Anonymous Referee #1

Reviewer Opening Statement

The authors present an instrument for quantifying PM associated ROS using 9,10-bis(phenylethynyl) anthracene-nitroxide, (BPEAnit), as probe. Particles were collected directly by a combination of a steam-aided growth chamber and a miniature cyclone with added reaction solution. Particle losses, sensitivity and response time are discussed in detail, exemplarily by analyzing cigarette smoke.

Author Response Statement

Comment 1

The instrument is not sufficiently described, e.g. size data of the "Insoluble Aerosol Collector" (IAC) should be added to estimate the flow regime.

Response 1

The authors agree, and have provided information on the internal IAC dimensions in Sect 2.2. in the updated manuscript.

Comment 2

The authors stated that the instrument is measuring ROS of particle matter (PM) – is that correct? ROS in gas phase (not associated completely with PM, e.g. H2O2) should be collected too, if the gas/particle distribution is shifted towards particles (droplets) after adding condensing water vapor. The relevance of this process should be discussed. If important, loss of gaseous ROS must be determined or measures as e.g. installing a charcoal denuder prior to PM collection should be considered. Perhaps the term "particle" should be replaced by "aerosol", defined as mixture of gas, particles and droplets.

Response 2

The collection of gas phase species was noted in Sect 5. However it has been moved and expanded upon in a dedicated Sect 4.3. in the updated manuscript. During measurement the instrument should alternate between filtered and unfiltered samples in order to account for the gas phase contribution. Another approach would be using a denuder as described by the reviewer. However, the concern with this method would be the losses of ultrafine particles in the denuder prior to sampling (Stevanovic et al., 2015).

Currently the IAC is only characterized for PM collection, with the gas phase collection of interest but still in the very early stages of investigation due to its inherent difficulty. The authors feel it would be premature to claim aerosol collection until the gas phase is fully characterized. Instead, in any sampling campaign the inlet will be periodically switched to sample after a filter to account for gas phase measurements to present a purely particle phase result. Gas phase data can be interpreted to some degree, however until characterization it is semi-quantitative at best.

Accounting for the gas phase contribution was not performed in the response time experiments as the total aerosol response was of interest.

Comment 3

In section 1 several probes and collection devices reviewed. It will be helpful, if the probe dependent targeted ROS species (O-centered-, C-centered-radicals, . . .) will be discussed more detailed to enable interpretation of the different end-points.

Response 3

Some information on the sensitivity of the different major probes discussed has been added in the updated manuscript in Sect 1.2.

Comment 4

Page1 line 18: Replace ". . .(Nel, 2005)(Penttinen et al.,2001); and . . ." by ". . .(Nel, 2005; Penttinen et al.,2001) and . . ."

Response 4

This has been corrected in the updated manuscript in Page 1, Line 18-19.

Comment 5

Page 2, line 26: ". . .are only sensitive to narrow ranges of ROS species; making them unsuited for quantification of total oxidative potential." Here a more detailed discussion on determined ROS species will be helpful

Response 5

The discussion regarding difference ROS species and the use of phrase oxidative potential has been added in Sect 1.2.

Comment 6

Section 1.3: Subtitle should be replaced by "online collection techniques", as chemical assays are discussed in section 1.2.

Response 6

This has been corrected in the updated manuscript at Page 3, Line 29.

Comment 7

Page 5 line 19 and page 6 line 9 and 10 and some other occurences: . . ."sample

resolution" means ". . .time resolution. . ."

Response 7

All incidents of sample resolution have been replaced with time resolution in the updated manuscript.

Comment 8

Page 7 line 7-8: Where is the aerosol flow rate measured?

Response 8

The aerosol flowrate is set prior to, and checked after measurement using a TSI 4043 mass flow meter placed in line between the sampling line and the PINQ inlet. This was found to be stable over long periods (24 hours with no significant variance) and more reliable than a mass flow controller which suffered from issues with condensation. This has been updated in the current manuscript at Page 7, Line 16-17.

Comment 9

Page 8 line 9: A mass flow in g.min-1 will be more exact, additionally the dew point temperature of the supersaturated aerosol flow will be a vivid parameter.

Response 9

A mass flow of g.min^{-1} would be more exact, however the peristaltic pump is a volumetric device and hence a volume flow is provided. 1.5mL.min^{-1} provides an excess of supersaturation which will still be achieved with small variances caused by density changes caused by changes in different laboratory environments. If the instrument is operated in extreme environments with significantly elevated or lowered temperatures tests would have to be performed to ensure viability. This clarification has been included in the updated manuscript.

In regards to dew point temperature, the goal of the system is to provide excessive supersaturation to grow even the smallest hydrophobic particles into liquid droplets. As such the resultant aerosol will be well below the dew point temperature in all circumstances, and hence it is not a parameter of interest here.

Comment 10

Page 8 line 13: Why is the excess condensation drain volume not measured for calculation of the steam dilution factor? Can the excess drain water be analysed further for cross checking particle losses and removal of gaseous components?

Response 10

The steam dilution factor cannot be calculated using the chamber drain line, as you would also need to account for the water collected in the liquid trap and any condensation in tubing connected to the exhaust line of the instrument. The IC analysis during the ammonium sulphate collection experiments provided a significantly more accurate and direct way of measuring this value at Page 8 Line 1-4.

As shown in the manuscript, the PM mass collected by the IAC is within error of the aerosol sample mass. Whilst there is inevitably some particle losses in the chamber, these losses constitute a very small mass portion of the aerosol. Beyond issues regarding how effectively the chamber is washed by the condensation to remove particle deposition, the concentrations of ammonium sulphate in the mass concentration in the chamber drain would be below the limit of detection of the IC system.

The removal of gaseous components could be potentially significant and is of potential interest in the future. However, the gas phase collection is not considered in this publication.

Comment 11

Section 3.1.2: Did the authors check, if the charcoal denuder really removes all ethanol vapour from DEHS particles? If there is only a small amount of ethanol left on the surface of the particles, the still have a hydrophilic character.

Response 11

The charcoal denuder will remove a substantial portion of the ethanol from the aerosol source. The aerosol is then effectively diluted at a ratio of 10 to 1 inside the SMPS due to the sheath air interaction, and diluted again at a ratio of 15.7 to 1 when mixed with the makeup aerosol to generate the required flowrate. Given the volatility of ethanol is so high and the combination of two dilution stages the

authors are confident that ethanol will only be present in trace concentrations and will not influence the hydrophobicity of the particles.

Comment 12

Page 11 line 29-30: Particle mass increases with 3rd order to particle diameter/size, not exponentially

Response 12

This has been corrected in the updated manuscript at Page 12, Line 16.

Comment 13

Page 12 line 10 and page 16 line 3: "Sect. 0" is not defined

Response 13

This has been corrected in the updated manuscript

Anonymous Referee #2

Reviewer Opening Statement

This paper reports on the development of a steam-particle-growth system coupled to a cyclone for droplet collection followed by analysis of the liquid for particle bound ROS with a fluorescence probe. Recently, a number of papers have been published describing various designs aimed at measuring particle-bound ROS. This paper adds an additional method to this group. The authors have done a series of careful experiments testing the performance of the instrument, however there are a number of major issues to address. 1) The particle collection system of the instrument is nearly identical to other instruments already reported in the literature, with the exception that the cyclone design differs; exactly how it differs is not totally clear since exact details are not provided. 2) The instrument described measures only ROS associated with particles, yet it equates measurements of particle bound ROS with other assays that measure completely different particle species associated with the aerosols ability to induce oxidative stress. This conflation adds to the confusion that seems to exist in the new field of aerosol research. Prior to publication, these two major issues should be addressed.

Author Response Statement

The lines listed by the reviewer in their comments corresponds to the original submitted manuscript and not the one published for online discussion. As such the lines and pages listed by the reviewer or not relevant to the comments.

Comment 1

A major issue is that the instrument described in this paper is essentially identical to a PILS with a cyclone droplet collector instead of impactor. Orsini et al (2008) describes an instrument with PILS coupled to a cyclone (which the authors cite), and Peltier et al (2007) specifically describes and tests a PILS-mini cyclone system (not cited in this work). Since the proposed instrument is so similar to these existing instruments, details of how the new instrument differs, such as what are the technical advances in this new instrument over existing technology. For example, why not just utilize the existing methods? It appears that the authors are implying that the cyclone design is novel, ie, that it produces what they call a standing vortex. If this is indeed the main novel feature, the exact details of how the cyclone was designed and constructed to achieve this should be discussed in more detail. As it stands it is doubtful a reader could reproduce the results of this paper due to insufficient detail.

Answer 1

The authors disagree with this statement strongly. This paper is titled "An instrument for the rapid quantification of PM oxidative potential: the Particle Into Nitroxide Quencher (PINQ)" and as such is a paper regarding an instrument (the PINQ) which measures the oxidative potential of PM. The PILS is a particle collector, which is an entirely different category of instrument altogether.

The PINQ uses a combination of chemistry and purpose built collection and measurement stages which is clearly different than any other instrument published or commercially available for this purpose. This has been done in order to create an OP measurement instrument with as high time resolution and sensitivity as possible (< 1 minute). The authors believe the reviewer has mistaken the purpose of this paper as a discussion of the IAC, the particle collection stage of the PINQ. A large portion of the paper is dedicated to the design and collection efficiency of the IAC, which is entirely necessary given that the PINQs performance is predicated on this and it has not been described in a publication previously. However, the IAC is a single, if important piece in the larger PINQ. It is

predominantly named separately in order for readers to easily distinguish between discussion regarding the particle collection stage and those regarding the PINQ instrument as a whole.

Despite this important note, the IAC itself is distinct from the PILS and other commercially available and published steam collection devices. The initial inspiration for the IAC does indeed come from the modified PILS with a "wetted-wall cyclone" described in Orsini et al (2008). However, the variations from this system are substantial and include (but are not limited to): A liquid cooling system on the growth chamber to improve heat removal efficiency for elevated temperature applications; a completely new steam generator design to improve system stability and flowrate changes; and the development of a solvent resistant version of the wetted-wall cyclone compatible with DMSO which was termed a vortex collector. The decision to introduce this new term is not due to a change in mechanism from the one described by Orsini (2008), in this papers abstract it also describes "a standing liquid vortex which coats the inside deposition surface". Instead this was intended to separate the design clearly from that of a traditional PM cyclone as their purposes and design focus are different as discussed in Sect. 2.2. Some modifications have been made to the manuscript in Sect. 2.2 to emphasize these differences and their purpose in the development of an oxidative potential monitor.

The authors were not aware of Peltier et al (2007). It is relevant to this study and has been integrated into the manuscript.

As to the comment regarding the reproducibility of this study, all key conceptual information and design considerations, as well as published resources used in the development, construction and testing of this system are provided. As requested by Referee #1, more detail has been added on internal dimensions of the system. Further information regarding detailed construction information, schematics, etc would require a manuscript several times the length of the current one and would provide little utility. Instead, the following statement has been added to the data availability:

For a more detailed description on the design and construction of the instrument or interest in instrument evaluation, please contact the corresponding author.

Comment 2

A second major issue with this paper is the conflation of particle bound ROS and aerosol species that produce ROS in vivo, which is now often referred to as oxidative potential (OP). The title states that this is a method to measure PM OP, but it is more precisely a measure of ROS associated with particles. The title should be more specific, eg, possibly changed to something like . . . rapid quantification of ROS associated with particles ... Also, in the abstract it should be clearly stated that particle bound ROS is being measured. Throughout the paper care should be taken to delineate the two. Thus, it would be best not to equate what is being measured in this work with OP, eg, Pg 2 line 17 states: In order to achieve ROS quantification, termed herein oxidative potential, ... The two, particle ROS and OP should be delineated as they are associated with different aerosol chemical species and have potentially different health effects. Particle ROS, what the authors call exogenous ROS is what this paper is measuring and which has not been associated with any adverse health effects in population studies; at least this reviewer does not know of any. Maybe the authors can add citations supporting why particle-bound ROS is an important thing to measure. An example may be direct inhalation of combustion products, like cigarette smoke? In contrast to particle-bound ROS, endogenous ROS, which is often referred to as OP and typically measured with the DTT or GSH assay, has been associated with adverse cardiorespiratory adverse health effects in some studies (Abrams et al 2018; Bates et al., 2015; Weichenthal et al., 2016; Yang et al., 2016). Thus, it is strongly suggested that the term oxidative

potential be removed throughout the paper and replaced with particle-bound ROS, or similar notation, except in the cases where DTT assay is specifically referenced, eg, Table 1. Overall, the point is that this research area lacks an agreed upon terminology, but no matter what the authors decide to call what they measure, it is very important that it be made clear that it is fundamentally different than certain other assays that measure aerosol chemical species that generate ROS in vivo (eg, DTT or GSH, etc). Related to this, if particle-bound ROS is so reactive and has a short life-time, the justification for this instrument, why would one expect it to be a significant health hazard to a large segment of the population? It seems the instrument is most useful for measuring particle-bound ROS associated with very fresh combustion emissions. Where specifically would one then expect to deploy this instrument. A discussion along these lines should be added. This would further help clarify the difference between what this instrument is measuring vs methods using the DTT or GSH assays (ie, methods measuring aerosol oxidative potential not particle bound ROS).

Answer 2

The research supporting the association between the OP and health has been limited (to very few studies, mainly from 1 research group) and it is still in its pioneer stage. Insufficient evidence in this regard cannot be used to predict and suggest an explanation for observed health effects upon exposure to particulate matter.

Oxidative potential that depicts the presence and concentration of in-vivo present (or generated) redox species, measurable by the DTT, AA or GSH, is not a widely accepted terminology to the best of our knowledge.

There is no means to detect the total oxidative potential using any cell-free assay and thus it would not be accurate and representative to use the term oxidative potential for any of these techniques, including the DTT. In addition, ROS present on particles will also contribute to the OP. It has not been established what is the contribution of exogeneous ROS to the total OP, but excluding it will be inaccurate. It is also unclear what is the detection capacity of DTT for different particle types. So, saying that DTT is measuring the OP is also a bold statement as this approach is limited to certain solvents and reactive species.

We agree that in the lack of data supporting the link between the ROS and OP, we should use more precise terminology. To this end, a short note on the inability of current probes to described as a measure of oxidative capacity has been added in Sect. 1.2. Furthermore, the BPEAnit measurements performed with the PINQ are now referred to as measurements of PM-bound ROS.

Authors cannot agree with few comments highlighted by the Reviewer.

"The two, particle ROS and OP should be delineated as they are associated with different aerosol chemical species and have potentially different health effects." This statement is not supported by any piece of literature data and thus we could not consider modifying the discussion in the manuscript.

"Maybe the authors can add citations supporting why particle-bound ROS is an important thing to measure". Authors strongly believe that this is more than obvious and that the research in the area in the last 10 years demonstrates this. Importance of particle-bound ROS is beyond cardio-respiratory health effects. We believe that any atmospheric scientist is aware of the importance of particle-bound ROS. Once in the atmosphere, they will be oxidised easier, creating potentially more toxic form of pollutants, secondary pollutants. ROS on particles will change organic composition, that is found to be responsible for the OP, regardless of the approach used to measure it.

In regards to the last question: "Related to this, if particle-bound ROS is so reactive and has a short life-time, the justification for this instrument, why would one expect it to be a significant health hazard to a large segment of the population? It seems the instrument is most useful for measuring particle-bound ROS associated with very fresh combustion emissions. Where specifically would one then expect to deploy this instrument."

It is well known that the ROS on particles can be short-living and long-living. Persistent free radicals are also very important for the measurement of the oxidative reactivity of particles. This instrument is designed to measure the reactivity of particles in real-time and is not limited to the fresh combustion emissions. It can be deployed for atmospheric measurements, chamber studies, mechanistic studies, just to name a few. It can be also utilised to detect the change in oxidative reactivity over long periods of time. As indicated before, there is no doubt that the particle-bound ROS is very important for observed health effects, but only a very well designed, large cohort study (or a few of them) can shed more light into what is posing a health hazard to the large population.

Comment 3

Pg 2 last line is not correct as two online DTT systems have been developed, see Puthussery et al. (2018), and Eiguren-Fernandez, et al, (o-MOCA), which is cited.

Answer 3

Page 3, Line 3 has been clarified to indicate that the limiting factor is in reference to time resolution of the instruments possible rather than the inability to create a real time system.

For the referees interest there is also a third DTT system (Sameenoi et al., 2012). Puthussery et al. (2018) is not included as it was published after the submission of this manuscript.

Comment 4

Last paragraph of section 1.3.4: There is a difference between a solid insoluble particle and a hydrophobic particle. Can the authors give an example of an insoluble particle bound ROS species? For oxidative potential, this is extensively discussed in Fang et al, (2017). This is an important question since the authors are using this as design criteria. (More on this below).

Answer 4

The terms hydrophobic and insoluble were incorrectly used interchangeably as, in the case of the DCFH and DTT assays, the chemistry is performed in an aqueous solution and hence hydrophobic particles tend to be insoluble in that context. This has been corrected in the updated manuscript in several places including Sect 1.3.4.

The emphasis here is not on insoluble ROS, but on insoluble particles. The PINQ system collects these particles directly into the BPEAnit in DMSO solution, removing the requirement for particle solubility in the collection liquid used in several of the systems discussed in Sect 1.3.

Comment 5

Section 2.2.4, What specific system used a copper steam generation system the authors refer to? This is not common practice in most steam systems, including the commercially available PILS. References to the copper system should be removed unless specific instruments using it can be identified.

Answer 5

The authors agree that the use of copper is not common in these applications and have removed reference to it from the manuscript in Sect 2.2.4.

Comment 6

In the particle mass collection efficiency method was the aerosol neutralized after nebulization for the IAC leg, as done for the SMPS leg? If not the reason for not doing this and implications should be discussed since one may expect highly charged particles. Also, how is the impactor affected by these highly charged particles (if there was no neutralization)?

Answer 6

Neutralization in an SMPS is widely accepted standard practice to ensure correct sizing. The entire flow path was conductive to minimize electrostatic losses. Beyond this the authors do not believe that aerosol charge has any influence on the setup and the results presented. Charge plays no role in IAC collection and would not influence the impactor performance.

Comment 7

Why is the impactor installed before the particles are dried? Was the cut size of the impactor actually 0.1 μm or did it remove larger droplets, but ended up effectively removing dried particles with diameters less than 0.1 μm?

Answer 7

The purpose of the impactor was not to generate a sharp cut-off at 100nm, but to make the resultant size distribution as small as possible so that the mass distributions were predominantly in the ultrafine range. Placing the impactor first lowered the effective cut-off size once the particles are dried, enhancing this effect. The cut-off size can be estimated as ~74 nm based on the logistic function portion of the fitted curve for the particle size distribution with the impactor present (See Figure S4). This has been corrected and expanded in the updated supplementary material in Page S3, Lines 9-15.

Comment 8

Pg 16, line 8, if the particles are dried, depending on the RH achieved, the ammonium sulfate may not be spherical. Why not do a sensitivity test to see how the findings change if say the DMA sizing is corrected assuming non-spherical particles.

Answer 8

Ammonium sulphate particles are not perfectly spherical, however smaller particles tend towards sphericality (Zelenyuk et al., 2006). The particles in question here have a mean diameter between 30 - 40 nm which were dried to ~20 % RH. Whilst inevitably they will be slightly aspherical, they will only be marginally so. The most suitable dynamic shape factor found would be 1.02 (Biskos et al., 2006), which results in no significant change to the mass percentage present in the ultrafine range due to the significantly higher contribution of uncertainty from the function fitting (80 ± 10). Hence it represents a needless complication of the analysis. The supplementary material has been edited to add this justification of the sphericality assumption in Page S4, Lines 1-5.

Comment 9

Pg 16, line 10, why does the the Dp log scale make the area under the curve not proportional to fraction of overall mass when the size distribution is plotted as dN/dlogDp? That is precisely the point of the size distribution function.

Answer 9

dN/dlogDp normalizes each bin concentration by its size width in order to allow comparison between instruments with different bin resolutions. It is still a measure of particle size, not mass.

Particle mass of a chemically homogenous particle is equal to particle volume multiplied by density, and hence is not directly proportional to particle size. As stated in the manuscript the assumption is that the ammonium sulphate particles are approximately spherical, and therefore the volume of a particle can be estimated using the equation for volume of a sphere. Therefore, the particle mass distribution can be estimated by multiplying the particle number distribution by the volume of a sphere and the density of ammonium sulphate. As can be seen in Figure S3 this cubic relationship between particle size and particle mass results in the ultrafine particles accounting for a large portion of the number concentration, whilst at the same time accounting for only a small percentage of the mass concentration. Therefore, in order to investigate ultrafine collection using a mass based method it was necessary to further reduce the mean size of the distribution, as was shown in Figure S3 using an impactor. The supplementary material Sect. S2.3 has been edited to better explain this.

Comment 10

Pg 17 line 4, typo, 0?

Answer 10

The authors cannot find the typo listed in the online discussion paper.

Comment 11

Section 4.1.3. What is the difference between a hydrophobic particle and an insoluble particle? Is DEHS insoluble in very dilute systems? Does DEHS remain as the original sizes generated in the droplet collection system (ie, cyclone}? The point is the one thing that is unique about this instrument is the claim that it can measure at near 100 % efficiency insoluble particles, but only one form is tested. What about collection efficiency of solid particles? Will the instrument actually collect solid particles and thus have the ability to measure ROS associated with solid particle surfaces, say for example, fresh soot particles. Are comparisons of this vortex cyclone to the Orsini et al or Peltier et al mini-cyclone valid since their test were done with truly solid particles (PSL or soot}?

Response 11

The confusion between hydrophobic and insoluble particles has been responded to in Answer 4.

The authors have responded to the "uniqueness" of this system in Answer 1.

The IACs purpose is to entrain particles into a solution of DMSO and the BPEAnit probe in order for reaction between the probe and sample to occur. As a steam collection device, the collection efficiency is determined by: whether or sample particles form liquid droplets inside the growth chamber; and what the collection efficiency of grown droplets is.

The ammonium sulphate mass collection experiments addressed the question of the collection efficiency of grown particles. The results presented in the manuscript show that the mass of ammonium sulphate collected into the sample liquid was within error of unity with the sample aerosol mass for both fine and ultrafine mass concentration.

The DEHS experiments address the question of droplet formation. DEHS was selected not because it is insoluble in the DMSO collection liquid, but because hydrophobic DEHS particles are difficult to grow into water droplets. By showing that the collection efficiency for DEHS has a cut off size of < 20 nm, it is evident that the supersaturation achieved inside the chamber is sufficiently high to grow even very small hydrophobic particles. Whether the particles are solid or liquid phase does not influence this result.

The combination of these two experimental results shows that PM is collected into the capture solution regardless of size or chemical composition. While no direct measurements of solid insoluble particles collected into the liquid stream were performed, there is no mechanism that would somehow prevent these particles from being collected in the same manner as those tested. If the purpose of the IAC were to perform direct measurements on solid particles collected into the liquid, deposition of solid particles in the liquid flow path would be the only necessary effect not considered in this characterization. However, the IAC system was developed specifically for use with the BPEAnit probe in the PINQ system. The vortex collector ensures that the particles are collected directly into the liquid rather than impaction onto a plate where they could potentially adhere and not fully react with the probe. Once collected into the liquid the reaction between the probe and sample particles is diffusion limited. This means that any potential deposition of solid particles in the liquid line will not influence the final ROS measurement as reaction with the probe has already taken place.

Comparability between the IAC and the Orsini et al (2008) and Peltier et al (2007) systems would only be limited through differences in line losses in the instruments and the sensitivity of the detection methods. The efforts made to limit liquid residence time and volume would minimize this impact in the PINQ system. The updated manuscript highlights this consideration in the comparison between the different collectors.

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An instrument for the rapid quantification of PM- bound ROS~~oxidative potential~~: the Particle Into Nitroxide Quencher (PINQ)

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Abstract. ~~Presence or generation of r~~Reactive oxygen species (ROS) present on or generated by~~on/by~~ particulate matter (PM)
5   have been implicated in PM-induced health effects. Methodologies to quantify ROS concentrations vary widely both in detection and collection methods. However, there is currently an increasing emphasis on rapid collection and measurement due to observations of short half- ~~live~~ life ROS. To address this problem, this manuscript details the design and characterization of a novel instrument for the measurement of PM-bound ROS named the Particle Into Nitroxide Quencher (PINQ). This instrument combines the 9,10-bis (phenylethynyl) anthracene-nitroxide (BPEAnit) ROS assay in conjunction with a purpose-
10   built aerosol collection device, the insoluble aerosol collector (IAC). The IAC continuously collects PM regardless of size or chemistry directly into a liquid sample with a collection efficiency of > 0.97 and a cut-off size of < 20 nm. The sampling time resolution of the PINQ is one minute, with a limit of detection (LOD) of 0.08 nmol.m^{-3} in equivalent BPEAnit-Me concentration per volume of air. This high sample time resolution and sensitivity is achieved due a combination of the highly concentrated IAC liquid sample, minimized liquid sample volume and the rapid reaction and stability of the BPEAnit probe.

15   **1.   Literature Review**

1.1 Introduction

The World Health Organization (WHO) found ~~Atmospheric~~ air pollution ~~is~~ was responsible for more than 7 million premature deaths ~~each year~~in 2012. A large contributor to this ~~increased~~ mortality is atmospheric particulate matter (PM), which has been linked to: cardiovascular disease (Chow et al., 2006; Donaldson et al., 2001; Nel, 2005); increases in the prevalence of chronic
20   respiratory disorders (Nel, 2005; Penttinen et al., 2001)~~(Nel, 2005)(Penttinen et al., 2001)~~; and adverse effects in both embryonic and adult neuron activity (Morgan et al., 2011). Furthermore, studies have shown a link between exposure to PM in diesel exhaust and an increased lung cancer risk (Silverman et al., 2012). A consequence of these and other discoveries was

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that in 2012, diesel exhaust was classed as a type 1 carcinogen by the International Agency for Research on Cancer (IARC) (Benbrahim-Tallaa et al., 2012).

A key mechanism used to explain these adverse health effects is oxidative stress (Ayres et al., 2008; Li et al., 2002). Reactive oxygen species (ROS) are a group of free radicals which can be either: present on the surface of PM (~~exogenous~~ PM-bound
5 ROS)(Hung and Wang, 2001; Venkatachari et al., 2007); or generated through chemical reactions between PM and cells (endogenous ROS)(Donaldson et al., 2002). When inhaled, PM-associated ROS interact with cells to create oxidative stress, interrupting cell function and potentially leading to cell inflammation and death. The ultrafine particle range have been shown to be particularly hazardous in this respect. Their ability to penetrate deeper into tissues than their larger counterparts allows them to collect inside mitochondria, causing major structural damage to cells (Li et al., 2002).

10 Aerosols generated through combustion processes are of particular concern for oxidative stress as they are a major source of ultrafine particles (Brines et al., 2015; Posner and Pandis, 2015) and their potential for high ROS content (Cho et al., 2005; Kao and S., 2002; Mudway et al., 2005; Ristovski et al., 2012; Zhao and Hopke, 2012). Combustion emissions associated with vehicle emissions, power generation and biomass burning significantly contribute to the aerosol burden in many heavily populated urban areas (Harrison and Yin, 2000; Ma et al., 2017; Simoneit et al., 2004); making PM-associated ROS a key
15 issue in the assessment and understanding of the health impacts of air pollution. There have been many in vivo investigations involving both the monitoring of human exposure, and the exposure of animals and lab-cultivated cells to ROS-containing aerosols (Donaldson et al., 2002; Morgan et al., 2011; Sa et al., 2014; Shi et al., 2006; Shima et al., 2006). Whilst these studies provide us with an understanding of the aforementioned health impacts of PM-associated ROS exposure, they lack the ability to ~~quantify ROS concentrations~~quantify the oxidative potential of aerosols. In order to achieve ~~ROS~~ quantification, ~~termed~~
20 ~~herein oxidative potential,~~ a range of different in vitro methodologies have been developed.

1.2 Chemical Assays

The measurement of oxidative potential is a complex issue in terms of both sample collection and chemical analysis. In order for measurement to take place, PM~~-associated ROS~~ must in most cases be collected into a liquid and mixed with a chemical probe. The degree to which this probe reacts with the sample is then measured in order to ascertain a value ~~of oxidative~~
25 ~~potential~~related to oxidative potential. Many different chemical probes have been used for this purpose, ~~all with various~~ ~~benefits and shortcomings. A~~with a detailed review ~~of the most commonly used probes can be~~ found elsewhere (Hedayat et al., 2015). The reason for this diversity of probes is twofold. First, each probe is only sensitive to a specific range of ROS. Second, it is not known which ROS contribute to oxidative potential, and if they contribute equally. As such, the use of the term oxidative potential is contentious in the field of in vitro ROS measurement. While these probes measure a certain
30 contribution to oxidative potential, none are not true measures of total oxidative potential. This does not mean results are not valuable, as there have been good correlations between probe responses and oxidative stress response. However, all results must be considered in the context of the probe and methodologies used, and discussed accordingly.

Some probes, including p-hydroxyphenylacetic acid (POHPAA) (Hasson and Paulson, 2003) and ascorbic acid (AA) (Fang et al., 2016; Stoeger et al., 2009), are ~~only~~ sensitive to ~~sensitive to narrow ranges of ROS species~~transition metals~~; making them unsuited for quantification of total oxidative potential~~. The dithiotreitol (DTT) assay is commonly used (Eiguren-Fernandez et al., 2017; Fang et al., 2014; Gao et al., 2017; Li et al., 2002, 2009, Sameenoi et al., 2012, 2013) due to its ability to simulate the reaction responsible for the generation of ROS when PM interact with cells; making ~~it a suitable assay for the~~its quantification a measure of endogenous ROS. It is sensitive quinones and transition metals, as well as some water soluble organic compounds (WSOC) and humic-like substances (HULIS). DTT typically requires reaction times of up to 90 minutes with a sample for accurate quantification (Cho et al., 2005), ~~limiting~~which potentially limits time resolution of real time applications. However, new developments in microfluidic sensors have more recently allowed for DTT measurements with reaction times as low as 18 minutes (Koehler et al., 2014; Sameenoi et al., 2012).

2,7-dichlorofluorescein diacetate (DCFH-DA) combined with a horse radish peroxide (HRP) catalyst is currently the most commonly used ROS probe~~s~~ in literature for the ~~quantification~~ measurement of PM-bound~~exogenous~~ ROS (Fuller et al., 2014; Huang et al., 2016b, 2016a; King and Weber, 2013; Venkatachari et al., 2007; Venkatachari and Hopke, 2008; Wang et al., 2011; Wragg et al., 2016; Zhou et al., 2017). This is due to its relatively simple fluorescence-based quantification, potential for semi-continuous monitoring and sensitivity to several different ROS species. These species include organic peroxides, hydroperoxides, aldehydes, alcohols and hypochlorite. However, DCFH is prone to several issues, including: auto-oxidation upon exposure to air and sunlight (Stevanovic et al., 2012a); a high background fluorescence and a lack of sensitivity (Pal et al., 2012); a relatively complex chemistry setup for implementation, especially in the case of online measurements (Huang et al., 2016a; Wang et al., 2011; Wragg et al., 2016; Zhou et al., 2017); the catalytic activity of the HRP catalyst is dependent upon sample composition (Pal et al., 2012); and a minimum reaction time of 11 minutes for quantification with HRP (Zhou et al., 2017), and a 60 minutes without HRP (Pal et al., 2012). These attributes make this probe very difficult to work with in the field, and highlight the need for an alternative ROS probe for accurate oxidative potential measurements.

Profluorescent nitroxides (PFNs) are a group of chemicals consisting of a nitroxide group bound to a fluorophore (Fairfull-Smith and Bottle, 2008). Initially these molecules are only weakly fluorescent, however upon reaction with free radicals they become highly fluorescent (Blinco et al., 2011). Quantification of these reactions can be achieved by comparing the fluorescence intensities before and after reactions. Several different PFNs have been developed at the Queensland University of Technology, one of which is BPEAnit. When placed into solution with dimethyl sulfoxide (DMSO), BPEAnit has been shown to be sensitive to a broad range of ~~exogenous~~ PM-~~bound~~associated ROS (Stevanovic et al., 2012b), in particular those generated in combustion emissions (Miljevic et al., 2010; Stevanovic et al., 2012a). These include: carbon-centered radicals; nitrogen-centered radicals; sulphur-centered radicals; and peroxyl and hydroxyl radicals when in solution with Dimethyl Sulfoxide (DMSO) (Hedayat et al., 2015). Furthermore, its reaction is diffusion limited, allowing for ~~relatively~~comparatively quick measurement quantification. These characteristics make the BPEAnit a promising assay for the rapid online measurement of ~~exogenous ROS concentration and oxidative potential~~PM-bound ROS.

1.3 ~~Measurement Techniques~~Online Collection Techniques

Beyond chemical probes, there are several properties of ROS and combustion aerosols which complicate ~~oxidative potential measurements~~quantification. ~~Exogenous~~ PM-bound ROS react readily with the atmosphere and other surroundings (Fuller et al., 2014). This is a significant issue with standard filter capture techniques, as the concentration of PM-bound ROS ~~oxidative potential~~ can be skewed due to the decay of collected ROS ~~PM bound ROS~~ during long periods of collection and storage prior to measurement (Fuller et al., 2014; Zhou et al., 2017). Therefore, methodologies involving either: long periods of collection; or delays between collection and measurement, risk severely underestimating the ~~total~~ concentration of PM-bound ROS~~oxidative potential of aerosols~~in an aerosol. Additionally, extraction processes to remove ~~particle~~ PM from filters for analysis can introduce further positive and negative sample artefacts (Miljevic et al., 2014). To address these issues, methodologies have been developed to rapidly collect PM directly into liquid for more accurate quantification of ~~oxidative potential~~PM-bound ROS.

Instrument	Chemical Assay	Collection Method	Insoluble Particles	Sample Flowrate	Time Resolution	Limit of Detection
ROS Sampling-Analysis System	DCFH	PILS	No	16.7 Lpm	10 min	n/a
OPROSI	DCFH	PC	No	5 Lpm	$\leq$ 12 min	4 nmol.m^3
GAC-ROS	DCFH	GAC	No	16.7 Lpm	20 min	0.12 nmol.m^3
ROS Analyser	DCFH	PC	No	1.7 Lpm	8 min	2 nmol.m^3
o-MOCA	DTT	LSS	Yes	3 Lpm	3 hr	0.15 nmol.min^{-1}
Online DTT Monitoring System	DTT	PILS	No	16.7 Lpm	3 min	n/a

Table 1 List of online ROS instruments and their key characteristics including: ROS Sampling-Analysis System (Venkatachari and Hopke, 2008; Wang et al., 2011); OPROSI (Fuller et al., 2014; Wragg et al., 2016); GAC-ROS (Huang et al., 2016a); ROS Analyser (Zhou et al., 2017); o-MOCA (Eiguren-Fernandez et al., 2017); and Online DTT Monitoring System (Koehler et al., 2014; Sameenoi et al., 2012). Limit of detection (LOD) for DCFH systems is given as equivalent H_2O_2 concentrations per cubic meter of air. O-MOCA LOD is given as DTT consumption per minute.

1.3.1 Steam Collection Devices

Table 1~~Table 1~~~~Table 1~~ provides a list of the relevant online instruments developed for the quantification of ~~PM~~ different ROS species contributing to oxidative potential. Each instrument uses a different combination of either the DTT assay or DCFH assay with a method for direct capture of PM into liquid. The most predominant of these particle collection methods used are

5 steam collection devices (SCD) (Khlystov, 1995; Kidwell and Ondov, 2010; Simon and Dasgupta, 1995), including: the Particle Into Liquid Sampler (PILS) (Orsini et al., 2003; Weber et al., 2001) and the Gas Aerosol Collector (GAC) (Dong et al., 2012). SCDs utilize condensational growth to achieve high efficiency collection of ultrafine particles. When in operation, a sample aerosol is continuously mixed with a precisely controlled flow of steam and cooled, creating a supersaturated aerosol. Particles inside this aerosol undergo condensational growth, increasing them to a size typically between 1 and 4 µm in diameter

10 (Orsini et al., 2003). These grown particles are then collected into liquid with a very high efficiency through wetted impaction methods. The direct injection of steam allows for ~~high~~ effective supersaturations to be achieved with high~~er~~ flowrate~~s~~ s (Hering et al., 2014). For this reason, steam collection devices can achieve highly concentrated samples, as the ratio of aerosol sample flow to liquid collection flow can be maximized.

~~Both the PILS and GAC report very efficient collection of PM, with efficiencies of:~~The PILS reports a collection efficiency

15 of 97% particle number collection efficiency for particles between 0.03 – 10 µm (Orsini et al., 2003)~~;~~, while the GAC ~~and~~ shows a total mass collection efficiency of~~ ~~ > 99.5% (Huang et al., 2016a). The distinction between number collection efficiency and mass collection efficiency is important. Whilst the PILS system collects efficiency over all particle modes from fine to coarse, the GAC has a low collection efficiency for particles < 150 nm (Dong et al., 2012). This is due to high ultrafine losses inside a wetted annular denuder (WAD) (Simon and Dasgupta, 1993, 1995) used for the GACs gas phase measurements.

20 The collection method typically used to capture particles in SCDs involves the continuous deposition and washing off of particles on a solid surface. Hence, this method relies on particles being soluble in the collection liquid for its reported high collection efficiency. An alternative collection method was proposed in a publication focused on developing a system for the collection of virus aerosols. The impactor plate of a PILS was replaced with a wetted-wall PM cyclone which collects particles into a standing liquid vortex (Orsini et al., 2003). This prevents particles from depositing on a solid surface, allowing them to

25 be captured into the sample liquid for analysis regardless of solubility. Another miniature wetted cyclone system designed to continuously wash the walls of the cone rather than directly collect particles into liquid has also been coupled to a PILS system (Peltier et al., 2007). ~~None of the instruments for the measurement of oxidative potential discussed here have used this method.~~Neither of these alternative collection methods have been adapted for ROS measurement.

1.3.2 Particle Collectors

30 The particle collector (PC) (Takeuchi et al., 2005) is another particle collection method shared by published ~~oxidative potential~~PM-bound ROS devices. Names of similar devices include the mist chamber and aerosol collector. Variants of the PC are used in both the Online Particle-bound ROS Instrument (OPROSI) and the ROS analyser systems. The PC operates by

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collecting PM onto a hydrophilic filter which is continuously wetted with a fine mist of a capture solution. The capture solution drips off the filter into a collection reservoir underneath, removing the water-soluble portion of the collected PM for analysis. The use of a filter allows for the collection of ultrafine PM with a very high efficiency (97.7 % (Takeuchi et al., 2005)) without the need of a condensational growth stage. A disadvantage of the PC system that the collection reservoir limits the ~~sample~~ time

5   resolution of the system due to the continuous mixing of new and old sample.

1.3.3 Liquid Spot Sampler

The o-MOCA system (Eiguren-Fernandez et al., 2017) utilizes a Liquid Spot Sampler (LSS) (Hering et al., 2014) to collect particles for analysis. Similar to the SCDs, the LSS system utilizes a condensational growth process to collect ultrafine particles. However, the method of implementation is significantly different. Rather than mixing the sample aerosol with steam,

10   the aerosol instead undergoes a three-stage water condensational growth process (Hering et al., 2014). The sample aerosol is drawn through a wet-walled tube where it passes through three independently-controlled temperature regions. The induced temperature differentials combined with diffusion of water vapour from the wetted walls of the tube lead to condensational growth of < 10 nm particles (Hering et al., 2014). The grown particles are impacted into a small liquid volume over the period of 3 hours before being pumped off for analysis.

15   The reliance on diffusion to introduce water vapour to the sample limits the operational flowrate, leading the LSS to use three separate 1 L.min^{-1} growth tubes for a total sample flow of 3 L.min^{-1}. The direct impaction into liquid removes the reliance of the PM to be soluble in the collection liquid, allowing for solubility-independent collection.

1.3.4 Measurement Technique Comparisons

Ultrafine PM concentrations are heavily dependent upon source proximity and atmospheric conditions (Sabaliauskas et al.,

20   2013) which can lead to significant variations over short time periods and distances. This, coupled with the short half-life of some ~~exogenous~~ PM-bound ROS species (Fuller et al., 2014; Zhou et al., 2017)~~.~~; indicates that the ~~oxidative potential~~concentration of PM-bound ROS ~~of ambient PM~~ is dynamic and prone to significant changes over short distances and times. Therefore, in order to accurately measure and understand the health impacts of PM-bound ROS ~~oxidative potential~~, ~~ROS~~ monitors must have time resolutions sufficient to accurately quantify these variations.

25   The time resolution of the discussed instruments varies from widely from 3 minutes to 3 hours. It is clear that the SCD and PC based instruments offer much higher potential ~~sample~~ time resolutions than that of the LLS-based OPROSI. Within the SCDs, the PILS-based systems have, at a minimum, half the ~~sample~~ time resolution of the GAC-ROS due to its dual gas and particle phase measurements. This dual measurement also causes the GAC-ROS system to have a low collection efficiency in the ultrafine PM range, indicating that a SCD without a gas phase measurement stage is a superior choice for PM-~~associated~~ bound

30   ROS measurements. The PILS-based Online DTT Monitoring System has the highest ~~sample~~ time resolution of all the discussed instruments. This is ~~because~~ in part due to the total sample liquid volume ~~of the instrument is~~being much lower than

the PC-based systems as it does not ~~requiring~~ require a reservoir ~~as is the case of PC systems~~. For this reason SCDs currently offer the highest potential for high sampling resolution instruments for ~~oxidative potential~~PM-bound ROS measurements.

Aside from the OPROSI, a common disadvantage shared by all current systems is their inability to reliably collect ~~insoluble particles~~PM insoluble in the collection solution for analysis. This is problematic as a significant portion of primary combustion emissions are hydrophobic (Popovicheva et al., 2008), making them insoluble in the aqueous-based solutions used for the DCFH and DTT probes. ~~Furthermore, i~~This can result in an underestimation in measurements~~t~~ which is not possible to correct for ~~this insoluble fraction~~ in post-analysis of the data using known losses. This is because the water insoluble fraction represents a distinct group of PM with both a separate physiological impact (Delfino et al., 2010), and a different ~~oxidative potential~~ROS contributions (Verma et al., 2012). Future systems should endeavour to adapt or create new methodologies to allow for the collection of insoluble particles to improve the understanding and toxicity of aerosol oxidative capacity.

~~1.4 Manuscript~~1.4 Manuscript Focus

This paper discusses the design and testing of a novel instrument called the Particle Into Nitroxide Quencher (PINQ). The PINQ has been developed to address the need for an accurate and repeatable method of measuring the ~~oxidative potential~~PM-bound ROS present in ~~of~~ aerosols. Informed from the current literature on the field, the instruments collection mechanism is based on a steam collection device, with ~~a wetted-wall cyclone continuously collecting~~ PM collected directly into a miniature liquid vortex ~~solution~~ containing the BPEAnit ROS assay. The fluorescence increase of the BPEAnit probe is measured using a purpose-build flow through fluorimeter with a low internal volume and minimal flow-path length to ensure rapid quantification of ~~oxidative potential~~PM-bound ROS.

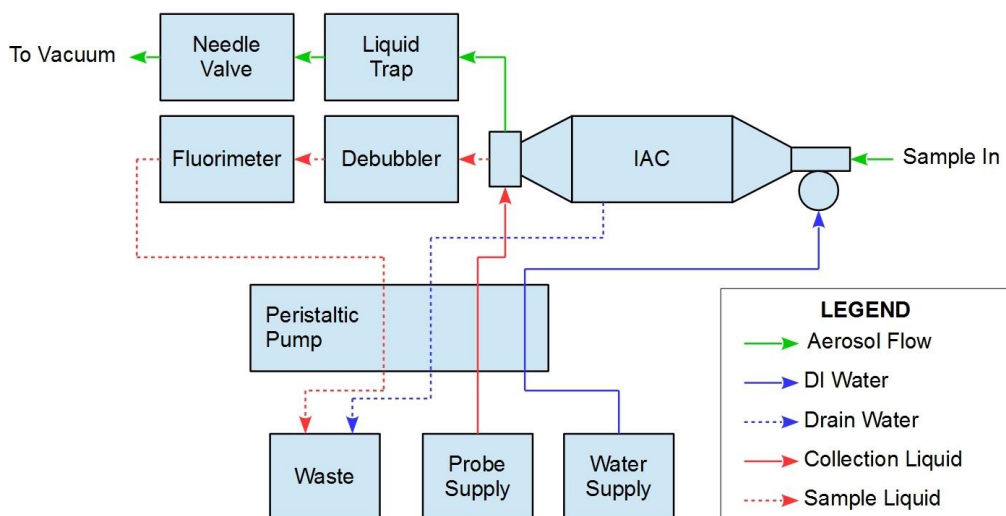## 2. Instrument Description
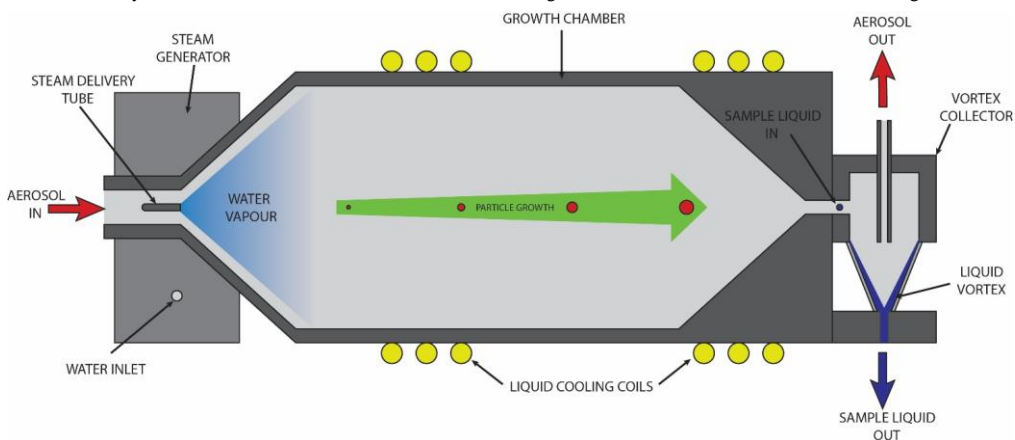
2.1 PINQ Layout

Figure 1 ~~Diagram of the PINQs Insoluble Aerosol Collector (IAC) showing key components including: the aerosol inlet, steam generator, growth chamber and vortex collector.~~*Diagram of the PINQ system showing all major components and the aerosol and liquid flow paths linking them.*

The flow diagram of the PINQ can be seen in *Figure 1*~~*Figure 1*~~~~Figure 1~~, including all key components of the system and their corresponding connections through liquid and aerosol flows. The aerosol is collected in a novel instrument called the Insoluble Aerosol Collector (IAC), in which PM is collected continuously into a liquid sample independent of size or chemical composition. The sample solution is then debubbled and passed through a purpose-build flow-through fluorimeter to quantify ~~oxidative potential~~PM-bound ROS.

The standard sample flow rate for the instrument is 16.7 L.min^{-1} (1 m^3.hr^{-1}), which is set prior to sampling using a needle valve connected to vacuum. This has been found stable over 24 hour sampling periods. The corresponding steam generator water supply for this flowrate is 1.5 mL.min^{-1}. ~~Aerosol flowrate through the system is regulated via a needle valve connected to a vacuum, whilst l~~All liquid flows are controlled using a peristaltic pump~~.~~ and hence are given in volumetric rather than mass units for completeness. The influence of temperature variation on liquid flow during normal laboratory conditions (20 - 30 ºC) results in a negligible impact on instrument performance. In more extreme temperature environments it may be necessary to regulate liquid reservoir temperatures and correct for variations. ~~The aerosol is collected in a novel instrument called the Insoluble Aerosol Collector (IAC), in which PM is collected continuously into a liquid sample independent of size or chemical~~

composition. The sample solution is then debubbled and passed through a purpose-build flow-through fluorimeter to quantify oxidative potential.

2.2 The Insoluble Aerosol Collector (IAC)

The PINQs aerosol collection stage, the IAC, is categorized as a steam collection device. The sample aerosol is mixed with water vapour to generate a supersaturated aerosol in which the PM ~~underdo~~ undergo condensational growth~~.~~. These grown particles are collected with a high efficiency into a continuously flowing sample solution inside a solvent resistant vortex collector. The system can be divided into four main sections: inlet; growth chamber; vortex collector; and steam generator.

Figure 2 Diagram of the PINQs Insoluble Aerosol Collector (IAC) showing key components including: the aerosol inlet, steam generator, growth chamber and vortex collector.

2.2.1 Inlet

The IAC inlet is a 10 mm inner diameter tube contain~~ings~~ a 1/16 in outer diameter~~fine~~ aluminium steam delivery tube concentric to the inlet, oriented in the direction of flow. A precisely controlled mass flowrate of water vapour is injected into the aerosol flow through this delivery tube. The aerosol and water vapour are then turbulently mixed through a~~n~~ 45 degree expanding cone, creating a homogenous supersaturated mixture. ~~The standard sample flow rate for the instrument is 16.7 L.min⁻¹ (1 m³.hr⁻¹) with a corresponding steam generator water supply of 1.5 mL.min⁻¹.~~

2.2.2 Growth Chamber

The supersaturated aerosol is passed through a~~n aluminium~~ cylindrical growth chamber (50 mm inner diameter, 140 mm length) to cool the mixture and allow time for particle condensational growth to occur. The chamber is actively liquid cooled

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to ambient temperature using a liquid cooling system and copper tubing compressed around the chamber to prevent any excess heat build-up in the system from the steam supply or the aerosol sample. A drain at the base of the chamber removes excess condensation on the chamber walls. Grown particles exiting the growth chamber are accelerated through a 30 degree contracting cone into the vortex collector.

2.2.3 Solvent-Resistant Vortex Collector

The vortex collector is a specially designed aerosol capture device which collects particles into liquid regardless of solubility. The concept was and dimensions are based on a wetted-wall cyclone described previously in literature (Orsini et al., 2008), with name vortex collector introduced here to differentiate it from the design of a standard miniature PM cyclone (Gussman et al., 2002; Kenny et al., 2000). . Both share similar It is similar to a miniature PM cyclone in design, with the dimensions of the internal cone and the inlet and outlet tubesgeometries which are selected in order to create a stable air cyclone inside the device. However, whilst the PM cyclone deposits particles onto the solid surface of the cone, the vortex collector deposits particles directly into a collection liquid. This is achieved through the continuous injection and removal of liquid at the top and base of the cone, respectively. The inertial force of the air cyclone acts on the liquid as it passes through the cone, causing the liquid to spread on the cone wall and form a standing liquid vortex. Grown particles entering into the cyclone collector from the growth chamber impact into this liquid vortex and are captured directly into the liquid stream.

In principle the design of a vortex collector is similar to that of a PM cyclone. However, whilst the cyclone design focus is on cut-off size and shape; the vortex collector is predominantly concerned with the formation of a stable liquid vortex. The condensational growth stage prior to the collector removes the significance of the cut-off size and shape which characterize PM cyclones. Instead, the main requirement is that particles are grown above the size at which maximum collection efficiency is achieved. As such, the dimensions specified in the literature regarding PM cyclones can be altered to achieve the desired standing liquid vortex without risking performance. In particular, the aerosol inlet and exit holes can be narrowed to accelerate the aerosol flow into the collector in order to better form a liquid vortex (Orsini et al., 2008). The location of liquid injection is also important, with the most stable vortex achieved when the liquid is injected into the aerosol stream before entering into the collector itself. Without these modifications the resulting collector does not form a standing liquid vortex for direct collection of PM into liquid (Peltier et al., 2007). Instead it could be more aptly described as a washed-wall cyclone, with a lower reported collection efficiency for insoluble particles.

Parameters influencing this includeBeyond these design points other parameters governing the performance of the vortex collector, including: dimensions; liquid and aerosol flowrates; sample liquid; temperature; materials; and surface finish,; making prediction of vortex formation difficult. To this end, the vortex collector was constructed using a combination of aluminium and stainless steel with a transparent fluorinated ethylene propylene (FEP) cone. This ensures the instrument is solvent resistant for use with DMSO in the PINQ system, whilst also allowing for visual confirmation of vortex formation. This device was chosen over simpler impaction methods for two reasons. First, the vortex collector collects particles directly into liquid allowing for solubility-independent particle collection. Second, the liquid vortex ensures that the collected PM is

homogenously mixed with the sample liquid exiting the cone base. When integrated into the PINQ, this factor coupled with the diffusion limited reaction between BPEAnit and collected ROS leads to the sample liquid exiting the base being fully reacted and ready for quantification.

2.2.4 Steam Generator

5 A stable and precisely controlled steam flowrate is essential for effective condensational growth of ultrafine particles. Initially a design similar to that described in literature was used (Orsini et al., 2003), in which a regulated water flow was input into a heated ~~copper~~ stainless steel tube. A similar design was attempted with both one and two stage heating, but was fraught with stability issues. This was attributed to the system having a low thermal mass, causing an unstable equilibrium point in the system. ~~Furthermore, the gradual corrosion of the copper tube lead to concerns over potential sample contamination.~~ To remedy
10 th~~ese~~is issue~~s~~, a new generator was proposed with a larger, insulated thermal mass.

 The new generator design consisted of a cylindrical aluminium block sheathed in thermally insulating polytetrafluoroethylene (PTFE). The aluminium block contains a sealed internal chamber with narrow inlet and exit holes bored perpendicularly at the base and top, respectively. The block is maintained at a constant temperature by the use of two heater cartridges and a thermocouple driven with a Novus N1020 PID controller. A flow of water regulated by a peristaltic pump is continuously
15 input into the base of the chamber through the inlet hole, where it vaporizes and expands, before being ejected through the exit hole. The aluminium steam delivery tube from the inlet section is inserted directly into the exit hole to minimize cooling and reduce system size. This design greatly improved stability and allows for long periods of unattended sampling.

2.3 Flow-Through Fluorimeter

A compact flow-through fluorimeter was designed to provide fast and accurate measurement of sample fluorescence for ROS
20 quantification. The sample liquid fluorescence is continuously measured in a small flow-through quartz cell contained within a stainless steel housing. The excitation source is a 450 nm diode laser, and the fluorescence response measured perpendicularly with an Oceanoptics USB2000+ spectrometer. The laser and spectrometer are directly mounted to the stainless steel housing to remove the need for optical fibre connections, reducing setup complexity and minimizing size. The setup is controlled using a dedicated LabVIEW-based application.

25 ### 3. Methodology

This study is divided into two investigations. The first is the measurement of the IAC collection efficiency. The second is the characterisation of the PINQ system fluorescence response. Flow diagrams of experimental setups, further methodology details, and calculations can be found in the supplementary material.

3.1 IAC Characterization

3.1.1 Particle Mass Collection Efficiency

The collection efficiency of the IAC for both fine ($PM_{2.5}$) and ultrafine ($PM_{0.1}$) particles was investigated through the comparison of mass concentration of ammonium sulphate (AS) collected with the IAC and those collected onto membrane filters. Sample aerosol was generated using a solution of AS ammonium sulphate in DI water in a Mesa Labs 6 Jet Collision Nebulizer. Sample was dried and diluted to provide the required sample flowrate before being sampled by the IAC, filter (Whatman Nuclepore polycarbonate membrane, 25 mm diameter, 0.2 µm pore size) and scanning mobility particle sizer (SMPS) (TSI 3071 Classifier, TSI 3772 Condensation Particle Counter, Aerosol Instrument Manager (AIM) software). IAC samples were collected into sealed quartz sample vials. Sample filters were collect and placed in quartz vials where they were sonicated for 5 minutes in 1 mL of solution. Samples were refrigerated until ion chromatography (IC) analysis was performed by the Central Analytical Research Facility (CARF) based at the Queensland University of Technology (QUT). Measurements were performed using a Dionex Integrion High Precision Ion Chromatography setup with a Dionex AS-AP autosampler. An AS18 Column (150 mm x 2 mm) with an isocratic 0.30 mL/.min⁻¹ flow was used. 0.1, 1, 5, 10, 20 and 100 ppm standards were used as calibration points.

3.1.2 Size Dependent Particle Number Collection Efficiency

The size dependent particle number collection efficiency was investigated using Di-Ethyl-Hexyl-Sebacat (DEHS) particles. This was chosen as the droplet activation diameter is not dependent on the composition of the particles if they are hydrophobic (Andreae and Rosenfeld, 2008). Particles were generated using a Mesa Labs 6 Single Jet Collision Nebulizer containing a solution of DEHS in ethanol. Monodisperse particle sizes were size-selected from the resulting polydisperse aerosol using a TSI 3071 Electrostatic Classifier for sizes between 30 and 300 nm. The aerosol was then diluted to provide sufficient sample aerosol flowrate. A 3-way valve was used to rapidly switch between pre and post instrument sampling, with particle concentrations for each size found by averaging a 60 s sample from a TSI 3025 butanol-based CPC after system had stabilized. A nafion dryer was attached to the CPC inlet to prevent the high humidity of the sample influencing measurements.

3.2 PINQ Characterization

The PINQ was assembled for characterization as per the layout described in *Figure 1Figure 1*Figure 1. A 1 µM solution of BPEAnit in DMSO was prepared as the sample solution for the PINQ. A 1.5 mL.min⁻¹ steam generator water feed rate and a 1 mL.min⁻¹ sample flowrate was used. The PINQ inlet was connected to a three way valve, with one port connected to a continuous supply of high purity nitrogen gas and the other connected to a combustion sample chamber. A cigarette was left to smoulder in the sample chamber for 5 min before being extinguished. The PINQ then sampled continuously, with the supply switched between nitrogen gas and cigarette smoke every minute for a total of eight samples.

The fluorescent response of the BPEAnit probe is expressed as an equivalent nanomolar increase in the concentration of the methyl adduct of the probe (BPEAnit-Me). The conversion factor for this is found through the slope of a calibration curve generated from fluorescence measurements of BPEAnit-Me standards of various concentrations. For PINQ measurements this equivalent response is then normalized against the ratio of liquid supply flowrate to aerosol sample flowrate; resulting in a measure of ~~oxidative potential~~PM-bound ROS in equivalent concentration of BPEAnit-Me per volume of air in nmol.m^{-3} using *Equation 1*~~Equation 1Equation 1~~. The limit of detection was calculated as three times the standard deviation of a set of 20 s blanks collected while sampling nitrogen.

Equation 1

$$C_{ROS} = FR * CF * \frac{q_{ls}}{q_A}$$

Where: C_{ROS} is the concentration of ROS in nmol.m^{-3}; FR is the fluorescence response of the spectrometer in unitless counts; CF is the calibration factor calculated from the calibration curve calculated as nmol.L^{-1}.counts^{-1}; q_{ls} is the liquid sample flowrate in L.min^{-1}; and q_A is the aerosol sample flowrate in m^3.min^{-1}.

4. Results and Discussion

4.1 IAC Characterization

4.1.1 Particle Mass Collection Efficiency

The IAC investigation was initially focused on mass collection efficiency in order to directly measure the fraction of aerosol collected into the sample liquid. As particle mass is ~~exponentially~~ proportional to the third order of particle size it was necessary to consider aerosols in terms of mass distribution when evaluating results. To this end, the averaged SMPS particle size distribution of the ammonium sulphate aerosol sample was fitted with a log-normal distribution and a corresponding mass distribution calculated. These distributions along with those of the ultrafine samples discussed below can be found in the supplementary material. The ultrafine particles (PM$_{0.1}$) correspond to ~~approximately~~ 3 ± 5 % of the total mass of the sample, whilst the entire mass distribution was in the fine particle size range (PM$_{2.5}$), hence the collection efficiency calculated using this aerosol is referred to fine particle collection efficiency. The averaged collection efficiency and standard error for the collected efficiency for fine particles is calculated as:

$$CE_{fine} = 1.00 \pm 0.04$$

As the majority of the mass in the previous tests was contained in the particles larger than 100 nm (~97 %) this result does not necessarily indicate a high collection efficiency of ultrafine particles. Therefore, these experiments were repeated with the larger ammonium sulphate particles removed from the sample using an impactor as detailed in the supplementary Sect. S2.1 ~~Sect. 4.1.1~~. The averaged SMPS particle size distribution over the sample collection period was fitted with a log-normal distribution multiplied by a logistic function to emulate the size cut-off generated by the impactor, and a corresponding mass

distribution was calculated. The ultrafine particles (<~100nm) correspond to ~~approximately~~ 80 ± 10 % of the total mass of the sample, which is considerably higher than the previous size distribution.

The generated particle mass concentrations with the impactor in front of the atomiser (ultrafine particle experiment) were over 60 times lower than the $PM_{2.5}$ experiments. In order to ensure the collected samples contained measurable concentrations of

5 sulphate ions, the flow through the vortex collector was reduced from 1.00 ml.min^{-1} to 0.15 ml.min^{-1}. This increased the residence time of the sample liquid in the vortex collector for the same aerosol flowrate, resulting in a more concentrated sample.

The averaged collection efficiency and corresponding standard error are calculated as:

$$CE_{ultrafine} = 1.05 \pm 0.06$$

10 The error of the ultrafine collection efficiency is larger than that of the fine collection due to the significantly lower aerosol sample concentration. However, the results are within error of each other, indicating that the IAC collects ~~ultrafine~~ both fine and ultrafine particles ~~as well as fine particles~~ with a very high efficiency. This is an expected result for steam collection devices, which will typically collect all particle sizes with equally high efficiency due to condensational growth of particles in the growth chamber well into the ultrafine size range.

15 **4.1.2 Steam Dilution Factor**

The sample liquid entering into the IAC was doped with a known quantity of sodium chloride. The steam dilution factor (SDF) was determined from the change in the chloride ion ~~Cl⁻~~ concentrations before and after the liquid feed passed through the vortex collector. Relevant measurements and individual calculated steam dilution factors for each sample can be found in the supplementary material. The average steam dilution factor for a standard liquid supply of 1 mL.min^{-1} (SDF_{SF}) was calculated

20 as:

$$SDF_{SF} = 0.882 \pm 0.004$$

This corresponds to a 0.134 ± 0.007 mL.min^{-1} contribution of condensed water into the sample flow.

The averaged steam dilution factor for a lowered liquid supply flowrate of 0.15 mL.min^{-1} (SDF_{LF}) was calculated as:

$$SDF_{LF} = 0.527 \pm 0.007$$

25 SDF_{LF} is lower than that that of the SDF_{SF}. This reduction indicates that the ratio of condensed water to sample flowrate has increased in the liquid sample exiting the PINQ. Despite this, the effective contribution of condensed water to the sample flow for SDF_{LF} was calculated as 0.136 ± 0.007 mL.min^{-1}; which is within error of the condensation water contribution calculated for SDF_{SF}. This shows that the condensation rate in the sample is independent of: liquid sample flowrate; PM mass; and particle number concentration (PNC). This indicates the principle source of condensation in the sample is from inside the cyclone

30 itself, which is directly proportional to the water flowrate input into the steam generator. This ensures that the steam dilution factor can be accurately corrected for in all measurements.

Lowering the liquid supply flowrate allows for higher concentrations of aerosol in the sample stream. In theory this could be further applied to improving the sensitivity of the PINQ. However, the corresponding increasing influence of steam dilution

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presents a limitation in the potential application of this. It is essential to keep the contribution of condensed water below 30% of the total sample (SDF > 0.7) when using a DMSO solution of the BPEAnit probe as larger percentages of water in DMSO will cause a nonlinear change in the fluorescent signal.

4.1.3 Size Dependent ~~Insoluble~~ Hydrophobic Particle Collection Efficiency

Ammonium sulphate was selected as the test aerosol for the mass collection efficiency investigation due to its ~~approximately spherical particle size~~shape being close to spherical (Biskos et al., 2006) and detectability with ion chromatography. However, due to its high hygroscopicity it will undergo condensational growth at a much lower supersaturation than those required for hydrophobic aerosols (Popovicheva et al., 2008). To ensure that the collection efficiency is independent on the chemical composition of particles, measurements of the number concentration collection efficiency with hydrophobic ~~insoluble~~ particles were conducted.

Size dependent hydrophobic particle number collection efficiency was measured through the size preclassification of DEHS aerosol, and corresponding measurements of PNC entering and exiting the PINQ. Collection efficiency was corrected for inlet and chamber losses which were estimated to be 1 minus the lower limit of the ultrafine mass collection efficiency. The calculated particle number collection efficiencies at each tested size are shown in Figure 3.
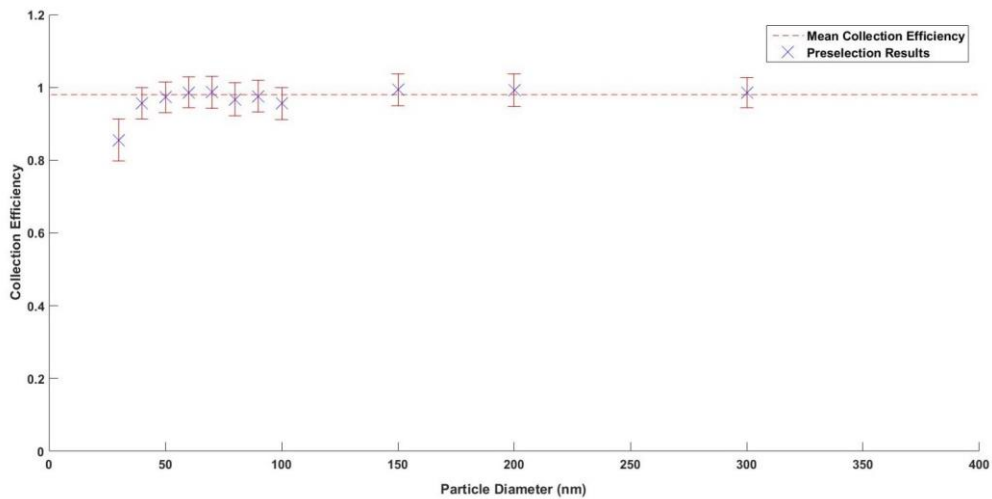
Figure 3 Calculated collection efficiencies for DEHS preselection measurements with standard error bars and mean collection efficiency

The mean collection efficiency was calculated as:

$$CE_{PNC} => 0.97$$

15

As it was not possible to generate sufficient DEHS test particles smaller than 30nm, the cut-off size corresponding to 50% of the maximum collection efficiency can only be extrapolated from the above graph to be < 20 nm. This is an improvement over significant improvement over a the earlier vortex-based wetted-wall cyclone design which reported a collection efficiency of > 0.88 with a cut-off size of 30 nm (Orsini et al., 2008). It is also higher than the 0.69 collection efficiency reported by the washed miniature cyclone developed for organic carbon measurements (Peltier et al., 2007).

An important note in these comparisons is that the two variants found in literature both used direct measurements of insoluble particles collected in liquid after exiting the instrument. The collection efficiency calculated here is the efficiency of initial collection into the liquid, and would need to be corrected for losses in the liquid flow path between collector and detector for a full comparison. This was not explored as liquid line losses are not an issue in the application of the IAC in the PINQ. Reaction with the BPEAnit probe is effectively completed instantaneously upon collection, meaning particles lost in the liquid path have already fully reacted with the BPEAnit probe.

This ensures that the IAC will be able to capture the majority of particles generated by various atmospheric sources.

4.2 PINQ Characterization – Response Time and LOD

The response time of the PINQ was separated into two parameters: a time delay between a source change and the corresponding start of change in fluorescence; and the mixing time taken for the fluorescence response to become completely independent of the previous source. An example of the fluorescence response of the BPEAnit probe when the instrument was switched from the ROS source (cigarette smoke) to nitrogen along with relevant key times is shown in Figure 4. In the 8 samples taken the signal strength of the cigarette smoke was approximately 60 times the magnitude of the background noise.
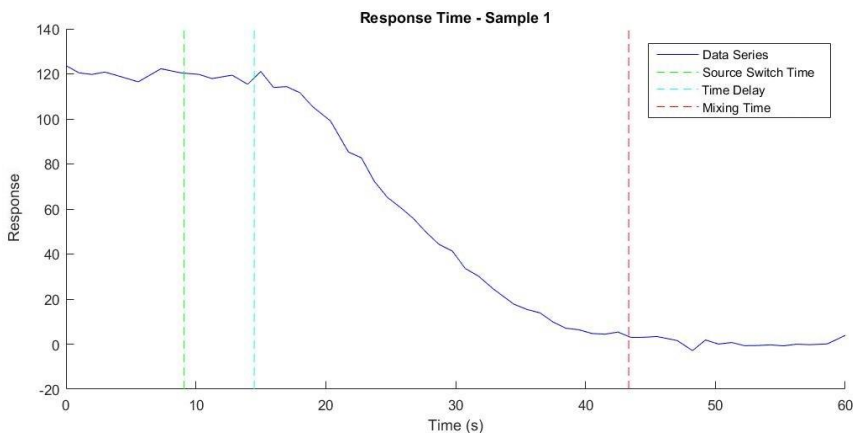
Figure 4 the fluorescence data series over time for Response Time - Sample 1, with: the time the source was switched from cigarette smoke to nitrogen (Source Switch Time); the time at which the fluorimeter began to measure a decrease in signal (Response Time Delay); and the time at which the signal reduced to background (Mixing Time Delay)

The averaged values of time delay and mixing time of the PINQ for the eight samples taken and corresponding standard errors were calculated as:

$$time\ delay = 6.3 \pm 0.6\ s$$

$$mixing\ time = 32 \pm 1\ s$$

The time delay of 6.3 s represents a small time correction factor which does not strongly influence instrument performance. In contrast, the mixing time of 32 s is a key value in determining the limits of instrument ~~sample~~ time resolution. This value indicates the minimum averaging time which provides independent data points, and is directly proportional to both: the liquid sample flowrate; and the internal liquid volume of the liquid sample flow path inside the instrument. An increased liquid sample flowrate above the tested 1 mL.min^{-1} will result in a faster time resolution. However, this will do so at the cost of a lower ratio of collection liquid flowrate to aerosol sample flowrate, diluting the aerosol and reducing instrument sensitivity. Internal liquid volume was minimized through the use of small bore 1/16" OD tubing for all flowpaths and a custom-made low internal volume fluorescence cell. An unavoidable limiting factor in reducing the mixing time is the internal volume of the cyclone, which cannot be minimized further without impacting instrument performance.

The results of this experiment indicate that the system requires a total of ~ 40 seconds to reach equilibrium response when connected to an aerosol source. When performing measurements on the ~~oxidative capacity of PM~~PM-bound ROS it is necessary to account for any contributions from the gas phase by alternating sampling between the total aerosol source, and the source after filtering to remove the particle-bound ROS. Therefore, the time resolution of the PINQ is determined by the sum of the total response time, and the time required to average the signal for an accurate measurement. An averaging period of 20 seconds was selected, leading the PINQ to have a time resolution of 1 minute when performing alternating gas and total phase measurements (See Sect. 4.3). A total of 234 blanks of 20 seconds averaging time sampled with nitrogen were collected and normalized as equivalent nmol of BPEAnit-Me per cubic meter of air as detailed in Sect. 00~~4.2~~. The limit of detection of the PINQ was determined as three times the standard deviation of these blanks.

$$LOD = 0.08\ \frac{nmol}{m^3}$$

The PINQ has a lower LOD than other online systems with responses normalized per volume of air sampled for two primary reasons. First, the IAC has a very small ratio of liquid sample flow to ~~aeprosol~~aerosol sample flow. The ensures a more highly concentrated sample than those of particle collector-based systems, which reported LODs between 4 nmol.m^{-3} (Wragg et al., 2016) and 2 nmol.m^{-3} (Zhou et al., 2017). The GAC-ROS system has similar aerosol and liquid flows, resulting in similarly concentrated sample and hence a closer LOD of 0.12 nmol.m^{-3} (Huang et al., 2016a). The second factor contributing to the lower PINQ LOD is the different ROS probe used. The BPEAnit probe does not autooxidise in the same manner that the DCFH probe used by the other system discussed here, resulting in more stable blanks and hence a lower LOD.

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4.3 PINQ Response –Particle and Gas Phase Contributions

As has been shown in Sect 4.1. the IAC stage of the PINQ collects PM with a very high collection efficiency. However, experiments with the PINQ system also show sensitivity to gas phase products. In order to accurately quantify the PM-bound ROS the PINQ response must be corrected for the gas phase contributions during measurements. This is achieved by alternately
5   sampling with and without a HEPA filter, resulting in both particle and gas phase measurements. This method was chosen over the use of a gas denuder for two reasons. First, gas denuders can cause significant losses of ultrafine particles (Stevanovic et al., 2015). Second, the gas phase can contain significant concentrations of ROS (Stevanovic et al., 2017) which cannot be investigated if scrubbed with a gas denuder.

The exact mechanism and efficiency with which the IAC collects the gas phase contribution is unknown. Likely it is a
10   combination of: the collection of water-soluble gas species during the condensational growth stage; and DMSO soluble species during interactions with the collection liquid inside the vortex collector. The quantification of these effects is a complex issue as it will likely be dependent upon each gas species solubility in both water and DMSO. As such the gas phase response is considered semi-quantitative, with its characterization beyond the scope of this manuscript. Hence the PINQ is presented here as an instrument for the measurement of PM-bound ROS only. ~~In order to quantify the particle phase ROS signal, it is necessary~~
15   ~~to alternately sample HEPA filtered and unfiltered air due the potential of contributions from the gas phase. This method was~~ ~~chosen over the use of a gas denuder as the gas phase can contain significant concentrations of ROS relevant to oxidative~~ ~~capacity (Stevanovic et al., 2017). The quantification of this gas phase signal is a complex issue as it will likely be dependent~~ ~~upon each gas species solubility in both water and DMSO. For this reason the quantification of the gas phase collection~~ ~~efficiency of the PINQ is beyond the scope of this paper, and any gas phase data presented in manuscripts will be semi-~~
20   ~~quantitative in nature until further study is undertaken.~~

5.   Summary

This manuscript's first focus was on the design and characterization of the IAC as a high efficiency aerosol collector for use in ~~ROS measurements~~the PINQ system. It is defined as a steam collection device, in which the sample aerosol is continuously
25   mixed with a stream of water vapour to generate a supersaturated mixture, growing the particles into large liquid droplets to ensure high efficiency capture independent of initial particle size. The grown droplets are collected ~~into a~~ continuous~~ly into a~~ liquid vortex ~~liquid sample stream~~ inside a specially designed vortex collector. ~~This component is similar to a miniature PM~~ ~~cyclone, in which a standing liquid vortex is generated in the cone section to collect aerosol directly into liquid.~~ This was designed over a simpler impaction system as it allows the capture of ~~insoluble particles by removing the necessity for an~~
30   ~~impaction surface~~insoluble in the collection liquid~~; which insoluble particles will typically adhere to rather than collecting into~~ ~~the liquid sample~~. The vortex collector ~~was designed to be solvent~~is also solvent resistant and allow~~s~~ for visual confirmation of the liquid vortex ~~to ensure suitability for application in the PINQ system.~~.

The IAC mass collection efficiency was determined to be within error of 1.00 for both fine and ultrafine ~~particle mass distributions~~ammonium sulphate particles. This result indicates that provided particles seed liquid droplets, they are collected with a very high collection efficiency. However, ~~This result was expected as the condensational growth mechanism used ensures high collection efficiency provided the particles form liquid droplets; and t~~hydrophilic particles like ammonium sulphate will undergo condensational growth more readily than hydrophobic particles~~he hydrophilic nature of the . ammonium sulphate particles allows for the easy formation of droplets in the supersaturated aerosol regardless of initial particle size~~. As the IAC must collect particle independent of chemical composition for use in the PINQ system, the number collection efficiency of highly hydrophobic DEHS test particles was also investigated. Using these particles the number collection efficiency was found to be > 0.97 with a cut-off size of < 20 nm. This result shows that the IAC is capable of collecting particles with a high efficiency independent of particle size and composition.

The PINQ was developed to measure ~~oxidative potential~~PM-bound ROS using the BPEAnit chemical probe in conjunction with the IAC. A 1 µM solution of BPEAnit in DMSO is used as the sample collection liquid, with particles collected directly into the probe solution inside the IAC vortex collector. The rapid mixing of liquid inside the vortex coupled with the diffusion limited reaction between the probe and any ROS collected ensures the liquid exiting the IAC is fully reacted. The sample liquid is then debubbled and input into a specially designed flow-through ~~through~~ fluorimeter. Finally, the fluorescence response measured is converted into ~~oxidative potential~~PM-bound ROS through calibrations performed on known concentrations of BPEAnit-ME, and are expressed in nmol.m^{-3}.

The PINQ is also sensitive to gas phase ROS. Therefore, in order to quantify PM-bound ROS it is necessary to account for gas phase contributions by periodically filtering the aerosol sample. ~~In order to quantify the particle phase ROS signal, it is necessary to alternately sample HEPA filtered and unfiltered air due the potential of contributions from the gas phase. This method was chosen over the use of a gas denuder as the gas phase can contain significant concentrations of ROS relevant to oxidative capacity (Stevanovic et al., 2017). The quantification of this gas phase signal is a complex issue as it will likely be dependent upon each gas species solubility in both water and DMSO. For this reason the quantification of the gas phase collection efficiency of the PINQ is beyond the scope of this paper, and any gas phase data presented in manuscripts will be semi-quantitative in nature until further study is undertaken.~~

Experiments on response time with a standard sample flowrate of 1 mL~~/~~.min^{-1} indicate that after switching sources the PINQ signal takes ~ 40 seconds to ~~stabilize~~reach equilibrium response. Therefore, with a 20 second sample averaging time the sample time resolution of the instrument is one minute when alternating between ~~HEPA~~ filtered and unfiltered samples. With this time resolution the LOD of the instrument was determined to be 0.08 nmol.m^{-3}. Both the time resolution and LOD of the instrument are considerably lower than other instruments currently found in literature, indicating the PINQ is a viable candidate for the quantification of ~~aerosol oxidative potential~~PM-bound ROS.

Data availability

Collection efficiency of PINQ data is available as part of an online Supplement. For a more detailed description on the design and construction of the instrument or interest in instrument evaluation, please contact the corresponding author.

Competing interests

The authors declare that they have no conflict of interest.

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