Sensors and Materials, Vol. 18, No. 5 (2006) 241–249
MYU Tokyo

S & M 0646

A Vanadium Oxide Nanotube-Based Nitric Oxide Gas Sensor

Yubo Li*, Zhiwei Huang[1] and Shiquan Rong

Cancer Research Institute, Nanhua University, Changshengxi Road 28,
Hengyang 421001, Hunan, China
[1]Electrical Engineering College, Nanhua University, Changshengxi Road 28,
Hengyang 421001, Hunan, China

(Received July 16, 2005; accepted May 16, 2006)

Key words: vanadium oxide nanotube, gas sensor, nitric oxide, exhaled nitric oxide

Accurately measuring exhaled nitric oxide (eNO) is still an unsolved problem. We report the fabrication of a novel nanotube-based gas sensor. The gas sensor consists of a gas-responsive multiwall vanadium oxide nanotube (VO_X-NT) layer deposited on a ceramic chip with two Ag-Pd electrodes, a gas sensor signal collecting system and a computer data-processing system. The absorption of different gases in the VO_X-NT layer changes the permittivity and conductivity of the material and consequently alters the voltage of the sensor. By measuring the voltage change of the sensor, different gas concentrations can be determined. Our results show that the sensor response to nitric oxide (NO) is both highly sensitive and reversible at room temperature. The VO_X-NT-based gas sensor only reponds to NO and water vapor in the exhaled air, and the response is concentration dependent. We suggest that the novel sensor can meet the demands of clinical diagnosis.

1. Introduction

Nitric oxide (NO), a very important compound physiologically, and plays many key roles in the physiological and pathological functions of all organ systems.[1,2] An analysis of exhaled nitric oxide (eNO) in breath provides the physician with a simple and noninvasive window into the activities of disease in the lower airways, including asthma, chronic obstructive pulmonary disorder and cystic fibrosis.[3] Various technologies have been proposed for the next generation of medical devices that will be capable of making routine eNO measurements of patients in a clinical setting. Chemiluminescence is the most recently proposed technique for this purpose and is the □"gold standard" today. However, endogenous and exogenous water vapor, carbon dioxide, and ammonia can contribute to inaccurate eNO measurements using chemiluminescence instruments,[4] and are most likely responsible for the large variations in results reported in various clinical studies.[5] Fourier-transform IR spectroscopy and gas chromatography coupled with mass spectrom-

*Corresponding author, e-mail address: Lyb108@hotmail.com

etry are selective and sensitive but cannot perform rapid trace-gas measurements, so they also are not applicable to this clinical diagnosis.

Interest in nanomaterials has been growing rapidly for the past several years. Among nanostructures, tubular materials are particularly interesting because their morphology is associated with an intrinsic multifunctionality that arises from four different contact regions. Recently, nanotube-based gas sensors[6] have received considerable attention because of their outstanding properties, such as fast response, high sensitivity and low operating temperature. However, they have several drawbacks concerning non-specificity of detection methods, re-usability of the devices and difficulty in fabrication.

Because of the selective response of vanadium oxide to NO_X,[7] we applied multiwall vanadium oxide nanotubes (VO_X-NTs) to the selective detection of exhaled nitric oxide (eNO) and measured changes in VO_X-NTs permittivity and conductivity with gas exposure. The transduction platform used in this work is an electronic semiconducting gas sensor. A thin layer of gas-sensitive VO_X-NTs is deposited on a ceramic chip with two Ag-Pd electrodes; as the permittivity and/or conductivity of the VO_X-NTs changes, so does the sensor voltage. The sensor signal collecting system and a computer data-processing system automatically collect the electric signal and process the data. The novel VO_X-NT-based gas sensor has been applied to measure the exhaled NO level.

2. Sensor Design and Operation

The sensor consists of a gas-responsive multiwall VO_X-NT layer deposited on a ceramic chip with two Ag-Pd electrodes (see Fig. 1). As the sensor is exposed to various gases, the relative permittivity and the conductivity[8] of the VO_X-NTs vary, consequently changing the voltage of the sensor. The relationship between test gas adsorption and the sensor voltage is discussed in § 4. These gases are nitric oxide (NO), ammonia (NH_3), oxygen (O_2), carbon dioxide (CO_2), carbon monoxide (CO), nitrogen (N_2), argon (Ar) and water vapor.

The experiments employ off-line methods with variable gas flow, but the test gas volume is always 1 L. When the sensor is in a work state, a test gas is poured into the front of a vacuum workroom with 1 L volume. The voltage curve for the sensor is obtained by the signal-collecting system and the computer data-processing system.

3. Experimental

3.1 *Sensor fabrication*

The VO_X-NTs (a gift from Prof. Wen Chen, Wuhan University of Technology, China) were 60 nm in average diameter (45 nm inner diameter and 80 nm outer diameter), 1 to 10 μm in length, and had 3 to 10 VO_X layers. A 12×20 mm rectangular sensor was fabricated by depositing the VO_X-NTs on a ceramic chip with two Ag-Pd electrodes (see Fig. 1). The VO_X-NTs layer was about 200 μm thick.

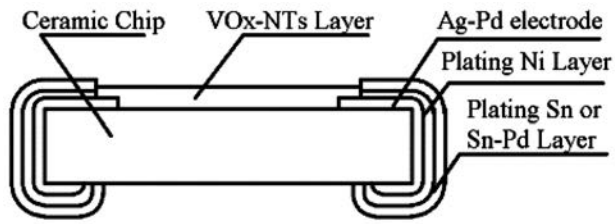

Fig. 1. Schematic drawing of the VO_x-NT gas sensor. A layer of gas-responsive VO_x-NT composite is deposited upon a ceramic chip with two Ag-Pd electrodes. The VO_x-NT gas-sensing layer is 200 μm thick. The ceramic chip is a 12×20 mm rectangle 1 mm thick.

3.2 *Experimental setup*

The sensor was placed inside a sealed Tedlar gas-collecting bag made of a high former with a volume of 1 L. It was maintained under vacuum before every test. After pouring 1 L test gas into the bag, the voltage was measured with a signal collecting system. A computer was used to analyze and process the measurement data. N_2 gas was the carrier gas for preparing different concentrations of test gas throughout the experiment.

The response of water vapor was investigated by humidifying the carrier gas. Different values of relative humidity were obtained by mixing dry N_2 gas that was completely saturated with water vapor by bubbling it through water, with dry air.[9] The dry N_2 gas flow rates were 1 L/min, 5 L/min, and 10 L/min. All measurements were performed at room-temperature (ca. 27°C).

4. Results and Discussion

4.1 *Different gas response*

Figure 2 shows the measured curves for various pure test gases. The sensor is highly sensitive to NO gas. Once NO gas molecules make contact, the sensor's voltage rises to about 2700 mV in 1 min. Under the same conditions, the highest output voltages of NH_3 and O_2 are almost 1500 and 800 mV, respectively. The sensor is non-responsive to other gases, such as CO, CO_2, Ar and N_2.

The absorption of different gases in the VO_X-NT layer changes the permittivity and conductivity of the material. The equilibrium geometries of various small molecules, such as NO, NH_3, O_2, CO_2, CO, N_2 and Ar, are different. The VO_X surface has an active site for NO. Each VO_X-NT has a very advantageous shape offering three different contact regions, namely, the inner and outer wall surfaces as well as the tube ends. The contact regions possess more damaged shells that can create more adsorption sites for NO molecules. This results in higher response to NO and lower or no response to other gases.

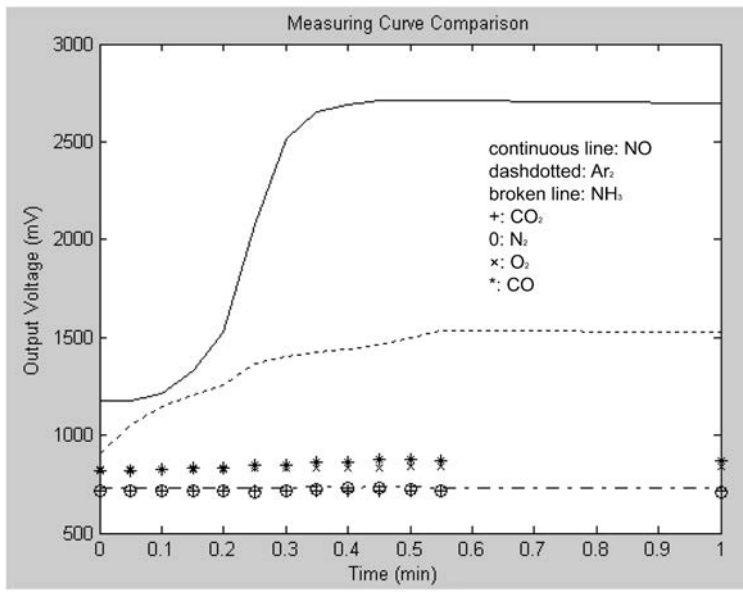

Fig. 2. The measured curves for various pure test gases.

4.2 *NH_3, O_2 , CO and NO detection*

Figures 3–5 show the measured curves for different concentrations of NH_3, O_2 and CO, respectively. The concentrations used were 100, 50 and 25%. The results show that the sensor response depends on gas concentration. As concentration decreases, the sensor response also decreases. The sensor becomes entirely non-responsive at 25% concentration.

However, the measured curves at 100, 50 and 25% concentration of NO are almost identical (see Fig. 6). This probably indicates that the VO_X-NTs are so sensitive to NO molecules that the absorption of NO is already in a super-saturated state at 25% concentration. We shall examine the relationship between the VO_X-NT sensor and NO gas concentration in the concentration range of parts per million (ppm) or parts per billion (ppb) in future studies.

4.3 *Water vapor response*

Figure 7 shows the measured curves for various humidity levels. The results show that the sensor response increased with increasing relative humidity. In sensors that use physical adsorption, water vapor is one of the main obstruction gases. This indicates that the VO_X-NTs surface absorbs both NO molecules and water molecules.

The composition of human exhaled air is 15% O_2, 3.6% CO_2, 74% N_2 and 6% water

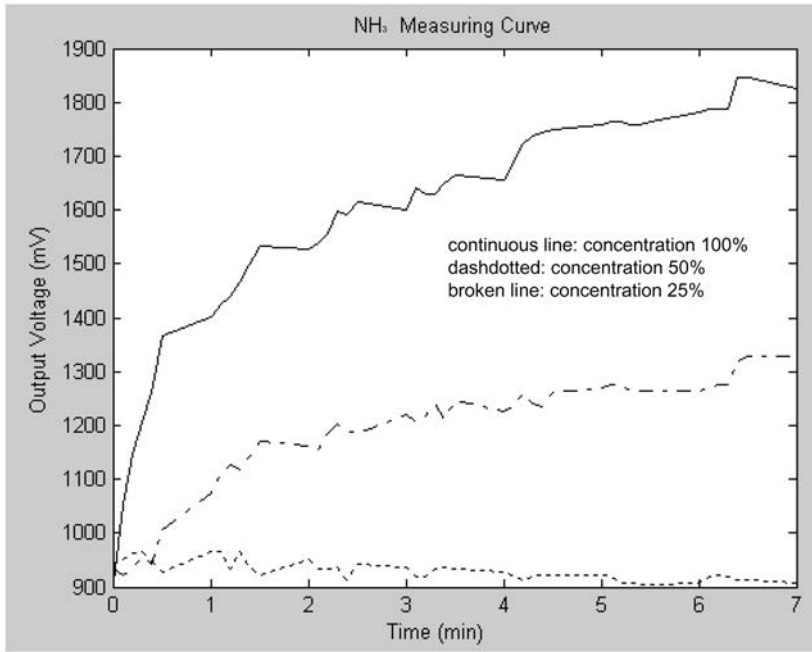

Fig. 3. The measured curves for different concentrations of NH_3.

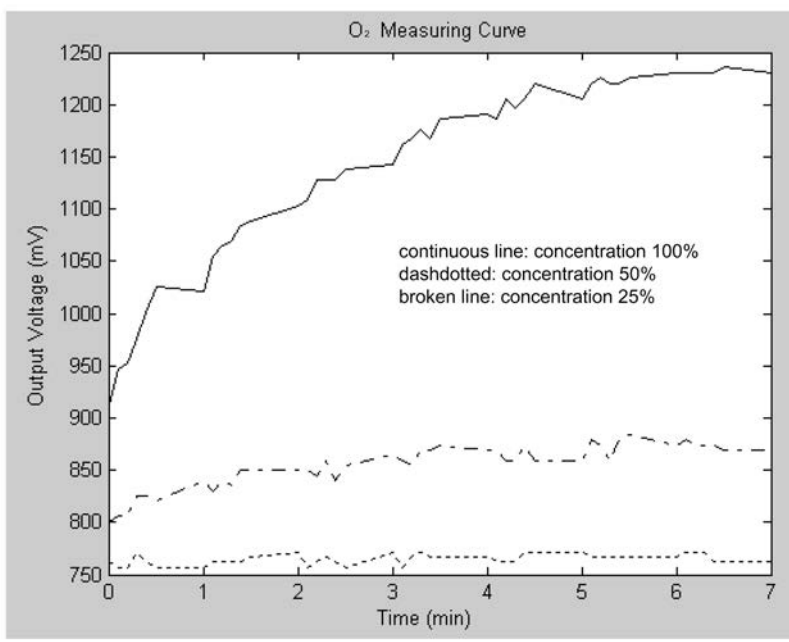

Fig. 4. The measured curves for different concentrations of O_2.

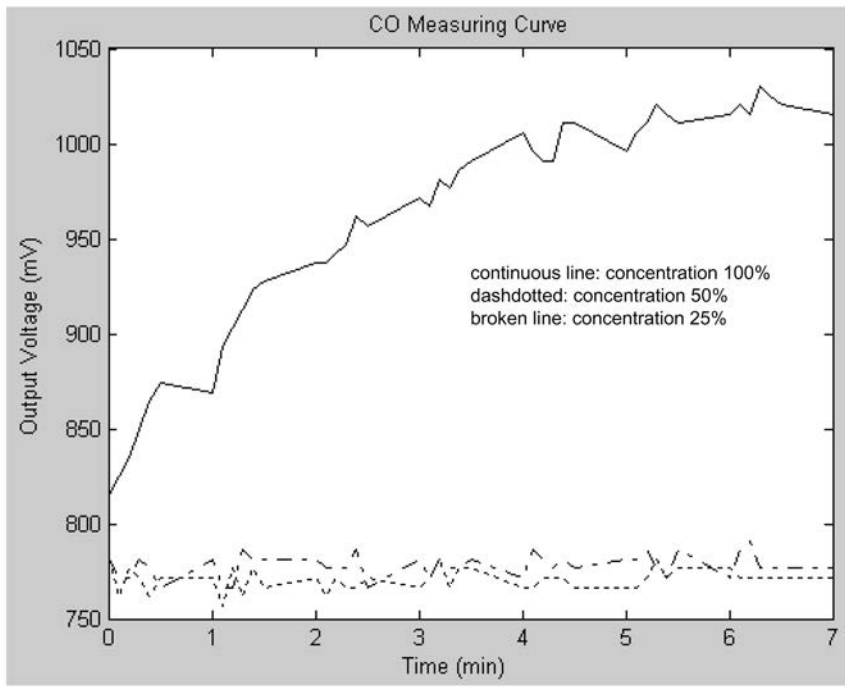

Fig. 5. The measured curves for different concentrations of CO.

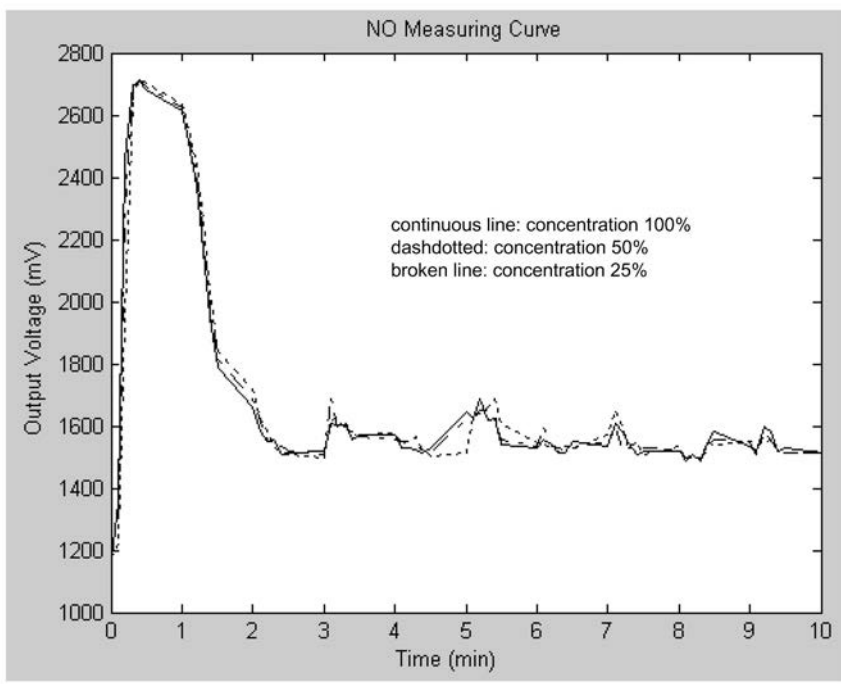

Fig. 6. The measured curves for different concentrations of NO.

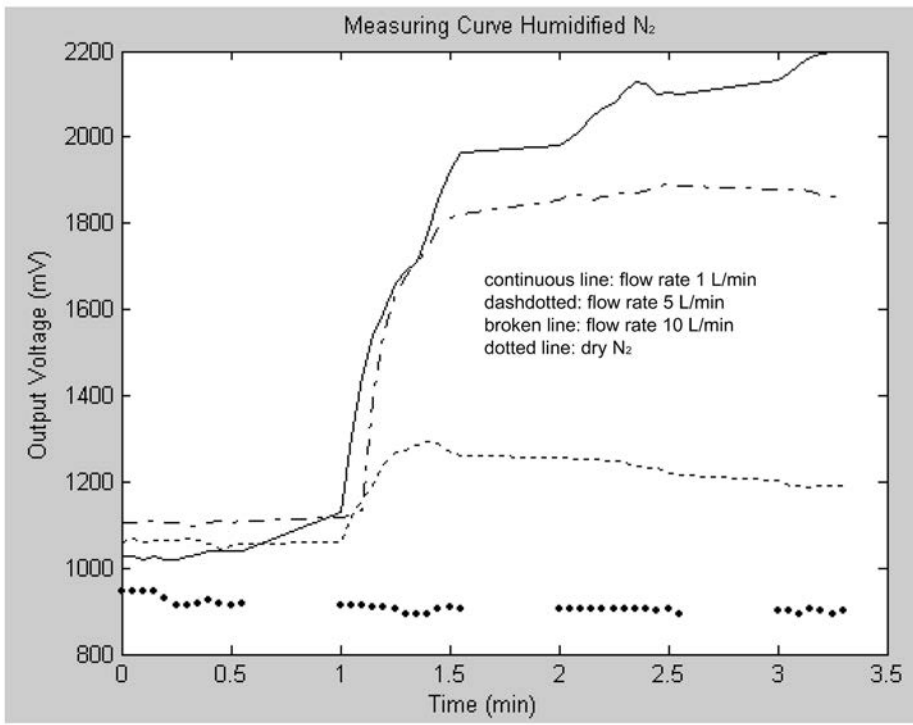

Fig. 7. The measured curves for various humidity levels.

vapor, in addition to 80–90 ppb NO,[10] 2 ppm CO,[11] 0–1 ppm NH_3, and other trace gases. The relative humidity of human exhaled air is about 63%. The VO_X-NT-based gas sensor responds to NO in the dehydrated exhaled air only, and the response is concentration dependent. The reasons for this are:

(1) The sensor is non-responsive to CO_2, N_2, 25% NH_3, 25% O_2 and 25% CO.
(2) The VO surface has an active site for NO and responds to NO.
(3) The results show that the sensor strongly responds to NO gas.
(4) The NO concentration in various populations is different.[12]

In future studies, we will generate calibration curves for NO concentrations covering the range 0 to 1000 ppb. Standard NO gases of known concentrations will be bought from National Research Center for Certified Reference Materials. These NO gases will then be measured with the VO_X-NT-based sensor. The mV reading of each NO gas will be noted and a graph of concentration vs mV reading will be plotted. Then, the NO concentration of the unknown gas will be able to be measured. The mV value of the unknown gas can then be located on the graph and the corresponding NO gas concentration can be determined.

4.4 *Reversible behavior*

Figure 8 shows the return curve after testing for NO. After continuous washing of the VO_X-NT sensor with N_2, the sensor voltage decreases as the NO concentration decreases.

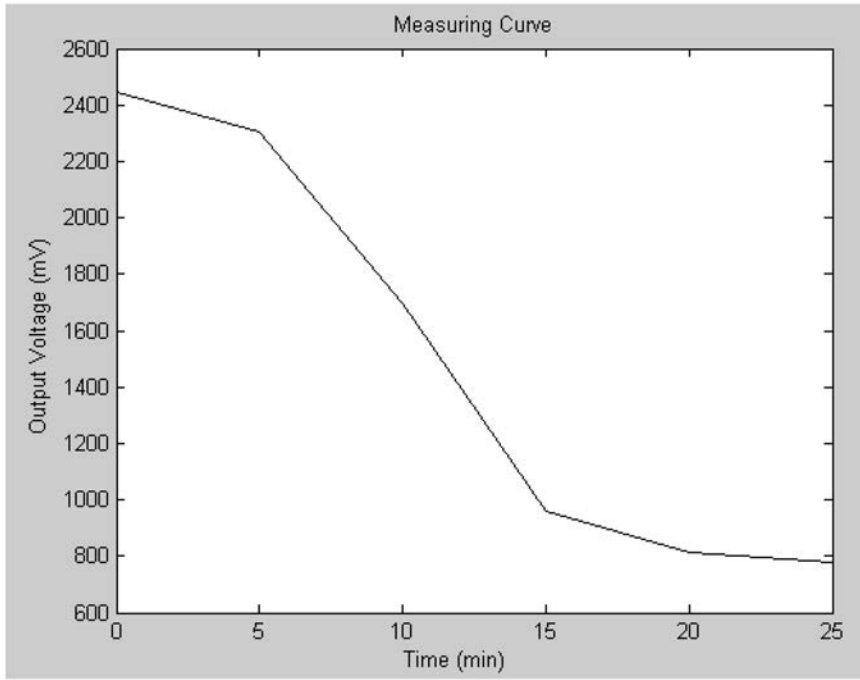

Fig. 8. Return curve after testing for NO.

Finally, the sensor voltage returns to the initial value starting point.

There are two possible modes in which gases interact with the nanotubes: physisorption, which is reversible, and/or chemisorption, which is irreversible. Our results indicate the presence of physisorption. Our results also show that sensor voltage varies directly with NO concentration.

5. Conclusion

To the best of our knowledge, this is the first time that a nanotube gas sensor has been fabricated with multiwall vanadium oxide nanotubes (VO_X-NTs). The sensor has high sensitivity and selectivity to nitric oxide (NO), and the response to NO is readily reversible. The results presented in this paper demonstrate that the VO_X-NT-based sensor only reponds to NO and water vapor among the gases in exhaled air. We have successfully developed a vanadium oxide nanotube-based gas sensor for measuring the NO concentration in human exhaled air. The features of the VO_X-NT-based gas sensor are:

(1) rapid trace-gas measurements with potential for clinical use,

(2) high sensitivity and selectivity to exhaled NO at room temperature,

(3) re-usability of the device,
(4) mass production possible with low fabrication costs (These informations are not opened to public.)

In future studies, we will generate a calibration curve for NO concentration and then establish a computer database of exhaled NO measuring curves. We will correlate these data with the state of health, to evaluate patients' conditions and help with the diagnosis of diseases. The clinical diagnosis using this device will be simple, non-invasive and immediate.

Acknowledgments

The project has been supported by the funds from special project of Hunan Province, China. The project number is 02SSY1005-1. The authors acknowledge Prof. Wen Chen, Wuhan University of Technology, China, for providing the vanadium oxide nanotubes used in this study.

References

1 P. L. Feldman, O. W. Griffith and D. J. Steehr: Chem. Eng. News **20** (1993) 26.
2 A. Baysal: Turk. J. Med. Sci. **31** (2001) 471.
3 D. H. Yates: Immunol. Cell Biol. **79** (2001) 178.
4 N. Binding, W. Muller and P. A. Czeschinski: Eur. Respir. J. **6** (2000) 499.
5 M. Bernareggi and G. Cremona: Pulmonary Pharmacol. Therapeut. **12** (1999) 331.
6 J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho and H. Dai: Science **287** (2000) 622.
7 Handbook of Heterogeneous Catalysis Vol. 4, eds. G. Ertl, H. Knözinger and J. Weitkamp (Wiley-VCH, Weinhaim, 1997).
8 S. Ramo, J. R. Whinnery and T. Van Duzer: Fields and Waves in Communication Electronics (Wiley, New York, 1984) Chap. 13.
9 St. John RE: Crit. Care. Nurs. Clin. North. Am. **11** (1992) 7.
10 S. A. Kharitonov, D. Yates, P. J. Barnes: Eur. Respir. J. **8** (1995) 295.
11 P. M. Kong, C. C. Chan, P. Lee and Y. T. Wang: Singapore Med. J. **43** (2002) 399.
12 L. Prieto: Alergol. Immunol. Clin. **17** (2002) 72.