DETERMINATION OF AEROSOL STRONG ACIDITY LOSSES DUE TO INTERACTIONS OF COLLECTED PARTICLES: RESULTS FROM LABORATORY AND FIELD STUDIES

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Abstract—Existing methods of measuring atmospheric aerosol strong acidity adequately prevent neutralization of fine-particle acidity by removing coarse alkaline particles and gaseous ammonia from air samples. However, these techniques do not consider particle interactions on the collection medium; therefore, they may still underestimate the actual aerosol acidity. Assessment of acid neutralization due to such interactions is made possible using annular denuder technology in conjunction with a newly designed filter pack. The amount of sulfate-related acidity neutralized by the collected ammonium nitrate (and possibly ammonium chloride and organic acid ammonium salts) is determined. Laboratory data suggest that large fractions of sulfate-related aerosol acidity are neutralized by ammonium nitrate particles during collection on filter media. Field data from the Harvard Acid Aerosol Health Effects Study also suggest that ammonium nitrate and possibly other ammonium salts, such as ammonium chloride, neutralize collected acid aerosols. For low-acid aerosol concentrations, the correction factor is significant; whereas, for high-acid concentrations, correction is negligible.

Key word index: Aerosol acidity, sulfuric acid, ammonium nitrate, acid neutralization, annular denuder, filter pack particle interactions.

INTRODUCTION

Acidic ambient sulfate aerosols can be formed through homogeneous gas or aqueous phase reactions as well as through heterogeneous reactions on particle surfaces. A number of gas–particle reactions occur among the strongly acidic particles and atmospheric gases. Among these, the neutralization reaction with ammonia is the most important from the perspective of atmospheric acidity.

Depending upon the availability of ambient ammonia, acid aerosol sulfates may be partially or totally neutralized. Furthermore, depending on the acid aerosol content and ambient relative humidity, the partially or totally neutralized atmospheric sulfates remain in the liquid phase or change to the solid phase. It is also possible that acidic particles contain both phases, where the partition coefficient is given by the phase diagram of the system: $H_2O–(NH_4)_2SO_4–H_2SO_4$ (Tang *et al.*, 1978). The liquid phase is an aqueous solution of NH_4^+, H^+, SO_4^{2-} and HSO_4^- ions and possibly undissociated H_2SO_4, if the solution is strongly acidic. The solid phase consists of pure sulfate salts, such as $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, NH_4HSO_4 or sulfate salt mixtures, such as $(NH_4)_2SO_4$ plus $(NH_4)_3H(SO_4)_2$ or $(NH_4)_3H(SO_4)_2$ plus NH_4HSO_4. The composition of the solid phase is also predicted by the sulfate phase diagram.

Ammonia vapor pressure is considerably lower above acid aerosol sulfates than it is over ammonium nitrate particles. The ammonium nitrate aerosol dissociation constant, $K(NH_4NO_3) = P(HNO_3) \cdot P(NH_3)$, depends on temperature and relative humidity (Tang, 1980; Stelson and Seinfeld, 1982). Assuming that there is no mechanism preventing the neutralization of acid aerosols by ammonia, the presence of acidic particles in ambient air implies that no ammonium nitrate exists simultaneously. For relative humidities below $\approx 98\%$, all nitric acid exists in the gas phase. Although ammonium nitrate and acid sulfate particles do not coexist in the sample air, they may be present at different times in a sampling period. Consequently, ammonium nitrate and acidic sulfate may be collected on the same multi-hour integrated sample.

The main objective of this paper is to examine losses of aerosol acidity on filter media during sampling due
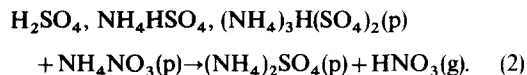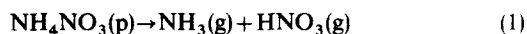
to interaction with ammonium nitrate. The paper focuses on the interactions between sulfate and nitrate particles because they are two of the most abundant aerosol species under typical atmospheres. Results from both laboratory and field studies are presented and discussed.

SAMPLING AND ANALYSIS

The Harvard/EPA Annular Denuder System (HEADS), designed for the sampling of atmospheric aerosols and gases, is presently being used to study health effects of acid aerosols on North American children. As depicted in Fig. 1, the sampler consists of a glass impactor, a series of annular diffusion denuders, and a filter pack. The glass impactor removes coarse particles, $d_a \geqslant 2.1$ μm, from the 10 ℓ min^{-1} air sample and allows gases and fine particles to pass into the annular denuders and filter pack components (Koutrakis et al., 1990). The first (Na$_2$CO$_3$-coated) annular denuder (D1) quantitatively collects acidic gases, such as HNO$_3$, HONO, SO$_2$, HCl, HCOOH and CH$_3$COOH (Possanzini et al., 1983). The second (citric acid-coated) denuder (D2) collects ammonia and protects the acid aerosols collected downstream on the Teflon filter from neutralization. Laboratory and field tests of the denuder collection efficiencies and capacities for HNO$_3$, HONO, SO$_2$ and NH$_3$ are described elsewhere (Koutrakis et al., 1988a; Brauer et al., 1989).

A filter pack containing three filters follows the series of annular denuders. The first filter (F1) is a Teflon membrane used to collect fine particles. The second

filter (F2) is a Na$_2$CO$_3$-coated glass-fiber filter used to trap HNO$_3$. The HNO$_3$ originates from two sources; (i) the dissociation of NH$_4$NO$_3$ collected on the Teflon filter (F1) given by Equation (1), and (ii) the displacement of the sulfate related hydrogen ion by ammonium nitrate (Equation 2):

$$NH_4NO_3(p) \rightarrow NH_3(g) + HNO_3(g) \qquad (1)$$

$$H_2SO_4, \ NH_4HSO_4, \ (NH_4)_3H(SO_4)_2(p)$$

$$+ NH_4NO_3(p) \rightarrow (NH_4)_2SO_4(p) + HNO_3(g). \qquad (2)$$

The last component of the three-stage filter pack is a citric acid-coated glass-fiber filter (F4) used to trap ammonia originating from the dissociation of NH$_4$NO$_3$ collected on the Teflon filter (Equation 1).

This filter pack is a modification of a previous design. According to the original filter pack design, two Na$_2$CO$_3$-coated glass-fiber filters (F2 and F3) are used to allow for correction of artifact nitrogen oxides on the filter medium (Slater et al., 1989). This original design assumes that the artifact reactions of ambient nitrogen oxides occurring on the second Na$_2$CO$_3$-coated glass-fiber filter (F3) are equivalent to those occurring on the first Na$_2$CO$_3$-coated glass-fiber filter (F2). Therefore, the nitrate and nitrite concentrations of the first filter (F2) are corrected by subtracting the nitrate and nitrite concentrations on the second filter (F3). However, an analysis of the first-year data of Harvard Acid Aerosol Health Effects Study suggested that this correction is minimal (less than 8% difference in the arithmetic means of H$^+$ (total), defined in Equation 3): thus, only one Na$_2$CO$_3$-coated filter (F2) is necessary for nitrate and nitrite collection.

After sampling, the denuders are extracted using deionized distilled water. The aqueous extract from the Na$_2$CO$_3$-coated denuder is analysed by ion chromatography coupled with a conductivity detector for SO$_4^{2-}$, NO$_3^-$ and NO$_2^-$ to determine SO$_2$, HNO$_3$ and HONO concentrations, respectively. The aqueous extract from the citric acid-coated denuder is analysed by ion chromatography for NH$_4^+$ to determine the NH$_3$ concentration.

All three of the filters in the filter pack are also extracted using deionized distilled water. One aliquot of the extracted solution from the Teflon membrane filter (F1) is analysed by ion chromatography to determine SO$_4^{2-}$, NO$_3^-$, NO$_2^-$ and NH$_4^+$ particulate concentrations. Another aliquot of the extracted solution from the Teflon membrane filter (F1) is analysed by a pH-meter with a semi-microelectrode to determine aerosol strong acidity (Koutrakis et al., 1988b). The extracts from the Na$_2$CO$_3$-and the citric acid-coated glass-fiber filters (F2 and F4) are analysed using ion chromatography for NO$_3^-$ and NO$_2^-$ and NH$_4^+$, respectively. The apparent aerosol strong acidity measurement for the Teflon filter (F1) (measured by the pH-meter) is corrected using the ion chromatography results by adding the moles of nitrate measured on the Na$_2$CO$_3$-coated glass-fiber filter (F2) and subtracting the moles of

FILTER PACK
AIR OUT TO SAMPLE PUMP
Citric Acid Coated Filter
Na$_2$CO$_3$ Coated Filter
Teflon Filter

2ND DENUDER
Citric Acid Coated

1ST DENUDER
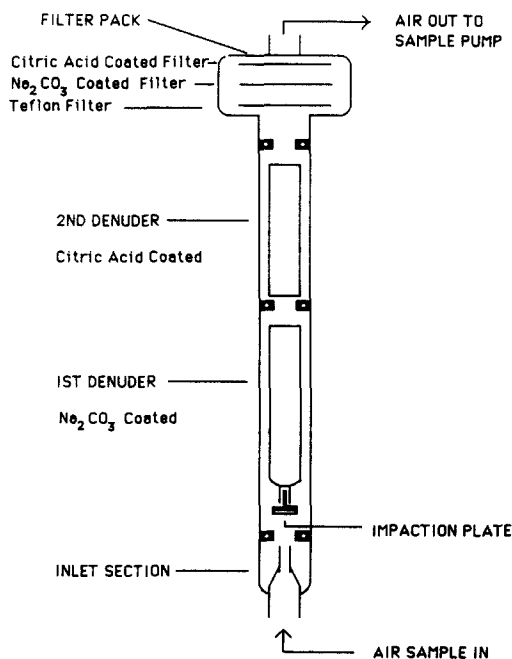Na$_2$CO$_3$ Coated

IMPACTION PLATE
INLET SECTION

AIR SAMPLE IN

Fig. 1. Schematic of the Harvard/EPA Annular Denuder System (HEADS).

ammonium measured on the citric acid-coated filter (F4) (Slater et al., 1989). This is demonstrated by Equations (3) and (4), where all concentrations are in moles per cubic meter. Nitrite does not appear in these equations because it is negligible:

$$H^+(total) = H^+(F1) + H^+(correction), \qquad (3)$$

where

$$H^+(correction) = NO_3^-(F2) - NH_4^+(F4). \qquad (4)$$

LABORATORY TESTS

The interaction of NH_4NO_3 and acid aerosol sulfates on Teflon membrane filters during sampling was studied in a series of laboratory experiments. For these tests, an aerosol generation system (described by Brauer et al., 1989) was used to deposit pure NH_4NO_3 and/or H_2SO_4 aqueous droplets on the Teflon membrane filters. The aerosol generation system, depicted in Fig. 2, includes an air-scrubbing system, a dilution system, a humidity controller and a baffled-jet nebulizer. The H_2SO_4 and NH_4NO_3 aerosols are produced using aqueous H_2SO_4 and NH_4NO_3 solutions, respectively. To minimize contamination, separate nebulizers, Teflon lines and mixing vessels are used for H_2SO_4 and NH_4NO_3 aerosols. The annular denuders are placed just upstream of the filter packs to remove any gaseous HNO_3 and NH_3 that may be produced in the sample stream by the dissociation of NH_4NO_3. The diameters of generated particles are chosen to be

Fig. 2. Schematic of the aerosol generation system.

approximately 1 μm, similar to those observed in previous atmospheric acid aerosol studies (Koutrakis et al., 1989). No impactor is required upstream of the annular denuder series for this system because the generated aerosols have diameters smaller than 2 μm.

Table 1 summarizes the results of the laboratory tests. The table shows the conditions for each experiment including: the compounds used in each experiment, the experiment numbers, the deposition times for each aerosol, the relative humidity used during the experiment and the sequence of the depositions for experiments 5–9. The table also shows the results of the experiments including: the depositions (in nmoles) of SO_4^{2-}, NO_3^-, H^+ and NH_4^+ measured on the Teflon filter (F1), the ion balance on F1 (the ratio of the cations to anions, which should be equal to one), the deposition of NO_3^- measured on the Na_2CO_3-coated filter (F2), the deposition of NH_4^+ measured on the citric acid-coated filter (F4) and the estimated total hydrogen ion neutralized in units of nanomoles and in percent.

Experiments 1 and 2 involve depositions of H_2SO_4 aqueous droplets. As expected, no NO_3^- was detected on F2,· and no NH_4^+ was detected on F4. The ion balance was generally good, but showed a slight contamination of ammonium detected on the Teflon filter. (Since it is very difficult to avoid ammonia contamination during sulfuric-acid particle generation, this unfortunate contamination was not too surprising.) Experiments 3 and 4 involve deposits of ammonium nitrate droplets only. Again, the analysis is good with excellent agreement between the ion balances. Since the annular denuders remove any gaseous HNO_3 or NH_3 from the sample stream, the NO_3^- and NH_4^+ detected on F2 and F4, respectively, must originate from the dissociation of NH_4NO_3 on the Teflon filter by Equation (1). Thus, the results of these two experiments show 5–7% of the NH_4NO_3 dissociated (Equation 1) with the HNO_3 detected as NO_3^- on F2 and the NH_3 detected as NH_4^+ on F4.

For experiments 5 and 6, the NH_4NO_3 particles are deposited first and the H_2SO_4 particles second. In these experiments, the acid on F1 was neutralized by the NH_4NO_3. On the Teflon filter (F1), neutralization occurred if the concentration of H^+ is lower than twice the concentration of SO_4^{2-} and the concentration of NH_4^+ exceeded the concentration of NO_3^-. Also, since the concentration of NO_3^- on F2 exceeded the concentration of NH_4^+ on F4, there is evidence of extra nitric acid from the neutralization (Equation 2). The amount of neutralization is the difference between the nitric acid measured on F2 and the ammonia measured on F4 in nanomoles (Equation 5):

$$H^+(neutralized) = NO_3^-(F2) - NH_4^+(F4). \qquad (5)$$

The percentage of neutralization is a comparison of the H^+ (neutralized) and the H^+ deposited on the Teflon filter as calculated from the sulfate (Equation 6):

$$H^+(\% \ neutralized) = 100 \cdot H^+(neutralized) /$$
$$(2 \cdot SO_4^{2-}(F1)). \qquad (6)$$

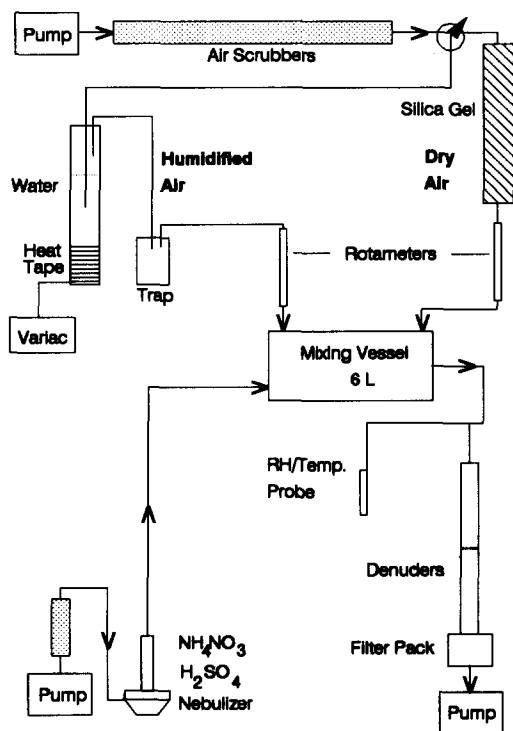The acid neutralization varies from 37 to 65% in these experiments. The percentage of neutralization appears to be related to the percentage of relative humidity (r.h.), with greater neutralization taking place at higher r.h.

For experiments 7-9, the H_2SO_4 particles were deposited first and NH_4NO_3 particles were deposited second. Extensive neutralization of the acid was again evident on the Teflon filter. For F1, the concentration of H^+ was lower than twice the concentration of SO_4^{2-} and the concentration of NH_4^+ exceeded that of the NO_3^-. Also, the concentration of NO_3^- detected on F2 greatly exceeded the low or absent concentration of NH_4^+ on F4. Experiments 7 and 8 show the highest neutralization because of the excess of ammonium nitrate deposited on the Teflon filter.

Discussion of laboratory tests

The results from these laboratory experiments suggest that the expected volatilization and neutralization reactions occur on the filter medium. These reactions accounted for 32-80% neutralization of the aerosol acidity observed in these experiments. Therefore, both Na_2CO_3 and citric acid-coated filters are needed to measure accurately the acidity lost from the Teflon filter. The degree of neutralization may be related to the relative amounts of H_2SO_4 and NH_4NO_3 particles, the order of deposition and relative humidity. Further experiments should investigate the particle interaction mechanisms on the filter collection medium. Two possible mechanisms are : (i) particle-to-particle interactions, when particulate ammonium nitrates react with acid sulfate particles; and (ii) gas-to-particle interactions, when ammonia originating from the dissociation of ammonium nitrate (already collected on the filter media) neutralizes the acid particles. At times

when the collected ammonium nitrate particles are not in equilibrium with the parent gases, ammonia and nitric acid, dissociation occurs.

FIELD STUDIES

Table 2 presents the results from acid aerosol measurements conducted as part of the epidemiological study "Acid Aerosol Health Effects in North American Children" (Speizer et al., 1989). According to the study design, yearly monitoring is conducted in eight North American sites. A total of 24 sites are being studied during the 3-year period of 1988-1991. Twenty-four-hour samples are collected using the annular denuder-filter pack system described above. For each site, sampling begins at 8 a.m. and samples are collected every other day (approximately 170 per year). Table 2 summarizes the results from acid aerosol measurements: 3 first-year sites (Dunnville, Ont; Hendersonville, TN; Morehead, KY) and 3 second-year sites (Charlottesville, VA; Oak Ridge, TN; Zanesville, OH). These sites, located at eastern and northeastern United States and southeastern Canada, were selected for this analysis because they present higher acid aerosol concentrations compared with the rest of the first-year and second-year sites. Data collected prior to mid-June of 1988 (for the first-year sites) are not included in this analysis because a filter blank problem invalidated the measurements of ammonium on the citric acid filters.

Figures 3-8 present the relationship between $H^+(F1)$, the apparent acidity measurement on the Teflon filter, and H^+ (correction), calculated using Equation (4). These figures reveal that for high $H^+(F1)$ concentrations, H^+ (correction) tends to be near zero.

Table 1. Neutralization of aerosol strong acidity by ammonium nitrate in laboratory experiments. All values are in units of nmoles

Aerosol: Experiment no.:	H_2SO_4 1	H_2SO_4 2	NH_4NO_3 3	NH_4NO_3 4	$NH_4NO_3+H_2SO_4$ 5	$NH_4NO_3+H_2SO_4$ 6	$H_2SO_4+NH_4NO_3$ 7	$H_2SO_4+NH_4NO_3$ 8	$H_2SO_4+NH_4NO_3$ 9
Deposition Time (h)									
H_2SO_4	3.1	3.0	—	—	3.1	3.0	3.0	3.0	3.0
NH_4NO_3	—	—	21.2	21.2	3.0	3.0	2.0	2.0	0.3
Relative humidity (%)	75	58	41	41	55	90	53	58	58
Teflon filter									
SO_4^{2-}	571	866	—	—	489	705	792	658	595
NO_3^-	—	—	73960	63560	197	144	4885	3103	70
H^+	1004	1822	—	—	714	125	173	157	740
NH_4^+	54	64	67800	60600	339	1270	6100	4062	518
Ion balance on Teflon filter (cations/anions)	0.89	1.09	0.92	0.95	0.90	0.90	0.97	0.95	1.0
Na_2CO_3-coated glass filter NO_3^-	—	—	3924	3311	732	1249	1272	963	386
Citric acid-coated glass filter NH_4^+	—	—	4476	4103	370	333	—	11	—
H^+ (neutralized)					362	916	1272	952	386
H^+ (% neutralized)					37	65	80	72	32

Table 2. Summary of field study results

Site (no. of samples)	Filter: Species:	F1 NO$_3^-$	F1 SO$_4^{2-}$	F1 NH$_4^+$	F1 HP*	F2 NO$_3^-$	F4 NH$_4^+$	HT†	BAL‡
Dunnville, Ont		11.7	66.0	117.1	26.3	14.8	15.1	33.8	1.0
(93)		22.6‖	65.7	116.3	49.2	13.6	36.6	51.2	0.3
Hendersonville, TN		1.1	60.8	83.8	30.9	8.7	11.4	36.3	1.0
(151)		4.9	45.5	64.5	39.0	10.0	31.1	38.1	0.3
Morehead, KY		3.4	65.3	93.3	36.6	6.5	8.9	39.9	1.0
(144)		9.3	55.3	69.6	47.6	4.9	29.2	47.1	0.2
Charlottesville, VA		3.2	59.9	91.7	31.5	4.0	3.0	34.1	1.0
(169)		10.9	49.7	57.3	35.7	3.9	13.7	36.8	0.2
Oak Ridge, TN		2.4	66.1	91.8	40.6	4.8	2.4	44.0	1.0
(171)		6.2	47.7	57.0	47.9	4.1	6.5	48.2	0.2
Zanesville, OH		12.5	63.3	97.7	28.5	6.7	5.6	32.3	1.0
(171)		18.2	56.3	66.0	49.0	6.1	17.4	49.9	0.3
Detection limit‡		9.8	8.8	11.8	8.0	3.2	9.6		

*HP = H$^+$(apparent) and HT = H$^+$(total).
†BAL = arithmetic means and standard deviations of the Ion Balances of the F1 filters, where Ion Balance = {[HP] + [NH$_4^+$]}/{[NO$_3^-$] + 2[SO$_4^{2-}$]}.
‡If the concentration is less than the detection limit, it is set to 1/2 of the detection limit.
§Arithmetic means, all in nmol m^{-3} except BAL (see note †).
‖Standard deviations, all in nmol m^{-3}, except BAL which are dimensionless (see note †).
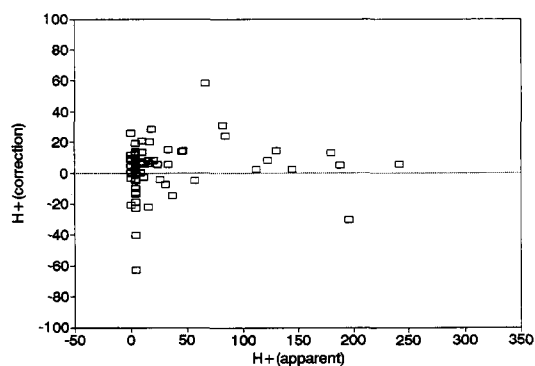

Fig. 3. H$^+$(correction) vs H$^+$(apparent) for data collected in Dunnville, Ont.
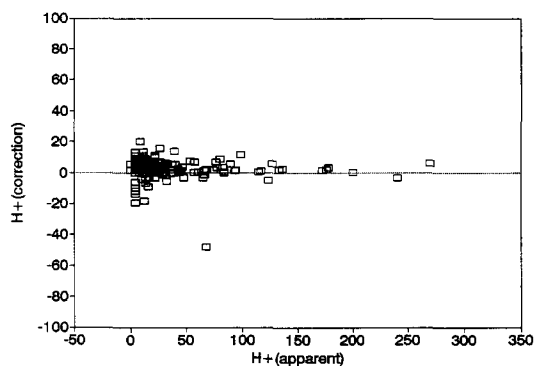

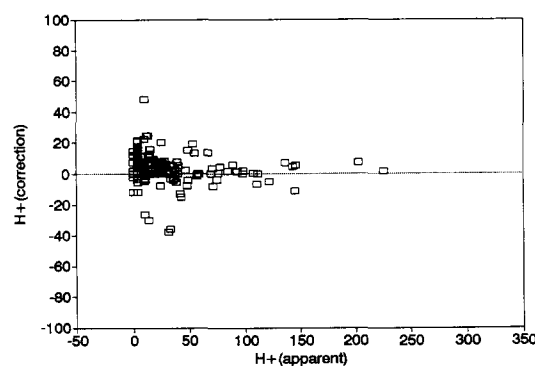Fig. 5. H$^+$(correction) vs H$^+$(apparent) for data collected in Morehead, KY.

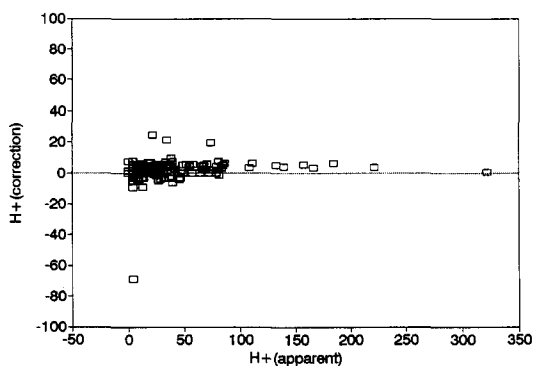Fig. 4. H$^+$(correction) vs H$^+$(apparent) for data collected in Hendersonville, TN.

Fig. 6. H$^+$(correction) vs H$^+$(apparent) for data collected in Charlottesville, VA.

In general, for H$^+$(F1) concentrations higher than approximately 40 nmol m^{-3} (or 2 μg m^{-3} of equivalent H$_2$SO$_4$), H$^+$(correction) represents only a small percentage of the total aerosol acidity, H$^+$(total), calculated using Equation (3). Therefore, for high-acid aerosol concentrations, the correction factor is negligible. This is expected because for samples corresponding to high acid aerosol concentrations, ammonia concentrations should be low during a great part of the 24-h sampling duration. As a result,
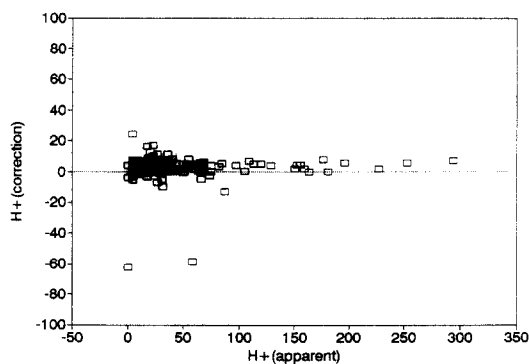
Fig. 7. H^+(correction) vs H^+(apparent) for data collected
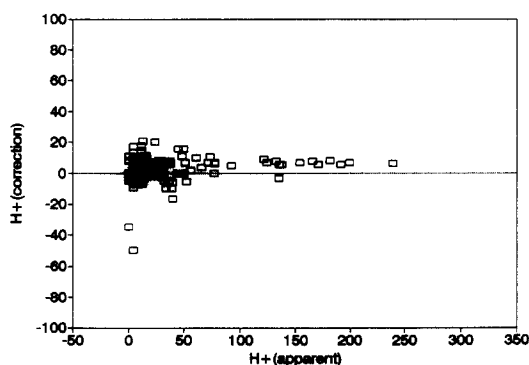in Oak Ridge, TN.

Fig. 8. H^+(correction) vs H^+(apparent) for data collected
in Zanesville, OH.

ammonium nitrate concentrations in these samples
are expected to be low and neutralization of acid
aerosol sulfate to be minimal.

Table 3 summarizes in more detail the acidity data
for the cities in Table 2. The table gives arithmetic
means for H^+(apparent) (which is the H^+(F1)), the
H^+(total) found using Equation (3), and the ratio of
the H^+(total) to the H^+(apparent). These means are
shown for the valid data collected during the sampling
period (approximately 1 year) and for both the high
and low acidity seasons. High season includes samples
collected between 1 May and 30 September and low
season includes samples collected the rest of the year
(Koutrakis and Mueller, 1989). The table also gives the
percentage differences between the corrected (HT) and
uncorrected (HP) averages. Finally, the last two
columns of the table give the relative rankings of the
cities for the sampling period and the high and low
seasons, without and with the correction, respectively.
The ranks based on the high-season acidity averages
do not change using the correction, which supports
the idea that the correction is not important for high
acidity concentrations. However, the rankings of these
cities for annual and low season averages do change

slightly when the correction is made. As this table
demonstrates, the rankings switch order for some
cities which have similar annual or low season aver-
ages. City rankings were changed only in those cases
where the averages were very close (< 10% difference
for both apparent and corrected H^+). In these cases,
the differences in concentration are probably not
significantly different in terms of health effects. There-
fore, we can conclude that the correction is probably
not needed for ambient studies whose goal is to
investigate relationships between respiratory health
effects and exposure to aerosol acidity. However,
corrections may be needed for indoor studies.

As mentioned above, for low H^+(F1) concentra-
tions, less than approximately 40 nmol m^{-3}, the cor-
rection factor becomes significant and H^+(correction)
values may be higher than H^+(F1). This is expected
because these conditions favor ammonium nitrate
formation. Interestingly, negative H^+(correction) val-
ues are depicted in Figs 3–8. Negative correction
numbers, down to ~ 10 nmol m^{-3}, are justifiable by
nitrate (F2) and ammonium (F4) analysis errors. How-
ever, the negative values lower than ~ 10 nmol m^{-3}
shown by Figs 3–8 suggest that NH_4^+ (F4) concentra-
tions are higher than NO_3^- (F2). Therefore, our as-
sumption that ammonium (F4) originates only from
the dissociation of ammonium nitrate collected on the
Teflon filter, (Equation 1), appears to be invalid. How-
ever, these high ammonium concentrations may be
explained by the following reasons:

(i) If the collection efficiency of the citric acid-
coated annular denuder is less than 100%, then part of
the ammonia passes through the citric acid-coated
denuder and is collected downstream on the citric
acid-coated glass-fiber filter (F4); and/or

(ii) If other unstable ammonium salts collected on
the Teflon filter dissociate, such as ammonium chlor-
ide and/or possibly ammonium salts of organic acids,
then NH_4^+ (F4) would originate from dissociation of
ammonium nitrate and these other ammonium salts.

The first hypothesis is tested by comparing
NH_3(D2) and NH_4^+(F4) concentrations. If the effici-
ency of the citric acid denuder is less than 100%,
negative correction numbers, H^+(correction), should
correspond to high ammonia concentrations. How-
ever, no relationship is found between negative correc-
tion numbers and ammonia concentration for any of
the six sites, suggesting that this hypothesis is not
valid.

For all of the sites, most of the significant negative
correction values are observed when aerosol acid is
low (when formation of ammonium nitrate and chlor-
ide is favored). Although the second hypothesis can
not be tested with this collected data because no Cl$^-$
(F2) measurements were made, it may explain the
observed phenomenon. The high NH_4^+(F4) concentra-
tions may be justified by the presence of unstable
ammonium salts, other than ammonium nitrate, like
those shown in Equations (7) and (8) where HA can be

Table 3. Summary of field study acidity results

|	HP*	HT	HT/HP†	Percentage difference	Rank HP	Rank HT
Dunnville, Ont						
annual mean	26.3	33.8	1.3	28.5	1	2
high season mean†	48.3	57.0	1.2	18.0	1	1
low season mean†	3.8	10.0	2.6	163.2	1	1
Hendersonville, TN						
annual mean	30.9	36.3	1.2	17.5	3	4
high season mean	59.6	62.2	1.0	4.4	4	4
low season mean	16.0	22.8	1.4	42.5	4	5
Morehead, KY						
annual mean	36.6	39.9	1.1	9.0	5	5
high season mean	78.3	79.6	1.0	1.7	6	6
low season mean	16.2	20.5	1.3	26.5	5	4
Charlottesville, VA						
annual mean	31.5	34.1	1.1	8.3	4	3
high season mean	56.3	59.1	1.0	5.0	3	3
low season mean	15.4	17.9	1.2	16.2	3	2
Oak Ridge, TN						
annual mean	40.6	44.0	1.1	8.4	6	6
high season mean	65.4	68.7	1.1	5.0	5	5
low season mean	22.2	25.7	1.2	15.8	6	6
Zanesville, OH						
annual mean	28.5	32.3	1.7	13.3	2	1
high season mean	53.8	57.2	1.1	6.3	2	2
low season mean	14.4	18.4	1.3	27.8	2	3

*HP = H$^+$(apparent) and HT = H$^+$(total). All concentrations are arithmetic means in nmol m^{-3}.
†HT/HP is the ratio of the arithmetic means given in this table. High season is from 1 May to 30 September. Low season is the remainder of the year.

an inorganic or organic acid:

$$NH_4Cl \rightarrow NH_3 + HCl \qquad (7)$$

$$NH_4A \rightarrow NH_3 + HA. \qquad (8)$$

Obviously, such ammonium salts may interact with acid aerosol particles on the Teflon filter, as in the case of ammonium chloride:

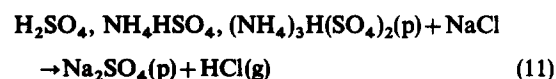$$H_2SO_4, NH_4HSO_4, (NH_4)_3H(SO_4)_2$$
$$+ NH_4Cl(p) \rightarrow (NH_4)_2SO_4(p) + HCl(g). \qquad (9)$$
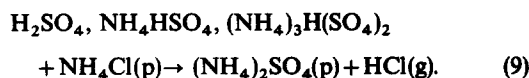
An analogous equation may be written for NH$_4$A. Then Equation (4) needs to be modified appropriately (Equation 10):

$$H^+(\text{correction}) = NO_3^-(F2) + Cl^-(F2)$$
$$+ A^-(F2) - NH_4^+(F4). \qquad (10)$$

Clearly, in future measurements, Cl$^-$(F2) and A$^-$(F2) concentrations need to be determined in order to test the second hypothesis and to estimate H$^+$(correction) more precisely. Since Cl$^-$(F2) blank concentrations are high and variable, determining Cl$^-$(F2) is a challenge. Due to the sampling and analysis handling, chloride contamination is inevitable; thus, measurements may be unreliable. Furthermore, NH$_4$A salts need to be identified and examined to determine which of them, if any, need to be included

in the correction Equations (4) and (10). Ammonium nitrite is formed when the concentration product P = [NH$_3$] [HONO] exceeds 2.4×10^9 ppb^2 at 25°C (Brauer et al., 1990); therefore, it is not expected to be present under usual atmospheric conditions. Ammonium formate and acetate salts are also very unstable and are unlikely to be present in ambient air (Grosjean, 1982). Other ammonium salts of organic acids, such as oxalic, malonic, adipic or glutaric, may also be collected on the Teflon filter. Since these organic acids have been identified by previous investigators (Ferek et al., 1983; Grosjean et al., 1982), the sodium carbonate-coated extraction solutions should be analysed for these organic acids. Unfortunately, due to the presence of microorganisms, organic acids decompose during storage and it is not possible to analyse samples collected previously. However, determination of Cl$^-$ and A$^-$ may be measured in future samples, provided that sampling and analysis protocols are appropriately modified.

Besides the ammonium salts, other salts and alkaline particles may react with acid sulfate particles on the collection media. Equations (11) and (12) show some examples:

$$H_2SO_4, NH_4HSO_4, (NH_4)_3H(SO_4)_2(p) + NaCl$$
$$\rightarrow Na_2SO_4(p) + HCl(g) \qquad (11)$$

H_2SO_4, NH_4HSO_4, $(NH_4)_3H(SO_4)_2(p)$

$$+ CaCO_3(p) \rightarrow CaSO_4(p) + CO_2(g) + H_2O(g) . \quad (12)$$
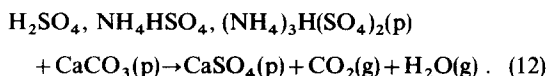
The reaction with NaCl can be taken into account if Cl^- (F2) is measured; however, the reaction with $CaCO_3$ or other carbonate salts can neutralize acidic sulfates and these acid losses can not be easily determined. Although $CaCO_3$ is mostly associated with coarse particles under usual atmospheric conditions, some of the $CaCO_3$ may be present in the fine-particle mode resulting in underestimation of aerosol strong acidity. Also, it is possible that bounce-off of alkaline coarse particles from the impaction plate could cause neutralization of fine particles collected on the Teflon filter. However, it is not possible to quantify the amount of neutralized acid through this process.

From the analysis and discussion above, it appears that for high-acid aerosol concentrations, acidity losses may be negligible and that correction may not be necessary; whereas, for low concentrations, underestimation of aerosol acidity is possible due to particle interactions. This can be explained because ammonium concentrations are minimal for high acid sulfate concentrations. In contrast, for low acid concentrations, ammonium salts present higher concentrations. Furthermore, negative H^+ (correction) values, shown in Figs 3–8, may be related to the presence of ammonium salts other than ammonium nitrate. Therefore, the H^+ (correction) determined using NO_3^- (F2) and NH_4^+ (F4) represents a minimum correction and negative correction values can be set equal to zero. The determined average and percentage corrections in Table 2 represent minimum corrections. The same table also gives the average concentrations of ammonium, hydrogen, sulfate and nitrate ions.

CONCLUSIONS

An annular denuder system in conjunction with a newly designed filter pack can be used to examine interactions between acid aerosol sulfates and other particles during sample collection. Both laboratory tests and field studies indicate that particle interactions occur and result in losses of aerosol acidity. Use of the annular denuder filter pack techniques allows for correcting the apparent aerosol strong acidity. For high aerosol acidity concentrations, correction was found to be unimportant; however for low concentrations, correction becomes very important and needs to be taken into account. Negative correction numbers may be related to the presence of ammonium salts other than ammonium nitrate, such as ammonium chloride or ammonium salts of organic acids. Thus, calculations assuming that aerosol strong acidity losses are due exclusively to the presence of ammonium nitrate represent a minimum acidity correction. It may be worthwhile to measure Cl^- or other

anions collected on the Na_2CO_3-coated glass-fiber filter to determine a more accurate correction.

Our results suggest that for concentrations above approximately 40 nmol m^{-3} of hydrogen ion (2 μg m^{-3} of H_2SO_4 equivalent) the neutralization percent is minimal. Therefore for our epidemiological studies, neglecting acid correction should not be an important omission since adverse human health effects, if any, are expected to be associated with higher acid exposures. However, for atmospheric chemistry and indoor studies, neutralization effects need to be taken into account.

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