Development of a spectroscopic integrated system for remote and continuous monitoring of volcanic gases

Scientific Coordinator
Name-Position Paolo De Natale, Research Director

Affiliation Istituto Nazionale di Ottica Applicata (INOA)

ACTIVITY REPORT –2nd YEAR

PROJECT PARTICIPANTS

<table>
<thead>
<tr>
<th>RU1</th>
<th>Istituto Nazionale di Ottica Applicata</th>
<th>Paolo De Natale</th>
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<tr>
<td>RU2</td>
<td>Dipartimento di Scienze Ambientali</td>
<td>Livio Gianfrani</td>
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<td>RU3</td>
<td>Cambridge University</td>
<td>Clive Oppenheimer</td>
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<td>RU4</td>
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<td>Frank K. Tittel</td>
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GENERAL OBJECTIVES

- Joint field campaigns at Solfatara, Vulcano island and Mt. Etna: Testing of the spectrometers at volcanic sites.
- Upgrading and modifications of the spectrometers based on the results of the field campaigns.

TASK 1 - FIELD CAMPAIGNS

- RU1, RU2, RU3
- Joint field campaigns at Solfatara, Vulcano island and Mt. Etna: Testing of the spectrometers at volcanic sites

2nd YEAR RESULTS

As shown in each research unit report, the scheduled joint campaign was performed in July 2002. Scientists from RU1, RU2, and RU3 took data at Solfatara on the 16th July, and from 22nd to 26th at Vulcano Island. Different measurement methodologies were used in these occasions. RU1 and RU2 deployed the Portable Diode Laser Spectrometer, in an open-path configuration, to measure CO$_2$ and H$_2$O concentrations in different locations of both sites. System control and continuous data acquisition was carried out using a program written under LabView platform. Concentrations up to 3300(100) ppm and 74000(1000) ppm for CO$_2$ and H$_2$O, respectively, were measured at Solfatara.

RU3 used the UV spectroscopic system already described in the scientific report of Year 1. SO$_2$ fluxes at Vulcano, Stromboli and Mt. Etna (averages of 14, 280 and 940 Mg d$^{-1}$, respectively) were measured. Unlike the conventional approach of traversing underneath the plume, this technique can be operated from fixed positions, providing higher (every few minutes) time resolution data. Side-by-side measurements for Etna with a COSPEC operated by a INGV group from Catania, providing an important intercomparison of the old and new methods (Figure 2), were also performed.

After a careful analysis of the peculiar technical problems due to the site, evidenced in the fieldwork of the three other RU, the portable modular gas sensor for measuring the $^{13}$C/$^{12}$C isotopic ratio in CO$_2$, developed by RU4, was considered to be not ready and robust enough for field work at Solfatara with the INOA, DSA and CU groups.

TASK 2 - UPGRADES OF THE OPTICAL SPECTROMETERS

- RU2, RU4
- Upgrading and modifications of the spectrometers based on the results of the field campaigns

2nd YEAR RESULTS

Most of the efforts of RU2 were devoted to the development of a novel method for $^{13}$CO$_2$/$^{12}$CO$_2$ isotope ratio measurements, based on diode laser spectroscopy. A compact and portable spectrometer has been implemented, in close collaboration with RU1, operating with a room-temperature DFB diode laser at the unusual wavelength of 2.007
micron. As a result of the accurate measurements of the absolute intensity for a large number of CO$_2$ lines, optimum $^{12}$CO$_2$ and $^{13}$CO$_2$ line pairs were selected. A BASIC code was developed for system control and continuous data acquisition, while spectra analysis and retrieval of the isotope ratio were carried out through a MATLAB code. A large variety of laboratory tests have been performed to determine the precision levels in the super-ratio determination. Earlier tests were performed using pure CO$_2$ samples, in a low pressure regime (about 1 Torr), and $^3$rd harmonic detection of the absorption signals. In this case, a $1\%$ precision was found (absolute statistical uncertainty corresponding to one standard deviation, over 30 repeated measurements) in both the short (over few hours) and long (over several days) terms. The situation drastically changed when using CO$_2$-$N_2$ mixtures at a total pressure of about 100 Torr. Indeed, although the absorption signals were reduced, the much wider lines observed enabled to improve the horizontal resolution, i.e. the number of acquired points for each line profile. Hence, the precision level was improved, using a 2 $\%$ mixture, up to a level of 0.2 $\%$.

RU4 has developed a system for $^{13}$CO$_2$/$^{12}$CO$_2$ isotopic ratio measurements that makes use of a difference frequency-based sensor operating around 4.35 microns ($\sim$2300 cm$^{-1}$). A portable modular gas sensor for measuring the 13C/12C isotopic ratio in CO$_2$ present in volcanic emissions with a precision of $1\%$ was completed. The main limitation factors of the system during laboratory tests were inherent detector noise and imperfect N$_2$ purging of the open path part of the sensor. These error sources can be significantly reduced by increasing the difference frequency generation (DFG) power, that is feasible with present technology of fiber amplifiers.

Another approach under development by RU4 is to utilize a less complex and more compact spectroscopic source (a thermoelectrically cooled, pulsed quantum cascade laser operating in a single frequency mode at 4.35 microns). For this reason an order of such a laser was placed from Alpes Lasers in Neuchatel, Switzerland., the only commercial source to date for such lasers. Although to-date Alpes has not been able to fabricate and deliver such a laser, it is expected at the beginning of 2003 and the rest of the set-up has already been built. This laser can be current and temperature tuned to two optimum $^{12}$CO$_2$ and $^{13}$CO$_2$ absorption lines at 2311 cm$^{-1}$ in order to measure changes in $^{13}$C/$^{12}$C with a precision of 0.1$\%$.

This precision value, together with the similar result achieved with the DFB diode laser spectrometer, could represent a breakthrough for continuous acquisition of isotopic ratio measurements in volcanic sites, though careful field testing will be necessary during year III of the Project.

On the basis of the field experiences acquired during the II year of activity, we plan to make other joint field campaigns during the II year, deploying improved and better suited instrumentation, with the aim to state the final levels of performance of each instrument as well as to define the combined data acquisition capabilities when all of them are deployed.

- **RESEARCH PRODUCTS OF THE PROJECT**
  - n° of articles published on international journals= 28
  - n° of articles published on national journals, proceedings, technical reports= 2
  - invited papers and talks= 1
  - Presentations at international meetings= 3
  - Presentations at national meetings= 4
  - Data base
  - Computation codes= 2
  - Other

**PUBLICATIONS LIST** (inclusive of papers in prints and accepted)


Development of a spectroscopic integrated system for remote and continuous monitoring of volcanic gases.

RU Responsible
Name-Position: Paolo De Natale, Research Director
Affiliation: Istituto Nazionale di Ottica Applicata (INOA)

ACTIVITY REPORT–2nd YEAR

RU PARTICIPANTS

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<tr>
<th>Name-Position</th>
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<tr>
<td>Dr. Paolo De Natale</td>
<td>INOA</td>
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<tr>
<td>Dr. Giuseppe De Natale, Research</td>
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<td>Director</td>
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<tr>
<td>Dr. Alessandra Rocco Post-Doc</td>
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<td>Roberto Abbate (Technician)</td>
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<td>Dr. Pablo Cancio Post-doc</td>
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<td>Paolo Bianchi (optical technician)</td>
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2nd YEAR OBJECTIVES

- Joint field campaigns at Solfatara, Vulcano island and Mt. Etna: Testing of the spectrometers at volcanic sites.
- Upgrading and modifications of the spectrometers based on the results of the field campaigns.

2nd YEAR RESULTS (max 1 page)

The second year activity of the project was mainly devoted to the improvement of the DLS spectrometer, especially concerning its use in field campaigns. Many test measurements were carried out at Solfatara Volcano, while a joint field campaign in collaboration with the Cambridge University Group was successfully performed in July 2002 both at Solfatara and at Vulcano Island.

The upgrading of the DLS involved both the acquisition technique and the optical layout. The acquisition system was switched to a combination of a portable, battery operated, oscilloscope, and a laptop computer to perform continuous data acquisition. To this aim a new program was developed, in collaboration with the DSA, which utilises the LabView© platform. The maximum acquisition rate is 1sec⁻¹ ("sample” mode, of the oscilloscope) but it was fixed to 0.2sec⁻¹ because the “average” acquisition mode increases the digital resolution of the oscilloscope. At present, up to 999 spectra can be continuously acquired.
The optical modifications of the spectrometer involved both the use of a portable breadboard where the 2\(\mu\)m diode laser system was mounted, and the implementation, to perform open-path measurements, of the Herriott multiple reflection cell especially designed for our system. The building materials for the cell, having an optical path length of approximately 20m, are stainless steel (316) for the body and gold for coating the spherical glass mirrors. In fact, the cell must withstand the particularly aggressive chemical compounds formed in volcanic emissions.

*Figure 1: Experimental configuration of the PDLS.*

The new design, shown in fig.1 was deployed during the July 2002 field campaigns. Using the DLS spectrometer, in-situ \(\text{H}_2\text{O}\) and \(\text{CO}_2\) concentration measurements were taken, vs. time. Examples of the retrieved values vs. time are reported in fig.2, where measurements taken at Solfatara crater are shown. The total observation time was approx. 900sec. The detection bench with the cell was positioned at a distance of approx. 1.5m from the fumarole, and at an height of 0.2m with respect to the ground.

The concentrations were retrieved from the acquired spectra by means of a non linear least-square fitting developed in a Matlab® environment. Data analysis required particular care in order to separate the contribution caused by background signal variations (due to change in the environmental conditions as well as wind, which caused oscillation of the optical fibres) from the variations in the concentrations of the molecules under analysis. The whole fitting procedure (robustness and accuracy) was deeply tested.

*Figure 2 : \(\text{CO}_2\) and \(\text{H}_2\text{O}\) concentrations vs. time, recorded at Solfatara Volcano on July, 16th 2002.*

Both field campaigns provided extremely useful information on the system. In particular, the field tests suggested modifications to the set-up, in order to increase its efficiency as well as its performances. As for the spectrometer building materials, stainless steel resulted to be very well suited for the Solfatara environment but still partly prone to chemical aggression when deployed on top of Fossa Grande crater, at Vulcano.
• RESEARCH PRODUCTS
  • Scientific publications:
    5 published in international journals
    1 accepted
    2 submitted
  • Conference presentations
    1 Invited talk
    2 oral presentations
    1 poster presentation
  • New geochemical data
  • Field-tested spectrometers

PUBLICATIONS LIST


“Generation of tunable far-infrared radiation using a quantum cascade laser”

D. Mazzotti, S. Borri, P. Cancio, G. Giusfredi, P. De Natale
“Low-power Lamb-dip spectroscopy of very weak CO₂ transitions around 4.25 µm”


S. Borri, P. Cancio, G. Giusfredi, D. Mazzotti, P. De Natale “Difference-Frequency Generation as a Precise Tool for High Resolution Spectroscopy”


CONFERENCE PRESENTATIONS

P. De Natale, “Recent advances in infrared sources for high resolution spectroscopy”


Project title:
Development of a spectroscopic integrated system for remote and continuous monitoring of volcanic gases.

RU responsible:
Livio Gianfrani, Associate Professor in Experimental Physics, Dipartimento di Scienze Ambientali (DSA), Seconda Università di Napoli

ACTIVITY REPORT–2nd YEAR

RU participants:

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<tr>
<th>Name-Position</th>
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<tr>
<td>Prof. Livio Gianfrani</td>
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<td>Dr. Gianluca Gagliardi, Post-Doc fellowship</td>
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<td>Dott. Antonio Castrillo, Ph.D. student</td>
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<td>Prof. Dario Tedesco</td>
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<td>Giovanni Casa, Technician</td>
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- 2nd YEAR OBJECTIVES
  - Spectroscopic measurements on $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$
  - Joint field campaigns at Solfatara and Vulcano island
  - Development of a novel diode-laser spectrometer for $^{13}\text{C}/^{12}\text{C}$ isotope ratio measurements in CO$_2$

- 2nd YEAR RESULTS (max 1 page)
  During the 2$^{nd}$ year of the project, the Environmental Optics Group at the Environmental Sciences Department in Caserta has contributed to the optimisation of the diode-laser spectrometer for H$_2$O and CO$_2$ concentration measurements in volcanic flows, also implementing a new method for CO$_2$ efflux measurements. We also participated to the joint field campaigns at Solfatara volcano.
  Nonetheless, most of the efforts were devoted to the development of a novel method for $^{13}\text{CO}_2/^{12}\text{CO}_2$ isotope ratio measurements, based on diode laser spectroscopy. Our goal is the demonstration that high resolution and high sensitivity laser spectroscopy can be used for accurate isotope ratio measurements in volcanic gases. We also started, on this topic, a collaboration with the Center for Isotope Research, University of Groningen (Holland).

  A compact and portable spectrometer has been implemented, operating with a room-temperature DFB diode laser at the unusual wavelength of 2.007 micron, in resonance with some interesting absorption lines belonging to the CO$_2$ ν$_1$+2ν$_2$+ν$_3$ vibrational combination bands.

  In the beginning, a spectroscopic investigation has been performed, aimed to find the optimum line pairs for isotope analysis, considering the temperature dependence of their linestrength, the possible overlapping with other atmospheric molecular species, the frequency separation as well as the ratio between the line intensities in natural abundant samples. For this purpose, the absolute intensity for a large number of CO$_2$ lines was accurately measured by means of a novel approach, based on the use of a Michelson interferometer in combination with pure absorption spectroscopy. As a results of the spectroscopic investigation, optimum $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ line pairs were selected.

  The spectrometer is based on the use of two multiple reflection cells, the former containing the sample and the latter the standard gas. Laser absorption is simultaneously observed in the two cells using wavelength modulation spectroscopy with a 1$^{st}$ or a 3$^{rd}$ harmonic detection. Two digital lock-in amplifiers are used for phase-sensitive detection of the absorption signals.

  A BASIC code was developed for system control and continuous data acquisition, while spectra analysis and retrieval of the isotope ratio were carried out through a MATLAB code. The development of the latter code has been done with a particular care, in order to satisfy a number of requirements, including the accurate determination of the $^{13}\text{CO}_2$ and $^{12}\text{CO}_2$ line centers, the
background subtraction in the detected spectra, as well as the non-linear least-squares fit of the sample-gas spectrum with the standard-gas one.

A large variety of laboratory tests have been performed to determine the precision levels in the super-ratio determination. The earlier tests were performed using pure CO$_2$ samples, in a low pressure regime (about 1 Torr), and 3$^{rd}$ harmonic detection of the absorption signals. In this case, we found a 1‰-precision (absolute statistical uncertainty corresponding to one standard deviation, over 30 repeated measurements) in both the short (over few hours) and long (over several days) terms. The situation drastically changed when using CO$_2$-N$_2$ mixtures at a total pressure of about 100 Torr. Indeed, although the absorption signals were reduced, the much wider lines we observed enabled us to improve the horizontal resolution, i.e. the number of acquired points for each line profile. Hence, we were able to improve the precision level, using a 2 % mixture, up to a level of 0.2 ‰.

- **RESEARCH PRODUCTS**
  - num of articles published on international journals: 5
  - presentations at international meetings: 2
  - presentations at national meetings: 4
  - Computation codes: 2

**PUBLICATIONS LIST**


**CONFERENCE PRESENTATIONS**


**Project title:**
Development of a spectroscopic integrated system for remote and continuous monitoring of volcanic gases.

**RU Responsible**
Name-Position: Clive Oppenheimer (Lecturer)
Affiliation: University of Cambridge

**ACTIVITY REPORT–2nd YEAR**

**RU PARTICIPANTS**

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<thead>
<tr>
<th>Clive Oppenheimer &amp; Andrew McGonigle</th>
<th>University of Cambridge</th>
<th>4 months</th>
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- **2nd YEAR OBJECTIVES**
- Joint field campaigns at Solfatara, Vulcano island and Mt. Etna: Testing of the spectrometers at volcanic sites.
- Upgrading and modifications of the spectrometers based on the results of the field campaigns.

- **2nd YEAR RESULTS (max 1 page)**

We continued to develop the UV spectroscopic system that we reported in Year 1. The results continue to look very encouraging, and already there has been a considerable interest in the methodologies following our presentations at the Mt. Pelee congress and other meetings. The Montserrat Volcano Observatory now has an operational UV system based on our original work last year, and INGV-Catania has recently invested in several UV instruments for deployment on Etna.

*Figure 1: Experimental configuration of the automated plume scanning device.*

The main new achievements this year have been to design a compact, portable scanning UV system (Figure 1), and to test it in collaboration with our GNV Project colleagues from LENS and INGV during a successful field campaign in July 2002. This work has been written up and is in review with *Journal of Geophysical Research*. We measured SO$_2$ fluxes at Vulcano, Stromboli and Mt. Etna (averages of 14, 280 and 940 Mg d$^{-1}$, respectively). Unlike the conventional approach of traversing underneath the plume, this technique can be operated from fixed positions, providing higher (every few minutes) time resolution data, and application to volcanoes where road traverses, airborne or ship
borne campaigns are impossible, impractical or uneconomic. This approach could readily be extended to measurements of other sources (e.g., industrial/agrochemical), and other UV absorbing species (e.g., NO$_2$). Importantly, we were able to make side-by-side measurements for Etna with a COSPEC operated by our INGV-Catania colleagues, providing an important intercomparison of the old and new methods (Figure 2).

A second field campaign at Solfatara and Vulcano is in progress now, with the UV system adapted for short path measurements using an artificial source. The aims of this work are to build a capability for optical measurement of SO$_2$/H$_2$S ratios. The results of this work will be reported next year.

Figure 2: SO$_2$ column amount versus distance traversed perpendicular to the plume transport direction for two traverses of Mt. Etna’s plume on the 25$^{th}$ July 2002. COSPEC data (diamonds), obtained in parallel, are also shown in the upper plot.

- **RESEARCH PRODUCTS**
In press and 2002 publications on volcanic volatiles measurements are reported below. In addition, we have presented the following papers:
- Invited paper for *Workshop on Melt Inclusions*, Seiano, 2002 (Oppenheimer et al.)

**PUBLICATIONS LIST** (inclusive of papers in prints and accepted)


**Project title:**
Development of a spectroscopic integrated system for remote and continuous monitoring of volcanic gases.

**RU Responsible**
Name-Position: Frank K. Tittel (Professor of Electrical and Computer Engineering)
Affiliation: Rice University

**ACTIVITY REPORT–2nd YEAR**

**RU PARTICIPANTS**

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<tr>
<td>Dr. M. Erdelyi</td>
<td>Rice University</td>
<td>2 months</td>
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<td>Dr. D. Richter</td>
<td>National Center for Atmospheric Research</td>
<td>1 month</td>
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<tr>
<td>Dr. A. A. Kosterev</td>
<td>Rice University</td>
<td>1 month</td>
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<tr>
<td>Prof. F. K. Tittel</td>
<td>Rice University</td>
<td>1 month</td>
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- **2nd YEAR OBJECTIVES**
  - Upgrading and modifications of the spectrometer
  - Joint field campaign at Solfatara

- **2nd YEAR RESULTS (max 1 page)**

The thrust of our research and development project was focused on three tasks:

1. $^{13}$CO$_2$/12CO$_2$ isotopic ratio measurements using a difference frequency-based sensor operating at 4.35 microns (~2300 cm$^{-1}$). A portable modular gas sensor for measuring the $^{13}$C/12C isotopic ratio in CO$_2$ present in volcanic emissions with a precision of $1^\circ$ was completed. Such an instrument can provide valuable information about CO$_2$ exchange processes in volcanic emissions that are useful in predicting increased volcanic activity. Details of this laser based spectroscopic sensor, the required specialized absorption cell and gas sampling, the experimental strategy for measuring isotopic ratios by means of direct absorption spectroscopy and the associated data acquisition methodology are described in Publ. 1, which can be viewed on our website [http://www.ece.rice.edu/lasersci](http://www.ece.rice.edu/lasersci). The main limitation factors of the system during laboratory test were inherent detector noise and imperfect N$_2$ purging of the open path part of the sensor. These error sources can be significantly reduced by increasing the difference frequency generation (DFG) power (e.g., using higher power seed laser sources or different DFG pump sources operating at ~1 and ~1.5 microns as described in Publ. 2). Hence, the instrumentation available in July 2002 was considered not to be ready and robust enough for field work at Solfatara with the INO/DSO and CU groups.

2. Design and implementation of a second advanced mid-IR difference DFG source based on experiences in task 1. This source will employ the latest enabling photonics technology available in 2003, tunable DFG radiation at 4.35 microns will obtained by mixing two pump wavelengths at 1.13 and 1.52 microns from a Yb$^{3+}$ doped DFB fiber laser and tunable DFB diode laser. Both lasers attain linewidths down to 100kHz, which is important for achieving good sensor selectivity in the presence of absorption by
interfering gas species. The power level of both pump lasers can be boosted by Yb and Er/Yb doped fiber amplifiers. Based on performance data from our previously developed DFG sources, the expected DFG power will exceed 0.1 mW if pumped with 0.2 W and 0.5 W at 1.52 and 1.13 microns, respectively

(3) Design and implementation of a quantum cascade laser source for high-precision $^{13}$CO$_2$/$^{12}$CO$_2$ isotopic ratio measurements.

Another approach is to utilize a less complex and more compact spectroscopic source that makes use of a newly developed thermoelectrically cooled, pulsed quantum cascade laser operating in a single frequency mode at 4.35 microns. For this reason we placed an order of such a laser from Alpes Lasers in Neuchatel, Switzerland, the only commercial source to date for such lasers. To-date Alpes has not been able to fabricate and deliver such a laser that can be current and temperature tuned to two optimum $^{13}$CO$_2$ and $^{12}$CO$_2$ absorption lines at 2311 cm$^{-1}$ in order to measure changes in $^{13}$del with a precision of 0.1$^{100}/0$. This requires achieving a near equivalence in the absorption for the minor and major CO$_2$ isotopes, which differ in abundance by ~100. In the meantime we have designed and built a suitable laser housing, and the necessary laser current and thermoelectric temperature control electronics to operate such a pulsed DFB quantum cascade (See Publ. 3)

- RESEARCH PRODUCTS
  - n° of articles published on international journals = 2
  - n° of articles published on national journals, proceedings, technical reports
  - invited papers and talks
  - presentations at international meetings = 1
  - presentations at national meetings:
  - Data bases
  - Computation codes
  - Other

PUBLICATIONS LIST (inclusive of papers in prints and accepted)