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Johnson, Graham R. and Fletcher, Catherine A. and Meyer, Nickolas K. and Modini, Robin L. and Ristovski, Zoran (2008) *A robust, portable H-TDMA for field use*. *Journal of Aerosol Science*, 39(10). pp. 850-861.

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## **A robust, portable H-TDMA for field use.**

G. R. Johnson, C. Fletcher, N. Meyer<sup>1</sup>, R. Modini, Z. D. Ristovski<sup>\*</sup>.

*International laboratory for Air Quality and Health, Queensland University of Technology, Brisbane Queensland, Australia.*

<sup>1</sup>Now at the Institute for Aerosol and Sensor Technology, FHNW, Switzerland.

<sup>\*</sup>Corresponding author. GPO Box 2434, Brisbane 4001, Australia. Tel.: +6173138-1129; fax: 6173138-9079. E-mail address: [z.ristovski@qut.edu.au](mailto:z.ristovski@qut.edu.au) (Z. D. Ristovski)

### **Abstract**

The complexity of a typical hygroscopicity tandem differential mobility analyser (H-TDMA) can make it an awkward instrument for fieldwork. An improved design is presented here which is both light weight and portable and permits very accurate, reliable hygroscopic growth, deliquescence and efflorescence measurements for aerosols over a continuous relative humidity range from 10% to 98% without reconfiguration.

The method achieves this through three significant advances in H-TDMA design: Firstly, the approach regulates the humidity by rapidly alternating the air flow between a dryer and a saturator, with the time spent in each path controlled by a feedback loop connected to the humidity sensor. Secondly the temperature of the aerosol humidifier is directly coupled to that of the wet DMA by enveloping the humidifier in the wet DMA's excess air flow. Thirdly, a novel arrangement of two Nafion<sup>TM</sup> tubes in the humidifier allows for high humidities without needing to pre-wet the aerosol flow.

Keywords: H-TDMA, Relative humidity, hygroscopic growth, deliquescence

# 1 Introduction

The ability of atmospheric aerosol to absorb water and grow with increasing relative humidity influences the light scattering, cloud condensation nuclei properties, lifetime, and chemical reactivity of these particles. The main two techniques that enable us to measure the change in the amount of water absorbed in an aerosol particle for varying relative humidity are the single particle levitation technique using an electrodynamic balance and the Hygroscopicity Tandem Differential Mobility Analyser (H-TDMA) technique. The second technique is commonly used when conducting field measurements because real time hygroscopicity data can be produced, and submicrometer particles (which make up the majority of the atmospheric aerosol) can be studied, neither of which can be done using an electrodynamic balance.

The HTDMA was first designed by Rader and McMurry (1986) and applied by McMurry and Stolzenburg (1989). This technique is an extension of the TDMA technique (Liu et al., 1978) with the addition of an aerosol humidifier between the two DMAs. A polydisperse aerosol sample enters the first differential mobility analyser (DMA) which selects a narrow particle size range; this aerosol flow is then brought to a chosen humidity before passing into the second DMA, where the resulting size distribution is determined. An increase in particle diameter with increasing humidity indicates absorption of water, and the relative change in diameter is called the Hygroscopic Growth Factor (HGF). As the humidity is higher in the second DMA, it will be referred to as the “wet DMA” or H-DMA.

Advances in H-TDMA design have seen improvements in the areas of humidity, temperature and flow control. These factors influence the accuracy and reproducibility of measurements. In the H-TDMA the roles of humidity and temperature are intrinsically linked, with accuracy in humidity control being strongly affected by temperature. Avoidance of this is generally achieved by placing systems in regions having minimal thermal gradients. These include air-conditioned laboratories (McMurry & Stolzenburg,

1989); water baths (Cubison et al., 2005; T. Hennig et al., 2005; Weingartner et al., 2002); temperature controlled cabinets (Cocker et al., 2001; Prenni et al., 2001) and passive, insulated regions (Virkkula et al., 1999). Humidity control has been achieved by mixing humid and dry air (Biskos et al., 2006; Cubison et al., 2005; McMurry & Stolzenburg, 1989; Weingartner et al., 2002), temperature control of a water bath over which the aerosol sheath air passes (Virkkula et al., 1999) and a combination of the two methods (Cruz and Pandis; 2000).

A new design for a hygroscopicity tandem differential mobility analyser system is presented which is both light-weight and portable and permits very accurate, reliable hygroscopic growth, deliquescence and efflorescence measurements for aerosols over a seamless continuous relative humidity range up to 98% without any reconfiguration. This has been achieved through several design improvements. The first design improvement was aimed to achieve swift adjustment of relative humidity but also be able to maintain steady relative humidity over an extended period of time. This was achieved with a rapid time-based switching between saturated and desiccated sheath air paths in combination with dew-point humidity sensing and a computer-controlled PID loop. Secondly the temperature of the humidifier assembly is directly coupled to that of the wet DMA by enveloping the humidifier in the wet DMA excess airflow. In this way temperature gradients within the part of the system that humidifies the aerosol flow were minimised. Finally, the system incorporates a unique two-stage humidifier which allows a continuous range of aerosol humidification from dry to greater than 98% without separately pre-wetting the aerosol or additionally cooling the system. The humidifier features two Nafion<sup>TM</sup> tubes: the first tube extracts some water vapour from the excess flow after it leaves the DMA, raising the humidity of the aerosol flow; this allows a higher final humidity to be achieved in the second stage Nafion.

## **2 Design Principles**

The following design principles have guided us in constructing the new H-TDMA.

### ***2.1 Requirements for accurate hygroscopic growth measurement***

Calculating the hygroscopic growth factor requires the measurement of the aerosol particle diameter at an accurately known relative humidity (RH).

- The diameter is determined during passage through the entire length of the DMA column. Therefore the humidity in the wet DMA should be as constant as possible throughout the column length.
- Since relative humidity and temperature are linked, the humidity must be measured in the wet DMA column itself, to eliminate the possibility of temperature variation between the point of humidity measurement and the region of diameter measurement.

### ***2.2 Requirements for accurate deliquescence measurement***

The objective of deliquescence measurements is to measure the relative humidity at which water uptake of a dry aerosol begins to occur (deliquescence), as indicated by an abrupt increase in the particle diameter with increasing RH. If the RH is then decreased again, the aerosol will remain in the liquid state, not reverting to the dry state again until the efflorescence relative humidity (ERH) is reached. As this is always significantly below the DRH, it is important that, once deliquesced, a particle is not permitted to experience a drop in RH before the size and humidity are measured. Otherwise deliquescence will appear to have occurred at a lower humidity than it actually did. Similarly, during efflorescence, once a particle has crystallised, it is important that the humidity does not then increase above the ERH before measurement, or it will appear to have crystallised at a humidity that is higher than the true ERH.

To achieve, for example, an accuracy of  $\pm 0.1\%$  RH in deliquescence measurement, one of two requirements must be fulfilled:

- RH must be constrained within  $\pm 0.1\%$  RH at all stages of the humidification and measurement process.

or

- the RH measurement must be at the point of highest RH in the humidified aerosol pathway, while ensuring that the RH doesn't ever drop below the efflorescence RH.

We have used the second approach.

### ***2.3 Requirements for accurate humidity control***

For a given water vapour concentration at constant pressure where surface adsorption of water is at equilibrium, the RH depends only on the air temperature - provided the RH never exceeds saturation where in which case water may be lost from the vapour phase through condensation. Therefore the problem of maintaining constant RH is largely one of maintaining constant temperature.

Temperature gradients can occur for a number of reasons. Local heat sources or sinks in the system will result in steady-state temperature gradients, as different elements will achieve different equilibrium temperatures depending on their proximity to the source or sink. These gradients can be minimised by thermal isolation.

Changes in the temperature of the aerosol or sheath air entering the system will result in temporary temperature gradients because of the thermal inertia of the system. Elements with large thermal inertia will take longer to adapt to a change in operating temperature and lag behind other elements of the system resulting in temporary thermal gradients. Temporary thermal gradients can be minimised by utilising strong thermal coupling between the various elements of the system.

The effect of these temperature differences on humidity is simple to calculate. An empirical expression for the dependence of the saturation vapour pressure of water on

temperature is given by  $p_s(T) = \exp [16.7 - 4060/(T-37)]$ , where the temperature  $T$  is in Kelvins and the saturation vapour pressure  $p_s$  in Pascals (Hinds, 1999). Relative humidity is the amount of water vapour  $p$  expressed as a percentage of the saturation vapour pressure at the appropriate temperature ( $RH=100p/p_s(T)$ ). To see how the relative humidity falls with increasing temperature, assume a constant amount of water vapour is present and consider the derivative with respect to temperature:

$$\frac{dRH}{dT} = \frac{-4060 \times RH}{(T-37)^2} \quad (1)$$

So at a roughly constant room temperature, the decrease in relative humidity with temperature is a linear function of the relative humidity. The RH variations are greater at higher humidities, and can be quite pronounced: at 25 degrees Celsius, a rise in temperature of 0.1 degree decreases the humidity by 0.1 percentage points at a relative humidity of 20%, while at 90% relative humidity the decrease is greater than 0.5 percentage points.

For a typical dew-point hygrometer, the accuracy of the temperature measurement is  $\pm 0.1^\circ\text{C}$ , meaning that the best routinely achievable absolute accuracy for a system using such a hygrometer is approximately  $\pm 0.6\%RH$  when operated at high humidities. The precision that is actually reported by the instrument is  $0.1\%RH$ , and the PID loop is capable of keeping the humidity stable to this level of precision. Thus, while the achievable short term stability may therefore be  $\pm 0.1\%RH$ , the long term repeatability may be no better than  $\pm 0.6\%RH$ .

## 3 Experimental Setup

### 3.1 General design

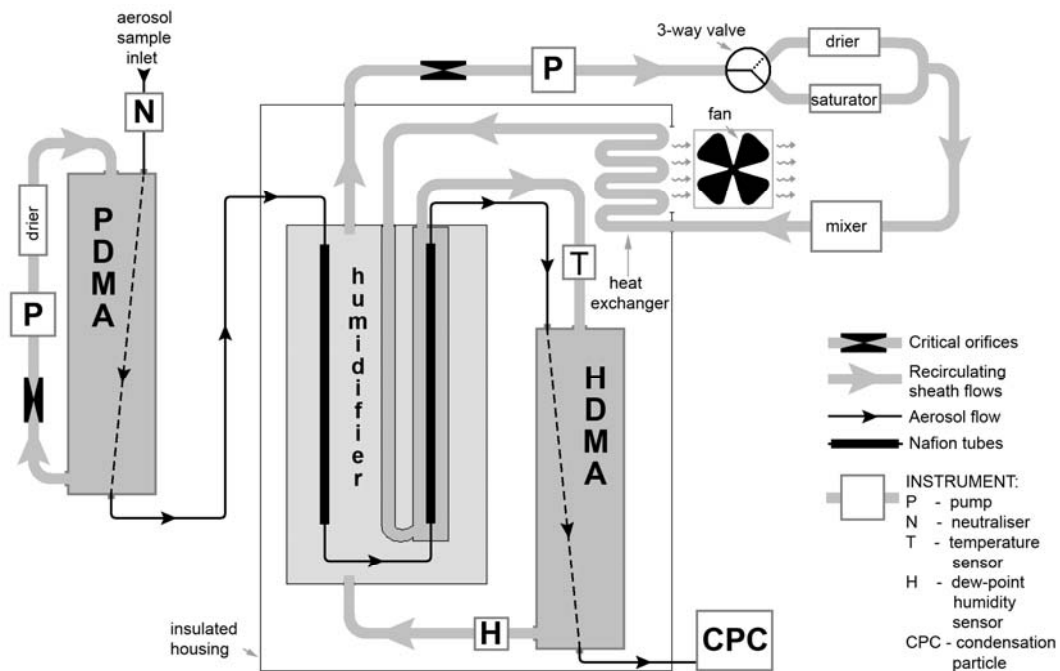
The schematic diagram of the HTDMA used in the current work is presented in Figure 1. There are three major parts of the system: the preclassifier, the aerosol humidification and measurement system, and the humidity control system. The preclassifier consists of a

bipolar neutraliser and a fixed voltage DMA (P-DMA), and is used to select a narrow size range of ambient aerosol.

The aerosol humidification and measurement system is enclosed in a thermally isolated chamber. It consists of a newly designed Nafion™ assembly that ensures the aerosol and sheath air entering the second classifier are at the same set humidity, followed by a second DMA (H-DMA) and a CPC. The second DMA and the CPC work as an SMPS (Scanning Mobility Particle Sizer) and are used to determine the hygroscopic growth of the particles selected by the first DMA.

Both DMAs used were of in-house design based on the TSI 3071 classifiers with some modification. The main modifications were a shorter length of the central column (31.25cm), reducing losses for smaller particle diameters, and fins on the outer side, increasing thermal coupling. Critical orifices are used to regulate the sheath flows, which are both recirculated using closed-loop arrangements (Jokinen & Mäkelä, 1997). As the humid excess air of the H-DMA is recirculated, the sheath air humidifier only adds a small amount of water vapour to the flow. This enables long term monitoring without requiring maintenance – the system could run continuously for more than two weeks without needing to add water to the saturator. The sheath flow rate in the H-DMA is usually 7.5 litres per minute, while the aerosol flow is 1 litre per minute. The P-DMA's recirculated sheath flow is passed through a diffusion drier filled with silica gel, which reduces the RH in the P-DMA below 15%.





**Figure 1: Schematic diagram of the H-TDMA. The preclassifier is shown on the left, the aerosol humidification and measurement system is in the central insulated region, and the humidity control system is shown on the upper right-hand side.**

The humidity control system consists of a saturator, drier and a high-speed 3-way valve. The 3-way valve switches the sheath flow between the saturator and drier. Humidification in the saturator was achieved by passing air through a diffusion dryer which contains wetted Perlite™. Humidity measurements were performed using a dew-point humidity sensor (Optidew Vision – Michell Instruments) placed in the excess air flow.

### **3.2 New aspects compared to previous designs**

#### *3.2.1 Multi stage Humidifier*

The sheath and aerosol air of the HDMA can be humidified independently or simultaneously. In the first case (Cubison et al., 2005; T. B. Hennig et al., 2004;

Svenningsson et al., 2006; Weingartner et al., 2002) a separate humidity control system is needed for the sheath and aerosol air and separate well-calibrated and adjusted sensors are needed. Prior to the humidified aerosol entering the humidification DMA (H-DMA) it is assumed that it should have reached equilibrium with the water vapour present, and no further drying or wetting of the combined sheath-aerosol flow can be permitted as it passes through the classifier column. Biskos et al. (2006) note the importance of this in their replication and discussion of the work of Hameri et al. (2000). They show that equalisation of the aerosol and sheath relative humidity *within* the DMA, and not prior to entering it, leads to erroneous results. If the aerosol and sheath air are not at the same humidity, the residence time of the aerosol in the DMA can influence the amount of hygroscopic growth, which is not desirable.

To ensure that the sheath and aerosol prior to entering the classifier column are at the same humidity, other approaches have also been used. The original approach (Cruz & Pandis, 2000; Johnson et al., 2004; McMurry & Stolzenburg, 1989) was by wetting of the aerosol by the sheath air in a laminar flow reactor, where water vapour diffuses from the sheath to the aerosol flow. As the flow rate of the aerosol is roughly one tenth of the sheath, the maximum relative humidity that can be achieved in this way without additional cooling of the two flows is around 90%. Higher RH can be achieved if the dry aerosol flow is pre-wetted in a separate process. If the pre-wetting process has to increase the humidity above the deliquescence point (in order to achieve the final desired RH) then measurement of the deliquescence points will not be possible. The aerosol will pass the deliquescence point in the pre-wetter and will remain in droplet form even if it is subsequently dried in the laminar flow reactor. Another disadvantage of the laminar flow reactors are the relatively large losses. When used in the field conditions with relatively small concentrations, such as those in remote marine environments, this could be a seriously limiting factor.

Instead of using laminar flow reactors to equalise the aerosol and sheath flows, Nafion<sup>TM</sup> or Gore-Tex tubes can be used (Biskos et al., 2006; Kreidenweis et al., 2005). These are made of a material that allows the passage of water vapour, so that the humidity on either

side of the tube wall can be equalised. When used as an aerosol humidifier, the dry aerosol air is passed through a Nafion tube, with the humid sheath air passing on the outside of the Nafion. If they pass in the same direction for a sufficient time, then after exiting the Nafion the aerosol air will have the same relative humidity as the sheath air. As with laminar flow reactors, the maximum humidity is limited to around 90% with this set-up in the absence of additional cooling.

To be able to equalise the sheath and aerosol humidity to values above 90%, a double Nafion arrangement as presented in Figure 2 has been used. In this arrangement the aerosol is humidified in a two step process. In the first step, the dry aerosol flow is wetted in the first Nafion by the excess air from the H-DMA. This means that the aerosol can come close to the humidity of the excess air but cannot exceed it, which is very important if one is to measure the deliquescence properties. The second humidification step brings the aerosol humidity to the desired sheath/excess humidity with a second Nafion. Here the aerosol flow passes through the Nafion and a wet sheath, with air coming from a saturator, passes on the outside of the tube in the same direction. After exiting the second Nafion the sheath and aerosol flow are in equilibrium at the same humidity. Further as the aerosol flow has been pre-wetted somewhat in the first Nafion, it will not take a large amount of water vapour from the sheath flow which envelopes the second Nafion.

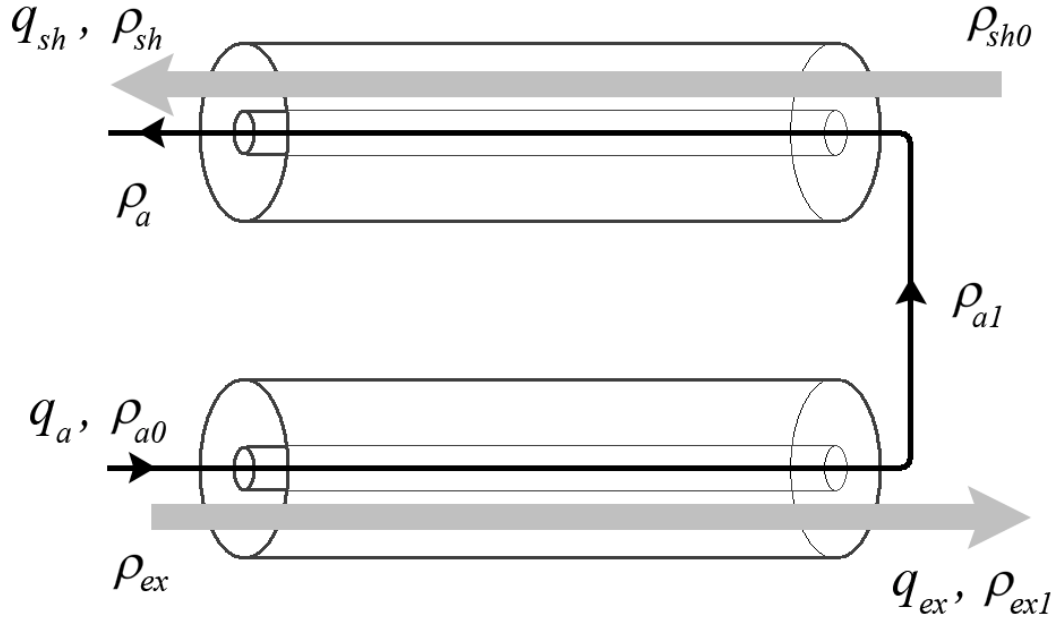
The maximum humidity that can be achieved in the aerosol and sheath air just before entering the classifier can be easily calculated. Assuming that there is no condensation inside the Nafions, and that all flow rates are in thermal equilibrium and at the same pressure, the total mass of water (in vapour phase) entering and exiting either of the two Nafions in unit of time has to remain constant. This can be expressed in the following way:

For the first Nafion:

$$q_a \rho_{a0} + q_{ex} \rho_{ex} = q_a \rho_{a1} + q_{ex} \rho_{ex1} \quad (2)$$

Where:  $q_a$ , is the aerosol flow rate;  $q_{ex} = q_{sh}$  the excess air flow which is equal to the sheath air flow;  $\rho_{a0}$  and  $\rho_{ex}$  are the water vapour densities of the dry aerosol flow and the

excess air before entering the first Nafion respectively,  $\rho_{a1} = \rho_{ex1}$  are the water vapour densities, which are in equilibrium, after exiting the first Nafion.



**Figure 2: Schematic diagram of the airflows through the Nafion tubing. The aerosol (subscript  $a$ ) has a flow rate of  $q_a$ , and goes through the two small Nafion tubes, which sequentially increase the water vapour density in the flow from  $\rho_{a0}$  to  $\rho_{a1}$  and finally to  $\rho_a$ . This water vapour is extracted from the humid air (shown in grey) which flows around each Nafion, at flow rates  $q_{sh}$  and  $q_{ex}$ , with water vapour densities  $\rho$  as labelled.**

The relative humidity can be expressed as the ratio of the water vapour density ( $\rho$ ) and the water vapour density at saturation ( $\rho_s(T)$ ).

$$RH = \frac{\rho}{\rho_s(T)} \quad (3)$$

The saturation water vapour density  $\rho_s(T)$  is only a function of the temperature and pressure, and in our case under the previous assumptions will be the same for all flow rates. Dividing Eq. 2 with the saturation water vapour density and setting the aerosol and sheath/excess flows to commonly used values ( $q_{ex} = q_{sh} = 7.5$ ,  $q_a = 1$ ) we obtain:

$$RH_{a0} + 7.5RH_{ex} = 8.5RH_{a1} \quad (4)$$

In a similar way the following can be written for the second Nafion:

$$RH_{a1} + 7.5RH_{sh0} = RH_a + 7.5RH_{sh} = 8.5RH_{ex} \quad (5)$$

Where  $RH_{sh0}$  and  $RH_{sh}$  are the relative humidity of the sheath air before and after passing through the second Nafion, respectively; Assuming that the relative humidities of the aerosol and sheath flows are equal (after exiting the second Nafion) and that there is no change in humidity in the classifier, then there the humidity will be equal to  $RH_{ex}$ . From the above equations one can obtain the expression for the relative humidity of the flows entering the classifier:

$$RH_a = RH_{sh} = RH_{ex} = \frac{RH_{a0} + 63.75RH_{sh0}}{64.75} \quad (6)$$

Under the assumption that  $RH_{a0} = 0\%$ , i.e. fully dry aerosol air entering the first Nafion and mixing with saturated air coming from the saturator at  $RH_{sh0} = 100\%$ , the theoretical maximum RH that can be achieved in the system is 98.5. Realistically however, the air from the saturator is not quite 100% saturated – the constant evaporation of water means that the saturator is at a slightly lower temperature to its surrounds, and the warming of the flow upon exit causes a drop in humidity. This means that in practice, 98% is the achievable maximum humidity at these flow rates. A slightly higher maximum could be achieved if required by increasing the sheath flow – for instance, 10 litres per minute would yield a maximum of 99.1%.

### 3.2.2 Thermal Management

To address the issue of thermal management the following changes to the designs previously reported in the literature were done:

#### ***Thermal Isolation***

The approach used for thermal isolation was to encapsulate the entire humidification and H-DMA part of the system in an insulated chamber to exclude radiative heat sources and sinks. The only remaining heat sources and sinks are then the sheath and aerosol inflows and any airflow through the chamber.

The temperature in the chamber is then coupled to the ambient temperature by drawing ambient air through the reservoir using a blower fan in the cabinet wall. This approach ensures that all measurements are conducted at the ambient temperature. Ambient air temperatures typically change at no more than several degrees per hour. This slow rate of change in combination with the inherently large thermal inertia and strong internal thermal coupling of the system ensures that the computer control PID loop will be able to maintain constant RH although not keeping the temperature constant.

### *Thermal coupling*

The approach used for thermal coupling was to treat the element with greatest thermal inertia as a thermal reservoir and to immerse all the remaining elements in that reservoir. The element with the largest thermal mass is the H-DMA. The large thermal mass of the H-DMA will change the temperatures of the sheath and aerosol flows. If a thermal gradient between the top and bottom of the H-DMA exists it will be observed through a difference between the temperature of the flows entering the top of the DMA (the sheath and aerosol flows) compared to the temperature of the flows exiting at the bottom of the DMA (the excess and monodisperse air flows). As mentioned previously such a temperature gradient could be a major cause of RH fluctuations in the system. Thermal gradients can also be caused by the differences in the temperatures of the two flows entering the H-DMA, the sheath and aerosol flows.

To reduce these differences, in our system, the sheath and aerosol flows were encapsulated in the Nafion assembly by the H-DMA excess air flow. In this way the sheath and aerosol flow rates were brought to closer thermal equilibrium with the element with the greatest thermal inertia (H-DMA) even before they came into contact with it. The further requirement for constant temperature throughout the H-DMA column length can be met by minimising the temperature difference between the incoming aerosol and sheath flows. This is done within the second Nafion.

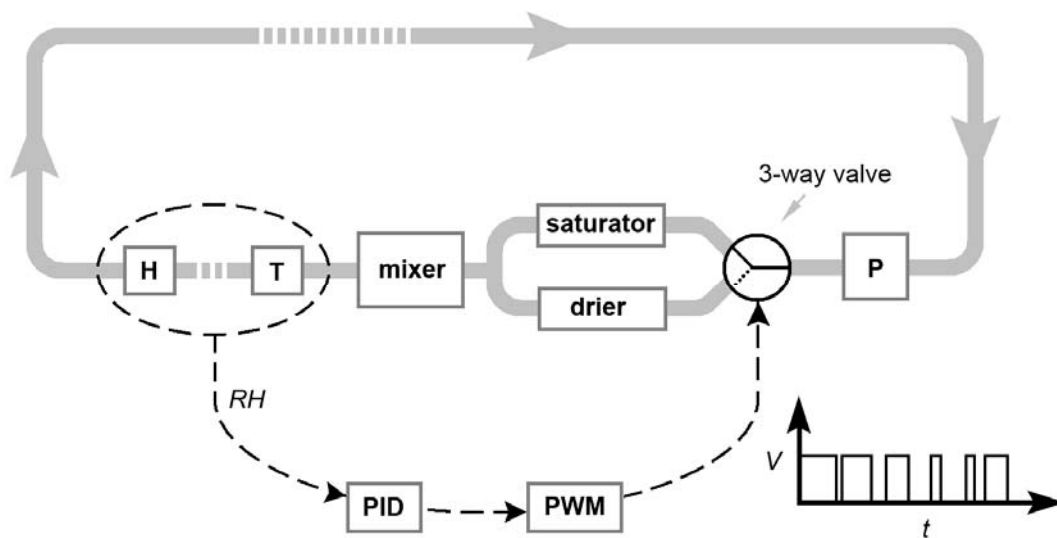
Previous designs have immersed the H-DMA in a water bath (Cubison et al., 2005; T. Hennig et al., 2005; Weingartner et al., 2002) to minimise the temperature gradients. In

our design we have tried to avoid immersion in water as that adds additional complexities to the system.

### 3.2.3 *Humidity Control via Timed Alternate Humidification and Drying with subsequent Mixing*

Humidity control is achieved through Timed Alternate Humidification and Drying with subsequent Mixing of the airflow (TAHDM), as illustrated in figure 3. Air from the pump (P) enters a high-speed 3-way solenoid valve (Festo MH4) and is alternately diverted to a drier and a saturator, with switching periods down to 4 milliseconds. The dry and saturated flows are recombined in a mixing volume to produce a steady average water vapour concentration which depends on the relative time fraction the flow spends in the dry and saturated arms of the flow path.

The TAHDM process is realised using a proportional-integral-derivative (PID) controller whose process input signal is the relative humidity output signal (*RH*) of a dew-point humidity sensor (H). The relative humidity is calculated from the absolute humidity measured by the mirror at location H combined with the temperature at the location T. The relative humidity is effectively controlled at the point T (which in our case is at the sheath inlet of the H-DMA), since the absolute humidity is constant between points T and H.



**Figure 3: Control of the humidity of the H-DMA sheath flow via Timed Alternate Humidification and Drying with subsequent Mixing of the airflow (TAHDM). The relative humidity signal  $RH$  from the humidity sensor is first compared to the set-point in the PID controller, which determines how much drying or wetting is needed. Then a Pulse Width Modulator then converts the PID output into a pulsed voltage which alternates the flow through the valve between the saturator and the drier to achieve the desired change in humidity.**

The TAHDM approach has distinct advantages over a control process involving continuous adjustment of the relative flows in saturator and dryer arms. Firstly the control valve requirements are not as stringent since the solenoid valve is required to simply turn on or off rather than provide a continuous range of adjustment. This does away with the need for a mechanical system which must give a precise continuous response to an input signal and the associated problems of non-linear response, hysteresis and backlash. Also because the valve is always either fully open or fully closed the response does not deteriorate at the extremes of operating range. In fact the operating humidity range is effectively unlimited, being a simple function of the relative times spent in the off and on states. Problems of obstruction by condensation at high humidity are also not an issue. The simplicity of the mechanical design of the solenoid valve actuation process also results in improved reliability and significantly lower cost than can be readily achieved by motor-controlled valves (mass flow controllers); further, these controllers lose their accuracy at high humidity. Lastly the valve control process is relatively simple to implement.

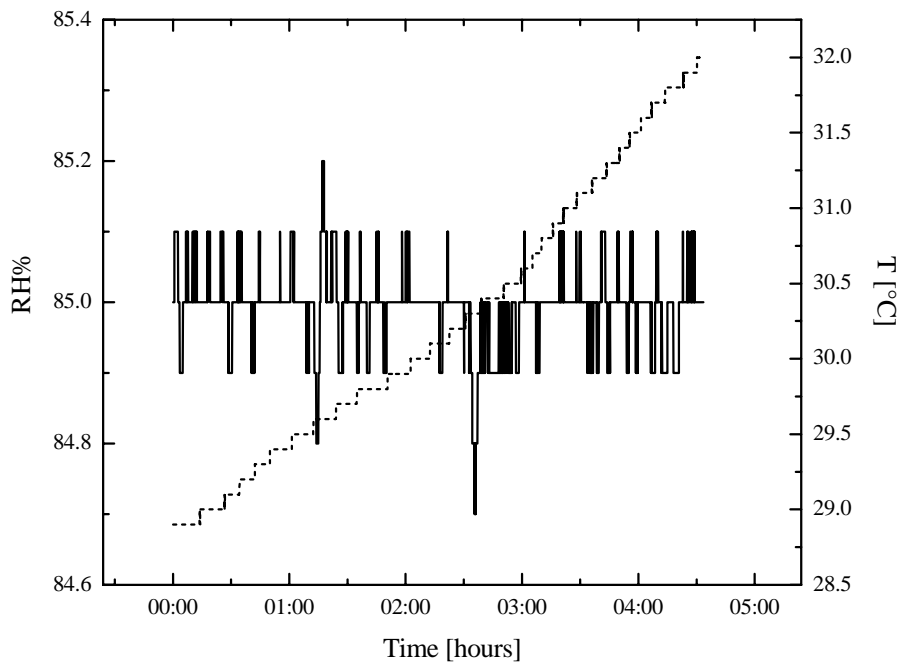


The valve switching is controlled by a Pulse Width Modulated (PWM) circuit responding to an analogue control signal output by a PID algorithm (contained in the NI PID toolkit within the Labview program), which is a function of the difference between the set point and measured relative humidities. Data acquisition and control interfacing is achieved using NI USB-DAQ-6009 acquisition devices. Automatic control of the system enables the measurement of both step function and ramped humidograms.

## **4 Results and Discussion**

### ***4.1 Stabilities/proof of concept***

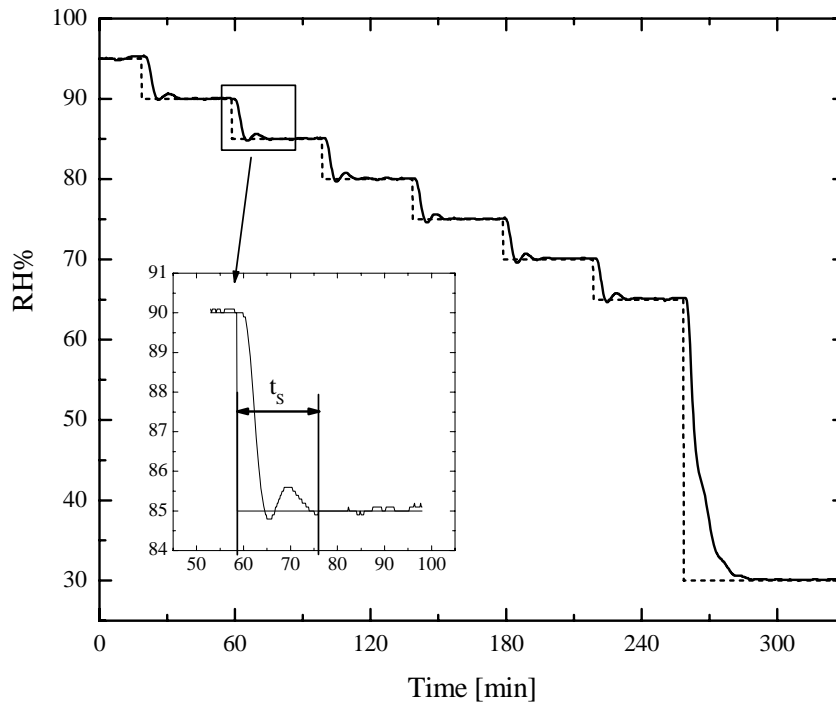
Figure 4 shows how well the system can maintain a stable humidity. Here the humidity set-point was left at a constant value of 85% for nearly 5 hours of system operation, and the humidity and temperature of the HDMA were logged. It can be seen that the measured humidity rarely deviated by more than 0.1% from the set-point, despite a gradual change in ambient temperature as the day progressed.



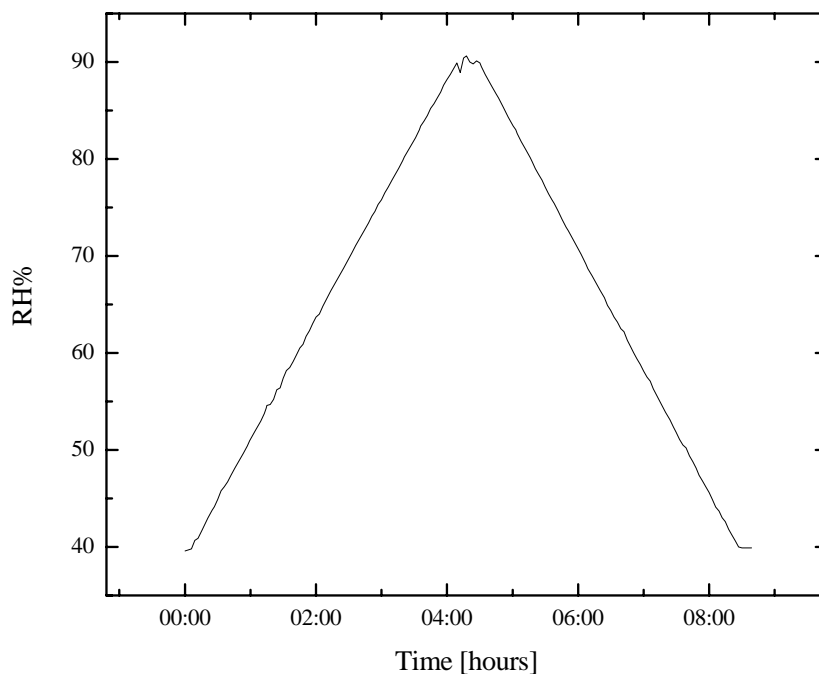
**Figure 4: Stability of relative humidity when set to a desired value of 85%. The humidity is shown as a solid line, and is unaffected by the increasing ambient temperature, plotted on the right-hand axis as a dotted line.**

Figure 5 shows how quickly the system re-establishes stability after the humidity set-point is changed. A small change in humidity requires only a few minutes for the system to adjust, while a radical change in humidity can take up to half an hour. These step changes in humidity can be entered manually, or can be programmed in when complete automation is required. Also the humidity can be programmed to ramp up very slowly, with a predefined slope, over a period of many hours (see figure 6). This can be used to perform automated deliquescence measurements. The particle diameter measurements are repeated every few minutes, and only take some tens of seconds to perform, so the

humidity is practically constant for each separate measurement.



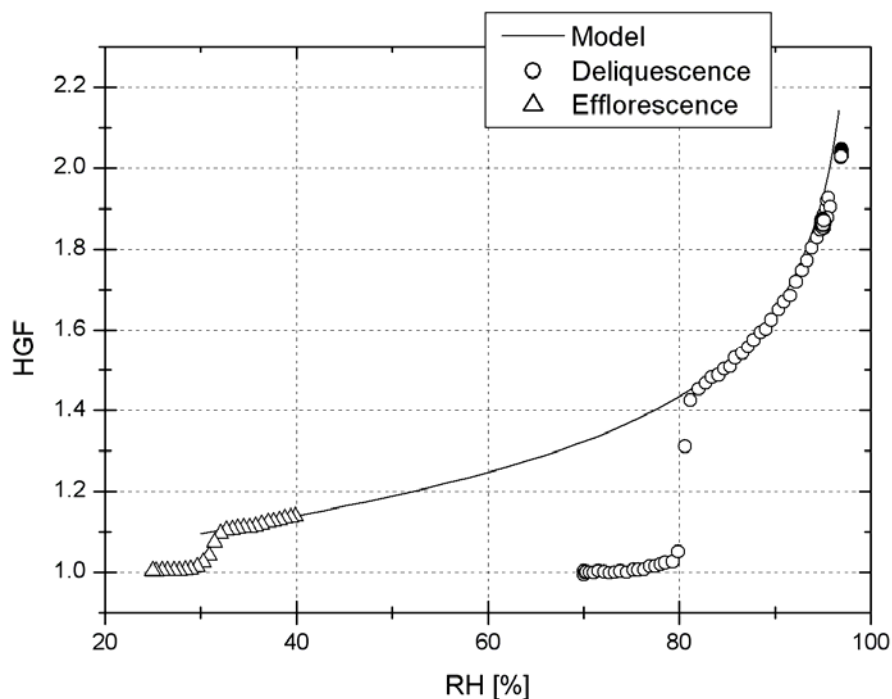
**Figure 5: Performance of the humidity control system. As the humidity set-point (dotted line) is reduced from 95% to 30% in steps, the measured humidity (solid line) is brought to the desired value with a minimum of oscillation by the PID controller.**



**Figure 6:** When programmed to automatically ramp up from 60% to 90% and back down, the humidity rises and falls in a very smooth monotonic fashion.

## 4.2 Hygroscopic Growth for Single Species

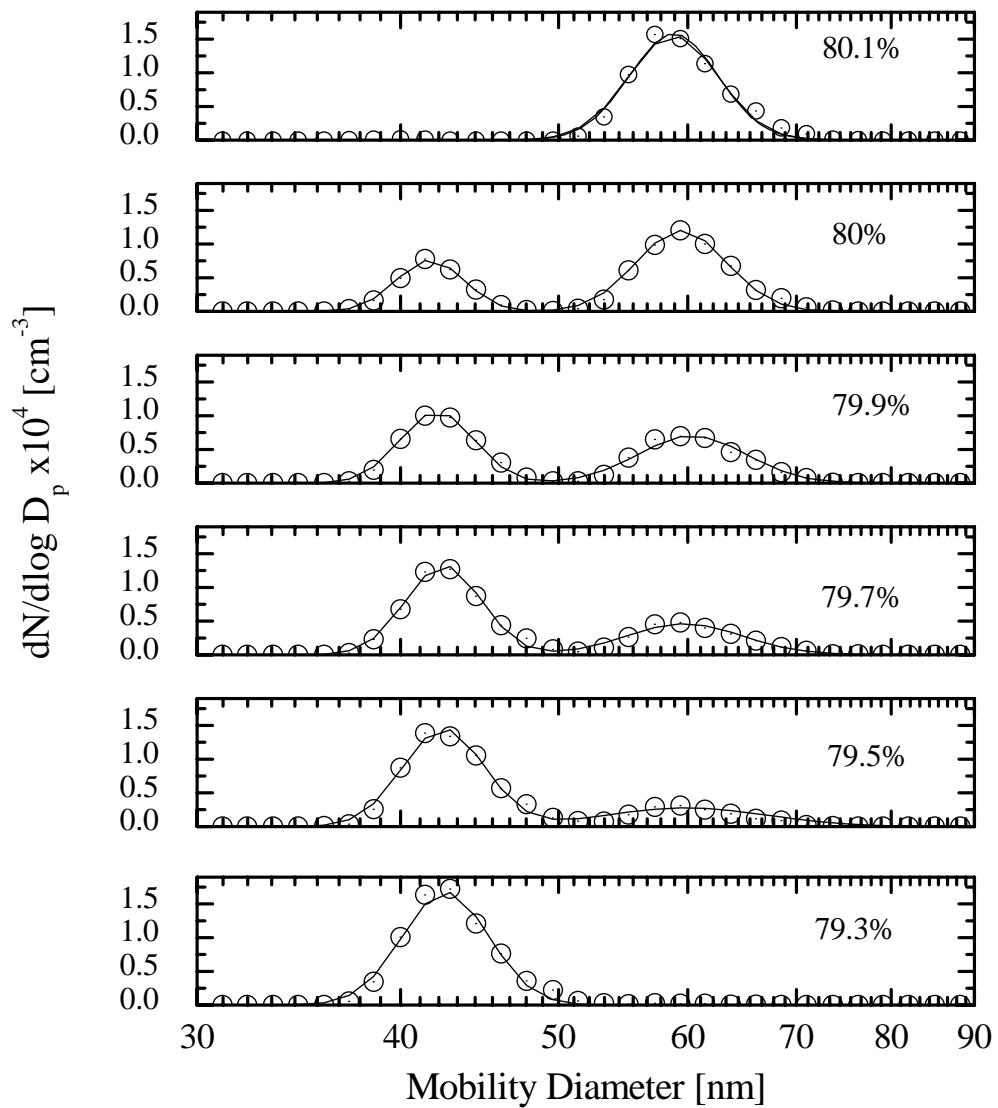
Figure 7 shows the deliquescence and efflorescence of 97nm ammonium sulphate particles as measured using the system described. The hygroscopic growth factor (HGF =  $d_{wet}/d_{dry}$ ) is shown for relative humidities between 25% and 97%, along with expected growth factors for ammonium sulphate according to the model of Biskos et al (2006). The particles effloresce at 32% humidity and deliquesce at 80% as expected, and the growth factors show good agreement with modelled values.



**Figure 7: Humidogram of 97nm ammonium sulphate particles, showing the hygroscopic growth factor as a function of relative humidity.**

The humidity control is so stable and precise that it is possible to watch the deliquescence in action by stepping up the humidity in tiny increments (see figure 8). As will be discussed in a subsequent paper, the particles selected by the P-DMA are not all exactly the same size, and will not all deliquesce at exactly the same humidity. Rather, the deliquescence occurs over a small range of humidities. At 79.3% humidity, none of the particles have deliquesced and the size distribution is monomodal; at 79.5%, a small percentage of particles deliquesce and form a separate peak with a growth factor of around 1.38; as the humidity is increased further in stages, the number of particles in the deliquesced peak steadily increases until by 80.1% all of the particles have deliquesced. The steady increase in the number of particles in the deliquesced peak in successive

stages demonstrates that the humidity is very stable and free of fluctuations – a fluctuation of just +0.2% at any time would be sufficient to deliquesce enough particles as to obliterate the difference between any two successive stages, and yet the differences are always clearly seen.



**Figure 8: Deliquescence of 43nm ammonium sulphate particles. The bottom panel shows the dry particles, the top panel shows the deliquesced particles which have grown to a diameter of 60nm, and the panels in between show stages in the deliquescence process.**

This level of precision compares favourably to values reported in the literature for other H-TDMA systems. The main sources of error are linked to the precision of the RH measurement and the level of control over the humidification process. The accuracy is not limited by gentle variations in ambient temperature throughout the day but the existence of temperature gradients within the system. The first HTDMA systems used passive temperature control methods (McMurry & Stolzenburg, 1989) ideally keeping their systems in air-conditioned rooms or insulating them from their surroundings. Active temperature control was applied to the already operating HTDMA system of Brechtel and Kreidenweis (2000) by Prenni et al. (2001). By holding the entire system to 30°C, variability as reported by Brechtel and Kreidenweis (namely an accuracy of  $\pm 0.8-1\%$ , and a precision of  $\pm 0.85\%$ ) was greatly reduced. The active control method was further developed by Weingartner et al. (2002) who utilised a water bath to minimise temperature gradients in their system to  $\pm 0.1^\circ\text{C}$ . This method was also employed by Cubison et al. (2005) however no indication was given as to the accuracy to which temperature could be controlled. Cocker III et al. (2001) and Weingartner et al. (2002) showed that regulation of temperature gradients to within  $\pm 0.2^\circ\text{C}$  and  $\pm 0.1^\circ\text{C}$  respectively minimise measured effects of the fluctuations between the gas and aerosol phase of the sample. During this experiment Weingartner et al. (2002) report accuracies of 1.1% to 1.6% RH. Hennig et al. (2005) have further enhanced the temperature control and showed that the absolute temperatures can be maintained within  $\pm 0.1\text{K}$  and with a long-term stability of 0.02 K. They have achieved a RH in the second DMA of 98% with an absolute accuracy of  $\pm 1.2\%$  and a long-term stability of  $\pm 0.1-0.4\%$  of set point values.

## **5 Summary and Conclusions**

The H-TDMA system presented in this paper was developed and honed over several years of use, both in the laboratory setting and in diverse field conditions including boat trips and trailers and other non-air-conditioned environments. The final system

represents what we believe to be a high level of accuracy and stability in measurement, while still keeping the setup robust and compact enough to be frequently transported for field work.

The design permits very accurate, reliable hygroscopic growth, deliquescence and efflorescence measurements for aerosols over a continuous relative humidity range from 10% to 98% with an accuracy of  $\pm 0.6\%$  RH.

This performance is made possible by three main improvements to the basic design of an H-TDMA. Firstly, a novel arrangement of two Nafion<sup>TM</sup> tubes is used to humidify the aerosol flow, which allows for high humidities without needing to pre-wet the flow, while keeping losses smaller than with laminar flow humidification. Secondly, temperature gradients during humidification and measurement are kept to a minimum by encapsulating the sheath and aerosol flows in the HDMA excess air-flow. This eliminates the need for unwieldy temperature control equipment. Thirdly, a switching valve is used to control the humidity, because it is rapid, feedback-controlled, simple, cheaper than using mass flow controllers, and again doesn't require temperature control.

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