

Optical Detection of Chlorine for Chemical Oxygen Iodine Laser

Mainuddin¹, Gaurav Singhal², A. K. Varshney³, R. K. Tyagi⁴, A. K. Maini⁵

^{1,2,3,4,5}Laser Science and Technology Centre,
 Defence Research and Development Organization,
 Metcalfe House, Delhi-110054, India

Abstract: This paper focuses on the implementation of optical technique for measurement of chlorine gas utilization which is one of the critical parameters for Chemical Oxygen Iodine Laser (COIL). COIL employs chlorine as one of the fuel components to generate singlet oxygen molecules after its reaction with Basic Hydrogen Peroxide (BHP) solution. The efficiency of COIL is strongly dependent on utilization of chlorine which in turn maximizes the laser output power. An optical absorption based in-house custom built chlorine detection system has been developed and interfaced with COIL.

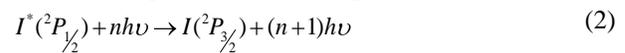
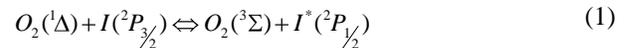
Keywords: Chlorine; Data acquisition; Chemical laser; Interface electronics; Graphical user interface

1. INTRODUCTION

COIL is one of the flowing medium infrared gas lasers [1-3] which utilizes various gas effluents and chemicals. It is the only chemical laser based on electronic transition. It has distinct benefits in terms of scalability, efficiency (>20%), shorter wavelength ($\lambda=1.315\mu\text{m}$) enabling fibre compatibility for remote operation and also good laser material interaction. Owing to these advantages it is highly sought after laser source for numerous applications. The pumping energy source for this laser is singlet oxygen $O_2(^1\Delta)$, which is an excited form of oxygen molecule with energy level very near to the atomic iodine. This allows possibility of a near resonant energy transfer. Singlet oxygen is required not only for pumping but also for dissociation of iodine molecules. It is produced using chemical method by the reaction between chlorine gas and BHP solution. The production of singlet oxygen is strongly dependent on the amount of chlorine reacted to the BHP solution. There is a need for development of non contact type method for estimation of chlorine utilization so that flow of laser gases does not disturb. An optical absorption based chlorine utilization measurement system has been developed for optimization of COIL.

COIL first demonstrated by McDermott [4] in 1978, is the only chemical laser with electronic transition. A two phase reaction between BHP solution and chlorine gas produces pumping medium, singlet oxygen $O_2(^1\Delta_g)$. This is diluted

with sufficient nitrogen buffer gas and mixed with the lasing species i.e. iodine. The total flow is then supersonically expanded into the laser cavity, where laser power at $1.315\mu\text{m}$ wavelength is extracted according to equations (1) and (2).



The pumping source, $O_2(^1\Delta)$ is an excited form of oxygen molecule with energy level very near to the atomic iodine and hence almost a near resonant energy transfer can be achieved. Various methods such as chemical, electrical (RF and Microwave discharges) and optical methods have been used for the generation of these pumping molecules. Amongst these, the chemical method is the only method till date that has been successful for the large-scale production of singlet oxygen with required yield. The chemical method is based on the reactions between chlorine gas (Cl_2) and BHP solution as,



The lasing medium (iodine atoms) is injected into the pumping medium in the gaseous form. In typical COIL operation, commercially available iodine crystals are converted into vapor form in an evaporator and supplied with the aid of heated nitrogen gas. Fig. 1 shows the functional block diagram of COIL, which exhibits interconnections of all subsystems.

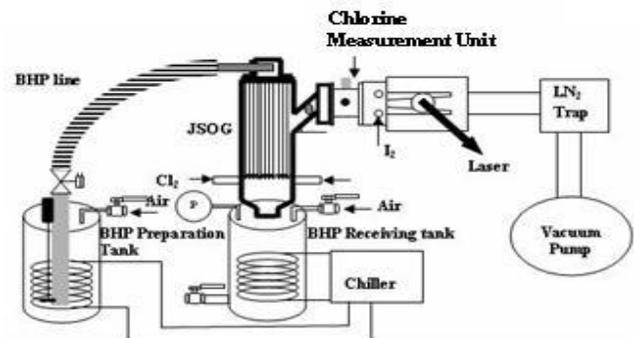


Fig. 1: Schematic of COIL System

The BHP solution is prepared in a separate storage tank and is supplied to singlet oxygen generator (SOG) reaction chamber in the form of jets. The chlorine is supplied to SOG reaction chamber from the bottom side so that it reacts with the surface of the liquid jets to produce singlet oxygen molecules. The supplied BHP through SOG is collected in receiving tank attached at the bottom of the SOG reaction chamber. The temperature of BHP solution has to be maintained at a temperature of -20° C from the safety and operational performance point of view. Thus, a cooling system attachment for both the BHP preparation and receiving tanks is essential.

SOG is an important subsystem in COIL. The input to SOG is chlorine and BHP solution. The concept of chemical based jet type singlet oxygen generator (JSOG) for the production of singlet oxygen for COIL applications was first demonstrated by Balan *et.al.* [5] and later implemented by Zagidullin [6]. Basically the generator consists of a large number of fine jets of BHP flowing through an atmosphere of chlorine.

The chemical generation of singlet oxygen involves a liquid–gas phase interaction and hence involves many fluid dynamic aspects. The parameters associated with the reaction i.e. chlorine utilization, molar flow rate and pressure of chlorine gas line, pressure, temperature and flow rate of BHP inside SOG are required to be controlled and monitored.

In this article, we present the optical absorption based chlorine utilization diagnostic system for COIL.

2. SYSTEM DESCRIPTION

A. Basic principle

The principle behind the estimation of chlorine flow is peak absorption of chlorine at ~ 330 nm [7, 8] with an absorption cross-section (σ) of $2.75 \times 10^{-19} \text{ cm}^2$. In COIL operation, known flow rate of chlorine is passed through SOG and reaction (3) utilizes the chlorine for singlet oxygen generation. Chlorine utilization measurement gives the percentage of chlorine molecules reacted with BHP for generation of laser pumping medium i.e. singlet oxygen.

In order to estimate the utilized chlorine, un-utilized chlorine is measured by applying Beer Lambert law at the exit of SOG. A probe beam ($\lambda \sim 330 \text{ nm}$) is passed through the optical cell containing measuring medium as shown in Fig. 1. Fig. 2 shows the schematic diagram of chlorine measurement. The intensity of the transmitted beam is given by the Beer Lambert's law:

$$\frac{I_v}{I_0} = \exp(-\sigma_v n L) \quad (4)$$

Where

I_v - transmitted light intensity at frequency 'v' (intensity with chlorine)

I_0 - incident light intensity (intensity without chlorine)

σ_v - absorption cross section ($2.75 \times 10^{-19} \text{ cm}^2$)

n - chlorine concentration (molecules cm^{-3})

L - length of the optical cell

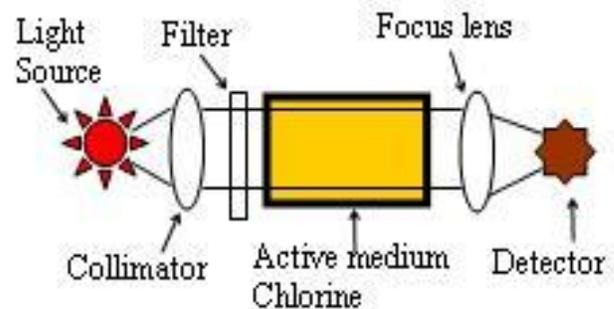


Fig. 2: Optical scheme for measurement of chlorine

From the above relation, the partial pressure of chlorine can be determined as,

$$P_{Cl_2} = \left(\frac{kT}{\sigma L} \right) \ln \left(\frac{I_0}{I_v} \right) \quad (5)$$

Where, k is the Boltzmann's constant and T is the temperature of the medium. In case of COIL operation, chlorine is carried to the laser head along with nitrogen and pressure measured in the optical cell is the total pressure of chlorine and nitrogen gas. Thus, unutilized chlorine molar flow rate ' $(M_{Cl_2})_{exit}$ ' at exit of SOG can be estimated using Dalton's law,

$$(M_{Cl_2})_{exit} = \frac{P_{Cl_2} \times M_c}{P_{tot} - P_{Cl_2}} \quad (6)$$

Where,

P_{tot} - Total pressure at the measuring optical cell

M_c - Molar flow rate of the carrier gas (N_2)

The flow rate of exit chlorine ' $(M_{Cl_2})_{exit}$ ' is estimated using relation (6) and chlorine input flow rate ' $(M_{Cl_2})_{input}$ ' is known using the principle of orifice under choke flow condition [9]. Hence chlorine utilization ' U_{Cl} ' is estimated using the relation (7).

$$U_{Cl} = 1 - \frac{M_{Cl_2_{exit}}}{M_{Cl_2_{input}}} \quad (7)$$

B. Experimental Setup

The singlet oxygen from generator along with nitrogen is passed through optical cell of 25 cm length and 2.54 cm diameter. The flow medium from the optical cell with traces of chlorine gas is continuously pumped out to liquid nitrogen trap. Ultra Violet mercury lamp is used as a light source along with an interference filter with 330±5 nm. The collimated light is passed through the cell and detected using silicon photodiode (RS component stock no. 303-674). The flow rate of exit chlorine ‘ $(M_{Cl_2})_{exit}$ ’ can be estimated using the relation (6) and chlorine input flow rate ‘ $(M_{Cl_2})_{input}$ ’ is known using the principle of orifice under choke flow condition. Fig. 3 shows the photograph of developed chlorine measurement system.

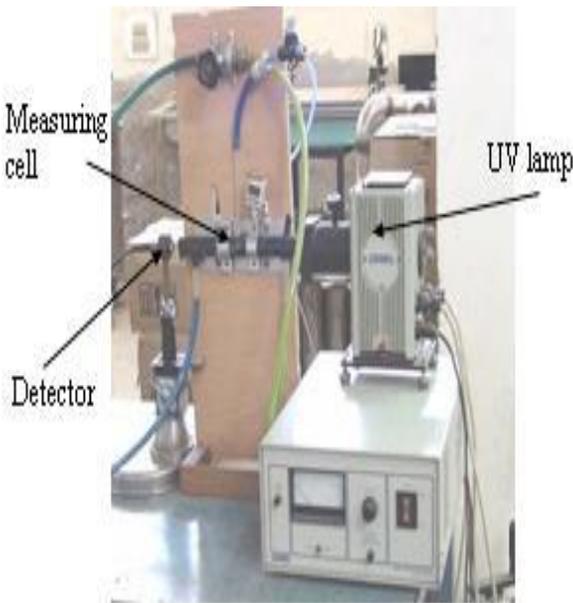


Fig. 3: Photograph of Chlorine measurement system

Initially total pressure in the transport duct (P_{tot}) was measured using a capacitance gauge (M/s Pfeiffer make Model No. CMR 262) due to its high accuracy (0.2%). However, these sensors require warm up time of about one hour for achieving accuracies of this order and moreover the water vapor and hazardous gases such as Cl_2 and I_2 adversely affect the performance. Therefore, diaphragm type pressure transmitters from M/s Metran of “Metran-22 series” have been used. These employ metallic diaphragm, which are suitable for corrosive environment as encountered in COIL application.

In these diaphragm type sensors, there is a monocrystalline sapphire plate with silicon film tensoresistors (silicon-on-sapphire-structure), connected fast to diaphragm of tensostransducer. Tensoresistors are connected into bridge circuit. Deformation of measuring diaphragm (deformation of tensostransducer’s diaphragm) causes proportional resistance change of tensoresistors and misbalance of bridge circuit. Electrical signal from bridge circuit output is fed to microprocessor based electronic module, where it is transformed into unified current output (4-20 mA). These operate at 24 V supply to produce 4-20 mA output current signal. The current signal is preferred because it is less likely to be affected by noise. The temperature of medium is monitored using resistance temperature detector Pt-100.

The continuous recording of temporal variation of pressure and photodiode signal is carried out using a dedicated PCI bus based data acquisition system (DAS). DAS [10] is not only require for diagnostic parameters estimation but also for real time operational control, acquisition, measurement, monitoring, display, storage and analysis of parameters. Fig. 4 shows the scheme of DAS which has been used for estimation of chlorine utilization as well as for other operational requirements of COIL.

C. Chlorine Safety System

A safety interlock scheme has been implemented to cater for any leakage of Cl_2 , and storage of BHP solution. Fig. 5 shows the general safety scheme adopted for safe operation of COIL.

For example, chlorine supply system is operated at sub-atmospheric pressure (500-600 torr) to avoid any leakage from the system. Chlorine leak detection system (Model no Advance 200) has been installed for detection of chlorine leakage. This system has option to set a threshold concentration of 1 and 10 ppm and produces an alarm signal (SS), which is compared with preset reference value (RF). If leakage exceeds this limit, data acquisition system issues a command to shut off the experiment and switch on the safety equipment (air ventilation system installed in the chlorine supply system).

The sensor produces 5 mA current output signal according to the concentration (1ppm or 10 ppm as per settings of threshold value) of chlorine. This current output is fed to a current to voltage converter to get a voltage output signal and is compared with a reference signal (5V) to activate air circulation system & alarm and the scheme is shown in Fig. 6. The ventilator output is passed through a scrubber (charcoal) to absorb the traces of chlorine before it is exhausted out of the chimney into the atmosphere.

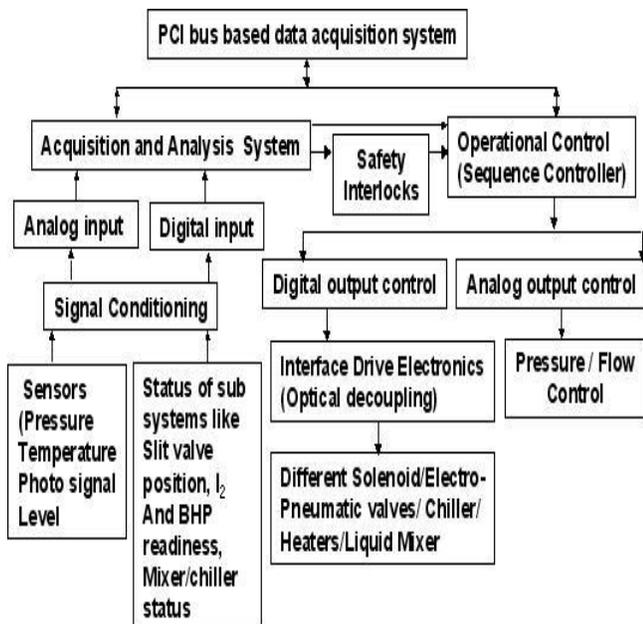


Fig. 4: Schematic of data acquisition system

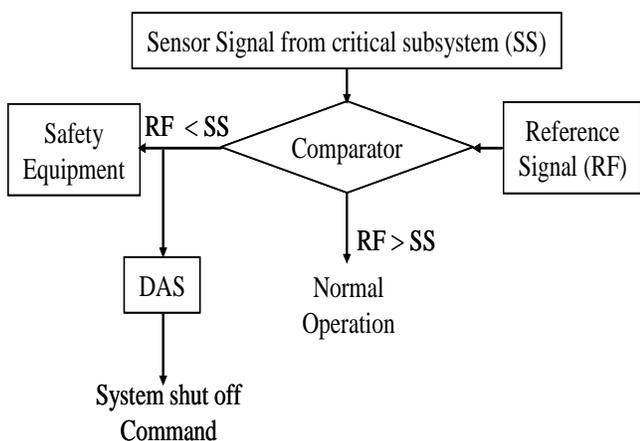


Fig. 5: Scheme for Safety Interlocks

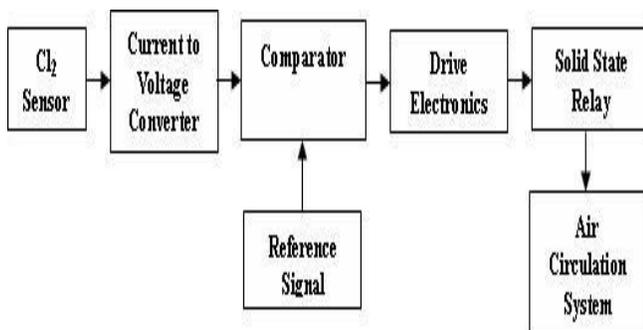


Fig. 6: Automatic control unit for chlorine sensor

D. Data Acquisition System

Chlorine utilization diagnostics system is interfaced with PCI bus based data acquisition system (DAS) which comprises of three modules: (i) acquisition and analysis, (ii) operational and sequence control and (iii) safety interlocks. DAS has been configured using Advantech PCI-1716 multifunction card and application software developed using VC++. Five user's friendly graphical user interfaces (GUI) have been designed for on line parameter acquisition, control and safety interlocks implementation. This card is a 16 bit high resolution multi function card with a sampling rate of 250 kS/s. It includes complete functions for data acquisition and control including A/D conversion, D/A conversion, digital input, digital output and counter/timer. Fig. 7 shows one of the GUI for display of acquired parameters as well as control switching and sequential functions.

The acquisition and analysis system is responsible for the acquisition of analog and digital parameters along with the storage and online estimation of diagnostics parameters in graphical form for analysis of performance of different subsystems. The analog input channels are required for acquiring the signals from transducers like pressure sensor, temperature sensor and photodiode. On the other hand, the digital input channels are used to indicate the status of various subsystems such as the system readiness status for laser firing and on/off status of various electro-pneumatic/solenoid /slit valves.

The operational and sequential control system is responsible for the sequential and switching control of electrical/ electro-pneumatic valves/devices and online control and adjustment of physical parameters like flow rates of gases involved in lasing action. This system also incorporates both analog outputs as well as digital output channels. The analog output channels are required for the flow rate control of different gas feed lines, whereas digital outputs are required for performing switching and sequential operations (on/off control) of various subsystems.

3. RESULTS AND DISCUSSIONS

The developed chlorine diagnostics system has been interfaced with COIL for estimation of chlorine utilization. The experiments have been conducted for large variation in Cl₂ flow rate conditions ranging from few tens of mmols⁻¹ to few thousands of mmols⁻¹.

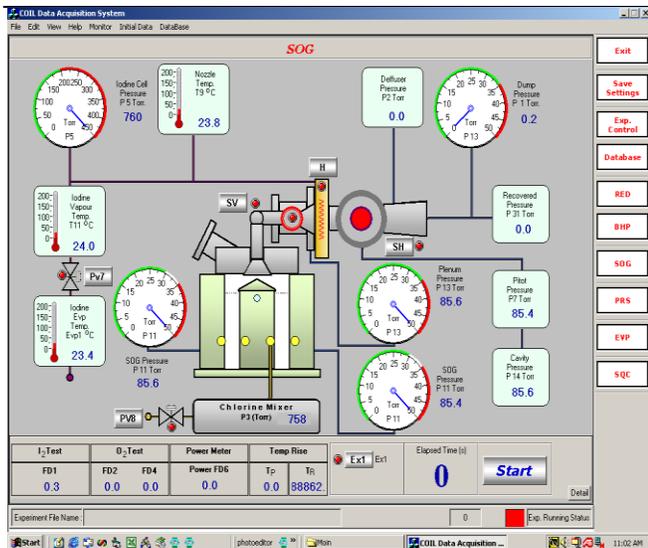


Fig. 7: GUI for display of parameters for COIL operation

The temporal variation of chlorine absorption signal, pressure and temperature signals are acquired by DAS in real time and the corresponding iodine flow rates are estimated and displayed on the PC in real time. The data acquisition card acquires the corresponding data from photo detector, pressure and temperature sensors via different analog input channels of data acquisition card and stored in the different files in the software, which are used for the online estimation of the unutilized chlorine flow rates. Fig. 8 shows typical curve of chlorine absorption signal detected by silicon detector. Initially there is no chlorine and we get a photo signal (I_0) and when chlorine is passed through the measuring cell, there is a dip in the photo signal (I_v) due to absorption of signal by chlorine molecules. This curve determines the partial pressure of chlorine gas using relation (4) and (5). Ultimately chlorine flow rates are estimated using relation (6) which is shown in Fig. 9.

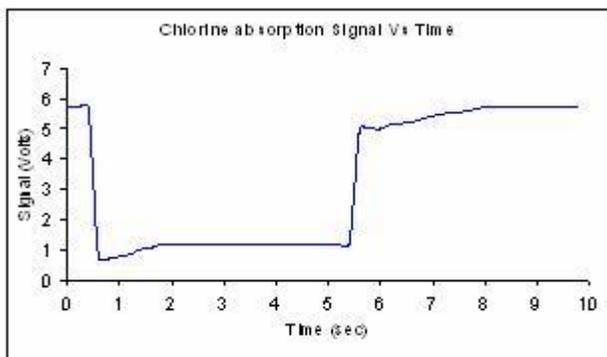


Fig. 8: Typical Chlorine absorption signal acquired by DAS

The observed unutilized chlorine flow rates are ~ 1.64 mmols^{-1} . The detailed experimentation in the present case corresponding to supplied input chlorine flow rates of ~ 27.5 mmols^{-1} , shows a typical chlorine utilization of nearly 94% using the relation (7).

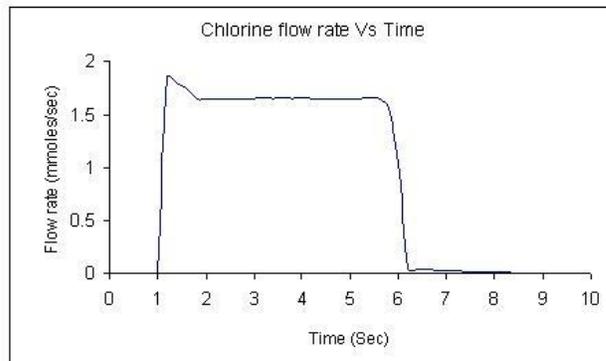


Fig. 9: Typical estimated unutilized Chlorine flow rate

The chlorine utilization is one of the important diagnostics because COIL power is a strong function of chlorine flow rates. Moreover unutilized chlorine can not be sent directly to vacuum pumps (which evacuate the laser chamber) as chlorine is a corrosive gas and affects the life of vacuum system. The unutilized chlorine was therefore trapped and neutralized by standard norms. In our system, we have developed a liquid nitrogen based trap for trapping the unutilized chlorine which is neutralized after experiments.

4. CONCLUSIONS

An on-line optical absorption based chlorine utilization diagnostics system has been developed for real time monitoring of chlorine utilization. The developed diagnostic system has been successfully incorporated with the COIL system and is being routinely used for COIL parametric studies.

5. REFERENCES

- [1] D. L. Carroll, "Overview of high energy lasers: Past, Present and Future", *AIAA paper*, 2011-3102, 2011.
- [2] I. Rego, K. N. Sato, Y. Miyoshi, T. Ando, K. Goto, M. Sakamoto, S. Kawasaki, "Studies on the characteristics of the gas dynamics laser with low CO_2 -concentration medium by a diaphragmless shock tube", *Proc. Of 34th EPS conference on plasma physics*, 31F, 0-4-036, 2007.
- [3] W. H. Behrens, P. D. Lohn, "Hydrogen and deuterium fluoride chemical lasers", *CRC Press (NY)*, N4, pp 341-367, 2007.
- [4] McDermott W. E, Pchelkin N. R, Benard D. J., Bonsek R. R., "An electronic transition Chemical Laser", *Applied Physics Letters*, 32(8), pp469-470, 1978

- [5] Balan N.F., Gizadulin R. M., Zagidulin M. V., Kurov A. Yu., Nikolaev V. D., Pichkasov V. M., Svistin M. I., “Investigation of a jet generator of $O_2(^1\Delta_g)$ ”, *Sov. J. Quantum. Electron.* pp1412, 1989.
- [6] Zagidullin M.V., Nikolaev V.D., Svitin M.I., Safonov V.S., Ufimtsev N.I.,(1996), “The study of buffer gas mixing with active gas on chemical oxygen iodine laser performance with jet SOG”, *SPIE*, 2702, pp310, 1996.
- [7] Jarmila Kodymova, and Otomar Spalek, “Performance characteristics of jet type generator of singlet oxygen for supersonic chemical oxygen iodine laser” *Japanese Journal of Applied Physics*, 37, pp117-121, 1998.
- [8] R. Rajesh, Gaurav Singhal, Mainuddin, R. K. Tyagi and A. L. Dawar “High throughput jet singlet oxygen generator for multi kilowatt SCOIL”, *Optics and Laser Technology*, 42, pp580-585, 2010.
- [9] Mainuddin, M. T. Beg, Moinuddin, R. K. Tyagi, R. Rajesh, Gaurav Singhal and A. L. Dawar, “Real time gas flow control and analysis for high power infrared gas lasers”, *International Journal of Infrared and Millimeter Waves*, 1, pp91-105, Jan. 2005.
- [10] Howard Austerlitz, “Data acquisition techniques using PCs”, 2nd edn., Academic Press, *Elsevier Science(USA)*, 2003.