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Spectrochimica Acta Part A 63 (2006) 923–928
SPECTROCHIMICA ACTA PART A
www.elsevier.com/locate/saa

Detection of HCl and HF by TTFMS and WMS

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Received 12 September 2005; received in revised form 27 October 2005; accepted 7 November 2005

Abstract

In this work we discuss on a compact spectrometer based on DFB diode lasers for detection of chloridric and fluoridric acids. HCl and HF concentrations are determined through optical absorption of the P(4) line ($\lambda = 1.7\ \mu m$) and the R(3) line ($\lambda = 1.3\ \mu m$), respectively. Both lines belong to first overtone vibrational bands and their linestrengths are 7.8×10^{-21} cm/molecule for HCl and 2.8×10^{-20} cm/molecule for HF. We chose these lines for their relative high intensities and because they are quite far from water vapour lines which represent the main interfering gas for trace-gases analysis. To detect these species we used two different high frequency modulation techniques: two-tone frequency modulation spectroscopy ($f_1 = 800$ MHz and $f_2 = 804$ MHz) was used for HCl while for HF we followed a simpler approach based on wavelength modulation spectroscopy ($f = 600$ kHz). We demonstrate that the two techniques provide comparable detection limit of about 80 ppbV at atmospheric pressure. Positive testing of our spectrometer makes it suitable for in situ measurements of exhaust gases coming from waste incinerators.

Keywords: Sensors; Gas-trace analysis; Frequency modulation spectroscopy; Acids; Incinerators

1. Introduction

The problem of atmospheric pollution has become increasingly important in recent years. The composition of atmosphere is changing rapidly as result of energy overuse for industrial purposes and lack of control of industrial emission. Since many atmospheric pollutants have a significant impact on the environment and human safety even in small concentration, the development of techniques for their fast, accurate, and sensitive detection is required [1–5].

Laser-based systems have attained an increasing attention in recent years, due to their high sensitivity and selectivity, which guarantee fast and accurate responses [6,7]. In particular, semiconductor diode lasers (DLs) emitting in the near-infrared region, have revealed particularly interesting thanks to their narrow bandwidth, their fast frequency modulation, and low amplitude fluctuations [8,9]. In addition, their small sizes and accessible cost make them very attractive for large scale commercial applications. In the near-IR region, combination or overtone vibrational transitions (and in some case also electronic transitions) occur for many molecules relevant for environmental or industrial monitoring applications [10]. Although these transitions exhibit linestrengths of about two orders of magnitude lower than transitions belonging to fundamental vibrational bands, optical absorption combined with high frequency modulation techniques have allowed to achieve sensitivity in the range of ppmV.

More recently, a new class of diode lasers, the quantum cascade diode lasers (QCDLs) [11], have opened new horizons for ultra-high sensitivity gas-trace analysis (ppbV range or below) since they make accessible the spectral region of the mid-IR, where lye the stronger fundamental vibrational bands. Although these lasers are very promising, they still suffer for some drawbacks like thigh costs, cryogenic temperature operation, and limited available wavelengths. On the contrary, conventional hetero-structures DLs continue to be quite versatile sources for monitoring pollutant species. Among them, HCl and HF are particularly interesting chemical species: both are very reactive and frequently generated or released during various industrial processes. In particular, HCl emissions depend mostly on the chlorine content in the fuel whereas HF emissions come primarily from aluminium plants, glass works, tile manufactures, incinerators and alkylation plants. The maximum permissible emission level of HCl and HF from industrial and domestic waste incinerators in Europe is now specified to not exceed 5 ppmV.

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doi:10.1016/j.saa.2005.11.009

Traditionally these chemical species have been measured by wet chemical methods: the gas is extracted from the source, preconditioned, and sent into the chemical reactor where the concentration is deduced. This procedure presents, however, several disadvantages: for instance, due to low concentration the extraction time is generally quite long. Moreover, there are many sources of errors related to extraction and preconditioning procedures, and the whole measurement is quite laborious. Instead, optical spectroscopic techniques can work well without preconditioning of the gas [12] and, therefore, their use for in situ measurements is more direct.

Optical techniques currently used are based on the combination of optical absorption with high frequency modulation techniques (FM) (see Ref. [13] for a review on this subject). In addition, the use of multipass cells [14] or high-finesse cavities [15,16], further improves the sensitivity, since the effective optical paths is increased up to several tens or hundreds of meters. Phase-sensitive technique, which is the core of FM techniques, reduces significantly the 1/*f* electronic noise achieving high detection sensitivity, which in most cases is only limited, by optical noise introduced by undesired optical fringes.

In this paper we show as HCl and HF can be detected by using two commercial distributed-feedback (DFB) diode lasers. We have applied two different high-sensitivity spectroscopic techniques: for HCl detection we used two-tone frequency modulation spectroscopy, TTFMS [17–19] while for HF we followed a simpler approach based on wavelength modulation spectroscopy, WMS [20,21].

For both HCl and HF we reached a detection limit of about 80 ppbV at an atmospheric pressure of nitrogen.

2. Experimental set-up

Fig. 1 shows the block scheme of our experimental apparatus. All the optical elements were fixed on a bread-board (60 cm × 75 cm) and they were properly designed to reduce as much as possible the dimensions and the mechanical instability.

As light sources we employed two different DFB diode lasers. An InGaAs/P DFB diode laser (Sensors Unlimited, Inc. SUI-1793-TE), emitting a power of about 1 mW in the range around 1742 nm, was used to detect the HCl P(4) line. A second DFB laser (Nanoplus 105/22-9), that emits about 2 mW around 1321 nm, was instead used to detect the HF R(3) line.

The laser wavelengths could be coarsely tuned by varying the laser temperatures, while fine tunings were accomplished by changing the laser diode injection currents. The output beams were collimated by appropriate objective lenses. The two laser chips were mounted so that the polarization of the laser beams resulted orthogonal each other in order to overlap them in a polarizing cube. The beams were focused by a lens ($f = 50$ cm) to the centre of a Herriott-type multipass cell. After 74 reflections, corresponding to about 30 m, the beams exit the cell and they were separated again in a second polarizing cube. The two beams were, finally, focused by short focal lenses onto two different fast photodiodes (mod. G8422-03 at 1.7 μm and G8376-03 at 1.3 μm, Hamamatsu, bandwidth 40 MHz).

Part of the laser beam at 1.7 μm was reflected by a beam splitter and sent through a sealed Pyrex reference cell (filled with a mixture of 5% HCl in Ar) for fast laser frequency calibration.

Detection of HCl was performed by using a commercial system (SIT, Scienza Industria Tecnologia) based on two-tone frequency modulation spectroscopy. That was realized by modulating the laser injection current at two near frequencies, 800 and 804 MHz; the signal collected from a fast photodetector was demodulated at the difference frequency. For HF detection, we used the wavelength modulation spectroscopy. The laser frequency was tuned around the molecular line at a frequency of 3 Hz by adding to the laser injection current a sinusoidal modulation at 600 kHz. Phase-sensitive detection was performed by means of a *lock-in* amplifier (time constant 10 ms). The dc outputs coming from the electronics of both schemes were sent to a digital oscilloscope for sampling and then transmitted to a PC for data acquisition.

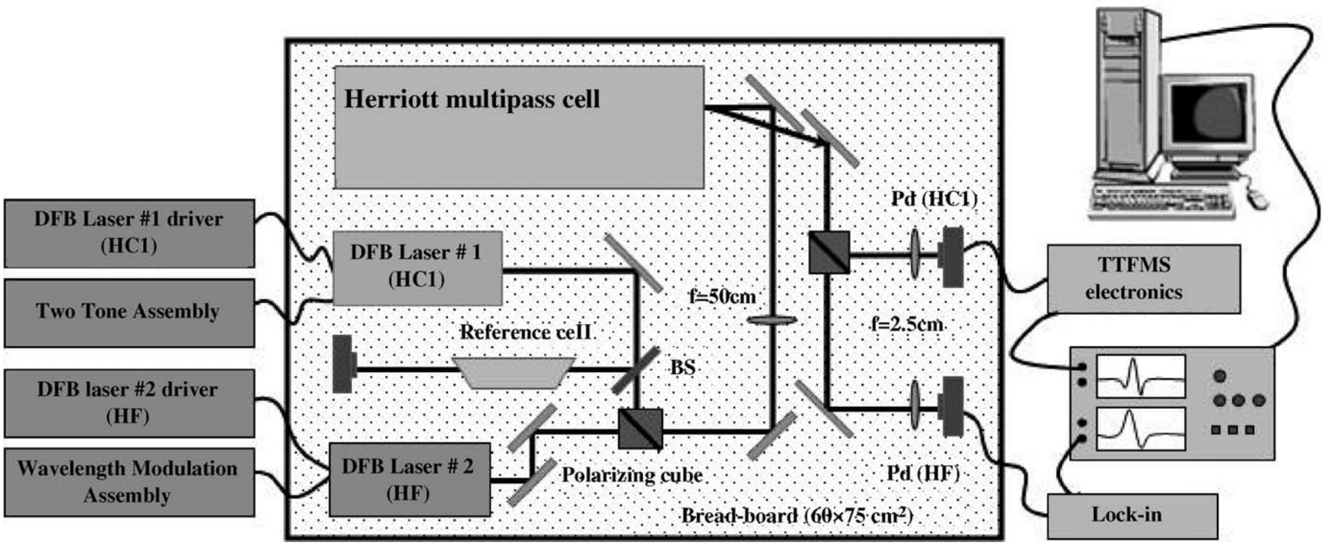

Fig. 1. Scheme of the absorption spectrometer developed in this work. BS stands for beam-splitter while Pd for photodetectors.