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Incoherent broad-band cavity enhanced absorption spectroscopy for sensitive and rapid molecular iodine detection in the presence of aerosols and water vapour

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ABSTRACT

The atmospheric chemistry of iodine is important in different environments, and particularly in case of a nuclear reactor severe accident. This paper describes the performance of an Incoherent Broad-Band Cavity Enhanced Absorption Spectroscopy (IBB-CEAS) device, based on a green LED source allowing the online detection of gaseous molecular iodine. High sensitivities and a wide dynamic range are obtained. The performances and limitations of the IBB-CEAS technique for measurements of iodine in the presence of aerosols and water vapour are discussed. The capabilities of this device to perform kinetics studies on iodine have been investigated in the framework of nuclear reactor accident research. The re-vaporization process of deposited CsI by optical monitoring of I₂ concentration–time profiles is presented. The aerosols used in the experiments have been well characterized (size, distribution, concentration and mass) before interaction with iodine by a NanoScan scanning mobility particle sizer (SMPS), a PEGASOR particle sensor PPS-M and a tapered element oscillating microbalance (TEOM).

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1. Introduction

During a nuclear power plant severe accident [1], radionuclides of iodine constitute one of the main concerns of post-accident management because of their high radiotoxicity induced by their affinity for the thyroid. Indeed, in the case of a nuclear power reactor core melt accident, the volatile fission products (iodine, caesium and molybdenum) can almost completely be released from the degraded fuel and transported through the reactor coolant system into the reactor containment building.

If core degradation cannot be stopped through cooling, the accident may ultimately lead to loss of containment integrity and large releases of radioactivity into the environment. The Fukushima-Daiichi accident in 2011 showed that external hazards (in this case, a tsunami triggered by an earthquake) with a magnitude greater than a facility's design basis could also lead to core meltdowns. This accident resulted in significant amounts of radioactivity being released into the environment [2].

The radioactive aerosols and gaseous iodine emitted into the atmosphere may interact with each other in the short term or with atmospheric aerosols. Thus, the interactions between iodine in the

gas phase and aerosols should be considered and need to be studied.

Over the past two decades, the French Institute for Radioprotection and Nuclear Safety (IRSN) has invested large resources on Severe Accident research. The overall aim of this work is to predict better the potential releases of fission products into the containment atmosphere and finally into the environment, with emphasis on iodine species.

However several issues remain to be addressed. With this in mind, to complete and better understand the volatile iodine formation, deposition and decomposition, several laboratory scale experiments have been performed at IRSN to examine the behaviour of iodine with aerosols transported in the Reactor Cooling System (CHIP-program Chimie de l'Iode dans le Circuit Primaire [3]) and in the reactor containment building (EPICUR program Experimental Program of Iodine Chemistry Under Radiation [1]). The Source Term Evaluation and Mitigation STEM/EPICUR tests (performed under the aegis of OECD/NEA/CSNI) were dedicated to study the release under radiation of iodine species deposited onto painted surfaces in the containment atmosphere. Further researches have been carried out within the framework of the French MIRE program [4] (Mitigation of Releases to the Environment in the event of a nuclear accident) in the strategy to investigate and to improve the mitigation of radioactive releases after a core melt accident.

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The second phase of the project named Source Term Evaluation and Mitigation 2 (STEM 2), coordinated by IRSN, will be focused on mid- and long-term iodine releases [3].

These experiments aimed at simulating the conditions of a severe nuclear accident at high temperature (100–1600 °C): the presence of aerosols (up to several mg/m³), carrier gas including air, hydrogen or water vapour (from 0% up to 100%) and a high dose rate in particular cases.

One of the main goals is to be able to determine the fraction of gaseous iodine (mainly I₂) at trace levels (~ ppbv) with a sufficiently high time resolution to allow kinetics studies.

It should be recalled that the experimental conditions for such studies are rather different from atmospheric conditions: (i) in the atmosphere, the water vapour distribution is highly variable spatially and temporarily. Water vapour varies from a trace to a few % (by volume). On the contrary, the amount of water vapour considered in this work is well above atmospheric levels (can be up to 100%). (ii) the amount of aerosols and iodine released in severe accident scenarios. The mass of aerosols (fission products, heavy nuclei, materials of the structures and control rods) released into the containment during fuel degradation may be high (i.e., around 1500 kg for a 900 MWe Pressurized Water Reactor (PWR) [1]. Following an accident with release into the atmosphere, these aerosols may agglomerate and settle. This results in a reduction for the aerosol mass suspended in the containment atmosphere by a factor of 2500 (48 h after the last releases). The 900 MWe reactor containment has a total volume of $\approx 60 \times 10^3 \text{ m}^3$ giving a mass density of aerosols of about 10 mg/m³.

The use of ¹³¹I to label iodine allows continuous γ -measurements in order to follow on-line the release of the gaseous iodine. Gamma-spectrometry features high sensitivity and a suitably short time resolution (~ min) to follow the kinetics of the studied reaction [1,5]. However, the use of radiotracers induces high costs, safety procedures and regulatory issues. When the use of radiotracers is not possible (high temperature studies, needs for stable iodine generation for several hours), more conventional systems have to be considered such as quartz aerosol filters followed by gas scrubbers filled with a sodium hydroxide solution (1M) in order to trap the gaseous iodine species. Besides the low time resolution of such system (at best ~30 min) the first tests in the CHIP line showed strong adsorption of gaseous iodine onto aerosols trapped on the inlet filter device, thus hindering accurate detection of low gaseous iodine concentrations. This system was then successfully replaced by a direct scrubbing of the transported flow (containing both the aerosols and gaseous iodine) into an organic phase in which only I₂ is retained [6]. It is the low time resolution (connected to the low sensitivity) which makes the previous technique mentioned inappropriate for the tests. Nevertheless, due to its low sensitivity (accumulation ~30 to 60 min), this system is not suited for kinetic studies. For this purpose, Johansson et al. [7] developed recently an on-line optical instrument based on an Incoherent Broad-Band Cavity Enhanced Absorption Spectroscopy IBB-CEAS and operating in the green spectral range 500–550 nm.

There are a few existing optical spectroscopy and mass spectrometry methods for molecular iodine measurements [8], such as Long-Path Differential Optical Absorption Spectroscopy (LP-DOAS) [9–12], Laser Induced Fluorescence (LIF) [13–15], denuder sampling followed by Inductively Coupled Plasma Mass Spectrometry (ICP/MS) [10,16–18], chemical ionization mass spectrometry [19] and cavity enhanced techniques such as Broad-Band Cavity Ring Down Spectroscopy (BB-CRDS) and Cavity Ring Down Spectroscopy (CRDS) [10,20,21]. All have good sensitivity, with reported detection limits being on the order of ~5 pptv (30 min acquisition time) for LP-DOAS [9], 20 pptv (10 min acquisition time) for BB-CRDS [20], 13 pptv for LIF (10 min integration time) [15] and

~26 pptv (1 min acquisition time) for IBB-CEAS [22]. The quoted detection limits will of course change depending on the presence and concentration of other species that absorb at the same wavelength as I₂.

LP-DOAS can be immediately disregarded for laboratory measurements, as it requires a single pass path length of tens of metres to kilometres. LIF is a very sensitive technique (a detection limit of $\sim 2 \times 10^9 \text{ molecule cm}^{-3}$ is reported in [13]) but it does not provide absolute measurements and therefore it requires calibration.

In order to achieve absolute measurements with a good sensitivity while retaining a compact device, a cavity enhanced technique is required. Of these there are two main techniques of interest: Broad-Band Cavity Ring Down Spectroscopy (BB-CRDS) and Incoherent Broad-Band Cavity Enhanced Absorption Spectroscopy (IBB-CEAS) [23].

CRDS data retrieval becomes more complicated when the spectral width of the incoming light is comparable to or broader than that of the absorption line of the species in question. The ring-down decay is no longer single-exponential, but becomes multi-exponential [24]. However, cavity ring-down techniques have some advantages, namely that it is not necessary to know the reflectivity of the mirrors, and the intensity fluctuations of the incoming radiation are not important, as it is the decay time that is being measured. By contrast, IBB-CEAS is more analogous to standard absorption experiments. There are multiple advantages of IBB-CEAS compared to other techniques: by virtue of the cavity enhanced nature of the technique, IBB-CEAS gains in terms of sensitivity, size and stability compared to both simple absorption and long path absorption techniques. This enables spectra to be taken at short integration times (depending on concentration and other interferences, seconds to minutes). The experimental design is simple compared to more complicated techniques that require fast electronics or sophisticated optics such as mode-locking, feed-back loops, optical isolators, Faraday switches, frequency comb spectroscopy. The use of broad band light sources such as xenon arc lamp [22,25,26], supercontinuum sources [27,28] and light emitting diodes (LEDs) [29,30] for probing spectral light allows simultaneous quantitative assessment of multiple atmospheric species [30]. The use of a LED light source is a very low cost solution, and by changing the LED and the mirrors, other wavelength ranges can easily be investigated from the ultraviolet (UV) to the visible, allowing access to the spectral regions that involve strong fundamental electronic transitions of gaseous molecules. This is also of importance when a measurement of one species in the presence of an unknown concentration of a secondary broad absorber is required, as will be seen later. Finally, no optical mode matching is involved as in some Cavity Ring Down Spectroscopy applications (CRDS), which makes IBB-CEAS apparatus much simpler, more stable and robust. There are two main drawbacks however; unlike CRDS, the sensitivity is dependent on the light source stability and the measurement accuracy of the transmitted intensity and it requires a reliable calibration procedure to determine baseline optical losses of the system (often performed by calibration of reflectivity as a function of wavelength using a sample of known concentration in the cavity). This can be calibrated by introducing a known concentration of an absorbing species into the cell. IBB-CEAS has been successfully used to measure a number of atmospheric trace gas compounds like I₂ [7,22,29], IO [22,38], OIO [22], NO₂ [29,31,32,38–41], NO₃ [29,31,40,42], O₂ [27,29,34,40], C₂H₂ [27], CO₂ [28], CH₄ [28], H₂O [29,32,38,40,41], HONO [30], CHOCHO [32,38,39,41], CH₃COCHO [38,39], CH₂O [33,37], O₃ [35,36], O₄ [38,40,41], N₂O₅ [42], Br₂ [36], BrO [36], SO₂ [36], OClO [37].

A few Cavity Enhanced Absorption Spectroscopy (CEAS) setups based on the coupling of a laser source to a high finesse cavity have been reported in the literature for our region of interest. High-

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