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Editorial

Analytical molecular and biomolecular spectroscopy: Basics and applications

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Traditionally, as compared to atomic spectroscopy techniques, analytical molecular spectroscopy on the whole comprises a greater extent of studies related to analysing various structural and (or) conformational characteristics, bonding, inter- and intramolecular interactions, etc., rather than merely quantitative analyses of molecular species. Of course, such molecular-level structure-and-bonding related information is directly pertinent to elucidating the mechanisms of chemical and physical processes underlying different analytical methods. Thus, molecular and biomolecular spectroscopy in the aforementioned broader scope is represented in a variety of analytical applications at each congress of the Colloquium Spectroscopicum Internationale (CSI), a major series in the broad field of analytical spectroscopy since the 1950s.

This Special Issue of *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* is devoted to CSI XXXVII which was held in Buzios, Rio de Janeiro, Brazil, from the 28th of August to the 2nd of September, 2011 (see the excellent detailed and 'colourful' report on this event by its Co-Chairman, Professor B. Welz [1]). It contains 28 selected articles in which the main results have been reported using a range of molecular spectroscopic techniques. According to our estimation, approximately about a third of the CSI XXXVII participants, whose contributions were within the scope of molecular or biomolecular spectroscopy, have submitted full papers to this Special Issue. Nonetheless, the latter appears to be well representative with regard both to the participants (as the authors' teams represent 16 countries) and to the spectroscopic techniques used, as shown by the following brief survey of the contributions comprising this Special Issue.

Three papers by Kim et al. deal with the very important and rapidly developing field of spectrochemical analysis related to the use of surface-enhanced Raman scattering (SERS) on noble metal nanoparticles. In the first two papers, the authors consider "nanogaps" between a flat Au or Ag metal surface and an Au, Ag or Pt nanoparticle as SERS-active "hot sites". Their third paper reports on the fabrication of SERS-active substrates, based on functionalised Au nanoparticles attached onto the inner surfaces of glass capillaries, for the detection of biogenic volatile organic compounds.

The next group of three papers presents experimental studies involving vibrational, ^{1}H and ^{13}C NMR and (in the first two papers) optical spectroscopic techniques, as well as theoretical calculations revealing the effects of a series of alkali metals on the electronic and molecular structures of the ligands in their salts with caffeic (3,4-dihydroxycinnamic) acid (Świsłocka), vanillic acid (Świsłocka et al.) and benzenesulfonic acid (Świderski et al.). In some cases, the antimicrobial activities of the salts towards a range of pathogenic microorganisms were compared and correlated with their molecular structures.

The following series of four papers are grouped on the basis of utilising various polymeric matrices for spectrochemical analyses. A solid-phase extraction of enrofloxacin, a fluoroquinolone antibiotic for veterinary applications, on an acrylic polymer was optimised to separate the drug from interfering components of biological matrices, with further phosphorimetric analysis after photochemical derivatisation, resulting in a nanogram-range absolute limit of detection and a linear analytical response over three orders of magnitude of the concentration (de Souza et al.). The application of magic angle spinning (MAS) solid-state ^{19}F NMR spectroscopy, combined with a chemometric approach, for analysing and probing structural variability of poorly water-soluble fluorinated pharmaceuticals, formulated as solid dispersions in polymer matrices, was presented (Urbanova et al.) with examples of a range of model systems with Atorvastatin incorporated in a polyvinylpyrrolidone matrix. Raman imaging spectroscopy was demonstrated (de Campos et al.) to allow monitoring the topography and surface characterisation of poly(dimethylsiloxane) rubbers modified by methacryloxypropyltrimethoxysilane (by

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polycondensation reactions), used as substrates for microchannel fabrication, applicable in micro total analysis systems. Magnetic nanocomposites of nanosized particles of maghemite (γ-Fe_2O_3, a ferromagnetic with a spinel structure) in a styrene–divinylbenzene copolymer template were characterised using photoacoustic spectroscopy, X-ray diffraction and transmission electron microscopy (Rodriguez et al.).

An accompanying paper by Rodriguez et al. using photoacoustic spectroscopy presents a simple and sensitive non-destructive method for the determination of optical properties of biological samples. The pigmentation in leaves of the tree *Blepharocalyx salicifolius* (Kunt) O. Berg, was inversely correlated to the soil moisture levels, leaf water content and leaf water potentials. A portable device for photoacoustic spectroscopy of plants and other photosynthetic tissues, cells and organelles was developed together with a method to measure photosynthesis in such biological objects.

A series of five papers featuring ^{57}Fe Mössbauer (nuclear γ-resonance) spectroscopy opens with a report on the keynote lecture presented at CSI XXXVII by Michael I. Oshtrakh, showing methodological advances related to the use of high-velocity-resolution Mössbauer spectroscopy, with several examples of the authors' studies of iron-containing biomolecules, pharmaceutical products, meteorite samples and nanoparticles emphasising the advantages of the high-velocity-resolution approach (Oshtrakh and Semionkin). The accompanying two experimental papers using Mössbauer spectroscopy with a high velocity resolution demonstrated its capability to reveal small variations in the ^{57}Fe hyperfine parameters related to differences in the ferric oxyhydroxide core structure in human liver ferritin, some of its pharmaceutical models and ferritin in chicken liver and spleen tissues (Alenkina et al.), as well as differences in Mössbauer parameters of iron oxide nanoparticles as-prepared and dispersed in Copaiba oil, an essential oil from South American trees of the genus *Copaifera* with a variety of uses (Oshtrakh et al.). Mössbauer spectroscopy, in addition to transmission electron microscopy and X-ray diffraction, was used to characterise magnetite (Fe_3O_4) based nanoparticles in mesoporous styrene–divinylbenzene microspheres (Rodriguez et al.). A mineralogical application of Mössbauer spectroscopy (with measurements at temperatures from 17 K and higher), together with X-ray diffraction and energy-dispersive X-ray spectroscopy, was presented in a characterisation of the heterosite (Fe–Mn orthophosphate) phase occurring in a pegmatitic rock sample (de Grave et al.).

Two papers (both by Luna et al.) describe the power of infrared (IR) spectroscopy in conjunction with chemometric methods for analysing edible vegetable oils. Canola, sunflower, corn and soybean oils were characterised, classified and discriminated using Fourier transform mid-IR spectroscopy, while near-infrared (NIR) spectroscopy, also together with multivariate classification, was shown to provide a rapid, nondestructive and reliable method to distinguish non-transgenic and transgenic soybean oils.

The final set of 10 papers represents a variety of techniques and samples studied. Fourier transform infrared (FTIR) spectroscopic measurements with band deconvolution analysis of ternary borate glasses immersed in dilute aqueous phosphate solutions showed a time-dependent formation of crystalline calcium phosphate (hydroxyapatite), while X-ray diffraction could be used to retrace the structural changes and degree of crystallinity of the prepared glasses (Abdelghany). For spectrofluorimetric determination of doramectin in milk samples with a significantly enhanced sensitivity, a new easy, clean and low-cost derivatisation reaction was proposed based on alkaline hydrolysis of ethanolic doramectin solutions at an elevated temperature, resulting in 10^3-fold stronger fluorescence signals and an extended linear response range (Maia et al.). Fourteen metal(II) complexes with two S-benzyl-N-(1-ferrocenyl-3-(4-X-benzene)acrylketone) dithiocarbazate ligands (with X = CH_3 or Cl) were synthesised, characterised using IR, ^{1}H and ^{13}C NMR (in deuterated DMSO) and UV–visible (in DMF solutions) spectroscopic techniques with regard to their coordination structure, and screened for their *in vitro* antibacterial and antifungal properties (Liu et al.).

Differences in the chemical profiles of plant material samples of river bushwillow (*Combretum erythrophyllum*), harvested from mine contaminated areas and those of natural populations, were characterised using NIR spectroscopy in combination with chemometrics (Mokgalaka-Matlala et al.). This approach is of importance for optimising phytoremediation of contaminated soils as an eco-friendly direction in environmental biotechnology.

In the field of archaeology, infrared spectroscopic analysis and laser-induced breakdown spectroscopy (LIBS), as well as pyrolysis-gas chromatography coupled with mass spectrometry and thermoluminescence were used for analysing the material of an ancient ceramic vase and its original content (Legnaioli et al.). For twenty-six commercial honey samples from six types of flowers (acacia, sunflower, forest, polyfloral, lime and sea buckthorn), a range of their physical and biochemical properties, including free radical scavenging activity monitored by EPR spectroscopy, were correlated with their botanical source (Cimpoiu et al.). For the determination of lapachol, a natural naphthoquinone found in trees of the genus *Tabebuia* (the *Bignoniaceae* family), in the presence of other naphthoquinones, lapachol-induced fluorescence (λ_{max} = 540 nm) quenching of 3-mercaptopropionic acid (3MPA)-capped CdTe quantum dots in aqueous dispersion was utilised (Aucélio et al.). Arsenic-loaded Mn_3O_4 magnetic composites obtained by As^{III} adsorption were studied using FTIR and Raman spectroscopic techniques, whereas XANES data were used to prove adsorbed As oxidation to arsenate, As^V (Silva et al.).

Spectrofluorimetric determination of tetrabenazine, a drug used for the symptomatic treatment of hyperkinetic movement disorder, was found to be significantly improved with regard to the analyte signal-to-blank ratio and an extended linear range after a UV irradiation-induced photochemical derivatisation of the drug in alkaline solution (Osório et al.). It was also found that the detection power could be improved at least 10-fold using solid phase extraction, which also allowed the separation of the analyte from matrix components, enabling the analysis of biological fluids.

In the final paper of this issue (Kamnev et al.), time-dependent changes of the integral bioluminescence intensity of live *Photobacterium phosphoreum* cells were monitored in the presence of ultra-trace concentrations of americium-241 (^{241}Am, an α-emitting radionuclide) and/or humic substances (HS, a possible detoxifying agent). In addition, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was used to control possible metabolic responses of the bacteria to the α-radioactivity stress and its alleviation by HS.

The present brief survey shows that a over a half of the papers deal with analyses of various biological, pharmaceutical or food samples or include their biological activity tests. This reflects the growing trend of using a wide range of spectroscopic techniques in diverse and often sophisticated bioanalytical applications.

Completing this Editorial, I would like to pay tribute to the excellent organisational work of the CSI XXXVII Chairman, Professor Reinaldo Calixto de Campos, who unfortunately passed away in February, 2012, and acknowledge the support and friendly collaboration of the whole team of the CSI XXXVII Organising Committee, with special personal thanks to the Co-Chairman, Professor Bernhard Welz.

The next CSI XXXVIII event will be held in Tromsø, Norway, June 16–20, 2013 (http://site.uit.no/csi2013/).

Reference

[1] B. Welz, Spectrochimica Acta Part B: Atomic Spectroscopy 71–72 (2012) 1–2.