TABLE OF CONTENTS

TIME SCHEDULE

Sunday, September 21

Arrival at "Hotel Napoca" and registration. The secretariat of the Conference will be functioning in the lobby of the hotel between 17 to 19 o'clock.

At 19^{30} o'clock "Ice breaking cocktail".

Monday, September 22

9^{00} - 9^{30}	Opening ceremony
9^{30} - 10^{15}	Yasuhiko Fujii et al. *CALCIUM ISOTOPE SEPARATION BY USING CROWN-ETHER RESIN*
10^{15} - 11^{00}	Kenji Takeshita *DEVELOPMENT OF LIGHT-DRIVEN EXTRACTION TECHNIQUE USING 'CIS-TRANS' PHOTOISOMERIZATION OF AZOPYRIDINE COMPOUND*
11^{00} - 11^{30}	Coffee break
11^{30} - 12^{15}	Ilie Hodor *THE THEORY OF THE ISOTOPIC SEPARATION COLUMN BASED ON MULTI-STEP CHEMICAL EXCHANGE*
12^{15} - 13^{00}	Gheorghe Vasaru *ENRICHMENT OF OXYGEN-17. A REVIEW*
13^{00} - 15^{00}	Lunch
15^{00} - 15^{30}	Katzlinger H. et al., *GC ISOLINK: A NEW CONCEPT FOR AUTOMATED MULTI-ELEMENT IRM-GC/MS*
15^{30} - 16^{00}	Maria Chiriac et al. *ENZYMATIC SYNTHESIS OF SOME L-AMINO ACIDS ISOTOPICALLY LABELED WITH* ^{15}N
16^{00} - 16^{30}	Paula Raica and D. Axente *DYNAMIC MODELLING AND SIMULATION OF* ^{15}N *ISOTOPE SEPARATION BY CHEMICAL EXCHANGE IN NITROX SYSTEM*
16^{30} - 17^{00}	Damian Axente et al.

	THE ^{14}N AND ^{15}N SIMULTAN SEPARATION BY ISOTOPIC EXCHANGE IN NO, NO_2 - HNO_3 SYSTEM UNDER PRESSURE
17^{00} - 17^{30}	Iulia Lupan et al. *THE UNIFORMLY AND SELECTIVE ^{15}N-LABELLING OF THIOL PEROXIDASE FROM 'BACILLUS SUBTILIS'*
17^{30}	Visit to the "Village Museum" and barbecue

Tuesday, September 23

9^{00} - 9^{45}	Jorge E. Spangenberg *STABLE ISOTOPE EXCHANGE BETWEEN WATER PHASES IN SYNTHETIC AND NATURAL SYSTEMS*
9^{45} - 10^{30}	Istvan Forizs, József Deák *FOOD QUALITY INSURANCE: AN APPLICATION OF STABLE ISOTOPE MEASUREMENTS FOR BOTTLED WATERS*
10^{30} - 11^{15}	Ana Voica-Bojar et al. *THE MIOCENE VOLCANISM IN THE STYRIAN BASIN, AUSTRIA : INSIGHTS FROM THE ISOTOPIC RECORD*
11^{15} - 11^{45}	Coffee break
11^{45} - 12^{30}	Gerhard Strauch *PROCESS ORIENTED ISOTOPE STUDIES IN ANTHROPOGENIC AFFECTED ENVIRONMENT*
12^{30} - 13^{00}	José Mauro Sousa Moura et al. *STABLE CARBON ISOTOPIC COMPOSITION (^{13}C-CH_4) AND CONCENTRATION OF METHANE IN AMAZON TROPICAL FORESTS*
13^{00} - 15^{00}	Lunch
15^{00} - 15^{45}	Jaleh Gashghaie et al. *METABOLIC ORIGIN OF ^{13}C OF DARK-RESPIRED CO_2: COMPARISON BETWEEN LEAVES AND ROOTS*
15^{45} - 16^{15}	Allan T. Emrén *CHLORINE-36 IN NUCLEAR WASTES - AN UNEXPECTED PROBLEM*
16^{15} - 16^{45}	Zaharie Modovan *APPLICATION OF ISOTOPE DILUTION TECHNIQUES FOR DETERMINATION OF MICROPOLLUTANTS IN WATER*
16^{45} - 17^{15}	Adrian Pamula et al.

	METAL CONTENT AND ISOTOPIC CHARACTERIZATION OF SOME ROMANIAN WINES. PRELIMINARY RESULTS
17^{15} - 17^{45}	Coffee break
17^{45} - 18^{15}	Stelian Pintea et al. *TPR STUDY OF SUPPORTED Ni CATALYST WITH APPLICATION IN ENVIRONMENT PROTECTION, ECOLOGY AND ISOTOPIC EXCHANGE REACTIONS*
18^{15} - 18^{45}	Petru Berdea et al. *ISOTOPIC MIXING MODEL IN LABORATORY SIMULATION EXPERIMENT WITH DEUTERIUM; RELEVANCE FOR NATURAL ISOTOPIC TRACKING*
18^{45} - 19^{45}	Poster session
19^{45}	Closing Ceremony
20^{00}	Conference Dinner

Wednesday, September 24

Post Conference Excursion.

INVITED LECTURES

CALCIUM ISOTOPE SEPARATION BY USING CROWN-ETHER RESIN

**Yasuhiko Fujii, Saori Umehara*), Kaneshiki Tositaka, Masano Nomura,
Tatsuya Suzuki, and Tadahumi Kishimoto*),**

*Research Laboratory for Nuclear Reactors, Tokyo
Institute of Technology
*) Department of Physics, Graduate School of Science,
University of Osaka*

Natural calcium consists of the isotopes, Ca-40, Ca-42, Ca-43, Ca-44, Ca-46, and Ca-48. Among them, Ca-48 is a double magic isotope and known as the double β nuclide. For the purpose of neutrino study, determination of Ca-48 double β decay constant is very important and enrichment of Ca-48 is desirable to this end.

Calcium isotopes have been separated by electro-magnetic method for long time. But the cost is too high to practically use the enriched isotopes for double β study. In addition, calcium isotope separation was studied by using amalgam process, ion exchange resin, electo-migaration etc. Chemical exchange process is desirable, but amalgam is nowadays not applicable due to the hazard material of mercury, and the separation coefficient of ion exchange is too small to be used as the isotope separation process.

In the present paper we tested crown ether resin as the isotope separation medium. The crown monomer 18-crown-6-ether was polymerized with phenol derivatives, and fine particle resins, ca 60 μ, were synthesized. Using the columns packed with the synthesized resin, we conducted ca isotope separation experiments. Calcium chloride dissolved in HCl solution was charged into the packed column. The effluent was sampled in fractions and the Ca concentration and the isotopic analysis of calcium were analyzed by flame photometry and Thermo-ionization mass spectrometry, respectively. The enrichment of the heaviest isotope Ca-48 was observed at the front end of ca adsorption band. The single stage separation coefficient ε of the crown ether system was observed to be proportional to the mass difference between the isotope in question and the major isotope Ca-40. The calculated ε was approximately $3\text{x } 10^{-3}$ for the pair of Ca-40 and Ca-48.

Presently fundamental study has been conducted to synthesize the crown ether resin and separation of Ca isotopes using the packed columns with the resin.

DEVELOPMENT OF LIGHT-DRIVEN EXTRACTION TECHNIQUE USING *CIS-TRANS* PHOTOISOMERIZATION OF AZOPYRIDINE COMPOUND

Kenji Takeshita

Chemical Resources Laboratory, Tokyo Institute of
Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-
8503, Japan,
E-mail: takeshita.k.ab@m.titech.ac.jp

Light-driven extraction technique using an azopyridine compound, bis(2,2’-dipyridyl-6-yl)diazene (BDPDA), was developed and the optical-response extraction of Au(III) with BDPDA was examined. In this extraction technique, as shown in Fig.1, An optical-response material, whose molecular configuration is changed reversibly by the irradiation of light with different wavelength, is used as an extractant. The complex formation between the extractant and a target metal is controlled by the configuration change of extractant. The extraction of Au(III) was promoted by changing the configuration of BDPDA from *trans* to *cis* under irradiation of UV light (340 nm). $AuCl_4$ was complexed more stably with *cis*-BDPDA and extracted as $AuCl_3$(BDPDA) in organic phase. However, the distribution ratios under the UV irradiation were less than 3 times those under VIS irradiation (465nm). Further promotion of Au extraction by UV irradiation is required for practical use.

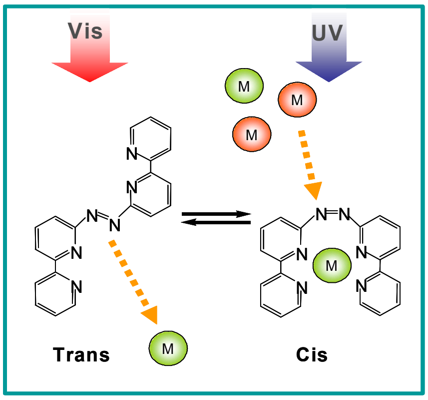

Fig.1 Concept of Light-driven Extraction.

For the improvement of light-driven extraction technique, synergistic extraction of Au using carboxylic acid as a synergist was tested. Octanoic acid was an effective synergist and was complexed mainly with $AuCl_3$(*cis*-BDPDA) formed by the coordination of $AuCl_4$ and *cis*-BDPDA. In the presence of more than 3 mol/L octanoic acid, the distribution ratio of Au was increased under the UV irradiation and reached to 10 times that under the VIS irradiation. The back extraction of Au from the organic phase proceeded effectively at lower temperature. At 5˚C, about 16% of Au extracted in the organic phase was recovered by one back-extraction operation using an aqueous solution with pH3 and the ionic strength of 0.1. These results suggest that the light-driven extraction technique using a suitable synergist such as octanoic acid is applicable to a practical separation process.

THE THEORY OF THE ISOTOPIC SEPARATION COLUMN BASED ON MULTI-STEP CHEMICAL EXCHANGE

Ilie Hodor

National Institute for R&D of Isotopic and
Molecular Technologies, Cluj-Napoca, Romania
hodor@itim-cj.ro

The isotopic separation column based on multi-step chemical exchange is theoretically treated as a particular application of a general theory of the separation column previously developed by the author [1-3]. The theory is developed for binary isotopic mixture, for low isotopic effects and for an arbitrary number of chemical species participating to the chemical exchange.

The result of the theory is an equation of the transport of one isotope through the column. The equation is useful both for experimental research and for the design and optimization of the separation column.

The theory is then specialized for the separation of ^{13}C by the chemical exchange method between CO_2 and amine in a nonaqueous solvent. The result is compared with the theoretical procedure proposed by Kitamoto and Takeshita [4].

References

[1] I. Hodor, *An Overall Theory of Separation on Column or on Square Cascade,* Isotopenpraxis, **20(9)**, 330 (1984)

[2] I. Hodor, *A general theory of the separation column as applied to thermal diffusion column*, Thermodiffusion: Basics&Applications (Proc. of IMT7-2006, eds. M. M. Bou-Ali & J. K. Platten, Mondragon Univ., 67)

[3] I. Hodor, *The Theory of the Thermodiffusion Column with Arbitrary Cross-Section*, The 8th International Meeting on Thermodiffusion, 9-13 June 2008, Bonn, Germany

[4] A. Kitamoto and K. Takeshita, *A Two-Step Model for Advanced Separation of ^{13}CO by Chemical Exchange Method between CO_2 and Amine in a Nonaqueous Solvent*, Proceedings of the International Symposium on Isotope Separation and Chemical Exchange Uranium Enrichment, Tokyo, Oct 29 – Nov 1, 1990; Fujii, Y., Ishida, T., Takeuchi, K., Eds.; Bull. Res. Lab. for Nucl. Reactors, Tokyo Institute of Technology, Tokyo 1992, pp. 376

ENRICHMENT OF OXYGEN-17. A REVIEW

Gheorghe Văsaru

National Institute for Research and Development of
Isotopic and Molecular Technologies, Cluj-Napoca
Aleea Tarniţa Nr. 7, Apt. 11, 400659 Cluj-Napoca ,
ROMANIA e-mail: g.vasaru@from.ro

Development of a variety of isotope separation processes is an important R&D activity, because there is no one isotope separation process which is economically superior to all others for every isotope. The best method of separation can be chosen only after an evaluation of the chemical and physical properties of nuclides involved, the degree of separation desired, the scale of the operation, the capital investment, the energy consumption, and the operating and maintenance costs for each competing separation process. The availability of a variety of isotope separation methods also allows the option of combining two or more processes for a more economical isotope production.

Oxygen exists in seven isotopic forms. The isotopes of mass 14, 15, 19 and 20 are radioactive, having half-lives of two minutes or less. Those of mass 16, 17 and 18 are stable; their normal abundance is 99.762 %, 0.038 % and 0.200 %, respectively. Until some times ago, research involving oxygen tracing has been performed almost exclusively with ^{18}O. This isotope can be concentrated conveniently by several techniques, and it is currently available in purities up to > 99.5 %. However, use of ^{18}O is sometimes inconvenient since elaborate recovery procedures may be necessary to prepare the sample for analysis by existing methods. Some research cannot be performed at all because of conflicting conditions required in the sample recovery step. Prior the development of the Nuclear Magnetic Resonance (NMR) there was no alternate course; now, with the NMR spectrometer, it is feasible to use ^{17}O as a tracer. In certain instances the analysis may even be performed without interfering with the experiment.

^{17}O can be used as a tracer in the study of cerebral oxygen utilization. Compounds labeled with ^{17}O (nuclear spin $I = 5/2$) are used in NMR experiments. Researches are currently exploring the use of ^{17}O to provide improved lung images.

Use of the NMR technique depends upon the availability of oxygen enriched in ^{17}O. Small quantities of low purity oxygen-17 have become available, largely as a by-product of ^{18}O enrichment, but no highly enriched material has been or is available. In response to this need, there has been constructed at the Oak Ridge National Laboratories the world's first facility designed for the production of research quantities of highly enriched ^{17}O purities of 50% and greater. The enrichment process is a combination of two different isotopic separation methods: distillation of water and thermal diffusion of oxygen gas. ^{17}O is first concentrated from 0.038 % to 3.67 % in a cascade of water distillation column. The partial enriched water from this process is electrolyzed and the resulting ^{17}O is concentrated to 50% in a cascade of hot-wire thermal diffusion columns.

This paper reviews the methods used for separation of ^{17}O. The separation processes are considered both from a laboratory and a commercial viewpoint.

STABLE ISOTOPE EXCHANGE BETWEEN WATER PHASES IN SYNTHETIC AND NATURAL SYSTEMS

Jorge E. Spangenberg
Institute of Mineralogy and Geochemistry, University of Lausanne, Switzerland, Jorge.Spangenberg@unil.ch

The stable isotope composition of water (δ^2H and $\delta^{18}O$) is a powerful tracer of fluid sources, pathways, mixing processes, phase separations and dissolved constituents. In this lecture we present the results of two case studies of variation of δ^2H and $\delta^{18}O$ values of waters stored in PET bottles, and waters from mine tailings in different climatic environments.

Permeability, sorption, desorption, diffusion and solubility of water, water vapor, oxygen, carbon dioxide, nitrogen, and methane in organic polymer films varies with film thickness, relative humidity, polymer crystallinity and temperature. Water sorption and diffusive transfer of water molecules through the wall of the PET bottle may cause isotopic exchange between water within the bottle and water vapor in air near the PET-water interface. In this study, a set of bottled waters from a single natural spring, has been used to examine the effects of storage in plastic polymer material on the isotopic composition of the water. The chosen bottled water is the natural spring water of Evian, which is distributed throughout most of the world in PET and locally also in glass bottles. This permits examination of the changes in the stable isotope composition of water stored in the same type of PET bottle, presumably produced and cleaned via the same procedures, but where the water was stored and transported within these bottles for different times and at different conditions of temperature, pressure, and humidity. 30 bottles of Evian bottled water were obtained from 27 locations in 19 countries. Changes of about +4‰ for δ^2H and +0.7‰ for $\delta^{18}O$ have been measured for water after 253 days of storage within the PET bottle.

The stable isotope composition of waters can be used as natural tracer of hydrologic processes in systems affected by acid mine drainage. We investigated the δ^2H and $\delta^{18}O$ values of pore waters from four oxidizing sulfidic mine tailings impoundments in different climatic regions of Chile (Piuquenes at La Andina with Alpine climate, Cauquenes and Carén at El Teniente with Mediterranean climate, and Talabre at the Chuquicamata deposit with hyperarid climate). No clear relationship was found between altitude and isotopic composition. The observed displacement of the tailings pore waters from the local meteoric water line towards higher $\delta^{18}O$ values (by ~ +2‰ $\delta^{18}O$ relative to δ^2H) is partly due to water-rock interaction processes, including hydration and O-isotope exchange with sulfates and Fe(III) oxyhydroxides produced by pyrite oxidation. In most tailings, from the saturated zone towards the surface isotopically different zones can be distinguished. Zone I is characterized by an upward depletion of ^2H and ^{18}O in the pore waters from the saturated zone and the lowermost vadose zone, due to ascending diffused isotopically light water triggered by the constant loss of water vapor by evaporation at the surface. In the zone II, the capillary flow of a mix of vapor and liquid water cases an evaporative isotopic enrichment in ^2H and ^{18}O. At the top of the tailings in dry climate a zone III between the capillary zone and the surface contain isotopically light diffused and atmospheric water vapor. In temperate climates, the upper part of the profile is affected by recent rainfall and zone III may not differ isotopically from zone II.

FOOD QUALITY ASSURANCE: AN APPLICATION OF STABLE ISOTOPE MEASUREMENTS FOR BOTTLED WATERS

<u>István Fórizs</u>[1], József Deák[2]

[1] *Institute for Geochemical Research, Hungarian Academy of Sciences, 1112 Budapest, Budaörsi út 45, Hungary*
[2] *GWIS Ltd., 2120 Dunakeszi, Alkotmány u. 45, Hungary*

As globalization of market is going on, the importance of quality assurance of food is growing. Especially in Europe, where the inner borders are opened for the free movement of food. In many cases quality is connected with geographical origin, so EU adopted measures (EU-regulation 2081/92)[1] to protect the origin assignment.

In the recent years a significant work has been made around the regulation of use of water for different purposes in EU including tap water and bottled water (EU Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption). The laws adopted in EU level have changed the national regulations on drinking and bottled waters in many EU countries (in Hungary too).

Usually brand name or indication of geographical origin (source of water) help the consumer, but a brand name can be misleading if waters of different locations are bottled under the same brand name and difference is indicated by very small letters.

Similar to many other foods (e.g. wine, milk, juice) the geographical origin of bottled water can be traced by natural tracers as stable isotopic or chemical components. The easiest way of characterizing the geographical origin of bottled waters would be to make a δ^{18}O map of EU as proposed by Voerkelius[2]. Principle of this map is that δ^{18}O of precipitation (and of groundwater) follows a characteristic regional distribution within Europe. Regarding the Carpathian Basin this simple model is expected not to work, because a significant ratio of the groundwater is of Ice Age origin (more than ten thousand years old) characterized by a stable isotopic composition more negative than the recently infiltrated groundwater[3].

To check this idea 12 brands of bottled waters bottled in Hungary and Romania have been studied for their stable oxygen and hydrogen isotopic composition. Results confirm that a significant number of bottled waters are of Ice Age origin: characterized by δ^{18}O and δD values ranging from -14‰ to -11‰, and from -100‰ to -80‰ in contrary to average values of -9,3‰ and -65‰ of the Holocene infiltrated groundwater in Hungary.

---

[1] CEC (1992) Commission of the European Communities Council Regulation (EEC) No. 2081/92 of July 14 1992. Official Journal of the European Communities 208/1.

[2] Voerkelius, S. (2007). *Geographical Specifications for Mineral Water*. Proceedings in: 3rd annual meeting TRACE: Perspectives from Science, Supply Chain and the Consumers, Limenas Hersonissou - Crete - Greece, 26-27 April 2007, 42.

[3] Stute, M. - Deák, J. (1989) *Environmental isotope study (^{14}C, ^{13}C, ^{18}O, D, noble gases) on deep groundwater circulation systems in Hungary with reference to paleoclimate.* Radiocarbon 31(3):902-918

THE MIOCENE VOLCANISM IN THE STYRIAN BASIN, AUSTRIA : INSIGHTS FROM THE ISOTOPIC RECORD

Ana Voica - Bojar (1), S. Halas (2), H.-P. Bojar (3), J. Szaran (2)

(1) Institute for Earth Sciences, Graz University, Austria, ana-voica.bojar@uni-graz.at
(2) Mass Spectrometry Laboratory, Institute of Physics, Lublin, Poland,
(3) Department of Mineralogy, Landesmuseum Joanneum, Graz, Austria

The Styrian basin was formed during Miocene eastward tectonic extrusion and orogen-parallel extension. The Miocene to Pliocene volcanic rocks are found as an arc, extended between the Styrian basin to the west and lake Balaton to the east. The Miocene volcanics are characterised by high-K trachyandesites, trachites and basaltic trachyandesites. The age of the volcanism extend from 16.8 to 14.2 Ma. The Gossendorf volcanic body is the only one in the Styrian basin, showing extensive hydrothermal alteration. In this study we investigated the age of rocks and alterations as well as the source of fluids by determining the stable isotopic composition of mineral concentrates from the magmatic body and alteration zone. The study allows to constrain the origin of Gossendorf hydrothermal alteration and to associate it with other Miocene hydrothermal alterations from the Alpine-Carpathian-Pannonian area.

The sulphur, oxygen and hydrogen stable isotope composition of the alteration products such as opal, barite, pyrite and alunite combined with mineralogical investigations as XRD indicate temperatures between 150 and 200°C for the formation of the alteration zones. Sulphur isotopic compositions of sulphur, sulphides and sulphates indicate disequilibrium, and progressive oxidation. This fact combined with the mineral zonation of the alteration zone reflects not only change in the pH but also change in the fO_2 of the ascending fluids.

During the Miocene, in the Alpine-Carpathian-Pannonian area a non-subductional volcanism occurred in the Apuseni Mountains as well. Similar to the Styrian basin the Miocene volcanism from the Apuseni is related to deep-seated shear zones active during the Miocene escape tectonic, although the Apuseni rocks are largely hydrothermal altered. The reduced extensional component in the Styrian basin may explain the low influx of exogene fluid and thus the limited extent of volcanic alterations.

PROCESS ORIENTED ISOTOPE STUDIES IN ANTHROPOGENIC AFFECTED ENVIRONMENT

Gerhard Strauch
Helmholtz-Zentrum für Umweltforschung – UFZ,
Permoserstraße 15, D-04318 Leipzig, Deutchland

In the 21th century the water resources will increasingly appear on the agenda of economy, politics and human needs. Many of water resources are unprotected; they are affected by pollutants of different origin and ecotoxicity. Several efforts are done to overcome the status of polluted water systems. One of those is the European Water Framework Directive having the goal of a "good status of water" in surface and groundwater. To support such regulations a lot of scientific studies are dealing with the impact and sources of contaminations, the degradation of pollutants, and the assessment of water resources. In all these studies the isotope methods play an important role to understand processes for improving the quality of water.

Some of typical anthropogenic impacts on the natural water cycle are presented by three examples of isotope investigations on water systems.

Nitrate pollution from agricultural activities often persistently affects groundwater quality due to long residence times in the vadose and saturated zone. In a drinking water area in the loess region of Saxony, Germany, the risk of nitrate pollution and its development for the next dozens of years was evaluated. In this study we used nitrogen and oxygen isotopes to evaluate the source of nitrate which is caused by soil organic matter and organic fertilizers. By means of tritium, ^{3}He and CFC we estimated the residence time of groundwater and nitrate from the agriculturally used drinking water catchment.

The rehabilitation process in mining areas influences the long term development of the groundwater quality. Typical processes like the acidification of groundwater by pyrite oxidation, the hydrodynamic of mineralised pore and lake water, but also sulphate reduction and the saturation of the dump site influence the water quality. An example is presented from the Lusatia lignite mining site, East Germany. H/O isotopes characterize the hydrodynamic of pore and lake waters. Qualitative evidence of bacterial sulfate reduction could be detected by S and O isotope fractionation. Concluded by those isotope studies is that sulfate reduction is an increasing dominant process in mining sites which may improve the water quality in dump sites.

Urban water systems are polluted by diffuse and direct contributions from anthropogenic activities. For assessing the impact of human activities on the urban water system, isotope analyses seem to be a useful tool to estimate the origin of contaminants, possible transformation processes ongoing within the aquatic environment, and their distribution within the urban water system. Here, we present a study on the urban water components of the cities of Leipzig and Halle, Germany, using a multi-isotope approach of analysing the stable isotopes of H/O from water, S/O from sulphate, N/O from nitrate, and boron isotopes in connection with hydrochemical data

METABOLIC ORIGIN OF ^{13}C OF DARK-RESPIRED CO_2: COMPARISON BETWEEN LEAVES AND ROOTS

Camille Bathellier (1), Guillaume Tcherkez (1,2), Richard Bligny (3), Elisabeth Gout (3), Franz W. Badeck (4) & Jaleh Ghashghaie (1)

(1) Laboratoire d'Ecologie, Systématique et Evolution, CNRS-UMR 8079, Bât 362, Université Paris-Sud, 91405-Orsay cedex, France.
(2) Plateforme « Métabolisme-Métabolome », IFR « Plante et son Environnement », Institut de Biotechnologie des Plantes, Bât 630, Université Paris-Sud, 91405-Orsay cedex, France.
(3) Laboratoire de Physiologie Cellulaire Végétale, CEA, 38054 Grenoble Cedex 9, France.
(4) Potsdam Institute for Climate Impact Research (PIK), 14412, Potsadm, Germany.

The photosynthetic discrimination against ^{13}C leads to a ^{13}C-depletion of plant organic matter while the CO_2 left in the atmosphere gets ^{13}C-enriched. Thus, records of the variation of the isotopic composition of CO_2 above ecosystems can be used to distinguish between photosynthetic and respiratory fluxes. However, the generally accepted hypothesis in such studies that no discrimination occurs downstream photosynthetic fixation is now questioned [1], especially concerning respiration. Several studies have thus shown that the CO_2 respired by leaves in the dark is ^{13}C-enriched compared to organic matter, while it is ^{13}C-depleted in the case of roots [2, and references therein]. Although the relation between the metabolism and the ^{13}C of respired CO_2 has been explored in leaves [3], no such metabolic rationale is available for roots. A better understanding of root respiratory processes is thus necessary, especially since root respiration is a major contributor to soil CO_2 efflux, and so an important component of ecosystem respiration. To address this issue, we conducted ^{13}C-analysis on CO_2 and metabolites in typical conditions or in continuous darkness, both under natural abundance and following labelling with ^{13}C-enriched glucose or pyruvate (in specific carbon atom positions) using IRMS and NMR techniques. Surprisingly, it was found that the $\delta^{13}C$ of root-respired CO_2 remained constant (around -27.5‰) under continuous darkness, despite the decrease in the respiration rate and respiratory quotient. Indeed, we have previously shown that the $\delta^{13}C$ of leaf-respired CO_2 decreased together with the decrease in respiratory quotient leading to a linear relationship between these 2 parameters [3]. This strongly suggested that the variation in $\delta^{13}CO_2$ is a direct consequence of a substrate switch to feed respiration: carbohydrate oxidation producing ^{13}C-enriched CO_2 and β-oxidation of fatty acids producing ^{13}C-depleted CO_2 compared to organic matter. This is consistent with the assumption that the $\delta^{13}C$ of dark-respired CO_2 in the leaves is determined by relative contribution of the 2 major decarboxylation processes occurring in the dark: pyruvate dehydrogenase activity and the Krebs cycle. Labelling experiments on roots allowed us to infer, in typical conditions, an important contribution of the pentose phosphate pathway to respiration (22%) and fluxes that appeared quite similar along glycolysis and the Krebs cycle. Continuous darkness mainly affected the Krebs cycle which seemed to become notably reduced, the ongoing synthesis of glutamate being sustained by the anaplerotic action of PEPc [4]. It is concluded that the invariance in the isotope composition of root respired CO_2 under continuous darkness is driven by compensations between both the different fractionating steps and the composition of the respiratory substrate mix.

Comparison between autotrophic organs (leaves) and heterotrophic organs (roots) will be discussed.

[1] Badeck *et al,* (2005) *Rap Comm in Mass Spec* 19: 1381-1391.
[2] Bathellier *et al*, (2008a) *New Phytol* 117: 406-418.
[3] Tcherkez *et al,* (2003) *Plant Physiol* 31: 237-244.
[4] Bathellier *et al*, (2008b) *New Phytol (accepted).*

ORAL PREESENTATIONS

GC ISOLINK: A NEW CONCEPT FOR AUTOMATED MULTI-ELEMENT IRM-GC/MS

H. Katzlinger*, D. Juchelka, M. Krummen**, A. Hilkert** and J.B. Schwieters****

**Thermo Fisher Scientific, Austria*
***Thermo Fisher Scientific (Bremen) GmbH, Germany*

About 30 years ago D. E. Matthews and J.M. Hayes have introduced *c*ompound *s*pecific *i*sotope *a*nalysis (CSIA) by *i*sotope *r*atio *m*onitoring GC/MS (irm-GC/MS). At the beginning the challenge was the development of a suitable reaction interface that provides quantitative conversion of compounds while maintaining chromatographic integrity.

Today two different conversion technologies, combustion and high temperature conversion (pyrolysis) are applied to determine the isotope ratios of the major bioelements C, N, O and H.

irm-GC/MS together with other continuous flow applications have revolutionized *i*sotope *r*atio *m*ass *s*pectrometry (IRMS) within the last 20 years. Continuous flow techniques can be found in all fields of application with improved performance on sample size, throughput, multiple isotope methods, overall precision and ease of use. Multi-element and multi-component analyses are performed to deduce unambiguous isotope fingerprints.

The growing interest and appreciation in isotope ratio applications requires new features and functionalities of the instrumentation.

The GC IsoLink follows a new concept for an automated multi-element irm-GC/MS. It includes automated switching between a combustion reactor and a high temperature conversion reactor only by changing the gas flow direction. The combustion mode has been redesigned so that C and N isotope ratios can be determined with the same reactor setup.

The concept incorporates the ConFlo IV as the interface to the IRMS. All ConFlo IV capabilities are available for irm-GC/MS, e.g. injection of up to five reference gases, reference gas dilution and automatic H_3^+ factor determination.

The principle of the device is discussed with respect to the dynamic range, precision, accuracy together with the requirements on sample size. Examples for multi-element and multi-component isotope analysis will be shown.

ENZYMATIC SYNTHESIS OF SOME L-AMINO ACIDS ISOTOPICALLY LABELED WITH ^{15}N

<u>Maria Chiriac</u>[1], Iulia Lupan[2], Flavia Popa[1] , N. Palibroda[1], O.Popescu[2]

[1]National Institute for Research and Development of Isotopic and Molecular Technologies; 400293 Cluj-Napoca, P.O. BOX 700, Romania.
[2]Molecular Biology Center, Institute for Interdisciplinary Experimental Research, Babeş-Bolyai University, Cluj-Napoca, Romania.

Stable isotope-labelled amino acids a useful for biological studies of amino acid metabolism, for examining the tertiary structure of proteins by NMR spectroscopic techniques and in medical and agricultural researches to study biochemical and nutritional problems.

L-amino acids labelled with ^{15}N are frequently either commercially unavailable or prohibitively expensive. Chemical synthesis of the amino acids usually produces a racemic product, although there is occasionally a strong bias towards a single isomer.

Enzymatic synthesis however can be made to produce the L-isomer alone. Such enzymatic synthesis has been carried out by conventional fermentation techniques, or by biosynthesis using either isolated cells, or enzyme extracts

In this paper we report a simple enzymatic procedure for preparation of L-[^{15}N]-serine, L-[^{15}N]-metionine and L-[^{15}N]-glutamic acid from corresponding α-keto acids as substrate, using bacterial NAD-dependent amino acids dehydrogenase: alanin dehydrogenase (AlaDH), leucine dehydrogenase (LeuDH) and glutamate dehydrogenase (GDH) as a catalyst.

The reaction mixtures included glucose dehydrogenase (GlucDH) for NADH regeneration with glucose as an electron donor.

As isotopically labelled material we used $^{15}NH_4Cl$ 99 at.%^{15}N produced at National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania.

The reactions are simple and efficient for producing in gram quantities of ^{15}N –labelled amino acids, with good yield .

The amino acids were purified by ion exchange chromatography or by classical methods.

All compounds were fully characterized by Mass Spectrometry analyses, by FT-IR Spectroscopy and RX Diffraction, and the isotopic label was determined by MS on the molecular compounds.

REFERENCES

[1]. **J.E. Rose, P.D. Leeson, D. Gani**, J. Chem. Soc., Perkin Trans. 1, p.1563 (1992).

[2]. **A. Martin, G. Chassaing, A. Vanhove**, „Synthesis and Applications of Isotopically Labelled Compounds", eds. J. Allen, R. Voges, Wiley, New York, p. 761 (1995).

[3]. **W.F.J. Karstens, H.J.F.Berger, E.R. van Haren, J. Lugtenberg, J. Raap**, J. of Lab. Compds. and Radiopharm., 11,p.1077 (1995).

[4]. J. **Hanners, R. Gibson, K. Velarde, J. Hammer, M. Alvarez, J. Griego, C.J. Unkefer**, J. of. Lab. Compds. and Radiopharm., Vol. XXIX, Nr. 7, p. 781-790 (1991)

[5]. **A. Galkin, L. Kulakova, T. Yoshimura, K. Soda, N. Esaki**, Appl. Environ. Microbiol., p. 4651-4656 (1997).

[6]. **F. Jeanjean, N. Perol, J. Gore, G. Fournet**, Tetrahedron Letters, vol.38, nr. 43, p. 7547-7550 (1997).

[7]. **W. Greenaway, F.R. Watley**, Febs Letters, vol. 75, nr.1, p. 41-43 (1997).

[8]. **J.A. Chanatry, P.H. Schafer, M.S. Kim, D.M. LeMaster**, Analytical Biochemistry, 213, p.147-151 (1993).

[9]. **Cl. Audigié, G. Dupont, F. Zonszoin**, *"Biosciences et techniques principes des méthodes d'analyse biochimique"*, ed. 3, vol. 1, p. 202 (1992).

[10]. **J. A. Charatry, P. H. Schafer, M. S. Kim, D. M. LeMaster**, *Anal. Biochemistry,* 213, p. 147-151 (1993).

[11]. **T.E. Walker, R.E. London, „Appl. Environ. Microbiol**.", Vol. 53, Nr. 1, p. 92-98 (1987).

DYNAMIC MODELLING AND SIMULATION OF ^{15}N ISOTOPE SEPARATION BY CHEMICAL EXCHANGE IN NITROX SYSTEM

Paula Raica[1], D. Axente[2]

[1]*Technical University of Cluj-Napoca*
15 C.Daicoviciu Str., 400020 Cluj-Napoca, Romania
e-mail: Paula.Raica@aut.utcluj.ro
[2]*National Institute for Research and Development of*
Isotopic and Molecular Technologies
400293 Cluj-Napoca 5, P.O.Box 700, Romania
e-mail: axente@itim-cj.ro

The dynamic behavior of a ^{15}N separation process by chemical exchange in NO,NO_2-HNO_3 system has been analyzed based on an accurate mathematical model. A nonlinear system of first-order partial differential equations was determined, by considering the multiple exchange reactions between the components of the gaseous mixture (NO, NO_2, N_2O_4 and small quantities of N_2O_3) and the liquid phase constituents (NO_3^-, NO_2^-, solved nitrogen oxides, HNO_3, HNO_2). The mathematical model of the process describes the space-time variation of the ^{15}N concentration (mole fraction) in gas and liquid phases of the separation column and provides a better understanding of plant operation limits and decision support in process design and optimization.

References

1. Paula Raica, D. Axente, *Modeling and Steady-State Analysis of ^{15}N Isotope Separation by Chemical Exchange in Nitrox System*, 5th Conference on Isotopic and Molecular Processes PIM 2007, Cluj-Napoca, September 20 – 22, (2007),
2. D. Axente, M. Abrudean, A. Bâldea, *Separation of isotopes ^{15}N, ^{18}O, ^{10}B, ^{13}C by isotopic exchange* (in Romanian), Casa Cărții de Ş tiință, (1994)
3. D. Axente, M. Abrudean, A. Bâldea, *Nitrogen isotope ecxhange between nitric oxide and nitric acid*, J.Radioanal.Nucl.Chem., Vol. 207, No. 1, (1996), 163 – 170
4. A. Kitamoto, K. Takeshita, *A Two-Step Model forAdvanced Separation for ^{13}C by the Chemical Exchange Method between CO_2 and Amine in a Nonaqueous Solvent*, Proc. Of The International Symposium on Isotope Separation and Chemical Exchange Uranium Enrichment, 1990.
5. Paula Raica, D. Axente, *Enrichment of ^{13}C by chemical exchange between CO_2 and amine carbamate in nonaqueous solvents*, J. Radioanal. Nucl.Chem., Vol. 251, No. 3, (2002) 443–449.
6. Paula Raica, D. Axente, Analysis of 235U Enrichment by Chemical Exchange in U(IV)-U(VI) System on Anionite, Sep.Sci.Technol., Vol. 42, No.5, (2007), 1065-1077.

THE ^{14}N AND ^{15}N SIMULTAN SEPARATION BY ISOTOPIC EXCHANGE IN NO, $NO_2 – HNO_3$ SYSTEM UNDER PRESSURE

Damian Axente, Cristina Marcu, Ancuţa Mureşan, Martin Kaucsar, Ioan Mişan, Gabriel Popeneciu, Nicolae Gligan, Gabriela Cristea

National Institute for R. & D. of Isotopic & Molecular
Technologies, 400293 Cluj-Napoca, Donath Str. 65-103,
P.O. Box 700, Romania
axente@itim-cj.ro

In the natural abundance compounds the stable isotopes of nitrogen have the following isotopic concentrations: 99.635 at. % ^{14}N and 0.365 at. % ^{15}N. The less abundant isotope, ^{15}N, is utized for synthesis of an important number of organic and inorganic labelled compounds, destined to research activities in agrochemistry, biology, medicine, chemistry, environmental sciences, etc.

^{14}N, highly depleted of ^{15}N, has several applications in nuclear physics, chemical and industrial research.

The heavier isotope of nitrogen, ^{15}N, is produced at more than 99 at. % concentration by isotopic exchange in the system NO, $NO_2 – HNO_3$.

In this paper an experimental study on simultan separation of both isotopes ^{14}N and ^{15}N, using the same isotope exchange system under pressure, is presented.

The experiments were performed on a laboratory pilot plant with a stainless steel separation column of 100 cm length and 18 mm inside diameter, packed with triangular wire springs of 1.8x1.8x0.2 mm. The separation column has two refluxers: in the product refluxer, 700 mm length, 52 mm i.d., made of hastelloy, with 3-4 mm ceramic packing, nitric acid is quantitatively converted into nitrogen oxides, by reaction with sulfur dioxide.

In the waste refluxer, 77 cm length, 34 mm i.d., made of stainless steel, packed with stainless steel triangular wire springs 1.8x1.8x0.2 mm in two sections with a space between them, the oxides of nitrogen are converted to nitric acid by reaction with oxygen and water.

At 1.8 atm (absolute) and 3.14 ml/cm^2.min, 10M HNO_3, HETP is practically equal with that obtained at atmospheric pressure and two times smaller flow rate. At steady state the isotopic concentration at the bottom of separation column was 0.554 at. % ^{15}N and in the top of the column was 0.113 at. % ^{15}N.

The HETP and flow-rate values, obtained in this experimental study in NO, $NO_2 – HNO_3$ system under pressure, allows the simultan separation of ^{14}N, highly depleted of ^{15}N, and of ^{15}N at more than 99 at. % ^{15}N concentration.

THE UNIFORMLY AND SELECTIVE ^{15}N-LABELLING OF THIOL PEROXIDASE FROM *BACILLUS SUBTILIS*

<u>Iulia Lupan</u>[1], Maria Chiriac[2], O. Popescu[1]

[1]Molecular Biology Center, Institute for
Interdisciplinary Experimental Research, Babeş-Bolyai
University, 400271, 42 August Treboniu Laurian street,
Cluj-Napoca, Romania
[2]National Institute for Research and Development of
Isotopic and Molecular Technologies; Cluj-Napoca,
Romania.

The *Escherichia coli* expression system is the most powerful system for expression of recombinant proteins. One of the major advantages of this system is represented by the ability to easy production of highly yields proteins.

The coding gene for thiol peroxidase (*tpx*) from *Bacillus subtilis* was cloned into pET28b vector from Novagen. Thiol peroxidase (thioredoxin peroxidase, thiol-specific antioxidant protein or peroxiredoxin) is a protector protein that eliminates H_2O_2 and alkyl hydroperoxides. The recombinant protein was expressed in bacterial system (*Escherichia coli* strain BL21(DE3)) on minimal media. This work describes the production and purification of uniformly ^{15}N-labeled thiol peroxidase and selective labeling of protein with ^{15}N-Leucine for MNR structure studies without the use of an auxotrophic strain.

STABLE CARBON ISOTOPIC COMPOSITION ($\delta^{13}C-CH_4$) AND CONCENTRATION OF METHANE IN AMAZON TROPICAL FORESTS

José Mauro Sousa Moura[1], Reynaldo Luiz Victoria[1], Christopher Sargent Martens[2], Marcelo Zacharias Moreira[1], Howard P Mendlovitz[2], Risonaldo Leal Lima[3]

[1]Centro de Energia Nuclear na Agricultura –CENA/USP, Avenida Centenário, 303, São Dimas, 13416-903, Piracicaba, SP, Brasil;

[2]Department of Marine Sciences, CB-300, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3300, USA;

[3]Projeto LBA-ECO, Rua Vera Paz, S/N, Salé, 68040-260, Santarém, PA, Brasil;

Here we present preliminary results of the stable carbon isotopic composition ($\delta^{13}C-CH_4$) and concentration of methane in atmospheric air samples from in upland tropical forest in the Amazon. This is the first dataset ever collected in the region for stable carbon isotopes analyses. The campaigns were carried out at the Tapajós National Forest (TNF) and Caxiuanã National Forest (CNF). Atmospheric air samples were collected in a vertical profile (0.2, 7.0, 15.0, 22.0, 35.0, and 45.0 m) in different times of the day (4:00, 16:00, 22:00, and 24:00h) during the wet (Dec-Jan) and dry season (Sep-Oct). The air samples were pulled through tubes by a battery-operated pump and then stored into glass flasks. The $\delta^{13}C-CH_4$ was determined by mass spectrometry (Finnigan Mat 252 equipped with HP 5890GC, interfaced to a CF/GCC/MS) and the concentration was determined by gas chromatography (Shimadzu 14A – Greenhouse). The $\delta^{13}C-CH_4$ varied from -49.46‰ to -46.00‰. The overall mean value found was equal to -47.51‰. The concentration varied from 1.82ppmv to 2.75ppmv, with overall mean equal to 2.09ppmv. $\delta^{13}C-CH_4$ and concentration were both in the range for values found for atmospheric methane. Both sites showed seasonal variation in $\delta^{13}C-CH_4$ and concentration, being more depleted in ^{13}C and more concentrated during the dry season than during the wet season. A spatial variation was observed only for $\delta^{13}C-CH_4$. The CNF showed a mean value of $\delta^{13}C-CH_4$ more depleted than the mean values measured at the TNF. The lightly depleted values observed at the lowest height (0.2m) suggests that microbial production might be an important source of the gas, however other sources with different origins could co-exist along the profile and could contribute differently to the isotopic composition of the CH_4 released.

CHLORINE-36 IN NUCLEAR WASTES - AN UNEXPECTED PROBLEM

Allan T. Emrén

Nuchem Research AB, Runnshultsv. 3, Tollered, Sweden
allan@nuchem.se

In the radioactive wastes from nuclear power plants, ^{36}Cl is merely a minor component. Thus, one would expect it to be of minor importance in the safety assessment of repositiories for spent nucler fuel and other radioactive wastes. In some scenarios, however it appears as the main component causing radioactive hazards to the environment.

It is formed in negligible quantities as fission products. Rather, the major source of this isotope is neutron activation of ^{35}Cl. Use of materials in which chlorine is a major component, is avoided in parts of the reactor subject to neutron irradiation.

Thus, the essential source of ^{36}Cl is impurities in the construction materials. As a consequence, the quantities present in nuclear wastes is small. In some cases, however, the nuclide turns out to the dominant nuclide contributing to the dose given off to the biosphere from a repository for spent fuel or other kinds of nuclear wastes.

The reason is a combination of long half life and the poor retardation by engineered and natural barriers. Cl^- is an important component in most groundwaters. Thus, any material that is able to sorb chlorine is saturated in the natural state, making ^{36}Cl appear like an inert species.

If transmutation is used to take care of nuclear wastes, ^{36}Cl is troublesome for a different reason. In the nuclear wastes, it is almost a trace nuclide mixed with major amounts of the stable isotopes ^{35}Cl and ^{37}Cl. Any attempt to get rid of ^{36}Cl by neutron irradiation will result in production of larger quantities.

Future fusion reactors will have far higher neutron fluxes than the fission reactors, causing the problem of ^{36}Cl to be even worse. So in the future, one will have to either be extremely careful about removing any traces of Chlorine from the construction materials or invent a cheap and very effective method for isotope separation.

APPLICATION OF ISOTOPE DILUTION TECHNIQUES FOR DETERMINATION OF MICROPOLLUTANTS IN WATER

Zaharie Moldovan,

National Institute of Research and Development for Isotopic and Molecular Technology, INCDTIM, Cluj-Napoca, Str. Donath 65-103, Romania, E-mail: zaha@.itim-cj.ro

Due to dilution and degradation, lower concentration levels of organic micropolutants are expected after they enter the aquatic environment[1]. To obtain detection limits down to lower ng/l range high enrichment and sensitive detection methods such as GC/MS, GC-MS/MS or LC-ES-MS/MS are essential[2].

The objective of the present study was to investigate the behaviour of selected Pharmaceuticals and Personal Care Products (PPCPs) during the transport in the river Somes by mass flow analysis.

Due to an incomplete elimination in wastewater treatment plant (WWTP) residue of pharmaceutical and personal care products are found both in waste and surface waters. Although most pharmaceuticals are designed to target specific metabolic pathways in humans and domestic animal, they can have numerous often unknown effects on metabolic systems of nontarget organisms. As analytes, the following were chosen: acidic pharmaceuticals (ibuprofen), neutral pharmaceuticals (caffeine, carbamazepine, diazepam, pentoxyfylline), musk fragrances (galaxolide, tonalide) and an anti-microbial compound (triclosan).

The analytes were concentrated by solid-phase extraction (SPE) procedures and subsequently measured by a GC/ITMS system[3]. For exact quantification of the target compounds the Isotope Dilution Technique was applied. The method has few main advantages: 1) The labeled compound has almost exactly the same chemical properties as the original or naturally occurring isotopes, they just differ in mass; 2) Improve precision and accuracy reducing the problems with calibration and sample preparation matrix effects. This is as close as it gets to a "perfect" internal standard or surrogate; 3) Predicted mass spectral effects. If the original compound has the molecular ion $M^{+\cdot}$ and base peak m/z= I_b the corresponding labeled compound will have molecular ion $[M+A]^{+\cdot}$ and base peak to m/z=$[I_b+B]^+$. *A* and *B* are mass difference due to heavy stable isotopes from the labeled compound and can be easy determined.

Quantification was performed using corresponding labelled internal standards: $^{13}C_3$-Ibuprofen, $^{13}C_3$-Caffeine, D_3-Tonalide, $^{13}C_{12}$-Triclosan, D_{10}-Carbamazepine, D_5-Diazepam added prior to enrichment. The limit of quantification (LOQ) ranged between 2.5 and 37 ng/l (ratio signal/noise 10) depending on the compound and the error was generally less than 5%.

References:

1) D. V. Kolpin, et al., *Environ. Sci. Technol.,* 2002, **36**, 1202-1211.
2) Sacher F, et al., *J. Chromatogr. **A**, 2001, 199-210.*
3) Z. Moldovan, et al., *J. Env. Monitoring, 2007, **9**, 986-993*

METAL CONTENT AND ISOTOPIC CHARACTERIZATION OF SOME ROMANIAN WINES. PRELIMINARY RESULTS

<u>A. Pamula</u>, Cezara Voica, Adriana Dehelean

National Institute for Research and Development for
Isotopic and Molecular Technologies,
Donath str. 65 – 103, P. O. Box 700, 400293 Cluj-Napoca, Romania

Eleven wine assortments from Romania and Moldavian Republic were investigated from the point of view of their metal content and isotopic ratios $^{206}Pb/^{207}Pb$ and $^{86}Sr/^{87}Sr$. The determination was performed by ICP-Q-MS.

Thirty metals with significant concentration were identified, from which potassium was the most abundant (0.5 μg/ml to 1.13μg/ml). Relative important concentration of chromium (230 μg/l to 46700 μg/ml) and nickel (59 μg/l to 66000 μg/l) are perhaps originating from the technological procedure of vinification (fermentation in stainless steel tanks).

Traces of Cd (0.14 μg/l to 1.13 μg/l), Hg (2.5 μg/l to 17.9 μg/l) and Pb (2.5 μg/l to 315 μg/l) were also found.

Isotopic ratios give information concerning the site where the grapes were cultivated and the possible source of lead contamination.

TPR STUDY OF SUPPORTED Ni CATALYST WITH APPLICATION IN ENVIRONMENT PROTECTION, ECOLOGY AND ISOTOPIC EXCHANGE REACTIONS

Stelian Pintea[1], Petru Marginean[1], Stefan Gergely[1], Vasile Rednic[2]
and Nicolae Aldea[1]

[1] National Institute for Research and Development of
Isotopic and Molecular Technologies,P. O. Box 700,
400293 Cluj-Napoca, Romania,
[2]Babes-Bolyai University, Department of Physics, Str. M.
Kogalniceanu 1, RO-400084, Cluj-Napoca, Romania.

Supported catalyst are very used in applications regarding environmental protection, ecology and H/D isotopic exchange (for instance: H_2+HDO=HD+H_2O and H_2+NH_2D=HD+NH_3. There are some specific characteristics of this materials to be used in catalytic processes. One of the necessary condition is to have them in reduced state, otherwise they don't have catalytic activity. But, if the reduction is done at high temperatures, Ni sintering could occur, leading to a strong decrease of the specific surface of the catalyst. The specific surface is strongly correlated with the catalytic activity.

The goal of this study is to investigate the influence of the active metal concentration and of the support type on reducing temperature. For this purpose, different samples were investigated by temperature programmed reduction method (TPR). The results were obtained after numerical analysis of the experimental data. For the dependence of the reducing temperature with the active metal concentration, supported Ni catalyst on Cr_2O_3 supports were prepared. The Ni concentrations used were: 100 at %, 85 at % and 60 at %. In order to obtain the reducing temperature as a function of the different support nature, the sample prepared were Ni catalyst with 60 at % of Ni supported on Cr, Al and Mg oxides.

For data acquisition, an interface connected to a PC was used. Data displaying and analysing have been done with LabView8 software that administrate directly and automatic the acquisition plate.

References

[1.] J.W. Niemantsverdriet, *Spectroscopy in Catalysis*, VCH, Wenheim, New York, Basel, Tokio, 1993.

ISOTOPIC MIXING MODEL IN LABORATORY SIMULATION EXPERIMENT WITH DEUTERIUM; RELEVANCE FOR NATURAL ISOTOPIC TRACKING

Petru Berdea, Stela Cuna, Mihaela Falub, Alina Magdas, Edina Melita Szilagy

*National Institute of Research and Development for
Isotopic and Molecular Technologies, Donath St. 65 -103,
400293 Cluj Napoca, Romania, E-mail: berdea@itim-cj.ro*

The study shows the model of constant rate asymptotic isotopic mixing between two sources. This model is verified by laboratory setup that mimics repeatedly mixing of two sources with different isotopic content. The relevance of the model in the future researches in theoretically modeling of animal feeding, or in isotopic tracking will be presented.

References

1 P. Berdea, S. Cuna, C. Cuna, G. Balas, *On the correction of memory effect in isotopic analyses,* J. Mass Spectrom., **41**, 2006, 1598-1599.

2 D.M.O'Brien, M. J. Wooller, *Tracking human travel using stable oxygen and hydrogen isotope analyses of hair and urine*, Rapied Commun. Mass Spectrom., **21**, 2007, 2422-2430

3. A. E. McKechnie, B. O Wolf ,. Martínez del Rio, C. *Deuterium stable isotope ratios as tracers of water resource use: an experimental test with rock doves,* Oecologia, **140**, 2004, 191 – 200

POSTERS

P.1. SMALL ANGLE SCATTERING AS RESOLUTION HARMING FACTOR FOR ISOTOPIC PEAKS IN MASS SPECTRA

D. Ioanoviciu[1], I. Albert[1], C-tin Ciortea[2], C. Cuna[1], D. Dumitriu[2], N. Lupsa[1], V. Mirel[1]

1)National Institute for Research Development of Isotopic and Molecular Technologies P O Box 700 Cluj-Napoca Romania
2)National Institute for Nuclear Physics and Engineering "Horia Hulubei" P O Box MG 6 Bucharest Romania

A comparative analysis has been performed concerning small angle scattering generated peak wings, in various types of mass analyzers. The resolution on isotopic peaks was determined in magnetic deflector, double focusing and time of flight mass spectrometers [1]. The intensity of the scattered wings was evaluated for various types of time of flight mass analyzers as reflectrons [2] and linear drift analyzers. The calculated results were compared to the mass spectra recorded experimentally.

1. D. Ioanoviciu, C. Cuna, S. Cuna *Forme des pics d'ions stables et metastables dans les spectrometres a temps de vol* Analusis 20 (1992) 9s.
2. D. Ioanoviciu, *Elastic scattering induced peak tails in time-of-flight mass spectrometers,* Nucl. Instrum. Methods Physics Res. 363A (1995) 454.

P.2. APPLICATION OF ULTRAFILTRATION ENHANCED BY SORPTION ON NATURAL SORBENTS FOR REMOVAL OF IONS OF RADIOACTIVE METALS FROM WATER SOLUTIONS

Grażyna Zakrzewska –Trznadel , Agnieszka Jaworska, Agnieszka Miśkiewicz, Marian Harasimowicz, Andrzej Dobrowolski

Institute of Nuclear Chemistry and Technology, Dorodna
16,03-19 Warsaw, Poland

The aim of this work was a possibility of application of hybrid ultrafiltration/sorption process for removal of radionuclides from water solutions. Model solutions of metal ions or radionuclides and the apparatus for membrane filtration equipped with Amicon cell and flat-sheet membranes from cellulose acetate and polyethersulfone and ceramic tubular membranes of different cut-off were applied. The following sorbent samples were used in the experiments: commercial chitosan of average molecular weight 700 kD and 46 kD, radiation-modified chitosan, irradiated in electron accelerator with dose in 20-250 kGy range, chemically modified chitosan (by H_2O_2 oxidation), chitosan modified by two methods: chemical and radiation, like above. The experiments showed similar sorption ability of both types of commercial chitosan samples (in 56-61 mg/g range); however these two forms exhibited different kinetics of sorption. Significant reduction of time to reach equilibrium was observed for chitosan with lower molecular weight. Irradiation by e-beam caused enhancement of sorption properties of chitosan samples (sorption of the metals in the range of 80-95 mg/g). The influence of chemical treatment was lower – sorption ability of the samples was not higher than 80 mg/g.

Another sorbents tested in the work were yeasts *(Saccharomyces)*. Mechanism of absorbing the metals by yeast cells can be attained in two ways: active absorption and concentration of metal or radionuclide by living organisms or passive sorption on the material (biomass) formed by dead yeasts cells. For sorption of the metals in the experiments, biomass from bakery yeasts *(Saccharomyces cerevisiae),* was used. Subsequent treatments of dead cells were applied to obtain the sorbent: dissolution in NaOH, heating in temperature of 120 °C and filtration in the centrifuge. The suspension was dried and grounded. The kinetics of sorption of metals was determined and the influence of pH, and sorbent amount was examined. The quantity of metal adsorbed on biomass depending on process conditions was 550-850 mg/g, and the separation factors for pH 7-8 were higher than 90%.

P.3. FUNCTIONALISATION OF SOLUBLE POLYMERS APPLIED FOR REMOVAL OF ^{60}CO FROM RADIOACTIVE WASTES

Laurent Dambies[1)], **Agnieszka Jaworska**[2)],
Grażyna Zakrzewska-Trznadel[2)]

[1)] Visiting researcher in the scope of Marie Curie Transfer of Knowledge Project AMERC (MTKD-CT-2004-509226), France
[2)]Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

Polymer assisted ultrafiltration (PAUF) is a relatively new process of separation for purifying water containing metal ions. PAUF combines the ion exchange or chelating properties of a functionalized water soluble polymer with the sieving power of an ultrafiltration membrane [1-3].

As far as the synthesis of water soluble polymers concerned, two approaches can be used which are the functionalization of an existing polymer or the synthesis of the polymer starting with the individual monomers by radical polymerization. In the present work the first method using polyvinylalcohol and polyethylene glycol to attach series of different ligands (sulfonic, phosphoric, EDTA) was chosen.

The 50 mL-ultrafiltration cell Amicon was used for all experiments. In the 100 mL-volumetric flask 1 mL of cobalt stock (1 mg or 0.017 mmole) and a suitable volume of polymer solution to give 0.17 mmole of acid groups were placed. Solution was completed to 100 mL with distilled water, mixed and transferred into a beaker with a magnetic stirrer. The solution was agitated for at least 2 hours and pH was checked and adjusted if necessary, then the solution was added to the ultrafiltration cell fitted with 10,000 MW cut-off membrane (PES Millipore)

The retention of cobalt in polymer enhanced ultrafiltration was higher when modified polymers as complexing agents were applied. Strongly acidic water soluble polymer prepared from polyvinylalcohol 10,000 can be used in PAUF to remove with high capacity Co^{2+} between pH 3 and pH 6 with the same efficiency. Sulfonated PVA 10,000 performed very well with a rejection rate above 95% between pH 3 and 6.

1. I.Korus, M.Bodzek, K. Loska, Removal of Zinc and nickel ions from aqueous solutions by means of the hybrid complexation-ultrafiltration process. Separation and Purification Technology,17,1999,111-116
2. R-S. Juang, C-H. Chiou, *Ultrafiltration rejection of dissolved ions using various weakly basic water-soluble polymers*. Journal of Membrane Science 177 (2000) 207–214.
3. D.D. Reynolds, W. O. Kenyon, *Polyvinyl sulfonates and process for their preparation*. US patent 2,531,468. 1949.

P.4. OXYGEN ISOTOPIC COMPOSITION OF LACUSTRINE CELLULOSE AND AUTHIGENIC CALCITE – NEW INSIGHT INTO LATE GLACIAL AND HOLOCENE TEMPERATURE CHANGES IN CENTRAL POLAND

Klisch[1] M.A., Rozanski[1] K., Edwards[2] T.W.D.

1-AGH-University of Science and Technology, Krakow, Poland
2-University of Waterloo, Waterloo, Ontario, Canada

The $\delta^{18}O$ of lacustrine calcite potentially provides information about both temperature and $\delta^{18}O$ of lake water. If the $\delta^{18}O$ of lakewater is strongly controlled by the $\delta^{18}O$ of local precipitation, such as in a groundwater-fed lake having rapid throughflow, and lakewater temperature covaries with climatic temperature, then $\delta^{18}O_{calcite}$ may serve as a direct palaeothermometer. The "calibration" of the thermometer will be determined by two opposing relationships: temperature-dependent changes in the $\delta^{18}O_{precipitation}$ (c. +0.64‰/K for Poland; Duliński et al., 2001) and changes in the temperature-dependent equilibrium fractionation between calcite and water (c. – 0.23‰/K; Craig, 1965):

$$\Delta\delta^{18}O_{calcite}/\Delta T = 0.64‰/K - 0.23‰/K \approx 0.4‰/K \quad (1)$$

Equations like (1) have been used in many situations to reconstruct palaeotemperatures, including, for example, the development of a Holocene palaeotemperature record from $\delta^{18}O_{calcite}$ in the sediments of Lake Gosciaz. A source of significant uncertainty in this approach, however, is the possibility that changes in the hydrologic balance of a lake may alter the relation between $\delta^{18}O_{precipitation}$ and $\delta^{18}O_{lakewater}$, potentially adding spurious non-temperature-dependent signals.

Here we report results from a pilot study to test the $\delta^{18}O_{calcite}$ thermometer in Lake Gosciaz sediments by using aquatic cellulose $\delta^{18}O$ to directly estimate the $\delta^{18}O$ of lakewater at times in the past. Since the isotopic fractionation between cellulose and lakewater is believed to be constant (Edwards and McAndrews, 1989; Wolfe et al., 2007), this allows us to isolate the effects of temperature-dependent calcite-water fractionation to obtain estimates of absolute temperature changes during and between selected intervals over the past 12,000 years, without interference from possible changes in the hydrologic balance of the lake. The calibration of the cellulose-calcite thermometer in this case is described by:

$$\Delta T = (\Delta\delta^{18}O_{calcite} - \Delta\delta^{18}O_{cellulose})/(-0.23 ‰/K) \quad (2)$$

Our data from Lake Gosciaz yield some striking differences in estimated temperature changes. For example, for the Younger Dryas/Preboreal transition, equation (1) gives an increase in lakewater temperature of about +5 K, meanwhile equation (2) suggests +20 K, because of the incorporation of a pronounced shift of +6.5 ‰ observed in $\delta^{18}O_{cellulose}$. This shift in $\delta^{18}O_{cellulose}$ almost certainly reflects the influence of increased evaporative enrichment of the lakewater in response to drier conditions, which obviously cannot be accommodated by equation (1).

References:

1. Craig H., 1965, *The measurement of oxygen isotopes paleotemperatures*, In Tongiorgi, E. (ed.): Stable Isotopes in Oceanographic Studies and Paleotemperatures. Spoleto, Consiglio Nazionale delle Ricerche, Laboratorio di Geologia Nucleare, Pisa, Italy, 161-182

2. Duliński, M., Florkowski, T., Grabczak, J., Różański, K., 2001, *Twenty-five years of systematic measurements of isotopic composition of precipitation in Poland*, Przegląd Geologiczny 49, 250-256 (in Polish)

3. Edwards, T.W.D, McAndrews, J.H., 1989, *Paleohydrology of a Canadian Shield lake inferred from* ^{18}O *in sediment cellulose*, Can.J.Earth Sci.26, 1850-1859

4. Wolfe, B.B., Falcone, M.D., Clogg-Wright, K.P., Mongeon, C.L., Yi Yi, Brock, B.E., St Amour, N.A., Mark, W.A., Edwards, T.W.D., 2007, *Progress in isotope paleohydrology using lake sediment cellulose*, Journal of Paleolimnology, Vol 37, No.2, 221-231

P.5. COMPOUND-SPECIFIC CARBON ISOTOPE ANAYSIS OF NITROAROMATIC COMPOUNDS IN WATER SAMPLES USING SPE WITH GC/IRMS

Malgorzata Derda[1,3], Farrukh Ahmad[2], Mindy Vanderford[2], R.Paul Philp[1]

[1]School of Geology and Geophysics, University of Oklahoma, Norman, Oklahoma, 73019; Email: Malgorzata.Derda-1@ou.edu

[2]GSI Environmental Inc., 2211 Norfolk, Suite 1000, Houston, Texas 77098-4054,

[3]Institute of Nuclear Chemistry and Technology, Warsaw, Poland

Compound-specific isotope analysis (CSIA) using gas chromatography coupled with isotope ratio mass spectrometry (GC/IRMS) has become an increasingly important analytical tool for the assessment of the origin and fate of organic compounds in the environment. CSIA has been applied to allocate sources of many groundwater contaminants, in many environmental forensic studies. Nitroaromatic explosives are present in the groundwater at many military installations in the United States and Europe. These nitroaromatic compounds, like many others organic compounds, can attenuate naturally by different chemical and physical processes. Monitoring and documenting these natural processes over time is referred to as monitored natural attenuation (MNA). There are numerous types of natural attenuation, including biological and physical forms. It is important to know what specific mechanism is responsible for the reduction of mobility, toxicity, or bioavailability of contaminants so the long term effectiveness of the mechanism can be evaluated.

The work presented in this paper is part of project to determine field-scale stable isotope enrichment effects for the purpose of evaluating MNA of explosives and other impurities in groundwater plumes.

In this talk it is proposed to present results from the optimization of a GC/IRMS analytical method for determining compound–specific $^{13}C/^{12}C$ stable isotope ratios of nitroaromatic in contaminated water samples. The specific objectives are to determine the experimental parameters for analyte enrichment in water samples by SPE using GC-ECD for quantification and to evaluate the SPE-GC/IRMS method for the analysis of $\delta^{13}C$ isotope signature of nitroaromatic compounds with limits of detection for $\delta^{13}C$ analysis by SPE – GC/IRMS below 50 ppb.

The SPE – GC/IRMS method is very useful for the determination of isotopic enrichment factors of various nitroaromatic compounds transformation processes and provides many possibilities to monitor fate and degradation mechanisms of these contaminants in soils and groundwater.

P.6. STABLE ISOTOPES STUDY OF CO_2 EFFLUX FROM SOILS: PRELIMINARY RESULTS

Gabriela Cristea, Stela Cuna, Valentin Mirel, Alina Magdas, Edina Szilagyi and Mihaela Falub

National Institute for Research and Development of
Isotopic and Molecular Technologies, 65-103 Donath Str.,
RO-400293 Cluj-Napoca, Romania
(www.itim-cj.ro)

Stable isotopes are a powerful research tool in environmental sciences and their use to study ecosystems is increasing [1, 2, 3]. Soils carbon is a major component of the terrestrial carbon cycle. Soils contain more carbon than the combined total amounts occurring in vegetation and atmosphere. Isotopic flux measurements of CO_2 above- and below-ground ecosystems can be used to separate the net ecosystem CO_2 exchange into its components. Here we used stables isotopes to identify the sources of soils CO_2 and estimate the effect of environmental factors on these sources [4, 5, 6]. We studied the mechanisms controlling carbon uptake and release from soils and vegetation in an urban area and a beech forest. The Keeling plot method was used to identify the CO_2 sources. The CO_2 efflux from soils was measured using the dynamic closed-chamber method. The conclusion was that the CO_2 efflux from soils is depending on the environmental factors. In the forest ecosystem, two areas were fertilized and two unfertilized, in order to verify if the soil carbon production is influenced by soil fertilization. The isotopic composition of CO_2 was measured with Delta V Advantage mass spectrometer by the dual inlet method. One aim of our work was to partition the soil respiration in its components: autotrophic and heterotrophic using isotopic mass balance. For this, we used samples of soil, roots, and litter.

1. Buchmann et al., *Soil Biology and Biochemistry* 32, (2000), pg. 1625
2. Kelting et al., *Soil Biology and Biochemistry* 30, (1998), pg. 961
3. Rochete &Flanagan, *Soil Science Society of Amer. Journ* 61, (1997), pg. 466
4. Takeshi & Moorcroft, *Global Change Biology* 80, (2006), pg. 217
5. G. Marland, B. Schladminger, *Energy 20*, (1995), pg. 1131;
6. Watson R.T., Noble I.R., Challenges of a Changing Earth, 2002 *Springer-Verlag*, New York, IGBP Series

P.7. STABLE ISOTOPES STUDY OF ECOSYSTEMS IN POLAR AREA

Stela Cuna[1], Petre Berdea[1], Negoita Teoedor[2], Gabriela Balas[1], Alina Magdas[1], Edina Szilagyi[1] and Mihaela Falub[1]

[1]National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath Str., RO-400293 Cluj-Napoca, Romania (www.itim-cj.ro)
[2]Romanian Polar Research Institute, C.P. 42-29, Bucharest 4, Romania

This study shows how stable isotopes are used in polar researches. The measurements of stable isotopes from water, snow and ice was carried out with the isotope ratio mass spectrometer. The study area was Antarctica between Growe Mountains (73^0 $06^{'}$ $01^{''}$ S; 75^0 $14^{'}$ $13^{''}$ E) and the coastal area with the coordinates 69^0 $23^{'}$ $16^{''}$ S; 76^0 $22^{'}$ $47^{''}$ E. A set of 39 samples were investigated for deuterium and ^{18}O isotopes. The water, ice and snow were sampled on the straight line of 500 km from the first coordinates. The sampling points were established at each 12.82 km on this straight line.

The results of our data show that the samples have the deuterium content in excess with negative values. These values ranged from -30‰ to -60‰. The negative values for the excess of deuterium are an indicator of the evaporative origin of the investigated samples. Using the variation of D and ^{18}O for the ice and snow samples we concluded that the origin of the precipitation is evaporative.

P.8. ISOTOPIC ANALYSIS OF WATER NITRATES USING $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ISOTOPIC RATIOS

Stela Cuna[1], Gabriela Balas[1], Alina Magdas[1], and Mihaela Falub[1]

[1]National Institute for Research and Development of
Isotopic and Molecular Technologies, 65-103 Donath
Str., RO-400293 Cluj-Napoca, Romania
(www.itim-cj.ro)

The $\delta^{15}N$ and $\delta^{18}O$ values of NO_3 from water were measured using ion exchange resin methods and isotope ratio mass spectrometry. The possible isotopic fractionations that could appear in each step of the ion exchange resin method were identified. The data show that an incomplete elution, leaving NO_3 on the column, caused an increase in $\delta^{15}N$ and $\delta^{18}O$ with respect to the real $\delta^{15}N$ and $\delta^{18}O$ values. The nitrates are enriched as a result of the isotopic fractionations caused by the competition for sites among NO_3, DOC and other anions (SO_4, CL, PO_4). The isotopic fractionations can be caused in oven-drying process and if the processing of the sample is delayed.

The conclusion of the study is that the anion exchange resin technique is an efficient method of collecting water for nitrogen and oxygen isotope analysis of water nitrates. However, the sample preparation using this technique have to be carried out without isotopic fractionations.

In summary, the isotopic fractionations can be caused by incomplete nitrate elution from the column, by competition for sites among the anions present in the water, in oven-drying process, and if the processing of the sample is delayed.

P.9. WATER MONITORING ALONG THE ROMANIAN DANUBE BASIN: PRELIMINARY STUDY USING ^{18}O AND D ISOTOPES

Alina Magdas[1], **Petre Berdea**[1], **Stela Cuna**[1], **Carmen Varlam**[2], **Gabriela Cristea**[1] **Edina Szilagyi**[1] **and Mihaela Falub**[1]

[1]National Institute for Research and Development of
Isotopic and Molecular Technologies, 65-103 Donath
Str., RO-400293 Cluj-Napoca, Romania
[2] National Research and Development of Cryogenics and
Isotopic Technologies, Ramnicu-Valcea, Romania

Isotope techniques provide invaluable information on the sources, movement and quantity of water in different environments, including rivers and lakes. Environmental isotopes such as deuterium (D) and ^{18}O are well recognized tools for studying dynamics of hydrological cycles on different spatial and temporal scales. In river systems, ^{18}O and D have been used mostly in small-scale investigations for separating different flow components [1].

Water flow in most river systems has two principal components: surface run-off of precipitation and groundwater. Their respective contributions differ in each system and depend on the physical setting of the drainage basin, as well as on climatic parameters. In most rivers, contributions from different surface and sub-surface sources, each with their characteristic isotope contents, will determine the water isotopic composition [2].

In this work, the analyzed samples were collected between April and June 2007. The results show a spatial variation of the ^{18}O and D isotopes, indicating that the isotopic content increases from upstream to downstream. The increase is not a linear one; it presents an important decrease in the contact zone with the isotopic depleted water from Balta Ialomitei si Balta Brailei. Also, the temporal variation of the ^{18}O and D isotopes is small for the studied period of time. The (δ^{18}O, δD) plot indicate a meteoric origin for the Danube water and its tributaries. However, for the Danube Basin lakes the origin of water is evaporative.

1. Genereux, D. P., Hooper, R. P., *Oxygen and hydrogen isotopes in rainfall-runoff studies*, In: Isotope Tracers in Catchment Chydrology. C. Kendall and J.J. McDonnel, Elsevier (1998) 319-343
2. Gat J. R., *Groundwater*, in: Gat J. R., Gonfiantini R.(eds.), Stable Isotope Hydrology, IAEA Vienna, (1981), pp. 223-238

P. 9A SULPHUR ISOTOPIC FRACTIONATION IN SULPHUROUS MINERAL WATERS[1]

Mihaela Falub, Stela Cuna, Gabriela Cristea, Alina Magdas

National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath Str., RO-400293 Cluj-Napoca, Romania
(www.itim-cj.ro)

Analysis of the isotopic composition of sulfate and sulfide dissolved in water has many applications in the study of the chemistry and evolution of hydrologic systems [1]. This study presents an important application of the isotopic composition of sulfate and sulfide dissolved in water: determining the source of dissolved sulphur species, including natural sources such as gypsum or pyrite in rocks and anthropogenic sources such as fertilizer and acid rain. In order to perform our study, the first step was to elaborate a method to determine the sulphur isotopic composition ($\delta^{34}S$) by isotopic ratio mass spectrometry (IRMS) [2,3]. The precision of our method was ± 0.1‰. We have investigated 22 samples of sulphurous mineral waters from Olanesti, Romania and we have measured the characteristic $\delta^{34}S$ values by IRMS in order to determine the sulphur origin. The conclusion is that in the studied mineral waters the sulphur originates from dissolved sulfates, mineral deposits as sulfates, and hydrogen sulfides of biogenic nature.

1. Mayer, B., Fritz, P., Prietzel, J. and Krouse, H.R, *The use of stable sulfur and oxygen isotope ratio for interpreting the mobility of sulfate in aerobic forest soils*, Applied Geochemistry, vol. 10, (1995), pp. 161-173
2. Carmody, Rebecca, Plummer, L.N., Busenberg, E., and Coplen, T.B., *Methods for collection of dissolved sulfate and sulfide and analysis of their sulfur isotopic composition*, (1998), U.S. Geological Survey, Reston, Virginia
3. Rees, C.E., Holt, B.D., *The Isotopic Analysis of Sulphur and Oxygen* in "Stable Isotopes in the Assessment of Natural and Anthropogenic Sulphur in the Environment", (1991) SCOPE, Published by John Wiley & Sons Ltd.

---

[1] By a regretable error, this abstract was omitted from the printed version of the booklet

P.10. THE SYNTHESIS OF OROTIC ACID ISOTOPICALLY LABELLED WITH ^{15}N

Maria Chiriac, Flavia Popa, I.Bratu, Irina Kacso, G. Borodi, N. Palibroda, Adriana Vulcu

National Institute for Research and Development of Isotopic and Molecular Technologies; 400293 Cluj-Napoca, P.O. BOX 700, Romania.

Orotic acid is a precursor for the biosynthesis of pyrimidine derivatives, and this compound isotopically labelled is used for elucidating biosinthetic pathways.

Orotic acid plays a central role in the metabolism of folic acid and vitamin B-12, and may enhance the transportation of minerals across cell membranes. The biochemical is reportedly a remedy for liver-related complications, premature aging, and helps for treating the symptoms of multiple sclerosis.

The aim of this paper is to present the synthesis of orotic acid labelled with ^{15}N in positions 1 and 3.

The experimental procedure is an adaptation of the synthesis methods for the corresponding unlabelled compounds. As isotopically labelled material we used urea-$^{15}N_2$, 99 at.% ^{15}N produced at National Institute for Research and Development of Isotopic and Molecular Technologies, Cluj-Napoca, Romania.

Urea-$^{15}N_2$ was condensed with citric acid in fuming sulfuric acid yielding the labelled dioxo-pyrimidineacetic acid which by oxidation with potassium dichromate forms [1,3-$^{15}N_2$] orotic acid.

The compound was fully characterized by Mass Spectrometry analyses, by FT-IR Spectroscopy and RX Diffraction, and the isotopic label was determined by MS on the molecular compounds.

REFERENCES

[1]. **M.L. Tamayo, J.M. Gamboa, E.E. Alvarez**, Ann.Soc.Espan. Fis.Quim., 48B, pag. 889-891 (1952).
[2]. **L.L. Weed, D.W. Wilson**, J. Biol. Chem., 189, pag.435 (1951).
[3]. **I. Lieberman, A. Kornberg**, J. Biol.Chem., 207, pag.911 (1954); 212, pag. 909 (1955).
[4]. **A. Kornberg, I. Lieberman**, E.S. Simms, J. Biol. Chem., 215, pag. 389 (1955).
[5]. **C. Heidelberger, R.B. Hurlbert**, J. Am. Chem. Soc., 72, pag. 4704 (1950).
[6]. **L. Pichat, N. Audinot, P. Carbonnier**, Bull. Soc. Chim. Fr., pag. 1798 (1959).
[7]. **F. Korte, W. Paulus, K. Storik**, Liebigs Ann. Chem., 619, pag. 63 (1958).
[8]. **V. Jezdic, N. Razuwenic, M.Skakun, S.Albahari, J. Odavic-Josic**, J. Lab.Compd.,6, pag.88 (1970).
[9]. **G. Hilbert, J. Am. Chem. Soc**., 54, pag. 2076 (1932).
[10]. **S. Pinchas, I. Laulich**, Infrared spectra of labelled compounds, Acad. Press, New York, (1971).
[11]. **A. Hernanz, F. Billes, I. Bratu, R. Navarro**, Biopolymers (Biospectroscopy) 57, 187-198 (2000).

P.11. MASS SPECTRAL STUDY OF MOLECULAR CLEAVAGE PATHWAYS IN SOME NEWLY SYNTHESIZED ESTERS OF AMIDOTHIOPHOSPHONIC ACIDS

I. Fenesan[1], *Simona Nicoara[2,3], Monica Culea[4], A. Hantz[1], Al. Alexandri[5], G. H. Morgan[3]

[1] *Chemistry Institute "Raluca Ripan", Cluj-Napoca, Romania*
[2] *Physics Department, Technical University of Cluj-Napoca, 15 C. Daicoviciu str, 400020 Romania*
[3] *PSSRI, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK*
[4] *Faculty of Physics, "Babes-Bolyai" University, 1 Kogalniceanu str, Cluj-Napoca, Romania*
[5] *ALCEDO, Bucharest, Romania*

This work discusses the synthesis and the EI-MS fragmentation patterns for some biologically active cyanacetamid- and cyanethyl- acetate oximinic esthers of amidothiophosphoric acids, with insecticide and fungicide potential [1-4].

EI mass spectra at 70 eV, HR mass measurements and metastable ions spectra were used to elucidate the fragmentation processes of 2-cyano-2-(dimethyl-amino-cyclohexyl-thiophosphono-oximino)- acetamide (**1**), 2-cyano-2-(morfolinyl-cyclohexyl-thioposphono-oximino) acetamide (**2**), 2-cyano-2-morfolinyl-cyclohexyl-thiophosphono-oximino)- ethylacetate (**3**), and 2-cyano-2-(diethylamino-phenyl-thiophosphono-oximino)-acetamide (**4**). Their chemical structure was confirmed by analytical data, IR, ^{1}H-NMR and MS spectrometry.

Low abundance molecular ions in the mass spectra of compounds **1-4** reflect the instability due to the cyan-acetyl-oximinic group. Simple fission processes of the P-N and P-C bonds respectively led to abundant ions in spectra of **1,3** and **4**. Important series of ions were initiated by the cleavage of the P-O and O-N bonds, and H rearrangements with migration from the cyclohexyl group were observed and compared to literature data of similar comounds [5,6].

References

1. W. Kromer, H-J Riebel, Bayer A.G., DE 3429434 A1.
2. W. Lorentz, Ch. Fest, I. Hammann, M. Federmann, W. Fluke, W. Stendel, Farbenfabriken Bayer A.G., DAS 1238902.
3. M. Safta, A. Hantz, Rom. P. 100.896.
4. I. Fenesan, A. Hantz, M. Culea, S. Alexandrescu, *Proc. "Timisoara Academic Days",* **1995**: 123-124.
5. I. Fenesan, R. Popescu, C. T. Supuran, Simona Nicoara, Monica Culea, N. Palibroda, Z. Moldovan, O. Cozar, *Rapid Commun. Mass Spectrom.*, **2001**; **15**: 721-729.
6. Monica Culea, N. Palibroda, Z. Moldovan, Simona Nicoara, I. Fenesan, R. Popescu, V. Muresan, E. Postoi, V. Znamirovschi, *Rapid Commun. Mass Spectrom.*, **1998**; **12:** 1808-1812.

P.12. STUDY FOR CIRRHOSIS DIAGNOSIS BY GC/MS

M. Culea[1],C. Mesaros[1], M. Chiriac[2]

[1] *"Babes-Bolyai" University, Str. M. Kogalniceanu, Nr. 1, Cluj-Napoca, 400084, Romania, mculea@phys.ubbcluj.ro,*
[2]*INCDTIM Str. Donath, Nr. 71-103, Cluj-Napoca, 400293, Romania*

A study of the pharmacokinetic data for cirrhosis diagnosis by isotopic dilution-gas chromatography-mass spectrometry (ID-GC/MS) is presented. Isotopic dilution measurements are very important for pharmacokinetic studies, metabolic studies, clinical applications for treatment and diagnosis [1-3]. The selected ion monitoring (SIM) mode was used in caffeine test measurements by adding known amounts of the^{15}N labelled internal standard. A single dose of 4 mg/kg p.o. of caffeine was followed by blood concentrations measurements at two points, 1h and 9 h. Caffeine clearance, measured in patients with cirrhosis and chronic hepatitis, was reduced and half live time was increased in children with liver disease as compared with control.

Keywords: Cirrhosis, Cafeine test, GC-MS

References

[1]. M. Culea, D.L. Hachey, *Determination of Multiply Labeled Serine and Glycine Isotopomers in Human Plasma by Isotope Dilution Negative Chemical Ionization Mass Spectrometry,* Rapid Commun. Mass Spectrom., 9, (1995) 655- 659.
[2]. M. Culea, P. Panta,, M. Nanulescu, N. Palibroda, O. Cozar, I. Vintilă, *Theophylline determination in plasma and saliva,* Balcanic Physics Letters, 5, (1997) 1861-1864.
[3].M. Culea, N. Palibroda, P. Panta Chereches, M. Nanulescu, *Comparative of isotopic dilution methods for determination of theophylline in the plasma and saliva of infants and children,* Chromatographia, 53, (2001) S387- S390.

P.13. AMINO ACIDS TRANSMEMBRANAR TRANSPORT STUDY BY RED CELL MEMBRANE

M.Culea[1], S. Neamtu[2], I. Turcu[2], M. Chiriac[2]

[1] "Babes-Bolyai" University, Str. M. Kogalniceanu, Nr. 1,
Cluj-Napoca, 400084, Romania, mculea@phys.ubbcluj.ro,
[2]INCDTIM Str. Donath, Nr. 71-103, Cluj-Napoca, 400293,
Romania

A study of the amino acid transmembranar transport in human red cells is presented. The quantitation of amino acids, as trifluoroacetyl butyl ester derivative, was performed on a chromatographic column coupled to a mass spectrometer (GC-MS). The method was validated for small values of the amino acid transmembranar transported to determine the amino acids glycine and leucine. The isotope dilution GC/MS technique was used in the SIM mode. The efflux of ^{14}N labelled amino acid was calculated by using as internal standard the ^{15}N labelled amino acid.

References

[1]. M. Culea, D.L. Hachey, *Determination of Multiply Labeled Serine and Glycine Isotopomers in Human Plasma by Isotope Dilution Negative Chemical Ionization Mass Spectrometry,* Rapid Commun. Mass Spectrom., 9, (1995) 655- 659.

[2]. M. Culea, S. Neamtu, N. Palibroda, M. Borsa, S. Nicoara, *Study of amino acid transmembranar transport in human red cell and rat hepatocyte,* J. Molec. Structure, 348, (1995) 377-380.

[3].M. Culea, N. Palibroda, P. Panta Chereches, M. Nanulescu, *Comparative of isotopic dilution methods for determination of theophylline in the plasma and saliva of infants and children,* Chromatographia, 53, (2001) S387- S390.

P.14. GAS-CHROMATOGRAPHIC ANALYSIS OF MIXTURES OF HYDROGEN ISOTOPES USING DIFFERENT SAMPLES LOOPS

Anisoara Preda[1], Anisia Bornea[1], Claudia Pearsica[1], Felicia Vasut[1], Cristina Barbu[2], Alexandru Popescu[3]

[1]National R & D Institute for Cryogenics and Isotopic Technologies – ICIT Rm. Valcea,Valcea, Romania,
[2]Spiru Haret University, Craiova, Dolj, Romania
[3]Department of Chemistry, Craiova University, Craiova, Dolj, Romania

Abstract

Gas-chromatography is considered to be the most appropriate of many analytical techniques used to determine the composition or purity of gases.

A gas chromatographic system for the analysis of gas species of hydrogen is very important for the separating of hydrogen species by cryogenic distillation, catalyst isotopic exchange and another processes.

In this paper, for the analysis of gas mixtures containig hydrogen isotopes, we present the analysis of different mixtures of hydrogen isotopes using capillary molecular sieve 5A column and different sample loops.

It is realised a comparative study to develop or improve existing methods for the qualitative and quantitative determination of the composition of gas mixtures of hydrogen isotopes.

As results there are presented chromatograms for different H2, HD, D2 mixtures and different operated parameters.

Keywords: gas chromatography, pulsed discharge helium ionization detector, 5 Å molecular sieve, sample loops.

References

[1] Raymond Peter William Scott, *Techniques and Practice of Chromatography*, Marcel Dekker, Inc.: New York, Basel, Hong Kong, (1995), page 10.

[2] L. Szepesy, *Gas Chromatography*, Akademiai Kiado, Budapest, (1971), pages 11-13.

[3] R. Vogd, H. Ringel, H. Hackfort, T. Schober, C. Dieker, *Gas Chromatography Separation of Hydrogen Isotopes on Molecular Sieves*, Fusion Technology, (1988), 14, page 574.

[4]. Sessions, Alex; *J. Sep. Sci.*, , (2006), 29, pages 1946 – 1961.

P.15. THE STUDY OF THE DISTRIBUTION OF SOME HEAVY METALS ON THE MAIN TRIBUTARIES OF THE JIU RIVER COURSE USING ICP-MS

Cristina Barbu[1], Dan Selisteanu[2], Anisoara Preda[3], Alina Ghitulescu[3],

[1]Spiru Haret University,
cristina_barbu2000@yahoo.co.uk, Brazda lui Novac
Street, No. 4, Craiova, Dolj, Romania, telephone number
40 251 598265, fax 40 251 598265.
[2] University of Craiova, Automation, Computers and
Electronics Faculty, A.I. Cuza Street, No. 13, Craiova,
Romania, telephone number 40 251 438198, fax 40 251
438198, dansel@automation.ucv.ro,
http://www.automation.ucv.ro.
[3]National R & D Institute for Cryogenics and Isotopic
Technologies – ICSI Rm. Valcea, Uzinei Street, No. 4,
Rm. Valcea, Romania, telephone number 40 250 732744,
fax 40 250 732744.

The most important tributaries of the Jiu River are: Motru, Gilort, and Amaradia. Concerning the industrial pollution, it is much more difficult to establish the quantity of the pollutants. Most frequently are met detergents, solvents, heavy metals, organic acids, washing agents, ammonia. The most toxic inorganic products are: Arsenic, Zinc, Cadmium, Selenium, Mercury etc. Heavy metals are a cause of environmental pollution (heavy-metal pollution) from a number of sources, including lead in petrol, industrial effluents, and leaching of metal ions from the soil into lakes and rivers by acid rain. To determine the content of heavy metals in the samples of water taken from several points of the Motru River, Gilort River, and Amaradia River, an analytical method has been used: Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Keywords: environment, heavy metals, inductively coupled plasma mass spectrometry.

P.16. POLLUTANTS MEASUREMENTS FROM ENVIRONMENTAL GASEOUS SAMPLES IN THE ATMOSPHERE

Diana Florescu, Gili Saros, Roxana Ionete, Vasile Stanciu

National Institute for Isotopic Separation and Cryogenic Technology, Department of Research and Development –
I.C.I.T. RM. VALCEA, Uzinei Street, no. 4, OP 4, CP 10,
E-mail address for author: dianaf@icsi.ro

All the research in this field gives us the effects of atmospheric pollution (changes of climatic effects) and takes risk about major changes, but the first culpable it is human nature because it is the generator of atrophic pollution, with repercussions on urbane population and to the materials in the polluted area.

There are many methods to analyze the atmospheric pollutants from environment, in function to the treatment place and method, in function to the pollutant type or quality analyzes or with the quantitative value of this [1, 2].

We choose to measure the concentrations of these atmospheric pollutants with two different, but complementary methods: Mass Spectrometry and Gas Chromatography. The equipments are located in the National Institute R&D for Isotopic Separation and Cryogenic Technology – ICIT Rm. Valcea, Department of Research and Development.

References:

1. W. Bucherberger and Pola Zaborsky, *Acta Chim. Slov* (2007) 54, 1-13.
2. M. Mezcua, A. Aguera, J.L. Libera, M.A. Cortes, B. Bago and A.R. Fernandez-Alba, *J. Chromatogra. A*, 1109 (2006), 222-227.

P.17. PRECISE POSITION MAINTAINING OF THE REACTION ZONE IN THE PRODUCT REFLUXER OF ^{15}N SEPARATION PLANT USING A SIMPLE ON-OFF CONTROLLER

M. Kaucsár, D. Axente, V. Cosma, Cristina Marcu, Anca Mureşan

National Institute for Research and Development of
Isotopic and Molecular Technologies
65-103 Donath Str., P.O.Box 700, RO-400293
Cluj-Napoca 5, Romania

One of the most important tasks in optimizing the isotope separation process in ^{15}N production plant is the precise position control of the $HNO_{3(e)} - SO_{2(g)}$ reaction zone in the product refluxer [1], [2].

The first important step in this control is the accurate localization of the reaction zone in which the following exothermal reactions take place:

$3SO_2 + 2HNO_3 + 2H_2O \leftrightarrow 3H_2SO_4 + 2NO$

$SO_2+2HNO_3 \leftrightarrow H_2SO_4$

The localization is realized by determining the parameters of the temperature peak along the product refluxer, therefore it is provided with a temperature sensor array. The temperature gradient curve along the refluxer is computed by using a special spline interpolation and the position of the temperature peak is given by the first derivative zero crossing point [3]. The position of the reaction zone is determined by two main parameters: the flow rate of the nitric acid solution and the flow of the sulfur dioxide to product refluxer.

The nitric acid solution flow rate is maintained at constant level by using a metering pump. The flow of the sulfur dioxide is controlled by means of an on-off controller [4] in order to minimize the shifts in the isotopic gradient caused by the movement of the reaction zone in the product refluxer.

During the operation of the isotope separation plant a constant flow of sulfur dioxide to the product refluxer was maintained, this primary flow being slightly less than the stoichiometric one required to holding the reaction zone at a constant level – hence the peak of the temperature moves downward. When it passes under the setpoint an on-off valve is opened and adds over the primary sulfur dioxide flow a much smaller secondary flow. The amount of this flow is sufficient to move the reaction zone very slowly upward. When the reaction zone passes over the setpoint then the secondary flow is stopped and the cycle repeats.

The sensitive on-off controller maintains very precisely the reaction zone in its optimal position and results a smooth ^{15}N separation column operation.

Bibliography:

1. Benedict, M., Pigford, T.H., Levy, H.W. – *Nuclear Chemical*

Engineering, McGraw-Hill Book Co., Boston, 1998.
2. Axente, D. – *Metodica separării pe coloane a izotopului ^{15}N*, Studii cercetări chimie, tom.19, nr.4, p.395-415
3. Kaucsár, M., Cosma, V., Axente, D., Bâldea, A., Popescu, Şt., Dobocan, I., Zotoiu, D. – *An accurate reaction zone control in the product refluxer of ^{15}N separation plant*, 4-th Conference Isotopic and Molecular Processes PIM – 2005, Cluj-Napoca, 22-24 September 2005
4. Love, J. – *Process Automation Handbook*, Springer London, 2007, Part I, Section 4, pp. 191-194

P.18. EXPERIMENTAL CASCADE FOR THE SEPARATION OF ^{13}C BY CRIOGENIC DISTILLATION OF CARBON MONOXIDE

M. Gligan, A. Baldea, S. Dronca, V. Stoia

National Institute for Research and Development of
Isotopic and Molecular Technologies, Donath Street nr.
65 – 103, P.O.Box 700, 400293 Cluj-Napoca, Romania

The stable isotope ^{13}C has multiple applications as labeled compounds in the fields of biology, chemistry, medicine, environment agro-chemistry, etc. The progress in isotope analysis methodologies increased the interest in producing and using this isotope. The most used method production of large quantities of ^{13}C is cryogenic distillation of carbon monoxide in a cascade of several stages containing columns of different diameters with packing.

Cryogenic distillation uses the differences between vapor pressures of different isotopic species, $^{12}C^{16}O$ and $^{13}C^{16}O$, at temperatures lower than 85 K. This ratio, that is regularly named relative volatility or separation factor α equals 1.01 at 70 K and 1.007 at 81 K.

The experiments were performed on experimental device in which are used columns as high as 7 m with inside diameters of 16 and 26 mm respectively. A cascade consisted of two vertical sections, the inner column 26 mm and 2.5 m height and the lower of 16 mm inside diameter and 4.5 m length, both of them containing Helipack packing. The cooling agent used in the condenser was liquid nitrogen bailing at atmospheric pressure. The boilers were electrically heated at variable power supply.

The plant is an automation system head by a PC.

On this plant a values of HETP between 18.5 and 23 mm were obtained.

After a productive experiment of the plant a product of 7.5 at. % of ^{13}C were obtained. The obtained results fit fairly with theoretical calculus.

References

1. Schwind R.A., *Chem. Proc. Eng*., 7, 1969, 75
2. Stable Isotopes Catalogue, Mound Laboratory,Miamisburg, Ohio, September 1968.
3. G. Văsaru, P. Gheţe, I. Covaci, Marieta Atanasiu, Proceedins of Technical Communittee Meeting on Modern Trends in the Life Sciences, Leipzig, 14-18 Febr 1977, IAEA Vienna, 1977, 39-52
4. Page WEB Cambridge Isotope Laboratories Inc., http://www. isotope.com
5. Moulton-Barrett, R., U.S. Patent 5,542,419 , Aug. 6, 1996.
6. Clusius, K., Schleich, K., *Helv. Chim. Acta* 41, 1958, 1342
7. Asatiani, P., Kaminski, V.A., Oziasvili, E.D.,Tevzadze, G., *Isotopenpraxis*, 4,1966, 275
8. M. Gligan, A. Rădoi, Raport, Contr. I.T.I.M. 81b,1993, 2

P. 19. COMPARATIVE STUDY OF URANIUM ISOTOPES RATIO MEASUREMENTS ($^{235}U/^{238}U$) BY THERMAL IONIZATION MASS SPECTROMETRY AND INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY

Adriana Dehelean and Zoltan Balazs

National Institute for Research and Development of
Isotopic and Molecular Technologies, 400293 Cluj-
Napoca, Romania,zbalazs@oc1.itim-cj.ro

Determination of $^{235}U/^{238}U$ isotopic ratio is of great importance in nuclear power industry. The use of slightly enriched uranium ($^{235}U/^{238}U$ = 0.9% .. 1.2%) increases considerably the efficiency of reactors. The monitoring of this isotopic ratio gives also information related to the burning degree of the fuel. In geology – geochronology, $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ratios are used in dating.

This article reviews current analytical techniques available for ($^{235}U/^{238}U$) isotope ratio measurements, including:

- Positive thermal-ionization mass-spectrometry(PTIMS)
- Inductively coupled-plasma mass-spectrometry(ICP-MS)

The two analytical methods are compared. Thermal Ionization mass spectrometry appears to be a much more precise method, but very tedious. ICP-MS using quadrupole mass analyzers, though less precise, is often more useful in many applications where rapid results are needed.

P.20. ^{15}N ISOTOPE SEPARATION INSTALATION COMPUTED CONTROL

Adrian Bot*, Cornel Cuna*, Viorel Cosma *, Martin Kaucsar*, Stefan Popescu*, Florin Toadere*, Popescu Ana Voichita**

**National Institute for Research and Development of*
Isotopic and Molecular Technologies,
71-103 Donath Str., P.O.Box 700, RO-400293
Cluj-Napoca 5, Romania
***Tehnical Univertsity , Faculty of Automation and*
Computer Science, Computer Science Departament,
26-28 Baritiu Street, 400027, Cluj Napoca, Romania

Isotope separation

Is the process of concentrating specific isotopes of a chemical element by removing other isotopes, for example separating isotope ^{15}N (0.365 %) from isotope ^{14}N (99,35%). The National Institue of Rescherces and Development for Isotopic and Molecular Technologies (INCDTIM-Cluj) was constructed an industrial instalation for producing the isotope ^{15}N by the NO-HNO3 isotopic exchange tehnique. There is a cascade of two separation columns, C1 wich is feed with 0.365% HNO3 natural concentation of ^{15}N, and C2 which is feed with 10%HNO3 provided from C1. Between these two columns there are three refluxors, R1, R2, R3, which togheder with two cascaded columns C1 and C2 forms thre loops of isotope separations.On every separation loop we where mounted a continuous concentration detector, which on his tourn is programmed to send to National Instrument Device, on a PC, a logical level signal (Boolean signal), for a programmed, or local setup treshold level. This signal is recevid by the National Instrument M 6251 device digital port and procesed by our LabView 8.5 program. The answer to isotope concentration states is an individual command to the driver of the separation valves.These commands are resetted in time depending of the new isotopic product concentration.

Enrichment cascades

All large-scale isotope separation schemes employ a number of similar stages which produce successively higher concentrations of the desired isotope. Each stage enriches the product of the previous step further before being sent to the next stage. Similarly, the tailings from each stage are returned to the previous stage for further processing. This creates a sequential enriching system called a cascade. There are two important factors that affect the performance of a cascade. The first is the separation factor (the square root of the mass ratio of the two isotopes), which is a number greather than 1.The second is the number of required stages necessaries to obtain the desired purity.

P. 21. MATHEMATICAL SIMULATOR FOR DINAMICAL CONSTITUENS IN ATHMOSPHERIC METHANE FROM BLACK SEA REGION, ROMANIA

Adrian Bot*, Stela Cuna*, Stefan Popescu*, Gabriela Cristea*, Florin Toadere*, Popescu Ana Voichita**

**National Institute for Research and Development of Isotopic and Molecular Technologies,71-103 Donath Str., P.O.Box 700, RO-400293 Cluj-Napoca 5, Romania*
***Tehnical Univertsity , Faculty of Automation and Computer Science, 26-28 Baritiu Street, 400027, Cluj Napoca, Romania*

There are some atmospheric constituents like Carbon Monoxide, Carbon Dioxide, Methane, Hidrogen, so on, capable to forcing changes in the climate of Earth through modification of the atmospheric irradiative environment , for example greenhouse gases and aerosols . Each of this constituent has one or more sources, laic fossil, biomass burning or microbial produced . Each source has a isotopic signature. These signatures are essential to separating fluxes of atmospheric CO_2 (for example), between terrestrial biosphere and the ocean. Some international laboratories, laic NOOA / Climate Monitoring and Diagnostics Laboratory , U.S.A., CMDL / Cooperative Global Air Sampling Network created a WEB-based interactive atmospheric DATA visualization tool and Data-Base, which offer free measurement data sample. The Data-Files from this sources and from our own researches are used in this work as inputs for simulator of atmospheric and anthropogenic phenomena. Our research area is the Danube Delta – Black Sea at Constanta which is a important wetland region in Romania. Computers are physical systems designed to implement the idealized relationships on mathematical models. Modeling is usually regarded as an extension of thinking, its purpose being to develop or clarify the modelers understanding of the system or process modeled. The needed basis is usually found in mathematical forms which characterize the behavior of each system. There are various mathematical models for same dynamic system, each one suited to solve a particular problem associated with the system. To do a easier problem software modeling, today there is a powerful development environment, LabVIEW 8.5 . His output can be graphic , thus summarizing instantaneously the computer results. It seems likely, however, that interactive dynamic modeling (and models) will prove to be almost as important in communication with the researcher as in research properly. In their static form, computer program models are laic documents printed in natural language. In their dynamic form, however, computer-program models appeal to the people understanding directly through his perception of dynamic behavior.

Keywords : isotopic signature, wetland regions, greenhouse gases dynamic, modeling physicals processes, mathematical simulator.

P. 22. CO_2 ABSORPTION IN SOLUTIONS OF SECONDARY AMINES IN NON-AQUEOUS SOLVENTS

S. Dronca, V. Stoia, A. Baldea_C. Varodi, M. Gligan,

National Institute For Research And Development Of
Isotopic And Molecular Technologies, Cluj-Napoca ,
ROMANIA

The CO_2 absorption in amine is industrially used in the gaseous mixtures purification, the absorption mechanism and the kinetics aspects being well know. Most of these refer to the CO_2 reaction with amines in aqueous solutions [1]. Scientific literature does not offer enough informations about the CO_2 absorption in amine solutions in non- aqueous solvent, this system being utilized in ^{13}C separation by chemical exchange [2-4].

The experiments presented offer informations about the CO_2 absorbtion in two secondary amines: diethlamine (DEA) and di-(n-butyl) amine, in different non-aqueous polar solvent (methanol) and non-polar solvents(octan and trietilamina, TEA) in a stirred absorption stainles steel cell.

Three carbamate compounds: R_2NCOOH, $R_2NCOO^-R_2NH_2^+$ and R_2NCOO^- are formed by the chemical absorption of CO_2 into secondary amine (R_2NH), according to the following reactions [5] :

$$CO_2(g) + S \longleftrightarrow CO_2\,(l) \qquad (1)$$

$$CO_2\,(l) + R_2NH \longleftrightarrow R_2NCOOH \qquad (2)$$

$$R_2NCOOH + R_2NH \longleftrightarrow R_2NCOO^-R_2NH_2^+ \qquad (3)$$

$$R_2NCOO^-R_2NH_2^+ \longleftrightarrow R_2NCOO^- + R_2NH_2^+ \qquad (4)$$

Where S is the solvent, R is the ethyl or butyl radical, CO_2 (g) is carbon dioxide in gaseous phase and CO_2 (l) is carbon dioxide physic dissolved in solvent.

Carbon dioxide partial pressure was varied from 0.025 to 0.45 MPa, the temperature between 5^0C and 25 ^0C and concentration of amine were 1M and 2M. Equilibrium kinetic measurements and molar ratio between amine and absorpted CO_2 were also performed.

All these measurements help us to choose the best system amine-solvent and work conditions (temperature and pressure) for ^{13}C enrichment by ^{13}C / ^{12}C exchange in CO_2- carbamat system.

References:

1. Takesita K., Kitamoto A., *J. Chem. Eng. Japan*, 22(5), 447 (**1989**).
2. Raica P., Axente D. : *J. Rad. Nucl. Chem.*, 251 (3), 443-449, (**2002**).
3. Park S. W., Choi B. S., Lee J. W., *Korean J. Chem. Eng.*, 23, 138 (**2006**).
4. Dronca S.,Axente D.,Bâldea A.,Teacă C,*Rev.Chim.*,51,1 (**2000**)
5. Bratzer K. and Doerges A., *Hydrocarbon Proc.*, 4, 78 (**1974**)

P. 23. APLICATION OF STABLE ISOTOPE-LABELED COMPOUNDS FOR DETERMINATION OF THE SOLID-WATER DISTRIBUTION COEFFICIENT (K_D) FOR ORGANIC POLLUTANTS IN WASTEWATER TREATMEMT PLANT

Marincas Olivian[a] • Wick Arne[b] • Zaharie Moldovan[a] • Thomas Ternes[b]

[a]*National Institute for Research and Development of Isotopic and Molecular Technologies, 400293 Cluj-Napoca, Str. Donath 65-103, Romania, e – mail: itim@oc1.itim-cj.ro, Tel.: + 40 264 584037, Fax: + 40 264 420042*
[b]*Federal Institute of Hydrology (BfG), Am Mainzer Tor 1, D-56068, Germany*

The paper aim is the determination of the solid-water coefficient (K_d)[1,2] of several organic pollutants (Terbutryn, Terbuthylazine, Thiabendazole, Propiconazole, Diuron, Isoproturon, Imazalil and Carbendazim) using stable isotope-labelled compounds. Partition coefficients of selected compounds are determined in order to understand the environmental behaviour in sewage treatment plants.

The concentration determination of target compounds in samples collected from WWTP presents difficulties by interference of signal from other compounds. The exact measurements can be performed using a suitable internal standard. The better internal standard for this compounds is the corresponding stable labelled isotopes.

The paper presents the fallowing data:

- Name of target compounds and corresponding internal standards
- The diagnostic ions used for quantitation
- Experimental values of K_d

The labelled compounds used for this experiments are: Terbutryn-D5, Terbuthylazine-D5, Thiabendazole-D6, Propiconazole-D5, Diuron-D6, Isoproturon-D6, Imazalil-D5 and Carbendazim-D4.

For K_d determination, the concentrations of compounds were measured in aqueous and solid phase. The measurements were done with Liquid Chromatography/Mass Spectrometry (LC/MS/MS) in positive ionization mode.

Keywords. Distribution coefficient (K_d) • Stable isotope-labeled compounds • Organic pollutants • Liquid Chromatography/Mass Spectrometry • Wastewater treatment plant.

1. T.A. Ternes, N. Herrmann, M. Bonerz, T. Knacker, H. Siegrist, A. Joss, *Water Research* **2004,** 38, 4075 – 4084
2. M. Carballa, G. Fink, F. Omil, J.M. Lema, T. Ternes, *Water Research* **2008,** 42, 287 – 295

P. 24. C-13 AND C-14 LEVELS ALONG ROMANIAN DANUBE RIVER SECTOR[2]

<u>Ionut Faurescu</u>[1], Carmen Varlam[1], Stela Cuna[2], Gabriela Balas[2], Irina Popescu[1], Denisa Dobrinescu[1]

[1]National Institute R&D for Cryogenic and Isotopic
Technologies, Rm. Valcea
[2]National Institute R&D for Isotopic and Molecular
Technologies, Cluj Napoca
e-mail: ifaurescu@icsi.ro

The Lower Danube Basin covers the Romanian-Bulgarian Danube sub-basin downstream of Cazane Gorge up to Danube Delta. The Danube is of huge significance to Romania, since the country is almost entirely within the Danube Basin. In order to establish C-13 and C-14 concentration in Romanian Danube River Sector and it's most important tributaries we used a complete measurement procedure adequate for natural level water samples. We established 7 locations along Romanian Danube River Sector starting with Ieselnita near Cazane Gorge, to Tulcea in Danube Delta, and 4 locations on following tributaries: Cerna, Jiu, Olt and Arges. A study of the carbon species and the carbon isotopic composition of Dissolved Inorganic Carbon (DIC) was carried out in the Romanian Danube River Sector. Special cares have been done for sample preparation technique in order to obtain C-14 level along Danube. The "direct absorption method" has been used with few "home-made" improvements in order to increase the reproducibility and accuracy of this simple and less-time consumer method.

Determination of C-14 concentration in water sample collected was carried out using liquid scintillation counting (LSC), with ultra-low liquid scintillation spectrometer Quantulus 1220 specially designed for environmental samples and low radioactivity. Results obtained were around 100 pMC for Danube River, because surface water studied is in equilibrium with atmospheric carbon reservoir. $\delta^{13}C_{PDB}$ values varied between - 7,8 ‰ and - 11.1 ‰ for Romanian Danube River Sector and around 9 ‰ for most important tributaries.

---

[2] By a regretable error, this abstract was omitted from the printed booklet

AUTHOR INDEX

NOTES