Session 1. SPECIATION OF METAL IONS IN BIOMEDICAL, NUTRITIONAL AND ENVIRONMENTAL FIELDS

ELEMENT SPECIATION, SPECIFICALLY IN THE RIO-MEDICAL FIELD

B. Michalke

GSF-Research Center, Institute of Ecological Chemistry, Ingolstadter Landstr 1, 85764 Neuherberg, Germany.

Trace metals may have associated risks or benefits. Although, the need for trace and ultra-trace analyses is clear, the required information about mobility, bioavailability, and finally the impact of elements on biological organisms is not necessarily given by total element concentrations alone. The knowledge of the elemental species provides a better understanding of chemical and biochemical processes, bioavailability and more complete information about toxicity or essentiality. Elemental species may involve their oxidation states, organometallic forms, isotopic composition, or complexation states. A meaningful risk assessment should then require speciation analysis. Elemental speciation analyses and more specifically, metal speciation analyses, utilize methods to address this challenge.

Complete speciation schemes consist of sampling, sample preparation, species analysis and evaluation. Without proper sampling and sample preparation procedures, there is little chance that any speciation analysis will provide reliable data upon which human health or environmental decisions can be based. Certain metal species can easily be lost. Quality control approaches and statistical data handling are a must for providing reliable results. Reviews on sample collection, pretreatment and storage of a wide range of sample types as published by [1]. For quality control strategies review articles are available from [2] and [3].

The session organized on speciation will be strictly going along the definitions given by IUPAC [4]. In short terms:

Chemical species: Specific form of a chemical element defined as to molecular, complex, or nuclear structure, or oxidation state. **Speciation analysis:** The analytical activity of identifying and measuring species is called „speciation analysis“. **Speciation of an element:**

Distribution of defined chemical species of an element in a system.

It is planned to present lectures giving an overview on methodology and problems in speciation, new methods, e.g. in hyphenated systems or species preserving sample preparation as well as focussing on specific spots of research in bio-medical speciation, such as selenium speciation.

PROTON MICROPROBE TECHNIQUE IN ELEMENT ANALYSIS OF BIOLOGICAL LIQUIDS

[1] V.T. Punin, [1] S.N. Abramovich, [1] M.E. Buzoverya, [1] V.V. Chulkov, [2] I.D. Gorlachev, [2] S.N. Lyisukhin, [3] V.N. Shabalin, [3] C.N. Shatokhina

[1] Russian Federal Nuclear Center –All Russia Scientific Research Institute of Experimental Physics, Sarov, Russia; [2] Institute of Nuclear Physics of the National Nuclear Center of the Republic of Kazakhstan Alma-Aty, Kazakhstan; [3] Scientific-Research Institute of Gerontology of RF, Moscow, Russia.

Early diagnostics of various diseases is an actual problem of the present-day medicine. Russian scientists S.N. Shatokhina and V.N. Shabalin are the world-first to develop the pathogenetic method of the urolithiasis early diagnostics – Litos system. It is based on the urine structure characteristics analysis on its transition into solid state through dehydration. Solid fixed bio-liquid structure in this case is formed by salts and organic elements dissolved in it.

The Litos method allows nephrolithogenesis and its activity level to be found out and salts participating in the process to be determined. One of the basic stages in this technique is a comparative analysis of chemical elements content in glass urine samples peripheral and central zones. At the present moment the element analysis by the Litos system is carried out with the X-ray spectral microanalysis.

In the report there is presented a possibility of the proton microprobe technique use for determining main lithogenic elements in glass bio-liquids by the Litos system. There is shown a good convergence of the results of samples proton microprobing and X-ray spectral analysis.

ARSENIC SPECIATION IN BIOLOGICAL SAMPLES USING HPLC-ICP-MS

J.W. Ejnik, J. Caplan, M. Serra, J.A. Centeno

Armed Forces Institute of Pathology, 6825 16th St. N.W., Washington DC 20306 USA.

Background: Biomethylation of arsenic occurs in mammal's metabolic pathways of inorganic arsenic as a detoxification process. The speciation of arsenic metabolites is essential in determining the toxicity and health effects of arsenic.

Aims: To develop a method based on high pressure liquid chromatography-inductively coupled plasma mass spectrometry (HPLC-ICP-MS) to measure arsenic species in biological samples.

Method: Five arsenic compounds including arsenobetaine, methylarsonic acid, dimethylarsinic acid, arsenous acid, and arsenic acid were separated by HPLC on a Hamilton PRP-X100 anion-exchange column using carbonate and sulfate buffer gradient and detected by ICP-MS. This analytical procedure was applied to the speciation of arsenic compounds in urine, blood, serum, and tissues. A Perkin Elmer Elan 6100 DRC ICP-MS instrument was used for the analysis. The potential ArCl (m/z 75) interference was removed for the arsenic signal by using oxygen as the dynamic reaction cell gas, thus converting As (m/z 75) to AsO (m/z 91).

Results: Six human urine reference materials were analyzed with respect to the five arsenic compounds by HPLC-ICP-MS. Detection limits for the five arsenic species were 0.01 m g/L. The results were found to be within 20% of the certified total arsenic concentration in the reference materials. Blood, serum and tissue samples with the five arsenic species added had between 90%-110% recoveries.

Conclusions: A robust method for determining five arsenic species was applied to biological samples. The method was validated by obtaining excellent recoveries of all five arsenic species in certified reference materials.

INVESTIGATIONS ON SPECIES-PRESERVING EXTRACTION FROM LIVER SAMPLES

V. Nischwitz, B. Michalke, A. Kettrup

GSF — National Research Center for Environment and Health Institute of Ecological Chemistry, Ingolstдdter LandstraЯe 1, 85764 Neuherberg, Germany.

In biomedical research the qualitative and quantitative analysis of metal species in tissues is necessary to obtain a more detailed knowledge of metal species transport, transformation and function in organisms. Unfortunately there are no sufficiently sensitive and selective methods for the direct analysis of these compounds in solid matrices commonly available. Consequently, an extraction is necessary. But this is a critical step regarding species stability because the addition of an extractant in most cases changes chemical equilibria in the sample.

Therefore, the aim of this study is to develop mild extraction methods for metal species in solid samples combined with the proof of species stability during extraction. Metallothioneins (MT) and superoxide dismutase (SOD) are used as model compounds for the comparison of different extraction procedures. These species are characterized quantatively by HPLC-ICP-MS-online-coupling and in parallel identified by HPLC-ESI-MS-offline-coupling before and after extraction.

An approach in three steps is realized: First, extraction of the species alone, second, extraction of spiked liver samples and finally extraction of unspiked liver samples.

The results of the first step show differences of up to 50% in the recoveries of MT and SOD for different extractants. Preliminary results of the second and third step will be presented.

Various extraction procedures are compared; most of them are taken from the literature with minor or no modifications. From the investigations so far it can be concluded that there are significant differences in the ability of the extractants to stabilize MT and SOD during extraction.

SERUM SELENIUM AND MANGANESE ANALYSIS BY ICP-DRC-MS

O. Piraner, K.L. Caldwell, R.L. Jones

Centers for Disease Control and Prevention, 4770 Buford Hwy. NE, MS F18, Atlanta, GA 30341 USA.

Selenium (Se) and Manganese (Mn) are both essential nutrients to humans and are also known to be toxic at certain levels. Therefore, it is important to monitor the Selenium and Manganese content in biological matrices such as urine and serum. Normal U.S. serum Se levels are 95–165 mmg/L. Normal serum Mn levels are 7.7–

12.1 mg/L. Currently, determination of Selenium and Manganese in biological matrices is accomplished with a number of different techniques, such as graphite furnace atomic absorption spectrometry (GFAAS), flow injection hydride generation electrochemical atomic absorption spectrometry (HG-AAS) or conventional inductively coupled plasma mass spectrometry (ICP-MS), all of which suffer from limitations. In conventional ICP-MS isotopic interferences are a problematic limitation. However, Dynamic Reaction Cell (DRC) technology using methane as the reaction gas can eliminate isobaric background and allows analyzing Se and Mn in serum. Additional improvements are seen by adding ethanol, Triton X-100, and internal standards such as Gallium and Rhodium for Se and Mn correspondingly. With the recent introduction of a Dynamic Reaction Cell in the ICP-MS (ICP-DRC-MS), analysis of serum Selenium and Manganese can now be done using the most abundant selenium isotope (^{80}Se) which results in lower a LOD, and ^{55}Mn which is monoisotopic.

ARSENIC SPECIES ANALYSIS IN WOOL OF SHEEP AND HUMAN HAIR

A. Raab, J. Feldmann

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 1UE, UK. E-mail: a.raab@abdn.ac.uk

Hair and wool are part of the body metabolism and they are therefore during their growth influenced also by the presence of toxins and drugs. The fibre is formed in the root; during that time there is the possibility of inclusion of for example arsenic species. Since hair proteins contain a large amount of sulfhydryl groups and especially trivalent arsenic species have a high affinity to these groups, there is a high probability that these highly reactive arsenic species are enriched in hair. Trivalent arsenic species are under suspicion, that they are highly carcinogenic, but their concentration in most body fluids is too low to measure them. So hair and wool might be a good material to increase our knowledge about the metabolic changes of ingested arsenic species. To test this hypothesis we extracted wool from sheep feeding on seaweed (contains large amounts of organic bound arsenic) and human hair samples from people drinking arsenic contaminated well water. The fibres were extracted by boiling for 6 h with water. After filtration the samples were directly injected onto a HPLC column directly connected with an inductively coupled plasma mass spectrometer for the determination of arsenic. We used different separation techniques: anion and cation exchange chromatography and size exclusion chromatography. For the identification of the separated species we used standard species and standard addition. So long we have been able to identify As(III), As(V) and dimethylarsenate (DMA(V)) in both kinds of fibre. In wool we have in addition identified monomethylarsenate (MMA(V)), monomethylarsenite (MMA(III)) and dimethylarsenite (DMA(III)). In wool there are at least 4 until now not identified species.

SPECIATION AND METABOLIC STUDIES AS KEY FACTORS FOR INTERPRETING METAL TOXICITY AND CARCINOGENICITY

E. Sabbioni

European Commission, JRC-Ispra, Institute for Health & Consumer Protection (IHCP), ECVAM Unit, 21020 Ispra (Varese), Italy.

The toxicity of metal compounds has been traditionally regarded as a function of dose and potency of the metal itsel. However, it has become evident that several metals and metalloids undergo biotransformations in the cells, and that metal metabolism has important implications in clinical pharmacology as well as environmental and occupational health, affectoing the nature and intensity of the toxic response. In addition, most of metal exist in a variety chemical species to which humans are exposed leading to different toxic effects. Thus, metabolic-speciation studies are essential factors as a basic for interpriting metal toxicity.

The aim of the paper is to present the current in vitro research activities concerning metabolism, cytotoxicity and carcinogenicity potential of metal compounds as investigated by cell cultures according to the 3Rs approach (reduction, refinement and replacement)related to development and validation of toxicity testing for regulatory purpose. Application concern:

(i) screening studies concerning the cytotoxicity of more than 30 metal spesies in HaCaT (immortalised human keratinocytes), PC12 (rat pheochromocytoma), MDCK (Madine Darby Canine Kidney), Balb/3T3 (mouse fibroblasts) cell lines as models of dermal toxicity, neurotoxicity, nephrotoxicity and carcinogenenic potential of Pt-compounds (cisPt >> carbo Pt> PtCl > $PtCl_2$ > (NH_{42}) > $(NH_{42}PtC_{l4})$ as well as the toxic effects of As, Cr, Hg, Te, Ti and V species induced in the other cell lines considered.

(ii) uptake studies of As, Cr, V by using ^{74}As, ^{51}Cr and ^{48}V radiotracers and of Pt by inductively coupled plasma mass spectrometers (ISP-MS). The relations between the findings of the uptake with the cytotoxic responses are pointed out.

SELENIUM SPECIATION OF HUMAN BODY FLUIDS BY HPLC-HEX-ICP-MS

[1] J. Adair, [1] N.I. Ward, [2] F.R. Abou-Shakra, [2] H. Walker

[1] ICP-MS Facility, Department of Chemistry, University of Surrey, Guildford, GU2 7XH, UK; [2] Micromass UK Ltd., Floats Road, Wythenshawe, Manchester M23 9LZ, UK.

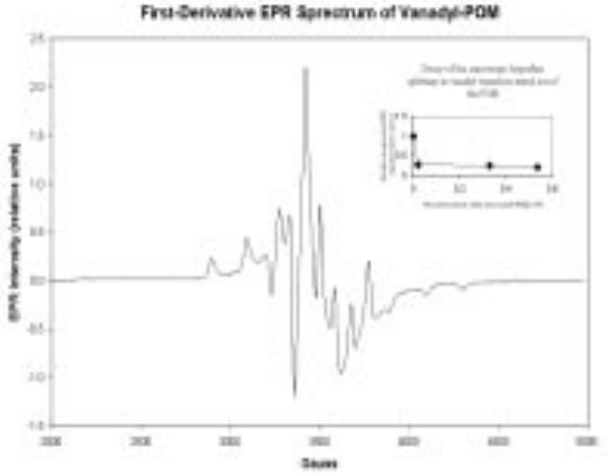
Selenium is a key component in a number of functional selenoproteins, required for normal health, *e.g.* antioxidant glutathione peroxidase. It also has a role in thyroid hormone metabolism, the immune system and in proper reproductive performance. Following our presentation at Munich on the preliminary study[1], further studies have been carried out and the data will be presented. Three forms of chromatography (reverse phase, ion pair and ion exchange) have been used in order to determine conclusively the speciation information within human body fluids, namely blood serum, urine and seminal plasma. Selenium speciation analysis of the human body fluids was collected from healthy individuals before (t = 0 days) and during a dietary selenium supplementation programme (t = 14 and 28 days) was analysed using HPLC-HEX-ICP-MS (hexapole collision/ reaction cell). This hexapole collision cell technology effectively removed all interfering species effectively. The Se supplements investigated were Se-methionine, Se-methyl-Se-cysteine and two commercial varieties of Se yeast (200 mmg per day). Inorganic (selenite/ selenate) and organo-species (Se-methionine, Se-cystamine, $TMSe^{+}$, Se-cystine, and Se-ethionine) were quantitatively measured. The three forms of chromatography along with spiking of selenium standards were used to conclusively prove the presence (or not) of both organic and inorganic selenium species in the human body fluids, unfortunately several selenium species present in the human body fluids are still unidentified.

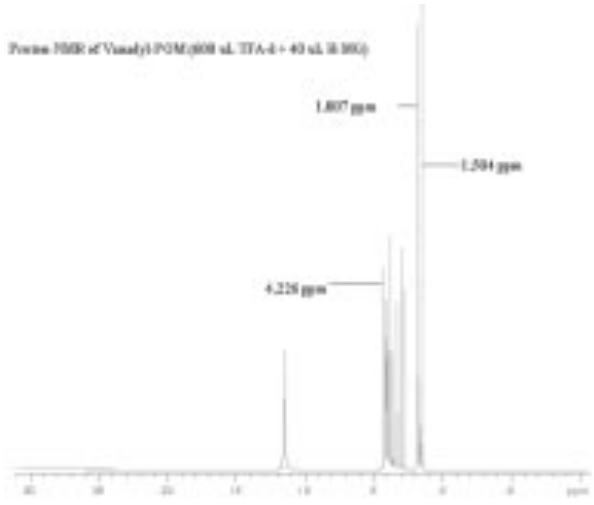
APPLICATION OF EPR AND NMR TO THE ANALYSIS OF POLYOXOMETALATES (POM) REACTING WITH THE MONOFUNCTIONAL SULFUR MUSTARD (H-MG)

[1] C.M. Arroyo, [1] J.M. Sankovich, [1] D.W. Kahler, [2] A.J. Carmichael, [1] E.H. Braue

[1] U.S. Army Medical Research Institute of Chemical Defense, 3100 Ricketts Point Road, Aberdeen Proving Ground, MD 21010-5400 USA; E-mail: Carmen.Arroyo@amedd.army.mil; [2] USAMRD, MCMR-UWB-L, Brooks AFB, TX 78235-5138 USA.

Polyoxometalates (POMs) are d^{o} [e.g. V (V), Mo (VI)] transition metal oxide cluster compounds, which readily undergo redox cycling. For this reason they are used to catalyze the oxidative breakdown of organic compounds and thus, are good candidates to inactivate chemical warfare agents such as sulfur mustard with a potential use in topical skin protective creams. This project deals with the application of EPR/NMR to study the reaction of a vanadium-containing POM ($H_5PV_2Mo_{10}O_{40}$) with a monofunctional sulfur mustard (butyl-2-chloroethyl sulfide, half-mustard, H-MG). Since the V_2-POM is synthesized with V (V), it should not have an EPR spectrum. However, the V_2-POM powder yielded the room temperature EPR spectrum shown in the top panel (right side). This spectrum is the typical EPR of the vanadyl cation (VO^{+2}) displaying 8 hyperfine lines due to the interaction of a single unpaired electron with the ^{51}V nucleus (99.7% abundant) with a nuclear spin, I = 7/2. In this case, the spectrum is anisotropic due to immobilization, a characteristic property of VO^{+2}. This result indicates that at sometime during the synthesis of the V_2-POM the vanadium was reduced from V (V) to V (IV),





which rapidly associates with oxygen forming VO^{+2}. In solution the V_2-POM EPR spectrum becomes more isotropic, typical of a more rapidly tumbling VO^{+2}. When H-MG is added to the solution the VO^{+2} EPR spectrum loses intensity. There are two possible mechanisms that can explain this result: (1) H-MG reacts directly with the VO^{+2} causing it to loose its EPR; (2) H-MG dismantles the cluster freeing the VO^{+2}, which may then form the EPR silent $VO(OH)_2$. To determine which of these mechanisms is occurring and what the overall mechanism of action for the V-POM is, the NMR of V_2-POM was obtained in the presence and absence of H-MG. The NMR spectrum obtained in the presence of H-MG is shown in the bottom panel. In both cases the NMR spectra are complex, and the peaks are still being assigned. How the characterization of the model reaction of vanadium with H-MG can be used to obtain information specific for other chemical warfare sulfur analogs will be presented and discussed.

ИЗУЧЕНИЕ КОМПЛЕКСООБРАЗОВАНИЯ В ВОДНЫХ РАСТВОРАХ ИОНОВ МЕТАЛЛОВ (II) С МОЛЕКУЛЯРНЫМ КИСЛОРОДОМ МЕТОДОМ ПЕРЕМЕННОТОКОВОЙ ВОЛЬТАМПЕРОМЕТРИИ

[1] П.М. Зайцев, [2] А.А. Ревина, [3] Д.В. Красный

[1] ОАО “НИУИФ”, Москва, Ленинский пр. 55; [2] Институт электрохимии РАН, Москва, Ленинский пр. 31; [3] НПП “ЭКОНИКС”, Москва, Ленинский пр. 31

В продолжение работ, находящихся в печати в ЖАХ и “Координационной химии” по изучению влияния O_2 на электрохимическое восстановление ионов металлов, исследовано его комплексообразование с ионами Zn^{2+}, Fe^{2+} и Cu^{2+} методом переменнотоковой вольтамперометрии по изменению высоты пика восстановления ($i_п$) реагирующих компонентов в растворах с pH 4–6 0,1M $NaClO_4$ ($NaNO_3$), насыщенных по кислороду воздуха. Рабочий электрод – висящая ртутная капля.

Ионы Zn^{2+} и Fe^{2+}, восстанавливающиеся при более отрицательных потенциалах, чем восстановление O_2 до H_2O_2 и H_2O_2 до H_2O, влияют на высоту, потециал пика восстановления O_2 и H_2O_2 и форму их вольтамперограмм. В присутствии Fe^{2+} наблюдаются дополнительно пики каталитического восстановления H_2O_2 ($i_к$) и скачкообразное смещение в анодную область потенциалов начала восстановления O_2.

Потенциал восстановления ионов Cu^{2+} незначительно отличается от такового для O_2. В их присутствии наблюдается одновременное появление новых пиков на вольтамперограмме в анодной и катодной областях потенциала относительно пика восстановления O_2. Высоты пиков увеличиваются с ростом $[Cu^{2+}]$.

Ионы Zn^{2+} в условиях избытка O_2 электрохимически неактивны, а при их избытке восстанавливаются при более отрицательных потенциалах, чем в отсутствии O_2.

Величина отношения $i_п^{Zn}/[Zn^{2+}]$ имеет максимальное значение при $Z=[Zn^{2+}]:[O_2]=2$, которое при дальнейшем росте Z, уменьшаясь, достигает постоянного значения при Z=4.

В присутствии O_2 восстановление Fe^{2+} протекает либо одноступенчато (избыток O_2), либо в две ступени при $Z=[Fe^{2+}]:[O_2]i0,8$, как и в отсутствии O_2. В этих условиях высота пика первой ступени увеличивается, а второй, наоборот, уменьшается с ростом Z.

Электрохимическое поведение изученных ионов металлов в присутствии O_2 и отдельно H_2O_2 существенно различается между собой.

Показано, что при избытке O_2 в растворе образуются ранее неизвестные комплексные соединения состава $[Me^{2+}\cdot(O_2)n]$, где n=1,2,3 и $Me^{2+}= Fe^{2+}$, Cu^{2+}, Zn^{2+}, а при избытке ионов металлов на примере Zn^{2+} образуются ди- и тетраядерные комплексы. Состав последних для Fe^{2+} в литературе известен.

Благодарности: Работа выполнена при поддержке РФФИ, проект 01-03-32-783.

AN *IN-VITRO* BIOAVAILABILITY STUDY ON SELENIUM SUPPLEMENTS - SPECIATION ANALYSIS BY HPLC-HEX-ICP-MS

[1] J. Adair, [1] N.I. Ward, [2] F.R. Abou-Shakra, [2] H. Walker

[1] ICP-MS Facility, Dept. of Chemistry, University of Surrey, Guildford, GU2 7XH, UK; [2] Micromass UK Ltd., Floats Road, Wythenshawe, Manchester M23 9LZ, UK.

Selenium has a high biological activity with its bioavailability and toxicity depending greatly on the chemical form available. Commercial Selenium supplements are available in a variety of different forms, *e.g.* selenite, selenomethionine, selenium yeast *etc.* Bioavailability is the “fraction of the ingested nutrient that is utilised for normal physiological functions or storage” (Jackson, 1997). An in-vitro bioavailability study, which mimics the human gut, was performed on selenium supplements in order to distinguish which species are

available for absorption after the supplements have been consumed. All samples were performed in triplicate and the method for bioavailability mentioned by Kapskefalou and Miller, 1991 was modified in order to be applicable to the supplements (Bentley 2001). Speciation data will be presented for selenomethionine, selenomethylselenocysteine and two commercial forms of selenium yeast. The results showed selenite and selenate within the supplements, some other selenium peaks were observed but unfortunately these were unidentifiable.

SOD LIKE ACTIVITY AND LIPOPHILICITY OF COPPER CHELATES WITH AMINOACIDS AND PEPTIDES

[1] G. Facchin, [1] M.H. Torre, [1] I. Viera, [1] E. Kremer, [2] E.J. Baran

[1]Qиmica Inorgбnica, DEC, Facultad de Qиmica, UDELAR, Gral. Flores 2124, CC1157, Montevideo, Uruguay; [2]CEQUINOR, Facultad de Ciencias Exactas, UNLP, Calle 47, 115, CC 962, La Plata, Argentina. E-mail: mtorre@bilbo.edu.uy

Many copper (II) complexes of aminoacids or small peptides have diverse pharmacological activities: anti-inflammatory, anticancer, anticarcinogenic, anticonvulsant or antiulcerous.

In general, it can be contended that copper complexes of low molecular weight can be useful to facilitate transport of the metal to the enzymatic active site. This allows activation or reactivation of a metal-dependent enzyme, like superoxide dismutase (SOD). This enzyme catalyses the dismutation of the toxic superoxide radical. It has a central role in defending life forms that use oxygen, from oxidative damage. It has also been shown that many pharmacologically active copper complexes disproportionate superoxide anion in a manner similar to SOD. Looking for new copper complexes useful as potential drugs, we have synthesised and characterised a number of Cu (II) complexes of different biological occurring aminoacids and dipeptides. As a continuation of this research, we present the results of the superoxide dismutase-like activity of these copper (II) complexes. This was done using the method based on the reduction of nitroblue tetrazolium (NBT) by O_2^- generated by the action of xanthine oxidase. We also present the results of lipophilicity tests (partition coefficient between octanol and water systems) of these complexes. The presented results were analysed in relation to the known structural characteristics of these Cu (II) complexes.

METHOD OF CALCIUM ION MEASURING IN BIOLOGIKAL MATERIAL WITH COMPLEXON ARSENAZO III

[1] A.I. Ovsjannikov, [2] S.A. Konkov, [1] V.K. Gurkalo

[1]N.N. Petrov's Institute of Oncology Ministry of Health RF, Clinical Laboratory, St-Petersburg Russia; [2] Laboratory of Xenobiotics, SPC "Eco-Servis", St-Petersburg Russia.

Method of photometric determination of concentration total calcium in serum and other biological liquids with use color complexon Arsenazo III is offered.

Physical-chemical characteristics Arsenazo III, e-factor of mol extinction, affinity to other ions, spectral characteristics of reagent and its complex with calcium are indicated.

On the results of measurement calcium concentration at 750 individuals are designed reference concentration total serum calcium is 2.15–2.75 mmol/l, average significance — 2.47 mmol/l. On semi-automatic method are CV % — about 5 %. Reactive is very convenient for work, especially on automatic analyzers, by that it monoreagent, durably stored at room temperature, gives stable results.

VIBRATIONAL AND NMR SPECTROSCOPIC STUDIES OF IRON COMPLEXES WITH SOME INDOLE DERIVATIVES

A.G. Shchelochkov, A.A. Kamnev

Laboratory of Biochemistry of Plant-Bacterial Symbioses, Institute of Biochemistry and Physiology of Plants and Microorganisms, Russian Academy of Sciences, 13 Prosp. Entuziastov, 410015 Saratov, Russia. E-mail: micbio@ibppm.saratov.su

Indole derivatives are known to play an important role in plant physiology and plant-bacterial interactions as a result of their plant growth-promoting effects (phytohormones of the auxin series) and their biosynthesis by many soil microorganisms [1]. The formation of their complexes with metal ions may essentially affect both their physiological [2] and chemical properties [3], in particular, as a result of alterations in the electronic structure of the aromatic system [4].

In this work, comparative investigations were performed on the structure and coordination of iron(III) with some indole derivatives including indole-3-acetic

acid (IAA; auxin); a product of its oxidation, and indole-3-butyric acid (IBA). For characterising the state of functional groups, Fourier transform infrared (FTIR) (for solid samples) and FT-Raman spectroscopy (also in solutions) were used; the structural information was complemented by ^{1}H NMR studies (300 MHz; in D_6-acetone). The obtained results show that iron(III) forms similar complexes with IAA and its oxidised derivative with a high degree of covalency. This is confirmed by the lower frequency of the stretching Fe–O mode (under 520 cm^{-1} in IAA complex), as well as by the presence of the carboxylic C=O band at 1710 cm^{-1} in both the IAA-related complexes (cf. the stronger C=O band at 1703 cm^{-1} in free IAA) which is absent in the IBA complex (as well as in many other carboxylates). Oxidation of IAA in air introduces a carbonylic group (1794 cm^{-1}) in the indole aromatic system. The data of ^{1}H NMR confirmed the effect of iron(III) coordination on the indole aromatic system in IAA proposed earlier on the basis of UV-Vis spectra [4].

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COMPOUNDS OF COPPER AND PRASEODYMIUM CHLORIDES WITH N-TETRAHYDROPYRANYL-D,L-AMINOACIDS

[1] S.A. Vasilyeva, [1] L.Kh. Kalimullina, [1] R.K. Gaifutdinova, [1] M.G. Safarov, [2] V.N. Baimatov

[1]Department of Organic Chemistry of Bashkir State University, 32, Frunze Street, 450074, Ufa, Russia; [2]Bashkir Agriculture University, 400087, Ufa, Russia

The interaction of copper and praseodymuim chlorides with the formerly unknown

N-Tetrahydropyranyl-D,L-amino acids (I a–d, glicine (a), Leicine (b), в-phenyl-б-alanine (c), methionine (d) has been investigated.

As a result new coordinate compounds (II a–d, III a–d) have synthesized and broad spectrum of the biological activity the mixed ligand complexes (II, III) is being carried out.