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Simultaneous study of gas phase and secondary organic aerosols' chemical composition

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Introduction

Secondary Organic Aerosols (SOAs) are formed in the atmosphere by gas-to-particle conversion of organic gases. Processes involve gas phase reaction of anthropogenic or biogenic Volatile Organic Compounds (VOCs) with atmospheric oxidants (OH, O₃, NO₃) leading to the formation of oxygenated Semi-Volatile Organic Compounds (SVOCs). SVOCs partition between gas and particulate phases is achieved either by condensation on pre-existing aerosols, or by nucleation (new particles formation). SOAs take part to the atmospheric physico-chemistry and influence :

- Climate regulation by reflecting and diffusing solar radiations and acting as Cloud Condensation Nuclei (CCN)
- Human health because of their submicron size allowing them to cross respiratory barriers.

However, if global processes are well known, due to excessive complexity of atmospheric chemistry and chemical composition of secondary organic matter, the community currently lacks of data to fully describe these multiphase phenomena, characterise SOAs formations pathways and accurately assess their climate and health impacts.

This analytical work intends to improve our understanding of SOAs life cycles providing access to chemical speciation of gaseous and particulate phases simultaneously and allowing :

- Characterization of secondary compounds partitioning according to environmental parameters, age of air mass, reactivity in both phases, etc, and confrontation with theoretical data
- Exploration of chemical processes in both phases leading to SOAs formation and evolution
- Evaluation of potential SOAs toxicity using chemical speciation data in structure-toxicity relationship models.

This original study is based on the development of a low-volume simultaneous sampling of gaseous and particulate phases and an analysis by a unique sensitive and fast analytical technique coupling thermal-desorption, gas chromatography and mass spectrometry (TD-GC-MS). The awkward point of this work is the necessary adaptation of derivatization techniques of polar secondary organic compounds, in gaseous and particulate phases, to the powerful TD-GC-MS analytical method. Here are presented the method development and validation by the use of complementary tools : dynamic atmospheric simulation chamber (INERIS), static atmospheric simulation chamber especially designed for multiphase chemistry (CESAM, LISA), and real atmospheres sampling. Same ways, simulated and real multiphase atmosphere sampling, are taken for first applications of the method.

Sampling and analytical methods

Exploration of chemical speciation of secondary atmospheric organic matter requires the use of an analytical technique meeting three principal characteristics : high sensitivity to detect trace compounds, powerful chromatographic separation to resolve very complex matrices and a detection system allowing structural identification of unknown compounds.

Thermal extraction of sampling material of gas and particulate phases enables high sensitivity minimizing manipulations and limiting losses and contaminations, in opposition to solvent extraction protocols. GC and MS techniques fulfill the sensitivity and identification requirements.

To fit with this analytical method, the gas phase is collected on Tenax TA sorbent tubes and particulate phase on quartz fiber filters, two sampling material which resist to the high temperatures required by thermal extraction (around 300 °C).

Both phases are collected simultaneously, during five hours for relevant atmospheric concentrations. For field campaign, the functional commercial sampling system Partisol Speciation (Figure 1) was adapted. It has four mass flow regulator and nine sampling lines, allowing to simultaneously collect two sets of gas/particules samples. Aerosols are collected on 47 mm quartz fibers filter using ChemComb system at a flow rate of 16,7 mL.min⁻¹. ChemComb integrates an impaction plate (PM 10, PM 2,5 or PM 1), a filters pack and the possibility to place ozone or VOCs denuder before filter (Figure 1). Gases are collected at around 100 mL.min⁻¹ on Tenax TA stainless steel tubes (from Perkin Elmer) or on other sorbents if needed. Flow rate can be adjusted as necessary for gaseous phase. To avoid unwanted aerosols collection on sorbent, Teflon filter, material limiting gas adsorption in comparison with quartz, is placed upstream the sorbent tube. For simulation chamber experiments, analog sampling systems are used.

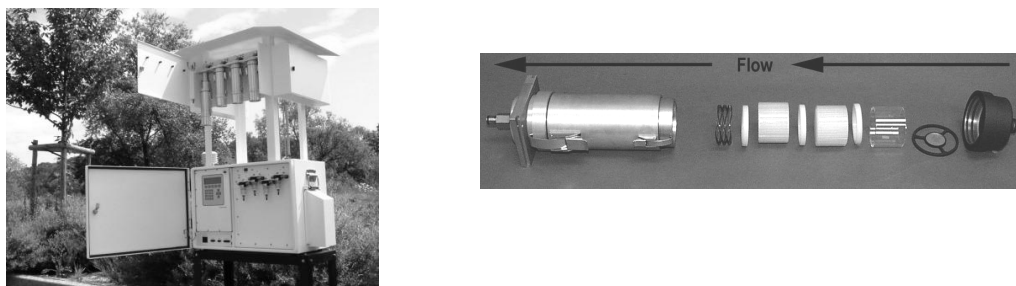


Figure 1 : Partisol Speciation (Model 2300, Thermo Scientific) and ChemComb system

If TD-GC-MS method is commonly used for a large range of primary compounds in gas phase, its application on secondary organic compounds, oxygenated and polar, requires analytical developments. Indeed, polar organic compounds are generally lost in the injection system and/or are not properly eluted in the chromatographic column leading to poor sensitivity. The use of reactive and oxygenated compounds derivatization, reduces polarity and so improves thermal extraction, chromatographic separation and also identification by characteristic fragmentations in mass spectrometry. Derivatization technique is commonly used in SOAs chemical speciation studies when using solvent extraction. However, its adaptation to thermal extraction, involving derivatization on solid support, represents an important challenge.

Derivatization of secondary organic compounds

One of the aims of this work is to adapt derivatization techniques of secondary oxygenated compounds on solid derivatization while maintaining the advantages of thermal extraction, as the minimization of samples manipulations.

Two derivatization reagents have been selected to react with two family compounds :

- O-2,3,4,5,6-(PentaFluoroBenzyl)HydroxylAmine (PFBHA) for carbonyl compounds (ketones, aldehydes). It is largely used by SOAs community when using solvent extraction (e.g. Jang and Kamens 2001; Reisen et al., 2003; Carrasco et al., 2007) The reaction of carbonyl with PFBHA proceeds in two step (Figure 2). As a consequence gas and aerosols samples need a 5-6 days storage before analysis to achieve complete derivatization. The reaction is normally achieved in aqueous solution. Besides, atmospheric ozone can potentially generate negative artifacts by reaction with derivatized compounds.

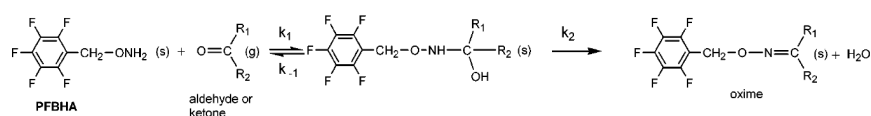


Figure 2 : PFBHA derivatization reaction of carbonyl compounds (Ho and Yu 2002)

- N-Methyl-N-(Tert-ButyldiméthylSilyl)TriFluoro-Acétamide (MTBSTFA) for hydroxyls compounds (alcohols, carboxylic acids) (Figure 3). It is less sensitive to hydrolysis than BSTFA, and is usually used by community (e.g. Spaulding et al., 1999; Jones and Ham 2008). Giving good responses in GC-MS (Schummer et al., 2009), this agent and its derivatised compounds is still influence by humidity and easily hydrolysed.

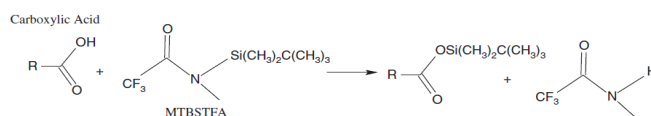


Figure 3: MTBSTFA derivatization reaction of hydroxyl compounds (Buch et al., 2006)

For gas phase collection, Tenax TA is coated with derivatization agent before sampling, which allows to couple sampling to derivatization in order to minimize manipulations, losses and contaminations. On-sorbent deposition is achieved by PFBHA sublimation under nitrogen stream at around 110°C during 20 min. MTBSTFA deposition is carried out by thermal evaporation of pure reagent under nitrogen stream allowing Tenax TA coating.

For particulate phase sampling on quartz fiber filters, derivatization is performed after sampling by filter exposure to derivatization reagent vapors to prevent gas collection from reacting with the coated agent. Humidity influence on derivatization efficiency is expected to be similar to on-sorbent gas phase derivatization. Derivatization of sample filter is performed in a 1,5 L glass vessel where reagent and sample(s) have been introduced for 2 hours. After complete procedure, filter is roll-on and introduced in an empty stainless steel tube suitable for thermal extraction system.

Special attention is drawn to humidity effects on derivatization processes regarding foreseeable behaviour of both reagents.

INERIS exposure chamber experiments

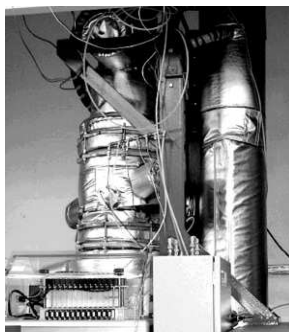


Figure 4 : INERIS exposure chamber

The INERIS continuous flow chamber is a cylindrical glass vessel with a usable volume of 150 L where samplings are performed. Temperature and humidity are continuously controlled and monitored. Gas phase pollutants atmosphere can be created by a generation system providing continuous control of dilution parameters from gas bottles. As a result, the INERIS exposure chamber is a very interesting tool for humidity influence study on gas collection and derivatization.

Indeed, humidity is expected to improve carbonyls derivatization with PFBHA, reaction being widely performed in aqueous solution. On the contrary, it is expected to penalize hydroxyls derivatization by MTBSTFA and derivatives hydrolysis. However these dependences have to be confirmed and characterised.

A preliminary test on the humidity influence on gaseous carbonyls collection was thus realised by generating a simulated atmosphere of simple aldehydes at relative humidities of 0 % and 50 %. Sampling was performed during five hours at 100 mL.min⁻¹ on Tenax TA coated with PFBHA on five sampling tubes simultaneously.

Results comparison of dry and wet sampling tests (Figure 5) show significant improvement of the collection efficiencies on one hand (around 3,5 times for benzaldehyde and around 2 times for

others compounds better at 50 %HR than in dry situation) and of reproductibility on the other hand (10 to 20 % error in dry situation, 8 to 12 % error at 50 % HR). Moreover, pentanal quantification by sampling results comparison with derivatization of pure compound in acetonitrile/water solution showed good agreement between theoretical generated concentration and sampling at 50 % HR (theoretical concentration : $14,3 \mu\text{g}\cdot\text{m}^{-3}$, quantification : $13,9 \mu\text{g}\cdot\text{m}^{-3}$).

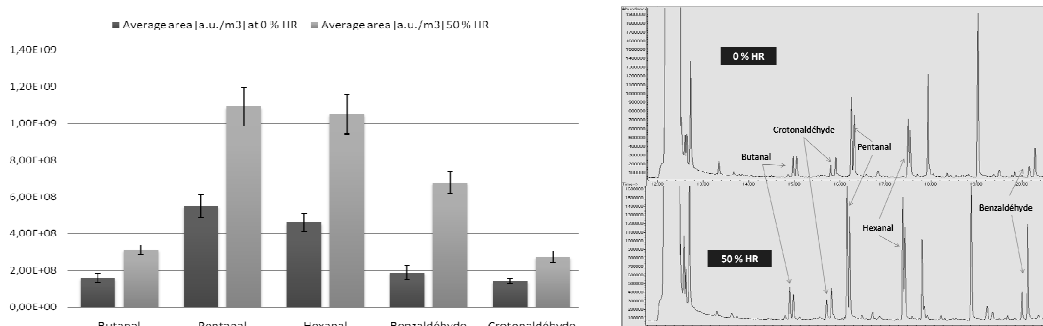


Figure 5 : Comparison of average area (in area units per cubic meter sampling) for five replicates of aldehydes sampling in a dry atmosphere and in a 50 % HR atmosphere. Examples of chromatograms.

These first results confirm the positive influence of relative humidity on carbonyl collection with PFBHA derivatization. Nevertheless, since the method is dedicated to relevant atmospheric conditions (i.e. rarely under 30 % HR or above 80 % HR), further characterization of humidity dependence is required. The aim is to evaluate if a minimum of 30 % HR is enough to achieve complete (or maximum) collection of carbonyls compounds or if a gas stream humidifier is required to achieve suitable results in all relevant atmospheric humidity conditions.

Thus, additional experiments were performed in the INERIS exposure chamber at 30, 50 and 80 % HR. In order to get closer to relevant secondary atmospheric compounds, an alternative series of 10 carbonyls is generated including unsaturated aldehydes (e.g. methacroleine), ketones (e.g. 4-heptanone) and one polyfonctional (hydroxyacetone). Data processing is still ongoing.

Similar experiments will be scheduled for relative humidity influence on hydroxyls collection on MTBSTFA if other experiments (for example CESAM chamber experiments, see below) do not provide complete characterisation.

MEGAPOLI field summer campaign

The European project "Megacities : Emissions, urban, regional and Global Atmospheric Pollution and climate effects" (MEGAPOLI) has been created in the aim to evaluate present and future impacts of megacities on air quality, atmospheric chemistry and climate at local, regional and global scales. The 2009 summer field campaign took place in the Paris area on several urban and suburban locations, and lumped together a varieties of measurement instruments (IR, PTR-MS, SMPS, TEOM-FDMS, AMS, EC/OC, ...).

This campaign has allowed confronting the method to real conditions, testing coating method and gas sampling parameters as flow rate or denuders suitability, and collecting real aerosols samples for particulate phase derivatization development. The adapted Partisol Speciation was used.

In the case of hydroxyls collection by on-sorbent MTBSTFA derivatization, results have highlighted poor derivatization issue (presence of non-derivatized compounds in samples) and expected relationship between ambient relative humidity and derivatization efficiency variability. Flow rate decrease, tested on a few samplings, seems to be a potential, but not ideal, pathway to fix poor derivatization problem. In order to minimize humidity influence sampling flow dryer system is going to be tested before the method optimization is continued. Nafion membrane appears as an appropriate tool. Indeed, double flux counter-current system seems limiting surface exchanges for potential losses. System has to be tested on known simulated atmosphere in order to quantify analytes losses and evaluate its viability and efficiency.

However, humidity variability during the campaign was not sufficiently significant to obtain suitable conclusions on its influence on carbonyls collection. An important outcome concerns

ozone scrubber influence (Sep-Pack Ozone Scrubber, Whatman®). Indeed, results clearly show quasi-total carbonyls retention by the ozone scrubbers which thus is going to be rejected for further tests.

Concerning particulate phase derivatization, it was evaluated in a first step if humidity adsorbed on quartz fiber filter during a five hours sampling is sufficient for complete (or maximum) carbonyls derivatization, or if additional humidity is required in derivatization protocol. In this aim, a filter obtain after a five hours sampling time (at a flow rate of 16,7 mL.min⁻¹ and at an humidity ration of 35 % on average) was cut in two equal parts. One part was derivatized by vapor PFBHA exposure in a nitrogen purge and dry atmosphere. The other part was derivatized by vapor PFBHA exposure in a purge atmosphere moisturized by a 1 mL liquid water reservoir. Both experiences took place under light nitrogen stream (60 mL.min⁻¹) to help reagent and water sublimation/evaporation.

On four compounds clearly identified as PFBHA derivative (but not rigorously identified), gains on peaks area for wet situation in comparison with dry situation vary between 18 and 72 %, clearly showing the needed additional water introduction in derivatization protocol (Figure 6). Such as carbonyls gas phase problematic, it is necessary to determine minimum humidity ratio in vessel atmosphere required to achieve complete (or maximum) derivatization efficiency in order not to saturate TD-GC-MS with an unnecessary amount of water. This work is currently in progress as the MTBSTFA derivatization protocol definition.

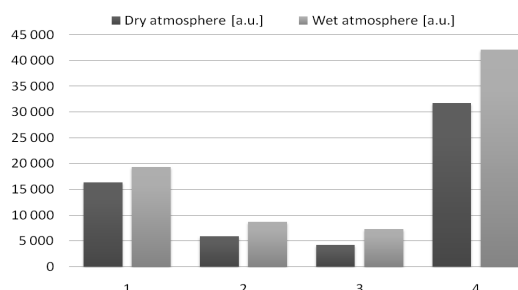


Figure 6 : Improvement of compounds (1 to 4) recovery (in area units) between dry and wet atmosphere aerosols derivatization protocols by PFBHA reagent.

Simulated multiphase atmosphere experiments in CESAM chamber

To refine previous results and apply the method to relevant but simplified atmospheric parameters (range of compounds, multiphase composition, low concentrations, ...), three series of experiments are scheduled in the CESAM chamber (Figure 7) in April and May 2010.

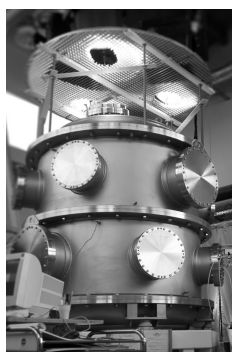


Figure 7 : Experimental Chamber for Multiphase Atmosphere Simulation (CESAM, LISA, Créteil, France)

The first experiments specifically concern the gas phase collection : non reactive gaseous atmosphere is generate from about twelve atmospheric relevant carbonyl and hydroxyl pure compounds (e.g. methacroleine, oxalic acid, limonene-1,2-diol) of which concentrations can be precisely monitored by FTIR in the CESAM chamber. These experiments, performed at different concentrations (from 200 to 20 ppb) and relative humidities, will provide more precise information on humidity influence on derivatization performance with both agents. For hydroxyls MTBSTFA derivatization, Nafion membrane to dry the sampling air is to be tested.

In a second step, one or two compounds, of which wall losses have been quantified in the previous experiments, are selected to create a known non reactive multiphase atmosphere by the simultaneous introduction of a gas compound and sulfate seeds in the chamber. Compounds concentration remaining in the gas phase is monitoring by FTIR. The aim is to evaluate the method capacity to give relevant gas/particles partitioning and the potential measurement artifacts (gas adsorption on filter, ...).

In a third step, SOAs generation experiments will be performed in order to confront the global method to more complex and atmospheric relevant mixture of compounds in gas and particulate phases. The multiphase atmospheres will be created from, in a first time, well known chemistry system, as the ozonolysis of limonene, biogenic VOC emitted by a large range of plants. This step will enable a complete method performance evaluation, facilitating compounds search and identification in both phases.

Conclusions and perspectives

The experiments carried out in real and simulated atmospheres in the aim to develop the proposed method, allowing simultaneous study of gas phase and secondary organic aerosols' chemical composition, have permitted to validate parts of protocols, as field sampling system or Tenax TA coating protocols, and test and adjust sampling parameters affecting gas phase derivatization, such as sampling flow rate or ambient relative humidity.

Besides, specific laboratory work has allowed characterizing the TD-GC-MS analysis method by the evaluation of thermal extraction efficiency from Tenax TA and quartz fiber filter and the determination of quantification and detection limits.

The original approach of SOA cycle life study providing by this new developed tool going to be applied in different topics as indoor air characterisation, simulated SOA chemistry experiments, and is included in the European project CHARMEX concerning atmospheric chemistry study of the Mediterranean basin. The area is indeed submitted to multiple anthropogenic sources of VOCs, under the marine salts influence and with strong sunshine periods, allowing an important photochemistry development. It is so a privileged zone for studying SOA formation and evolution pathways and taking all advantages and potentialities of the new instrument.

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