Off-line analysis of organic aerosols

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1 Introduction

Aerosols have been a primary issue due to both their public health concerns and their potential, and still not fully known, effects on climate. Aerosols have a wide range of origins, and part of the effort the scientific community has developed in this filed during the past decades has focused on the identification of the aerosol's sources and their quantification. Another part has been directed towards the understanding of the aerosol's role in various atmospheric processes.

For these purpose, the collection of the aerosol, either from the ambient air or directly at a source, for further analysis (both chemical and physical) has been employed.

2 Sampling

Mainly, the aerosol has been collected on various types of filters. The choice of the filter media composition (quartz or glass fiber, cellulose, nuclepore, ...) is related to the kind of analysis that is to be done after the sampling. Besides filters, aerosol may also be collected into liquid media. The liquid is then further analised.

In order to bring the aerosol to deposit onto the filter or dissolve into the liquid, air is pumped. A variety of air sampling systems may be used (high-volume, low-volume, ...).

3 Instrumentation

3.1 Chemical characteristics

3.1.1 Carbon

Elementar versus organic carbon determination Organic (OC) and elemental (EC) carbon can be determined by thermochemical oxidation and evolved gas analysis (CO_2 detection) of a filter sample by controlling the temperature and atmosphere in the instrument used (Figure 1), and by an optical feature that corrects for pyrolytically generated carbon, which can be formed during the analysis of some materials [1]. When analysing using this technique it is assumed that the sample is homogenously distributed since the instrument calculates the amount of OC, EC and total carbon (TC) from a small area of the filter. A punch of the filter is placed in the sample oven of the instrument (Figure 1) and the OC is volatilised from the filter whilst the temperature is stepped up to above 800° C. A carrier gas (helium) drives the evolved OC through granular MnO_2 (maintained at 870° C), which oxidises it to

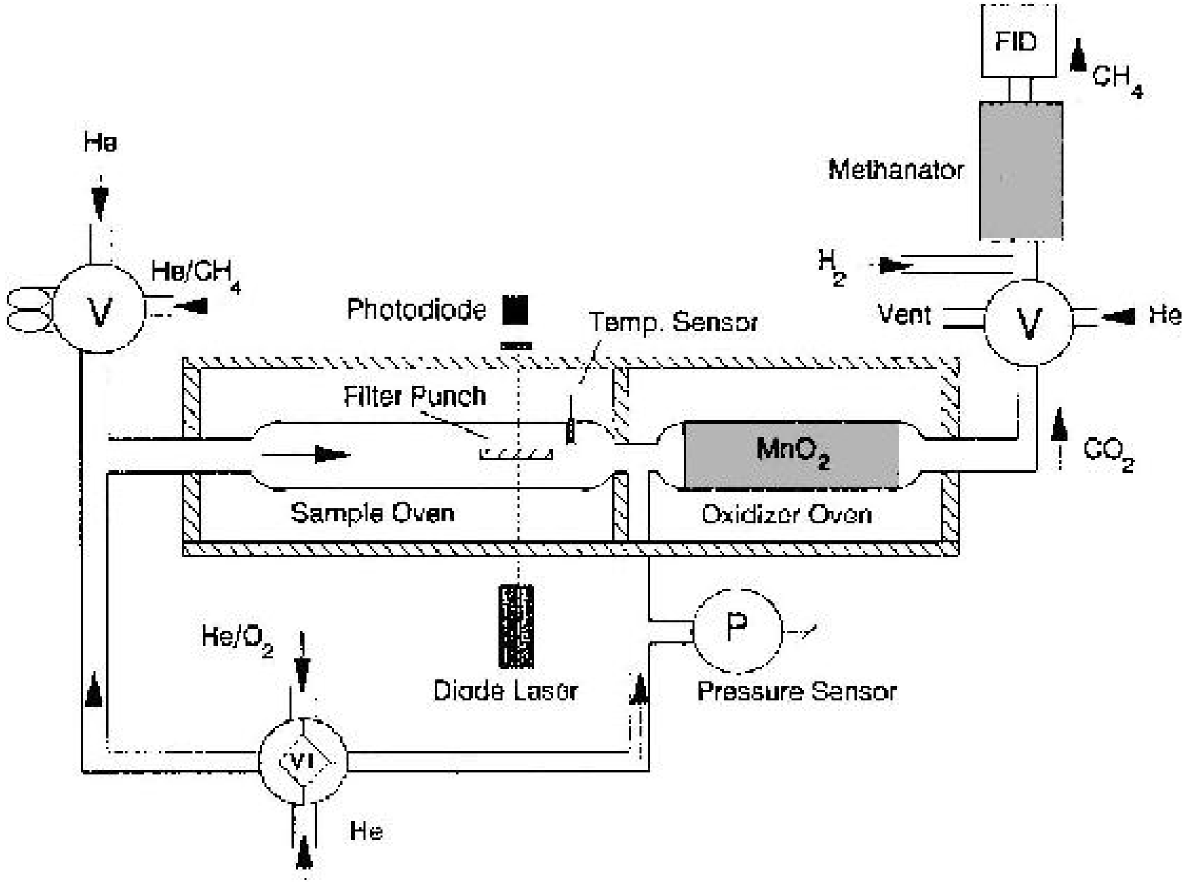

Figure 1: Schematic diagram of thermal-optical instrumentation [1].

CO_2. A hydrogen flow is then introduced and a nickel-firebrick methanator (held at 500° C) reduces the CO_2 to CH_4. A flame ionisation detector (FID) is used to quantify the CH4. The concentration of CH_4 measured is assumed to be the OC concentration, once a pyrolisis correction is applied. A typical thermogram produced by this instrument is shown in Figure 2, which includes the profiles of the laser transmittance, temperature and FID. In the next stage of the analysis the oven temperature is lowered and the carrier gas changed to O_2/He. The temperature is stepped up to above 800° C again, and the volatilised and oxidised EC is measured in the same way as with the OC. The transmittance is continuously measured throughout the analysis by a helium-neon laser and a photodetector. When pyrolisis occurs there is an increase in light absorption, resulting in a decrease in transmittance. When the sample comes into contact with O_2 the pyrolytically generated char (EC) is oxidised and increases the transmittance. The amount of char produced is the quantity required to return to the level of transmittance at the start of the analysis. By retrospectively assigning a portion of the elemental carbon peak to the organic fraction the pyrolised OC can be corrected for. A vertical line is drawn in the thermogram (Figure 2) to represent the split time, defined to separate the OC from the EC.

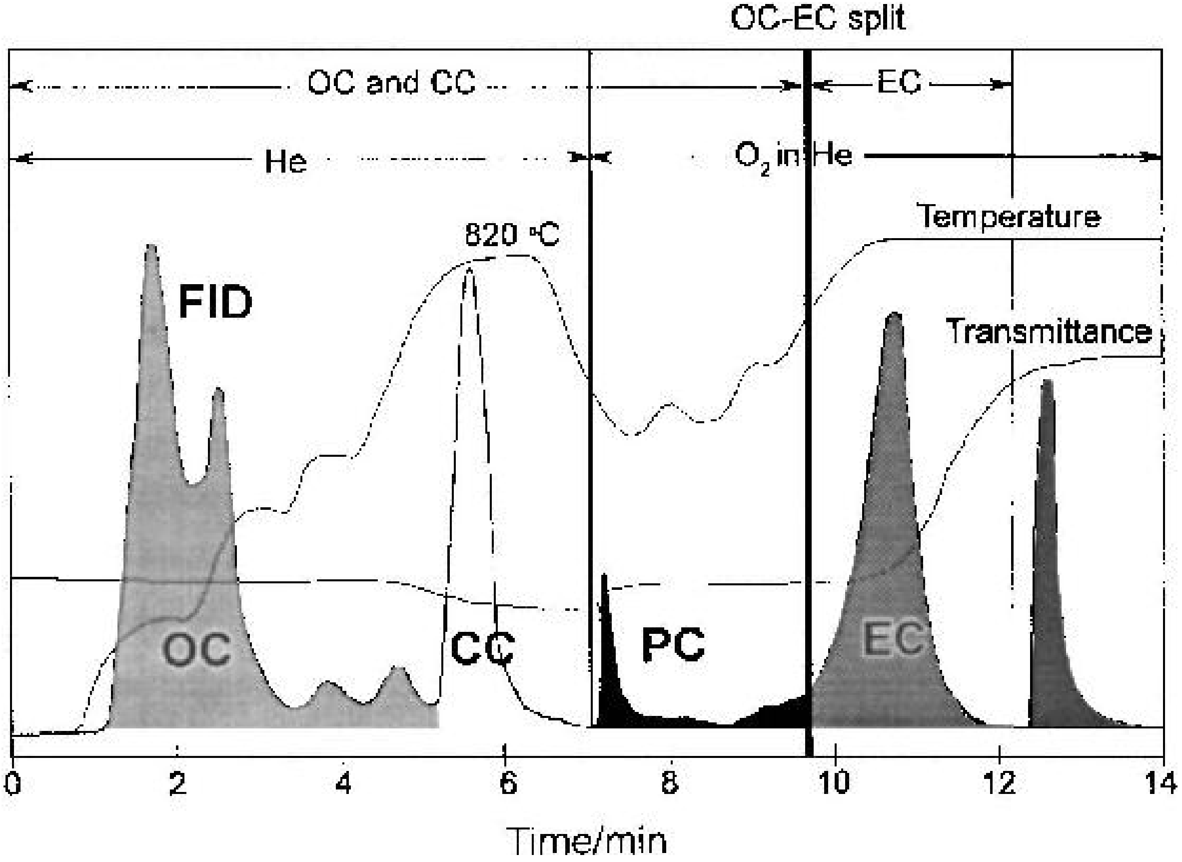

Figure 2: A typical thermogram from the thermal-optical instrumentation [1]. The three traces correspond to oven temperature, filter transmittance and FID response. Peaks correspond to organic (OC); carbonate (CC); pyrolytic (PC); and elemental (EC) carbon. The final peak is a methane calibration peak.

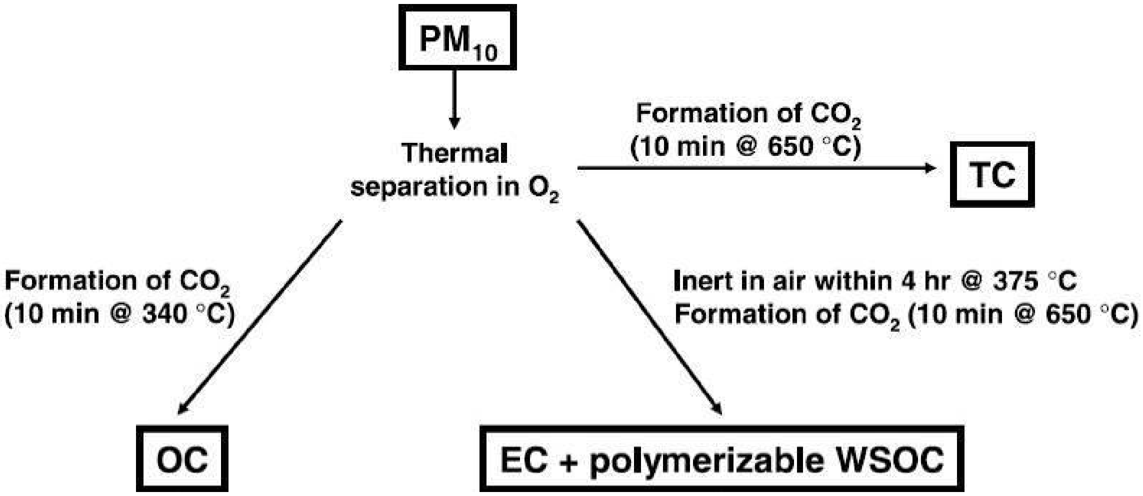

Figure 3: Separation scheme of the different carbon fractions. The ^{14}C was directly measured in OC, and the mixture EC + polymerizable WSOC. Modified from [3]

^{14}C Accelerator Mass Spectrometry (^{14}C-AMS) ^{14}C measurements of airborne PM are used to distinguish between OC and EC of fossil and contemporary carbon origin [2]. In this method OC and EC are transformed into CO_2 in a stream of O_2 at 340 and 650° C, respectively, and reduced to filamentous C to produce a target for subsequent 14C-AMS measurements (Figure 3). ^{14}C has a half-life of 5730 years so none is present in fossil carbon, whereas, contemporary carbon contains about 1 in 1012 atoms of ^{14}C, and this can be detected by the AMS. By measuring the amount of fossil and contemporary carbon present in the OC and EC fractions of filter samples a simple top down source apportionment can be made (Figure 4).

Stable isotope ratio mass spectrometry (SIMS) Cachier *et al.* (1986) [4] measured the carbon isotopic composition (δ ^{13}C) differences between aerosol from major continental and oceanic sources, showing that oceanic particles in the Northern Hemisphere are mainly of continental origin while those in the Southern Hemisphere are mainly of marine origin. However, a study of particles in the atmosphere of Sydney, Australia [5], reached the conclusion that δ ^{13}C data unfortunately do not provide clear indications of origin.

gas chromatography separation, followed by isotopic ratio mass spectrometer analysis (GC-IRMS) It is known that aerosols are formed from different emission sources (e.g., fossil fuel or biomass) through different formation processes (e.g., primary emission: high temperature combustion and secondary formation: low temperature photochemical oxidation). Huang *et al.* (2002) [6] developed a method to measure carbon isotopic compositions of bulk carbon fractions in aerosols, released at different temperature ranges and different redox conditions, including OC (organic carbon), CC (carbonate carbon) and EC (elemental carbon). The distribution of δ ^{13}C obtained from different temperature ranges may provide information about source and formation processes. The method uses a step-wise heating thermal desorption/combustion OC/EC analyzer coupled with GC-IRMS through a Pre-Con

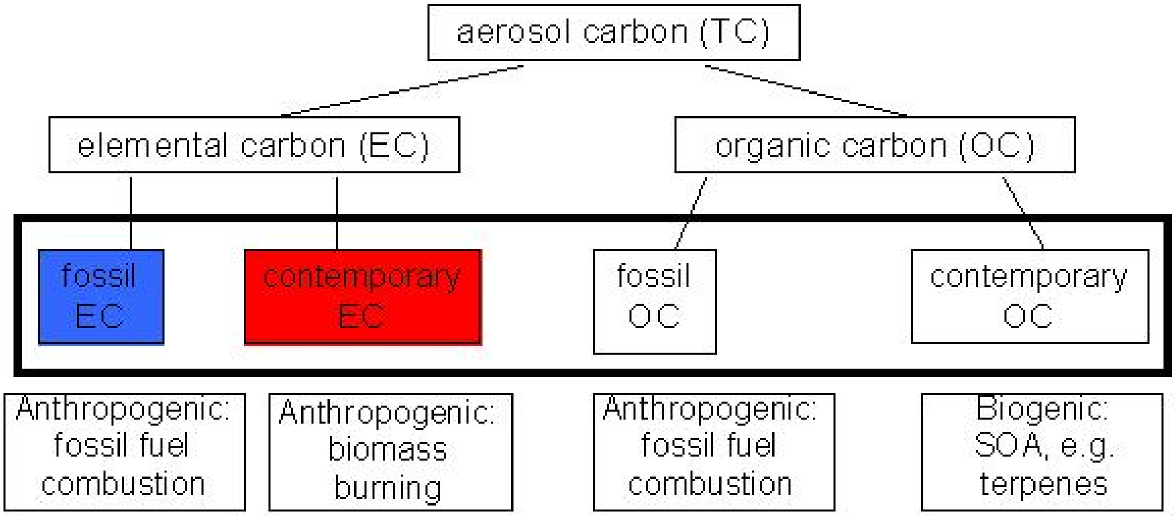

Figure 4: Top down source apportionment for fossil and contemporary carbon in OC and EC.

system. The overall precision of the whole method is about 0.3%, the average difference between on-line and off-line results is 0.1%. The combination of the isotopic compositions of different carbon components (i.e. the difference of δ ^{13}C between OC and EC) and the corresponding relative ratios of those components may be a powerful tool to constrain source apportionment for carbonaceous ambient aerosols [6]. Continiuos flow isotopic ratio mass spectrometry is usefull tool for investigation of non-volatile organic compounds (nVOC). Variation of nVOC composition in different sampling sites probably related to natural and anthropogenic activites. Recent natural release of hydrocarbons from plants have a clear predominance for the odd-carbon numbered n-alkanes. These C_{23}–C_{31} compounds are also systematically depleted in ^{13}C. The carbon isotope range between the odd and even compounds is up to 10 permil for the plant signatures. Anthropogenic and "aged" hydrocarbons have substantially lower molecular and isotope OEPs. This novel biogeochemical approach has good potential for estimating broad source apportionment and process control of nVOCs in rural and urban air masses [8].

The schematics of GC-IRMS system is shown in Figure 5. The GC is an standard capillary system with any of the usual injectors, split/splitless or on-column. The GC effluent is directed to a combustion reactor, which is normally a ceramic or quartz tube with capillary connections at the entrance and exit. The reactor is usually loaded with a metal oxide derived from oxidizing metal wire, such as Cu, along with Pt catalyst intended to promote completion of the oxidation reaction. At 600°C, CuO is a source of O_2 via

$$2CUO_{(s)} \longleftrightarrow 2Cu_{(s)} + O_{2(g)} \tag{1}$$

It is necessary to divert solvent GCC peaks away from the furnace, because solvent would otherwise prematurely deplete CuO. Most systems accomplish this diversion by a backflush switching of flow pressure under computer control so that He is forced back through the furnace toward the capillary column. CO_2 and H_2O are representative of the combusted organic analyte emerge from the furnace. Water must be removed prior to admission to the

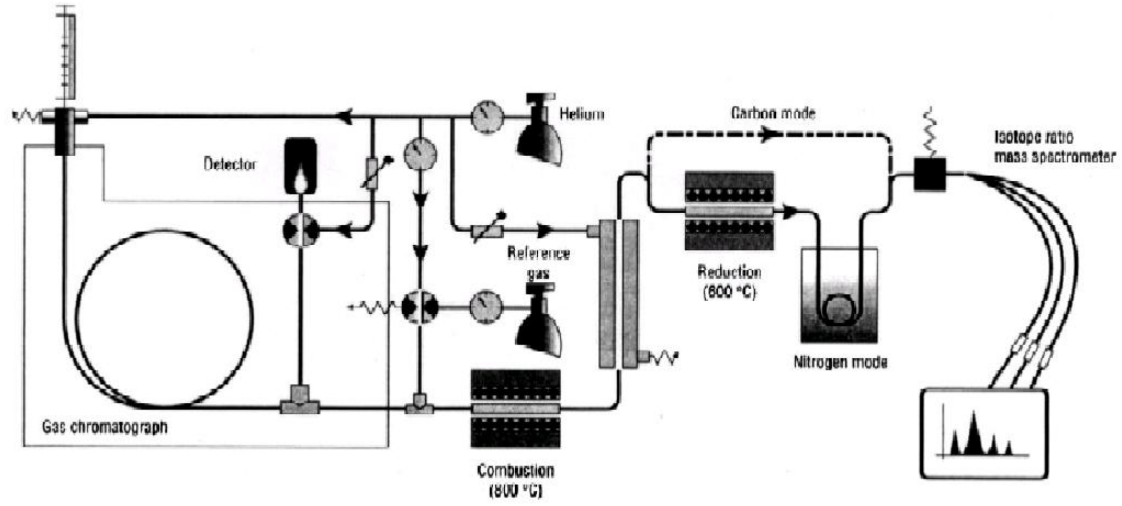

Figure 5: Set-up of an isotope ratio mass spectrometer coupled to a gas chromatograph via a combustion interface to measure $^{13}C/^{12}C$ (carbon mode) or $^{15}N/^{14}N$ ratios (nitrogen mode) [7].

ion source because it protonates CO_2 to produce HCO_2^+ , which interferes with analysis at m/z 45. Either a NafionTM tube or a cryogenic trap is employed to remove the water of combustion. Carbon isotope data from a single GC peak are shown in Figure 6. Three traces, representing masses 44, 45, and 46, are recorded as the analyte CO_2 passes through the ion source. Isotopic calibration can be accomplished if one of the peaks in the chromatograms is an internal standard. Precisions of SD(δ ^{13}C) <0.3 are routine for well-resolved, strong peaks that are integrated and calibrated in this way. For carbon, the minimum sample size required to yield a precision of this level is about one nmole carbon.

Elemental analyser coupled to isotope ratio mass spectrometer (EA-IRMS) Elemental analyzers provide an automated means for on-line high-precision isotope ratios for bulk analysis of solid and nonvolatile liquid samples. Samples are placed in a capsule, typically silver or tin, and loaded into a carousel for automated analysis (Figure 6). The sample is dropped into a heated reactor that contains an oxidant, such as copper oxide for C or S analysis, where combustion takes place in an He atmosphere with an excess of oxygen. Combustion products are transported by flowing He through a reduction furnace for removal of excess oxygen and conversion of nitrous oxides into N_2. A drying tube is used to remove any excess water in the system. The gas-phase products are separated by GC, and detected nondestructively by thermal conductivity before introduction to the IRMS. For all elements, initial sample sizes in the mg range are most easily analyzed with these instruments.

Stable isotopic ratio of carbon has been used extensively as a tracer of carbon sources in the environment. It has been documented that burning of C4 grasses resulted in significant depletion of ^{13}C in the charcoal while burning of wood and C3 grass did not [10].

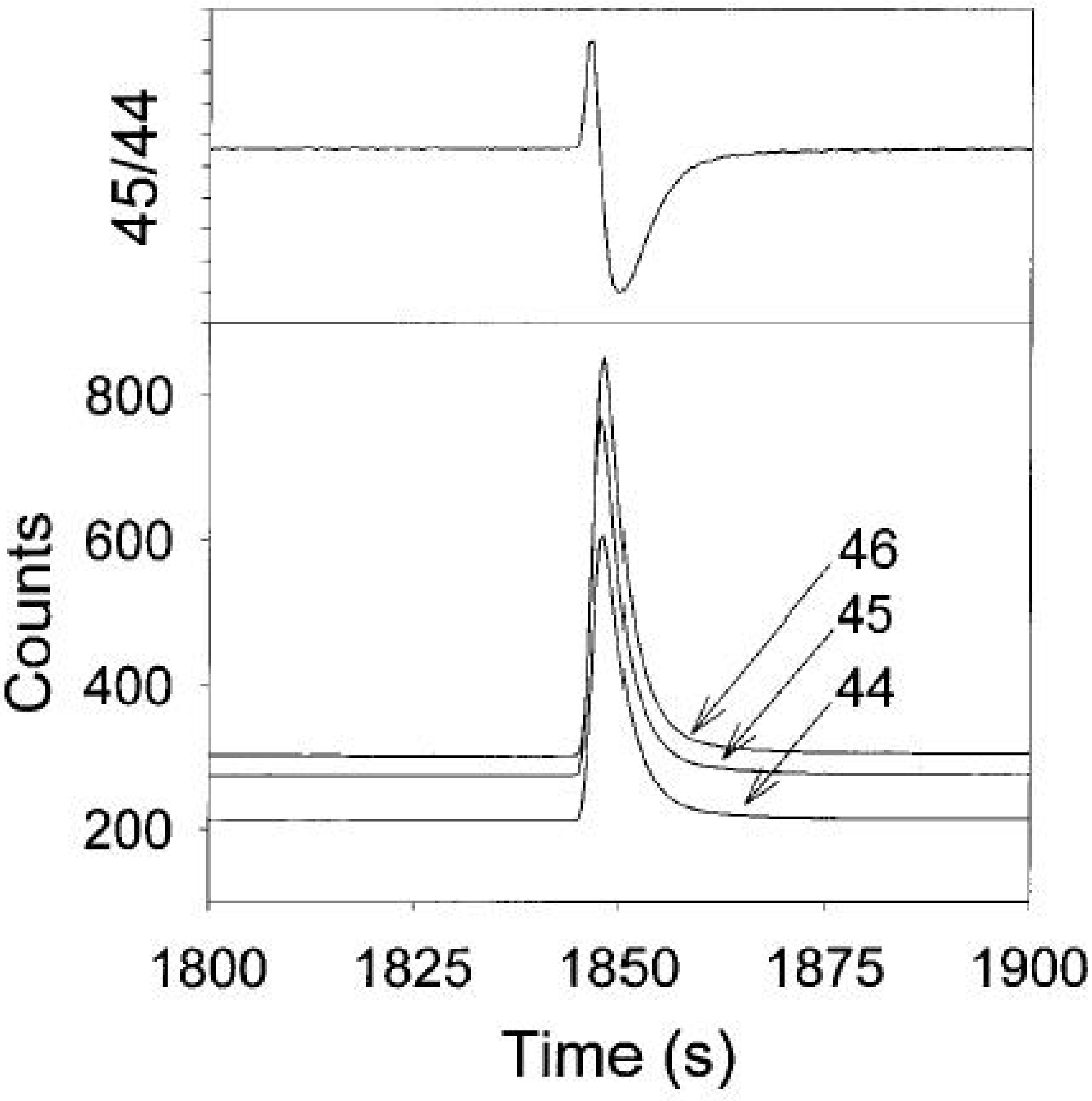

Figure 6: Traces of the m/z 44, 45, and 46 mass channels as a GC peak are analyzed in the IRMS [9].

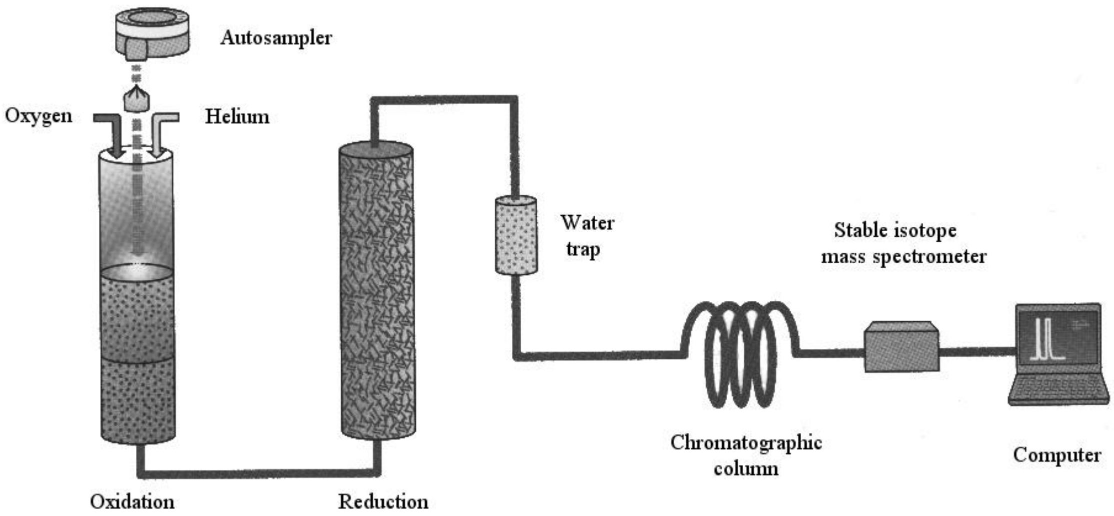

Figure 7: System for bulk carbon isotopic ratio determination

3.1.2 Organics at the bulk level

A range of sophisticated and sensitive chemical analytical techniques are now available that can help identify chemical characteristics of the carbon-containing part of PM. Use of these techniques on PM samples of varying spatial and temporal characteristics should help to reduce the current levels of uncertainty about their chemical composition. Attempts to characterise individual compounds in carbonaceous PM do not account for all of the species present. Therefore, analysis of the bulk properties of this fraction should give a better understanding of the overall chemical characteristics. The following is a brief overview of techniques that have been used to study the carbonaceous fraction of PM collected on filters.

Solid-Phase Extraction (SPE) WSOC removed from filters contains inorganic salts that can interfere with various analytical techniques. It is therefore beneficial to remove these interferences and enrich the organic material present in the aqueous solution.

An SPE method, capable of isolating about 60% of the WSOC from aerosol samples, was developed by Varga *et al. (2001)* [11]. It involved acidifying the water extract to pH 2 and applying it to an SPE cartridge, followed by elution in methanol (MeOH) (Figure 8). About 60% of the hydrophobic WSOC was recovered from the reversed-phase SPE cartridge using MeOH, whilst about 40% of the hydrophilic WSOC passed into the effluent, along with the inorganic components. The isolated organic matter (OM) was nearly free from inorganic ions, which are major constituents of atmospheric aerosol.

Another procedure entailed the adsorption of the WSOC fraction onto XAD-8 and XAD-4 resins, desalting the adsorbed organic material with ultra-pure water, and eluting the retained OM with 40% MeOH solution (Figure 9) [12]. Due to resin's different properties, and to certain hydrophobic/hydrophilic interactions between the resin polymers and the OM, two major fractions were obtained. About 58% of the WSOC was present in the XAD-8 eluate and consisted of partially acidic, highly conjugated compounds, containing hydrophobic functional groups. About 9% of the remaining WSOC was present in the XAD-4 eluate and consisted

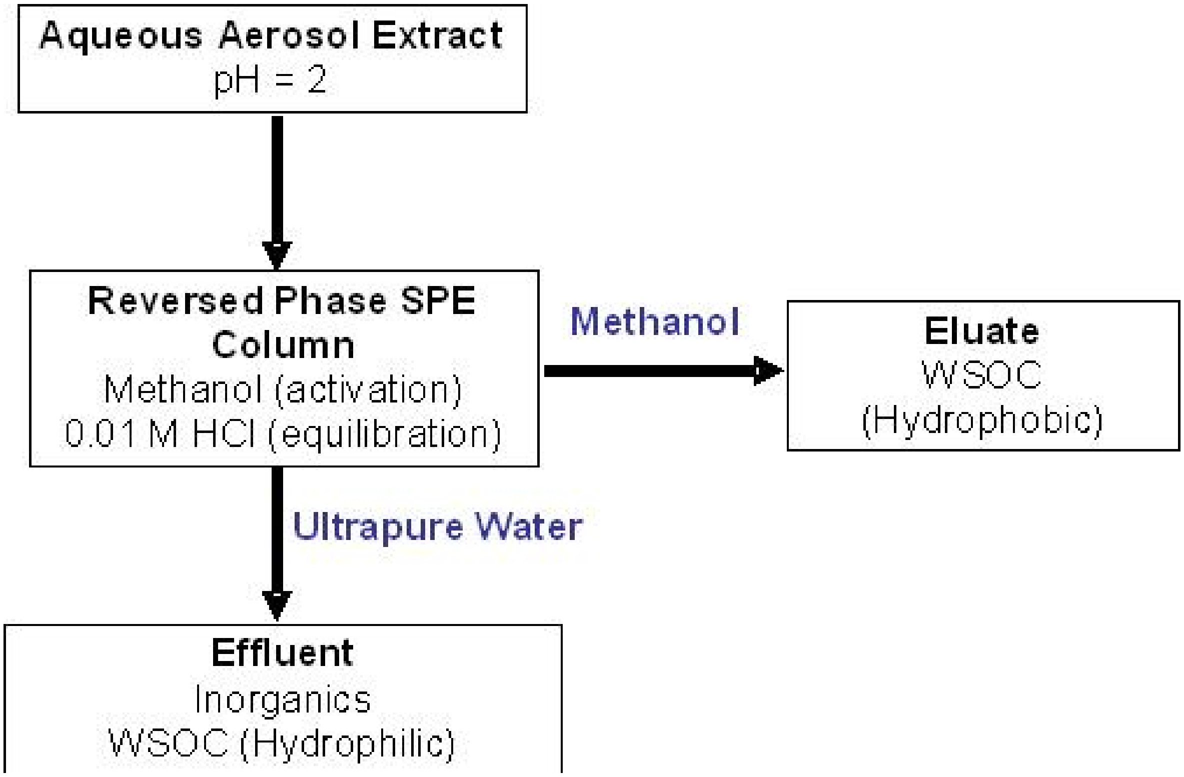

Figure 8: Schematic of the SPE procedure used by Varga *et al.* (2001) [11].

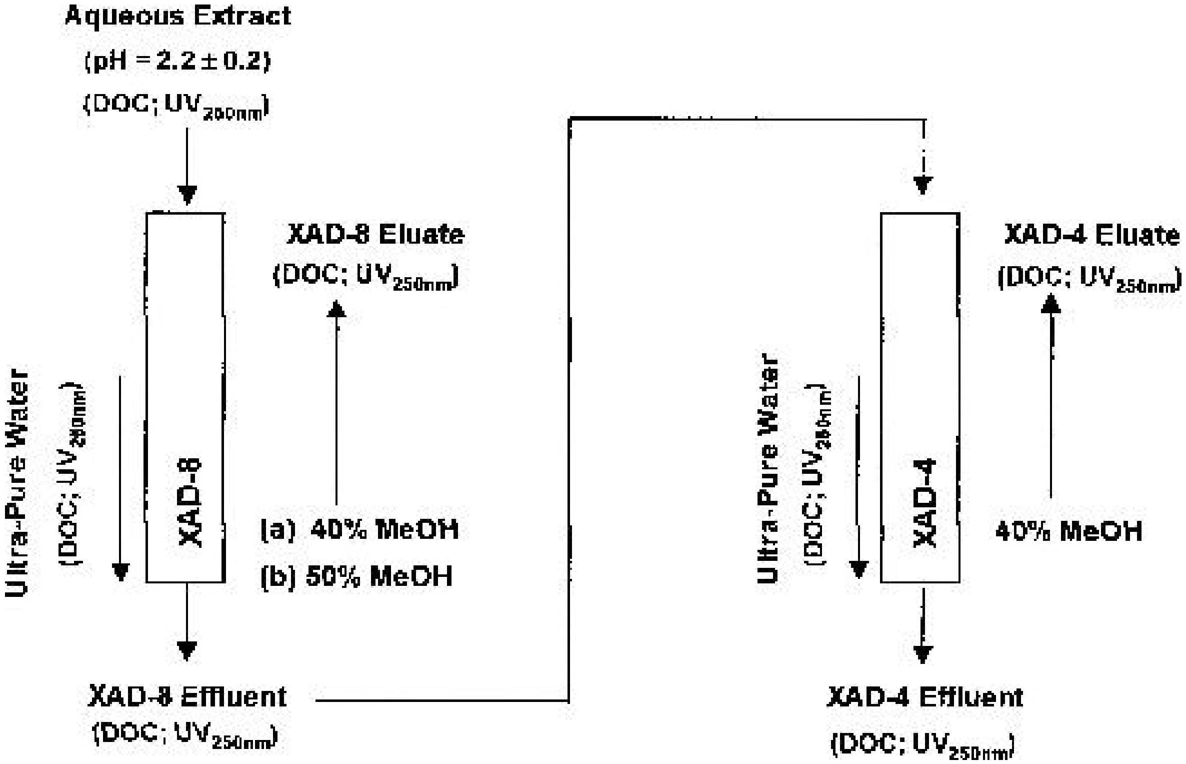

Figure 9: Scheme of the tandem XAD-8/XAD-4 isolation and fractionation procedure of the aerosol WSOC [12].

of fewer conjugated systems, with a lower molecular size, and a higher content of hydrophilic structures.

Ultraviolet-Visible (UV-VIS) Spectroscopy The UV-VIS spectra of WSOC from PM tend to be featureless, with a continuous absorption up to about 400 nm, which indicates the presence of conjugated double bond systems. More useful information may be gained by studying ratios of absorbances, for example, E250/E365 (E2/E3). The E2/E3 ratio has been found to be inversely correlated with molecular weight and aromaticity in aquatic humic substances [13] and could therefore be a useful indicator of molecular weight and aromaticity in WSOC. Duarte *et al.* (2005) [14] reported a higher E2/E3 ratio in summer samples than in autumn samples, indicating lower aromaticity in summer WSOC compared with autumn. The higher aromatic content in the autumn samples is typical of lignin breakdown products, highlighting the possible contribution of wood burning processes into the chemical properties of the WSOC fraction.

Fluorescence Spectroscopy Three-dimensional excitationemission matrix (EEM) fluorescence spectra of WSOC from aerosol samples have been measured by Duarte *et al.* (2004) [15]. The EEM profiles of the WSOC showed two well-defined excitation/emission (λExc/λEm) peaks at λExc/λEm 240/405 nm and λExc/λEm 310/405 nm. Compared with EEM profiles reported in the literature for natural dissolved organic matter (DOM), these were located at

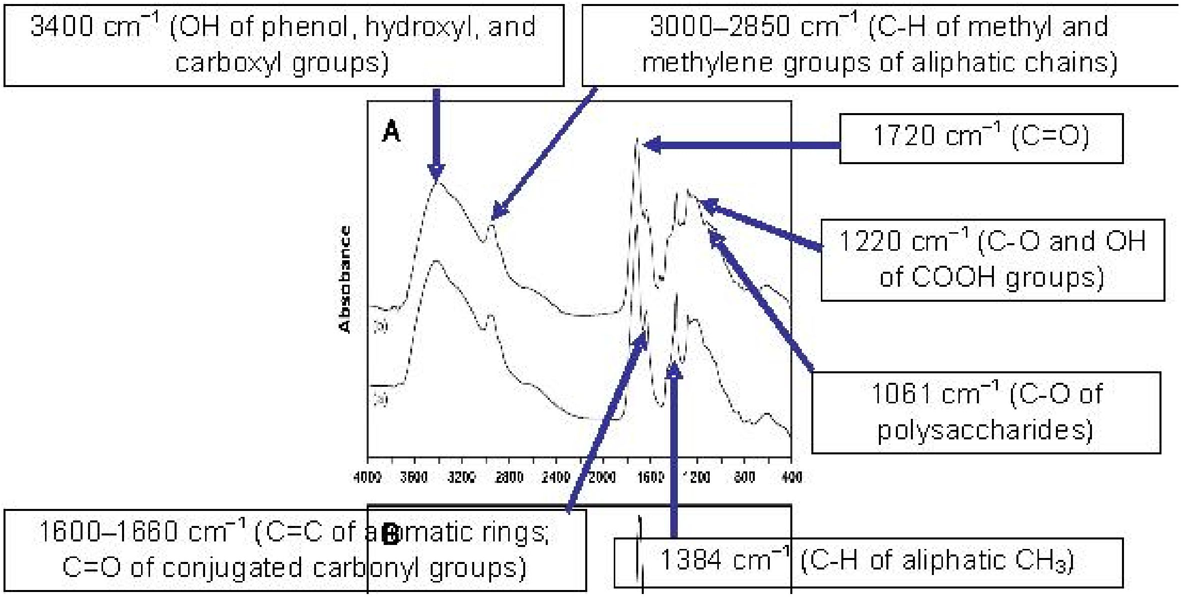

Figure 10: FT-IR spectra of the WSOC isolated from the aqueous extracts of the aerosol samples collected in the summer (a) and autumn (b) seasons [12].

shorter wavelengths, indicating a smaller content of both aromatic structures and condensed unsaturated bond systems in the WSOC fraction of PM [15].

Fourier Transform Infrared (FT-IR) Spectroscopy FT-IR spectra can be used to determine the chemical characteristics and functional groups present in bulk WSOC (Figure 10). A previous study [14] showed that autumn samples exhibited spectroscopic signals typical of lignin breakdown products (e.g. aromatics, phenols, ketones and methoxyl groups), highlighting the major contribution of wood burning processes into the chemical properties of the WSOC fraction.

Nuclear Magnetic Resonance (NMR) Spectroscopy

Solid-state The most common NMR method for the characterisation of natural organic matter (NOM), which can also be used for the analysis of PM, is solid-state NMR, mainly via cross polarization magic-angle spinning (CP-MAS) ^{13}C-NMR. Solid-state NMR has a number of benefits compared to liquid-state NMR, including: no concentration limit; no solvent effects; minimal sample handling; the ability to analyse highly insoluble fractions (e.g. black carbon BC); the stability of samples in the solid state; and the ability to analyse whole PM samples [16].

It has been reported that solid state ^{13}C-NMR of WSOC from PM can reveal differences between the chemical structure of summer and autumn samples from a rural part of Portugal. The autumn samples were richer in aromatic carbons, which would be typical for lignin breakdown products, highlighting a possible major contribution from wood burning processes (Figure 11) [12]. Solid-state ^{13}C-NMR results indicated that WSOC in urban Atlanta aerosol particles was mostly aliphatic in nature (about 95% by C mass). Of this C mass around 80%

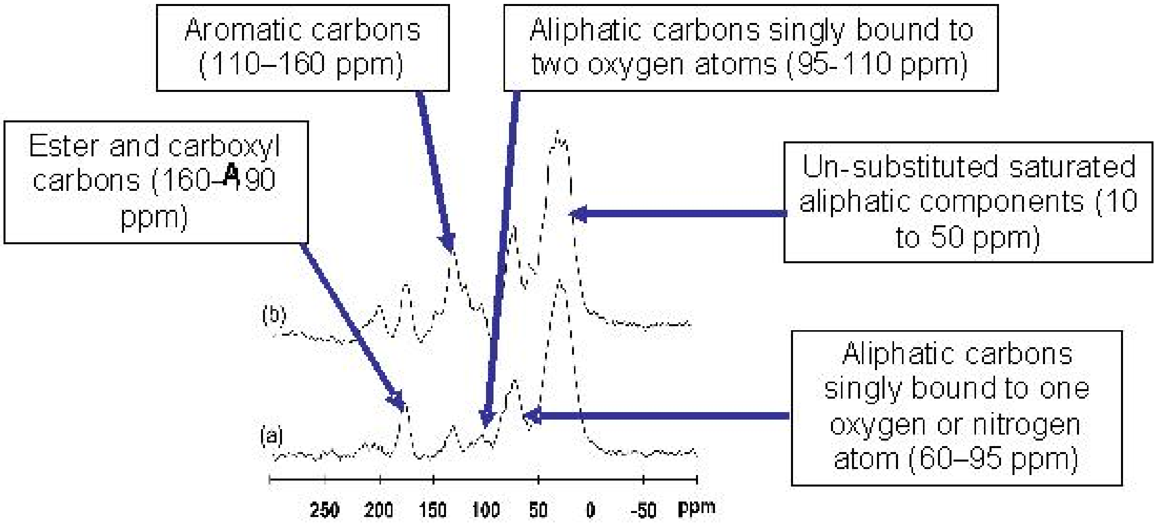

Figure 11: CP-MAS ^{13}C NMR spectra of the water-soluble organic matter isolated from the aerosol samples collected in the summer (a) and autumn (b) seasons [12].

came from alkyl and oxygenated alkyls, other approximately 10% from carboxylic acids, and about 4% from aromatic functional groups [17].

Liquid-state Proton NMR (^{1}H-NMR) is commonly used in chemistry for the investigation of small molecules, due to the high natural abundance and receptivity of protons. However, it may not be as useful for the study of WSOC in PM due to the very strong water signal in the ^{1}H-NMR spectrum and the lack of resolution compared to ^{13}C-NMR [16]. ^{1}H-NMR spectroscopy has other drawbacks for the analysis of organic compounds: although details on the chemical environment of protons can be obtained, alternative interpretations of the spectra are possible due to the lack of information on the carbon structures present. Also, acidic hydrogens (like those of -OH and -COOH groups) can undergo chemical exchange with the D_2O solvent and elude detection [13].

This can be used to determine the presence of certain functional groups and their quantities, which will help highlight seasonal differences and give an indication of the aerosol sources, e.g. emission of aromatic compounds by wood burning or slower degradation reaction of aromatics in winter [18]. Characteristic ^{1}H-NMR fingerprints can be derived for three major aerosol sources: biomass burning, secondary formation from anthropogenic and biogenic volatile organic compounds (VOCs), and emission from the ocean. These source fingerprints can be related to the chemical properties of the organic mixtures, which determine their reactivity and their physicochemical properties, and ultimately the fate of the organic particles in the atmosphere [19].

2D methods Due to the complexity of PM, peak overlap can be a major problem in its analysis by NMR. Therefore, being able to disperse the data into a second dimension could be highly beneficial. Most 2D NMR experiments used in the study of NOM are based on through-bond interactions (homonuclear and heteronuclear) and through-space interactions

[16]. Having control over how the data is dispersed is one of the reasons why 2D NMR could be a powerful and useful technique for the study of PM.

Elemental Analysis This is used to determine the percent of C, H, N O in a sample. Information about the chemical characteristics (e.g. the level of oxygenated functional groups and saturated systems) can be inferred from these values and the calculated O/C, H/C and OM/OC ratios. Results of WSOC from PM samples collected in Hungary indicated the predominance of oxygenated functional groups and a low H/C ratio, implying the presence of unsaturated or polyconjugated structures [20].

Size Exclusion Chromatography (SEC) This chromatographic method can be used to separate particles based on their molecular size. However, molecular weight determination by SEC can be inaccurate due to hydrophobic and electrostatic interactions between the stationary phase and the analyte [21].

Liquid Chromatography Electrospray Mass Spectrometry (HPLC-ESI-MS) Kiss *et al.* (2003) [22] used this technique to gain average molecular weight values in the 200300 Da range for the OM isolated from rural fine aerosol samples collected in Hungary, but no seasonal variation was observed. Possible sources of error using HPLC-ESI-MS are: fragmentation in the ESI source; formation of multiply-charged ions; and the differing ionization and detection efficiencies of different components [13]. However, high resolution MS techniques could be useful for identifying a number of chemical species present in PM and only require a small quantity of material to generate enough signal to produce a useful spectrum.

Laser Desorption Ionization Mass Spectrometry (LDI-MS) LDI-MS has been used to investigate the molecular weight of WSOC from PM. Test experiments suggested that fragmentation was not significant and did not lead to an underestimation of the molecular weight distribution. LDI-MS data are dominated by singly charged ions, compared to ESI-MS, reducing the likelihood of multiply charged ions leading to measurement artefacts when using this technique [21].

3.1.3 Organics at the molecular level

Organic molecular compounds are of utmost importance in aerosol research. They are used as tracer for specific sources. The quantification of the levels of various organic compounds at a given receptor site allow to quantify the contribution of the many sources that build up the ambient aerosol loadings. Such process is called *receptor modelling* and can be done by two ways: either by matrix reduction (e.g. factor analysis, positive matrix factorization) or by multi-linear combination with source profiles, which are the composition of various sources in respect to the same analysed compounds as in the ambient aerosol (chemical mass balance). Besides source apportionment, the other objective of aerosol molecular characterization is the mass closure of the aerosol organic mass.

Throughout aerosol science history, analytical techniques have evolved and form, nowadays, a complementary suite that allows the detection and quantification of a large number of organic compounds. The amount of organic compounds that make up the ambient aerosol is so large, that no technique is able, by itself, to identify and quantify a satisfying suite of compounds to resolve all the sources. Instead, the aerosol composition is so complex that only the grouping of the results from various analytical techniques, used in a combination of diverse statistical and mathematical methods, is able to bring some light on the still largely uncertain sources contribution quantification.

Chromatographic methods are the most widely used for the quantification of organic compounds at the molecular level. They include gas and liquid chromatography and are divided into three sequential steps: sample preparation, compounds separation and detection.

Gas chromatography The pre-treatment the sample undergoes is intrinsically linked with the separation and detection methods used (see below).

After being collected on a filter surface, the aerosol is usually extracted to a liquid medium, generally either using soxhlet (e.g. [23, 24, 25, 26]) or ultrasonication (e.g. [27, 28, 29, 30]). Pressurized fluid extraction (PFE) with an accelerated solvent extractor has also been reported [31].

The choice of the extracting agent is dictated by the polarity of the compounds at which the analysis is targeted. Dichloromethane is a less polar solvent than methanol and is commonly used to extract organics, by itself or in a mixture with methanol (e.g. [32, 33, 34, 35, 31]). Water extraction, to analyse the water soluble organic carbon (WSOC) fraction of the aerosol is also possible (e.g. [36, 37]. Often, a strategy of sequentially extracting the organics with solvents of increasing polarity is used (e.g. [38]), all extracts being combined thereafter.

The obtained extract or extracts can be further subdivided with sequential extractions (e.g. [39]) using solvents of increasing polarity on a flash [40, 37, 25, 26] or thin layer chromatography column (e.g. [41, 42]), or using C18 solid phase extraction [38], obtaining different fractions of the original aerosol organic loading (e.g. [43, 44]. The resulting fractions contain (in order of increasing polarity): saturated hydrocarbons including mainly n-alkanes, hopanes and steranes, PAHs, esters and ketones including n-alkan-2-ones, acids and sugars (e.g. [45, 43, 44].

This fractionation procedure has been reported to be done as the extraction step itself [46], using sequential extractions with solvents of different polarities and not combining the different extracts obtained. For example, extracting the filter twice, once with an apolar solvent (e.g. hexane) and consequently with a polar solvent (e.g. methanol), obtaining two extracts: the polar and the apolar organics (e.g. [47, 48, 49]).

Other extracting solvents are methylene chloride (e.g. [50]), benzene/propanol mixtures (e.g. [51, 52] acetone/hexane mixtures (e.g. [53]), ether/hexane mixtures [54].

Another step in the sample preparation, is the addition of an internal (or recovery) standard. Usually, the internal standard is an isotope-labelled compound representative for one class of compounds. It is used to trace back possible losses during the sample work-up and analysis.

Generally, extraction is done in a large volume of solvent that needs to be reduced by evaporation under vacuum and/or a gentle flow of nitrogen.

Derivatisation is often used in order to facilitate detection and quantification of polar organic compounds so that, once converted into less polar and more volatile compounds, they chromatographically elute. Derivatising agents are functional group-specific and the literature reports many possibilities. The basic process is to replace a hydrogen atom from an OH group by an organic radical in order to turn the molecule into a heavier analogue. Main derivatising agents are diazomethane, which converts organic acids to their methyl-esters analogues (methylation) (e.g. [55, 56]) and bis(trimethylsilyl)triuoro-acetamide (BSTFA, commonly used with trimethylchlorosilane (TMCS) as a catalyst) to convert the compounds with hydroxylic and carboxylic (alcohols, sterols, sugars and other organic species) groups into the corresponding trimethylsylil (TMS) ether or TMS ester derivatives, respectively (sylilation) (e.g. [57, 58, 59, 25]). It is also possible to sylilate subsequently to the methylation (e.g. [29]).

Other possible derivatising agents for trimethylsililation are N-trimethylsilylimidazole, a mixture of acetic anhydride and triethylamine (TEA) [34, 60], and N-methyl-N-trimethylsilyltri fluoroacetamide (MSTFA) with 1% trimethylchlorosilane (TMCS) [34, 61]. A BF3/methanol mixture esterifies the free alkanoic acids [27, 24]. A solution of 14% boron trifluoride in methanol etherifies fatty acids at 85° C [61]. Tetramethylammonium hydroxide (TMAH), and hexamethyldisilazane (HMDS) for methylation and silylation were used as derivatising reagents in direct pyrolysis (Py-) GC-MS [62]. BF3/n-butanol at 100° C derives the carboxyl groups to butyl esters and the aldehyde groups to dibutoxy acetals of the water-extracted organic fraction [63].

Some authors refer to the injection of non-derivatised extracts to obtain the concentrations of non-polar organic compounds such as n-alkanes (e.g. [64, 61, 65, 66]).

After injection (usually the splitless mode is used, [67, 68]), but the split mode has also been reported [69]), the gas-chromatographic separation process is achieved by repeated distribution of each sample component between two phases: a mobile phase for the transport of the mixtures components, and a stationary phase, to which the different mixtures components bind differently to achieve separation (selectivity). This process is fine-tuned with a temperature program (e.g. [70, 71, 72, 73]). Gas chromatographic columns most commonly used in aerosol research are capillary columns, whose inner walls are coated with the stationary phase. The carrier gas is usually helium. The interaction between component and phase is determined by the functional groups.

A large suite of detections strategies have been used in aerosol chemistry, generally mass spectroscopy (MS, either in scan or single electron monitoring modes) is used (e.g. [74]). The most common interface between GC and MS is the electron-impact quadrupole, with the electron energy being 70 eV [75, 76, 77, 78, 40, 44, 60, 79, 70, 55, 62, 80, 81, 82, 83].

Other detection procedures have been used. Ion-trap MS/MS [33, 35, 84, 85, 47, 86, 87, 88] presents operational advantages such as a minor propensity to contamination. Chemical ionisation is another possible interface [89].

Flame ignition detection (FID) can also be used [45, 34, 90], and some authors use this technique when they are looking for some specific compound classes (after appropriate extraction and derivatization): e.g. branched and linear alkanes [42] n-alkanes and n-alkan-2-ones [43, 44], PAHs [91], mono- and dicarboxylic acids [92, 38, 93]. Despite its greater accuracy and simplicity for compounds quantification, its limitations in terms of compounds identification when compared to mass spectrometry, however, make it very less common, and it is often used in tandem with MS detection for quantification, but not identification, purposes [38, 45, 34, 94].

Fourier transform infra-red spectroscopy (FTIR) is another alternative. Often, compounds that have the same mass spectrum (e.g. isomers), can only be separated using the information from the FTIR spectrum [95].

Techniques that do not employ extraction to a solvent have also been described in the literature. Neusüss and co-workers (2000) [96] developed the use of direct thermal desorption (flash evaporation) by Curie Point Pyrolysis in order to avoid solvent extraction of the collected aerosol and directly analyse semi-volatile organic compounds, but with serious limitations for the analysis of very polar organics [67, 24]. Fabbri and co-authors (2002) [62] and Fitzpatrick *et al.* (2007) [97] used Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) with and without derivatisation. Thermally assisted hydrolysis and methylation (THM), coupled online to GC/MS has been developed to analyse a variety of organic compounds, namely compounds already incorporated into a polymeric matrix, though with limitations in regard to quantification [98, 99]. These techniques are less labour and time consuming, and also need smaller amounts of particulate material.

Recent advances developed by the scientific community to further identify organics at the molecular level using GC, improving the chromatographic resolution, include GCxGC-TOFMS or GCxGC-FID (2D GC) [100]. Also, ion scanning mass spectrometry was used to determine organic nitro functional groups [101].

Liquid chromatography Though less resolving than GC, HPLC has the advantage of eluting polar organic compounds, avoiding the time and labour consuming derivatisation step. Although these were not developped for atmospheric sciences and despite of their higher cost, they are very promising in the filed of organic aerosol molecular speciation [102, 95, 103].

In general, sample preparation is much simpler for liquid chromatography than for gas chromatography. The basic principle that drives the separation is identical, though there is a large range of analytes characteristics that can be used to establish the affinity between the analyte and the mobile phase. In a same way, many more detectors have been used up to now.

This is particularly true for the MS detection (the most widely used for molecular speciation with LC), for which various alternatives have been described in the litterature. As ion sources, ESI (soft ionization technique to analyse polar, involatile compounds where the ions are produced by the addition of suitable charged particles to the solution) is a method of choice widely used, but alternatives such as atmospheric pressure pressure chemical ionization have been employed. The mass spectrometers themselves may be ion-trap, quadrupole, time of flight, or Fourier transform ion cyclotron resonance. Besides MS, pulsed amperometric detection is also quite common. This variety in the detection, allied to the variety of choices for the HPLC separation yields a wide range of possible combinations. The choice of the combination is done following the analyte(s) that is to be determined. The following paragraphs describe some examples.

Carboxylic acids may be analysed using C18 columns coupled to a hybrid mass spectrometer (MS/MS) (mostly quadrupole and Time-of-Flight) with an electronspray ion source (ESI) [104, 105, 106]. Elution is performed mostly under acetonitrile or methanol and water mixtures applying a concentration gradient (using formic or acetic acids to obtain an acidic pH) [103].

Microbore LC columns are an alternative to reverse-phase C18 [103]. A similar technique was used for the analysis of sugar-like compounds but using atmospheric pressure chemical ionisation (ACPI) by chloride attachment followed by ESI prior to MS.

Monosaccharide anhydrides were determined using a dC18 column for separation in the liquid phase [107, 108]. Aerosol extraction is done in a mixture of tetrahydrofuran and water, with the help of sonication (e.g. [109, 110, 111, 108]).

Monosaccharide anhydrides, along with other sugars, have successfully been measured using high pH anion exchange chromatography coupled to pulsed amperometric detection

(HPAE-PAD) [112, 113, 114]. Extraction is done in de-ionized water, and sample preparation requires no further step. Anhydrosugars were also measured with cation-exchange chromatography, with pure water as eluent. The detection was conducted with aerosol charge detection, where the eluent is converted into an aerosol, which is charged to produce current [115]. LC-MS, with ESI, was also used for this class of compounds [116].

Also based on ion chromatography, there is the possibility to use anion-exchange chromtography, coupled to either conductivity detection or different mass spectrometry strategies, to determine short-chain mono- and dicarboxylic acids [117, 118].

LC-MS methods are also in the forefront of research concerning nitrogen- and sulphate-bearing organic (possibly oligomeric) compounds [119, 103]. The technique is preferably used with ESI or ACPI and tandem or simple MS (ion trap) [120, 103], but also with Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS).

Non-chromatographic methods It is possible to specify the OC (e.g. Anhydrosugars, oligomers, organosulphates, organonitrates) directly into the ESI-MS(/MS) system [112, 121, 122, 123, 120, 124]. This technique has, however, the inability to distinguish between compounds with the same molecular mass.

Capillary electrophoresis (CE), where the separation relies on the ionic mobility, can be used to perform a separation prior to the ESI-MS [125, 126]. The target analytes from such methods include compounds that readily ionize in the eluent, and has been used for carboxylic acids, namely. Capilary electrophoresis was also used in conjuntion with pulsed amperometric detection for the analysis of anhydrosugars [127]. Similarly, oligomeric compounds were anlysed using FTICR-MS [124].

Further analysis at the molecular level without chromatographic separation of compounds include the measurement of cellulose with an enzymatic method [128, 129], and the measurement of genetic material (DNA and RNA) [130].

3.2 Physical characteristics

3.2.1 Morphology

Microscopy techniques Particle sampling for subsequent microscopy analysis is frequently carried out on inertial and/or filter based techniques. Particles are collected in superficial filters or substrates (depending on the technique) as they must be all in the same spatial plane to guarantee they are properly measured during the image measuring process (Figure 12).

Quartz and polycarbonate filters (Figure 12 a,b) are frequently used in filter based sampling techniques such as high volume or dichotomous samplers.

Quartz filters (Figure 12) are comprised of a great number of crystalline silicate fibers (from which) the air passes through. They are widely used for the different bulk chemical analysis methods but they result useless in microscopy techniques. Smaller particles fall into the bottom of the filter during sampling and the measurement is biased as only larger particles are retained in the outer surface. In addition, this type of filters reduces image resolution working with the same scope as particles are at a different depths and focusing frequently becomes challenging.

Polycarbonate filters (Figure 12) are superficial filters that present rounded pores of one to several cents of nanometers. This type of filters is widely used for microscopy purposes. They give a very good image response enhancing the microscope resolution and particles lay

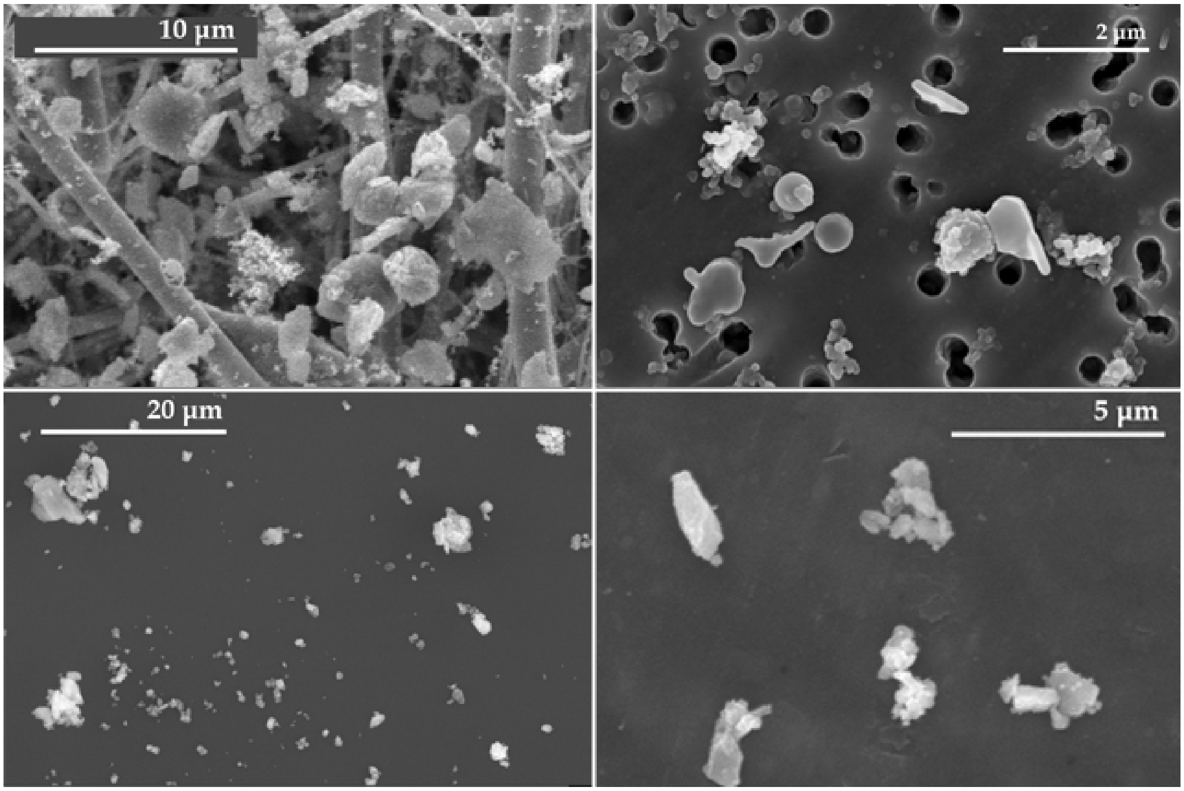

Figure 12: Images of Atmospheric aerosols collected in a quartz filter (a), polycarbonate filter (b), glass substrate (c), and aluminum substrate (d) with SEM.

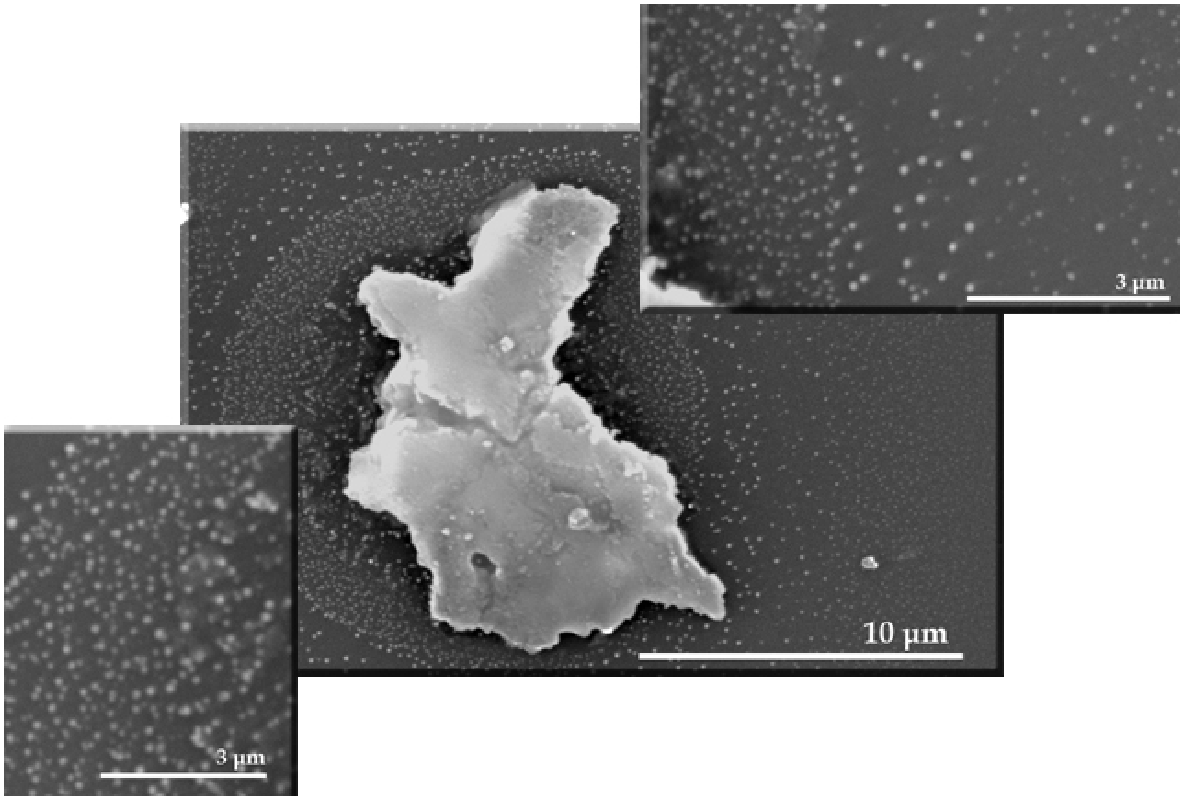

Figure 13: Crater shaped effect of small particles disintegrated from the large one with the impact produced during deposition.

on the same plane. Therefore, they are suitable for the image analysis purposes. However, they present certain disadvantages. Their carbon composition frequently interferes with the X-ray spectrum of the particle, the pores etches sometimes become bright and might be automatically segmented and labeled by the particle measurement program as a particle. In addition, they present certain roughness down to several nanometers level which generally makes difficult to distinguish from particles which limits the resolution to particles over 100 nm.

Glass fiber and aluminum substrates are used in the inertial not filtering based techniques such as cascade impactors. Glass fiber substrates (Figure 12) give a very good response in imaging. Nevertheless, the impact of the particles with the surface is severe and frequently produces the bouncing of the smaller particles that larger ones carry with them biasing the counting (Figure 13). Aluminum (Figure 12) substrates give also a good response in imaging and are very stable but its strong conductivity produces sometimes in non conductive particles a darkener effect that might leave to miscounting.

Microscopy is generally used to characterize the properties of aerosol particles in an individual basis. They present the advantage of obtaining chemical and physical information about particles together from single particles. Characterizing the physical structure of organic aerosols is important since it is closely related with other properties such as chemical composition, density and aerodynamic behavior. The structure of aerosol particles, and especially

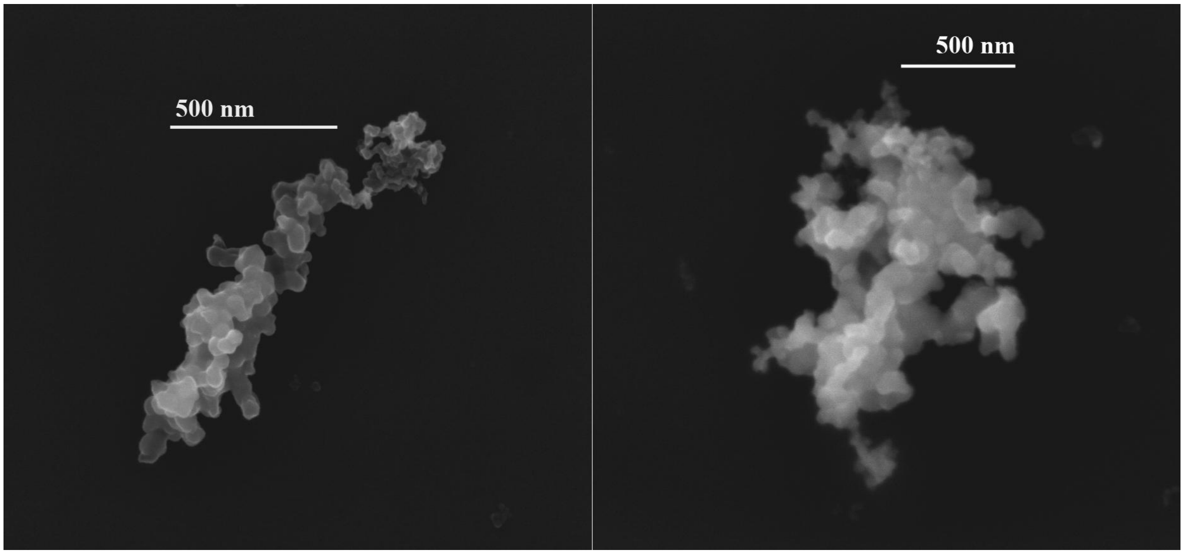

Figure 14: (a) Fresh diesel aggregate and (b) aged diesel aggregate

of organics, is generally heterogeneous, that is, they are comprised by a number of different compounds, mixed or layer structured depending on the formation and subsequent process in the atmosphere. For instance, particles from combustion tend to adopt the morphology of aggregates from carbonaceous and inorganic compounds in the form of spherules of several nanometers size covered by several layers of condensed matter, generally other organics or sulfates. When aggregates are in chain morphology, they are fresh, opposite, when they are in a closed porous structure, generally indicates aging (Figure 14). Microscopy studies have provided valuable information in the characterization of organic aerosols, but especially about their mixing state [131, 132, 133] and hygroscopic behavior [134, 135, 136, 137]

Microscope techniques applied in the characterization of aerosol particles are mostly based on electron and/or X-ray detection after bombardment and interaction with the specimen. These types of scope have higher resolution than optical. Spatial resolution is of especial importance in the characterization of organics since they fall into the fine range. Several different types of Electron Microscopes are available for the scientist: Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), Atomic Force Microscope (AFM) ... The different instruments and their related theoretic chemical and spatial resolution are presented in Figure 15. Chemical information content varies from elemental composition (the lowest) from carbon and heavier elements (in the newest instruments) to the identification of the functional groups (the highest) and is given by the X-ray signal. Spatial resolution ranges from more than one micron down to the nanometer and can be obtained from both electron and x-ray signal, being the first one associated to mucn higher spatial resolutions. The perfect situation is being able to choose the use of one or either other microscope based on the goals pursued on the research (chemistry-spatial resolution efficiency), but availability of these techniques is not always possible since they generally involve high economical disbursement. Hence, this problem generally leads to the inverse question focused on which problem can be solved with the available technique.

A basic electron (X-ray) microscope consists of a source of electrons (X-ray) that is fo-

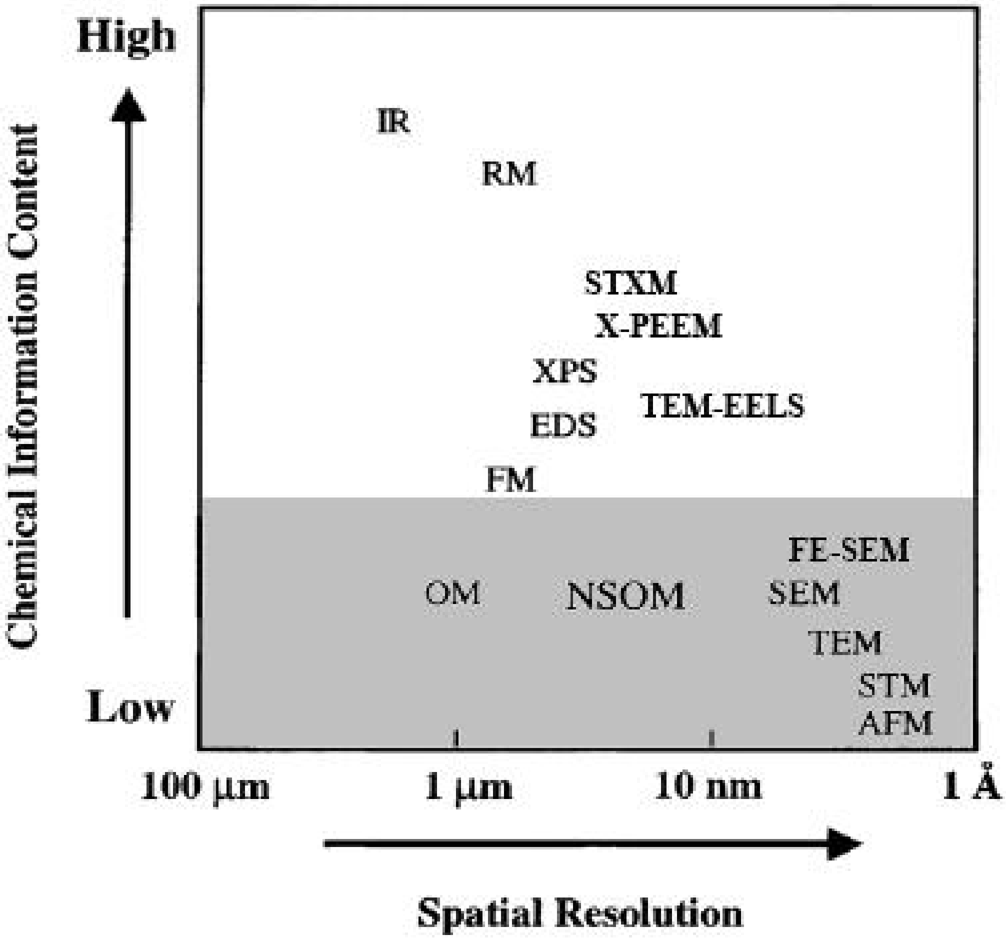

Figure 15: Chemical versus spatial resolution in the different microscopy techniques. Techniques onto the gray background give only image information unless coupled with any other technique such as EDS.

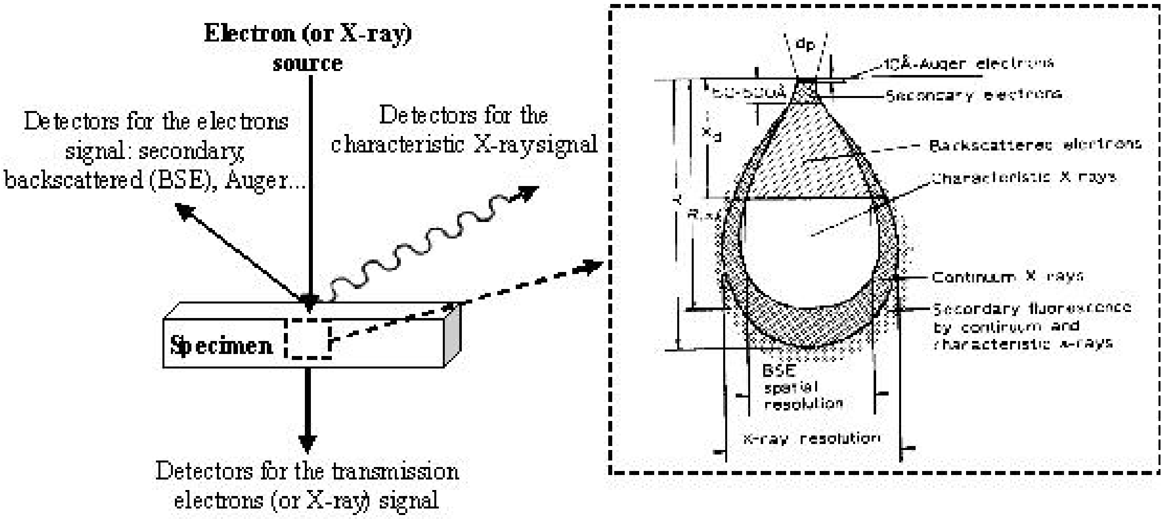

Figure 16: Schematic diagram of a general electron microscope and detail of the electron-specimen interaction of the different signals, their depth and resolution.

cused on the sample, producing an interaction with the specimen. In formation from several signals can be obtained as a result of this interaction (Figure 16). The length of the electron interaction determines the spatial resolution of the image, which means Auger electrons would give similar spatial resolution than the size of the electron beam (dp) and secondary a little bit larger (Figure 16). The rest of the signals have poorer resolution. Chemical information is obtained from the X-ray signal. The resolution of this signal depends on their energy. The higher the energy is, the higher chemical resolution obtained. For instance, common Energy Dispersive X-ray Spectroscopy (EDS) works around 100 eV of energy, while X-ray absorption spectroscopy based on its near edge fine structure (NEXAFS) works from 200-1200 eV. The first technique is able to give information about the elemental composition from carbon and heavier elements in the best conditions while the second one allows studying the functional groups.

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