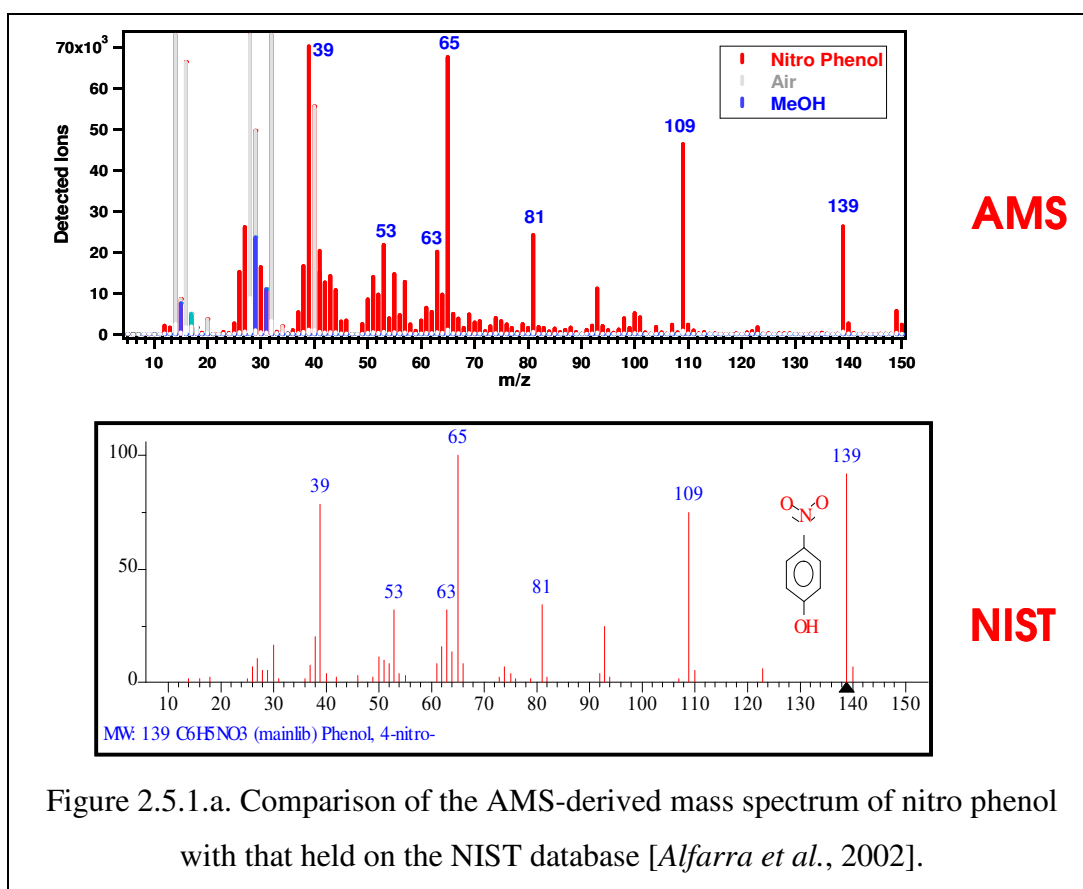


2.5. Instrument and technique validation

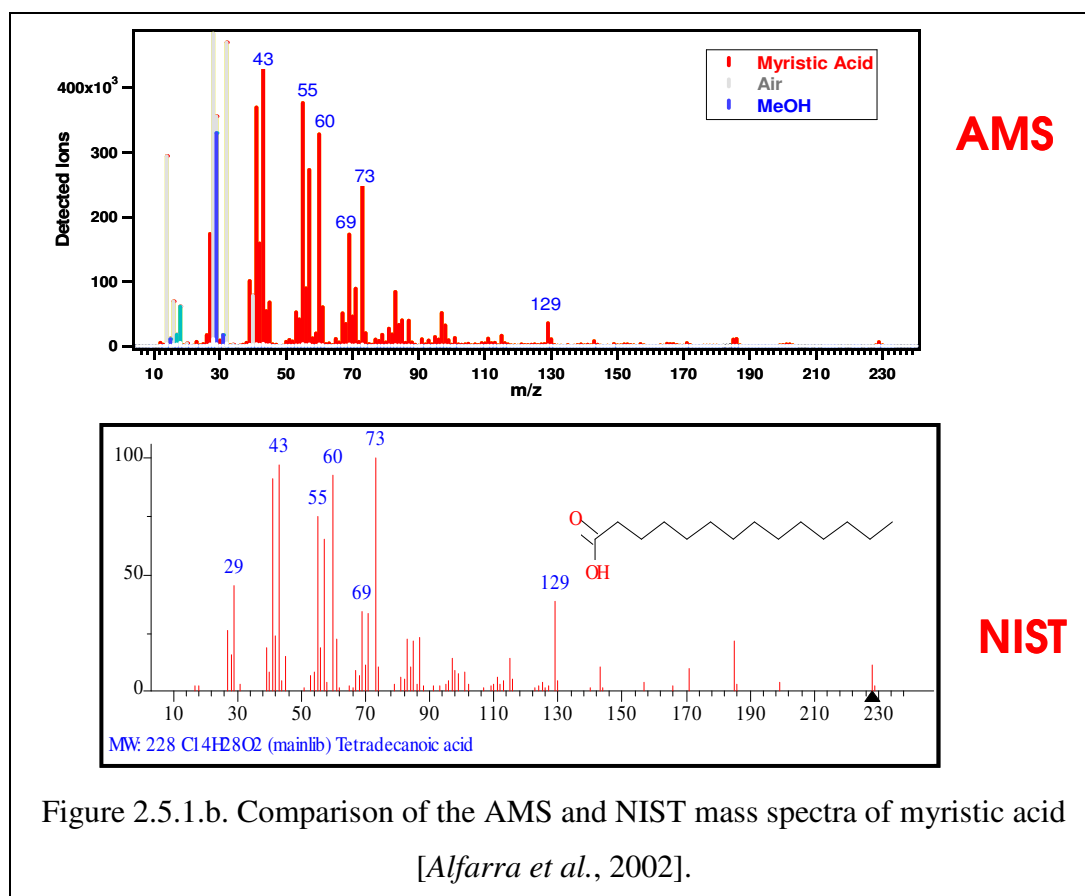
Part of the development process of the instrument and its data analysis techniques is the validation process, required in order to produce fully quality assured data. This is an ongoing process being performed by several groups worldwide, in tandem with the development work itself. The validation work performed at UMIST is detailed in this section, with some summarised validations performed by other groups.

2.5.1. Comparison of mass spectra with libraries



An important property of the AMS design is that it uses a standard quadrupole mass spectrometer with a 70 eV EI ion source. As this is already a very well established technique in mass spectrometry [McLafferty and Turecek, 1993], it should mean that any mass spectra generated should be similar to the mass spectra held in libraries such as that of the National Institute of Standards and Technology (NIST) [Linstrom and Mallard, 2003]. The one technical difference between the AMS and standard gas-phase mass spectrometers is the addition of the heated surface to the ionisation region. This may cause differences in the mass spectra produced in two ways. Firstly, the fact that the molecules being studied spend time in contact with the heated metal surface means

they may either undergo changes to their structure in the process of being vaporised, fragment slightly differently due to the increased amount of internal energy they possess or cause larger numbers to be released from the first dynode of the multiplier during detection due to their increased velocity. Secondly, the heater itself, as explained before, has a bias voltage placed on it so that it does not interfere with the ion optics. However, this bias voltage will affect the electrical potential of the central ionisation region, reducing the energy of the electrons from the 70 eV that is intended, which in turn may alter the fragmentation of the molecules. For these reasons, it is necessary to acquire mass spectra of known chemicals to ensure that they compare well with those in existing databases and if there are any differences, to characterise these and ensure that they do not impact on the abilities of the instrument. These comparisons were taken from *Alfarra et al.* [2002].



For most species, the m/z 's of the major peaks in the AMS spectra are in good agreement with the corresponding NIST spectra. Two examples, nitro phenol and myristic acid, are shown in figures 2.5.1.a and 2.5.1.b. There are extra peaks present in the AMS spectra, but these are due to the carrier gas (air) and the solvent used when generating the particles (methanol). While the organic peaks themselves are in

agreement, the sizes of the lower m/z peaks relative to the higher m/z peaks are higher in the AMS spectra when compared to those in the NIST spectra. This could be a manifestation of any of the effects of the heating of the molecules by the vaporiser discussed above. Further work is needed to explore these but they will not affect the quantitative nature of the instrument as all ions are being collected and will neither affect its ability to identify species, providing that characterisation work like this is taken into account when analysing data.

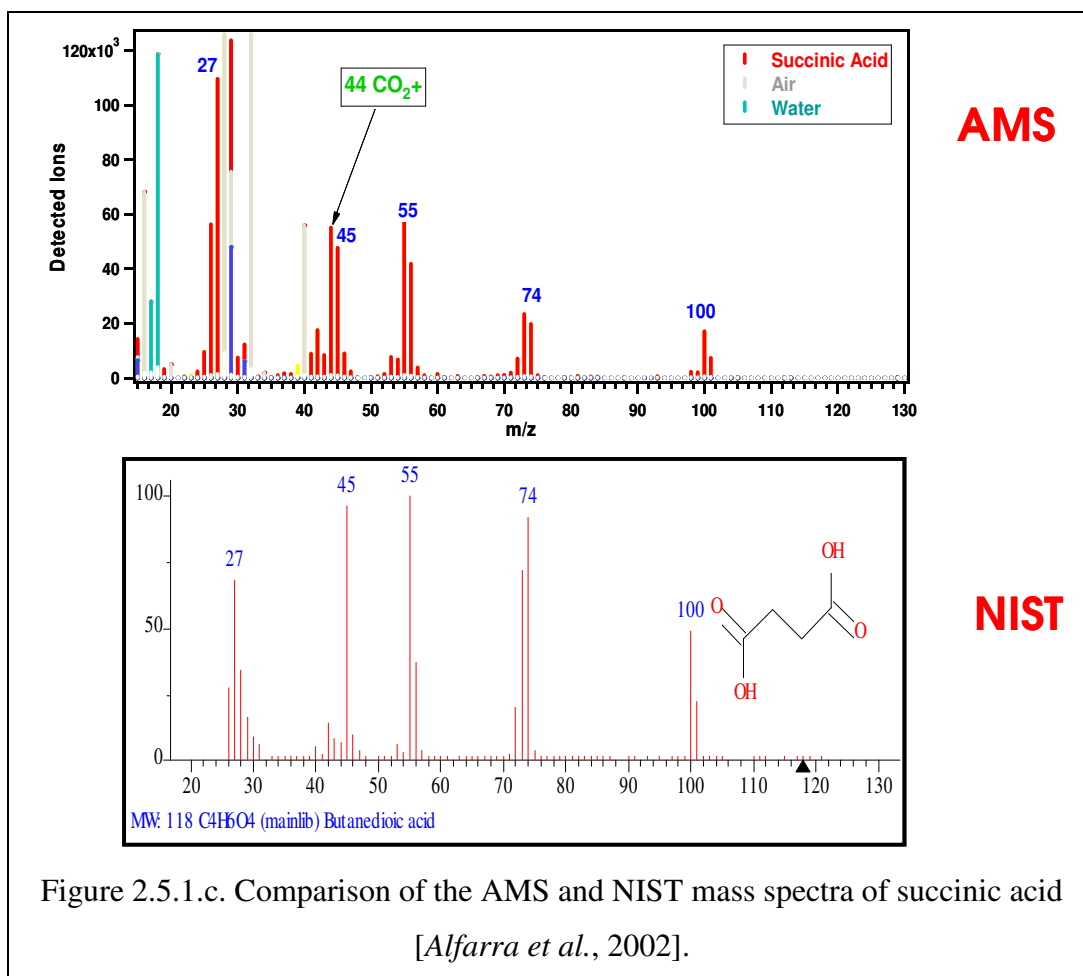


Figure 2.5.1.c. Comparison of the AMS and NIST mass spectra of succinic acid
[Alfarra *et al.*, 2002].

The break in the consistency between the AMS and the NIST database is observed with di- and polycarboxylic acids. An example, succinic acid, is shown in figure 2.5.1.c. In addition to the peaks listed by NIST, a peak is also found at m/z 44, which corresponds to CO_2^+ . This occurs because the heat of the vaporiser causes the function groups to decompose before the molecules enter the vapour phase. During other laboratory studies, a peak of identical size is also found at m/z 18, which corresponds to H_2O^+ . Assuming that the process being observed is the decomposition of two carboxylic acid groups, it can be predicted using stoichiometry that an additional peak should be formed at m/z 28 due to CO^+ ($2\text{COOH} \rightarrow \text{CO}_2 + \text{CO} + \text{H}_2\text{O}$), but this

fragment is hard to study because the m/z 28 channel is typically dominated by the N_2^+ ion from air. Work to investigate this is ongoing.

Again, this does not affect the quantitative nature of the instrument, providing that all ions are taken account of at the analysis stage and it has actually been proven useful when analysing ambient data, as is demonstrated in section 2.4, because the m/z 44 peak can be used very effectively as an indicator for these chemical species, which are associated with heavily oxidised organics in the particle phase.

2.5.2. External comparisons of field data

During field measurement campaigns when the AMS was deployed, other instruments at the same sites have provided comparable data to the AMS. These have allowed a number of comparisons to be performed with the AMS data for the purpose of validating the instrument and the data analysis techniques. Other results from these experiments are presented in section 3 of this thesis, but the comparisons are presented here, as they are more technical in relevance than scientific.

2.5.2.1. ACE-Asia

During the ACE-Asia campaign (described in more detail in diction 3.2.1.), many groups were operating impactors and filter packs at the Gosan supersite, where the AMS was located. As discussed earlier, these samplers do not have the same temporal or particle size resolution as the AMS, but the range of offline analysis techniques available means that more detailed chemical information can be derived. The following comparisons were originally presented by *Topping et al.* [2004a].

Amongst those deployed were two Berner impactors [*Berner et al.*, 1979; *Berner and Lurzer*, 1980], operated by UMIST and the samples analysed by CNR at Bologna, Italy. These cascade impactors consisted of 4 stages with the following approximate 50 % size cuts; $10 > D_a > 5.5 \mu\text{m}$, $5.5 > D_a > 1.5 \mu\text{m}$, $1.5 > D_a > 0.5 \mu\text{m}$ and $0.5 > D_a > 0.2 \mu\text{m}$. They were loaded with Tedlar (PVF, DuPont) substrates and also fitted with Tedlar filters after the impactor stages to collect all the particulate matter with an aerodynamic diameter of less than $0.2 \mu\text{m}$. However, much of the data derived from the base filter samples were unrealistically large and deemed unreliable.

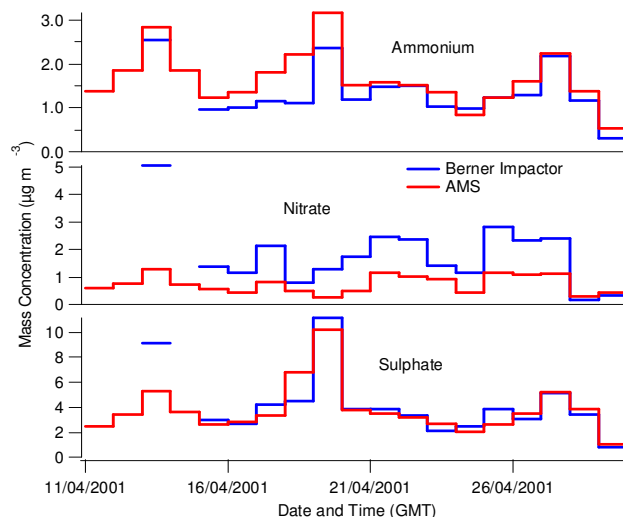


Figure 2.5.2.1.a. Comparison between the AMS-reported mass concentrations and those derived from the IC analyses of Berner impactor samples from ACE-Asia.

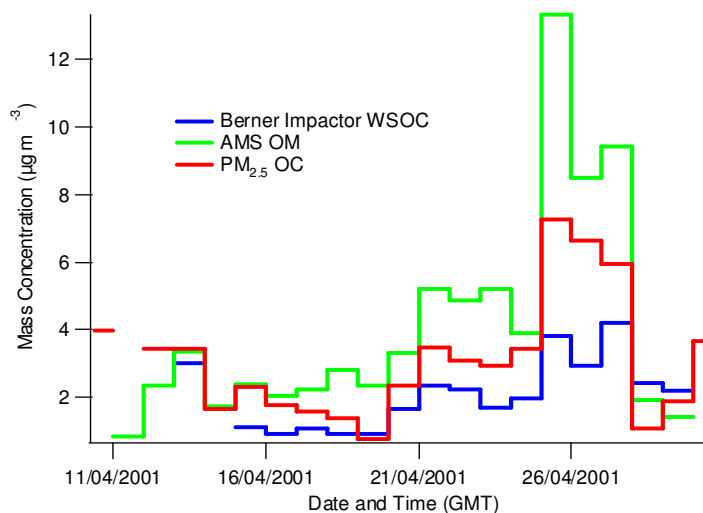


Figure 2.5.2.1.b. Comparison of AMS-derived organic matter (OM), Berner Impactor-collected water-soluble organic carbon (WSOC) and Lovel PM_{2.5} organic carbon (OC) from ACE-Asia.

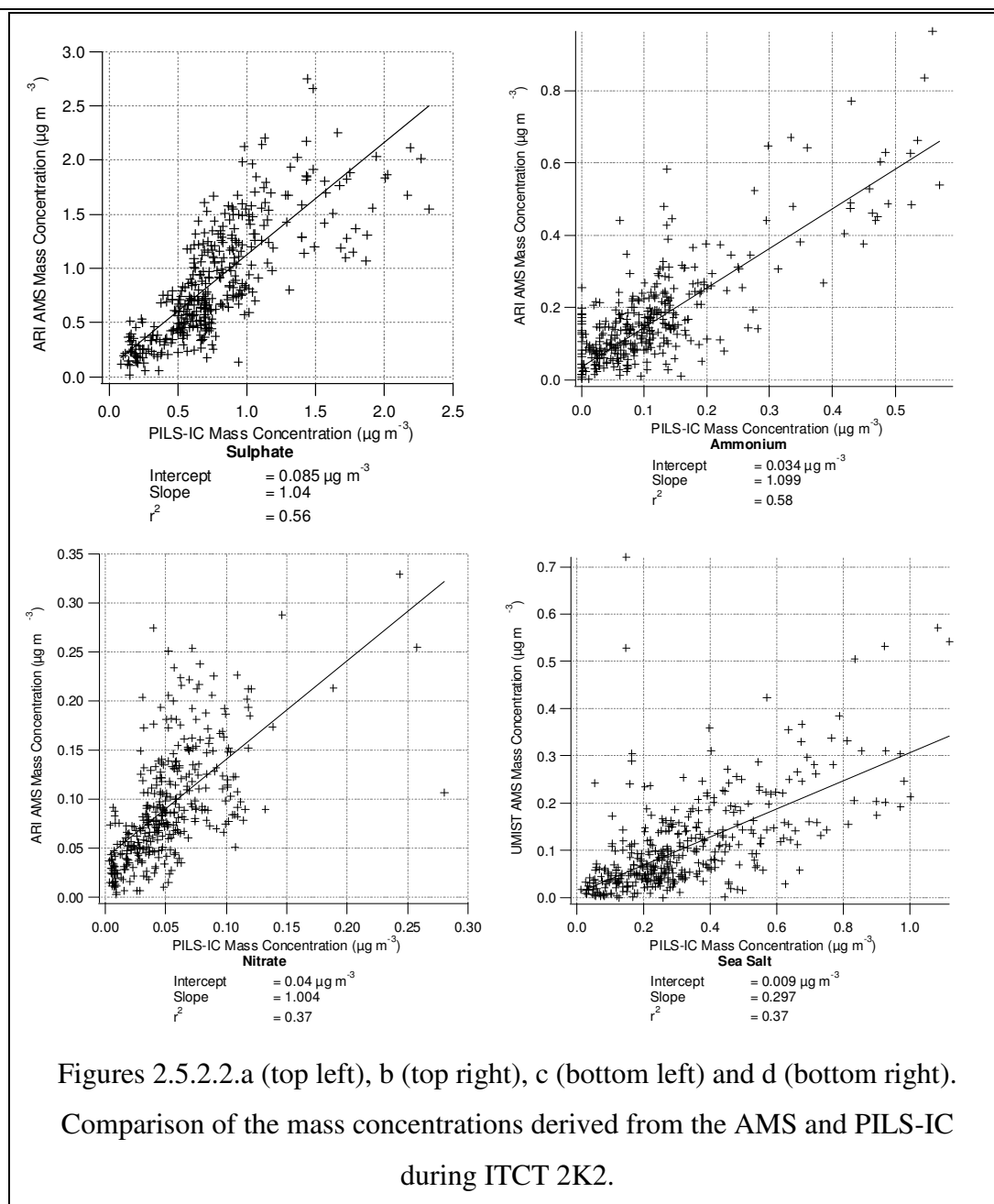
The graphs in figure 2.5.2.1.a show the comparisons between the total AMS-measured mass concentrations and the summed mass concentrations derived from the ion chromatography analyses of the second, third and fourth stages of the impactor samples ($5.5 > D_a > 0.2 \mu\text{m}$). As the sampling times varied, the data have been averaged into 1-day periods. Sulphate agrees well, both in terms of quantity and temporal variation. Ammonium's general temporal behaviour is matched, but during a 4-day period, starting at 16/4/2001, the AMS reported consistently more. This may be due to ammonia evaporating from the substrates during or after sampling. The nitrate comparison is unfortunately unfavourable, as the impactor consistently saw much more

than the AMS. However, the majority of this mass is contained within the larger D_a stages, so these particles will have been too large for the AMS lens to focus properly. Also, this increase in nitrate in the larger sizes is not reflected by an increase in ammonium, rather cations such as calcium and sodium, suggesting that the majority of the nitrate mass is in the form of a mineral nitrate rather than ammonium nitrate, which the AMS will not be able to vaporise properly.

The Berner impactor samples were also analysed for water-soluble organic carbon (WSOC), using the methods described by *Decesari et al.* [2000]. This involves dissolving the sample in water before quantifying the amount of carbon present. While the temporal behaviour between these data and the AMS are closely matched, the AMS total organics are, on average, greater by a factor of 2.21. Also present were some low volume ('Lovol') filter samplers, operated by the University of Wisconsin at Madison [*Mader et al.*, 2003], whose samples were analysed for elemental and organic carbon [*Schauer et al.*, 2003]. The data used in this comparison were taken from a quartz fibre filter downstream of a 2.5 μm cutoff cyclone and a carbon-impregnated glass denuder, designed to remove volatile organic carbon prior to sampling. These data were again averaged into 24-hour periods. As can be seen in figure 2.5.1.2.b, the temporal agreement between the Lovol OC measurement and the AMS-derived organic mass measurements was also good, but the AMS was greater by a factor of, on average, 1.43.

2.5.2.2. ITCT 2K2

The ITCT 2K2 experiment, which took place during the spring of 2002, is described in more detail in section 3.2.2. During this experiment, the AMS was co-located with a PILS-IC (see section 1.2.2.), operated by the Georgia Institute of Technology and the NOAA Pacific Marine Environment Laboratory. The advantage of this system compared to the AMS is that its data has a much higher signal to noise ratio due to its higher sample volume and it is less subject to particle collection issues but unlike the AMS, it cannot deliver size-resolved data. This comparison was originally presented by *Allan et al.* [2004c].



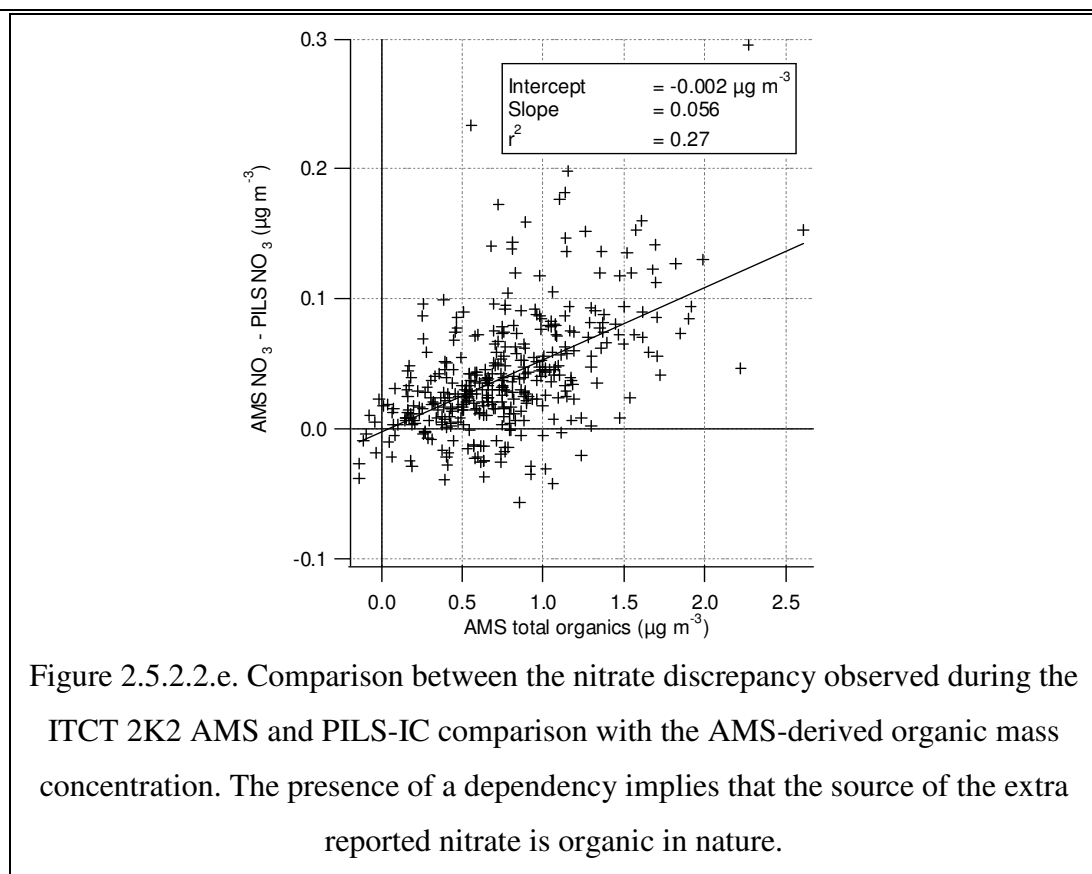
Comparisons between the PILS-IC earlier and the AMS have been performed on numerous other occasions and have generally been very favourable (see section 2.5.2.3.). The results from both instruments are directly comparable, as they both measure mass concentrations of ambient ionorganic ions in submicron particles. Scatter plots comparing the results can be seen in figures 2.5.2.2.a-d, along with the outputs of linear regression analyses. The measured sulphate compares very well, giving a slope agreement within 4 % and a relatively small intercept of $0.085 \mu\text{g m}^{-3}$, as does the ammonium, with a slope within 10 % and an intercept of $0.0034 \mu\text{g m}^{-3}$.

During this experiment, as described in part 2.2.1.3., one of the AMSs was configured to allow the study of sea salt particles. Despite the low signal to noise ratio

of the AMS data, the sea salt compares reasonably well, but the absolute loadings measured by the PILS are greater than those measured by the AMS by a factor of around 3. This will be partly because the two instruments used different inlet systems with slightly different 50 % cutoff points (1 μm for the PILS). As both cutoffs are within the coarse mode, where most of the sea salt resides, this will be significant. Also, there will almost certainly be an aerodynamic lens focusing issue related to the sea salt particles, as it tends to form cubic crystals in the solid phase. This may be reflected in the calibration data, where pure sodium chloride particles only achieved a collection efficiency of 17 %, although a component of this may also be bounce from the vaporiser.

The nitrate comparison is less favourable, possessing a significant positive intercept ($0.04 \mu\text{g m}^{-3}$) and showing many departures from the fit line that do not resemble purely random noise. The implication is that there is a species that is contributing to the AMS-measured nitrate signal that is not simply inorganic nitrate. There is a nitrate peak in the AMS size-resolved distribution that occurs at the same diameter as the sulphate, ammonium and organics, at around 300 to 400 nm. However, the ratio of the m/z 30 and 46 signals is around 5, which is too high to be purely ammonium nitrate. One potential additional source of this signal is mass spectral interference from the organic nitrates, as these can also produce NO^+ ions, without the amount of NO_2^+ that would be expected from ammonium nitrate. These peaks have been reported for certain organic nitrate compounds under laboratory conditions (M.R. Alfarra, unpublished lab data, 2004), but more extensive characterisation work is required. The amine family of compounds are another possibility because according to mass spectral libraries such as NIST, they can give a signal at m/z 30 (due to NH_2CH_2^+ or its isomers), with no measurable signal at 46.

The hypothesis that one or more nitrogen-containing organic chemicals are responsible for the discrepancy is strengthened by the analysis shown in figure 2.5.2.2.e, where the differences between the nitrate concentrations reported by the AMS and the PILS-IC are plotted against the AMS-reported organics. There is a degree of positive correlation shown by the linear regression ($r^2 = 0.27$), with an intercept close to zero ($-0.002 \mu\text{g m}^{-3}$), suggesting that the extra nitrate reported by the AMS is somehow linked to the organics in the particle phase.



2.5.2.3. Other comparisons

As mentioned before, the AMS has been co-deployed with IC-based instruments on other occasions. *Jimenez et al.* [2003a] and *Drewnick et al.* [2003] presented favourable comparisons with these, which included the PILS. *Allan et al.* [2003b] performed a comparison with the IC analysis performed on samples obtained in Edinburgh using a Micro Orifice Uniform Deposit Impactor (MOUDI). While the agreement was good for the modal diameters and the total loadings of sulphate in particular, the low number of valid MOUDI samples prevented a statistically significant comparison. During Pacific 2001 (see section 3.1.4.), comparisons have been made between the AMS data and the IC analysis of MOUDI samples [*Alfarra et al.*, 2004; *Boudries et al.*, 2004]. The comparisons based on the data taken at the Langley site were particularly good.

Size-resolved external comparisons are more difficult, as cascade impactors do not possess the equivalent resolving power of the AMS. Comparisons with the volume-convolved size distributions produced by counting instruments such as the SMPS are possible, although it does require effective density values to make the conversion between particle mobility and vacuum aerodynamic diameters. These can be prescribed,

based on the observed chemical compositions. By using non-linear least squares fits of summed lognormal modes, *DeCarlo et al.* [2004] were able to reach closure between the AMS and the SMPS-measured size distributions and parameterise the observed modes and the densities of the particles. Parameters have to be added to account for the refractory fraction as well. This technique was demonstrated using data from the 2002 Pittsburgh EPA Supersite.

It is generally difficult to directly compare the data produced with the AMS with those of an LDI-based aerosol mass spectrometry instrument, as they are fundamentally different in nature and LDI data is generally not quantitative. Also, on many occasions where the AMS was co-deployed with an LDI instrument, the other instrument was not using an aerodynamic lens and therefore not optimised for the submicron particles that the AMS detects. However, *Middlebrook et al.* [2003a] managed to successfully link the ratios of nitrate to sulphate, rather than their absolute loadings, with those derived from the NOAA Aeronomy Laboratory's PALMS instrument, using data from the Atlanta supersite project originally presented by *Jimenez et al.* [2003a] and *Lee et al.* [2002; 2003].

2.5.2.4. Summary

To this date, IC-based analysis, both offline and in situ, has provided the best source of external comparisons with the AMS for the total mass concentrations of the inorganic ions. Generally speaking, it has been the sulphate that has compared most favourably, as it tends to have a very high signal to noise ratio in the AMS and does not generally suffer from interferences or artefacts. Also, unlike ammonium nitrate, ammonium sulphate does not suffer from interchanges with the gas phase when sampled using impactors or filters.

Nitrate in particular has tended to be problematic when making external comparisons. If the main source of nitrate in the particles is in the form of ammonium nitrate, agreement is generally good. However, disagreements arise when there are significant amounts of other refractory forms such as sodium or calcium nitrate, which the AMS does not measure efficiently. Also, there are potentially some interferences in the AMS from organic nitrogen species such as organic nitrates and amines, although these require further investigation.

Generally, it is difficult to provide an absolute measure of total organic matter (OM) from ambient data [*Huebert and Charlson, 2000*], so a definitive external

comparison with the AMS-derived organic loadings is not possible based solely on the data presented here, as these simply measure the OC or WSOC present. The definitions of ‘organic’ and ‘water soluble’ in these instances are also mainly operational in nature, as is the organic matter that the AMS is capable of detecting, which will be dependent on the vapouriser temperature used. However, it is very encouraging to see that the temporal behaviours of all three methods are matched and the derived OM/OC and OM/WSOC ratios are similar to estimates that have been quoted previously in the literature [*Russell, 2003*].

