

# APARATURA

## BADAWCZA I DYDAKTYCZNA

### Analytical methods applied in standards for the analysis of environmental pollution

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#### **ABSTRACT:**

The environment in which humans live is polluted with chemical substances such as elements and chemical compounds. They can often be found in ambient air, water and soil in the amounts that may have a negative impact on human health and natural environment. There are lots of methods and analytical techniques applied in the analysis of the environmental pollution. The most reliable ones are the procedures described by the Polish Standards. Currently, most Polish Standards meet European and International Standards as well. Those standards for environmental pollution analysis most often apply chromatography and atomic spectrometry.

Environmental samples usually require meticulous preparation of analytes. The general purpose of sample preparation for analysis is to change the template matrix, remove impurities and concentrate (or very rarely dilute) analytes. The method of sample preparation for analysis is often an important part of an analytic standard. The stage of sample extraction and preparation is very important. Mistakes made during this stage may never be corrected, making the sample analysis useless.

The standards applied in analysis include methods and techniques which reflect the current state of analytical knowledge. As knowledge progresses, the standards are updated on a regular basis.

# Metody analityczne stosowane w normach dotyczących analizy zanieczyszczeń środowiska

**Słowa kluczowe:** ochrona środowiska, zanieczyszczenia, procedury analityczne, chromatografia, spektroskopia

## STRESZCZENIE:

Środowisko, w którym żyje człowiek, jest zanieczyszczone substancjami chemicznymi w postaci pierwiastków i związków chemicznych. Często występują one w powietrzu atmosferycznym, wodzie i w glebie w ilościach, które mogą negatywnie wpływać na zdrowie człowieka oraz na przyrodę. Istnieje wiele metod i technik analitycznych, które są stosowane do analizy zanieczyszczeń środowiska. Najbardziej miarodajne są procedury opisane w Polskich Normach. Polskie Normy obecnie są w większości jednocześnie Normami Europejskimi i Międzynarodowymi. W tych normach do analizy zanieczyszczeń środowiska najczęściej używane są techniki chromatograficzne i spektrometrii atomowej.

Próbki środowiskowe wymagają zwykle starannego przygotowania analitów. Ogólnymi celami przygotowania próbek do analizy jest zmiana matrycy, usunięcie zanieczyszczeń i zatężenie (bardzo rzadko rozcieńczenie) analitów. Sposób przygotowania próbek do analizy jest często ważną częścią normy analitycznej. Etap pobierania i przygotowania próbek jest bardzo ważny. Na tym etapie można popełnić błędy, których nie da się naprawić, i analiza takich próbek jest bezwartościowa.

Normy stosowane do analizy obejmują metody i techniki, które odpowiadają aktualnemu stanowi wiedzy analitycznej. W miarę postępów tej wiedzy normy są uaktualniane.

## 1. INTRODUCTION

Knowledge about the type and level of pollutants plays an important role in actions aimed at protecting the environment. This knowledge should not only refer to the current state, but also to the changes in the quality and level of pollutants in time. Having this knowledge allows us to follow the changes in the environmental pollution. Information about such changes may be used to identify the emitters of pollutants and thus reduce the emissions.

Chemical analysis is the basic source of knowledge about environmental pollution of individual elements of the environment, which include ambient air, water, sewage and soil. There are a lot of analytical methods and techniques used in environmental analyses. Such analyses are conducted by the laboratories of the Inspectorate of Environmental Protection, Sanitary and Epidemiological Stations, company laboratories, e.g. sewage processing plants and water treatment plants. From time to time research shows that there are certain areas where the amount of various pollutants is considerably higher than the acceptable level. In the past sometimes analyses which produced the results were not conducted in a proper way. Therefore, it is very important

that the analyses are conducted according to reliable standardised procedures.

Reliable standardised procedures for environmental analyses are described in the Polish Standards which fall within the remit of Technical Committees (KT): KT nr 280 for Air Quality, KT nr 121 and 122 for Water Quality and KT nr 191 for Soil Chemistry.

This paper reviews the Polish Standards within the remit of individual committees, which deal with the analysis of environmental pollutants. The review presents a perspective from which factors polluting individual elements of the environment are currently analysed and what methods and analytical procedures are used for this purpose.

## 2. ANALYSIS OF POLLUTANTS IN AMBIENT AIR

### 2.1 Analysis of carbon monoxide and organic pollutants

Air pollutants can take a form of gases, vapours and dust. Each of these forms can be directly or indirectly analysed using gas or liquid chromatography. The PN-ISO 8186 Polish Standard [1] describes the procedure intended for determining carbon monoxide coming from emissions with

concentrations below  $25 \text{ mg m}^{-3}$  with gas chromatography. The procedure may also be used to determine higher carbon monoxide concentrations.

Chromatography is also applied in determining the concentration of aromatic compounds and hydrogen chlorine derivatives. [2-5] The PN-Z-04031-9 Standard [2] describes determining aniline vapours occurring in single-phase samples using gas chromatography with flame ionization detector (GC-FID). According to the standard, the detectability of aniline amounts to  $2 \text{ } \mu\text{g m}^{-3}$  of air. Benzene is another aromatic organic compound which can be determined with the GC-FID system [3]. The PN-EN 14662-2 European Standard [3] specifies the measurement of its concentration ranging from  $0.5$  to  $50 \text{ } \mu\text{g m}^{-3}$  in an air sample with a volume of  $1 \text{ m}^3$ , which is usually extracted within 24 hours [3].

Analysis of polycyclic aromatic hydrocarbons (PNAs) in the air is very important. The procedure described in the standard [4] applies to the analysis of benzo(a)pyrene (BaP) present in the particles of PM<sub>10</sub> dust. BaP is sampled from the dust extracted for 24 hours with an organic solvent, and then it is analysed with high-performance liquid chromatography with a fluorescent detector. The analysis may also be conducted with gas chromatography – mass spectrometry. The described method is applied in measuring benzo(a)pyrene with concentrations ranging from  $0.04$  to  $20 \text{ ng m}^{-3}$ , and its detectability falls below  $0.04 \text{ ng m}^{-3}$  [4].

Determination of pairs of hydrogen chloride compounds (1,2-dichloromethane, trichloroethylene and tetrachloroethylene) in ambient air is specified in the PN-Z-04237 Standard [5]. The lowest concentrations of compounds which can be determined with the described method amount to:  $15 \text{ } \mu\text{g m}^{-3}$  for dichloromethane,  $20 \text{ } \mu\text{g m}^{-3}$  for 1,2-dichloroethane,  $0.3 \text{ } \mu\text{g m}^{-3}$  for trichloroethylene and  $0.1 \text{ } \mu\text{g m}^{-3}$  for tetrachloroethylene. The determined compounds which are found in the air either in mixtures or individually are absorbed in activated charcoal, desorbed in *p*-Xylene and determined in extract with gas chromatography – electron capture detection method [5].

## 2.2 Analysis of non-organic pollutants

Atomic absorption spectroscopy (AAS) is used to analyse non-organic substances (including heavy metals) in airborne dust. Heavy metals (arsenic,

chromium, cadmium, manganese, copper, nickel and lead) and their non-organic compounds are most frequently stored in filters, diluted in a mixture of acids and then analysed [6-11]. If glass fibre filters are used, the samples are diluted with nitric (V) and hydrofluoric acid. If polytetrafluoroethylene, polyvinyl chloride and nitrocellulose filters are used, the samples may be diluted in a reflux condenser with a mixture of nitric (V) and hydrochloric acid or nitric acid (V) and hydrogen peroxide. Microwave ovens may also be used for diluting the samples [10].

The lowest possible determined concentration of copper and its compounds in 30-minute and average daily ambient air samples is specified in the PN-Z-04106-4 Polish Standard [6]. The concentration of copper amounts to  $0.3 \text{ } \mu\text{g m}^{-3}$  for temporary samples and  $0.005 \text{ } \mu\text{g m}^{-3}$  for average daily samples [6]. The method of determining the metallic concentration of nickel and its compounds in airborne dust is specified in the PN-Z-04124-4 Polish Standard [7]. According to the procedure described in the standard, the lowest concentration of nickel and its non-organic compounds can be determined with atomic absorptive spectrometry method in average daily samples as calculated for nickel and amounts to  $0.01 \text{ } \mu\text{g m}^{-3}$  [7].

The PN-Z-04125-4 Standard [8] specifies the procedure for determining metallic manganese and its non-organic compounds in airborne dust. The lowest concentration of this metal and its compounds which can be determined with AAS method as calculated for manganese in average daily samples amounts to  $0.005 \text{ } \mu\text{g m}^{-3}$  [8]. If different metals can be found in selected air samples at the same time, they can be determined in a single analytical sample [6-8].

Chromium is one of heavy metals found in airborne dust. The procedure for determining this metal and its compounds is specified in the PN-Z-04126-5 Standard [9]. The lowest possible concentration determined with atomic absorptive spectrometry method according to this standard amounts to  $0.01 \text{ } \mu\text{g m}^{-3}$  [9].

The determining of heavy metals (Pb, Cd, Cu, Cr, Mn, and Ni) and their non-organic compounds in airborne dust with AAS method was specified in the PN-Z-04254 Polish Standard [10]. The lowest concentrations of metals and their compounds in average daily samples which can be determined with the method amount to:  $0.01 \text{ } \mu\text{g m}^{-3}$  for lead,  $0.005 \text{ } \mu\text{g m}^{-3}$  for cadmium,  $0.01 \text{ } \mu\text{g m}^{-3}$  for copper,

0.01  $\mu\text{g m}^{-3}$  for chrome, 0.01  $\mu\text{g m}^{-3}$  for manganese and 0.01  $\mu\text{g m}^{-3}$  for nickel and 0.03  $\mu\text{g m}^{-3}$  for copper in 30-minute samples. Iron interference with chrome determination is eliminated during the analysis by adding a solution of lanthanum to the samples. Other metals do not interfere with the analysis [10].

The concentration of heavy metals in airborne dust can be determined by atomic absorption spectroscopy in an atomic graphite furnace (GF-AAS) and ICP-MS. The Standard PN-EN 14902 [11] specifies a standard method of determining lead, cadmium, arsenic and nickel in the PM10 fraction of airborne dust in ambient air. The standard can be applied to measure the concentration of elements with GF-AAS method in a range of: 1-4,000  $\text{ng m}^{-3}$  for lead, 0.1-50  $\text{ng m}^{-3}$  for cadmium, 0.5-350  $\text{ng m}^{-3}$  for arsenic and 2-100  $\text{ng m}^{-3}$  for nickel. The measurement of absorption with GF-AAS method for Pb should be conducted with  $\lambda = 283.2 \text{ nm}$  or  $217 \text{ nm}$ , for Cd  $\lambda = 228.8 \text{ nm}$ , for As  $\lambda = 193.7 \text{ nm}$ , and for Ni  $\lambda = 232 \text{ nm}$ . If necessary, the matrix can be modified by adding  $\text{NH}_4\text{H}_2\text{PO}_4$ ,  $\text{Mg}(\text{NO}_3)_2$  or  $\text{Pb}(\text{NO}_3)_2$ .

When applying ICP-MS method, the analysis of individual heavy metals can be performed in the following ranges: Pb 0.5-2.1  $\text{ng m}^{-3}$ , Cd 0.03-0.16  $\text{ng m}^{-3}$ , As 0.2-0.5  $\text{ng m}^{-3}$ , Ni 1.1-1.3  $\text{ng m}^{-3}$ . During the measurement of individual analytes a mass of one or more isotopes can be used. For lead, recommended isotopes are:  $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ , and internal patterns include:  $^{103}\text{Rh}$ ,  $^{85}\text{Re}$ ,  $^{209}\text{Bi}$  and  $^{175}\text{Lu}$ . For cadmium, isotope  $^{111}\text{Cd}$  and patterns  $^{89}\text{Y}$ ,  $^{103}\text{Rh}$  and  $^{111}\text{In}$  are recommended. For arsenic and nickel, isotopes  $^{75}\text{As}$  and  $^{60}\text{Ni}$  are recommended, respectively. For both elements, recommended patterns are  $^{45}\text{Sc}$ ,  $^{89}\text{Y}$  and  $^{103}\text{Rh}$  [11].

### 3. ANALYSIS OF WATER AND SEWAGE POLLUTANTS

Most analyses concern the pollutants in sewage and both surface and drinking water. There are numerous techniques applied to determine organic and non-organic pollutants in waters. As with air, chromatographic techniques and flame absorption atomic spectroscopy are of the biggest significance.

#### 3.1 Analysis of non-organic pollutants

The PN-EN ISO 14911 Standard [12] specifies a method for determining cations of lithium, so-

dium, potassium, ammonium, manganese, calcium, strontium and barium with ion chromatography (IC) with the application of conductometric detection (CD). The IC-CD technique allows for determining individual ions in the following ranges of concentrations:  $\text{Li}^+$  0.01-1  $\text{mg dm}^{-3}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$  0.1-10  $\text{mg dm}^{-3}$  and  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$  0.01-1  $\text{mg dm}^{-3}$  and  $\text{Ba}^+$  1-100  $\text{mg dm}^{-3}$ . The determining might be interfered by organic compounds, e.g. amino acids and aliphatic amines. If the mobile phase does not contain strong complexing agents such as 2,6-Pyridinedicarboxylic acid or suppression technique is not used, other cations may act as interfering agents such as  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ . During the determination of ions in ammonia and sodium, piques may overlap if there is a significant difference in concentrations of cations [12].

For determining anions dissolved in water ionic liquid chromatography with conductometric detection (CD), spectrophotometer (UV) and ampere meter (AD) can be used. The procedure specified in the PN-EN ISO 10304 standard [13] is applied to determine individual ions in the following ranges with a UV detector: chromates 0.05-50  $\text{mg dm}^{-3}$  with  $\lambda = 355 \text{ nm}$ , iodides (I) 0.1-50  $\text{mg dm}^{-3}$  with  $\lambda = 205-236 \text{ nm}$  (such a range of measurement is achieved with a CD detector, too), sulphites ( $\text{SO}_3$ ) 0.5-50  $\text{mg dm}^{-3}$  with  $\lambda = 205-220 \text{ nm}$  (with a CD detector 1-50  $\text{mg dm}^{-3}$ ), for thiocyanates ( $\text{SCN}$ ) and thiosulfates ( $\text{S}_2\text{O}_3$ ) the range of measurement amounts to 0.1-50  $\text{mg dm}^{-3}$  with  $\lambda = 205-220 \text{ nm}$ . When analysing samples containing iodides, thiocyanates and thiosulfates, it is possible to use an AD detector with a working range from approximately 0.7 to 1.1 V. Ammonium exchanges with low capacity are recommended as stationary phases. Mobile phases are usually water solutions of salts of monobasic and dibasic acids. In order to accelerate elution or decrease the pique tailing (during the analysis of highly polarised iodide, thiocyanate and thiosulfate ions), organic reagents can be added to the eluent such as 4-hydroxybenzotrile or organic solvents [13].

The IC technique applied with the abovementioned detectors is also used to determine the soluble chlorate, chloride and chlorine anions in waters with low pollution. This method allows for the measurement of individual ions with a CD detector in the following concentration ranges: chlorates 0.03-10  $\text{mg dm}^{-3}$ , chlorides

0.1-50 mg dm<sup>-3</sup> and chlorines 0.05-1 mg dm<sup>-3</sup>. The IC method with a UV detector allows for a measurement of chlorines concentration in a range of 0.1-1 mg dm<sup>-3</sup> with  $\lambda = 207-220$  nm, and with an AD detector the range amounts to 0.4-1.0 V. Organic acids or side products of disinfection interfere with the determination, as well as the presence of fluorides, carbonates, nitrites and nitrates. Moreover, when determining chlorites and chlorates, a high concentration of chlorides and bromides can also interfere with the process, but they can be removed with special exchangers [14].

In the standard flow analysis with photometric or potentiometric detection it is recommended to determine chlorides in waters [15]. Both methods can be used in the analysis of waters and sewage containing the analysed ions in concentrations ranging from 1 to 1,000 mg dm<sup>-3</sup>. Samples with a concentration higher than 1,000 mg dm<sup>-3</sup> can be analysed after being previously diluted. The potentiometric detection method can be used in turbid and coloured samples. Chemical compounds releasing thiocyanates and bromides in concentrations higher than 30 mg dm<sup>-3</sup> interfere with the determination in flow injection analysis and constant flow analysis with photometric detection and produce coloured substances with an applied agent. Another interfering factor is the natural colour of the sample. If the colour is an issue, it is recommended to dilute the sample or conduct its in line dialysis. It is recommended to filter the samples which contain particles over 100  $\mu\text{m}$ , and their pH value must range from 3 to 10. When determining with the flow method with potentiometric detection, ions creating insoluble compounds or complexes with silver can interfere with the process. If the analysed sample contains sulphides, 0.5 cm<sup>-3</sup> of hydrogen peroxide per 100 cm<sup>-3</sup> should be added and the analysis should be conducted after 5 minutes. If the sample contains ions Br<sup>-</sup> and S<sup>2-</sup> in concentrations to 0.1 g dm<sup>-3</sup> per sample, it should be mixed with a solution containing potassium bromate and nitric acid in a ratio of 1:2, and the analysis should be conducted after 10 minutes [15].

Alkali metals and alkaline earth metals present in water and sewage are most frequently analysed with AAS method [16-21]. The PN-EN ISO 7980 Standard [16] describes the procedure of determining soluble calcium and magnesium with furnace atomic absorption spectrometry (F-AAS).

The method is applied in the analysis of raw and drinking water, which contains up to 50 mg dm<sup>-3</sup> of calcium and up to 5 mg dm<sup>-3</sup> of magnesium. If air/acetylene flame and the dilution ratio of 1:10 are used, the optimum range of concentrations for the determined calcium ions amounts from 3 to 50 mg dm<sup>-3</sup>, and for magnesium ions from 0.9 to 5 mg dm<sup>-3</sup>. In order to reduce the influence of interfering factors, lanthanum chloride should be added to the water before the analysis when air/acetylene flame is used, and caesium chloride when applying nitrous oxide / acetylene flame. For calcium the measurement of absorption is conducted with  $\lambda = 422.7$  nm, and for Mg with  $\lambda = 285.2$  nm [16].

Other elements which can be determined with the F-AAS method are sodium and potassium [17-21]. For determining sodium in the sewage, the procedure described in the PN-ISO 9964-1 Standard is applied [17] and for potassium – in PN-ISO 9964-2 [18]. The mass concentration for both analysed samples should range from 5 to 50 mg dm<sup>-3</sup> [17, 18]. For determining sodium in raw and drinking water with furnace atomic absorption spectrometry, methods applied are specified in the PN-ISO 9964-1 Standard [19]. The method is used to analyse sodium in water in concentrations ranging from 5 to 50 mg dm<sup>-3</sup>. Caesium chloride should be added to the samples and the absorption measurement is conducted with  $\lambda = 589$  nm [19]. Potassium in the same range of concentrations can be analysed with the AAS method according to the standard [20]. According to the procedure described in the standard the sample is sucked directly into the air/acetylene flame and the absorption measurement is taken with a wave  $\lambda = 766.5$  nm [20].

Sodium and potassium level can be determined in water with furnace atomic emission spectrometry. The standardised procedure is applied in analysing raw and drinking water with the concentration of sodium and potassium not exceeding 10 mg dm<sup>-3</sup> [21]. If otherwise, small volume samples should be analysed. The determination of both elements is lower than 0.1 mg dm<sup>-3</sup>. When applying this method to determine analytes, ionisation interference is eliminated if suppressants are added [21].

The AAS method and other methods of sample atomisation are used to determine the level of heavy metals in waters [22-27]. The PN-EN 1233 Standard [22] specifies two procedures of de-

termining total chrome with the furnace AAS and electro-thermal atomisation AAS. The first procedure is used to analyse water and sewage when the concentration of chrome in a sample ranges from 0.5 to 20 mg dm<sup>-3</sup>. Levels below this range can be determined after careful evaporation of the acidified sample to a smaller volume, avoiding the formation of a precipitate. In order to decrease the interfering influence of the matrix, lanthanum salt should be added to the samples and absorption should be measured with  $\lambda = 357.9$  nm. The second procedure specified in the standard [22] is suitable for determining the concentration of chrome within a range from 5 to 100  $\mu\text{g dm}^{-3}$  for samples with a volume lower than 20  $\mu\text{l}$ .

The AAS method with nitrous oxide / acetylene flame atomisation is used to determine the concentration of aluminium in water with the mass concentration ranging from 5 to 100 mg dm<sup>-3</sup> [23]. Applying this method for lower concentrations is possible after careful evaporation of a sample acidified with nitric acid, until a precipitate is formed. When determining the total level of aluminium, the sample should be mineralised. However, during the mineralisation process, siliceous and oxygen aluminium compounds may not be determined quantitatively. If the concentrations of sulphates, chlorides, phosphates, sodium, potassium, magnesium, calcium, iron, nickel, cobalt and lead exceed 10,000 mg dm<sup>-3</sup>, they may interfere with the determination process. Other interferents include fluorides and cadmium with concentrations exceeding 3,000 mg dm<sup>-3</sup>, fluoroborates above 2,000 mg dm<sup>-3</sup>, titanium exceeding 1,000 mg dm<sup>-3</sup>, and silicates exceeding 200 mg dm<sup>-3</sup>. It is also recommended that the total concentration of salt in the analysed solution should not exceed 15 g dm<sup>-3</sup> and the electrical conductivity should not be higher than 2,000 mS m<sup>-1</sup>.

The second procedure described in the standard [23] which uses electro-thermal atomisation AAS is used to determine the content of aluminium in water and sewage with total concentrations ranging from 10 to 100  $\mu\text{g dm}^{-3}$ . The working range can be extended to higher concentrations by diluting the sample or using one with a smaller volume. Chlorides, sulphates, phosphates, acetates, sodium, calcium and potassium do not interfere with this method if their total concentrations do not exceed 1,000 mg dm<sup>-3</sup>. If the concentrations ex-

ceed 100 mg dm<sup>-3</sup>, silicates, 4-fluoroborates and ions of iron, copper, nickel, cobalt, cadmium and lead may interfere with the process. Fluorides decrease the signal even in a low concentration. Therefore, it is recommended to add sulphuric acid(VI), which compensates their interference in concentrations even up to 50  $\mu\text{g dm}^{-3}$ . Determination of low levels of aluminium may be interfered by its common occurrence [23].

Cadmium is another element whose content in water and sewage can be determined with the standardised F-AAS method. The procedure described in the PN-EN ISO 5961 Standard [24] can be used when the concentration of cadmium ranges from 0.05 to 1 mg dm<sup>-3</sup>. Higher concentrations can be determined after diluting the sample. The method can be used with lower concentrations after evaporating the water and acidifying the sample with nitric acid (V). Cadmium can be quantified in sewage and bottom residues after applying an appropriate mineralisation process, which prevents the formation of a precipitate. Sulphates, phosphates, chlorides, sodium, potassium, magnesium, copper and cobalt may interfere with the determination if their concentrations exceed 10,000 mg dm<sup>-3</sup>. Calcium, iron, nickel and titanium may also interfere if their concentrations exceed 3,000 mg dm<sup>-3</sup> and silicon is an interferent if its concentration is above 1,000 mg dm<sup>-3</sup>. The total concentration of salt in the analysed solution should be lower than 15 g dm<sup>-3</sup>, and electrical conductivity should be below 20,000 mS m<sup>-1</sup>. Cadmium can be determined in water with the electro-thermal atomisation AAS method if the concentration ranges from 0.3 to 3  $\mu\text{g dm}^{-3}$  with a 10  $\mu\text{l}$  dose. Ions of iron, copper, nickel, cobalt and lead interfere if their concentrations exceed 100 mg dm<sup>-3</sup>. Sulphates, chlorides, sodium, potassium and magnesium do not interfere with the analysis if their mass concentrations do not exceed 1,000 mg dm<sup>-3</sup> [24].

The PN-ISO 9965 Standard [25] specifies the method for quantifying the level of selenium in organic compounds in drinking, underground and surface water with hydride generation atomic absorption spectroscopy (HG-AAS). The procedure can be applied for concentrations ranging from 1 to 10  $\mu\text{g dm}^{-3}$ . Higher concentrations of selenium can be determined after diluting the sample. In this method only Se (IV) forms quantitative hydride. In order to avoid unreliable results, all ions of selenium occurring in the sample should be in

the oxidation state IV and absorption should be measured with  $\lambda = 196 \text{ nm}$  [25].

The PN-EN ISO 15586 Standard [26] specifies the procedure of determining trace content of elements (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Tl, V and Zn) in surface, underground and drinking water, sewage and residue with the GF-AAS method. The limit of detection in each element depends on the sample matrix and the device used, as well as on the used chemical modifiers. If the water sample has an uncomplicated matrix, the limit of detection comes near the limits of detection of the spectrometer. The lowest acceptable values of limits of detection and optimal ranges of concentrations of individual elements in samples with a volume of 20  $\mu\text{l}$  can be found in Table 1 [26].

**Table 1** Limits of detection and optimal ranges of concentrations of individual elements [26]

Analyte	Limit of detection value [ $\mu\text{g dm}^{-3}$ ]	Range of concentrations [ $\mu\text{g dm}^{-3}$ ]
Silver	0.2	1-10
Aluminum	1	6-60
Arsenic	1	10-100
Cadmium	0.1	0.4-4
Cobalt	1	6-60
Chrome	1	6-60
Copper	0.5	3-30
Iron	0.5	3-30
Manganese	0.5	1.5-15
Molybdenum	1	6-50
Nickel	1	7-70
Lead	1	10-100
Selenium	2	15-150
Titanium	2	20-200
Vanadium	2	20-200
Zinc	0.5	0.5-5

Some samples, most frequently of sewage, and solutions of mineralised residue in which metals are determined in accordance with the Standard [26] can include significant amounts of interfering substances. High concentrations of chlorides may have a negative impact on the results of the analysis, as a consequence of increased volatility of elements and their losses during the thermal processing of the sample. The negative impact of the matrix can be partially or even totally eliminated by optimising the temperature programme, using

pipes and platforms coated with pyrolytic graphite, using chemical modifiers, using the method of pattern addition, and correcting the background. The PN-ISO 8288 Standard [27] describes three procedures of content analysis for cobalt, nickel, zinc, cadmium and lead with the F-AAS method. The first procedure is the method of direct determination of the abovementioned elements after chelating with ammonium pyrrolidinedithiocarbamate (APDC) and extracting with methyl isobutyl ketone (MIBK). The method is applied when the concentrations of the determined elements are relatively high and no interfering agents occur. This method should not be applied with complex samples of unknown origin or samples with a high concentration of dissolved salts. The first procedure should be applied when determining the level of cobalt and nickel in the range of 0.1-10  $\text{mg dm}^{-3}$ , copper 0.05-6  $\text{mg dm}^{-3}$ , cadmium 0.02-2  $\text{mg dm}^{-3}$  and lead 0.2-10  $\text{mg dm}^{-3}$ . Depending on the kind of the device, the ranges of concentrations of elements may slightly differ. The second procedure is used for quantifying the content of six metals with the F-AAS method after chelating (APDC) and extraction (MIBK), and the third one is used for quantifying the content with the F-AAS method after chelating with hexamethylene ammonium – hexamethylene dithiocarbamate (HMA-HMDC) and extraction with diisobutyl ketone (DIBK) and xylene. Both procedures are used when the concentrations of determined elements in the sample exceed 0.05  $\mu\text{g dm}^{-3}$ . The second procedure can be used for determining the level of cobalt, cadmium and nickel in the range of 1-200  $\mu\text{g dm}^{-3}$ , zinc and cadmium in the range of 0.5-50  $\mu\text{g dm}^{-3}$  and lead in the range of 5-200  $\mu\text{g dm}^{-3}$ . The third method is applied if the concentration of cobalt, nickel and copper ranges from 0.5 to 100  $\mu\text{g dm}^{-3}$ , zinc and cadmium from 0.2 to 50  $\mu\text{g dm}^{-3}$  and lead from 2 to 200  $\mu\text{g dm}^{-3}$ . The ranges of concentrations for the abovementioned elements are given for analytic samples with a volume ratio to the extracting solvent 20:1 [27].

### 3.2 Analysis of organic pollutants

Gas and liquid chromatography (HPLC) is used to analyse organic compounds in waters. The PN-EN ISO 23631 Standard [28] specifies the determination of derivatives of halogen acids (dalapon and trichloroacetic acid – TCA) in underground and drinking water with the GC-ECD or GC-MS

methods. Samples for analysis are prepared in liquid-liquid extraction and derivatization with diazomethane. Depending on the matrix, this standardised procedure may be used for analytes with concentrations ranging from 0.5 to 10  $\mu\text{g dm}^{-3}$ . The limit of detection with the GC-MS method for TCA and dalapon is approximately 0.05  $\mu\text{g dm}^{-3}$  and additionally allows for the identification of analytes. The application of the GC-ECD method allows for reducing the limit of detection [28].

There are standardised methods of analysis of organonitrogen and organophosphorus compounds such as pesticides in sewage, underground, surface and drinking waters. The PN-EN ISO 10695 Standard [29] specifies the procedure of analysis of these substances with gas chromatography method with the nitrogen-phosphorus detector. Samples of waters and sewage for analysis are prepared in liquid-liquid extraction with dichloromethane and then concentrated. The occurrence of organic substances, suspension and colloids in the amount exceeding 0.05  $\text{g dm}^{-3}$  may interfere with the analysis. These substances increase the value of the limit of detectability. For this reason surface, underground and drinking water samples in which the concentration of suspension is higher than 0.05  $\mu\text{g dm}^{-3}$  are prepared in liquid-solid extraction.

The values of limits of detection for individual chemical compounds in sewage in liquid-liquid extraction (method 1) and in drinking, underground and surface water in liquid-solid extraction (method 2) are shown in Table 2 [29].

Volatile organic compounds (VOCs), including aromatic ones, are another type of organic pollutants in waters and sewage. The PN-EN ISO 15680 Standard [30] describes the procedure of determining volatile organic compounds in water, including their extraction with the Purge and Trap technique and thermal desorption with GC. The final determination should be done with electron ionisation mass spectrometer. The limit of detectability depends largely on the type of applied detector and conditions of the analysis. The limit usually amounts to 10  $\text{ng dm}^{-3}$ . The standard is significant in determining VOCs with concentrations up to 100  $\mu\text{g dm}^{-3}$  in drinking, surface and sea water and in diluted sewage. Any chemical compound with retention time and mass spectre values close to the determined analyte may interfere with the determination [30].

**Table 2** Limits of detection for pesticides [29]

Chemical name	Limit of detection (method 1) $\mu\text{g dm}^{-3}$	Limit of detection (method 2) $\mu\text{g dm}^{-3}$
Atrazine	0.5	0.015
Fenpropimorph	1.0	0.059
Dimethoate	0.1	0.024
Vinklozolin	1.0	0.061
Metolachlor	0.5	0.060
Iso-chloridazon	0.5	0.060
Metazachlor	0.5	0.060
Simazine	0.5	0.012

Polycyclic aromatic hydrocarbons (PNAs) are common water pollutants. The PN-EN ISO 17993 Standard describes their determination with high-performance liquid chromatography with fluorescent detection, after liquid-liquid extraction with hexane [31]. The described procedure can be applied to determine the levels of naphthalene, benzo(a)pyrene, acenaphthene, phenanthrene, fluoranthene, benzo(a)anthracene, benzo(a)fluoranthene, dibenzo(a,h)anthracene, fluorene, anthracene, pyrene, chrysene, indeno (1,2,3-c,d)pyrene, benzo(ghi)perylene. PNAs can be determined in concentrations higher than 0.005  $\mu\text{g dm}^{-3}$  for drinking and underground water, and in concentrations higher than 0.01  $\mu\text{g dm}^{-3}$  in surface waters. Compounds which are fluorescent or hindering fluoridation, or any compounds which are simultaneously removed with the determined PNAs may interfere with the determination process. Moreover, an incomplete removal of solvents used for the sample preparation may result in low repeatability of retention time and splitting or halving of the piques [31].

#### 4. ANALYSIS OF SOIL POLLUTANTS

A lot of organic and non-organic pollutants, including heavy metals, can be found in soil. They can come from industrial and municipal waste and from substances used in agriculture.

##### 4.1 Analysis of organic pollutants

The PN-ISO 11264 Standard specifies the quantitative and qualitative determination of various herbicides with the RP-HPLC technique with UV detection in the soil [32]. Herbicides are extracted from soil with a mixture of acetone and water.

The extract is analysed with a chromatograph in a reversed phase with acetonitrile and water as a gradient of the mobile phase. The procedure described in the standard can be applied to determine the level of triazine, including the product of its transformation in the soil and phenylurea compounds, among other things. The limit of detectability of these compounds in dry soil amounts to approximately  $0.01 \text{ mg kg}^{-1}$  and depends on both the type of analyte and soil matrix. According to the procedure described in the PN-ISO 13877 Standard, PNAs in soil can be quantitatively analysed with the HPLC method with ultraviolet or fluorometric detectors, with fluctuating excitation and emission wavelengths [33]. If the soil is unpolluted or slightly polluted, PNAs extraction should be conducted with acetone without drying (method 1). If the soil is polluted, PNAs are extracted with toluene after drying (method 2). In 20 grams of soil extracted and during the analysis with a UV detector, the limit of detectability of individual compounds amounts from  $0.1 \text{ mg kg}^{-1}$  to even less than  $0.03 \text{ mg kg}^{-1}$ . With fluorometric detector, the limit of application of the method for a single PNA amounts to  $0.01 \text{ mg kg}^{-1}$ .

PNAs in soil can be analysed with the GC-MS technique. The method described in the PN-ISO 18287 Standard [34] can be applied for all types of soil and allows for determining PNAs from  $0.01 \text{ mg kg}^{-1}$  of dry soil. The extraction is conducted with acetone and petroleum ether.

#### 4.2 Analysis of non-organic pollutants

Heavy metals occurring in soil are analysed with standardised spectral methods. The atomic absorptive spectrometry technique is used in analysis of content of heavy metals in soil extracts. The analysis procedure including the sample preparation with aqua regia is described in standards [35, 36]. The procedures of determining the content of mercury in soil extract with the methods of cold vapour atomic absorption spectrometry (CV-AAS) and cold vapour fluorescent atomic absorptive spectrometry (CV-AFS) were described in the PN-ISO 16772 Polish Standard [35]. The limit of detection of the method amounts to at least  $0.1 \text{ mg kg}^{-1}$ , and absorption is measured with an analytic wavelength  $\lambda = 253.7 \text{ nm}$ .

For measurements conducted with both CV-AAS and CV-AFS method, the atomic absorption spectrometer should be equipped with a mercury

lamp with a hollow cathode or electro-free discharge lamp. It is also recommended that atomic fluorescence spectrometer (AFS) should be equipped with a mercury lamp with a 254 nm filter and a photomultiplier to detect fluorescent radiation [35].

According to the standard [36], flame atomic absorption spectroscopy (F-AAS) and electro-thermal atomic absorption spectroscopy (ET-AAS) are used to determine the content of cadmium, chrome, cobalt, copper, lead, manganese, nickel and zinc in soil extracts. The level of cadmium, manganese and zinc in soil extracts can be determined with the F-AAS method, as calculated for dry mass, for over  $2 \text{ mg kg}^{-1}$ , for copper for over  $5 \text{ mg kg}^{-1}$ , chrome, cobalt and nickel for over  $12 \text{ mg kg}^{-1}$ , and lead for over  $15 \text{ mg kg}^{-1}$ . For values below the abovementioned the ET-AAS method should be applied.

If chrome and manganese levels are determined with the F-AAS method in air/acetylene flame, a solution of lanthanum chloride (II) should be added to the sample. The measurement of absorption for nickel should be conducted with an analytical wavelength  $\lambda = 232 \text{ nm}$  and the spectrum width of  $0.2 \text{ nm}$  should be selected to separate the analytical line from the neighbouring non-absorbent lines. The measurement of cadmium absorption should be conducted with  $\lambda = 228.8 \text{ nm}$ , chrome with  $\lambda = 357.9 \text{ nm}$ , cobalt with  $\lambda = 240.7 \text{ nm}$ , copper with  $\lambda = 324.8 \text{ nm}$ , lead with  $\lambda = 217 \text{ nm}$ , manganese with  $\lambda = 279.5 \text{ nm}$  and zinc with  $\lambda = 213.9 \text{ nm}$ . When determining chrome levels, the main interfering agents include iron, aluminium, calcium and magnesium. When determining manganese levels, ions of iron and silicon are interfering agents. When applying the ET-AAS method, the measurement of absorption for individual elements is conducted with the same wavelengths as with AAS [36].

## 5. CONCLUSIONS

The review of current standards for analysis of environmental pollutants leads to the conclusion that there exist standards allowing for conducting numerous analyses and these standards should be applied in order to learn about the condition of our environment. Analytical procedures described in standards for the analysis of environmental organic pollutants most frequently apply chromatography, whereas for the anal-

ysis of non-organic pollutants they apply atomic spectrometry.

The review facilitates the choice of a standardised technique and analytical procedure depending on the need for an analysis of pollutants in

individual elements of the environment and the availability of analytical equipment in the laboratory. This review helps to specify the range of concentrations of pollutants, which can be determined with individual standards.

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