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## Selected papers of the 1st International Workshop on “Stable Isotope Ratio Infrared Spectrometry

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## **Selected papers of the 1st International Workshop on “Stable Isotope Ratio Infrared Spectrometry: New Developments and Applications” (SIRIS), September 6–8, 2004, Vienna, Austria**

### **Preface**

The first international workshop on “Stable isotope ratio infrared spectrometry: new developments and applications” (SIRIS 2004) was held at the Vienna International Center from September 6 to 8, 2004. A total of 45 scientists in the fields of laser spectroscopy, laser development, and stable isotope ratio measurements, participated in the workshop. This and the following issue of *Isotopes in Environmental and Health Studies* together contain 16 selected papers presented at the workshop that give a good impression of the state-of-the art methods in the field. The meeting represented the first forum specifically aimed at bringing together scientists in infrared spectroscopy and isotope ratio research. Particularly, widely-recognized experts in the fields of laser spectroscopy, semiconductor laser physics, and non-linear optics were given the opportunity to closely interact with leading researchers in a wide variety of fields (ranging from atmospheric science to ecology and bio-medicine), who all use isotope ratio measurements as their primary research tool, in order to identify the most promising experimental approaches and techniques, as well as to determine the needs of the different fields of applications.

There were 34 high-quality oral presentations and a good handful of posters. An authoritative overview was given of the most advanced spectroscopic techniques, which already find, or have a great potential for, fruitful application in accurate isotope ratio analyses. Similarly, the status was outlined of recent technologies for generation of laser radiation in the infrared region, likely to be employed for spectroscopic applications. At the same time, the usefulness of stable isotopes was illustrated with examples from a range of relevant research areas (including carbon cycle and biosphere-atmosphere gas exchange, troposphere-stratosphere exchange, and biomedical energy metabolism). Practically all areas of research are hampered by the difficulty or plain impossibility of performing *in-situ* and continuous isotope ratio measurements with the currently available IRMS instrumentation. Laser spectrometry holds the potential of building reliable, robust, portable, easy to use, on-site instrumentation, which would clearly provide a big boost to the fields of research mentioned above. In fact, in some areas, such progress is already being made, as demonstrated by the commercial availability of  $^{13}\text{CO}_2$  breath analysis instruments, on-site volcanic  $^{13}\text{CO}_2$  monitoring, and recent airborne water isotope measurements.

The round-table discussions were deemed to be very fruitful by all involved, especially in determining the main obstacles (of scientific, technical, financial, or other nature) to converting advanced optical measurement techniques into field-deployable technologies. The isotope community stressed the importance of calibration to international standards, over extended periods of time and under ‘real-life’ circumstances, in order to have the new methods fully accepted. Also, scientists involved in laser spectroscopy had the important opportunity to compare the different laser-based methods and discuss each method’s main advantages and limiting factors.

We would like to share with the reader a few observations and conclusions:

- Stable Isotope Ratio Infrared Spectrometry (SIRIS), has a problem reaching the extremely high levels of precision routinely achieved by IRMS, in all but a number of special cases (such as  $\delta^2\text{H}$  of water). However, it should be noted that IRMS has by now benefited from almost half a century of commercial development. In addition, SIRIS has some unique advantages over IRMS that are only beginning to be explored. For example, there is the possibility of building more compact, low-power consumption instruments for *in-situ* and remote operation (Mars . . .). Of special interest for commercialization is that optical instruments can be built at lower cost and generally require less maintenance. In part, these advantages can be traced back to the conceptual simplicity of the optical technique: Lambert-Beer absorption processes can be described in great quantitative detail, in contrast to, *e.g.*, the ionization process inside an IRMS ion-source. This results in scale contraction factors in the calibration procedure that are usually very close to unity. This is in contrast to the case of IRMS, where, *e.g.*, the  $\text{H}^{3+}$  correction can easily amount to 10% or more.
- Non-Dispersive InfraRed (NDIR) spectroscopy is a mature technology, especially for  $^{13}\text{CO}_2$  breath analysis in medical diagnostics. Efforts are being made to improve the sensitivity by about two orders of magnitude to make the technique useful for  $^{13}\text{C}/^{12}\text{C}$  measurements at atmospheric  $\text{CO}_2$  concentrations.
- Fourier Transform IR (FTIR) spectroscopy, in spite of the complexity of the spectral analysis procedures, has a high potential for *in-situ* measurements on multiple species (*e.g.*, combined  $^{13}\text{CO}_2$  and HOD) with a relatively simple and robust instrument, as amply demonstrated by the work of Griffith and Bryant at the University of Wollongong. Apart from the convoluted data analysis, the technique also becomes less attractive when a very high spectral resolution is required (*e.g.*, to “see”  $\text{H}^{18}\text{OH}$  or  $^{16}\text{O}^{12}\text{C}^{18}\text{O}$ ), as the instrumentation quickly becomes large and heavy in this case.
- An extension of the laser assisted ratio analyzer (LARA) technique to  $^{14}\text{C}$ -counting in  $\text{CO}_2$  has been presented. LARA is based on the use of fixed-frequency  $\text{CO}_2$  (-isotope) gas lasers and sensitive detection via the opto-galvanic effect. The success of this effort will depend largely on the development of a high-power  $^{14}\text{CO}_2$  laser. If successful, the technique will present an interesting alternative to currently available, expensive instrumentation (like Accelerator Mass Spectrometry), but is likely to remain limited to experiments using (strongly) enriched  $^{14}\text{C}$  material.
- Optical Cavity-based techniques, like cavity ring-down spectroscopy (CRDS) and cavity enhanced absorption spectroscopy (CEAS), generally appear to be the best choice to push the detection sensitivity to extremely high levels. A possible alternative, for molecules exhibiting a permanent dipole moment (like  $\text{H}_2\text{CO}$ , or possibly even  $\text{H}_2\text{O}$ ), was presented by Werle and co-workers, who implemented sample modulation through the Stark-effect. In combination with frequency-modulation spectroscopy, a very sensitive spectrometer can be designed that allows integration over relatively long time periods. Hence, the perspective of detecting atmospheric trace constituents, and their isotopologues, is now a concrete

possibility, especially when combining cavity-based methods with new coherent sources in the mid-IR.

- The development of laser sources in the mid-IR, where most relevant molecules exhibit strong fundamental absorption bands, has seen significant progress in the past few years. It is now fully realistic to expect inter-subband diode lasers to reach wavelengths exceeding 3  $\mu\text{m}$ , while maintaining ‘telecommunication properties’, (*i.e.*, *cw*, room temperature easy-to-use operation, with mW output power and good tunability), while at the same time (intra-subband) quantum cascade lasers can be made to work reliably in *cw* mode at room temperature at wavelengths below 4.5  $\mu\text{m}$ . It will only be a matter of time for these sources to close the gap between 3 and 4.5  $\mu\text{m}$ , where currently only relatively complicated and expensive non-linear frequency conversion devices are available. Of course, one has to keep in mind that detector performance quickly degrades as the wavelength is increased. In this respect, it is interesting to note that the development of QCLs was as a direct consequence of the observed difficulty of making good mid-infrared detectors with the same structures that later proved so powerful in the reverse direction. Also, at longer wavelengths the quality of high-reflectivity (“super”) mirrors needed in CRDS techniques is significantly lower than in the near-infrared region. Therefore, and especially when the excited molecular vibration concerns an X-H oscillator with relatively strong overtone transitions, the near-infrared region below 2 micron frequently presents a good compromise between sensitivity, or measurement precision, and availability, cost, and ease-of-use of the opto-electronic components.

We look forward to the second SIRIS workshop (to be held in September 2006 on the island of Capri), and are optimistic about the level of progress that will have been made in the two years between the meetings. The interaction between developers of optical isotope ratio instrumentation and the (potential) end users was deemed highly timely and very useful by all.

The workshop has already led to a number of joint research projects and collaborations. We will consider this first workshop even more successful if, at the next meeting, results of such collaborations will be presented.

The following sponsors have made the meeting possible; The Stable Isotopes in Biosphere-Atmosphere Exchange (SIBAE) program of the European Science Foundation, The Center for Isotope Research (CIO) of the University of Groningen, The Hydrology Section of the International Atomic Energy Agency (IAEA), and the Department of Environmental Sciences (DSA) at the Second University of Naples. We are particularly grateful to Michelle Davin and Manfred Gröning of the IAEA Hydrology section for local assistance with the organisation, and to the journal’s managing editor Erika Jäger for her efforts in keeping this issue on track.

*Guest Editors*  
*Erik Kerstel and Livio Gianfrani*