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REVIEW PAPERS

MANGANESE AND ITS SPECIATION IN ENVIRONMENTAL SAMPLES USING HYPHENATED TECHNIQUES: A REVIEW

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Abstract

Manganese is one of the most frequently used materials in industry, hence its elevated levels in the surrounding environment. Manganese is an essential nutrient, important in biochemical reactions of several enzymes; on the other hand, it can cause both acute and chronic diseases (eg. manganism). The importance of manganese in living systems remains poorly explored. Manganese compounds share with certain other elements the property of being essential for life, but certain manganese species and large doses are toxic. Manganese plays an important role in iron metabolism and is required for the brain's normal function. Chemical speciation is an important subject in the environmental protection as well as in toxicological and analytical research because toxicity, availability and reactivity of trace elements depend on the chemical forms in which they occur. This study deals with effects of manganese and manganese speciation forms on living organisms, particularly in aquatic environments. The review presents manganese speciation methods using sophisticated hyphenated techniques.The hyphenated techniques, in which a separation method is coupled with multi-dimensional detectors, have become a useful alternative. These techniques allow for a qualitative and quantitative analysis of the sample composition, wherein manganese may be present in various speciation forms. The article provides many examples of the hyphenated technique application in manganese speciation analysis.

Keywords: manganese, hyphenated techniques, speciation.

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INTRODUCTION

Manganese is an essential nutrient, important in biochemical reactions of several enzymes. It plays an important role in iron metabolism and is required for proper brain function. Toxicological data indicate that it is not the total content of the element, but the share of its various forms that is frequently critical to living organisms. Therefore, knowledge of the distribution of each speciation form of an element is frequently more important than determination of its total content. The research on the biological activity and toxicity of elements on living organisms reveals elements present mostly in the ionic form. All ions of an element in the environment may be in the form of free anions, cations or ions bound in a complex with organic or inorganic ligands. Given that manganese is a highly prevalent element in the Earth's crust, is can be found in many minerals, in which it appears in the form of oxides, carbonates and silicates.The term 'speciation' has often been used to indicate the analytical activity of identifying chemical species and measuring their distribution in a particular sample or matrix (TEMPLETON et al. 2000).

Chemical speciation can be also defined as the process of determining and identifying specific chemical species or binding forms; it allows one to discern the availability and mobility of metals in order to understand their chemical behavior and fate. The term 'speciation' defines chemical species, whereas fractionation is the process of classification of an analyte or a group of analytes from a certain sample according to physical or chemical properties (TEMPLETON et al. 2000). There are many examples of manganese fractionation and determination using FAAS (POHL 2007), AAS (SALAZAR et al. 2013, DHANAKUMAR et al. 2013), ICP-MS (JABŁOŃSKA-CZAPLA et al. 2014) or ICP-AES (SHEN et al. 2007).

Mobility and biological availability of trace metals (like Mn) depend not only on their total concentration but also on the physicochemical forms in which they occur (KALEMBKIEWICZ et al. 2008).

Chemical speciation is divided into four main categories (CAROLI 1995), i.e. screening, group, distribution and individual speciation. The first type determines only the most dangerous analyte present in the examined matrix. A good example is determining tribulytin in seawater or methylmercury in tissues. In group speciation, concentration levels of a given compound group or analyzed element at different oxidation states are determined. It deals with such problems as simultaneous determinations of Cr(III) and Cr(VI); Fe(I)and Fe(III); Mn(II), Mn(IV) and Mn(VII); BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand); and elemental or organic and inorganic mercury. Distribution speciation is used for biological samples, e.g. body fluids and blood serum. The last type, i.e. individual speciation, identifies and determines all individual chemicals that contain a given element in their composition in the sample.

Substances submitted to speciation analyses can be divided into two categories. The first one is composed of substances produced and introduced into the environment by humans, and is interesting for environmental analysis. The other one comprises natural chemical compounds formed as a result of biochemical transformations in living organisms or in the environment. Thus, they are chiefly researched by biochemists and ecotoxicologists.

Although speciation analysis is relatively expensive, it is gaining more and more importance. It helps to deal with situations that require both determination of the total element content and certain consideration of various forms in which these elements occur (KOT, NAMIEŚNIK 2000). Speciation analysis is used in studies on biochemical cycles of selected chemical compounds (ŁOBIŃSKI, SZPUNAR 1999), determination of the toxicity and ecotoxicity of elements, in quality control of food (CUBADDA 2004) and pharmaceuticals (MEERMAN, SPERLING 2012), in technological process control and in clinical analytics (MICHALKE, NISCHWITZ 2010).

Toxicological data analyses involve constant lowering of analyte detection limits, down to extremely low concentration levels. Unfortunately, many methods used so far cannot provide analysts with appropriate tools to perform such procedures. For this reason, various separation and detection techniques are combined and known as the hyphenated techniques (JABŁOŃSKA-CZAPLA et al. 2014, MICHALSKI et. al. 2011).

A proper hyphenated method should be selective towards determined analytes and sensitive in a broad concentration range. It should also allow possibly the best identification of determined substances. The selection of a hyphenated method should be conditioned by the analyte nature, possible combination of various methods, demanded determination sensitivity and apparatus availability. Chromatographic methods are mainly used for separation (ELLIS, ROBERTS 1997) whereas spectroscopic techniques enable detection. Hyphenated techniques also include couplings of several chromatographic methods (PURCANO et al. 2012). Although speciation analysis is dominated by chromatographic techniques, other solutions are also applied (GONZALVES et al. 2009).

Manganese is used in the metallurgic, chemical, ceramic, textile and many other industries. Human populations lving near industrial facilities may be exposed to doses of manganese of up to 200 μg 24 h^{-1} (in air) to 12.4 mg 24 h^{-1} in plant foods consumed. Mn has many anthropogenic sources, including refuse incineration, iron and steel manufacturing, mining, and gasoline, coal and oil combustion (WILLEY et al. 2009). Manganese is one of the most frequently used materials in industry, which leads to its elevated levels present in the surrounding environment. The metal has very low toxicity, except in humans, where chronic overdose called ‘manganism’ can lead to many diseases. There is a wealth of studies indicating that excessive intake of manganese can cause nervous system damage, leading to Parkinson’s disease, and also injury of arteries and the myocardium. Increased manganese use in manufacturing and in gasoline has raised concern about Mn-induced parkinsonism (Yokel, Crossgrove 2004).

Other studies (Reaney et al. 2002, Swan 1999) verify reasons to worry about increased environmental exposure to Mn in different oxidation states [Mn(II), Mn(III), and Mn(IV)], which may arise from combustion products of the gasoline antiknock additive methycyclopentadienyl manganese tricarbonyl (MMT). Much information about the speciation of methylcyclopentadienyl manganese tricarbonyl and its derivatives can be found in Butcher (2002).

The major anthropogenic sources of environmental manganese include municipal wastewater discharge, sewage sludge, mining and mineral processing, emissions from alloy, steel and iron production, combustion of fossil fuels and, to a much lesser extent, emissions from the combustion of fuel additives. Manganese is released to air mainly as particulate matter, and the fate and transport of the particles depend on their size and density as well as on the wind velocity and direction. Some manganese compounds are readily soluble in water. Over the last hundred years, Mn exposure has changed from acute, high-level exposure conditions, responsible for the occurrence of manganism, to chronic, low-level exposure to Mn. This change may have been brought about by the improved workplace protection measures designed for workers who are at risk of potentially high Mn exposure, such as welders, smelters, workers in battery factories, etc., thus limiting cases of acute manganism. On the other hand, there is an increased chronic Mn exposure among populations living close to industrial facilities with emission of Mn containing dust or close to busy traffic routes polluted with Mn-containing car exhaust fumes from fuel with added MMT (Michalke, Fernsebner 2014).

MANGANESE EXISTS IN THE AQUATIC ENVIRONMENT

Manganese may occur in all oxidation states between 0 and +7, of which +2, +4 and +7 are the most important. In an aquatic environment, manganese exists in two main forms: Mn(II) and Mn(IV). The highest oxidation state, Mn(VII), is difficult to find in the natural environment. For Mn, the +II oxidation state is relatively stable and the metal exist as an aqua ion in solutions, except at high pH, at which hydroxide will precipitate at a higher concentration. Hydroxide is easily oxidized by air and this fact is exploited in the wet chemical method used to measure oxygen in natural waters. Because of the insolubility of the hydroxides and oxides of Mn(III), its concentration in oxidized natural waters is generally much lower than in reduced environments. For manganese, the aqua ions tend to disproportionate to Mn(II) and Mn(IV) (Mason 2013). In a natural water system, dissolved manganese will be often in the +II oxidation state. The results indicate that Mn(II) predominates in most situations and it is often the most soluble chemical species of manganese, representing about 91.3% of all manganese. Complex species were 4.46% present as carbonates, 2.96% as sulphates and less than 0.3% bounded with other anions.

The movement between these two forms occurs *via* oxidation and reduction reactions, which may be abiotic or microbially mediated. The environmental chemistry of manganese is largely governed by pH and redox conditions. Mn(II) dominates at lower pH and redox potential, with an increasing proportion of colloidal manganese oxyhydroxides above pH 5.5 in non-dystrophic waters. Concentrations of dissolved manganese in natural waters that are essentially free of anthropogenic inputs can range from 10 to >10,000 μg L^{-1}. However, dissolved manganese concentrations in natural surface waters rarely exceed 1,000 μg L^{-1} and are usually less than 200 μg L^{-1}. Manganese concentrations in river sediments ranged from 410 mg kg^{-1} to 6,700 mg kg^{-1} dry weight; sediment from an urban lake receiving inputs from industrial and residential areas as well as windborne dust from old mine dumps contained manganese at concentrations reaching 13,400 mg kg^{-1} dry weight. Sediment manganese concentrations of 100-1,000 mg kg^{-1} dry weight have been reported for intertidal mudflats. Natural (background) levels of total manganese in soil range from <1 to 4,000 mg kg^{-1} dry weight, with mean values around 300-600 mg kg^{-1} dry weight (MASON 2013). The kinetics of Mn(II) oxidation are slow in waters with pH below 8.5 (ZAW, CHISWELL 1999). The input of Mn from hydrothermal sources, accounting for about 40% of the total input, is almost as high as the one entering the ocean from riverine sources. Atmospheric inputs are not important for manganese, or any of the other crustal metals, especially Al, Fe, and Co. For most metal(loid)s, the removal to deep ocean sediments is the major and dominant sink.

The sequence of reactions involving the oxidation of Mn(II) and subsequent precipitation as manganese dioxide includes the simultaneous occurrence of several manganese forms (i.e., dissolved Mn(II), hydrous oxides of Mn(III), Mn(II) adsorbed to particulates, and Mn(II)–ligand complexes), with individual concentrations dependent on such factors as pH, inorganic carbon, organic carbon, sulfate, chloride, temperature and time. In groundwater with low oxygen levels, Mn(IV) can be reduced both chemically and bacterially to the Mn(II) oxidation state (JAUDON et al. 1989). Manganese can contaminate drinking water by permeating into groundwater (BUSCHMANN et al. 2007).

Complexes of Mn(II) are of relatively low stability; Mn(II) (aq) is a relatively weak acid (pK1 ≈10.6) but Mn(III) (aq) is a much stronger acid (pK1≈0). The availability of Mn(II) to aquatic organisms depends on speciation, e. g., ‘free’ vs. complexed or solid-bound forms. Figure 1 illustrates connections among dissolved, precipitated and adsorbed forms of Mn. Figure 2 shows the so-called ‘manganese triangle’ Complexation, oxidation, adsorption and precipitation-dissolution are the key processes. Typical manganese concentrations are: 1-130 μg L^{-1} in natural waters, 0.03-0.8 μg L^{-1} in seawaters, and up to 1 mg L^{-1} in tap water.

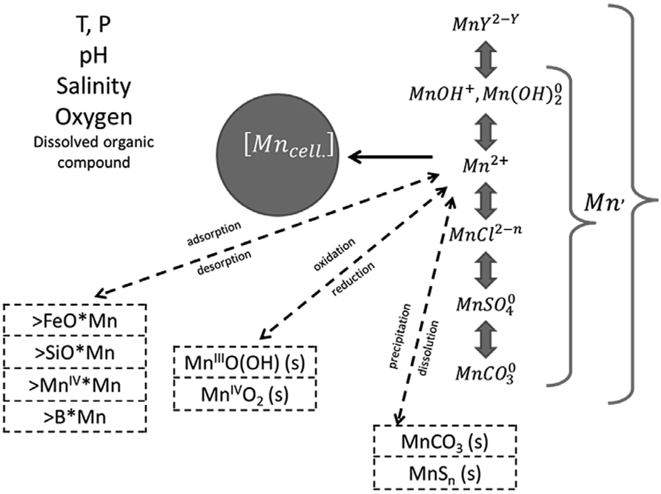

Fig. 1. Manganese speciation in natural waters (Morgan 2000)

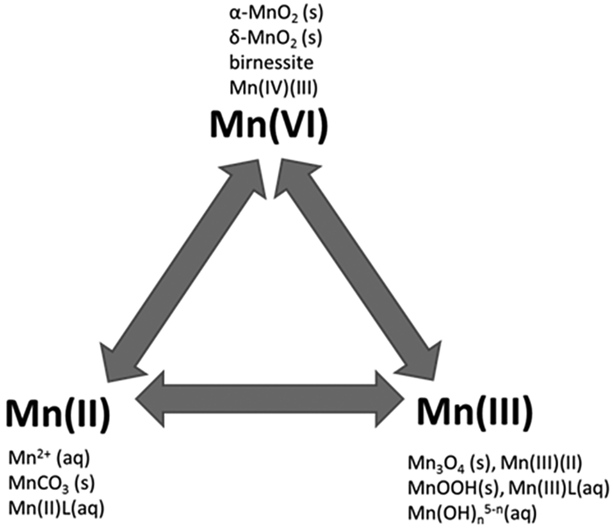

Fig. 2 The ‘manganese triagle’ for natural waters (Morgan 2000)

Divalent Mn salts are chemically most stable, and Mn(IV) (MnO_2) predominates in nature. Water-soluble $MnCl_2$ has been historically used to assess the toxicokinetic properties of manganese. In a natural water system dissolved manganese will be often in (+II) oxidation state. Mn(II) is predominate in most situation s and it is often the most soluble chemical species of manganese and represented about 91% of the manganese (Ellingsen et al. 2006, Pearson, Greenway 2005).

Dissolved, colloidal and particulate manganese concentrations were measured in rainwater (Willey 2009). It was concluded that wet deposition is an important source of soluble, stable Mn to surface seawater. However, the bioavailability of manganese from MnO_2 and Mn_3O_4 has been found to be significantly lower than that from an equal amount of $MnCl_2$ (PEARSON, GREENWAY 2005).

EXAFS (Extended X-Ray Absorption Fine Structure), XANES (X-ray Absorption Near Edge Structure) and LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) techniques were used in redox-dependent changes in manganese speciation sediment samples from the Baltic Sea in (LENZ et al. 2014). The authors investigated three major groups of Mn phases. The most abundant manganese species in the Baltic Sea sediments was Mn-carbonate.

Several publications highlight the negative role of suspension with surface-adsorbed contaminants, mainly heavy metals, in aquatic environments, while stressing the negative impact of suspensions on the reducing capacity of water bodies (ZHENG et al. 2013). Slurry is generally observed to be more toxic impurity than sediments (SABRI et al. 1993). The adverse effect of suspensions on the aquatic environment is much stronger than that of bottom sediments, as the latter are just a potential source of pollution with immobilized contaminants, whereas heavy metals present in suspensions are often a real threat. Therefore, it is important to know the content and type of ionic forms of manganese in both the sediments and suspension.

MANGANESE INFLUENCE ON LIVING ORGANISM

The importance of manganese in living systems remains poorly explored. Manganese compounds share with certain other elements the property of being essential for life, but certain manganese species and large doses are toxic. The biochemistry of manganese largely results from its association with enzymes and proteins, in which it has predominantly the valences (II) and (III). Generally, Mn(II) does not form metalloproteins but exchangeable metal complexes with proteins. Speciation of manganese in body fluids and tissues is very difficult for two reasons. Firstly, the total concentration is low, typically 0.5 $\mu g\ L^{-1}$ in serum. Secondly, the risk of contamination with exogenous manganese is very high because of the omnipresence of this element in air (dust) and on various surfaces or instruments. Manganese is an essential element for human and animal organisms. It plays an important role in the metabolism of carbohydrates, lipids, connective and osseus tissue formation, growth and reproduction. Excess manganese is particularly harmful to the nervous system. Divalent manganese compounds are approximately three times more toxic than trivalent. Long-term chronic manganese poisoning is often irreversible. High doses of Mn affect DNA replication and repair, and cause mutation (Gerber et al. 2002). Carcinogenicicty of Mn follows the order $MnCl_2 < KMnO_4 < MnSO_4$ (Pearson, Greenway 2005). The major storage sink of manganese is in the bones (about half), and excretion of Mn takes place through the liver. Excessive or long-term exposure to Mn can cause the overload of the liver. Nevertheless, it is an essential element in the human diet, and Mn deficiency can lead to dysfunctions of the central nervous system. Manganese helps to maintain healthy nerves and the immune system and to regulate blood sugar (Wang et al. 2010).

The oxidation state of manganese is thought to be an important aspect of its toxicity. Risk to the human health has been documented upon exposure to organic manganese-containing pesticides, such as manganese ethyl-bis-dithiocarbamate (Ferraz et al. 1988), inorganic manganese dust (Roels et al.1987) and also MMT used as an antiknock fuel additive in the United States and Canada. Manganese is an essential trace element for several enzymes involved in metabolic processes (Michalke et al. 2007*a*). It is needed for the normal functioning of the nervous and immune systems. Neurotoxicity is a major concern in cases of exposure to aforementioned manganese compounds (Newland et al. 1984). They are known to accumulate in the brain (Barbeau 1984), where they interfer with cellular functions (Michalke et al. 2007*b*).

The affinity of divalent Mn(II) towards an endogenous ligand is relatively low. Divalent Mn(II) does not readily complex with suphfhydryl (-SH) group or amides, and it shows little variation in its stability constants for endogenous complexing ligands such as glycine, cysteine, riboflavin and guanosine. Within the plasma, approximately 80% of Mn is bound to globulins and albumins, while a small fraction of trivalent Mn(III) is bound to transferrins (Aschner et al. 2007).

MANGANESE SPECIATION USING HYPHENATED TECHNIQUES

The choice of hyphenated techniques depends primarily on the research objective. The separation component of a coupled system becomes of particular importance when the target species have similar physicochemical properties. It may even be necessary to combine two or more separation mechanism in series to assure that a unique species arrives at the detector at a given time. The choice of a detector becomes crucial when the concentration of analyte species in a sample is very small and therefore low limits of detection are required (Łobiński, Szpunar 1999).

Many different techniques have been applied to the measurement of total Mn, including polarography (Kanchi et al. 2012), neutron activation analysis (NAA) (Chettle 2006), flame atomic absorption spectrometry (FAAS)

(Montes et al 2008) and inductively coupled plasma atomic emission spectrometry (ICP-AES) (Rodriguez-Agudelo et al. 2008) or mass spectrometry (ICP-MS) (Batista et al. 2008). Development of Mn speciation has generally involved the combination of several analytical techniques e.g. electrochemical (Boughriet et al. 1992), chromatographic (Kobayashi et al. 2007) and elemental analysis methods (Pohl, Jamroz 2011). A speciation procedure based on the coprecipitation of Mn(II) with $Zr(OH)_4$ has been developed for the investigation of levels of manganese species. The determination of manganese levels was performed by flame atomic absorption spectrometry (FAAS). Total manganese was determined after the reduction of Mn(VII) to Mn(II) by ascorbic acid (Citak et al. 2010). Speciation of dissolved and particulate manganese in the Seine River's estuary was the main subject studies by Oudanne et al. (1987). In other research, a simple solid phase extraction system based on applying the nickel-aluminium layered double hydroxide (Ni-Al LDH) as a nano-sorbent was developed for the speciation analysis of manganese by flame atomic absorption spectrometry (FAAS). The method was based on the fact that Mn(VII) oxyanion could be adsorbed on the Ni-Al(NO_3^-)LDH and/or exchanged with LDH interlayer NO_3^- ions at pH 6.0, whereas Mn(II) cations passed through an LDH-packed column without retention (Abdolmohammad-Zadeh, Sadehi 2012). Madison et al. (2011) proposed a spectrophotometric protocol for the simultaneous determination of soluble Mn(III), Mn(II) and total Mn [sum of soluble Mn(II)] in sediment (pore)waters using a water soluble meso-substitued porphyrin [α,β,γ,δ-tetrakis(4-carboxyphenyl)porphine (T(4-CP)P]. They use UV-Vis (*Ultraviolet or Visible)* spectrometry to determine Mn(III) and Mn(II) species. Similarly, UV-Vis spectrometry was used in chemical speciation of manganese in other environmental samples (Kalembkiewicz et al. 2008). The speciation of iron and manganese compounds retained by membrane filtration of dam water samples was studied via electron spectroscopy for chemical analysis (ESCA) [also known as X-ray photoelectron spectroscopy (XPS)]. Various of Mn(II), Mn(III) and Mn(IV) compounds were found to occur down the water column, namely Mn(IV) compounds predominated in the epilimnion, while both Mn(II) and Mn(IV) compounds prevailed in the epilimnion and hypolimnion (Zaw, Chiswell 1995).

Size Exclusion Chromatography (SEC) is based on a molecular sieve effect and enables species to be separated according to their size and, to a lesser extent, shape. Mn speciation in human milk was conducted using size exclusion chromatography (SEC) and strong anion exchange chromatography (SAX) with ICP-MS detection. This identified low-molecular- weight Mn-citrate species. However, it is a complex and analytically demanding method (Michalke, Schramel 2004). Liver extracts were analyzed using a mass calibrated size exclusion chromatography column coupled to ICP-MS (Quintana et al. 2005). Dietrich et al. (2012) studied the Mn transport mechanism across the blood-brain barrier into the brain using SEC-ICP-MS (size exclusion chromatography inductively coupled plasma mass spectrometry). Manganese metabolism involves numerous Mn species specifically affecting

Mn-homeostasis. Low molecular mass Mn species potentially facilitate Mn accumulation in the brain. The flow injection (FIA) of manganese in aqueous solution using the spectrophotometry (UV) method for detection was presented in other work (Kargosha, Noroozifar 2003). Capillary electrophoresis coupled to inductively coupled plasma mass spectrometry CE-ICP-MS holds great potential for speciation analysis, due to its superior efficiency, more rapid separation and small sample-size requirement as compared to chromatography (Rosen, Hieftje 2004, Dąbek-Złotorzyńska et al. 1998, Michalke 2004). CZE-ICP-MS (Capillary Zone Electrophoresis coupled to Inductively Coupled Plasma Mass Spectrometry) was used to analyze manganese speciation form in human cerebrospinal fluid (Michalke et al. 2007*c*). Michalke et al. (2007*c*) monitored 13 Mn species in CSF (cerebrospibal fluid) samples.

The couplings of HPLC to ICP-MS are technically fairly simple and consist in connecting the exit of a chromatographic column to a nebulizer. The principles of the HPLC separation mechanism used in metal speciation analysis include size exclusion, ion exchange and reversed phase chromatography. Because of the complex nature of metal-biomolecules systems, a combination of these separation mechanisms is often needed to identify correctly the trace element species. But there is an example of using HPLC-ICP-MS (high performance liquid chromatography inductively coupled plasma mass spectrometry) in manganese speciation (Kobayashi et al. 2007). Kobayashi et al. (2007) examined whether manganese was bound to the MT (metallothionein) in the liver, amd the distribution profiles of manganese, zinc, and copper in the soluble fraction of the liver of $MnCl_2$-treated mice were analyzed by a speciation analysis using HPLC-ICP-MS. The column used for the analysis (TSK gel G3000SW) can separate MT-I (metallothioneine I) and MT-II (metallothioneine II) isoforms in a single elution.

CONCLUSION

Recent research in manganese chemistry indicates that there is still much to be discovered. In particular, scientists are interested in the use of combined techniques such as HPLC-ICP-MS, IC-ICP-MS and other increasingly sophisticated connections. Due to the increasing environmental pollution and amount of anthropogenic origin manganese in the environment, there is growing interest among researchers in manganese speciation forms and in their impact on living organisms. On the other hand, manganese is an essential component of human diet, although its excess can cause a variety of diseases.

ABBREVIATIONS

AAS – Atomic Absorption Spectrometry
BOD – Biochemical Oxygen Demand
CE-ICP-MS – Capillary Electrophoresis Inductively Coupled Plasma Mass Spectrometry
COD – Chemical Oxygen Demand
CSF – Cerebrospibal Fluid
CZE-ICP-MS – Capillary Zone Electrophoresis Inductively Coupled Plasma Mass Spectrometry
ESCA – Electron Spectroscopy for Chemical Analysis
EXAFS – Extended X-Ray Absorption Fine Structure
MMT – Methycyclopentadienyl Manganese Tricarbonyl
FAAS – Flame Atomic Absorption Spectrometry
FIA – Flow Injection Analysis
HPLC-ICP-MS – High Performance Liquid Chromatography Inductively Coupled Plasma Mass Spectrometry
ICP-AES – Inductively Coupled Plasma Atomic Emission Spectrometry
ICP-MS – Inductively Coupled Plasma Mass Spectrometry
LA-ICP-MS – Laser Ablation Inductively Coupled Plasma Mass Spectrometry
NAA – Neutron Activation Analysis
SEC – Size Exclusion Chromatography
SAX – Strong Anion Exchange Chromatography
SEC-ICP-MS – Size Exclusion Chromatography Inductively Coupled Plasma Mass Spectrometry
UV-Vis – *Ultraviolet or Visible*
XANES – X-ray Absorption Near Edge Structure
XPS – X-ray Photoelectron Spectroscopy

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