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Solid-phase-extraction procedures for atomic spectrometry determination of copper

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ABSTRACT

For many years, copper has found fundamental application in metallurgy and electrical industry due to its ductility and excellent electrical conductivity. Nowadays, biostatic properties of this element are exploited in fungicides and wood preservatives, and components of water-treatment agents have attracted growing interest, resulting in its spread in various areas of human life. The need for copper determination at lower and lower concentration levels requires the involvement of dedicated analytical tools. Atomic spectrometric methods are still the most frequently used, but, in some applications, both enhancement of selectivity and increase in sensitivity are required and are realized by introducing solid-phase extraction (SPE) with sorbents selective towards copper. We present the most frequently applied sorbents dedicated to copper preconcentration, new trends in the methods for modifying them and the aspect of copper speciation using sorbents. We pay special attention to construction of on-line and off-line SPE set-ups.

Contents

1. Copper in the environment

Copper is a biogenic element regulating photosynthesis, transcription of RNA or transformation of nitric compounds in plant organisms. Any reduction of copper concentration in a plant results in a decrease in plant yield. Binding copper in the form of protein complexes and their storage in intercellular canals and formation of copper sulfide on the surface of a cell membrane are protective mechanisms of plants against high concentrations of copper in the environment. Water plants, invertebrates and fishes are very sensitive to copper ions present, especially in reservoirs characterized by low salinity and low pH. In an animal organism, copper ions are components of more than 30 enzymes (e.g., ceruloplazmin, superoxide dismutase, cytochrome oxidase or tyrosinase), but long-term exposure to high concentrations of copper leads to chronic toxicosis. The function of copper in living organisms, and its deficiency or excess effects have been described in detail in numerous books [1–3] and reports [4–7].

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In the environment, copper concentration is affected by natural sources (e.g., wind-blown dust, native soils, volcanoes, forest fires and sea spray) and anthropogenic sources (e.g., wastewater, combustion of fossil fuels and wastes, wood preservation, and phosphate-fertilizer production). Due to the wide spectrum of applications of copper and its compounds, the contribution of the anthropogenic sources is especially significant.

Copper and its compounds are in common use in different areas of life (e.g., metal industry, agriculture, medicine, food industry or even cosmetics). Due to the ductility and the malleability of metallic copper, it is a very useful material in the production of pipes, valves, coins, roof covering, and rainspouts). Bronze, brass, new silver or copper-nickel guarantee a wider range of potential applications, assuring the required stiffness, malleability and strength of a manufactured product. Metallic copper is an excellent electrical conductor, widely used in the production of electric cables, electromagnets and integrated circuits.

Both copper and its compounds have biostatic properties that are exploited in fungicides, algaecides, insecticides, wood preservatives, and components of water-treatment agents. Even in the cosmetic industry, some shampoos utilize nano-copper as an anti-dandruff component. New hospital equipment containing copper (e.g., toilet seats, sets of tap handles and door push plates at the entrances to wards) is being tested to reduce microbial contamination [8]. Also, new antibacterial packings for food, containing copper, are being tested [9]. Copper complexes with chlorophyllin and chlorophyll are popular food additives, used in the food industry as coloring agents [10]. Moreover, the quality of Emmental cheese is strongly influenced by the contact of the cheese pulp with a copper vat or additives of copper compounds, resulting in modification of bacterial/enzymatic metabolic activity used during production [11].

Copper released into the environment migrates with solvents, and its bioavailability is strongly affected by pH and the presence of oxygen and organic matter. Formation of non-labile forms of copper with organic matter, sulfates, sulfites and carbonates dominates in soil. Organic soils are therefore rich in copper but the bioavailability of copper is low. There is a similar situation in soils when fertilizers (e.g., phosphates or lime) immobilize copper, periodically changing its bioavailability. In water systems, copper ions are complexed by carbonate or hydroxide anions. Formation of insoluble malachite is one of the most frequent mechanisms regulating the concentration of copper in water. Humic acids present in freshwater systems can bind more than 90% of total copper ions, while in seawater only 10% of copper is immobilized [2].

On account of many kinds of anthropogenic sources of copper and the possibility of copper accumulation in living organisms, monitoring of its content in the environment, food and drinking water is necessary. Water systems are especially sensitive to exposure to copper. Copper concentration in fresh waters is typically about 0.5–50 $\mu g{\cdot}L^{-1}$, but, near mines and industrial areas, its concentration can increase several times. Copper concentration in tap water is at the $\mu g{\cdot}L^{-1}$ level, but, when water is sampled from a copper-made installation system, the concentration of copper can reach several $mg{\cdot}L^{-1}$ just after opening the tap.

2. Determination of copper using atomic spectrometric methods

Atomic spectrometric techniques, due to their different working ranges and limits of detection (LODs), are useful tools for analysis of environmental and biological samples that vary in their levels of copper concentration. The simplest and the cheapest technique – flame atomic absorption spectrometry (FAAS) – has an LOD of several $\mu g{\cdot}L^{-1}$(Table 1). Usually, copper is atomized in an air-acetylene flame and determined at the wavelength of 324.8 nm. Typical characteristic concentration range is 70–100 $\mu g{\cdot}L^{-1}$, while the calibration working range is 0.5–5 $mg{\cdot}L^{-1}$. The characteristic concentration decreases to 25 $\mu g{\cdot}L^{-1}$ when high-sensitivity nebulizers are used. The slotted tube atom trap (STAT) extends the atom-residence time in the optical path, so the sensitivity of FAAS can be increased by a factor up to 5 [15]. This method was successfully applied to copper determination in human thyroid tissues [16] or plant leaves [17]. A further increase sensitivity was obtained when the surface of the tube was coated with nanometer silica, which captured copper ions and increased their residence time inside the STAT [18].

Table 1
Limit of detection (LOD) for copper obtained with different atomic spectrometry methods

Technique	LOD ($\mu g{\cdot}L^{-1}$)		
FAAS	3 [12]	1 [13]	1.5 [14]
ICP-OES	0.3 [12]	0.9 [13]	0.4 [14]
ET-AAS	0.07 [12]	0.02 [13]	0.014 [14]
ICP-MS	0.0001 [12]	0.001 [13]	0.0002 [14]

Sample injection directly into a nickel or quartz tube situated in the middle of a flame (flame furnace AAS, FF-AAS) also eliminated problems with incomplete sample introduction into the atomizer. FF-AAS was applied to copper determination in fruit juices [19], wines [19], beer [20] and milk [21].

Copper can also be determined by inductively-coupled plasma optical emission spectrometry (ICP-OES) at 324.8 nm. The typical LOD declared by the manufacturers is in the range 0.3–0.9 $\mu g{\cdot}L^{-1}$. As a multi-element technique, ICP-OES is often used for quality evaluation of many types of samples (e.g., plants or water). In order to reduce interference effects, a sample can be introduced into the ICP-OES spectrometer via an electrothermal vaporization (ETV) system. Evaporation of the matrix before atomization and excitation of atoms in the plasma reduces the matrix effect and improves trueness and precision. ETV-ICP-OES with solid sampling or slurry sampling was applied to determination of As, Cd, Cu, Mn, Pb, and Zn in soils and sediments [22].

The LOD is improved by using electrothermal atomic spectrometry (ET-AAS) due to the longer atom-residence time in the atomizer system. A great advantage of this technique is the possibility to determine a given element in a small (μL) sample volume, which is not available for other atomic spectrometry methods. Unfortunately, ET-AAS suffers from high background and matrix interferences. The background interferences can be eliminated using a Zeeman correction method, while the matrix interferences require application of a proper chemical modifier and temperature-program optimization designed for the sample matrix. Application of diluted nitric acid, ammonium nitrate, palladium nitrate or magnesium nitrate is typically recommended to modify a matrix. For copper determination, Lima et al. [23] proposed impregnation of tube platform with a W–Rh modifier, which remained stable for 300 determination cycles and increased the tube lifetime up to 1370 analytical measurements. ET-AAS is especially useful for analysis of the solid samples, which can be injected into graphite tubes in the form of a slurry {e.g., tablets of antibiotics [24] or plant material [25]}, often stabilized by addition of a surfactant and use of ultrasound.

The best possibility of ultra-trace determination of copper uses ICP mass spectrometry (ICP-MS) to obtain LODs lower than 1 $ng{\cdot}L^{-1}$. Copper can be observed via detection of one of the two isotopes ^{63}Cu and ^{65}Cu. However, there can potentially be interference from certain molecules (e.g., $NaAr^+$, $MgAr^+$, $SO2^+$, $PO2^+$), especially in samples of high salinity. The most popular method for reducing polyatomic interferences in copper determination is application of a dynamic reaction cell with ammonia.