Working group On-line instruments

Erik Engström, Meteorological Department, Stockholm University.
Inga Rimselyte, Atmospheric pollution research laboratory, Institute of Physics, Lithuania.

Introduction

Through out the history of atmospheric science, one of the main goals has always been to establish what the atmosphere around us is made up of. The very first instruments early scientists (or philosophers) had at hand were there own senses. They could look at the air and see the colour, clouds, raindrops and large particles such as dust. They could also smell the salt ocean air. Later the thermometer, hygrometer and barometer where invented and represented the first technical instruments. During the last century an accelerating development of available analysing techniques have taken place. A major achievement is when physical and chemical techniques have been combined instead of being separated in different instruments.

Offline measurements are often filter based and usually requires subsequent treatments and analyzing procedures that are both time consuming and can cause loss off analyte. In contrast, online methods can provide more data in less time and is less sensitive to sample loss and contamination. This also lowers the limit of detection which is a critical parameter due to the low levels of concentrations often found in the atmosphere.

There are some important aspects to consider when discussing instrumental detection and identification of aerosols. The choice of technique has traditionally been a trade off between the wish of gaining detailed information about the chemical composition and structure of the sample, the wish of analysing as much as possible of the sample and high time resolution. A selection of analysing techniques will be described in the following section to elucidate this challenge.

Motivation

Atmospheric aerosol particles have been shown to have an effect on both climate through the radiation balance and cloud formation (IPCC 2007) and on health damaging the respiratory system (Pope, 2000; Thurston 2005). Of the atmospheric aerosols the fraction made up of organic carbon (OC) is the least understood (Fuzzi et al. 2006) even thou they present a substantial amount of the total aerosol mass. Typically the organic matter (OM) account for 20-50% of the PM2.5. (Chow et al. 1993; Schauer and Cass 2000; Kim et al. 2000; Christoforou 2000). Important sources of OM are bio fuel burning and biogenic processes. The organic carbon compounds present a wide range structures, compositions and properties which make a general definition difficult.

Particle number and size distribution

There are a number of available techniques to measure a particle population’s number and size distribution. Examples for counting particles are the Optical Particle Counter (OPC) introduced by Gucker et al. (1947 a, b), where a light beam is intercepted by passing particles and in that way counted or Condensational Particle Counter (CPC) (Mavliev et al., 2004) where the particles are grown to improve the detection. To acquire a size distribution a Differential Mobility Analyzers (DMA) (Hewitt, 1957; Knutson and Whitby, 1975; Winklmayr et. al., 1991) can be used. In this instrument the particles are charges at sent through an electrical field. The electrical field bend the travel path of the particles according to their mobility (size). These techniques give important information on the particle number and size distribution but tell nothing about the chemical composition.

Particle number measurement techniques

Condensation particle counter

The total number concentration of the aerosol particles as the integral of the number size distribution can be measured with a high time resolution. State of the art instruments to determine the particle number concentration are continuous flow condensation particle counters (CPC's) (Agarwal and Sem, 1980). This type of instrument counts each individual aerosol particle and therefore has an upper detection limit in particle concentration. Common CPCs have lower detection efficiency diameters of 10-15 nm, and an upper number concentration limit of about 10,000 cm^{-3} without significant coincidence. The development of the Ultrafine-CPC (Stolzenburg and McMurry, 1991) enabled number concentration measurements down to 3 nm in diameter with an upper detection limit of 100,000 cm^{-3}. Measurements of particle number concentration and size distribution in the range below 8 nm became possible by the Pulse Height-Analysis-UCPC (Weber et al., 1998).

Optical particles counter

These are instruments which size each individual aerosol particle according to their optical properties. The particles are aspirated into a scattering chamber and then directed into the centre of a beam of laser or a white light. The light is scattered by the particle; its intensity is related to the size of the particle via Mie theory for homogeneous spheres. In order to suppress sizing ambiguities due to oscillations of the Mie curves, the scattered light is collected over a wide angular region or a white light source is used. During sampling and within the scattering chamber the particles are dried and therefore the particles are not sized in ambient, undisturbed conditions (Strapp et al., 1992). Further problems are caused by the refractive index and shape-dependence of the measurements. With intra-cavity laser illumination, lower size detection limits of such instruments of 70 nm can be reached. As other single particle counters OPCs have upper concentration limits which are given by the probability of particle coincidence in the sensing volume. In combination with a DMA the OPC can be used to quantify external mixtures of light absorbing and light scattering particles in the size range about 0.3 μm (Covert et al., 1990).

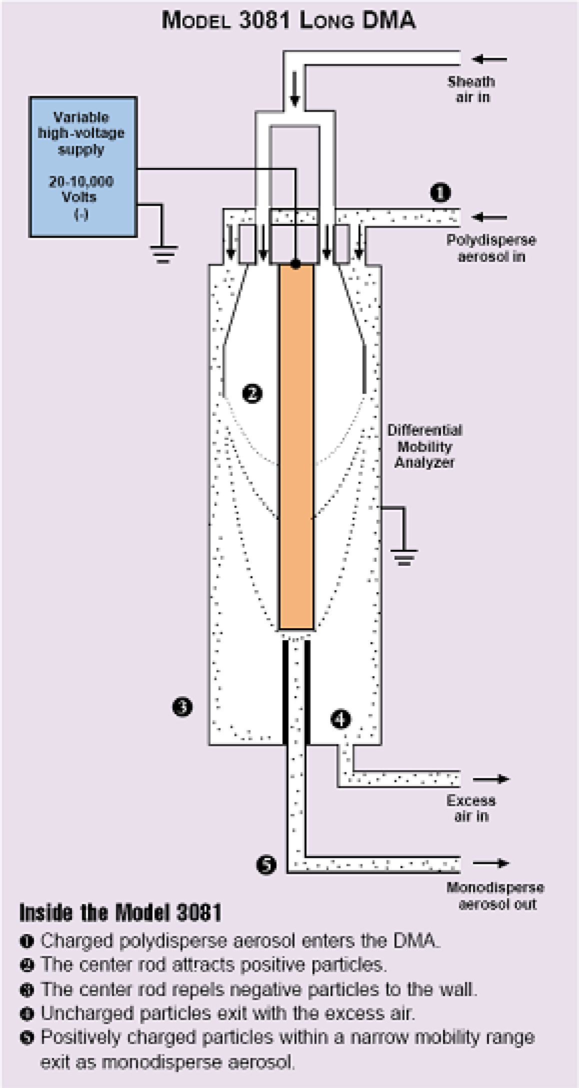
Particle size measurement techniques

DMA

They can be used to select monodisperse slices of “unknown” aerosols such as atmospheric aerosols for use for studies of aerosol properties. Size is determined from its known dependence on electrical mobility, classifying voltage and flow rates.

Polydisperse, submicrometer aerosol passes through a radioactive bipolar charger, establishing a bipolar equilibrium charge level on the particles. Nearly all particles from 20 to 300 nanometers in diameter receive either a single positive, single negative, or zero charge. The particles then enter the differential mobility analyzer (DMA) and are separated according to their electrical mobility. This parameter is inversely related to particle size. An electric field inside the DMA influences the flow trajectory of the charged particles. The DMA contains an inner cylinder that is connected to a negative power supply (0 to 10,000 VDC). This charged element provides a precise negative potential. Particles with negative charge are repelled towards and deposited on the outer wall. Particles with a neutral charge exit with the excess air. Particles with a positive charge move rapidly towards the negatively charged element. Only particles within a narrow range of electrical mobility have the correct trajectory to pass through an open slit near the DMA exit (TSI products).

DMA-based size spectrometers



Inside the Model 3081

❶ Charged polydisperse aerosol enters the DMA.
❷ The center rod attracts positive particles.
❸ The center rod repels negative particles to the wall.
❹ Uncharged particles exit with the excess air.
❺ Positively charged particles within a narrow mobility range exit as monodisperse aerosol.

Fig. 1. Differential Mobility Analyzer

The development of DMA-based size spectrometers, in the last years, enabled number size distribution measurements almost over the whole submicrometer size range. Two different sizing systems are presently used for atmospheric measurements. DMPS systems (Differential Mobility Particle Sizer) measure stepwise while SMPS (Scanning Mobility Particle Sizer) systems continuously scan through the size range. DMPS-systems need a scan time of 10-15 min and provide relatively good counting statistics in each size bin. In contrast, SMPS-systems can scan much faster (1-5 min), possibly leading to higher statistical uncertainties and artificial distortions at the ends of the size distributions. Those artefacts may lead to large errors in calculations of higher moments of the size distribution such as surface area, scattering coefficient, volume, or mass. DMPS systems are commercially available since the eighties, however, were limited only to the size range above 10 nm. The development of DMAs for nanometer particles (<10 nm) and the availability of the UCPC (UCPC =Ultrafine Condensation Particle Counter) led to the design of "ultrafine"-DMA based size spectrometers (Birmili *et al.*, 1999a; Russell *et al.*, 1996). However, the statistical uncertainty in the range below 10 nm is still quite large for atmospheric measurements in each DMA based sizing system due to decreasing DMA penetration efficiency, low charging probability and the low aerosol flow rate of the UCPC (Wiedensohler et al., 1994).

Hygroscopic-TMDAs

The tandem differential mobility analyzer (TDMA) has been used to infer water content. This instrument system involves the use of two DMAs operated in series (Rader and McMurry, 1986). The aerosol classified by the first DMA is humidified or dehumidified between the DMAs, and the second DMA measures the effect of humidity on particle size (McMurry and Stolzenburg, 1989; Svenningsson et al., 1994). TDMA data can provide information on variations in water uptake among particles of a given size. TDMA measurements have shown that when atmospheric particles of a given size are brought to high humidity, they often separate into two distinct types, which have been termed “more” and “less” hygroscopic.

Based on comparison with known materials, it is found that measured growth factors are typically accurate to within 2%. Because number concentrations of particles larger than about 0.5 μm are too low to permit TDMA measurements, all atmospheric data reported to date applies to smaller particles. Also, while the TDMA provides accurate information on the dependence of size on relative humidity, it does not provide direct information on particulate water mass concentrations. TDMA data can be used together with size distribution data, however, to obtain estimates of humidity-dependent mass concentrations. The TDMA has provided valuable insights into hygroscopic properties of atmospheric aerosols, but due to its high cost and complexity it is likely to remain a research tool rather than a monitoring device.
Other versions of the tandem DMA configuration exist such as the organic tandem DMA, which grows the particles in an organic chemical (e.g. propanol) instead of water, and the volatility tandem DMA, which subjects the particles to a high temperature between the DMAs rather than growing them. These can be used to obtain further information on other aspects of the particle compositions.

Particle mass measurement technique

More recently, beta-attenuation monitors (BAMs, e.g. BAM-1020, Met One Instruments Inc., Grants Pass, OR, USA) have become the standard method of PM10 and PM2.5 monitoring, as they have a much higher time resolution than is achievable with offline weighing of samples. These collect particles on a filter, where β-radiation is passed through the sample and the reduction in the radiation passing through measured. The degree of attenuation is proportional to the total number of electrons present in the molecules that make up the sample, which to a close approximation is proportional to its total mass. Also used for this measurement is the Tapered Element Oscillating Microbalance (Patashnick and Rupprecht, 1991), which collects particles onto a filter on the end of a tapered tube, which is vibrated electrically. Changes to the resonant frequency of the system are measured and linked to the mass of the sample. This technique too has very high time and mass resolutions but negates the need for radioactive sources.

Chemical techniques

Aerosol mass spectrometry

The universal nature of mass spectrometric detection for atomic and molecular species recommends the technique as a comprehensive and sensitive technique to characterize the chemical content of atmospheric PM. Over the past decade, several research groups have made major strides in adapting mass spectrometric techniques to meet this challenge, and this work has been the subject of several review articles (Suess and Prather, 1999; Noble and Prather, 2000; Sullivan and Prather, 2005).
The basic principle of an aerosol mass spectrometer is to introduce airborne particles into the instrument, vaporise and ionize the material. Once the ions are formed, they are analysed by mass spectrometry. Aerosol MS instrumentation may be classified into several discrete sections: sample introduction, aerosol sizing techniques, ionization techniques (inductively coupled plasma (ICP), secondary ion, surface or thermal, electron impact (EI), laser desorption/ionization (LDI), and mass spectrometer types (magnetic sector, quadrupole, ion trap, and time-of flight).
The most widespread commercially available particle mass spectrometers are the Aerosol Mass Spectrometer (AMS-Aerodyne Research, Inc.) and Aerosol Time-of-Flight Mass

Spectrometer (ATOFMS, model 3800-TSI Inc.) and a brief overview of these instruments is given in the next subparagraphs.

TSI model 3800 Aerosol Time-of-Flight Mass Spectrometer (ATOFMS). The ATOFMS provides continuous, real-time detection and characterization of single particles from polydisperse samples, providing information on particle size and composition (Prather et al., 1994; Gard et al., 1997). Briefly, air is introduced into a vacuum system region through a converging nozzle and two skimmers create a narrow collimated particle beam. The particles then travel through a sizing region where the aerodynamic diameter of individual particles is determined by detecting scattered light from two timing lasers positioned at known distance apart. After being sized, the particles enter the mass spectrometer source region where a pulse from a Nd:YAG laser (frequency quadrupled, λ=266 nm) is triggered at the appropriate time – based on the transit time of the particle measured in the sizing region – to desorb and ionise material from the sized particle. The mass-to-charge ratios of both positive and negative ions of single particles are then determined simultaneously in two time-of-flight reflectron mass spectrometers. Briefly, it was found that the response of the ATOFMS follows a power law dependency in the range 0.53–1.9 μm, and is affected by a substantial matrix effect in the super-micron size mode depending on the chemical composition of the aerosol sampled at the time, which is reflected in variations in the hit-rate of particles with the main desorption-ionization laser as they enter the sensing zone of the instrument. It is currently a matter of debate whether this effect is due to the inherent absorptive properties of the particles, or due to the hygroscopic properties and a low hit rate for solution droplets (Dall'Osto et al., 2004). However, the laser ablation technique can provide quantitative information on an ensemble of particles of a similar matrix. The unique feature of the ATOFMS is it can provide information on real-time changes in the size-resolved mixing state (internal/external) of the single particle sampled. The instrument is able to measure the size and the chemical composition of individual airborne particles in the size range roughly between 0.3 and 3.0 μm (TSI model 3800).

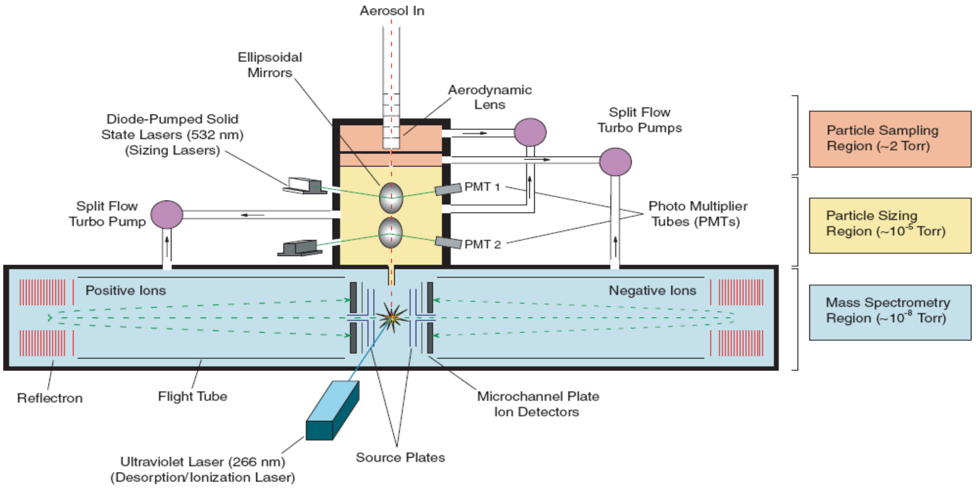
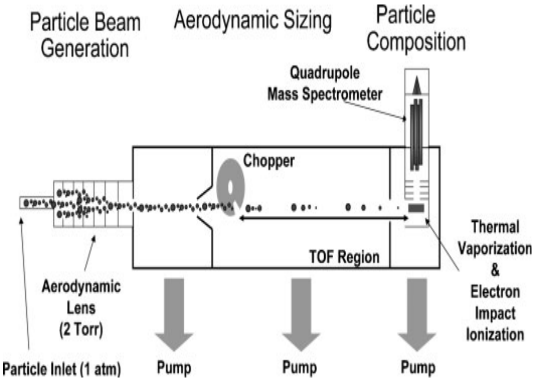
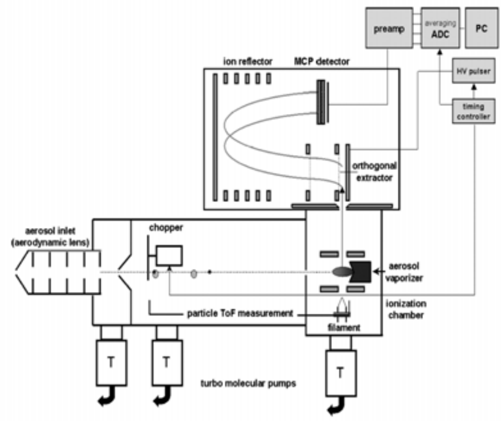


Fig. 2. Schematic of the aerosol time-of-flight mass spectrometer (TSI3800 ATOFMS).

The Aerodyne Aerosol Mass Spectrometer (AMS) (Jayne et al., 2000; Jimenez et al. 2003; Allan et al., 2003a) provides online, real time measurements of the mass of non refractory components of aerosol particles as a function of their size. Briefly, the AMS draws sample air into a high vacuum through a critical orifice and focuses particles with an aerodynamic lens. The particle diameter is measured by the same principle used in the ATOFMS which is time-of-flight. A chopper wheel delivers a slug of particles into the time of flight vacuum region, where their speed is proportional to their size. The particle beam is then delivered onto a heated surface, maintained at 500°C, at a vacuum pressure of 10^{-8} torr, which is located in the centre of an electron impact ioniser. Here the particles are deposited on the hot surface and the volatile and semi-volatile components of the aerosol are vaporised. The mass collection efficiency is almost 100% for spherical particles with aerodynamic diameters between 60 and 600 nm. The molecules are then ionised by electron impact (70 eV) and analysed by quadrupole mass spectrometry. The AMS alternates between two data acquisition modes: the "Time-of-flight" (ToF) mode and the "Mass Spec" (MS) mode (Jimenez et al., 2003; Alfarra et al., 2004). In the ToF mode the quadrupole mass spectrometer is set to scan pre-selected fragment ions and measure their mass as a function of the particle size. In the MS mode the averaged chemical composition of the non-refractory aerosol components is determined by scanning the full mass spectrum (1–300 m/z units) with the quadrupole mass spectrometer. In this mode the AMS measures the ambient submicron aerosol ensemble. The AMS can quantify the size resolved organic carbon, sulphate, ammonium and nitrate mass loadings of aerosol in the size range between 60 and 600 nm. However, it cannot detect refractory material such as elemental carbon, dust and sea salt particles. The standard quadrupole version of the AMS cannot resolve single particle composition, and therefore cannot explicitly determine the chemical mixing state of the particles. However, an AMS fitted with a time of flight mass spectrometer is currently being developed and will overcome this limitation. The ATOFMS can provide mass spectral information on a single particle basis and therefore information on the mixing state of single particles. Furthermore, it is sensitive to refractory material and so can probe sea salt, dust and elemental carbon, as well as more volatile components. The commercial version of the ATOFMS (without an aerodynamic lens system which is now available – TSI 3800-030) has a size dependent sampling efficiency and samples far fewer particles per unit time than the AMS. The complementarity of the two particle mass spectrometers is a very powerful combination for characterising ambient particles.



a)



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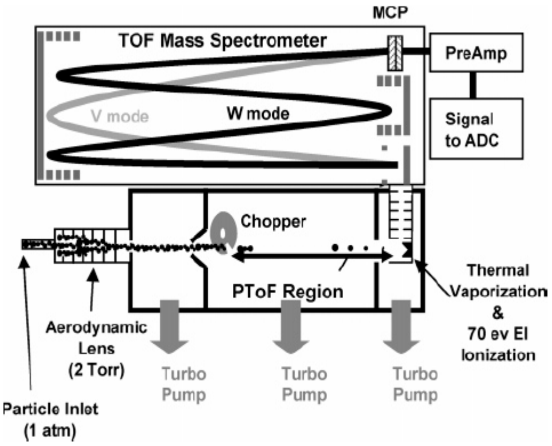

c)

Fig. 3. Schematic of an Aerodyne aerosol mass spectrometers: a) Q-AMS; b)ToF-AMS; c) HR-ToF-AMS.

Recently, the quadrupole in the AMS instrument has been replaced with a time-of-flight mass analyzer (ToF-AMS) (Drewnick et al., 2005; DeCarlo et al., 2006). The properties of the three versions are summarized in the table 1**.** The standard ToF-MS spectrometer is referred to as the C-ToF due to the shape of the ion path in the instrument resembling a ‘‘C.’’ Recently, a HR-ToF-AMS capable of resolution ranging from 2,500 (in V-mode) or 4,500 to 5,000 (in W mode) has been developed, where the V and W represent the path of the ions in the flight chamber (DeCarlo et al., 2006). In V-mode, ions follow a traditional reflectron path, whereas in W-mode, the ions are reflected three times, thereby increasing the effective drift length. The high mass resolution allows the separation of each unit mass peak into separate contributions for specific elemental compositions based on small differences in mass defect (Fig.6). Algorithms are being developed which allow elemental analysis (C, H, N) of HR-ToF-AMS data.

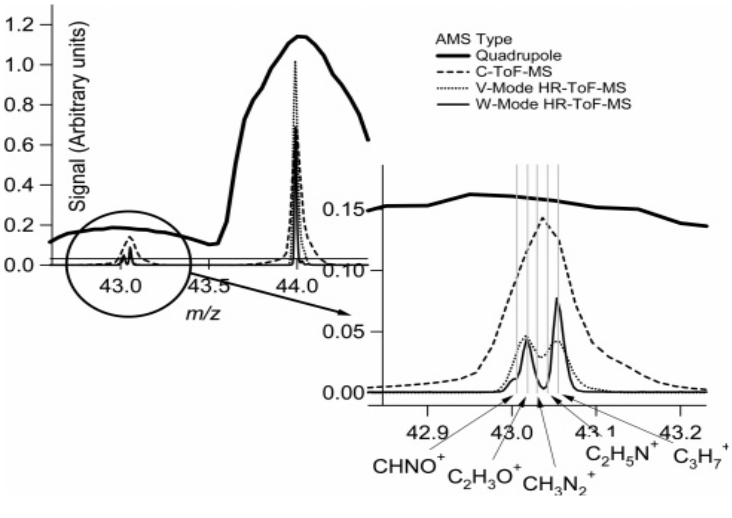

Fig. 4. Peak comparisons for the four versions of the AMS. Resolution improvements are obvious in the progression from Q- AMS to C-ToF-AMS to V-mode to W-mode of the HR-ToF-AMS (DeCarlo at al., 2006).

Table 1. Characteristics for the three versions of AMS (from http://www.aerodyne.com/products/aerosol_mass_spectrometer.htm).

	Detection Limit* (μg/m^3)	Mass Resolving Power (m/Δm)	Mass Range (m/z)
Q-AMS	0.01	300	1-300
C-ToF-AMS	0.002	800	1-800
HR-ToF-AMS (V-mode)	0.003	2500	1-1200
HR-ToF-AMS (W-mode)	0.05	4500	1-1200

* Detection limits depend on chemical species. Typical values for nitrate are listed.

Remaining development challenges for the AMS include improving its quantification capability, interpreting the mass spectral complexity, particularly for organic species, and extending its capability to detect refractory species. The flexibility of the AMS detection approach allows for progress in these directions through the development of aerodynamic inlets that have higher transmission efficiencies for supermicron (transmission range 0.2-2.5μm) and small particles (30-300nm), new vaporizer designs that could reduce bounce-related collection efficiency losses, soft ionization schemes that could simplify mass spectral fragmentation patterns, and the incorporation of other techniques such as light scattering that can be used to detect non-refractory species.

EC/OC

In an EC/OC analyzer a quarts fibre filter with pre-collected aerosol particles is heated controlled by a temperature program (Fig. 1). First the organic carbon is removed at 340 ºC. Subsequently the elemental carbon is oxidized to CO_2 and detected with a FID (Chachier et.al., 1989). An uncertainty of this method is that the choice of temperature program will affect which fraction of the sample that is detected as EC and which as OC. In recent years, the method has been combined with optical measurements to correct for charring by pyrolysis of OC to EC during the combustion process (Chow et al., 2001).

The EC/OC technique is limited in time resolution by the time demanding oxidation of the sample, but is an important complement to on-line techniques. Only two different classes of compounds can be identified, EC and OC.

Turpin et. al. presented an online set-up of the EC/OC analyzer with a time resolution of 1.5 hours (Turpin et. al., 1990). A complement to this technique is the Sunset Labs semi continues ECOC instrument. The instrument is equipped with an internal filter that collects the aerosols and then oxidizes and detects OC and EC using a non-dispersed infrared detector (NDIR) quantifying the produced CO_2.

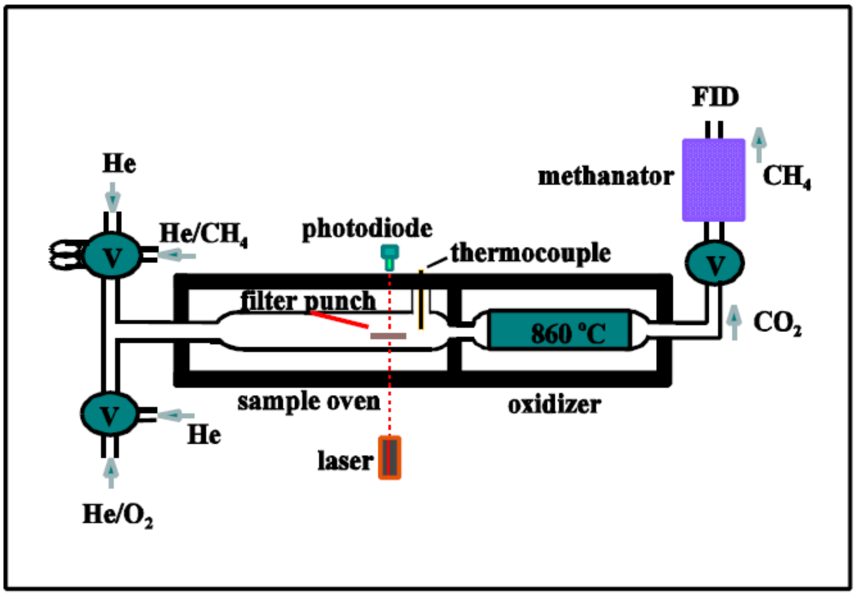

Fig 5. Schematic drawing of an OC/EC analyzer (NIOSH Manual of Analytical Methods (NMAM), Fourth Edition, Sunset Laboratory)

GC-MS

In gas chromatography molecules are separated in the column according to volatility and polarity. The advantage of this technique is the possibility to detect individual compounds, but the technique is limited by that the analyte has to be volatile enough to evaporate in the GC. Specific organic compounds may not make up large part of the aerosol mass, but can provide valuable information as traces for particle sources. The GC provides quantitative information with a Flame Ionisation Detector (FID) if reference sample are available. If a Mass Spectrometer (MS) detector is also used qualitative information will be generated.
The time resolution for the GC technique is limited by the time needed for the compounds to eluate with required separation. This gives often a time resolution around one hour but can be pressed down to minutes.

TAG

The thermal desorption aerosol GC/MS-FID instrument can analyze the chemical composition of organic aerosols with a time resolution of 1 hour (Williams et. al. 2006). The method is automated in a two step procedure. First the aerosol particles are humidified and the collected by inertial impaction. Secondly the compounds are thermally desorbed and transferred with a helium carrier gas in to the gas chromatograph column. In the column the chemical compounds are separated and then reach the MS-FID detector (Fig 2).

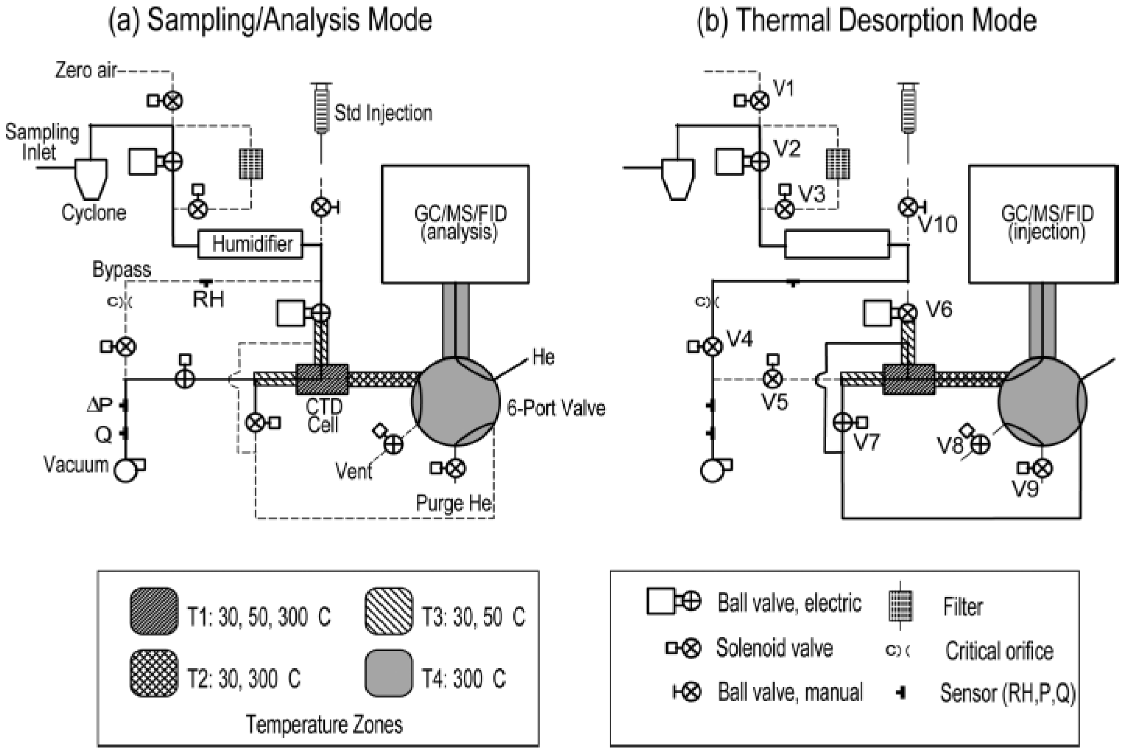

Fig 6. Schematic of the TAG system, showing flow configuration for two modes of operation: (a) concurrent sampling and analysis, and (b) thermal desorption. The thermal desorption mode is used for transfer of collected sample onto the chromatography column. (Williams et. al. 2006)

The method provides a large amount of information and can profit of the extensive body of knowledge available for quantification of organic aerosol from past research using filter-based GC/MS analyses. Below is an example of a chromatogram from Berkeley California (Fig 3).

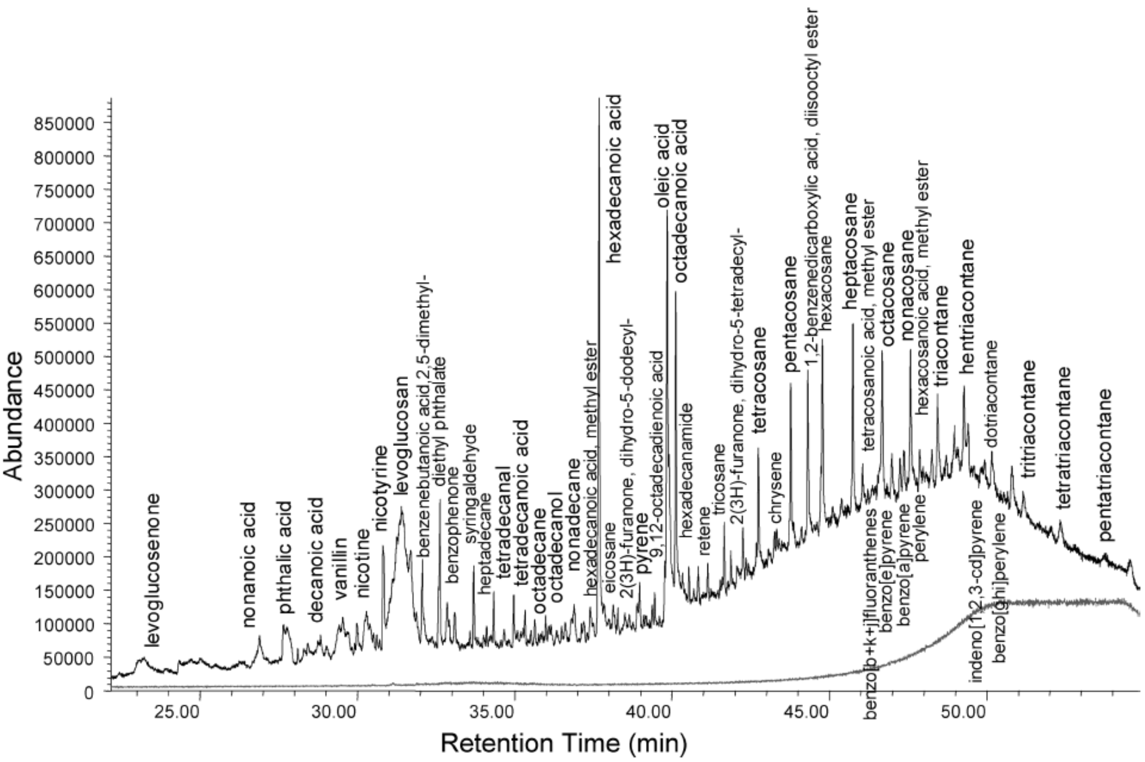

Fig 7. TAG Chromatogram from Berkeley California, with many of the identified peaks labeled. Volume of air sampled is approximately 0.4 m3. Lower gray line shows signal from blank. The rise in background signal after 40 minutes is a result of typical column bleed. (Williams et. al. 2006)

2D-TAG

To further increase the separation in GC two columns connected in line can be used. One column that separated due to volatility and a second one due to polarity. This is called Double column 2D-TAG (Goldstein et.al., 2008) and has a thermal desorption cell for sample collection and a mass spectrograph (MS) as detector. The use of an air cooled two-stage thermal modulator makes it appropriate for an automated in-situ field measurement. With a technique this specific a lot of information is generated, which raise the demand on improved data processing routines. There is no use with more information if we can't handle it.

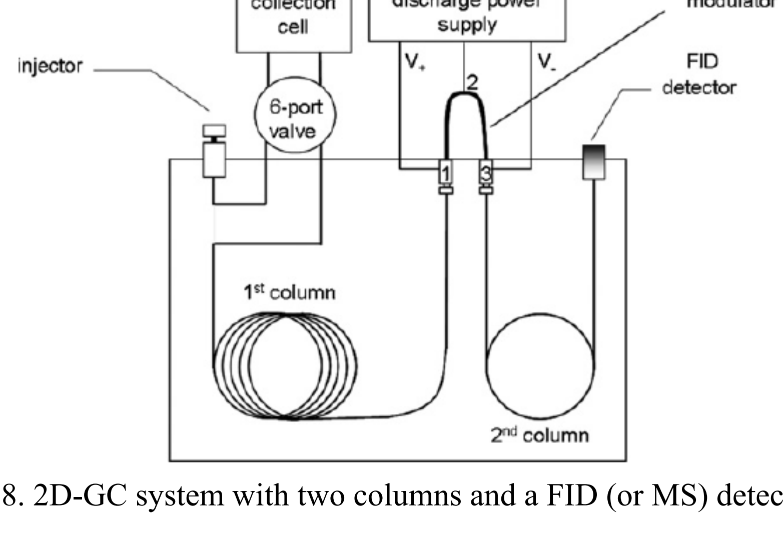

Fig 8. 2D-GC system with two columns and a FID (or MS) detector. (Goldstein et.al., 2008)

PILS-WSOC

Particle-Into-Liquid Sampler (PILS) coupled with a Total Organic Carbon (TOC) analyzer is a method to measure water-soluble organic carbon online (Peltier et. al. 2007). The aerosol sampling was performed with a cyclone which transferred the insoluble aerosol particles into a liquid stream. This instrument agreed within 5% when compared with the Sunset Labs ECOC technique measuring WSOCs. However, a size dependency was observed when measuring water insoluble OC, and the method showed not to be effective for particles larger than 110 nm.

Summary

Today wide ranches of techniques are available to the atmospheric scientist, who would like to study aerosol particles and the development is continuing. The characteristics of the techniques are all from those that measure all particles but do not distinguish between then, to those that only detect specific groups of compounds but gives detailed information of the chemical composition and the molecule structure. So it is a delicate choice to be made concerning which technique to be used when a study is planned. And another, not irrelevant, consideration not discussed here is the wide span in the costs for the different instruments.

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