HYBRID SPECTROSCOPIC STUDIES ON THE PRECONCENTRATION AND DETERMINATION OF HEAVY METAL IONS: SORPTION-ATOMIC ABSORPTION SPECTROSCOPY

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ABSTRACT

This article provides a comprehensive review of spectroscopic studies focused on the determination of heavy metal ions, specifically Cu(II), Zn(II), and Fe(III), in environmental samples using preconcentration techniques prior to analysis. Particular emphasis is placed on sorption-atomic absorption spectroscopy. The results and performance characteristics of various analytical methods for heavy metal ion determination are compared. Furthermore, the comparative characteristics of different studied methodologies involving the use of various sorbents and reagents are presented.

Keywords: spectroscopy, heavy metals, sorbent, reagent, atomic absorption spectroscopy, sorption determination, immobilization, concentration copper, iron, zinc, lead, spectrophotometry.

INTRODUCTION

Scientific and technological progress continuously intensifies the anthropogenic impact on the natural environment. A significant portion of accumulated and ongoing waste can be utilized to recover both metals and other valuable components that were previously incompletely extracted. A fundamental solution for the rational use of natural resources and the protection of the environment from pollution lies in the widespread implementation of low-waste and resource-saving technologies, which would allow for a more comprehensive utilization of natural mineral resources.

Heavy metal pollution is among the most hazardous types of contamination for the Earth's biosphere, entailing diverse adverse consequences for both human health and the vital functions of living organisms. The most critical "metallic poisons" include compounds of barium, bismuth, cadmium, manganese, copper, mercury, lead, silver, thallium, chromium, zinc, as well as compounds of certain non-metals (arsenic, antimony) [1-3]. Heavy metals enter aquatic systems - such as streams, lakes, rivers, and groundwater - as a result of various human activities, including mining and industrial processes involving the use of metals or substances containing metallic contaminants [4-5].

LITERATURE REVIEW

According to the World Health Organization (WHO), environmental factors determine 20% of human health status by exerting either a direct or a provocative influence. Therefore, reducing the negative impact of environmental factors on public health is a priority for any state.

In the course of studying the chemistry of metals and their biochemical cycles in the biosphere, a dual role in physiology is observed: on one hand, most metals are essential for the normal maintenance of life; on the other hand, at elevated concentrations, they exhibit high toxicity, exerting a harmful effect on the condition and activity of living organisms [6-7].

Table 1.

Determination of heavy metal ions using spectroscopic analytical methods.

№	Analytical Method	Metal	Reagent	Sorbent	Analysis Objects	Ref.
1	Extraction absorptiometry	Cu(II)	Brilliant green	-	Industrial wastewater	[8]
2	Sorption-colorimetric and test determination	Cu(II)	Lead diethyldithiocarbamate	Silochrom S-80	Tap and sea water	[9]
3	Flow-injection photometry	Cu(II)	Hydroquinone, hydrogen peroxide	-	Natural fresh and salt waters	[10]
4	Sorption-colorimetry	Cu(II), Mn(II), Co(II), Ni(II)	-	Cation exchanger KB-2E-7 (Na-form)	-	[11]
5	Spectrophotometry	Cu(II)	4-(2′-Benzothiazolylazo-) salicylic acid	-	Pharmaceuticals, water samples	[12]
6	Solid-phase spectrophotometry	Cu(II)	Neocuproine	Polymethacrylate matrix	Drinking water	[13]
7	Photometry	Cu(II), Fe(III)	Picramine epsilon, Sulfosalicylic acid	-	Wastewater	[14]
8	Spectrophotometry	Cu(II), Fe(III)	Sulfosalicylic acid	-	Wastewater	[15]
9	ICP-OES with preconcentration	Al(III), Ca(II), Cd(II), Co(II), Cu(II), Fe(II), Fe(III), Mg(II), Ni(II), Pb(II), Sr(II)	Polyhexamethylene guanidine, Arsenazo I	Silica	Natural waters	[16]
10	ICP-OES	Zn(II), Cr(III), Cd(II), Cu(II), Ni(II), Pb(II), Fe(III), Mn(II), Mg, Ca	-	-	Surface waters	[17]
11	Ultrafiltration	Pb(II), Cu(II), Zn(II), Ni(II)	-	Bentonite, zeolite, vermiculite	Wastewater	[18]
12	Sorption determination	Zn(II)	-	Nanocrystalline akaganeite	Wastewater	[19]
13	Solid-phase spectrophotometry	Pd(II)	1-(2-pyridylazo)-2-naphthol (PAN)	Polymethacrylate matrix	Aqueous solutions	[20]
14	Sorption-precipitation immobilization of HM	Cu(II), Zn(II), Pb(II), Cd(II), Co(II), Ni(II)	-	Calcite, dolomite	Aqueous solutions	[21]
15	Sorption spectroscopy	Cu(II), Zn(II), Cd(II), Pb(II)	Rhodamine B	Clay mineral	Aqueous solutions	[22]
16	Extraction photometry	Cu(II), Hg, V, Mn, Fe(III), Co(II), Ni(II)	-	Dimercaptophenols (DP) and hydrophobic amines (Am)	Technological solutions	[23]
17	Sorption spectroscopy	Cu(II), Zn(II)		Amberlite – antipyrine-2COOH	Water bodies	[24]
18	Spectrophotometry	Cu(II), Zn(II)	-	Diethyldithiocarbamate (DDC)	Water and oil samples, pharma, food	[25]

In examining studies on the sorption-atomic absorption determination of copper and iron ions, the characteristics for determining heavy metal ions using various spectroscopic methods - incorporating different sorbents and reagents - were also studied and compared (Table 1).

SORPTION-SPECTROSCOPIC METHODS FOR THE DETERMINATION OF HEAVY METAL IONS

In the determination of trace metal ions present in various samples - such as natural and wastewater, biological samples, and alloy specimens - direct determination by various instrumental methods is often impossible due to the matrix effect and the low concentration of metal ions in the sample. Therefore, the determination of trace elements frequently requires preconcentration and/or separation of the analytes from the matrix to improve the detection limit and selectivity [26].

The determination and monitoring of metallic pollutants in the natural environment is an ongoing challenge due to their release from numerous anthropogenic sources. For this reason, a significant number of studies have been devoted to the development, modification, or optimization of analytical methodologies capable of ensuring the determination of multiple metallic pollutants in natural environments. From an analytical perspective, selecting an appropriate method is not always a straightforward task, as it depends on many factors related to the available detection equipment, required detection limits, reproducibility of the method, and potential interferences caused by the sample matrix composition. As a result of the synergistic effect of all these factors, a compromise must be sought when determining multiple analytes [27].

The sorption of Co(II), Cr(III), Mn(II), Ni(II), and Pb(II) was investigated using phytosorbents FS-728, FS-744, and FS-745, based on sawdust and rice husks modified with phosphate and primary amino groups. These sorbents quantitatively extract non-ferrous and heavy metal ions from aqueous solutions within a pH range of 3–9, with a sorption equilibrium time not exceeding 10 minutes. Desorption of metal ions is achieved using dilute inorganic acid solutions. A methodology for the sorption-atomic emission determination of metals in natural and industrial waters has been developed, involving sorption preconcentration, elution of the sorbed elements, and their subsequent determination in the desorbing solution [28].

The possibilities of sorption-spectroscopic determination of total rare earth elements (REEs) were studied using La, Gd, and Yb as representatives of the beginning, middle, and end of the REE series. Determination is performed following sorption from solutions at pH 3 onto polyacrylonitrile fibers filled with the Chel 100 ion exchanger, followed by complexation with chlorophosphonazo III. A dynamic variant of the sorption-spectroscopic determination of the sum of La, Gd, and Yb was developed within a concentration range of 5–30 mg/mL, with a limit of determination of 3 mg/mL. The method was validated through the analysis of model solutions of $CaCl_2$, $FeCl_3$ and $TiCl_4$, with $Sr < 0.2$ [29].

A sensitive and simple electrothermal atomic absorption spectrometry (ETAAS) method was developed for the determination of Cr(III) following separation/preconcentration on a microcolumn packed with nano-sized zirconium phosphate. Total chromium was determined after the reduction of Cr(VI) to Cr(III) using 10% (w/v) aqueous ascorbic acid. The detection limit for Cr(III) was 1,5 ng/L with an enrichment factor of 300. The static adsorption capacity of the sorbent for Cr(III) was 9.34 mg/g. The relative standard deviation (RSD) was 3,2% ($n = 7$, $c = 10$ ng/mL). The method was successfully applied to the determination of Cr(III) and Cr(VI) in natural water samples [30].

A new online flow-injection solid-phase extraction method was developed for the determination of chromium(VI) and lead using flame atomic absorption spectrometry (FAAS). The use of hydrophobic polychlorotrifluoroethylene (PCTFE) beads as an adsorbent in an online preconcentration system was evaluated. Effective formation of ammonium pyrrolidine dithiocarbamate complexes and subsequent retention in the PCTFE column is achieved within the pH ranges of 1,0–1,6 and 1,5–3,2 for Cr(VI) and Pb(II) ions, respectively. The sorbed

analyte was efficiently eluted with isobutyl methyl ketone (IBMK) for rapid FAAS determination. The proposed packing material demonstrated excellent chemical and mechanical stability, along with fast adsorption kinetics for Cr(VI) and Pb(II), allowing for high sample flow rates of at least 15 mL/min without loss of retention efficiency [31].

A dithiooxamide-immobilized polysiloxane was utilized for the preconcentration of trace silver(I) in an aqueous matrix. The results indicated that silver(I) is selectively adsorbed from the solution within a pH range of 2,5 to 6,0. The maximum adsorption capacity of the polysiloxane was found to be 1,15 pm 0,07 mmol/g. The amount of silver(I) in model solutions and real samples (drinking water, semiconductor paste, and radio tubes) was determined using the adsorption-atomic absorption method. Under optimized conditions, the limit of quantification (LOQ) for the proposed method was 30 μg, and the calculated relative standard deviation (RSD) for 10 replicate measurements was 2,1% [32].

A new method utilizing pretreated silica gel as an adsorbent for the simultaneous preconcentration of trace Cd(II) and Pb(II) prior to flame atomic absorption spectrometry measurement was developed. The effects of pH, shaking time, elution conditions, and coexisting ions on the separation/preconcentration conditions of the analytes were investigated. Under optimized conditions, the static adsorption capacities for Cd(II) and Pb(II) were 45,5 and 27,1 μg/g, the relative standard deviations were 3,2% and 1,7% (n = 11), and the obtained detection limits were 4,25 and 0,60 ng/mL, respectively. The method was validated by analyzing GBW 07304a certified reference materials (stream sediment) and successfully applied to the analysis of various treated wastewater samples with satisfactory results [33].

Direct and sorption-atomic absorption methods have been developed for the determination of dissolved and suspended forms of Cd, Pb, and Tl in marine and river waters [34]. The proposed approach allows for the improvement of the metrological characteristics of the results when determining volatile metals in samples with a high organic matter content.

For the sorption separation and determination of Fe(III) and Fe(II), silica sequentially modified with polyhexamethylene guanidine (PHMG) and pyrocatechol-3,5-disulfonic acid (Tiron) has been proposed (SiO2–PHMG–Tiron sorbent). It was demonstrated that the sorbent quantitatively extracts Fe(III) from solutions at pH 2,5–4,0, and Fe(II) at pH 6,0–7,5, with the sorption equilibrium established in no more than 5 minutes. The use of a dynamic mode enables the quantitative separation and preconcentration of Fe(III) at pH 3,0 and Fe(II) at pH 6,0–7,0. The developed methodology was validated for the determination of Fe(II) and Fe(III) in natural artesian well waters [35].

The authors of [36] obtained sorbents based on zirconium oxide sequentially modified with polyhexamethylene guanidine, ferrozine, and ferene S. Optimal conditions for the modification of the aminated zirconium oxide surface with ferrozine and ferene S were determined. The sorption capacity for the organic reagents is 25 μg/g for ferrozine and 5 μg/g for ferene S. The synthesized sorbents quantitatively extract iron(II) from solutions within a pH range of 2,5–7,0. During sorption, intensely colored iron(II) complexes are formed on the surface of the sorbents, exhibiting a broad band in the diffuse reflectance spectrum with maxima at 560 and 600 nm for sorbents with ferrozine and ferene S functional groups, respectively. Maximum color intensity develops within 20 minutes at pH 2,5–5,0. The formation of colored complexes on the sorbent surface was utilized in developing methodologies for the sorption-photometric and test-determination of iron(II). Calibration curves are linear in the range of 0,1 to 4,0 μg/0,1 g. The detection limits for iron(II) by the sorption-photometric method, calculated using the 3 *s*-criterion, are 0,006 μg/0,1 g and 0,015 μg /0,1 g for ferrozine and ferene S functionalized sorbents, respectively. The methods were applied to determine the total iron content in natural waters. The accuracy of the techniques was validated by inductively coupled plasma atomic emission spectrometry (ICP-AES).

An atomic absorption method for the determination of Co(II) in drinking and natural waters is described, based on the preliminary preconcentration of the element using a polymer chelating sorbent, polystyrene-(azo-1)-2-hydroxy-3-carboxy-5-rhodanobenzene. The

determination is not affected by n 10^5-fold mass amounts of K and Na; n 10^4-fold amounts of Ca, Mg, Ba, and Sr; or n 10^2-fold amounts of Cu, Cd, Ni, Zn, Pb, Al, Fe, and Ti. Quantitative extraction of the element occurs under static conditions at pH 5,5–6,5. The accuracy of the methodology was verified using the standard addition method. The relative standard deviation (RSD) is 0,02–0,03 for the determination of Co(II) concentrations in the range of n 10^{-6} to n 10^{-7}%. The detection limit is 0,1 μg/L [37].

Sorbents based on aluminum, zirconium, and titanium oxides, sequentially modified with polyhexamethylene guanidine (PHMG) and bathocuproine disulfonic acid (Batocuproinesulfo), have been proposed for the sorption-photometric and test-determination of copper using the indicator tube method. Effective immobilization of the reagent on the surface of the inorganic oxides, pre-modified with PHMG, is achieved within the pH range of 3,0–7,0. The maximum surface concentration of Batocuproinesulfo on the PHMG-modified inorganic oxides is 22, 11, and 7 μmol/g for Al_2O_3, ZrO_2 and TiO_2, respectively.

During the sorption of Cu(II) in the presence of a reducing agent (hydroxylamine hydrochloride), a Cu(I) : Batocuproinesulfo = 1 : 2 complex is formed on the sorbent surface. This complex exhibits an orange color and a maximum at 490 nm in the diffuse reflectance spectra. Quantitative extraction of Cu(I) by the inorganic oxides modified with PHMG and Batocuproinesulfo is achieved from solutions at pH 6,0–7,0 and is independent of the sorbent matrix nature. The maximum color intensity of the surface Cu(I) complex is maintained within the pH range of 6,0–7,0. The formation of colored Cu(I) complexes on the sorbent surfaces was utilized to develop methodologies for its sorption-photometric determination using diffuse reflectance spectroscopy. The methodology utilizing aluminum oxide as the sorbent matrix exhibits the highest sensitivity. The detection limit for Cu(I), calculated based on the 3s-criterion, is 0,02 μg/0,1 g of sorbent. The linearity of the calibration curve is maintained within the range of 0,1–15,0 μg of Cu per 0,1 g of sorbent. Using aluminum oxide modified with PHMG and Batocuproinesulfo as a test system, a methodology for the test-determination of copper in natural waters was developed based on the length of the colored zone, with a minimum detectable concentration of 2 μg/L. The accuracy of the methods was validated using the "added-found" (recovery) method and by comparison with results obtained via an independent method - ICP-AES [38].

In study [39], a solid-phase extraction (SPE) method was developed based on the use of cobalt oxide nanoparticles (NPS Co_3O_4) as a novel nanosorbent for the preconcentration and extraction of zinc(II) ions from various real samples, followed by flame atomic absorption spectrometric determination. Under optimal conditions, the detection limit was 0,25 ng/mL, and the calibration curve was linear in the concentration range of 0,4–32 ng/mL with a correlation coefficient of 0,9951. The applicability of the developed SPE-FAAS method was evaluated by measuring zinc concentrations in various samples, including tap water, river water, well water, milk, and milk powder samples; the relative recoveries for the spiked samples ranged from 94.5% to 103,5%.

SORPTION-ATOMIC ABSORPTION METHOD FOR THE DETERMINATION OF HEAVY METAL IONS

Preliminary sorption preconcentration allows for the reduction of the detection limits of the target components by several orders of magnitude, while the use of sorbents modified with specific reagents enables enhanced analytical selectivity. The advancement of this research direction, based on the use of ion exchangers modified with selective organic reagents, is closely linked to the development of the theory and practice of producing modified sorbents and the study of the physicochemical parameters of sorption [40].

The necessity of wastewater quality control and its specific characteristics requires the availability, development, and refinement of the analytical instrument base, as well as the provision of methods for determining pollutants, including heavy metals. In study [41], the methods of elemental atomic absorption and atomic emission for the eco-analytical control of

wastewater, which are of the greatest practical interest, are characterized. Particular attention is paid to methods utilizing separation and preconcentration operations for heavy metal impurities.

The extraction of metal ions using a sorbent based on N-2-sulfoethyl chitosan with a hydrogen atom substitution degree of the amino group of 0,5 (SECH 0.5) under dynamic conditions is presented in [42]. It was demonstrated that from an ammonium-acetate buffer solution containing a range of transition and alkaline earth metal ions, SECH 0,5 selectively extracts copper(II) and silver(I) ions. A methodology for the sorption-atomic absorption determination of copper in natural and drinking waters with preliminary preconcentration on SECH 0,5 under dynamic conditions has been proposed. This method is characterized by high selectivity and allows for the determination of copper(II) within the concentration range of 0,001–0,1 mg/dm³.

Silica gel chemically modified with mercaptopropyl groups was used for the isolation and preconcentration of metal ions from highly mineralized natural waters, enabling the concentration of cadmium, copper, lead, zinc, nickel, and bismuth in both static and dynamic modes. The developed sorption-atomic-spectroscopic methodologies were applied to determine metal contents in high-salinity lake waters [43].

Data on the sorption properties of the VION KH-1 chemisorption fiber toward non-ferrous and heavy metals are presented. The possibility of group extraction of Zn(II), Cd(II), Pb(II), Co(II), Ni(II), Cu(II), Fe(III,II), and Mn(II) from solutions at pH 4-6 was demonstrated. The sorbed elements are quantitatively eluted with 1-3 M inorganic acid solutions and determined directly in the eluate using atomic spectroscopic methods. The developed sorption-atomic absorption and sorption-atomic emission (with inductively coupled plasma) methodologies were utilized for the analysis of tap and natural waters [44].

The results of the sorption preconcentration of several heavy metal ions, followed by their determination using electrothermal atomic absorption spectrometry (ETAAS) in natural and drinking waters, are provided. The processes of sorption and desorption (0,01–1 M HNO_3) of lead, copper, iron, cobalt, and manganese ions from aqueous media were optimized and investigated using nanofiber samples. These nanofibers were obtained from polyacrylonitrile (PAN) followed by targeted modification with a 1,25 M NaOH solution under heating (70°C) (designated as PAN*). The nanofibers were produced via needleless electrospinning from PAN solutions in dimethylformamide. This method allows for the production of nanomaterials with specified properties and offers several advantages, including instrumental simplicity, high energy efficiency in nanofiber production, versatility, and flexibility in controlling process parameters. The extraction recovery values (95.8–99.5%) and selectivity coefficients for competing pairs of metal ions were calculated: $\beta_{Pb/Cu}$ = 1,2; $\beta_{Pb/Co}$ = 2,8; $\beta_{Pb/Mn}$ = 3,2; $\beta_{Cu/Co}$ = 1,7; $\beta_{Cu/Mn}$ = 3,7; $\beta_{Co/Mn}$ = 2,5 [45].

A methodology has been developed for the preliminary preconcentration and subsequent sorption-atomic absorption determination of copper, cobalt, and nickel in environmental samples with varying degrees of contamination. The methodology was validated during the monitoring of heavy metal content in water, soil, and silt samples from areas of increased ecological hazard in the Kursk region [46].

A sorption-atomic absorption method has been developed for the determination of Co, Cr, Cu, Fe, Mn, and Ni in high-purity niobium (V) oxide. The method is based on the preliminary preconcentration of impurities using S, N-containing heterochain sorbents, followed by the determination of analytes via high-resolution continuum source electrothermal atomic absorption spectrometry (HR-CS-ETAAS). The extraction of Co, Cr, Cu, Fe, Mn, and Ni using OKS, MTX, and GLSh sorbents reached 100%, 80%, and 76%, respectively. The OKS sorbent, which ensured maximum analyte recovery, was selected for further studies. Sorption conditions in chloride solutions were studied and optimized across various acidities (0,1–3 M HCl). Under the established sorption and HR-CS-ETAAS analysis conditions, trace impurities of Co, Cr, Cu, Fe, Mn, and Ni were determined with a relative standard deviation (RSD) of less

than 5%. The accuracy of the results was verified using the "added-found" (recovery) method. The developed method allows for the determination of the following analyte concentrations ppm: 0,02–0,20 Co, 2,0–3,3 Cr, 0,2–1,5 Cu, 6,0–21,0 Fe, 0,6–0,8 Mn, and 2,8–3,5 Ni. The proposed methodology can be successfully applied to the determination of various trace elements in other high-purity inorganic materials [47].

In study [48], an online flow-injection procedure for the preconcentration of copper at the μg/L level was developed for industrial water analysis using a novel chelating resin and flame atomic absorption spectrometry. Amberlite XAD-2, functionalized with dithizone, was packed into a flow-injection minicolumn. Parameters such as pH, sample and eluent flow rates, and eluent concentration were optimized to ensure maximum recovery of Cu(II). The influence of coexisting ions on Cu(II) sorption was also investigated. For a preconcentration time of 180 s, the enrichment factor and detection limit were 76 and 0,6 μg/L, respectively. The resin provided a precision of 1,0% for seven consecutive determinations of 100 μg/L Cu(II). The resin remained stable for over 300 sorption-desorption cycles without a noticeable loss in efficiency. The accuracy of the preconcentration procedure was confirmed by spike recovery studies in industrial water using NIST-certified copper nitrate, yielding recoveries of over 96%. Validation was performed by analyzing a standard reference material.

A column [49] packed with Amberlite XAD-16 resin was utilized for the preconcentration and determination of the chemical forms of heavy metals, such as Cr, Ni, Cu, Cd, and Pb, in lake water samples. The concentrations of metals bound to humic substances and free metal ions were determined following their sorption-elution on the resin. Recoveries were quantitative for all investigated elements (95%). The detection limits (μg/mL) were 0,007 for Cu; 0,002 for Cd; 0,022 for Pb; 0,038 for Cr; 0,008 for Co; 0,015 for Mn; and 0,054 for Ni (n=20, 3 s). Precision values for these elements ranged from 1,3 to 2,4% (n=10).

A sensitive and selective solid-phase extraction methodology was developed for the determination of trace Cu(II), Zn(II), Pb(II), and Fe(III). Sodium dodecyl sulfate (SDS)-coated alumina, modified with meso-phenylbis(indolyl)methane (MPBIM), was utilized for the preconcentration and determination of these ions via flame atomic absorption spectrometry (FAAS). The relative standard deviation (RSD) of the method was found to be less than 3,0%. The presented methodology was successfully applied to the determination of analytes in real samples [50].

Polychlorotrifluoroethylene (PCTFE) beads were employed as a packing material for online flow-injection preconcentration and separation systems coupled with flame atomic absorption spectrometry (FAAS). Its performance characteristics were evaluated for the determination of trace copper in environmental samples. The detection limit for Cu(II) was c_L = 0,07 μg/L (corrected from μ/L or trace analysis context), with a precision of 1,8% at the 2,0 μ/L level. For the determination of lead, the detection limit was c_L = 2,7 μg/L, with a precision of 2,2% at the 40,0 μ/L level. The accuracy of the developed method was evaluated by analyzing certified reference materials and recovery measurements in spiked natural water samples [51].

The authors of [52] proposed a methodology for the determination of Cu, Hg, Cd, Pb, and Zn in freshwater, based on the preliminary preconcentration of these metals as complexes using poly-3-pyridyl-5-thioxo-4-allyl-4,5-dihydro-1H-1,2,3-triazole-1-carbodithioic acid, followed by atomic absorption measurement. The detection limits for the metals are 5, 8, 20, 5, and 20 ng/dm^3, respectively.

Polypyrrole chloride was investigated as a novel sorbent for the preconcentration of copper(II) using solid-phase extraction prior to determination by flame atomic absorption spectrometry. The sorbent demonstrated extremely high selectivity toward copper(II) in the form of an anionic chelate, i.e., Cu (Pyrocatechol Violet)$_2^{2-}$, within the pH range of 4 -7. Copper(II) in the form of this complex was selectively retained on a column containing 1,0 g of polypyrrole chloride and was quantitatively eluted with 3 mL of 2,0 mol/L nitric acid. The calibration curve was linear with a correlation coefficient of 0,999 at levels near the detection

limit and up to at least 50 g/L. When applied to the preconcentration and determination of copper in tap water, wastewater, and hot spring water, recoveries were found to be 96%, 101%, and 95%, respectively, with high precision (relative standard deviation < 4%) and a low detection limit (0.87 g/L) [53].

A sensitive and simple solid-phase extraction method for the simultaneous determination of trace toxic metals in food samples is based on the adsorption of zinc, nickel, iron, and lead onto sodium dodecyl sulfate (SDS)-coated alumina, which is also chelated with bis(2-hydroxyacetophenone)-1,3-propanediimine (BHAPN). The retained analyte ions on the modified solid phase were eluted using 8 mL of 4 M HNO_3 [54].

A simple, sensitive, and low-cost method [55] based on flow-time was developed for the online preconcentration and determination of copper, lead, and chromium(VI) at sub-mg/L levels in natural waters and biological samples using ammonium pyrrolidinedithiocarbamate and flame atomic absorption spectrometry. The detection limits were 0,2, 1,8, and 2,0 μg/L, while the precision, expressed as relative standard deviation (S_r), was 2.8% (at 10 μg/L), 3.4% (at 50 μ/L), and 3.6% (at 50 μ/L) for Cu(II), Pb(II), and Cr(VI), respectively.

In study [56], a sorption-atomic absorption method was developed for the determination of the total content of elements in natural waters. The method involves the simultaneous preconcentration of both dissolved and suspended forms directly within a multifunctional crucible atomizer packed with a diethylenetriamine tetraacetate sorbent. It was demonstrated that the proposed approach reduces matrix effects and improves the performance characteristics for the determination of elements in water samples.

A sensitive methodology has been developed for the determination of trace Cu(II) in various samples following column preconcentration by adsorption onto pulverized Amberlite XAD-4 loaded with N-benzoylphenylhydroxylamine (BPHA). Several experimental parameters, such as the XAD-4 particle size, adsorption flow rate, and sample solution pH, were optimized. The dynamic range, correlation coefficient (R_2), and detection limit obtained using the proposed methodology were 1,0–60 ng/mL, 0,9953, and 0,83 ng/mL, respectively. Based on the experimental results, it was established that the proposed methodology can be successfully applied to the determination of Cu(II) in various real samples [57].

A new chelating resin, 1-(2-pyridylazo)-2-naphthol (PAN) supported on Amberlite XAD-1180 (AXAD-1180), was prepared and utilized for the preconcentration of Cd(II), Mn(II), Ni(II), Pb(II), and Zn(II) prior to their determination by flame atomic absorption spectrometry (FAAS). The optimal pH for simultaneous retention and the best eluent for simultaneous elution were found to be pH 9,5 and 3 M HNO_3, respectively. The sorption capacity of the resin was 5,3 μg/g for Cd and 3,7 μg/g for Ni. The detection limits for Cd(II), Mn(II), Ni(II), Pb(II), and Zn(II) were 0,7, 10, 3,1, 29, and 0.8 μg/L, respectively. The influence of interfering ions on the quantitative sorption of metal ions was investigated. The concentration factors of the method ranged from 10 to 30. The obtained recoveries were quantitative (>95%). A certified reference material (GBW07605 tea sample) was analyzed to verify the accuracy of the described method. The proposed method was successfully applied to the analysis of various water samples, urea fertilizers, and tea [58].

A separation/preconcentration procedure using solid-phase extraction (SPE) was proposed for the flame atomic absorption spectrometric determination of trace copper and nickel in various samples. Analyte ions were sorbed in the form of chelates with 5-methyl-4 (2-thiazolylazo)resorcinol. The procedure allows for the determination of copper and nickel with detection limits of 1,03 and 1,90 μg/L, respectively, and a precision of 7% and 8% for copper and nickel concentrations at the 200 μg/L level. The developed method was successfully applied to the determination of copper and nickel in real samples [59].

The authors of [60] investigated and optimized the conditions for the micellar-extraction preconcentration of Cu(II) as a complex with 6,7-dihydroxy-4-methyl-2-phenylbenzopyrylium chloride into the micellar phase of the non-ionic surfactant Triton X-100. It was demonstrated that the introduction of ammonium benzoate into the system to establish a pH of 4,5, with a

Triton X-100 concentration of 0,4%, initiates the formation of the micellar phase at room temperature. A methodology for the atomic absorption determination of Cu(II) following its micellar-extraction preconcentration was developed. The calibration curve is linear in the concentration range of 5,0–213 μg/L, while the limits of detection (C_{min}) and quantification (C_{lim}) are 1,5 and 5,0 g/L, respectively. The proposed methodology was validated through the analysis of natural and drinking waters, with the relative standard deviation (s_r) not exceeding 0,04.

The parameters and characteristics of sorption-atomic absorption methods for the determination of heavy and toxic metal ions using various sorbents and reagents were studied and compared (Table 2).

Table 2.

Comparison of performance characteristics for the sorption-atomic absorption determination of various metals using different sorbents and reagents.

№	Analyte Metals	Sorbent	Reagent	Eluent	Optimal Reaction Conditions	Detection Limit (LOD)	RSD (Sr %)	Ref.
1	Cu(II), Ni(II), Co(II), Pb(II,IV)	Activated carbon	4,6-Dihydroxy-2-mercaptopyrimidine (DHMP)	HNO_3 in acetone	pH≈6	Ni^{2+} - 3,5 ng/mL; Co^{2+} - 3,4 ng/mL; Cu^{2+} - 2,9 ng/mL; Pb^{2+} - 8.4 ng/mL;	1.3 1.4 1.2 1.4	[26]
2	Cu(II), Zn(II), Cd(II)	Amberlite IRA-400 (High-basic anion exchanger)	3-[(4-antipyrine)azo]-6-[(3-sulfophenyl)azo]-chromotropic acid (Ant3SO3H)	EDTA	pH=10,0	$n.10^{-3}$ – $n.10^{-1}$ mg/L	0,01 – 0,06	[39]
3	Cu(II)	Polychlorotrifluoroethylene (PCTFE)	Diethyldithiophosphate	Isobutyl methyl ketone (IBMK)	pH=1-2	0,07 mg/L	1,8%	[51]
5	Cu(II), Hg(II), Cd(II), Pb(II), Zn(II)	Poly-3-pyridyl-5-thioxo-4-allyl-4,5-dihydro-1H-1,2,3-triazole-1-carbodithioic acid (PPTA)	-	H_2SO_4	Hg(II) - pH 1,5-2; Cd(II) - pH 3,5-4; Pb(II) - pH 3,5-4; Zn(II) - pH 6-8; Cu(II) - pH 6-8.	5 ng/dm^3 8 ng/dm^3 20 ng/dm^3 5 ng/dm^3 20 ng/dm^3	0,04-0,09 (n = 6)	[52]
6	Cu(II)	Amberlite XAD-4	N-benzoylphenylhydroxylamine (BPHA)	HCl	pH=8,0~10	2,1 ng/mL	6 %	[57]
7	Cd(II), Mn(II), Ni(II), Pb(II), Zn(II)	Amberlite XAD-1180	1-(2-Pyridylazo)-2-naphthol (PAN)	HNO_3	pH 9,5	0,7 μg/L 10 μg/L 3,1 μg/L 29 μg/L 0,8 μg/L	-	[58]
8	Cu(II)	Triton X-100 (Surfactant)	6,7-Dihydroxy-4-methyl-2-phenylbenzopyrylium chloride	-	pH 4,5	1,5 μg/L	0,04	[60]
9	Au(III)	Silica gel	Rubeanic acid	$CS(NH_2)_2$, HNO_3	pH=3,5	0,8 ng/mL	1,7%	[61]
10	Fe(III)	Octadecyl silica	Bis-(4-nitrophenylazo) salicylidine-1,3-diaminopropane (Schiff base ligand)	H_2SO_4	pH=2-4	20 (±0,7) ng/L	1,5%	[62]
11	Cu(II)	PPF-1 (Modified)	Thorin	HNO_3	pH=6-8	0,05 mg/L	3,3 %	[63]
12	Fe(III)	PPF-1 (Modified)	Sulfosalicylic acid	HNO_3	pH=2-4	0,005 - 4 μg/mL	0,033	[64]

CONCLUSIONS

In summary, environmental pollution by heavy metals remains one of the primary challenges threatening public health and living organisms, necessitating continuous monitoring and the development of cutting-edge analytical methods for their determination. We anticipate a significant surge in the development of novel matrices or their modification in the coming years, specifically aimed at enhancing selectivity for heavy metal detection.

In recent years, the preconcentration of heavy metals prior to their determination has garnered immense attention due to improved sensitivity and selectivity, lower reagent

consumption, and the rapid execution of analysis. The low concentrations of heavy metals, coupled with the insufficient sensitivity and selectivity of conventional instrumental methods, have provided the impetus for the development and hybridization of analytical techniques utilizing modified sorbents.

This review presents the recent advances in the synthesis of various sorbents and the development of sorption-spectroscopic and sorption-atomic absorption methodologies. It highlights the progress of their application for the determination of diverse metal ions - including copper, iron, zinc, lead, cadmium, chromium, and mercury - in water samples. The immobilization of various organic reagents or the modification of functional groups on the sorbent surface can significantly enhance their stability, improve analytical parameters, and increase sensitivity toward metal ions. Consequently, the application of sorption-spectroscopic and sorption-atomic absorption techniques for the determination of heavy metal ions in environmental samples will remain crucial research directions for environmental monitoring.

REFERENCES

1. Zinina, O.T. (2001) 'Influence of some heavy metals and microelements on biochemical processes in the human body', *Selected Issues of Forensic Medical Examination*, 4, pp. 99–105.
2. Madusmanova, K., Khalilova, L.M., Zhumaeva, E.Sh., Gafurova, D.A., Smanova, Z.A. and Tozhimukhamedov, Kh.S. (2022) 'Nitrosonaphthol derivatives as analytical reagents for cobalt ions', *Journal of Analytical Chemistry*, 77(1), pp. 26–34.
3. Rakhimov, S.B., Ermatova, O.A., Zhumaeva, E.Sh., Smanova, Z.A. and Ruzmetov, U.U. (2020) 'Immobilized phenylfluorone as a sensitive layer of an optical sensor for vanadium ions', *Scientific Bulletin of SamSU*, 3, pp. 49–53.
4. Usmanova, Kh.U., Bobozhonov, Kh.Sh., Zhumaeva, E.Sh. and Smanova, Z.A. (2022) 'Sensitive layers of optical sensor devices for determination of toxic metal ions', *Trends in the Development of Science and Education*, 89(1), pp. 46–52. doi:10.18411/trnio-09-2022-12.
5. Abu Kassim, N.S., Ghazali, S.A.I.S.M., Bohari, F.L. and Abidin, N.A.Z. (2022) 'Assessment of heavy metals in wastewater plant effluent and lake water by atomic absorption spectrophotometry', *Materials Today: Proceedings*, 66(1).
6. Zhumaeva, E.Sh., Smanova, Z.A., Usmanova, Kh.U. and Bobozhonov, Kh.Sh. (2022) 'Application of immobilized Eriochrome Red B for sorption–spectroscopic determination of toxic metals in waters', *Original Research*, 12(8), pp. 109–118.
7. Chernykh, N.A. and Baeva, Yu.I. (2004) 'Heavy metals and human health', *RUDN Journal of Ecology and Life Safety*, 1(10), pp. 125–134.
8. Arstamyan, Zh.M. and Mangasaryan, S.G. (2007) 'Extraction–absorptiometric determination of copper with brilliant green in natural and wastewater', *Chemical Journal of Armenia*, 60(3), p. 471.
9. Ivanov, V.M. and Kochelaeva, G.A. (2001) 'Sorption–colorimetric and test determination of copper in waters', *Moscow University Bulletin*, 42(2), pp. 103–105.
10. Mozzhukhin, A.V., Moskvin, A.L. and Khudyakov, Yu.S. (2013) 'Flow-injection photometric determination of trace copper(II) in natural waters', *Journal of Analytical Chemistry*, 68(3), p. 247.
11. Bobkova, L.A., Odnostorontseva, T.V. and Kozik, V.V. (2009) 'Sorption–colorimetric and test determination of Mn(II), Co(II), Ni(II) and Cu(II) ions in natural waters', *Polzunovsky Bulletin*, 3, pp. 209–214.
12. Hashem, E.Y., Seleim, M.M. and El-Zohry, A.M. (2011) 'Spectrophotometric determination of copper(II) in pharmaceutical, biological and water samples using 4-(2′-benzothiazolylazo)-salicylic acid', *Journal of Applied Spectroscopy*, 78(4), pp. 625–632.

13. Gavrilenko, N.A., Saranchina, N.V. and Gavrilenko, M.A. (2016) ‘Solid-phase spectrophotometric determination of copper(II) using neocuproine immobilized in a polymethacrylate matrix’, *Analytics and Control*, 20(4), pp. 330–336.
14. Varlamova, I.A., Kalugina, N.L. and Medyanik, N.L. (2007) ‘Adaptation of photometric determination of copper(II) ions with picramine epsilon for wastewater analysis of mining enterprises’, *Socio-Economic and Technical Systems*, 3, p. 5.
15. Vernigora, A.N., Volkova, N.V. and Guskova, E.N. (2017) ‘Simultaneous spectrophotometric determination of copper(II) and iron(III) as complexes with sulfosalicylic acid’, *Bulletin of Penza State University*, 2(18), pp. 85–91.
16. Losev, V.N., Buyko, O.V., Trofimchuk, A.K. and Zuy, O.N. (2015) ‘Silica sequentially modified with polyhexamethylene guanidine and Arsenazo I for preconcentration and ICP-OES determination of metals in natural waters’, *Microchemical Journal*, 123, pp. 84–89.
17. Chochorek, A., Bobrowski, A., Kiralyova, Z. and Mocak, J. (2010) ‘ICP-OES determination of select metals in surface water: a metrological study’, *Polish Journal of Environmental Studies*, 19(1), pp. 59–64.
18. Katsou, E., Malamis, S. and Haralambous, K.J. (2011) ‘Industrial wastewater pretreatment for heavy metal reduction using a sorbent-assisted ultrafiltration system’, *Chemosphere*, 82(4), pp. 557–564.
19. Deliyanni, E.A., Peleka, E.N. and Matis, K.A. (2007) ‘Removal of zinc ions from water by sorption onto iron-based nanoadsorbents’, *Journal of Hazardous Materials*, 141(1), pp. 176–184.
20. Saranchina, N.V. and Gavrilenko, N.A. (2012) ‘Solid-phase spectrophotometric determination of palladium(II) using PAN immobilized in a polymethacrylate matrix’, *Bulletin of Tomsk Polytechnic University*, 321(3), pp. 96–100.
21. Savenko, A.V. (2016) ‘Experimental modeling of immobilization of heavy metals on a carbonate sorption–sedimentation geochemical barrier’, *Geochemistry International*, 8, pp. 748–756.
22. Ramazanov, A.Sh. and Esmail, G.Q. (2015) ‘Determination of copper, zinc, cadmium and lead in water using diffuse reflectance spectroscopy’, *Analytics and Control*, 19(3), pp. 259–267.
23. Kuliev, K.A. and Verdizade, N.A. (2019) ‘Spectrophotometric determination of heavy metals in soils’, *Industrial Laboratory. Diagnostics of Materials*, 85(5), pp. 18–27.
24. Magomedov, K.E., Tataeva, S.D. and Zeynalov, R.Z. (2010) ‘Sorption preconcentration and spectroscopic determination of copper(II) and zinc(II) using Amberlite modified with an azo dye’, *Bulletin of Dagestan State University*, 6, pp. 115–120.
25. Uddin, M.N., Salam, M.A. and Hossain, M.A. (2013) ‘Spectrophotometric measurement of $Cu(DDTC)_2$ for simultaneous determination of zinc and copper’, *Chemosphere*, 90(2), pp. 366–373.
26. Ghaedi, M., Ahmadi, F. and Shokrollahi, A. (2007) ‘Simultaneous preconcentration and determination of copper, nickel, cobalt and lead by FAAS’, *Journal of Hazardous Materials*, 142, pp. 272–278.
27. Tsogas, G.Z., Giokas, D.L. and Vlessidis, A.G. (2009) ‘Graphite furnace and hydride generation AAS determination of cadmium, lead and tin traces in surface waters’, *Journal of Hazardous Materials*, 163, pp. 988–994.
28. Losev, V.N., Buyko, O.V. and Velichko, B.A. (2010) ‘Sorption–atomic emission determination of heavy metals using phytosorbents’, *Journal of Siberian Federal University*, 3(1), pp. 73–78.
29. Dedkova, V.P., Shvoeva, O.P. and Savvin, S.B. (2011) ‘Sorption–spectroscopic determination of lanthanum, gadolinium and ytterbium using chlorophosphonazo III’, *Journal of Analytical Chemistry*, 66(10), pp. 1055–1058.

30. Fan, Z. and Yang, B. (2012) ‘Speciation analysis of chromium in natural waters after preconcentration with nano-zirconium phosphate’, *Journal of Analytical Chemistry*, 67(5), pp. 499–503.
31. Anthemidis, A.N. and Koussoroplis, S.-J.V. (2007) ‘Determination of chromium(VI) and lead in water samples by on-line sorption preconcentration coupled with FAAS’, *Talanta*, 71(4), pp. 1728–1733.
32. Kholmogorova, A.S., Chernysh, M.L., Neudachina, L.K. and Puzyrev, I.S. (2020) ‘Adsorption–atomic absorption determination of silver(I) using modified polysiloxane’, *Reactive and Functional Polymers*, 152.
33. Xu, H., Wu, Y., Wang, J., Shang, X. and Jiang, X. (2013) ‘Simultaneous preconcentration of cadmium and lead using silica gel and determination by FAAS’, *Journal of Environmental Sciences*, 25, pp. 45–49.
34. Oreshkin, V.N. and Tsizin, G.I. (2008) ‘Determination of trace elements in marine and river waters by AAS using electrothermal crucible atomization’, *Journal of Analytical Chemistry*, 63(11), pp. 1164–1168.
35. Didukh, S.L. and Losev, V.N. (2017) ‘Sorption separation of Fe(III)/Fe(II) and their AES-ICP determination using Tiron-modified silica’, *Analytics and Control*, 21(4), pp. 298–306.
36. Didukh, S.L., Mukhina, A.N. and Losev, V.N. (2014) ‘Sorption–photometric and test determination of total iron using zirconium oxide-based sorbents’, *Analytics and Control*, 18(4), pp. 430–437.
37. Basargin, N.N., Oskotskaya, E.R., Karpushina, G.I. and Rozovskii, Yu.G. (2008) ‘Preconcentration and AAS determination of cobalt(II) in drinking and natural waters’, *Industrial Laboratory*, 74(9), pp. 11–13.
38. Didukh, S.L. and Losev, V.N. (2017) ‘Sorption–photometric and test determination of copper using modified inorganic oxides’, *Analytics and Control*, 21(1), pp. 49–56.
39. Abdolmohammad-Zadeh, H., Ayazi, Z. and Hosseinzadeh, S. (2020) ‘Application of Co_3O_4 nanoparticles as an efficient nanosorbent for extraction of zinc(II)’, *Microchemical Journal*, 153, 104268.
40. Zeynalov, R.Z. and Tataeva, S.D. (2013) ‘Sorption–AAS determination of Cu(II), Zn(II) and Cd(II) in drinking waters’, *Bulletin of Dagestan State University*, 1, pp. 188–193.
41. Dalnova, O.A. *et al.* (2017) ‘Modern methods for determination of heavy metals in wastewater (review)’, *Industrial Laboratory. Diagnostics of Materials*, 83(6), pp. 5–13.
42. Petrova, Yu.S. *et al.* (2015) ‘Sorption–AAS determination of copper in natural and drinking waters using sulfoethyl chitosan-based sorbent’, *Industrial Laboratory. Diagnostics of Materials*, 81(1-1), pp. 11–16.
43. Losev, V.N. *et al.* (2005) ‘Sorption–AAS and sorption–AES determination of metals using mercaptopropyl-modified silica gel’, *Analytics and Control*, 9(1), pp. 81–85.
44. Losev, V.N. *et al.* (2003) ‘Determination of heavy metals using chemosorption fiber Vion KN-1’, *Analytics and Control*, 7(3), pp. 270–275.
45. Danchuk, A.I. *et al.* (2019) ‘AAS determination of Pb(II), Cu(II), Co(II), Mn(II) and Fe(III) with electrothermal atomization after preconcentration on nanofibers’, *Industrial Laboratory. Diagnostics of Materials*, 85(12), pp. 14–19.
46. Kichigin, O.V. *et al.* (2009) ‘Sorption–AAS determination of copper, cobalt and nickel in environmental objects’, *Ecological Systems and Devices*, 5, pp. 6–9.
47. Eskina, V.V. *et al.* (2017) ‘Determination of impurities in high-purity niobium(V) oxide by high-resolution AAS after sorption preconcentration’, *Journal of Analytical Chemistry*, 72(6), pp. 562–568.
48. Saxena, R., Meena, P.L. and Tiwari, S. (2016) ‘Determination of copper in industrial water by flow injection FAAS’, *Instrumentation Science & Technology*, 44(2). doi:10.1080/10739149.2015.1089275.

49. Tokalioglu, S., Kartal, S. and Elci, L. (2000) ‘Speciation and determination of heavy metals in lake waters after sorption on Amberlite XAD-16’, *Analytical Sciences*, 16, pp. 1169–1174.
50. Ghaedi, M. *et al.* (2008) ‘FAAS determination of trace heavy metals after solid-phase extraction using SDS-coated alumina’, *Journal of Hazardous Materials*, 155(1–2), pp. 121–127.
51. Anthemidis, A.N. and Ioannou, K.I. (2006) ‘Evaluation of PCTFE as sorbent for on-line SPE and FAAS determination of copper and lead’, *Analytica Chimica Acta*, 575, pp. 126–132.
52. Sukharev, S.N. (2012) ‘Determination of heavy metals in natural waters by the sorption–AAS method’, *Journal of Water Chemistry and Technology*, 34(4), pp. 190–194.
53. Sönmez, S., Divrikli, U. and Elci, L. (2010) ‘Polypyrrole chloride for selective preconcentration of copper prior to FAAS determination’, *Talanta*, 82, pp. 939–944.
54. Ghaedi, M. *et al.* (2009) ‘FAAS determination of Zn, Ni, Fe and Pb after SPE on SDS-coated alumina’, *Journal of Hazardous Materials*, 166, pp. 1441–1448.
55. Anthemidis, A.N., Zachariadis, G.A. and Stratis, J.A. (2002) ‘On-line preconcentration and FAAS determination of Cu, Pb and Cr(VI)’, *Talanta*, 58, pp. 831–840.
56. Oreshkin, V.N. and Tsizin, G.I. (2004) ‘Determination of trace elements in natural waters by sorption–AAS with fractional evaporation’, *Journal of Analytical Chemistry*, 59(9), pp. 988–992.
57. Lee, Y.N. and Choi, H.S. (2007) ‘Determination of copper(II) after column preconcentration on Amberlite XAD-4’, *Journal of Analytical Chemistry*, 62(9), pp. 936–942.
58. Hazer, O., Kartal, S. and Tokahoglu, S. (2009) ‘Preconcentration of Cd, Mn, Ni, Pb and Zn on Amberlite XAD-1180 prior to AAS’, *Journal of Analytical Chemistry*, 64(6), pp. 627–632.
59. Tuzen, M. *et al.* (2009) ‘Preconcentration system for determination of copper and nickel in water and food samples’, *Journal of Hazardous Materials*, 162, pp. 1041–1045.
60. Snigur, D.V., Dubovyi, V.P. and Chebotarev, A.N. (2020) ‘AAS determination of copper after micellar extraction’, *Moscow University Bulletin*, 61(6), pp. 414–419.
61. Sabermahani, F., Taher, M. and Bahrami, H. (2016) ‘Preconcentration of trace gold prior to FAAS determination’, *Arabian Journal of Chemistry*, 9, pp. 1700–1705.
62. Mashhadizadeh, M.H. *et al.* (2008) ‘FAAS determination of Fe(III) after solid-phase extraction using modified C18 disks’, *Spectrochimica Acta Part B*, 63, pp. 889–892.
63. Ruzmetov, U.U., Jumayeva, E.Sh. and Smanova, Z.A. (2024) ‘Adsorption–atomic absorption determination of Cu(II) in technogenic waters’, *Journal of Analytical Chemistry*, 79(5), pp. 578–584.
64. Ruzmetov, U.U., Zhumaeva, E.Sh., Orzikulov, B.T. and Smanova, Z.A. (2023) ‘Sorption–atomic absorption determination of iron in waters’, *Industrial Laboratory. Diagnostics of Materials*, 89(9), pp. 22–30.