4. Reagents and materials

Only reagents of specified analytical grade and distilled water or water of equivalent purity are used in the analysis process.

4.1 Caustic soda 2 mol/dm$^3$, solution.

Dissolve 8 g of caustic soda in 100 cm $^3$ of distilled water. Store in a plastic bottle.

Note: Take measures to avoid atmospheric carbon dioxide pollution.

4.2 Ethylenediaminetetraacetic acid, standard titrated solution, with $(Na_2EDTA)_=$ 10 mmol/dm$^3$.

4.2.1 Preparation

Dry a portion of the disodium salt of ethylenediaminetetraacetic acid dihydrate ($C_{10}H_{14}N_2O_8Na_2 \cdot 2\ H_2O$) at a temperature of 60 °C for 2 hours. Dissolve 3.725 g of dry salt in water, then dilute to 1000 cm$^3$ in a volumetric flask. Store the ethylenediaminetetraacetic acid solution in a polyethene bottle and check its concentration regularly.

4.2.2 Calibration

Calibrate the solution (see 4.2.1) against the calcium standard solution 4.3. using the procedure specified in section 7. Use 20.0 cm$^3$ of the calcium standard solution (see 4.3) and dilute to 50 cm$^3$.

4.2.3 Concentration calculation

The concentration of a solution of ethylenediaminetetraacetic acid, $C_1$, expressed in millimoles per cubic decimeter, is calculated using the equation:

$$\mathrm{C1} = \frac{\mathrm{C2} \cdot V1}{V2} \qquad (1)$$

$C_1$ – concentration of the standard calcium reference solution (see 4.3), mmol/dm$^3$;

$V_1$ – volume of standard reference calcium solution, cm$^3$;

$V_2$ - volume of ethylenediaminetetraacetic acid solution used for Calibration, cm$^3$;

4.3 Calcium, standard reference solution, C ($CaCO_3$) = 10 mmol/dm$^3$.

Dry a sample of pure calcium carbonate for 2 hours at 150 °C, then cool it to room temperature in a desiccator.

Place 1.00 g in a 500 cm$^3$ conical flask and moisten with water. Add 4 mol/dm$^3$ hydrochloric acid dropwise until all the carbonate is dissolved. Do not add too much acid. Add 200 cm$^3$ water and boil. for a few minutes to remove carbon dioxide. Cool to room temperature and add a few drops of methyl red solution. Add 3 mol/dm$^3$ ammonia solution to colour the solution orange. Transfer the solution to a 1000 cm$^3$ single-mark volumetric flask and make up to volume with distilled water.

1 cm$^3$ of solution contains 0.4008 mg (0.01 mmol) of calcium.

Note: Industrial solutions can be used.

4.4 Calconcarboxylic acid, indicator.

Mix thoroughly 0.2 g of H SN [2-hydroxy-1 (2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid] ($C_{21}H_{14}N_2O_7S\ 3H_2O$ and 100 g of sodium chloride (NaCl).

Note: This indicator is also known as "calconecarboxylic acid." Another indicator that can be used for calcium is calcein {2,7-bis[N,N-di- (carboxymethyl)-aminomethyl] fluorescein ($C_{30}H_{26}N_2O_{13}$).

4.5 Equipment

Usual laboratory equipment and: burette, capacity 25 $cm^3$, with a graduation value of 0.05 $cm^3$ according to ISO 385-1, class A, or equivalent equipment.

## 5. Preparing to take measurements

5.1 Sample collection and preparation

Samples should be taken in accordance with the relevant parts of DSTU ISO 5667.

5.2 Preparation of the working part of the sample

The working portion of the sample should contain from 2 $mg/dm^3$ to 100 $mg/dm^3$ (0.05 $mmol/dm^3$ to 2.5 $mmol/dm^3$) of calcium. If a concentration higher than 100 $mg/dm^3$ (2.5 $mmol/dm^3$) is expected, dilute a known volume of the sample solution so that its concentration is within the specified limits and note the dilution factor F.

If the working portions of the sample have been acidified for storage, they shall be neutralised with the calculated amount of caustic soda solution (see 4.1). Any dilution of the sample or working portion of the sample with acid (alkali) shall be taken into account when calculating the results.

## 6. Definition

Pipette 50.0 $cm^3$ of the test solution into a 250 $cm^3$ conical flask. Add 2 $cm^3$ of sodium hydroxide solution (see 4.1) and approximately 0.2 g of chalcone carboxylic acid indicator (see 4.4). Mix and titrate immediately. Add the ethylenediaminetetraacetic acid solution (see 4.2) from the burette, stirring continuously. Titrate more rapidly at the beginning and more slowly at the end. The endpoint is reached when the colour changes to blue. The colour should not change further when another drop of ethylenediaminetetraacetic acid solution is added.

## 7. Processing the results

The calcium content, $C_{Ca,}$ expressed in millimoles per $dm^3$, is calculated using the equation:

$$\mathrm{C(Ca)} = \frac{\mathrm{C1}\cdot V3}{V0} \qquad (2)$$

$C_1$ – concentration of ethylenediaminetetraacetic acid solution, $mmol/dm^3$;

$V_0$ – volume of the working part of the sample, $cm^3$;

$V_3$ - volume of ethylenediaminetetraacetic acid solution used during titration, $cm^3$.

If necessary, the calcium content, $\rho_{Ca}$, $mg/dm^3$, is calculated using the equation:

$$\rho(\mathrm{Ca}) = \frac{C1 \cdot V3}{V0}\mathrm{A} \quad (3)$$

Where A is the relative atomic weight of calcium (Ca) – 40.08;

The calculation must be modified accordingly, using the dilution factor F.

7.1 Accuracy

Results obtained on the same test solution in different laboratories should agree within ±5 mg/dm$^3$ in the range from 30 mg/dm$^3$ to 100 mg/dm$^3$.

## 8. Interference

Caution! Sodium cyanide is poisonous. Appropriate safety precautions must be taken when working with this chemical compound. Do not oxidise a solution containing sodium cyanide.

Aluminium, barium, lead, iron, cobalt, copper, manganese, tin, and zinc ions affect the determination because they may titrate as calcium or cause the colour to darken at the endpoint. Orthophosphate at concentrations greater than 1 mg/dm$^3$ precipitates calcium during pH titration. Calcium carbonate may precipitate if the determination is performed too slowly or if the calcium content is very high, above 100 mg/dm$^3$ or 2.5 mmol/dm$^{3.}$ Interfering metal ions may be masked. Interference from iron at concentrations of 30 mg/dm$^3$ or less can be masked by adding 250 mg of sodium cyanide or a few cubic centimetres of triethanolamine to the sample just before titration. Cyanide also minimises interference from zinc, copper, and cobalt, as well as from triethanolamine with aluminium. Before adding sodium cyanide, ensure the solution is alkaline.

If interference cannot be eliminated, the atomic absorption method must be used. This method will be the subject of a future standard.

## 9. Test protocol

The test report must contain the following information:

- reference to this standard;
- complete identification of the sample;
- The result is expressed in milligrams per cubic decimeter (mg/dm$^3$) with an accuracy of 1 mg/dm$^3$ or in millimoles per cubic decimeter with an accuracy of 0.02 mmol/dm$^3$;
- titration of the working part of the sample;
- any deviations from the procedure specified in this standard or any other circumstances that may affect the result.

# CHAPTER 6

# Water quality - Determination of selected parameters using discrete analysis systems

## Part 1: Ammonium, nitrate, nitrite, chloride, orthophosphate, sulfate, silicate, with photometric detection adopted as a national standard by confirmation method by designation DSTU ISO 15923-1:2018 (ISO 15923-1:2013)

ISO (International Organisation for Standardisation) is the world federation of national standards bodies. The preparation of International Standards is carried out through ISO technical committees. Each member body interested in the subject for which a technical committee has been established is entitled to be represented on that committee. International organisations, governmental and non-governmental, that cooperate with ISO also participate in the work. The procedures used for the development of this document and those intended to support its further development are described in Directives 150/IEC, Part 1. This document has been prepared in accordance with the drafting rules of Directives 150/IEC, Part 2 (www.iso.org/directives). Some elements of this document may be the subject of patent rights. ISO is not responsible for identifying any or all such patent rights www.iso.org/patents. Any trade name used in this document is provided for the convenience of users and does not constitute an endorsement. The responsible committee for this document is 150/TC 147, Water quality, Subcommittee SC 2, Physical, chemical and biochemical methods. ISO 15923 consists of the following parts under the general title “Water quality – Determination of selected parameters using discrete analysis systems”: Part 1: Ammonium, nitrates, nitrites, chlorides, orthophosphates, sulphates and silicates with photometric detection. Many photometric determinations can be automated using a discrete analysis system. A large number of different parameters can be determined with a single instrument, and the parameters to be determined can be specified for each sample. Working with small volumes requires less sample and reagent material.

This part of ISO 15923 specifies methods for the automatic determination of ammonium, nitrates, nitrites, chlorides, orthophosphates, and silicates with photometric detection, and for the turbodimetric determination of sulphates using a discrete analysis system. The field of application is water (groundwater, runoff, surface water, waste water, eluates, boiler water).

## 6.1 Water quality - Determination of selected parameters using discrete analysis systems

### **Part 1**: Ammonium, nitrate, nitrite, chloride, orthophosphate, sulfate and silicate with photometric detection

WARNING: Persons using this part of ISO 15923 should be familiar with standard laboratory practice. This part of ISO 15923 does not claim to address all safety issues, if any, associated with its use. The user is responsible for establishing appropriate safety and health practices and for ensuring compliance with any national regulatory requirements.

IMPORTANT - It is essential that tests conducted in accordance with this part of ISO 15923 are performed by suitably qualified personnel.

### 1. Scope of application

This part of ISO 15923 specifies methods for the automated performance of spectrophotometric and turbodimetric analyses using a discrete analysis system for the determination of ammonium, nitrates, nitrites, chlorides, orthophosphates, sulfates and silicates. The scope is ground, water-soluble, surface, waste, eluate and boiler water.

### 2. Normative references

The following documents, in whole or in part, are normatively referenced in this document and are essential for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the cited document (including any amendments) applies.

ISO 3696, Water for analytical laboratory use - Specification and test methods ISO 5667-3, Water quality - Sampling - Part 3: Storage and handling of water samples ISO 8466-1, Water quality - Calibration and evaluation of analytical methods and performance evaluation - Part 1: Statistical evaluation of a linear calibration function

ISO 8466-2, Water quality - Calibration and evaluation of analytical methods and performance evaluation - Part 2: Calibration strategy for second-order nonlinear calibration functions

### 3. Principle

The Discrete Analysis System is an automated system for spectrophotometric and turbodimetric determinations.

The colour reactions occur in reaction cells, which may be cuvettes, in an incubator. A separate reaction cell is used for each determination. Pre-set volumes of sample and reagents are pipetted into the cells and mixed.

After the incubation period, the solution's absorbance is measured at the wavelength used for the determination. This is done by passing the cuvette through a photometer or by transferring the measuring solution from the reaction cells to a flow-cell photometer.

## 4. Interference

Particles present in the sample may cause clogging and interfere with photometric measurements. It is recommended to filter all samples through a 0.45 μm membrane filter, except for the determination of total phosphate and nitrogen by Kjeldahl (see Appendices B and E). Particles can also be removed by settling, centrifugation or dialysis.

This method applies to samples with pH values between 5 and 9, which cover most natural waters.

Samples outside this range may require pH correction.

The sample's inherent colour or turbidity interferes with the analysis. For prevention of such interferences, see Appendix A. Interferences specific to each parameter are discussed in Appendices B - H.

NOTE: The effect of intrinsic colour must be compensated for by measuring the absorbance of the sample before adding the chromogenic reagent (sample banking) or by using a compensation solution (measurement solution without the chromogenic compound). For more information, see Appendix A. A safe procedure for correcting turbidity cannot be provided. The Beer-Lambert law does not apply to turbid solutions. In addition, many chromogenic reagents and colour complexes are adsorbed on particles.

## 5. Reagents

Reagents for each parameter are listed in Appendices B to H. Use only reagents of recognised analytical grade unless otherwise specified in the appropriate appendix. Dry all solid reagents for at least 1 hour at (105 ± 5)°C, provided they are thermally stable. Store the dried solid in a desiccator before weighing. The reagent volumes listed in Appendices B to H may be adjusted to suit local requirements or the specifications of different instruments.

5.1 Water conforming to class 1 as defined in ISO 3696.

## 6. Apparatus

6.1 A discrete analysis system typically consists of the following components:

6.1.1 Sample introduction device, for automatic or manual control.

6.1.2 Sample container.

6.1.3 Reagent container, refrigerated or not.

6.1.4 Temperature-controlled incubator that maintains a constant temperature, e.g. 37 °C.

6.1.5 UV/VIS detector, e.g. spectrophotometer, suitable for a wavelength range, typically 340 nm to 880 nm.

6.1.6 Control, and data processing unit.

6.1.7 Recording device, e.g. PC with software for data acquisition and evaluation.

## 7. Sample collection and preparation

Use clean sampling vessels. Turbidity or particles interfere with spectrophotometric detection. Clarify samples by filtration through a 0.45 µm membrane (sedimentation, centrifugation or dialysis can also be used). To avoid contamination of the filter membrane, discard the first 20-30 ml of filtrate. Samples for total phosphate determination should not be filtered. See Appendix F.

Prepare and store the sample in accordance with Annexes B to H, or with ISO 5667-3, unless specific instructions are given in the relevant Annexe.

Prepare the water sample (5.1) in the same way as the sample to be used as a reservoir.

Prepare a control standard solution from the primary control standard containing an analyte concentration similar to that of the samples. Perform the analysis as a sample at appropriate intervals in the batch, according to local requirements. A minimum interval of once every 20 samples is recommended.

## 8. Calibration

### 8.1. Calibration function

During the first evaluation of the analytical system and at regular intervals thereafter, set the calibration function for each parameter (see ISO 8466-1 or ISO 8466-2) as follows:

Using the primary calibration standard, prepare the appropriate series of calibration solutions for the relevant parameter, as described in Appendices B to H, including a zero-concentration solution.

Analyse the calibration solutions in accordance with Section 9 and the instrument manufacturer's instructions.

Confirm the validity of the data obtained and use it to calculate the regression line as specified in ISO 8466-1 or ISO 8466-2.

Verify the continued validity of the established calibration function by analyzing the appropriate calibration standard solution at regular intervals according to the accuracy requirements or at least at the end of the batch.

Recalibrate if necessary.

### 8.2. Checking the accuracy of the calibration

If the full calibration function is not set up daily, perform an initial calibration validity check by analysing two calibration standard solutions in the lower and upper thirds of the calibrated working range after the setup procedure (see Section 9).

Verify the continued validity of the established calibration function by analysing an appropriate calibration standard solution at regular intervals according to accuracy requirements or at least at the end of the batch.

Recalibrate if necessary.

## 9. Procedure

Set up the discrete analysis system according to the instrument manufacturer's instructions.

Calibrate the system in accordance with Section 8 and the instrument manufacturer's instructions.

Prepare samples according to Section 7 and Appendices B to H. Consistent temperature and incubation time are essential for the stability of absorbance measurements. Refer to Appendices B-H for guidance on recommended temperatures and incubation times. Please note that the incubation times given in Appendices B to H are guidelines and may vary based on experience.

Measure the absorbance of the samples using the conditions given in Appendices B–H and the instrument manufacturer's instructions. Measure the sample according to Appendix A and the instrument manufacturer's instructions.

If the sample absorbance exceeds that of the upper calibration solution, dilute the sample or reduce the sample amount by an appropriate factor to bring it to the upper half of the calibration range, and re-analyse. If necessary, adjust the sample absorbance (see Appendix A).

The procedures in Appendices B to H can be modified for different instruments or to adjust the method's range or sensitivity for different parameter concentrations or sample types.

## 10. Calculation

Calculate the mass concentration (ρ) of the test parameter in micrograms per litre (μg/l) or milligrams per litre (mg/l) from the calibration line (see Calibration Section) using the resulting corrected absorbance values (see Procedure Section) as specified in ISO 8466-1 or ISO 8466-2. Take into account any dilution factors. This calculation can usually be performed automatically by the instrument software.

## 11. Expression of results

Results should be expressed to a maximum of three significant figures.

EXAMPLES Phosphate = mg/l P (3 significant figures), 1.1 mg/l P (2 significant figures), 1 mg/l (1 significant figure). The corresponding conversion factors are given in Table 1.

Before reporting results, it is essential to determine the required units of expression. For example, ammonium, nitrate, and nitrite can be expressed as·N or as the corresponding ion. Results for orthophosphate can be expressed as $P^-$ or $PO_4^{3-}$, and for silicate can be expressed as $SiO_4$, $SiO_2$, or Si.

Table 1

Conversion factors

| Parameter | Units | Conversion factor | Converted units |
|---|---|---|---|
| Ammonia | mg/l N | 1.2860 | mg/l $NH_4$ |
| Ammonia | mg/1 $NH_4$ | 0.7778 | mg/L N |
| Nitrate | mg/I N | 4.4270 | mg/l $NO_3$ |
| Nitrate | mg/l $NO_3$ | 0.2259 | rng/l N |
| Nitrate | mg/I N | 3.2850 | mg/l $NO_2$ |
| Nitrate | mg/l $NO_2$ | 0.3044 | mg/IN |
| Orthophosphate | mg/I P | 3.0660 | mg/l $PO_4$ |
| Orthophosphate | mg/l $PO_4$ | 0.3261 | mg/l P |
| Silicate | mg/l Si | 3.2790 | mg/l $SiO_4$ |
| Silicate | mg/l $SiO_4$ | 0.3050 | mg/l Si |
| Silicate | mg/l Si | 2.1390 | mg/l $SiO_2$ |
| Silicate | mg/l $SiO_2$ | 0.4674 | mg/I Si |
| Silicate | mg/l $SiO_2$ | 1.5330 | mg/l $SiO_4$ |
| Silicate | mg/l $SiO_4$ | 0.652 5 | mg/l $SiO_2$ |

## 12. Test report

The test report shall contain at least the following information:

- the test method used, together with a reference to this part of ISO 15923 (i.e. ISO 15923-1:2013);
- details necessary for the identification of the sample;
- analysis date;
- analysis results (see the section on expressing results);
- any deviation from this method and a report of the impact on the results.

## 6.2 Appendix A
## Colour correction

### A.1 General provisions

Two possibilities for correcting intrinsic colour are described in A.2 and A.3. Turbidity cannot usually be corrected. In many cases, particle-induced interference can be prevented by careful filtration, settling, centrifugation, or dialysis of the samples.

### A.2 Sample blanking

Sample adjustment is only possible when reaction cells are used, which also serve as cuvettes. The measurement (adjustment) is carried out after the sample and, if applicable, one or more reagents that can change the sample's colour (e.g., due to pH effects) are added, but before the chromogenic reagent. This adjustment value is subtracted from the final absorbance of the measuring solution, with the ratio of the volumes of the measuring solutions taken into account. Standards are measured in the same way.

### A.3 Use of compensation solution

When using a compensation solution, a second measuring solution is prepared, consisting of the same volumes of sample and reagent, in which the compound responsible for the colour formation is absent. This can be done by adding an equal volume of water instead of the chromogenic reagent, or by preparing a separate reagent lacking the chromogenic compound. The absorbance of the compensation solution is subtracted from the absorbance of the sample solution.

## 6.3 Appendix B

## Ammonium determination

### B.1 Principle

Ammonium reacts with hypochlorite, which is formed by alkaline hydrolysis of sodium dichloroisocyanurate, and with salicylate at a pH of approximately 12.6 in the presence of sodium nitroprusside as a catalyst, to form a brown-colored compound. The reagent contains citrate to mask interference from cations, such as calcium and magnesium. The absorbance at 660 nm is a measure of the ammonium content.

NOTE: This method is based on the same chemical processes as in ISO 7150-1.

### B.2 Interferences

Interferences from cations, especially calcium and magnesium ions, are masked by citrate. In saline samples, these interferences can occur when the citrate's complexing capacity is exceeded. This can be prevented by distillation in accordance with ISO 7150-1. Distillation is also recommended for intensely colored samples.

Excessively high or low pH values of samples may affect the result. Primary amines and components that can reduce hypochlorite may affect the determination, but they are rarely present in concentrations that affect the result in water samples. If the presence of any of these substances that affect the result is suspected, the magnitude of the interference should be assessed before analysis.

### B.3 Reagents

B.3.1 Nitric acid solution, pH ($HNO_3$), approximately 4 g/l.

Carefully add (4 ± 0.4) ml of concentrated nitric acid [$HNO_3$] to 800 ml of water in a 1 L volumetric flask and mix. Make up to the mark with water.

This solution is stored for 1 year at room temperature.

B.3.2 Sodium nitroprusside reagent

In a 250 ml volumetric flask, dissolve (32.5 ±0.3) g of sodium salicylate [$C_7H_5O_3Na$] and (32.5 ± 0.3) g of sodium citrate [$HO{-}C(CH_2COONa)_2COONa$] in approximately 200 ml of water. Ensure the pH is < 8.0. If necessary, acidify with nitric acid (B.3.1). Add (0.243 ±0.002) g of sodium nitroprusside [$Na_2(Fe(CN)_5NO)\ 2H_2O$] and dissolve. Make up to the mark with water. Store this solution in a dark bottle at 2°C to 8°C for 1 week.

NOTE: If necessary, add a suitable detergent, such as polyoxyethylene lauryl ether, to prevent air bubbles from adhering to the cuvette wall when mixing the sample and reagents.

B.3.3 DIC (dichloroisocyanurate) reagent.

In a 250 ml volumetric flask, dissolve (810 ± 0.1) g of sodium hydroxide [NaOH] in approximately 200 ml of water, mix, allow to cool, and add (0.500 ± 0.005) g of sodium dichloroisocyanurate [$Cl_2Na(NCO)_3 \cdot 2H_2O$] and dissolve. Make up to the mark with water. This solution is kept for 1 week in a dark bottle at a temperature of 2 °C to 8 °C.

B.3.4 Primary calibration standard ammonium, pH = 300 mg/l.

In a 1-litre graduated flask, dissolve (1.415±0.001) g of ammonium sulphate [$(NH_4)_2SO_4$] in approximately 750 ml of water and make up to the mark with water. This solution is kept for 3 months at 2 °C to 8 °C.

B.3.5 Primary ammonium control standard, pH = 200 mg/l.

Prepare a control standard using a different starting material than that used for the primary calibration standard.

For example, diammonium hydrogen citrate [$(NH_4)_2HC_6H_5O_7$] can be used as a starting material.

In a 1-litre graduated flask, dissolve (1.615 ± 0.001) g of diammonium hydrogen citrate in approximately 750 ml of water and make up to the mark with water. This solution is stored for 3 months at 2 °C to 8 °C.

**B.4 Procedure**

B.4.1 Sample pre-treatment

To determine nitrogen content by the Kjeldahl method, samples must first be decomposed.

NOTE: ISO 5663 can be used for splitting.

B.4.2 Calibration

The calibration curve is usually first order.

B.4.3 Analysis

The incubation temperature is between 30 °C and 40 °C. Prepare the measurement solution, which generally consists of the following:

- maximum 10 parts of the sample by volume;
- 1 part by volume of sodium nitroprusside reagent (B.3.2). Mix the measuring solution after each addition;
- (1 ±0.2) parts by volume of DIC reagent (B.3.3). Mix the measuring solution after each addition. The recommended incubation time after adding the DIC reagent is 480 s.

After the incubation time, measure the absorbance at 660 nm.

NOTE: The typical calibration range for this method is 0.05-2.0 mg/l N.

## 6.4 Appendix C
## Determination of the sum of nitrates and nitrites by the hydrazine method

### C.1 Principle

Nitrate is reduced to nitrite using hydrazine sulfate. Both the nitrite formed from this reaction and the nitrite present in the sample then react with sulfonamide and N-(1-naphthyl)ethylenediamine dihydrochloride (NED) to form a red-colored diazide compound.

The absorbance at 540 nm is a measure of the combined amounts of nitrite and nitrate.

NOTE 1 This method is based on the same chemistry as ISO 13395, except that ISO 13395 uses a cadmium column for nitrate reduction (Note 3).

NOTE 2. This method determines the amount of nitrogen that is completely oxidised. To obtain an accurate nitrate concentration, the amount of nitrite must be subtracted. Nitrite is determined by omitting the hydrazine reduction step from the method. See Appendix D.

NOTE 3. Nitrates can also be reduced to nitrites using a cadmium column instead of hydrazine sulfate.

### C.2 Interference

Sulfide concentrations up to 10 mg/L can cause a 10% negative result. Chloride concentrations above 100 mg/L can also cause a negative result. Nitrates are converted to nitrites before determination. See Appendix D.2 for further discussion of interference.

### C.3 Reagents

C.3.1 Cupric sulfate solution, ρ = 3.9 g/l.

In a 100 ml volumetric flask, dissolve (0.39 ± 0.01) g of cuprous sulfate [$CuSO_4 \cdot 5H_2O$] in 100 ml of water. This solution is stored at room temperature for 6 months.

C.3.2 Zinc sulfate solution, ρ = 45 g/l.

In a 100 ml volumetric flask, dissolve (4.5 ± 0.1) g of zinc sulfate [$ZnSO_4 \cdot 7H_2O$] in 100 ml of water. This solution is stable for 6 months at room temperature.

C.3.3 Sodium hydroxide solution, ρ = 8 g/l.

In a 100 mL volumetric flask, dissolve (0.80 ± 0.04) g of sodium hydroxide [NaOH] in 100 mL of water. This solution will keep for at least 1 week when stored in a closed container.

NOTE: If necessary, add a suitable detergent, such as polyoxyethylene lauryl ether, to prevent air bubbles from adhering to the cuvette wall when mixing the sample and reagents. To reduce precipitation of $Ca^{2+}$ and $Mg^{2+}$, 0.3 mL of phosphoric acid (85%) can be added to the sodium hydroxide solution.

C.3.4 Reducing reagent

ml volumetric flask, dissolve (0,163 ± 0,001) g of hydrazine sulphate ($N_2H_4$ $H_2SO_4$) in approximately 200 ml of water. Add (0,375 ± 0,005) ml of copper sulphate solution (C.3.1) and (2,50 ± 0,05) ml of zinc sulphate solution (C.3.2) and make up to the mark with water.

This solution is stable for 2 weeks at 2°C to 8°C.

The optimal hydrazine concentration in the reducing solution may vary from batch to batch and should be determined for each new batch.

Determine the recovery yield by analysing a nitrate and nitrite solution with the same N concentration, which is approximately 100 % of the $NO_3$-N measuring range. The absorbance of the nitrate solution should be between 95 % and 110 % of the absorbance of the nitrite solution. If the absorbance of the nitrate is lower than that of the nitrite solution, the nitrate conversion is not complete. The hydrazine content should be increased until the absorbance is within this range.

C.3.5 NED reagent

In a 1 L volumetric flask, carefully add 50 mL of phosphoric acid [$H_3PO_4$] (85%) to 500 mL of water. Add (5.0±0.1) g of sulfonamide [$C_6H_8N_2O_2S$] and dissolve. Add (0.25 ± 0.01) g of N-(1-naphthyl) ethylenediamine dihydrochloride [$C_{12}H_{16}Cl_2N_2$] (NED), dissolve and make up to volume with water. This solution will keep for 1 month if stored in a dark bottle at 2 °C to 8 °C.

C.3.6 Primary calibration standard of nitrate, $\rho(N) = 600$ mg/l.

Dry the potassium nitrate ($KNO_3$) for at least 2 hours at (105±5) °C. Cool in a desiccator for at least 45 minutes and dissolve (4.331±0.001) g in approximately 750 ml of water in a 1-litre volumetric flask. Make up to the mark with water. This solution is stable for 3 months at 2 °C to 8 °C.

S.Z. 7 Primary control standard of nitrate, $\rho(N) = 400$ mg/l.

Prepare a reference standard using a different starting material than that used for the primary calibration standard. For example, sodium nitrate [$NaNO_3$] can be used as the starting material. Dry the sodium nitrate for 2 hours at (105 ± 5) °C. Cool in a desiccator for 45 minutes and dissolve (2.427 ± 0.001) g in approximately 750 ml of water in a 1 L volumetric flask. Make up to the mark with water. This solution is stable for 3 months at 2 °C to 8 °C.

### C.4 Procedure

C.4.1 Calibration

The calibration curve is usually first order.

C.4.2 Analysis

The incubation temperature is between 30 °C and 40 °C. Prepare the measurement solution, which usually consists of the following:
-1 part by volume of sodium hydroxide solution (C.3.3.);
-(1 ± 0.1) parts sample by volume. Mix the solution after each addition. The recommended incubation time after sample addition is 180 s.
-(1 ± 0.2) parts by volume of the reducing reagent (C.3.4). Mix the solution after each addition. The recommended incubation time after addition of the TON-2 reagent is 420 s.
-(1 ± 0.5) parts NED reagent (C.3.5) by volume. Mix the solution after each addition. The recommended incubation time after adding the NED reagent is 300 s. After the last incubation, measure the absorbance at 540 nm.

NOTE: The typical calibration range for this method is 0.1-6.0 mg/L N.

To determine nitrate, subtract the nitrite value (see Appendix D) from the result obtained using this procedure.

## 6.5 Appendix D
## Nitrites determination

### D.1 Principle

In an acidic medium, nitrites react with sulfonamide and naphthyl ethylenediamine (NED) to form a red-colored diazide compound. The absorbance at 540 nm is a measure of the nitrite content.

NOTE: This method is based on the same chemistry as ISO 6777 [3].

### D.2 Interference

High alkalinity causes interference. Samples with bicarbonate alkalinity > 300 mg/L should be diluted or phosphoric acid added before analysis to ensure a pH of 1.9 after treatment with the chromogenic reagent. Free chlorine, chloramines, high levels of polyphosphate, iron(III) or thiosulfate may also cause interference. If any of these interferences are suspected in the sample, the magnitude of the interference should be assessed before analysis.

### D.3 Reagents

D.3.1 NED reagent

In a 1 L volumetric flask, carefully add 50 mL of phosphoric acid [$H_2PO_4$] (85%) to 500 ml of water. Add (5.0 ± 0.1) g of sulfonamide [$C_6H_8N_2O_2S$] and dissolve. Add (0.25 ± 0.01) g of N-(1-naphthyl) ethylenediamine dihydrochloride [$C_{12}H_{16}Cl_2N_2$], dissolve and make up to the mark with water. This solution is suitable for storage for up to 1 month in a dark bottle at 2 °C to 8 °C.

D.3.2 Primary calibration standard of nitrite, $\rho(N) = 200$ mg/l.

Dry the sodium nitrite [$NaNO_2$] for 1 hour at (105 ± 5) °C. Cool in a desiccator for 45 minutes, then dissolve (0.985 ± 0.001) g in a 1-litre volumetric flask containing approximately 750 ml of water. Make up to the mark with water. Store this solution for 1 month at 2°C to 8°C.

D.3.3 Primary nitrite reference standard, $\rho(N) = 125$ mg/l.

Prepare a reference standard using a different starting material than that used for the primary calibration standard.

For example, potassium nitrite [$KNO_2$] can be used as a starting material. Dry for at least 2 hours at (105 ± 5) °C. Cool in a desiccator for at least 45 minutes, then dissolve (0.759 ± 0.001) g in a 1-litre volumetric flask containing approximately 750 ml of water, and make up to the mark with water. This solution is kept for 3 months at 2 °C to 8 °C.

### D.4 Procedure

D.4.1 Calibration

The calibration curve is usually first order.

### D.4.2 Analysis

The incubation temperature is between 20 °C and 40 °C. Prepare the measurement solution, which usually consists of the following:

- maximum 5 parts of the sample by volume;
- 1 part by volume of NED reagent (D.3.1). The recommended incubation time after addition of NED reagent is at least 360 s. Mix the solution after each addition. After incubation, measure the absorbance at 540 nm.

NOTE 1 The typical calibration range for this method is 0.01 mg/l N to 0.6 mg/l N.

NOTE 2 A compensation solution for intrinsic colour can be prepared by omitting sulfonamide and N-(1-naphthyl) ethylenediamine dihydrochloride from NED reagent (D.3.1 ). See also Appendix A.

## 6.6 Appendix E

## Determination of chloride by the thiocyanate method

### E.1 Principle

The chloride reacts with mercuric thiocyanate to form unionised (but soluble) mercuric chloride and an equivalent amount of free thiocyanate, which forms a red complex with iron (III). This method is based on the same chemistry as ISO 15682 [7].

The chloride content is measured by absorption at 480 nm.

### E.2 Interference

Compounds that release free thiocyanate from mercury(II) thiocyanate, such as bromide and iodide, will interfere. Bromide causes significant interference above 30 mg/L. If the concentration of the interference is known, it can be taken into account in the calculation. Sulfide interferes and can be removed by adding 5 ml of 30% hydrogen peroxide (commercially available). The magnitude of any suspected interference should be assessed before analysis.

### E.3 Reagents

E.3.1 Mercury thiocyanate solution, $\rho = 4.16$ g/l.

In a 100 mL volumetric flask, dissolve (0.416 ± 0.001) g of mercuric thiocyanate. [$Hg(SCN)_2$] in 100 mL of methanol. Mix and filter if necessary. This solution is stable for up to 3 months when stored in a dark bottle at room temperature.

E.3.2 Ferrous nitrate solution, $\rho = 202$ g/l.

In a 100 ml volumetric flask, dissolve (20.2 ±0.1) g of ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] in 50 ml of water. Carefully add (4.44 ±0.04) ml of concentrated nitric acid. Make up to the mark with water. This solution is stable for up to 3 months if stored in a dark bottle at room temperature.

E.3.3 Chromogenic reagent, CI.

Measure (75 ± 1) ml of mercuric thiocyanate solution and (75 ± 1) ml of ferric nitrate solution into a 500 ml volumetric flask. Make up to the mark with water and mix. This solution is stable for up to 3 months in a dark bottle at room temperature.

E.3.4 Primary calibration standard of chloride, $\rho = 50$ g/l.

Dry the sodium chloride [NaCl] for 4 hours at (105 ±5) °C. Cool the salt in a desiccator for 45 minutes, then dissolve (41.21 ±0.01) g in a 500 ml volumetric flask with approximately 350 ml of water, making up to the mark with water. This solution is stable for up to 3 months when stored at 2°C to 8°C.

E.3.5 Primary chloride reference standard, $\rho = 15$ g/l.

Prepare a control standard using a different starting material than that used for the primary calibration standard.

For example, potassium chloride [KCl] can be used as a starting material. Dry the salt for at least 2 hours at (105 ±5) °C. Cool the salt in a desiccator for at least 45 minutes, then dissolve (31.54 ±0.01) g in approximately 250 ml of water in a 1 l volumetric flask, and make up to the mark with water.

This solution is stable for up to 3 months when stored at 2°C to 8°C.

### E.4 Procedure

E.4.1 Calibration

The calibration curve is usually second order.

E.4.2 Analysis

The incubation temperature is between 20°C and 40°C. Prepare the measurement solution, which usually consists of the following:

- 6 parts by volume of chromogenic reagent, CI (E.3.3.). The incubation time after addition of chromogenic reagent, CI, is not less than 240 s;
- maximum 1 part of the sample by volume. The recommended incubation time after adding the sample to the reagent is 180 s.

After the last incubation, measure the absorbance at 480 nm.

NOTE: The typical calibration range for this method is 5 mg/l $CI^-$ to 400 mg/l $CI^-$.

## 6.7 Appendix F
## Definition of orthophosphate

### F.1 Principle

Phosphate reacts with molybdate and antimony potassium tartrate in an acidic medium. The complex thus formed turns dark brown upon reduction with ascorbic acid. The orthophosphate content is measured at 880 nm.

NOTE: This method is based on the same chemistry as ISO 6878.

### F.2 Interference

Arsenate has a similar colour to orthophosphate. These interferences can be eliminated by reducing arsenate to arsenite. High concentrations of silicate (> 5 mg/l), sulfide (> 2 mg/l), nitrite (> 3 mg/l), chromium, iron, and copper (> 10 mg/l) may also interfere. If any of these interfering substances are suspected in the samples, their concentrations should be determined before analysis.

### F.3 Reagents

F.3.1 Ammonium molybdate solution, ρ=40 g/l.

In a 100 ml volumetric flask, dissolve (4.0 ± 0.1) g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$] in 100 ml of water. This solution will keep for 1 month if stored in a polyethene bottle at 2 °C to 8 °C.

F.3.2 Antimony potassium tartrate solution, ρ = 3.2 g/l.

In a 50 ml volumetric flask, dissolve (0.16 ±0.01) g of potassium antimony(III) oxide trihydrate [$C_8H_4K_2O_{12}Sb_2\cdot 3H_2O$] in 50 ml of water. This solution will keep for 2 months if stored in a polyethene bottle at 2 °C to 8 °C.

F.3.3 Sulfuric acid solution, ρ = ($H_2SO_4$) approximately 250 g/l.

Carefully add (70±2) ml of concentrated sulfuric acid [$H_2SO_4$] to 400 ml of water in a 500 ml beaker and make up to 500 ml. This solution is stable for 1 year if stored at room temperature.

F.3.4 Ascorbic acid solution, ρ = 18 g/l.

In a 250 ml volumetric flask, dissolve (4.5 ± 0.1) g of ascorbic acid [$C_6H_8O_6$] in 250 ml of water. This solution is stable for 1 week if stored in a polyethene bottle at 2 °C to 8 °C.

F.3.5 Molybdate tartrate reagent.

In a polyethene bottle, add 75 ml of ammonium molybdate solution (E.3.1) to 250 ml of sulfuric acid solution (E.3.3). Then add 25 ml of antimony potassium tartrate solution (E.3.2). This solution will keep for 2 months if stored in a polyethene bottle in a refrigerator.

F.3.6 Chromogenic reagent, $PO_4^{3-}$.

In a reagent container, mix (14 ± 0,5) ml of molybdate tartrate reagent (E.3.5) with (6 ± 0,2) ml of ascorbic acid solution (E.3.4).
Prepare the solution fresh on the day of use.

F.3.7 Primary phosphate calibration standard, ρ(P) = 100 mg/l.

Dry the potassium dihydrogen phosphate [$KH_2PO_4$] for 2 hours at (105 ±5) °C. Cool in a desiccator for 45 minutes and dissolve (0.439 ± 0.001) g in approximately 750 ml of water in a 1-litre volumetric flask. Make up to the mark with water. This solution is suitable for storage for up to 3 months at 2 °C to 8 °C.

F.3.8 Primary phosphate reference standard, ρ (P) = 30 mg/l.

Prepare a control standard using a different starting material than that used for the primary calibration standard.

For example, disodium hydrogen phosphate [$Na_2HPO_4$] can be used as a starting material. Dry the disodium hydrogen phosphate for 2 hours at (105 ± 5) °C. Cool in a desiccator for 45 minutes and dissolve (0.1375 ±0.0002) g in approximately 750 ml of water in a 1 l volumetric flask. Make up to the mark with water. This solution is suitable for storage for up to 3 months at 2 °C to 8 °C.

## F.4 Procedure

F.4.1 Sample pre-treatment

To determine the total phosphate content, the samples are first decomposed using an appropriate method.

NOTE: ISO 6878 can be used for the schedule.

F.4.2 Calibration

The calibration curve is usually first order.

F.4.3 Analysis

The incubation temperature is between 30 °C and 40 °C. Prepare the measurement solution, which generally consists of the following:

- 6 parts of the sample by volume;
- 1 part of the chromogenic reagent, $PO_4^{3-}$, to 6 parts by volume of the sample (E.3.6). Mix the solution after each addition. The recommended incubation time after adding the chromogenic reagent, $PO_4^{3-}$, is 540 s.

After incubation, measure the solution's absorbance at 880 nm.

NOTE 1: The ratio between sample and reagent must be kept constant; otherwise, the final pH value will be incorrect. This will lead to a loss of sensitivity.

NOTE 2: Absorbance can also be measured at 660 nm with lower sensitivity.

NOTE 3. The typical calibration range for this method is 0.01-1.00 mg/L P.

NOTE 4: A solution of sulphuric acid (E.3.3) diluted 1:1 with water is suitable for compensation of internal colour. See also Annexe A.

## 6.8 Appendix G

## Determination of sulfate by the turbidimetric method

### G.1 Principle

Sulfate forms a precipitate with barium chloride in an acidic medium. The solution is turbidity at 540 nm, a measure of sulfate content.

### G.2 Interference

High concentrations of carbonate, bicarbonate and chloride may interfere with the determination. Silica at concentrations > 500 mg/L will interfere. Differences may also occur with highly colored and/or turbid samples. If any of these interferences are suspected in the samples, the magnitude of the interference should be assessed before analysis.

### G.3 Reagents

G.3.1 Turbidimetric reagent.

In a beaker, dissolve approximately 0.125 g of gelatin in hot water (approximately 80 °C) and stir for at least 1 hour. Cool and transfer to a 500 mL volumetric flask. Add (5.0 ± 0.1) g of barium chloride [$BaCl_2 \cdot 2H_2O$] and (5.0 ± 0.1) g of sodium chloride [NaCl]. Then carefully add (2.5 ± 0.1) ml of concentrated hydrochloric acid and make up to the mark with water.

This solution is stable for up to 1 week when stored at 2°C to 8°C.

G.3.2 Primary calibration standard of sulfate, $\rho = 2000$ mg/L.

Dry the sodium sulfate [$Na_2SO_4$] for 2 hours at (105 ± 5) °C. Dissolve (2.957 ± 0.001) g in approximately 250 ml of water in a 1-litre volumetric flask and make up to the mark with water.

This solution is stable for 3 months when stored at 2°C to 8°C.

G.3.3 Primary sulfate reference standard, $\rho = 150$ mg/L.

Prepare a reference standard using a different starting material than that used for the primary calibration standard. For example, ammonium sulfate [$(NH_4)_2SO_4$] can be used as a starting material. Dry the ammonium sulfate for 2 hours at (105 ±5) °C. Dissolve (0.2063 ± 0.0002) g in approximately 250 ml of water in a 1 L volumetric flask and make up to the mark with water.

This solution is stable for 3 months when stored at 2°C to 8°C.

### G.4 Procedure

G.4.1 Calibration

The calibration curve is usually second order.

G.4.2 Analysis

The incubation temperature is between 20 °C and 40 °C. Prepare the measurement solution, which usually consists of the following:

- maximum 1 part of the sample by volume;
- 1 part by volume of turbidimetric reagent (G.3.1). Mix the solution after each addition.

The recommended incubation time after addition of the turbidimetric reagent is 240 s. After incubation, determine the turbidity of the measurement solution by measuring the absorbance at 540 nm.

NOTE 1: Different wavelengths can be used for turbidimetric measurement.

NOTE 2: The typical calibration range for this method is 5 mg/L $SO_4$ to 200 mg/L $SO_4$.

NOTE 3: If the sample colour is experimental, a different wavelength can be used. Alternatively, the colour can be corrected by measuring the absorbance of the sample after mixing with water in a 1:1 ratio, rather than using the turbidimetric reagent. This value is subtracted from the turbidimetric reagent value.

## 6.9 Appendix H
## Definition of silicate

### H.1 Principle

Molybdate forms a yellow silicate molybdate complex with simple silicates in acidic media. Reduction with ascorbic acid produces a yellow silicate molybdate complex. Oxalic acid is added to counteract interference caused by phosphate. The absorbance at 810 nm is a measure of silicate content. If an 810 nm filter is not available, an 820 nm or 880 nm filter may be used.

NOTE: This method will only partially remove the polymeric silicate particles. Results should be reported as molybdate-reactive silicate. If removal of all forms of silicate is desired, an alternative method may be appropriate.

### H.2 Interference

Phosphate interferes with the determination because it also forms a colored compound with molybdate. The addition of oxalic acid counteracts this effect. High concentrations of arsenic, sulfide, and ferric iron may also interfere. If the presence of any of these components in the samples is suspected, the magnitude of its influence should be assessed before analysis.

### H.3 Reagents

H.3.1 Sulphuric acid solution, C($H_2SO_4$) approximately 0.05 mol/l.

In a 1 L beaker, carefully add (2.8 ± 0.1) mL of concentrated sulfuric acid [$H_2SO_4$] to 1 L of water. This solution is stable for 6 months at room temperature.

H.3.2 Ammonium molybdate solution, $\rho = 10$ g/l.

a 250 ml volumetric flask, dissolve (2,5±0,1) g of ammonium molybdate [$(NH_4)_6Mo_7O_{24}\ 4H_2O$] in 250 ml of 0,05 mol/l sulphuric acid (H.3.1).

This solution is stable for 2 months if stored in a polyethene bottle at 2°C to 8°C.

H.3.3 Oxalic acid solution, $\rho = 50$ g/l.

In a 250 ml volumetric flask, dissolve (12.5 ± 0.2) g of oxalic acid [$C_2H_2O_4$] in 250 ml of water. This solution will keep for 2 months if stored in a polyethene bottle at 2 °C to 8 °C.

H.3.4 Ascorbic acid solution, $\rho = 18$ g/l.

In a 250 ml volumetric flask, dissolve (4.5 ± 0.1) g of ascorbic acid [$C_6H_8O_6$] in 250 ml of water. This solution is stored for 1 week in a polyethene bottle at 2 °C to 8 °C.

H.3.5 Primary calibration standard, sorbate solution, $\rho(Si)=120$ mg/l.

Dry sodium hexafluorosilicate [$Na_2SiF_6$] for 2 hours at (105 ± 5) 0°C. Dissolve (0.804 ± 0.001) g of sodium hexafluorosilicate in approximately 250 ml of water in a 1 L volumetric flask and make up to the mark with water. This solution is stable for up to 6 months if stored in a polyethene bottle at 2 °C to 8 °C.

H.3.6 Primary control standard, sorbate solution, ρ (Si) = 76.3 mg/l.

Prepare a reference standard using a different starting material than that used for the primary calibration standard. Potassium hexafluorosilicate [($K_2SiF_6$], for example, can be used as the starting material. Dry the potassium hexafluorosilicate for 2 hours at (105 ±5) °C. Dissolve (0.598 ±0.001) g in approximately 250 ml of water in a 1 L volumetric flask and make up to the mark with water. This solution is stable for up to 6 months when stored in a polyethene bottle at 2°C to 8°C.

**H.4 Procedure**

H.4.1 Calibration

The calibration curve is usually first order.

H.4.2 Analysis

The incubation temperature is between 20°C and 40°C. Prepare the measurement solution, which usually consists of the following:

- maximum 4 parts of the sample by volume;
- 2 parts by volume of ammonium molybdate solution (N.3.2).

Mix the solution after each addition. The recommended incubation time after adding the ammonium molybdate solution is 180 s.

- (1 ±0.2) parts by volume of oxalic acid solution (H.3.3). Mix the solution after each addition. The recommended incubation time after addition of the oxalic acid solution is 200 s.
- (1 ±0.2) parts by volume of ascorbic acid solution (H.3.4).

Mix the solution after each addition. The recommended incubation time after addition of the ascorbic acid solution is 500 s. After the last incubation, measure the absorbance at 810 nm. If an 810 nm filter is not available, an 820 nm or 880 nm filter may be used.

NOTE: The typical calibration range for this method is 0.05-6.00 mg/L Si.

# ANNEX I
# Chemical parameters

In accordance with Article 5 of Directive (EU) 2020/2184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (recast Drinking Water Directive), parametric values for chemical parameters are set out in Annex I, Part B.

| Chemical parameter | Parametric value | Units of measurement | Notes and conditions of use |
|---|---|---|---|
| Acrylamide | 0.10 | µg /l | The value refers to the residual monomer |
| Trumpet | 10 | µg /l | |
| Arsenic | 10 | µg /l | |
| Benzene | 1.0 | µg /l | |
| Benz (a) pyrene | 0.01 | µg /l | |
| Bisphenol A | 2.5 | µg /l | |
| Boron | 1.5 | mg/l | For desalinated water – up to 2.4 mg/l |
| Bromate | 10 | µg /l | |
| Cadmium | 5.0 | µg /l | |
| Chlorate | 0.25 | mg/l | Up to 0.70 mg/l with certain disinfection methods |
| Chlorite | 0.25 | mg/l | Up to 0.70 mg/l with certain disinfection methods |
| Chrome | 25 | µg /l | Transitional value until 12.01.2036. |
| Copper | 2.0 | mg/l | |
| Cyanides | 50 | µg /l | |
| 1,2-dichloroethane | 3.0 | µg /l | |
| Epichlorohydrin | 0.10 | µg /l | Residual monomer |
| Fluorides | 1.5 | mg/l | |
| Haloacetic acids (sum) | 60 | µg /l | The sum of five haloacetic acids |
| Lead | 5 | µg /l | 10 µg/l until 12.01.2036 |
| Mercury | 1.0 | µg /l | |
| Microcystin -LR | 1.0 | µg /l | At risk of cyanobacterial blooms |
| Nickel | 20 | µg /l | |
| Nitrates | 50 | mg/l | The formula with nitrites is used |
| Nitrites | 0.50 | mg/l | A formula with nitrates is used |
| Pesticides (each) | 0.10 | µg /l | |

|  |  |  |  |
|---|---|---|---|
| Pesticides (amount) | 0.50 | μg /l |  |
| PFAS (sum of list) | 0.10 | μg /l | List in Annexe III |
| PFAS (total) | 0.50 | μg /l |  |
| Polycyclic aromatic hydrocarbons | 0.10 | μg /l | The sum of identified PAHs |
| Selenium | 20 | μg /l | Up to 30 μg/l under regional conditions |
| Tetrachloroethene + trichloroethene | 10 | μg /l | Total value. |
| Trihalomethanes (sum) | 100 | μg /l | Sum of four TGMs |
| Uranus | 30 | μg /l |  |
| Vinyl chloride | 0.50 | μg /l | Residual monomer |

Source: Annexe I, Part B of Directive (EU) 2020/2184. Legal mandatory text published in the Official Journal of the European Union. Applies in conjunction with Article 5 of the Directive (parametric values).

# ANNEX 2

## Drinking and wastewater indicators

Table

Comparison indicators DSanPiN and Directives EU

| No. | Indicator | Unit. measurement | DSanPiN 2.2.4-171-22 | Directives EU 2020 |
|---|---|---|---|---|
| | **Sanitary and toxicological indicators** | | | |
| 1. | Aluminum** | mg/l | ≤ 0.200 | 0.2 |
| 2. | Beryllium* | mg/l | ≤ 0.0002 | |
| 3. | Boron** | mg/l | ≤ 0.500 | 1.50 |
| 4. | Bromates | mg/l | ≤ 0.010 | 0.01 |
| 5. | Cadmium** | mg/l | ≤ 0.001 | 0.005 |
| 6. | Cobalt** | mg/l | ≤ 0.100 | |
| 7. | Silicon** | mg/l | ≤ 10 | |
| 8. | Arsenic** | mg/l | ≤ 0.01 | 0.01 |
| 9. | Molybdenum** | mg/l | ≤ 0.07 | |
| 10. | Sodium** | mg/l | ≤ 200 | |
| 11. | Nickel | mg/l | ≤ 0.02 | 0.02 |
| 12. | Nitrates (by No$_3$) | mg/l | ≤ 50 | 50 |
| 13. | Nitrites** | mg/l | ≤ 0.5 | 0.50 |
| 14. | Mercury* | mg/l | ≤ 0.0005 | 0.001 |
| 15. | Lead** | mg/l | ≤ 0.01 | 0.005 |
| 16. | Selenium** | mg/l | ≤ 0.01 | 0.020 |
| 17. | Strontium** | mg/l | ≤ 7.0 | |
| 18. | Trumpet (antimony)** | mg/l | ≤ 0.005 | 0.005 |
| 19. | Fluorides ** | mg/l | 0.7- 1.5 | 1.50 |
| 20. | Chlorates | mg/l | ≤ 0.7 | 0.25 |
| 21. | Chlorites | mg/l | ≤ 0.7 | 0.25 |
| 22. | Chrome general | mg/l | ≤ 0.05 | 0.25 |
| 23. | Cyanides (general, the number of all their forms)* | mg/l | ≤ 0.05 | |
| 24. | Acrylamide | μg /l | ≤ 0.1 | |
| 25. | Polynuclear aromatic hydrocarbons (sum concentrations) | μg /l | ≤ 0.1 | 0.1 |
| 26. | Benz (a) pyrene * | μg /l | ≤ 0.005 | 0.010 |
| 27. | Benzene** | μg /l | ≤ 1.0 | 1.0 |
| 28. | Vinyl chloride | μg /l | ≤ 0.5 | 0.50 |
| 29. | Dibromochloromethane ** | μg /l | ≤ 10 | |
| 30. | 1.2 - dichloroethane ** | μg /l | ≤ 3 | 2.0 |
| 31. | Epichlorohydrin | μg /l | ≤ 0.1 | 0.10 |

| | | | | |
|---|---|---|---|---|
| 32. | Pesticides | µg /l | ≤ 0.1 | 0.1 |
| 33. | Pesticides (sum) | µg /l | ≤ 0.5 | 0.50 |
| 34. | Trihalomethanes (sum) | µg /l | ≤ 100 | 100 |
| 35. | Carbon tetrachloride ** | µg /l | ≤ 2 | |
| 36. | Trichlorethylene and tetrachlorethylene (sum) ** | µg /l | ≤ 10 | 10 |
| 37. | Formaldehyde** | mg/l | ≤ 0.05 | |
| 38. | Chloroform** | µg /l | ≤ 60 | |
| | **Physico-chemical indicators** | | | |
| 39. | General rigidity* | mmol/l | ≤ 7.0- 10.0 | |
| 40. | Copper | mg/l | ≤ 1.0 | 2.0 |
| 41. | Polyphosphates (by $PO_4^{3-}$) | mg/l | ≤ 3.5 | |
| 42. | Dry remainder* | mg/l | ≤ 1000- 1500 | |
| 43. | Chlorine residual-free | mg/l | ≤ 0.5 | |
| 44. | Petroleum products | mg/l | ≤ 0.1 | |
| 45. | Superficially active anionic substances | mg/l | ≤ 0.5 | |
| 46. | Chlorine residual bound | mg/l | ≤ 1.2 | |
| 47. | Bisphenol AND | µg /l | | 2.5 |
| 48. | Haloacetic acids ( HAAs ) | µg /l | | 60 |
| 49. | Microcystin - LR | µg /l | | 1.0 |
| 50. | PFAR general (a combination of per- and polyfluoroalkyl substances) | µg /l | | 0.50 |
| 51. | PFAR sum | µg /l | | 0.10 |
| 52. | Uranus | µg /l | | 30 |

*Note: Indicators for which standards do not coincide are highlighted in blue; new indicators in the EU are in green; “free cells” - the indicator is missing

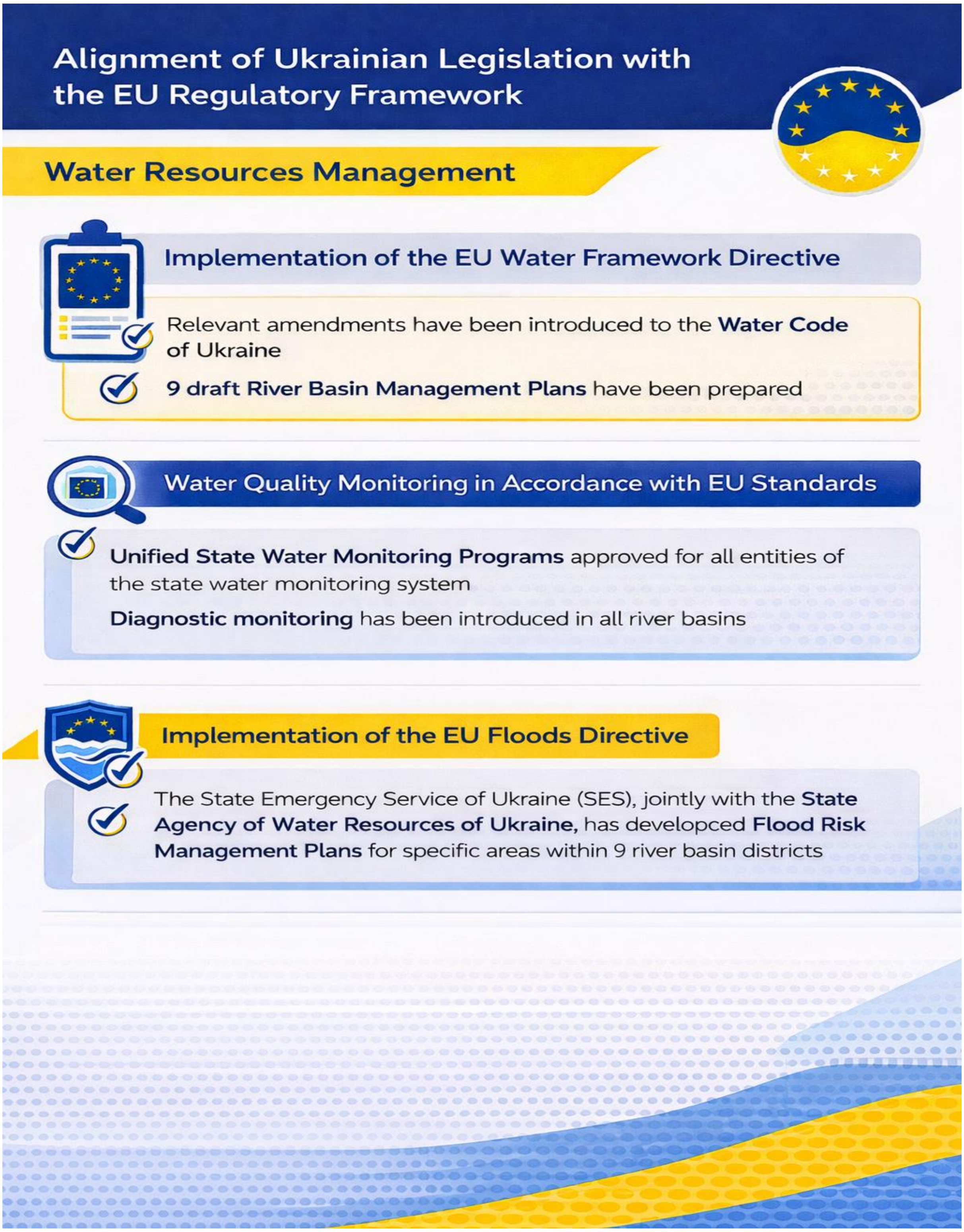
# ANNEX 3

## Requirements for the warehouse and properties sewage water, which is reset to the centralised sewage system

| No. | Indicators qualities sewage water | Unit of measurement | Maximum permissible value of the indicator |
|---|---|---|---|
| 1 | Reaction environment ( pH ) | units pH | 6.5 - 9.0 |
| 2 | Temperature | °C | +40 |
| 3 | BOD complete | mg/dm$^3$ | According to the project, no more than 350.0 |
| 4 | COD | mg/dm$^3$ | 500.0 |
| 5 | Ratio of COD: $BOD_5$ | - | < 2.5 |
| 6 | Suspended substances and substances, that pop up | mg/dm$^3$ | 300.0 |
| 7 | Nitrogen (sum nitrogen, organic and ammonium) | mg/dm$^3$ | 50.0 |
| 8 | Phosphorus general ( $P_{total}$ ) | mg/dm$^3$ | 5.0 |
| 9 | Oil and petroleum products | mg/dm$^3$ | 10.0 |
| 10 | Fats, vegetable and animal | mg/dm$^3$ | 50.0 |
| 11 | Chlorides ( $Cl^-$) | mg/dm$^3$ | 350.0* |
| 12 | Sulfates ($SO_4^{2-}$) | mg/dm$^3$ | 400.0* |
| 13 | Sulfides | mg/dm$^3$ | 1.5 |
| 14 | Anionic SPAR | mg/dm$^3$ | 10.0 |
| 15 | Phenols | mg/dm$^3$ | 0.25 |
| 16 | Iron ( Fe ) | mg/dm$^3$ | 3.0 |

# ANNEX 4

## Infographics on the agreement legislation in Ukraine with the EU regulatory framework regarding the management of water resources



Alignment of Ukrainian Legislation with the EU Regulatory Framework

**Water Resources Management**

**Implementation of the EU Water Framework Directive**

✓ Relevant amendments have been introduced to the **Water Code of Ukraine**

✓ **9 draft River Basin Management Plans** have been prepared

**Water Quality Monitoring in Accordance with EU Standards**

✓ **Unified State Water Monitoring Programs** approved for all entities of the state water monitoring system

**Diagnostic monitoring** has been introduced in all river basins

**Implementation of the EU Floods Directive**

✓ The State Emergency Service of Ukraine (SES), jointly with the **State Agency of Water Resources of Ukraine,** has developced **Flood Risk Management Plans** for specific areas within 9 river basin districts

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