

Information from Ions in Extracts from Acidic Gas Denuders Used in the PM_{2.5} Chemical Speciation Sampling Network

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ABSTRACT

Three of the four designs of PM_{2.5} chemical speciation collectors employ magnesium oxide (MgO) coated denuders prior to the filters that collect PM for ion analysis. The denuders remove acidic gases, such as nitric acid vapor, from the air stream and prevent such gases from reaching the filter surface. MgO-coated denuders remain in use for up to 30, 24-hour sampling days. Exploratory work to determine the "catch" of the RAAS MgO denuders was undertaken.

■ Extraction methods and recovery estimates

A method for aqueous and buffered extraction of ions (due to acidic species) from the denuder surfaces is described. Ions at concentrations representative of ambient air acidic gas concentrations were spiked into the MgO slurry that becomes the denuder coating. Recoveries of nitrate and sulfate ion spikes were reasonable, ranging from 107 to 116 percent. The capacity of the denuder for absorption of acidic gases is reviewed.

■ Comparison of acidic gas concentrations across PM_{2.5} sites

Concentrations of acidic gases such as nitric acid vapor (in terms of micrograms HNO₃ per cubic meter of air) are determined via IC analysis of denuder extracts. Average nitric acid vapor concentrations (for a sample gathered over three months at a frequency of every 3rd day) are compared for several sites in the network.

OBJECTIVES

- Assess the reproducibility of application of MgO coating to the RAAS and MASS denuder types.
- Devise an extraction procedure for semi-quantitative removal of nitrate and sulfate ions from exposed MgO denuders.
- Evaluate the capacity of the RAAS denuder for absorption of acidic gases as it is used in the PM_{2.5} Chemical Speciation Monitoring Network.
- Compare acidic gas "catch" across several sites in the PM_{2.5} Chemical Speciation Monitoring Network.

EXPERIMENTAL PROCEDURES

Reproducible Coating of the RAAS Denuder

An improved procedure for coating the RAAS denuder was devised that applies the MgO slurry only to the glass annular denuder surfaces with better precision than before. The steps are:

- Clean used denuder with 2N hydrochloric acid. Rinse well with deionized water, N₂ gas blast, dry overnight to constant weight (nearest 0.1 gram).
- Use jig consisting of neoprene O-rings and stoppers to seal one end of denuder.
- MgO in ethanol slurry prepared consistently, kept in suspension by magnetic stirrer.
- Reproducibly timed slurry application, denuder handling, and drying steps.
- Clean any excess MgO from entry ports, threads. Weigh coated denuder and seal.

View of RAAS Denuder and Sealing System



Denuder Extraction Procedure

RAAS denuder surfaces were extracted as follows:

- Cap one end; add 30 mL of extracting solution (deionized water or IC buffer)
- Seal denuder tightly
- Shake at room temperature overnight, 12 hours
- Pour off extract, repeat extraction process, shaking 1 hour
- Repeat 12 and 1 hour extractions twice more
- Submit separate or combined extracts for IC analysis

RESULTS AND DISCUSSIONS

Reproducibility of MgO coating of RAAS Denuders

Number of Denuders Coated	Avg. Mass Applied, grams	% RSD	Comments
22	0.341	16.3	Regular procedure
3	0.453	7.7	Improved procedure (thinned slurry)
5	0.69	5.9	Improved procedure (standard slurry)

RAAS Denuder Extraction Results

Denuder Identify (amount of MgO present)	Nitrate Ion, micrograms (% recovery)	Sulfate Ion, micrograms (% recovery)
Blank denuder (0.45 g)	3.8	671.1
Spiked denuder (0.31 g)	839 ⁽¹⁾ (109.7)	2854 ⁽¹⁾ (116.4)
Spiked denuder (0.29 g)	766 ⁽¹⁾ (107.6)	2710 ⁽¹⁾ (118.9)
IL (1) site ⁽²⁾	712	3554
MD (1) site ⁽²⁾	1094	5635
WA (1) site ⁽²⁾	341	1608
TN site ⁽³⁾	1467	3306
GA (C) site ⁽³⁾	416	1500
WA (2) site ⁽³⁾	445	1496
MD (2) site ⁽³⁾	1119	4110
GA (M) site ⁽³⁾	258	1303
NH site ⁽³⁾	544	3377
GA (S) site ⁽³⁾	544	3770
GA (A) site ⁽³⁾	1426	3878

⁽¹⁾ Value is blank-corrected.

⁽²⁾ In use 1/15/2002 through 4/16/02.

⁽³⁾ In use 4/17/2002 through 7/16/2002.

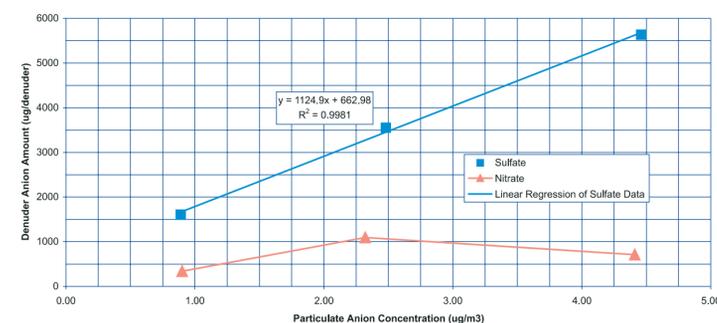
RAAS Denuder Capacity for Acid Gas Absorption Capacity based on amount of MgO available for reaction

- Amount of MgO on RAAS denuder has varied from 0.32 to 0.72 g (8,430 to 17,900 μmoles)
- RAAS denuder is exposed to ~ 302 m³ of air during 90 days of 1 in 3-day sampling
- Upper ranges of published values for acidic gases are: SO₂ (30 μg/m³), HNO₂ (2 μg/m³), HNO₃ (15 μg/m³)
- Sum of acidic gases above corresponds to 227 μmoles in 302 m³ of air
- Capacity factor for MgO coating is at least [8,430 μmoles / 227 μmoles] = 37
- CO₂ absorption by MgO produces MgCO₃, itself an acid-absorbing species
- Conclusion assumes all MgO is available for acid gas absorption/reaction

SUMMARY AND CONCLUSIONS

- A reproducible procedure was developed for coating RAAS PM_{2.5} denuders with MgO.
- A multi-step extraction procedure was developed that successfully removed nitrate and sulfate ion from spiked and exposed denuders.
- Average recoveries for denuders spiked with nitrate and sulfate ion were 109% and 117%, respectively.
- Nitric acid concentrations, based on concentrations of nitrate ion extracted from denuders at three PM_{2.5} sampling sites during January – April 2002, ranged from 1.2 to 3.7 μg/m³. Acidic sulfur species, expressed as SO₂, ranged from 3.5 to 12.4 μg/m³.
- For another set of sites that sampled in the period April – July 2002, nitric acid concentrations ranged from 0.9 to 4.9 μg/m³ and acidic sulfur species, expressed as SO₂, ranged from 2.9 to 9.1 μg/m³.
- On a stoichiometric basis, the RAAS MgO denuder has a greater than 30-fold excess capacity for higher values of ambient acidic gas concentrations.
- Relationship between amount of sulfur acidic species absorbed on denuder and sites' particulate sulfate anion concentrations is strong, but data set is very small. More data, across other seasons, are needed.
- Other anions present in the denuder extracts may be identifiable and of interest.

Magnesium Oxide Denuded catch versus Average PM_{2.5} Anion Concentrations



Three Types of MgO-coated Denuders Used in the PM_{2.5} Chemical Speciation Sampling Network



Left: SASS Aluminum Honeycomb Denuder
Center: MASS Downtube Glass Annular Denuder
Right: RAAS Glass Annular Denuder