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Interactive comment on “Sulfur isotope analyses of individual aerosol particles in the urban aerosol at a central European site (Mainz, Germany)” by B. Winterholler et al.

Anonymous Referee #2

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General comments Despite the fact that this technique looks promising as already exposed in Winteroller et al., 2008 (Int J. Mass Spectrom.) and will certainly used in the future (provided that one can have access to a Nano -SIMS ion probe !), I had a very hard time to read the manuscript and sorted out the essence of the observation (not their conclusion). Actually, as in all single particle analysis, its best friend is also its worst enemy. What you win in scale precision and details tend to be buried by the profusion of data and their heterogeneity. Unfortunately, it is what is happening here. I find the description of the result very confusing, mixing group classification and sample description in the same paragraph (4.2). The profusion of tables and data doesn't help either. Why not plotting table 6 for instance in stacked bars so that

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anyone can quickly see the main chemical features of each sample and crossed this data with table 7. I wonder also if table 8 is really necessary! What would a manuscript using an aerosol time flight mass spectrometer look like if results were tabulated for each single analysis! Furthermore I strongly disagree with the authors about their interpretation. They are ignoring Castelman et al, 1974, Leung et al, 2001, Baroni et al., 2007 who all demonstrated using different approaches that SO₂+OH reaction enriches SO₄ in 34S and not the reverse. Leung theoretical work proposes a fraction factor of ca 1.14 at ground level, stratospheric measurements of Castelman (where SO₂+OH is the only relevant reaction there) show an increase of 34SO₄ just after of volcanic injection of SO₂, same thing for the ice core measurements of Baroni in central Antarctica. Theoretical work of Saltzman and Tanaka are supported by no experimental or observational facts. Thus serious questions arise about the author interpretations when they decided to consider a fractionation constant of 0.991 for the SO₂+OH! This has a strong implication for SO₂, the origin of the sulphur found in their filter and thus the branching ratios btw homo and hete reaction pathways. What would have been the discussion if instead of using -9%; for the homogeneous reaction, they have used +14%? With a nano SIMS drawing a Raleigh distillation process in an atmospheric chamber producing H₂SO₄ through SO₂+OH should be fast and easier than the current IRMS technique, I think the authors should have explored this possibly first. Finally, I wonder if an urban environment is the best place to apply the nano-SIMS analysis and demonstrate its capabilities. May be going above clearly defined sources of sulphate would have been a better strategy and a major achievement in the field of sulphur isotope just as laboratory experiments. Apply a new analytical technique in a very complicate environment like the urban atmosphere is, to my point of view a mistake. The move should from simple to complexity, not the reverse.

specific comments I also found the EDX description in 3.2 not very helpful and or confusing notably about the retrieval of the diameter of particles and about the scanning of the filter to avoid multiple sampling of the same particle.

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The IMF is really an issue here as no equivalent standard to atmospheric aerosol composition exist. In their previous 2008 paper they presented a method to correct for IMF, however this technique is based on the diameter of pure sulphate salt. How this correction can be applied for internally mixed atmospheric particle? Should they behave like pure sulphate salt? What is the influence of the chemical composition of the particle sulphur isotope measurements? Is there really not chemical interaction and recombination in the ionisation chamber that can make the instrumental fractionation sensitive to chemical composition of the particle?

Page 9361 line 2: I have a hard time here too to understand the comparison between their PM10 and PM2.5 with the state agency measurements. I don't understand how they can claim that the diff PM2.5-10 agree well with monitoring stations? I don't see that in their table 3.

Page 9361 lines 21-23: why group 4b is not also included, I don't see any significant different between this group and the others listed? Furthermore sample 5 has a very different isotope signature for group 5 and 6 than the other filters, why it is grouped with all other sample excepted sample 4?

Page 9362 line 3: here it is claimed that sample 4 is different why? There is no more difference for sample 4 than sample 5 with the other samples. Sample 5 have different group 5 and 6 while sample 4 it is group 3a and 4b that differ. Also, dry day also occurred during sample 2, such argument can not be used to highlight the sample 4.

Page 9362 line 22: where did they get this 18%; value for ammonium sulphate process by homo and hete reactions?

Pages 9371 line 3-10 O₃ oxidation becomes important only above pH 5.5 so change in pH btw 4.4 to 4.9 will not change drastically the way SO₄ is produced in aqueous phase. H₂O₂ is the dominate oxidant, just as increasing of O₃ by a factor of 2 will not impact the way heterogeneous reaction occurs (See Seinfeld and Pandis book)

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Pages 9367 line 23-30. Using Cl to calculate nss sulphate in aged sea salt particles is justified only if dechlorination is a minor process. How they can be sure that Cl was not severely lost during NaCl + H₂SO₄ reaction?

Technical corrections cut of instead of cutoff, facouring instead of favouring Lee and Thiemens reference missing

In conclusion I do not support the publication of the manuscript without major modifications and a complete rethinking of the paper with the inclusion of Leung, Castelman and Baroni data. Using alpha = 1.14 for OH reaction will have changed completely their interpretations and conclusions.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9347, 2008.

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