South African Spectroscopic Society

NEWSLETTER

2002 issue 2

The Young Spectroscopist Symposium

18 September 2002

Twelve participants contributed to a programme of diverse and interesting talks. Many noteworthy papers were presented and as always it was a pity to only award three winners. The first prize, a CD player sponsored by Panalytical, went to Malebogo Legodi from the University of Pretoria, for his colourful and absorbing presentation on the use of Raman spectroscopy on the clays and pigments used in Ancient Artefacts. The second and third prizes, both book vouchers sponsored by SASS, went to Anton du Plessis from Stellenbosch University and Samantha Jansen van Vuuren from Rand Afrikaans University respectively. The participants presented aesthetically impressive slide shows that were clearly structured and easy to follow. The abstracts are attached below.

Professor Jan Boeyens from the University of Pretoria opened the event, followed by an introduction by the president of SASS, Janette Cawood. Maggi Loubser chaired this year's Young Spectroscopists' Symposium.

The programme was rounded off by a motivational talk presented by Zuanda Ramadwa entitled *Nurturing a Culture of Innovation and Development in Technology by bringing SET Literacy to our Nation* (SET – an acronym for science, engineering and technology). The main focus of the talk was that it does not help to only support pupils who do well in scientific subjects, focus should lie in awakening interest and curiosity in talented candidates. The talk conveyed a sense of optimism and promise for positive scientific development in our country.

Janette Cawood concluded the meeting by thanking the participants, judges and sponsors.

C. Canario, Technikon Pretoria

Atomic Absorption Spectrometric Determination of Cd, Pb and Mn in Urine with the Transverse Heated Filter Atomiser.

Abstract

The performance of the Transverse Heated Filter Atomizer (THFA) was tested in the direct atomic absorption determination of Cd and Pb in urine samples. The THFA design was modified to provide full recovery of both elements independent of the origin of sample without the use of chemical modifiers.

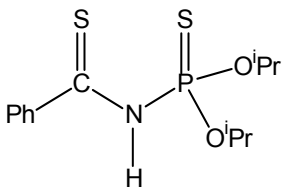
The developed procedure includes 5-times sample dilution with 0.2% HNO3 and injection of the solvent in the THFA at 150ºC. The omission of drying step shortens the thermal program significantly. The vapor filtration through the heated graphite filter reduces spectral interferences. A single THFA can be used for more than 500 firings. The method permits simultaneous quantitative determination of both elements in the urine samples below the levels corresponding to SRM "URINE BLANK" (0.35 mg/L for Cd and 3 mg/L for Pb).

S. Mtongana, University of Stellenbosch

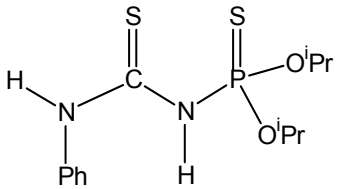
The structural elucidation of platinum(II) chelates of N-diisopropoxythiophosphoryl thioamide and Ndiisopropoxythiophosphoryl- N'-phenylthiourea by means of multinuclear magnetic resonance spectroscopy.

Abstract

N-diisopropoxythiophosphoryl thiobenzamide, **I** and *N*-diisopropoxythiophosphoryl-*N'*-phenylthiourea, **II** form stable chelates with many transition metals.[1,2,3] In this study, the coordination chemistry of **I** and **II** to platinum(II) has been investigated.



I

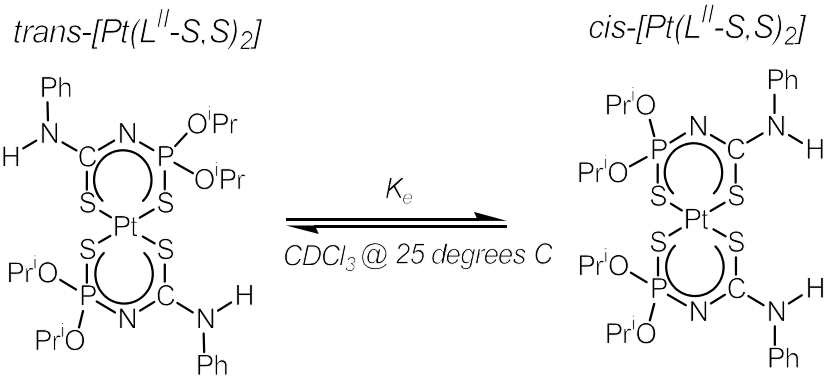


II

The platinum(II) chelate formed from **I** is exclusively the *trans*-[Pt(L^{I}-*S,S*)$_2$] isomer as determined by means of $^{31}P\{^{1}H\}$ NMR spectroscopy and verified by the crystal structure of the complex. The coordination chemistry of **II** significantly differs from that of **I** in that the platinum(II) chelates formed may either be exclusively *trans*-[Pt(L^{II}-*S,S*)$_2$] or a mixture of *cis*-[Pt(L^{II}-*S,S*)$_2$] and *trans*-[Pt(L^{II}-*S,S*)$_2$] isomers, depending on the mode of complex preparation. This is revealed by the $^{31}P\{^{1}H\}$ NMR spectrum, which shows two peaks at 43.6 ppm with a $^{2}J(^{195}Pt\text{-}^{31}P)$ value of 106Hz and at 44.5 ppm with a $^{2}J(^{195}Pt\text{-}^{31}P)$ value of 101Hz. The $^{195}Pt\{^{1}H\}$ NMR spectrum confirms the presence of the two isomers with two ^{195}Pt peaks at -3964 ppm and -3956 ppm for the *trans*-[Pt(L^{II}-*S,S*)$_2$] and the *cis*-[Pt(L^{II}-*S,S*)$_2$] respectively.

In chloroform solution, pure *trans*-[Pt(L^{II}-*S,S*)$_2$] isomerises to a mixture of isomers. The *trans*/*cis* isomerisation kinetics was followed by means of $^{31}P\{^{1}H\}$ NMR spectroscopy and the

equilibrium is reached in approximately 300 hrs. The equilibrium constant for the isomerisation, K_e = *cis*-[Pt(L^{II}-*S,S*)$_2$]/*trans*-[Pt(L^{II}-*S,S*)$_2$] at 25˚C was determined to be 8.53 x 10^{-1}.



References:

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A. du Plessis, University of Stellenbosch

A Tunable, Pulsed Raman Laser for IR spectroscopy.

Abstract

Tunable pulsed lasers in the infrared are of great interest, particularly for selective multiphoton excitation of molecules. For linear spectroscopy continuous-wave diode lasers are available, but for such non-linear processes tunable pulsed lasers are required, because of their higher peak powers. The laser sources available for such spectroscopy include well-known systems such as dye lasers and parametric oscillators (OPPOs). Here we present the characteristics of a lesser-known system: the tunable, pulsed Raman laser. This system can be used to extend the wavelength range of the available tunable sources, by utilizing stimulated vibrational Raman scattering of laser pulses in hydrogen, which generate Stokes-shifted laser pulses.

N. Mhlahlo, University of Cape Town

Analysis of Spectroscopic Observations of the Cataclysmic Variable, TX Col.

ABSTRACT:

Cataclysmic variables are two stars that are bound together by gravity and orbit each other with short orbital periods (typically from 0.29 to 47 hours). As a result, material flows between them due to the greater gravitational pull of one of the stars. Cataclysmic variables are used to understand the accretion dynamics in the universe including that of Black holes.

My presentation will be based on the analysis of spectroscopic observations of the cataclysmic variable, TX Col.

Using a grating Spectrograph with CCD detector, data was collected and stored for analysis.

It will be shown how the analysis of the spectroscopic data enable me to do emission line measurements and to investigate the accretion dynamics of the TX Col system.

S Govender, University of Cape Town

Lead concentration and isotopic composition by mass spectrometry and their implication for anthropogenic components at farms in Philippi, W. Cape – a pilot study.

Abstract

The first Pb isotope ratios for soil and vegetables from the Philippi agricultural area in the Western Cape are presented. The 206Pb/207Pb ratio is used to distinguish between natural and anthropogenic Pb. Two analytical techniques, thermal ionisation mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS), were used, allowing the evaluation of these methods as routine environmental monitoring tools in the Department of Geological Sciences, UCT.

A soil (>40cm deep) and residues from sequential extraction experiments revealed natural rock derived lead of less than 3mg/kg with radiogenic 206Pb/207Pb: 1.184 - 1.280. Some near-road soils with elevated lead levels, compared to background, have 206Pb/207Pb: 1.086 - 1.120, providing evidence of anthropogenic inputs similar to those obtained by international investigators for leaded fuel and freeway soils from Israel, France and Germany, and aerosol samples from inner-city Cape Town in a global study. Green leafy vegetables revealed a Pb concentration up to 6.09mg/kg and 206Pb/207Pb: 1.145 - 1.158, some quite different to the soil in which they were grown but similar to Pb isotope signatures obtained for leaded fuel from Russia. Since soils are a sink for heavy metals they reflect the anthropogenic Pb inputs over a longer period than the vegetables that are harvested seasonally. Perhaps this is an indication that locally a change in the source of leaded petrol additive may have taken place as the phasing out of leaded petrol has only began recently in South Africa.

Keywords: Lead isotopes; Lead concentration; sequential extraction; ICP-MS; TIMS; environmental monitoring.

Acknowledgements - I would like to thank Assoc Prof S H Richardson and Dr A Späth for the opportunity to undertake this project in the Radiogenic Isotope Facility and ICP-MS Laboratory, Department of Geological Sciences, UCT. Invaluable discussions with and advice from Dr R E Zartman, visiting scientist in the Department of Geological Sciences, UCT (April 2001 and April 2002), are gratefully acknowledged. Assistance with sampling and sample preparation by S Sheldon and F Wewers, from the Department of Physical Sciences, Peninsula Technikon and transport arranged by Botany Department, University of the Western Cape has made this collaborative study possible. My colleagues E Stout, S Davids, F Rawoot, R Bailie and D Jamal, for your help, interest and encouragement, I thank you all.

J. Mnisi, Vista University, Soweto Campus

Development of a Novel Method for Slag Sampling, employing XRF Spectrometry.

Abstract

Secondary Basic Oxygen Furnaces slag samples require the development of a novel technique for sample preparation which would yield a homogenous and representative sample of the material and that would simultaneously be fast, inexpensive and be practical to apply.

The specimens for X-ray fluorescence analysis of slags are usually prepared by the briquette method. This method entails some problems connected to analytical accuracy due to such factors as particle size, differences in packing, and the segregation of elements. It has

recently become evident that a fusion or glass bead method can be used for specimen preparation. This method has been applied mainly to the analysis of Basic Oxygen Furnaces Secondary slags. Fusion method provides better accuracy and precision than the usual briquette method if flux, crucible, fusion temperatures, casting operation and other variables are controlled in an appropriate manner.

Older methods of slag analysis were in many cases complicated and time consuming requiring a lot of work. It was decided to develop a novel method for analyzing the slag samples taken by a new kind of probe.

P. Swafo, University of South Africa

FT-Raman Spectroscopic Study of Hydrogen Bonding in Water-Methanol Mixtures.

Abstract

The interaction between methanol and water has been investigated by applying near-infrared spectroscopy (1); it cannot be measured using mid-infrared spectroscopy, because water absorbs very strongly in this spectral region. Since water is a very poor Raman scatterer, we have investigated the interactions between methanol and water over the entire composition range of mixtures. The interaction between the two components is evident from the shifts in the peaks of the functional groups of methanol as the compositions of the mixtures change: the CH3 vibrational bands shift to higher wave number with increasing concentration of water, whereas the C-O vibrational bands shift to a lower wave number.

The Raman spectra of the mixtures were analysed with methods such as PCA (Principal Component Analysis) and Derivative Methods. Based on the results of this analysis, it was possible to propose a model for the interaction between the methanol and the water in the mixtures.

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M Legodi, University of Pretoria

Raman Spectra of Clays and Pigments used in Ancient Artefacts.

Abstract

The technique of Raman spectroscopy was used to examine the composition of clays (found on Portuguese shipwrecks off the south African coast) and the reddish-brown clay pot, together with their associated pigments. Three samples of red clays, two samples of gray clays, and the reddish-brown clay pot were investigated. Each object appeared to have two predominant regions: dark and uncoloured. The dark regions on all the three red clay samples and the clay pot gave similar spectra, characterized by secondary aluminosilicates[1] and pigments[2]: hematite (292, 407 cm^{-1}), quartz (462 cm^{-1}), halloysite (1124 cm^{-1}), nacrite (737 cm^{-1}) and amorphous carbon (1317 cm^{-1}) [3].

The Raman spectra of the dark regions of the two gray clays showed common features of quartz (459 cm^{-1}), amorphous carbon black (1597 cm^{-1}), halloysite (1122 cm^{-1}), dickite (560 cm^{-1}) and nacrite (677 cm^{-1}). The uncoloured regions of all the objects investigated were dominated by high fluorescence.

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N. Krusberski, Rand Afrikaans University

The Evaluation of Different Calibration Strategies using Emulsions for Wear-metal-in-oil Analyses.

Abstract

The detection and identification of metallic elements in lubricating oil is of key importance for the timely maintenance of engine components. Elemental analysis in used lubricating oils suffers from matrix problems caused by the complexity of the oil matrix. Emulsification of the oil with surfactants and water reduces the organic content of the sample, which is especially beneficial for ICP-MS. When the oil is evenly dispersed in the water phase, the sample behaves similar to an aqueous solution. This approach is more cost efficient than using organometallic oil standards. Aqueous-, aqueous emulsion- and oil emulsion standards have been used for calibration of the ICP-OES determination of emulsified wear-metals-in-oil samples and their results reported. An evaluation of these calibration strategies is discussed in detail.

S. Jansen van Vuuren, Rand Afrikaans University

The Simultaneous Separation and Determination of Cr(III) and Cr(VI) species by Ion Chromatography – Inductively Coupled Plasma – Optical Emission Spectrometry.

Abstract

A hyphenated technique coupling ion chromatography to inductively coupled plasma - optical emission spectroscopy (ICP-OES) was developed for the simultaneous separation and determination of Cr(III) and Cr(VI) species. Separation was carried out on Dionex guard (AG 9) and separation (AS 9) columns using a carbonate - hydrogencarbonate eluant. The separation was preceded by the complexation of Cr(III) with ethylenediaminetetraacetic acid (EDTA) to form a stable anion. The parameters affecting retention times and resolution were optimised and interferences due to the presence of other metals were studied. The detection limits were found to be 0.2 µg/ml for both species. The method was applied to the determination of Cr(III) and Cr(VI) in plating bath effluent.

Z. Foldvari, University of Pretoria

Determination of the Stereoselectivity of Sharpless Epoxidation/Kinetic Resolution of (3RS)-7-[(tertbutyldimethylsilyl) oxy] –hept-1-en-3-ol by Nuclear Magnetic Resonance Spectroscopy.

Abstract

The synthesis of enantiomerically pure compounds is one of the most important goals in organic synthesis and is a major target in industrial syntheses of physiologically active compounds. The 1980s witnessed the emergence of reagent-control strategy that employs powerful enantiomerically pure catalysts and auxiliaries for the purpose of constructing chiral molecules in a diastereo- and enantioselective fashion. In 1980 Katsuki and Sharpless reported an unusually efficient method for the epoxidation of primary allylic alcohols and later the kinetic resolution of secondary allylic alcohol. This new strategy involves epoxidation by a transition-metal catalyst in the presence of chiral auxiliaries in order to achieve stereochemical control.

Sharpless epoxidation/kinetic resolution was applied in the epoxidation and resolution of racemic allylic alcohol, (3RS)-7-[(tert-butyldimethylsilyl)oxy]-hept-1-en-3-ol, which is an intermediate in the synthesis of TA and TB, toxins isolated from Alternaria alternata, a fungal contaminant of tomato plants. Nuclear magnetic resonance spectroscopy was used in the determination of the stereoselectivity of the asymmetric epoxidation reaction.

A. Whaley, University of Pretoria

Selective Ionisation Techniques for Mass Spectrometry.

Abstract

Most spectroscopists seem to spend hours in sample preparation, increasing the concentration to a workable range and minimizing the effects of the matrix or other constituents. For example, in Polyaromatichydrocarbon (PAH) analysis, rigorous sample preparation needs to be undertaken in order to remove the thousands of compounds which overlap with PAH's in chromatographic results. Hundreds of researchers seem to dedicate their lives on just this aspect, refining our knowledge, and improving sample preparation techniques.

Yet, what if other alternatives exist?

This problem can be tackled from another angle: Improving our technology in order to remove the need for extensive sample preparation. By improving our instruments' selectivity, we can easily improve their sensitivity.

From the many possibilities, I will focus on two areas, Negative Chemical Ionisation (NCI) Mass Spectroscopy, and Laser Ionisation Mass Spectroscopy.

A brief description of mass spectrometry, describing electronic ionization, chemical ionization and negative chemical ionization will be given. The background to Laser Ionization and the techniques of Single Photon Ionisation (SPI-VUV) and Resonance Enhanced Multi-Photon Ionisation (REMPI) will also be provided.

Results on Dioxin and PAHs samples will be presented.

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