

Prototype Compact Denuders for Ambient Air Sampling

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Overview

CASTNet currently uses a multiple-filter approach for sampling all target species. Unfortunately, particulate nitrate volatilizes from the initial filter and is collected on a secondary nylon "gas phase collection" filter; thus, nitric acid is overestimated and particulate nitrate is underestimated. Since the gaseous and particulate phases have much different deposition velocities, this bias interferes with the accurate determination of nitrogen deposition. Ammonia, which is an important yet poorly quantified contributor to nitrogen deposition and fine particle formation, is measured only in the particulate phase and is also subject to loss via volatilization. To address these shortcomings, a compact, extractable denuder has been designed to fit into the Met One, Inc. Speciation Air Sampling System (SASS), to provide a more complete and accurate inventory of nitrogen species concentrations and partitioning.

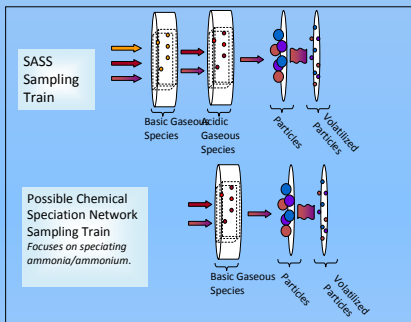


Table 1: Comparative CASTNet and SASS denuder analytical capabilities

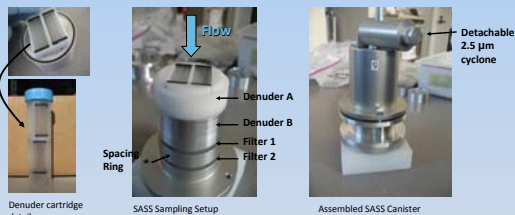
Species	Current CASTNet	SASS Prototype
Particulate		
NH ₄ ⁺	✖	✖
SO ₄ ²⁻	✖	✖
NO ₃ ⁻	✖	✖
Ca ²⁺ , Cl ⁻ , Mg ²⁺ , Na ⁺ , K ⁺	✖	✖
Quantity volatilized particulates	---	✖
Gaseous		
NH ₃	---	✖
HNO ₃	✖	✖
SO ₂	✖	✖

* Subject to artifact from volatilized particles

Two prototype denuders were designed and tested. Each was designed to fit into an extended length canister to be operated using the Met One SASS sampler. Collection surfaces in each denuder were made by sawing quartz into plates. The sawn edges provided appropriate roughness for retaining coating solution.

SASS Denuder Prototype 1

SASS denuder Prototype 1 featured two removable 'denuder cartridges' that fit within a holder in the SASS canister. These cartridges could be removed and fit into a 25mL test tube for extraction, washing, and coating (1% phosphorous acid solution was tested for ammonia collection).



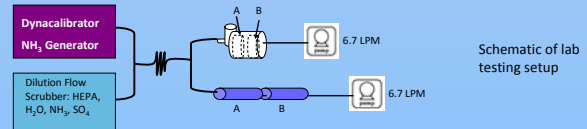
SASS denuder Prototype 2 was modified both in design and construction. Polypropylene was used for improved chemical compatibility with a stronger (5% phosphorous acid coating solution to increase denuder capacity for ammonia collection. The denuder design was modified to permit coating and extraction using caps attached to both ends. The required extraction volume was reduced (to ~ 7 ml) to improve sensitivity for use in low concentration environments.

SASS Denuder Prototype 2



Lab and Ambient Testing Approach

- ◆ The SASS compact denuder performance was compared in both lab and field environments.
- ◆ Tests included denuder-behind-denuder measurements to evaluate ammonia collection efficiency and side-by-side comparisons against a URG annular denuder sampling system.
- ◆ Lab tests utilized a stream of ammonia generated using a permeation tube. Ambient tests sampled outdoor air, including particles and gases, in Fort Collins, Colorado.



Findings

Prototype 1: Ammonia Testing Results

- ◆ SASS Prototype 1 denuder efficiency measured 89.8 +/- 14.5 %, below target (>95%) efficiency levels.
- ◆ Prototype 1 efficiency decreased in the presence of high loads, indicating insufficient load capacity.
- ◆ Extensive handling of denuder inserts required in Prototype 1 made extraction and coating inconvenient and prone to contamination.
- ◆ Delrin materials in Prototype 1 proved incompatible with the phosphorous acid coating solution

Prototype 2: Ammonia Testing Results

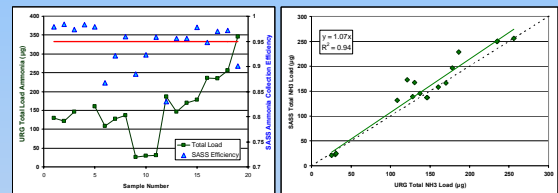


Figure 1: Lab testing of Prototype 2 revealed improved collection efficiency and no relationship between collection efficiency and total applied ammonia load.

Figure 2: Similar total ammonia loads were collected by URG denuders and Prototype 2 SASS denuders operated in parallel during lab tests.

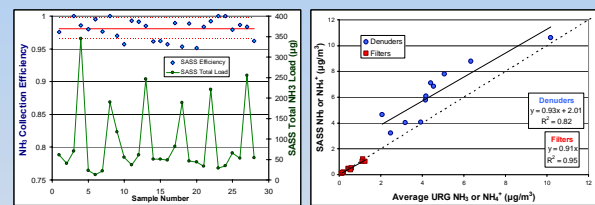


Figure 3: During ambient air testing, the Prototype 2 ammonia collection efficiency averaged 97.9 +/- 1.6%. Again, no correlation ($r^2 = 0.0078$) was observed between collection efficiency and total ammonia load.

Figure 4: An intercomparison of PM_{2.5} ammonium and gaseous ammonia collected by the modified SASS and the URG samplers showed good agreement for filter ammonium. SASS Prototype 2 denuders collected somewhat higher ammonia amounts than were observed with URG denuders.

Conclusions

- ◆ A compact denuder has been designed and successfully tested for use with the SASS sampler. This denuder has high efficiency for ammonia collection and sufficient capacity for daily or weekly sampling in most ambient environments. The denuders can be prepared with low background (blank) concentrations (< 2 µg).
- ◆ The compact nature of the denuder makes it easier to ship and to deploy on sampling towers. Drop "tests" demonstrate that the denuder is robust against breakage.
- ◆ Additional testing is planned in the coming year as part of a measurement methods intercomparison.
- ◆ Deployment of a denuder/filter-pack system can provide a more accurate determination of the split between gas (e.g., ammonia and nitric acid) and particle (e.g., ammonium and nitrate) species than is possible with a filter-pack sampling approach. Accurate knowledge of the phase partitioning split is crucial to improving estimates of reactive nitrogen deposition.

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