

Application of the VH-TDMA Technique to Coastal Ambient Aerosols.

G. Johnson, Z. Ristovski, L. Morawska

International Laboratory for Air Quality and Health, Queensland University of Technology, Brisbane, Australia

An edited version of this paper was published by AGU. Copyright [2004] American Geophysical Union

Johnson, Graham and Ristovski, Zoran and Morawska, Lidia (2004) Application of the VH-TDMA Technique to Coastal Ambient Aerosols. *Geophysical Research Letters* 31 L16105.

Abstract A newly developed VH-TDMA has been used for the first time to measure the volatile fractions and post volatilization hygroscopic growth factors of ambient aerosols in the coastal marine and urban environments. The results are compared with comparable data for laboratory generated aerosols of known composition.

Measurements conducted on coastal Aitken mode particles showed volatilization behavior similar to laboratory generated aerosols composed of methane sulfonic acid and ammonium sulfate. Measurements conducted on 60 nm particles during nucleation events contained a greater fraction of material with similar volatility to ammonium sulfate than was found at other times. These particles were hygroscopic but less so than pure ammonium sulfate.

Measurements conducted in the Brisbane central business district during sea breeze conditions show similar behavior to the coastal aerosol, but with additional low volatility species. This aerosol may originate from urban sources or from marine particles acquiring additional secondary aerosol species during transport.

I. Introduction

Measurement of thermal volatilization temperatures can reveal the presence of lower volatility species within aerosol particles (Clarke, 1993; Orsini et al., 1996; Sakurai et al., 2003; Schmid et al., 2002). By measuring the hygroscopic behavior of the aerosol after volatilization the solubility of these low volatility residues can also be examined. A volatilization and humidification tandem differential mobility analyzer VH-TDMA system was recently developed for this purpose and the design of this system as well as its performance with respect to a variety of laboratory generated aerosols representing species thought to exist in coastal marine ambient aerosols has been previously described (Johnson et al., 2004). The current work demonstrates the application of this system in examining ambient aerosols including those found in coastal marine and urban environments.

II. Experimental

The VH-TDMA system is used to examine the effects of volatilization on particle size as well as the effects of subsequent humidification of the non-volatile residue particles exiting from the volatilization process. The diameter hygroscopic growth factor measured at a given relative humidity (RH), is defined as the ratio of the humidified particle diameter to the dry particle diameter ($G_{RH}=D_{wet}/D_{dry}$) where the dry diameter is measured at a relative humidity of 15% or lower.

Measurements were conducted at a coastal site and at an urban site on the subtropical coast of Australia as shown in Figure 1. The coastal site is located within the Moreton Bay Marine Park, 19 km to the north of the Gold Coast city. The urban site is located in the Brisbane central business district (CBD).

The coastal site is in a sandy tidal area approximately 10 km from the nearest road. The site is surrounded by mangrove forest and sand areas which are exposed at low tide. The region to the east of the site consists of tidal sandbanks and small areas of dune vegetation with the Pacific Ocean beyond. During easterly winds air arrives from the ocean with influences from local nucleation events occurring upwind to the east of the measurement site. Tidal areas rich in marine algae have been associated with nucleation bursts (O'Dowd et al., 2002) during low tide under high solar radiation intensity conditions and such nucleation bursts were clearly observed on many occasions during dynamic mobility analyzer (DMA) size distribution scans. Such nucleation events were identified in the DMA scans by a distinct nucleation mode below 30 nm.

Aerosols at the coastal site were examined from a boat with the aerosol collected from an inlet tube projecting 1 m from the forward end of the upper deck of the boat, 4.8 m above the water line. During sampling, the boat was orientated into the wind to avoid interference from onboard activities.

The urban aerosol sampling site is located in the Brisbane CBD. A diurnal sea/land breeze cycle operates on warm sunny days throughout the summer months bringing coastal air over the city of Brisbane during afternoons. Aerosols were examined during sea breeze conditions in order to detect the growth of the marine aerosol during transport through the intervening polluted urban area.

The VH-TDMA scans generate size data for the aerosol after volatilization conditioning and after subsequent humidification conditioning over a range of volatilization temperatures. This process takes 10-120 minutes to complete depending on the number of temperature steps required. In most cases the hygroscopic growth of the conditioned aerosol was recorded for all conditioning temperatures, however in the case of the coastal aerosol Aitken mode, hygroscopic growth was recorded only at the initial and final volatilization temperatures in order to allow one CPC to be used for simultaneous size distribution measurements of the unconditioned aerosol.

Temperatures given for the volatilization process refer to the maximum temperature achieved by the aerosol when passing through the thermodenuder (volatilization conditioner). The uncertainty in these temperatures is ± 3 °C.

For the laboratory and CBD based measurements the RH of the humidification process was checked at regular intervals using dry 100 nm NaCl aerosol. The error in the RH for the laboratory based and CBD measurements is estimated to be ± 0.5 %RH.

The RH given for the humidification step in the coastal aerosol measurements performed on the boat is based on measurements using an inline humidity sensor in the excess air exiting from the DMA used for post-humidification size determination. The error associated with these humidity measurements is estimated to be ± 2 %RH while the variation during a VH-TDMA scan is typically ± 0.5 %RH.

III. Results

The graphs in Figure 2 show diameter hygroscopic growth factor data and volatilization data presented in terms of the particle volume fraction remaining after volatilization. The volume fractions were calculated from the diameter after volatilization (D_T) and the initial diameter (D_{T0}) as the cube of D_T/D_{T0} .

Figure 2(a) shows the VH-TDMA results from the coastal marine sampling site, when the wind was from the southeast with no nucleation apparent. The volatility of 60 nm Aitken mode particles was examined from 26 °C (ambient temperature) to 460 °C and the diameter hygroscopic growth factor at 85% relative humidity was recorded before volatilization and after volatilization at 282 °C.

The maximum thermodenuder temperature (T_{Max}) and the relative humidity (RH) of the humidity conditioning used for the growth factor measurements in this discussion are indicated in parenthesis (T_{Max} °C, RH%) in each case below. The minimum temperature was in all cases the ambient temperature which always fell within the range 23 to 28 °C.

Figure 2(b) shows the results ($T_{\text{Max}}=225$ °C, RH=85%) for 60 nm coastal marine aerosol Aitken mode particles recorded during a nucleation event. The VH-TDMA scan was commenced after persistent nucleation activity had been observed in repeated DMA scans over a period of 45 minutes, two hours before the point of maximum solar radiation and with low tide approaching. In this case (and all further cases), the diameter hygroscopic growth factor was determined at each volatilization conditioner temperature. Also shown in Figure 2(b) are the results for laboratory generated 100 nm particles consisting of 10% v/v MSA and 90% v/v ammonium sulfate ($T_{\text{Max}}=215$ °C, RH=90%).

Figure 2(c) shows the results ($T_{\text{Max}}=400$ °C, RH=90%) for 60 nm diameter particles in the Brisbane CBD for the dominant particle type present for particles of this size during a sea breeze. Also shown in Figure 2(c) are the results ($T_{\text{Max}}=215$ °C, RH=90%) for laboratory generated 100 nm particles consisting of 50% v/v methane sulfonic acid (MSA) and 50% v/v ammonium sulfate.

The results from each VH-TDMA scan shown in Figure 2 are summarized in Table 1. The table gives the description of each aerosol type followed by designations for the various chemical species detected (by volatilization) within the aerosol, and the particle volume fraction lost during volatilization of the species. The remaining three columns contain the pair of temperature settings between which volatilization of the chemical species began, the pair between which this volatilization ended, and the diameter hygroscopic growth factor of the particles at the volatilization temperature setting immediately below that at which the species began to volatilize.

Samples taken from the coastal marine site in the absence of simultaneous nucleation are denoted CM while those with simultaneous nucleation are denoted CM-N. The samples from the Brisbane CBD site are denoted CBD.

The 60 nm CM particles were found to be an external mixture of two distinct particle types denoted CM_A and CM_B . The CM_A type was composed of three species CM_A^{V1} , CM_A^{V2} and CM_A^R with distinct volatilization behavior while the CM_B particles contained a volatile species CM_B^V and a non-volatile fraction CM_B^R . Prior to volatilization, the CM particles contained two hygroscopically distinct particle types. These are labelled CM_α and CM_β in the legend of Figure 2(a) and are assumed to correspond in some way to the two distinct volatilization particle types CM_A and CM_B . The number of particles in the two volatilization categories were approximately equal as were those in the two hygroscopicity classifications, preventing clear matching between volatilization and hygroscopicity type. Both particle types were insoluble after volatilization at 282°C.

The CM-N aerosol appeared to contain a single particle type within the 60 nm size fraction examined. These particles appear to be composed of at least two species with different volatilization temperatures. One species (CM-N^{V1}) comprising 14% of the particle volume was completely removed within the temperature range 86 – 138 °C. The range for removal for the second species (CM-N^{V2}) which comprises most of the remaining volume is uncertain (due to the lack of higher temperature data) but completion of removal clearly occurs above 195 °C and the bulk of this material is removed before 224 °C. The residue present at 224 °C may be the remainder of species CM-N^{V2} or a refractory species. The sudden decrease in hygroscopic growth during CM-N^{V2} volatilization suggests the presence of a third low volatility insoluble species, CM-N^R comprising <4.3% of the original particle volume and giving rise after volatilization to residue particles of diameter <22 nm.

There appear to be four distinct species present within 57 nm CBD particles and these species have been denoted CBD^{V1} , CBD^{V2} , CBD^{V3} and CBD^{R} where the superscripts denote distinct volatilization temperature ranges which are representative of each species. The volatilization curve shows a number of volume reductions within the CBD^{V2} volatilization range suggesting that this material contains several low volatility species.

IV Discussion

There are similarities between behavior in the VH-TDMA of the CM and CM-N aerosols. Both samples show initial volatilization within the 25 – 173 °C range and a second volatilization within the range 109 - 231 °C leaving an insoluble residue.

Laboratory generated mixed MSA/ammonium sulfate particles (Figure 2b, Figure 2c) show very similar volatilization behavior to the marine case suggesting that the species CM-N^{V1} and CM-N^{V2} may be MSA and ammonium sulfate (or bisulfate) respectively. The hygroscopic growths of the coastal aerosols remain consistently smaller, throughout the volatilization process, than the laboratory generated sulfate/MSA aerosols. Therefore a composition consisting mostly of sulfate and MSA, would suggest the presence of additional species which volatilize with the above or which can impair their solubility when present in proportionately minute amounts.

The CM-N marine aerosol shows a marked increase in growth factor ($G_{85\%} = 1.19 - 1.30$) during the volatilization of species CM-N^{V1} and in fact the particle diameter of the humidified aerosol actually increased during this volatilization, implying that this species was not simply of lower hygroscopicity than CM-N^{V2} but that CM-N^{V1} reduced the solubility of CM-N^{V2} . Such behavior may be consistent with the amphipathic nature of the MSA molecule. If the MSA molecules form a coating on the surface of the sulfate particle with the polar end of the MSA molecule embedded in the polar sulfate core and the hydrophobic methyl group facing outward the particle would present a somewhat hydrophobic particle surface. Similar masking behavior has been observed using the VH-TDMA system using NaCl particles coated in insoluble organic material (Johnson et al., 2004).

The fact that the laboratory generated aerosol does not show an increase in hygroscopicity as the MSA component evaporates may be a result of the different aerosol formation processes. In the laboratory generated aerosol the two species were dissolved in water then atomized and dried which is likely to result in the two components being well mixed in the dried particle. In contrast the proposed ambient particle is likely to be formed first from the sulfate species with subsequent condensation of the MSA onto the outer surface. A further possibility is that the laboratory generated particle has a different layered structure influenced by the migration of water molecules drawing hydrophilic components to the particle surface during drying.

The observations suggest that the CBD^{V2} species is soluble but somewhat less hygroscopic than ammonium sulfate. Possible candidates include ammonium nitrate, MSA, sulfuric acid and particle bound water. The changes in hygroscopic growth suggest the presence of at least one organic species able to reduce overall particle hygroscopicity. The volatilization temperature range for the species CBD^{V3} is consistent with ammonium sulfate while the species CBD^{V2} most closely resembles ammonium nitrate in its volatilization temperature and hygroscopic growth.

V. Conclusions

The application of the VH-TDMA system was successfully demonstrated for ambient aerosols. The system is capable of distinguishing between volatile species within ambient submicrometer aerosols and of examining the influence of these species on the particles diameter hygroscopic growth.

Aitken mode coastal marine aerosol contained two physicochemically distinct particle types (CM_A and CM_B). The volatility of the CM_A particles, was consistent with a mixture of ammonium sulfate and MSA and one of the particle types was somewhat hygroscopic while the other did not show significant hygroscopic growth. The CM_B particle type was composed of a refractory material and a smaller quantity of volatile material.

Particles of similar size, examined during nucleation showed similar volatilization behavior to the CM_A type but with a larger volume fraction of a species showing similar volatility to ammonium sulfate. The volatile species in these particles were somewhat hygroscopic but the particles showed lower hygroscopic growth than laboratory generated aerosol containing only ammonium sulfate and MSA.

Similarities between samples taken from the coastal site during nucleation and those from the CBD site during sea breeze conditions suggest a possible coastal marine physicochemical signature. The similarities include possible evidence of MSA and ammonium sulfate in the volatilization curve and the direction of the hygroscopic growth changes accompanying volatilization although the consistently smaller hygroscopic growth of the coastal aerosols leaves this assignment open to question. An additional less hygroscopic, more volatile species comprising as much as 30% of the particle volume was present in the CBD aerosol but not in the coastal aerosols. The results suggest the possibility of a coastal marine physicochemical signature sufficiently robust to remain detectable after the aerosol has traversed polluted urban terrain. Secondary species apparently acquired by marine aerosol during transport over the urban terrain show high volatility and appear to reduce the hygroscopic growth of the aerosol.

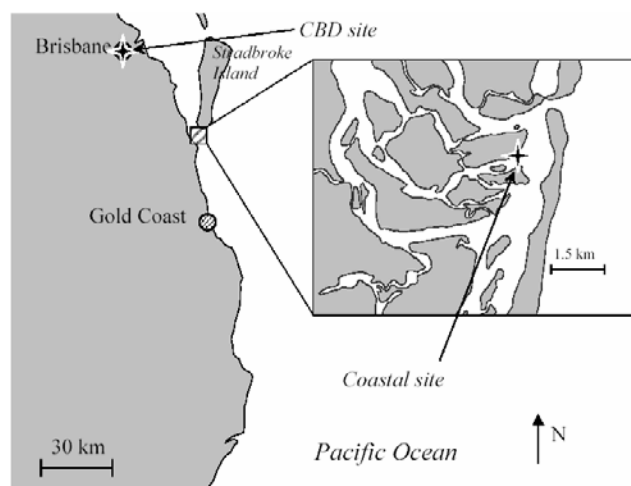


Figure 1: Locations of the sampling sites.

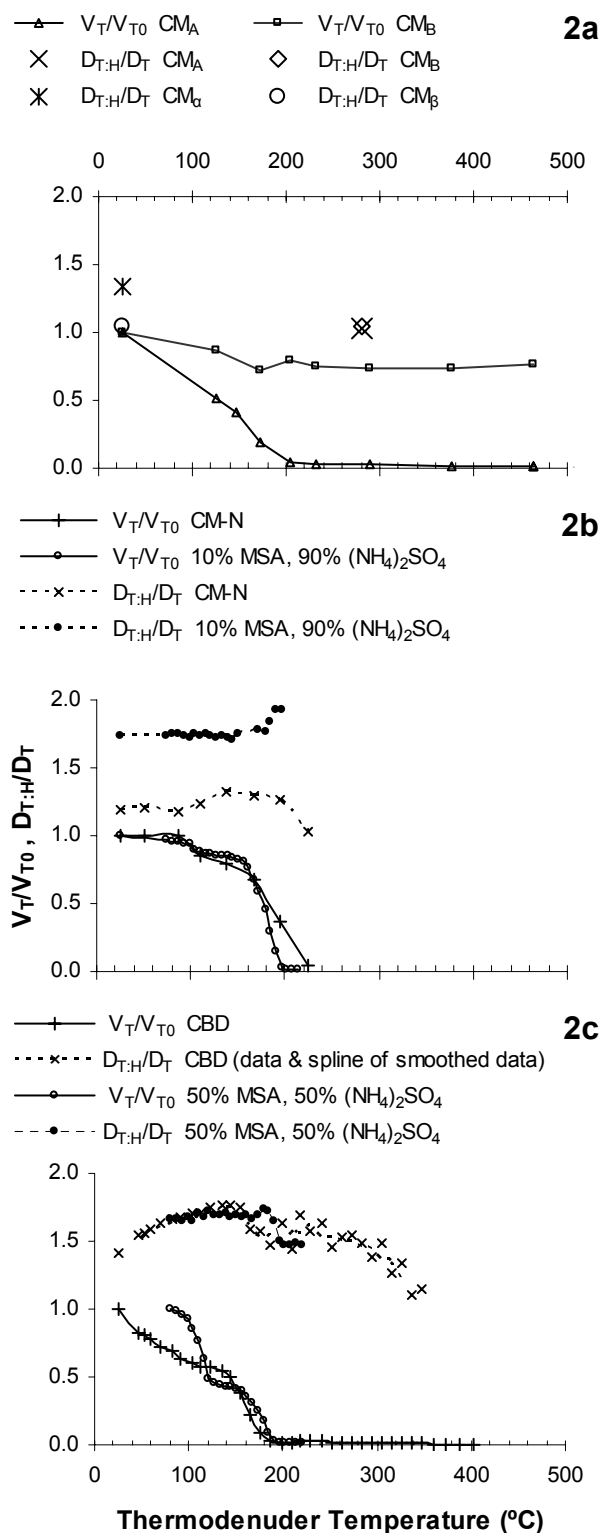


Figure 2: Ratio of particle volume after volatilization to that before volatilization (V_T/V_{T0}), and diameter hygroscopic growth factor ($D_{T:H}/D_T$), versus thermodenuder temperature; (a) for 60 nm particles from the coastal site with nucleation absent. (b) for 60 nm particles from the coastal site during nucleation. Also shown is the volatilization curve for laboratory generated particles consisting of 10% v/v MSA and 90% v/v ammonium sulfate. (c) for 57 nm ambient particles from the Brisbane CBD site. Also shown is the volatilization curve for laboratory generated particles consisting of 50% v/v MSA and 50% v/v ammonium sulfate.

Table 1: Summary of aerosol properties for the ambient and laboratory generated aerosols. Column 2 shows the notation used in the text for chemical species removed by volatilization. Column 3 shows the volume fraction by which particles shrank when the species was removed. Column 4 shows the temperature range within which the species began to volatilize (commencement of volume shrinkage). Column 5 shows the temperature range within which shrinkage stopped. Column 6 shows the hygroscopic growth factor of the aerosol prior to the volatilization of the species.

*Insufficient data existed in this case to assign this growth factor to a particle type (CM_A , or CM_B).

Aerosol examined { F_{th} = thermodenuder flow rate}	Species	Fraction removed	T_{start} (°C)	T_{finish} (°C)	G_{RH} before species removal
Marine Aitken mode type A Particles, D=60 nm { F_{th} =0.6 lpm}	CM_A^{V1}	58%	25≤ T≤ 126	146≤ T≤ 173	* $G_{85\%}$ =1.34 or 1.04
	CM_A^{V2}	40%	146≤ T≤ 173	204≤ T≤ 231	?
	CM_A^R	2%	> 400	> 400	$G_{85\%}$ =1.04
Marine Aitken mode type B Particles, D=60 nm { F_{th} =0.6 lpm}	CM_B^V	24%	25≤ T≤ 126	126≤ T≤ 173	* $G_{85\%}$ =1.04 or 1.34
	CM_B^R	76%	> 400	> 400	$G_{85\%}$ =1.04
Marine Aitken mode particles during nucleation, D=60 nm { F_{th} =0.6 lpm}	$CM-N^{V1}$	14%	86≤ T≤ 109	109≤ T≤ 138	$G_{85\%}$ =1.19
	$CM-N^{V2}$	82-86 %	109≤ T≤ 138	195≤ T≤ 224	$G_{85\%}$ =1.30
	$CM-N^R$	≤ 4 %	>224	> 224	$G_{85\%}$ =1.03
Brisbane CBD Aitken mode particles, D=60 nm { F_{th} =1.3 lpm}	CBD^{V1}	19%	25≤ T≤ 46	60≤ T≤ 82	$G_{90\%}$ =1.41
	CBD^{V2}	23.50%	71≤ T≤ 82	112≤ T≤ 124	$G_{90\%}$ =1.56
	CBD^{V3}	55.50%	124≤ T≤ 135	187≤ T≤ 198	$G_{90\%}$ =1.76
	CBD^R	2.00%	> 400	> 400	$G_{90\%}$ =1.57
Sulfuric Acid, D=100 nm, { F_{th} =0.6 lpm}			58±9	142±4	$G_{90\%}$ =1.68
Ammonium Sulfate, D=100 nm { F_{th} =0.6 lpm}			161±8	210±4	$G_{90\%}$ =1.70
MSA, D=100 nm { F_{th} =0.6 lpm}			95±3	165±4	$G_{90\%}$ =1.57
Ammonium Nitrate, D=100 nm, { F_{th} =0.6 lpm}			48±5	78±4	$G_{90\%}$ =1.50
			51±4	89±4	
Sodium Chloride, D=100 nm, { F_{th} =1.2 lpm}					$G_{90\%}$ =2.31

- Clarke, A.D., 1993. Atmospheric Nuclei in the Pacific Midtroposphere: Their Nature, Concentration, and Evolution. *Journal of Geophysical Research-Atmospheres.*, 98(D11): 20633-47.
- Johnson, G.R., Ristovski, Z. and Morawska, L., 2004. Method for measuring the hygroscopic behaviour of lower volatility fractions in an internally mixed aerosol. *Journal of Aerosol Science*, 35(4): 443-455.
- O'Dowd, C.D. et al., 2002. Coastal new particle formation: Environmental conditions and aerosol physicochemical characteristics during nucleation bursts. *Journal of Geophysical Research-Atmospheres*, 107(D19): 8107.
- Orsini, D., Wiedensohler, A. and Covert, D., 1996. Volatility Measurements of Atmospheric Aerosols in the Mid and South Pacific Using a Volatility-Tandem-Differential-Mobility-Analyzer. *J Aerosol Sci*, 27(Suppl 1): S53-S54.
- Sakurai, H. et al., 2003. On-line measurements of diesel nanoparticle composition and volatility. *Atmospheric Environment*, 37(9-10): 1199-1210.
- Schmid, O., Eimer, B., Hagen, D.E. and Whitefield, P.D., 2002. Investigation of Volatility Method for Measuring Aqueous Sulfuric Acid on Mixed Aerosols. *Aerosol Science & Technology*, 36: 877-889.