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Detection of brake wear aerosols by aerosol time-of-flight mass spectrometry

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HIGHLIGHTS

- Brake wear particles are an important constituent of urban aerosol.
- ATOFMS identifies brake dust from Fe and Ba signals.
- High laser pulse energies are needed to detect the Ba^+ ion.
- Data from several field campaigns are presented.

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ABSTRACT

Brake dust particles were characterised using an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) operated using two inlet configurations, namely the aerodynamic lens (AFL) inlet and countersunk nozzle inlet. Laboratory studies show that dust particles are characterised by mass spectra containing ions deriving from Fe and Ba and although highly correlated to each other, the Fe and Ba signals were mostly detected using the nozzle inlet with relatively high laser desorption energies. When using the AFL, only [^{56}Fe] and [$^{-88}FeO_2$] ions were observed in brake dust spectra generated using lower laser desorption pulse energies, and only above 0.75 mJ was the [^{138}Ba] ion detected. When used with the preferred nozzle inlet configuration, the [$^{-88}FeO_2$] peak was considered to be the more reliable tracer peak, because it is not present in other types of dust (mineral, tyre, Saharan etc). As shown by the comparison with ambient data from a number of locations, the aerodynamic lens is not as efficient in detecting brake wear particles, with less than 1% of sampled particles attributed to brake wear. Five field campaigns within Birmingham (background, roadside (3) and road tunnel) used the nozzle inlet and showed that dust particles (crustal and road) accounted for between 3.1 and 65.9% of the particles detected, with the remaining particles being made up from varying percentages of other constituents.

1. Introduction

Both exhaust and non-exhaust emissions are now the focus of air quality research as tightening policies are reducing the contribution of engine exhaust to the total airborne particulate matter budget, such that non-exhaust emissions are becoming more prominent (Lenschow et al., 2001; Harrison et al., 2001; Querol et al., 2004; Boulter et al., 2006). It is recognised that road traffic is frequently a dominant, but mitigatable, source of particulate matter (PM) accounting for 5–80% of airborne concentrations of PM depending on site and location (Pant and Harrison, 2013). In the UK, the Air Quality Expert Group identified non-exhaust primary PM emissions from road transport as a priority area of uncertainty, and stated the need to update and refine the associated methodologies and estimates (AQEG, 2005). Other, international assessments have also highlighted the need for action (Denier van der Gon et al., 2013; Amato et al., 2014).

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Non-exhaust emissions arise from mechanical abrasion and corrosion processes leading to particles with a large proportion in the coarse size range. The most important direct emission sources are associated with the wear of tyres, brakes, clutch and road surfaces through abrasion, and vehicle bodywork through corrosion. Compared to tail-pipe emissions, the coarser nature of non-exhaust emissions implies that they are more likely to be deposited onto the road surface and then be resuspended into the atmosphere both due to vehicle-generated turbulence and by action of the wind (Harrison et al., 2001). The common assumption that most of the primary fine particles ($PM_{2.5}$) and the coarse particles ($PM_{2.5\text{-}10}$) arise from exhaust and non-exhaust emissions respectively is not well supported by measurement of non-exhaust PM. There is evidence showing that non-exhaust particles contribute to both the fine and the coarse mode (AQEG, 2005) implying a need for measurement of both size fractions.

The frictional contact between a brake pad/shoe and disc/drum rotating with the wheel of the vehicle converts the linear motion of the vehicle into thermal energy. Associated with this process is the gradual wear of the contacting components which in turn liberates brake dust. The brake disc/drum is generally fabricated from cast iron and the contact material of the pads/shoes is made from a range of materials (Thorpe and Harrison, 2008). Recent information on the composition of brake pads used in Europe is available from Hulskotte et al. (2014). Major element components on average comprised 23% Fe, 11% Cu, 5% Zn, and 3% Sn as the dominant metals. Non-metal components in the discs were 2–3% Si, 3% S and 26% carbon. Hulskotte et al. (2014) do not report measurements of Ba, but cite reported values of 0.07–6.9% from Spain and 12% from Japan. Correlations have been observed between Cu, Ba, and Fe observed in ambient particulate matter (Birmili et al., 2006) and with measurements at roadside (Gietl et al., 2010). Furthermore, using the robust ratio between Fe and Cu found at the kerbsides, a 70% and 30% estimate of the contribution of brake pads and brake discs (consisting almost entirely of metal with iron being the dominant element >95%) to total brake wear respectively was made.

Using data from roadside and local background locations, Gietl et al. (2010) estimated that barium comprises 1.1% of brake wear (PM_{10}) particles from the traffic fleet as a whole, allowing its use as a quantitative tracer of brake wear emissions at traffic-influenced sites. By using real time aerosol data, Dall'Osto et al. (2013) found that Fe and Cu together can also be used as a tracer of brake wear. Other studies have reported that the abrasion of brakes produces particles characterised by high concentrations of Cu, Ba, Zn and Fe (Sanders et al., 2003; Johansson et al., 2008). Iron is often considered to be related to crustal elements and resuspension of road dust (Sternbeck et al., 2002; Heal et al., 2005; Lough et al., 2005). However, Harrison et al. (2003) in devising a pragmatic mass closure method from analyses of particulate matter collected at UK sites, found that the iron concentration within coarse dusts was much greater at roadside sites than at urban background sites and this was considered indicative of road traffic and most probably the vehicles themselves as a source. Birmili et al. (2006) confirmed that iron in coarse particles could be used as a tracer of vehicle-generated particles, whilst calcium is primarily a tracer of particles from soil, as also concluded by Harrison et al. (2003). Birmili et al. (2006), compared trace metal concentrations collected at four different measurement sites representing different degrees of traffic influence. The size-fractionated ambient PM analyses showed Fe, Ba and Cu correlated closely in the fraction $1.5 < D_p < 3.0$ μm in urban air. This finding supported the concept that most of these particles are not due to vehicle-induced resuspension but are directly emitted from abrasion processes.

Mass spectrometry of atmospheric aerosol has recently been established and has quickly become the most essential and fastest growing area of aerosol research (Laskin et al., 2012). Currently none of the available mass spectrometry instruments reaches ideality. For example, the Aerosol Mass Spectrometer (AMS) provides great quantitative information on limited number of chemical components (Jimenez et al., 2009), but does not analyse any species which does not volatilise at 600 °C (i.e. Sea salt, dust, Elemental carbon). The Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) provides information on many more chemical components (both refractory and non-refractory, size range 200–3000 nm) than the AMS, but the information is only semi-quantitative (Pratt and Prather, 2012). However, the ATOFMS' unique strength relies in the fact that it can monitor in real time variations in the single particle composition. Previous studies have indeed focused on the MS of different types of dust particles (Silva et al., 2000; Sullivan et al., 2007, 2009, Dall'Osto et al., 2010, 2014).

This paper extends such work by application of an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) to characterisation of brake wear particles in the size range between 0.3 and 3.0 μm. Mass spectral fingerprints of different dust particles have been determined and information at a single particle level is presented from both laboratory studies and from a number of different field studies in very different environments (at background, roadside and road tunnel sites). The ATOFMS results shown herein provide information on single dust particles at very high time resolution (minutes), hence allowing characterisation of the mixing state of brake wear particles, and comparison of their temporal trends with other dust particle types and meteorological conditions. We first report the characterisation of single particle mass spectra of brake wear aerosol generated in the laboratory, with specific key m/z markers. We then report ambient data across a number of environments, and we discuss the differences encountered. Finally, correlations between different types of dust and traffic volume data are used to conclude the study.

2. Experimental

2.1. Instrumentation

This work reports the use of an Aerosol Time-of-Flight Mass Spectrometer (TSI ATOFMS 3800) for the study of brake dust particles. Since its introduction in the late 1990s, the ATOFMS has given valuable insights into the size and composition of individual airborne particles (Gard et al., 1997; Pratt and Prather, 2012). In essence, this instrument provides an aerodynamic diameter and a positive and negative mass spectrum for each particle ionised by a pulsed UV laser.

Two different versions of the ATOFMS have been commercially available: ATOFMS TSI model 3800-100 and ATOFMS TSI Model 3800. In the ATOFMS TSI model 3800-100, particles are sampled through an orifice and accelerated through the aerodynamic lens to the sizing region of the instrument (Su et al., 2004). By contrast, the ATOFMS TSI Model 3800 utilizes a nozzle/skimmer interface for the inlet (Gard et al., 1997). In terms of particle collection efficiency, the aerodynamic lens provides a major improvement toward smaller particle sizes compared to the nozzle/skimmer inlet. Both instruments measure the aerodynamic diameter of particle sizes between 100 nm and 3 μm by calculating their time of flight between two orthogonally positioned continuous wave lasers ($\lambda = 532$ nm). However, a number of factors affecting the potential to extract fully quantitative information on particle size distributions - i.e. the transmission efficiency of the nozzle/skimmers used to create the particle beam in the instrument's inlet (Dall'Osto et al., 2006) - make the size responses of the two instruments quite different. Generally speaking, whilst the ATOFMS equipped with