SPECIATION OF TOXIC METALS

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Abstract: Speciation is the Science of Determination of the Chemical form & Oxidation State of a certain metal. One of the primary techniques to achieve this is to separate the chemical species and then measure the concentration with a coupled tool. Various separation modes of chromatography such as GC & LC (Ion Exchange, reversed-phase. Spectroscopic tools such as AAS, ICP-AES or ICP-MS are used for coupling measurements and affinity) were applied for the separation of metal species. Assessment of a metal exists in different chemical forms/species. The environmental chemistry of metals is typically complex and includes the formation of different chemical species with each metal species displaying unique chemical and physical properties. The metals speciation in abiotic and biotic environmental media strongly influences their bioavailability, bioaccumulation and toxicity to receptor organisms.

Keywords: Speciation, Toxic Metals, Chemical Speciation.

1.Introduction:

Metal species determination “METAL SPECIATION” has had a pressing necessity (Donard and Martin, 1992). In small doses, several components are essential for plant, animal and human health (Olle *et al.*, 2013). Most of these elements are taken through food, water and air into the human body. Rocks, via weathering processes, are broken down into soils on which crops and animals are raised. Through the food chain and the inhalation of dust, human health is exposed. The natural constituents of metals and metal compounds are moving between the environment, with all the habitats, the lithosphere, biosphere, and hydrosphere (Florea and Bu¨sselberg, 2006). Environmental contamination from organometallic compounds and other sources of elements is considered a major disaster, because of the high toxicity of these species (Ph. Quevauviller *et al.*, 1992). The toxicity of metal species is primarily based on their chemical composition (Ebdon *et al.*, 2001). Toxicological investigations clearly showed the various compounds – species - of the same variable might be largely different in effects that are adverse or essential (Olle *et al.*, 2013). There are ubiquitously distributed organometallic species in the environment, both natural and anthropogenic. These species are often more toxic concentration compared to the relevant inorganic compounds or compounds of metal ions (Douglas and Frech, 1993). Analytical chemists have come to realise that the sum chemical element concentrations are unable to supply details about their versatility, bioavailability and eventual availability effect on natural processes of life beings. Only knowledge of an element's chemical species is capable of providing details on potential chemical and biochemical compounds. Responses contribute to a greater understanding of toxicity or essentiality. Consequently, the commitment of the content of the element itself is not sufficient to ensure adequate risk declaration. Recognizing that the levels of total metals and metalloids are not adequate for determining their effect on the environment, their bioavailability, and that their toxicity has stimulated the development of species-selective analytical methodologies (Ebdon *et al.*, 2001). Mercury, Ge, Sn, Pb, As, Sb, Se and others are among the elements are to be added to the list of growing interest to clinical chemists in metal-containing drug metabolite monitoring. In energy-related samples such as crude oils and gasoline, the identification of specific species is also important due to variations in behaviour in combustion and refinery processes (Harrison and Rapsomanikis, 1989). Heavy metals and metallic elements that have a density equal to or greater than 6.0 g/cm^3; harmful to living organism even at low concentrations; cannot be destroyed by biological or chemical processes (can only be reduced by leaching or by biological uptake)

2. General Metal Speciation:

An appealing technique in speciation research to achieve accurate determinations which includes the online application of Isotope Dilution (ID) methodologies both with the HPLC-ICP-MS or GC-ICP-MS pairings was viewed. All the intrinsic benefits of this technique (Precision and accuracy) were added to the method of separation/determination and it is likely to be a broader future work (**Alonso *et al*., 2001).** Hyphenated techniques, which undergo rapid and continuous growth, give the widely accepted approach to speciation analysis (**Donard and Martin, 1992**). Biological cells are flexible due to their extensive metal remediation and metal remediation applications speciation and preconcentration (**Ting Yang *et al*., 2016)**. A five-step method of sequential extraction was used in sediment samples for the speciation of fractions of five heavy metals (**Jing Lin *et al*., 2009)**. They used a technique to distinguish five fractions of heavy metal exchangeable, bound to carbonate, attached to iron/manganese oxide, attached to residual fraction and organic matter. An ion-exchange preconcentration technique was used to assess the concentrations of trace metals in Texas Rivers, with varying fractions **(KUO-TUNG JIANN, 1999)**. Three metal fractions that have dissolved (labile, organic and inert), total concentrations of dissolved metals, total concentrations of recoverable and inert metals, concentrations of particulate metals were measured and compared to environmental conditions.

Chemical speciation and bioavailability was achieved in freshwater **(John David Murimboh, 2001).**

Minerals of the high quality gold and platinum category as sysertskite, nevyanskite, ruthenplatosmiride, ruthe niridosmine and rutheniridosmine, Pt- bearing, were discovered for the first time in the concentration of gravity **(Chernyshov and Ponamareva, 2012)**. A technological mineralogical sample of jaspilite in the weathering crust of the deposit of Mikhailovka Magnetic phenomenon of Kursk (KMA), thus identifying a comprehensive deposit creation strategy. The distribution of geochemical speciation of five metals (Cu, Fe, Ni, Pb and Zn) was calculated **(Eduardo *et al*., 2017).** The geochemical speciation of Cu, Fe, Ni, Pb and Zn metals was performed using the changed three-stage BCR protocol. Metal were determined using atomic absorption spectrometry. X-ray diffractometry (XRD) was the tool used to classify crystalline phases of minerals.

3. Coupled Gas Chromatography-Atomic Absorption Spectrometry:

Consideration of the theoretical aspects of the performance of GC-AAS detectors is necessary **(Douglas and Frech, 1993)**. The expressions are derived to describe the relative sensitivity values of the detector (peak height/area) and Chromatographic efficiency and resolution in terms of the ratio of the analyte's time of residence in the atomizer and the standard deviation from the GC system by the (assumed) Gaussian peak eluting from the chromatographic system. There were various detector designs employed, the most critical one with regard to detection Limits of electrothermal graphite atomizers Type of tube and Quartz Tube flame electrically-heated atomizer or hydride generation (HGAAS) **(Dimiter Tsalev, 1999)**. Automated flow injection and continuous flow injection HGAAS methods using accurate hyphenations with on-line sample/analyte (pre- or post-hydride generation) treatments or both. The potential caused by gas chromatography of microwave atmospheric pressure helium Plasma atomic emission spectrometry (GC-MIP-AES) is listed for organometallic and organometalloid compound of Hg, Ge, Sn, Pb, Ni, V, Fe and Se speciation research **(Ryszard and Adams, 1993)**. Although GC techniques are useful for the study of volatile organometallics, the GC packed column also does not have sufficient resolution power to characterise complex environmental samples adequately **(Alexander *et al*., 1992).** The recent available microwave-induced industrial capillary GC Atomic Emission Spectrometer of plasma (GC-MIP-AES) using state-of-the-art methods of coupling has resulted in increasing the number of elemental speciation studies in these complex samples. Currently, however, GC-MIP-AES Needs high-purity, costly reagent gases and solvent venting to avoid the instability of plasma and accumulation of carbon. Similar issues are encountered on the discharge tube in GC-MIP-MS, where the mass cones of the spectrometer may be blocked, too. An automated technique that is sensitive and interference free for the simultaneous study of speciation of methylated species of mercury, tin and lead, and also inorganic mercury in water as well, with purge-and-trap injection-gas chromatography-atomic chromatography spectrometry of pollutants, established **(MICHIEL AND ADAMS, 1996)**.

4. Arsenic:

Arsenic and its compounds are known to have adverse health effects on humans, including cancers of the skin, bladder, kidney & lung, and diseases of the blood vessels of the legs and feet (**Psanalytical, 2018)**.The toxicity of arsenic depends very heavily on the two main chemical forms, inorganic arsenic and organic arsenic. Inorganic arsenic species (arsenite, arsenate) in ground water have caused tremendous epidemic poisoning across the globe. Organic arsenic species (typically MMA, DMA) are common metabolites found in the human body and are much less toxic. Some other arsenic forms which are very commonly presented and account for the majority of the arsenic abundance in the marine environment (arsenobetaine, arsenocholine, arsenosugars etc), are completely non-toxic. The total concentration of arsenic cannot be used solely to explain the toxicity of arsenic in the environment. Up to four arsenic species; arsenite (AsIII), dimethylarsinic acid (DMA), monomethyl-arsonic acid (MMA) and arsenate (AsV) can be separated on a simple system. For the determination of non-reducible arsenic species such as arsenobetaine (AsB), arsenocholine and Trimethylarsine oxide ((TMAO) and arsenosugars. Determination of five arsenic species, arsenobetaine (AsBet), arsenite (AsIII), dimethylarsinic acid (DMA), monomethlyarsonic acid MMA and arsenate (AsV) was achieved by commercially available high performance liquid chromatography coupled to hydride generation and atomic fluorescence spectrometry (HPLC-HG-AFS).

Arsenic containing human urine samples was filtered before being injected into a C18 column (PSA C2 or equivalent). Five arsenic species were separated using a phosphate mobile phase. The eluted species were converted to volatile arsines by the addition of hydrochloric acid and sodium borohydride solutions. The volatile arsines were separated from the liquid phase using a gas-liquid separator and measured as arsenic using atomic spectrometry. Excess hydrogen from the reaction of reagents provided the hydrogen diffusion flame which atomised the arsenic species.

The speciation of arsenic species including the non-reducible arsenic species (arsenobetaine and arsenosugars) requires the use of UV oxidation system. This, in conjunction with an oxidising reagent, helps the breakdown of non-reducible arsenic species to a form that will react with NaBH4 so these can be quantified. As a result, a slight modification to the system is necessary.

5. Antimony:

Although it has been used in medicine by man for several thousand years, antimony is found to be non-essential and toxic to human body (**Psanalytical, 2018)**. However, the toxicity of antimony is also expected to be specie and form dependent. Elemental antimony is more toxic than its salt, and trivalent Sb is generally ten times more toxic than pentavalent Sb species. Antimony trioxide is found to cause serious lung cancer by inhalation. Whereas some antimony containing salts are commonly used as therapeutic treatment of parasite such as leishmaniasis. The concentration and more importantly the speciation of antimony must be understood before its toxicity can be assessed The separation of SbIII and SbV can be carried out in less than 3 minutes using a simple isocratic elution program and a strong anion exchange column. Species in real samples are identified on the basis of their retention times.

6. Chromium:

Chromium (III) is considered essential, while Cr (VI) is classified as carcinogenic **(Olle *et al*., 2013).** These species are polar and are Thermo-labile and thus liquid isolation of chromatography speciation research has acquired high importance.

7. Lead:

The interface of an inductively coupled plasma mass spectrometer with a capillary gas chromatograph was Outlined **(Alexander *et al*., 1992).** The interfacing only required a simple adjustment to the traditional inductively coupled plasma torch for mass spectrometry (ICP-MS) and the creation of a heated transfer line. Chromatography of capillary gases ICP-MS is sensitive and element-specific with a high chromatographic resolving power. The process demonstrated a strong potential for the study of a wide variety of volatile organometallics to become a very useful tool of compounds in a complex hydrocarbon mixture of alkyl lead compounds with a detection limit of 0.7 pg and is also applicable to the study of organometallics that are relatively involatile.

8. Mercury:

Organometals are present in the environment either as a consequence of direct methylation or as a consequence of direct anthropogenicity **(DONARD, 2001)**. A very small proportion of the total is expressed in the solution. Under particular circumstances, natural methylation responses occur and the yield of these reactions, both in natural waters is usually very low an in sediments. Methylmercury is more toxic than metallic mercury. Mercury is less dangerous than arsenic. Nonetheless, these modifications are in the form of the presence of the element results in significant changes to its physico-chemical nature properties, which can have a major effect on the toxicity and translocation between the numerous environmental compartments**.**

Two new and easy analytical techniques for obtaining volatile mercury and methylmercury species were described **(Craig *et al.* 1992)**. This makes it possible to classify non-volatile analyte solutions by element-specific and species-selective solutions. Compounds of mercury (ii) and/or methylmercury (ii) non-volatile aqueous solutions $NaBH_4$ or LiB (C_2H&H) are converted into volatile forms (including hydrides), followed by gas chromatographic separation. Atomic absorption detects the volatile derivatives divided by a column spectrometry or the mass spectrometry. Toxicity of Mercury, CH_3Hg>1000 times toxic than Inorganic Hg. Mercury has the greatest affinity for complex formation in the periodic Table. It is therefore important to be able to separate and measure species of mercury in order to avoid a tragedy similar to that at Minamata Bay **(Psanalytical, 2018)**. In order to determine levels of the individual mercury species, separation techniques such as such as HPLC (usually partition or ion chromatography) and/or GC are widely used. Using suitable extraction procedures, these techniques combined with sensitive detectors such as an Atomic Fluorescence spectrometer, offer the analyst a reliable and inexpensive system for mercury speciation.

For the HPLC speciation of mercury, a column suitable for the separation of the organo-mercury species is connected to an HPLC pump fitted with solvent handing accessory and manual injection valve. The column outlet is connected to the PSA 10.025 Millennium Merlin where the separated mercury species are oxidised to Mercury^{2+}. Stannous chloride is added in the gas liquid separator where mercury^{0} vapour is released which is measured, using Atomic fluorescence spectrometry operating in continuous flow mode. Automated mercury speciation can be achieved simply by the addition of an autosampler and automated valve.

9. Selenium:

Selenium can be presented in both inorganic (selenite, selenate, hydrogen selenide etc) and organic forms (selenomethionine, selenocysteine and selenoproteins etc). Among them, hydrogen selenide is extremely toxic while selenomethionine is essential and nutritional to the human body. The forms and the concentrations of selenium define its role in the environment and in the living systems. The field of selenium speciation has been receiving increasing attention over the past decades. Research and routine analysis of selenium is undertaken in plants, soils, nutritional supplements, and biological samples (urine etc.) in many environmental institutions and agencies. Using a reverse phase column with a modifier five selenium species (selenocystine, selenomethionine, selenoethionine, selenite and selenate) can be separated.

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إنتواع المعادن الثقيلة

أيمن السيد محفوظ حسن

قسم بحوث متبقيات المبيدات و تلوث البيئة – المعمل المركزى للمبيدات – مركز البحوث الزراعية – الدقى - الجيزة

الملخص العربى:

الانتواع هو علم تحديد الشكل الكيميائي وحالة الأكسدة لمعدن معين.تتمثل إحدى التقنيات الأساسية لتحقيق ذلك في فصل الأنواع الكيميائية ثم قياس التركيز باستخدام أداة مقترنة. تم تطبيق طرق فصل مختلفة للكروماتوغرافيا مثل) GC & LC التبادل الأيوني ، الطور العكسي. تستخدم الأدوات الطيفية مثل AAS أو ICP-AES أو ICP-MS لقياسات الاقتران والتقارب (لفصل الأنواع المعدنية. يوجد تقييم المعدن في أشكال / أنواع كيميائية مختلفة. عادةً ما تكون الكيمياء البيئية للمعادن معقدة وتتضمن تكوين أنواع كيميائية مختلفة مع عرض كل نوع معدني خصائص كيميائية وفيزيائية فريدة. يؤثر انتواع المعادن في الوسائط البيئية اللاأحيائية والأحيائية بشدة على توافرها البيولوجي وتراكمها الأحيائي وسميتها للكائنات الحية المستقبلة.