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Interactive comment on “Measurement of gas-phase ammonia and amines in air by collection onto an ion exchange resin and analysis by ion chromatography” by M. L. Dawson et al.

Anonymous Referee #2

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General comments: This paper provides a method for measuring ammonia and amines in air which avoids some of the pitfalls of existing methods, by concentrating the analyte on an ion-exchange cartridge, similar in principle to the use of ion-exchange cartridges for sampling rainfall composition, developed over the past 30 years, see e.g. Fenn et al., 2002.

However, it fails to deal with the biggest problem in measuring atmospheric ammonia, and to a lesser extent, amines, which is the possibility of phase transfer between gaseous and particulate phases. There is a long history of methods which attempt to separate ammonium particles from ammonia prior to sampling and analysis, the prob-

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lem being the volatilization of trapped particles to give ammonia gas, or reaction of ammonia gas with acidic gases on the filter surface. It would appear that this ‘new’ method also measures the sum of ammonium and ammonia, rather than simply ammonia gas concentration. Even with a pre-filter (not mentioned in the sampling method) breakthrough of volatilized ammonia from trapped particles would generate a positive artefact. The problem with particulate amines is less severe, given their lower volatility, but without a pre-filter the method described here samples both gases and particles; with a pre-filter, the method may be acceptable for use in the field for measuring gaseous amines, but not gaseous ammonia.

The methods usually adopted for separating gaseous ammonia from particulate ammonium rely on the very large difference between gas-phase diffusion of gases and particles. It is surprising that these techniques are not mentioned. For online sampling with hourly time resolution, denuder based systems are widely used and commercially available, for example the MARGA (ten Brink et al., 2009) or AIM-IC (Markovic et al., 2012). Although these work well for ammonia, detection limits may be rather high for gaseous amines. On longer time scales, passive diffusion samplers are effective (Tang et al., 2001), and also avoid positive artefacts from particulates – there is no reason in principle why such techniques should not be used for sampling gaseous amines. Long-term integrating denuder sampling is also possible for ammonia (Tang et al., 2009), but may be impractical for amines.

The method is demonstrated by measuring close to a cattle feed lot over several days. While instructive, the field demonstration gives no indication of the likely reproducibility of the measurement technique. I would have expected to see parallel sampling to indicate method reproducibility – indeed, the results from analysis of the gas-phase standards (Figure 6), while demonstrating linearity, show considerable variation even in near-ideal conditions.

In conclusion, the method may well be appropriate, when combined with a suitable inlet filter, for analysis of gas-phase amines, but further work is needed to show whether

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the method is reproducible both in the laboratory (reproducibility of different cartridges operated in parallel) and in the field.

Specific comments:

P1576 I23: the indophenol blue spectrophotometric method for measuring ammonium in solution has been used for over 3 decades – citation of a 2010 paper is not appropriate unless the authors present therein a major improvement on the 'historical' methods, e.g. EPA Method 350.1.

P1577 I1: the measurements here are for a lab-based system – exposure to humid ambient air may increase or decrease such sorption.

P1578 uptake on glass: can the authors demonstrate that there was uptake on glass, as opposed to microbial degradation during storage – which can be very rapid in non-sterile conditions? What type of glass beads was used? Soda glass is notorious for cation exchange, usually exchanging Na⁺ for solute cations. A better test would have been to compare storage in (borosilicate) glass and plastic vials. Reversible adsorption of cations, including ammonium (and presumably amines) is a recognized but not well documented problem in non-metal IC systems (e.g. PEEK) when analyzing samples with high concentrations of organic matter (Cape et al., 2001), where sorption of organic solutes with anionic moieties to the plastic tubing can lead to the development of weak cation exchange surfaces on tubing (also removed by acid).

P1578 I14: was any attempt made to quantify the cylinder contents directly, for example by sorption into an acidic solution through a fritted bubbler (or similar)? This would provide a check on the actual cylinder contents at the time of use, i.e. a check on surface losses since manufacture of the standards.

P1580 I8: how critical is the volume added to avoid introducing bubbles into the IC? How can overfilling and loss of analyte be prevented?

P1581 I23: this method of calculating the detection limit requires a literature reference.

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P1583 I19: demonstration of linearity gives little indication of method reproducibility – see general comments above.

P1583 I29: see comments above on P1578.

P1584 I6: although there was no degradation in efficiency, what was the within-cartridge and between-cartridge reproducibility over time?

Table 2: these are the concentrations as measured by the described method, but there is no comparison with other techniques to demonstrate whether they are even close to reality, nor replicate (parallel) measurements to show likely uncertainty using the described method.

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