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Development and Characterization of an Annular Denuder Methodology for the Measurement of Divalent Inorganic Reactive Gaseous Mercury in Ambient Air

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Atmospheric mercury is predominantly present in the gaseous elemental form (Hg^0). However, anthropogenic emissions (e.g., incineration, fossil fuel combustion) emit and natural processes create particulate-phase mercury ($\text{Hg}(\text{p})$) and divalent reactive gas-phase mercury (RGM). RGM species (e.g., HgCl_2 , HgBr_2) are water-soluble and have much shorter residence times in the atmosphere than Hg^0 due to their higher removal rates through wet and dry deposition mechanisms. Manual and automated annular denuder methodologies, to provide high-resolution (1–2 h) ambient RGM measurements, were developed and evaluated. Following collection of RGM onto KCl-coated quartz annular denuders, RGM was thermally decomposed and quantified as Hg^0 . Laboratory and field evaluations of the denuders found the RGM collection efficiency to be >94% and mean collocated precision to be <15%. Method detection limits for sampling durations ranging from 1 to 12 h were 6.2–0.5 pg m^{-3} , respectively. As part of this research, the authors observed that methods to measure $\text{Hg}(\text{p})$ had a significant positive artifact when RGM coexists with $\text{Hg}(\text{p})$. This artifact was eliminated if a KCl-coated annular denuder preceded the filter. This new atmospheric mercury speciation methodology has dramatically enhanced our ability to investigate the mechanisms of transformation and deposition of mercury in the atmosphere.

Introduction

It has been recognized for many years that the accurate measurement of relevant atmospheric mercury species, not just total mercury, is necessary to help elucidate the processes of emission, transport, transformation, and deposition of

atmospheric mercury. Brosset (1, 2) hypothesized that divalent mercury species might explain the decreasing mercury concentration gradients observed from industrialized Central Europe to Northern Europe. This led to development of the first methodologies to attempt to measure different atmospheric gas-phase mercury species, which Brosset and Iverfeldt correctly acknowledged was likely to produce artifacts (3). During the same time period, Schroeder and Jackson also recognized the need for a viable atmospheric mercury speciation method (4, 5). On the basis of our current understanding of atmospheric mercury speciation, the Schroeder and Jackson methodology likely had biases, but their use of selective adsorption based on the chemical and physical behavior of the different mercury species was a key concept used for future method development efforts, including this work.

With the advent of cold vapor atomic fluorescence spectroscopy (CVAFS) for mercury detection, Bloom and Fitzgerald were able to directly quantify gas-phase mercury species in the atmosphere at low pg m^{-3} levels (6). Other researchers applying CVAFS to the detection of atmospheric mercury were then able to quantify and describe particulate-phase mercury ($\text{Hg}(\text{p})$) patterns and transport in urban, rural, and remote locations at the low pg m^{-3} level (7, 8). However, it became clear in the early 1990s that water-soluble (divalent) inorganic forms of mercury (e.g., HgCl_2 and HgBr_2 , hereafter referred to as reactive gaseous mercury (RGM)) were a significant fraction of mercury emissions from municipal waste and coal-fired power plants (9). Unlike gaseous elemental mercury (Hg^0), RGM is readily scavenged by precipitation and has an extremely high dry deposition velocity (often compared to that of nitric acid 1–5 cm s^{-1}) (10, 11). This led a multiagency international expert panel to identify the development of a low pg m^{-3} method for measuring concentrations of RGM in the atmosphere as a high priority research topic (12). On the basis of the recommendations of the expert panel, three separate research groups developed a method to measure ambient RGM: (i) refluxing mist chambers (11, 13, 14), (ii) ion-exchange membranes behind particulate filters (15, 16), and (iii) potassium chloride (KCl)-coated tubular denuders (17). The advantages and disadvantages of the methods have been discussed previously (15), and the mist chamber method is critiqued in the following discussion. The international mercury research community has subsequently recommended that emission inventories, ambient air measurements, and atmospheric modeling efforts include at least Hg^0 , RGM, and $\text{Hg}(\text{p})$ species because of their different atmospheric behavior (18). Two international atmospheric mercury measurement intercomparison studies have shown that there can be significant differences between the various research based RGM methods (16, 19).

The U.S. Environmental Agency (EPA) and the Florida Department of Environmental Protection also recognized the need to develop methods for the determination of atmospheric mercury species in ambient air after the 1995 South Florida Mercury Monitoring and Modeling Study (20) revealed mercury emissions from municipal and medical incinerators were dominated (78–95%) by water-soluble RGM. This finding was significant to investigators evaluating the relative importance of local sources to mercury deposition to the Everglades (21) as well as other scientists and modelers trying to elucidate atmospheric mercury chemistry. On the basis of past studies and future research goals, we recognized that an advanced RGM methodology must meet the following criteria: (i) could be operated and maintained by a trained

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technician, (ii) could be operated under a wide temperature range (e.g., -40 to 50 °C), (iii) would be specific for RGM (e.g., no interference from Hg^0 and the much larger Hg^0 component), (iv) has a method detection limit (MDL) low enough to allow background concentrations to be quantified at 1-h resolution, and (v) would minimize the possibility of contamination. Neither the impregnated ion-exchange membrane nor the refluxing mist chamber ambient air RGM measurement methodologies being used at the time satisfied all five criteria. However, Klockow et al. (22) successfully used KCl and elemental silver (Ag)-coated tubular denuders in series to collect RGM and Hg^0 from stack gases, respectively. Xiao et al. (17) subsequently utilized KCl-coated tubular denuders for ambient measurements; unfortunately, the low flow rate ($\sim 1 \text{ L min}^{-1}$ (lpm)), low capacity, and wet chemical extraction procedure made them incapable of achieving the required MDL for high-resolution ambient applications. We felt that the denuder concept was the best option to pursue based on past success using denuders for other ambient reactive gases such as sulfur dioxide, ammonia, and nitric acid over the last two decades (23).

EPA, Florida Department of Environmental Protection, and Tekran Inc. began scientific collaboration that ultimately led to three key modifications necessary to satisfy the aforementioned criteria and apply the denuder methodology for ambient RGM sampling (i) use of a quartz annular denuder, (ii) etching of the active collection surface, and (iii) thermal desorption of the denuder (Tekran, patent pending). The annular denuder design allowed for higher sample collection flow rates while maintaining $>99\%$ theoretical collection efficiency. Etching both the outer surface of the annulus and the inner surface of the denuder tube dramatically increased its KCl holding capacity and produced a uniform coating. Thermally desorbing the quartz denuder at 500 °C in a mercury-free air stream decomposes RGM and allows for quantification as Hg^0 without chemical extraction or sample preparation. Thermal desorption provides for rapid analysis in the field, minimizes the possibility of contamination, and allows the denuder to be immediately reused without further preparation. The immediate reuse of the denuder was the key element necessary for successful automation of RGM determinations. This paper will outline the development and performance characteristics of the quartz annular denuder for both manual and automated collection and analysis for RGM. In addition, we will present and discuss standardized procedures to obtain optimal results.

Quartz Annular Denuder Design. A classic diffusion denuder is a cylindrical tube that is chemically coated to remove selected gas-phase species that diffuse to the walls and react or adhere the surface during the passage of a laminar air stream (24). Fine particles ($<2.5 \mu\text{m}$) pass through the denuder in the laminar air stream unaffected because they have insufficient diffusion coefficients to be deposited to the walls of the denuder (25). Klockow et al. (22) successfully used tubular denuders to speciate RGM and Hg^0 from the flue gas of fossil fuel combustion facilities and waste incinerators. They used KCl-coated denuders to capture RGM and Ag-coated denuders to collect Hg^0 . After collection, the denuders were extracted using nitric acid and subsequently analyzed using cold vapor atomic absorption spectrophotometry (CVAAS). Xiao et al. (17) subsequently adapted KCl-coated tubular denuders for ambient applications using a hydrochloric acid extraction procedure. Unfortunately, the tubular denuders' low flow rate (~ 1 lpm), low capacity, and wet chemical extraction procedure made them unsuitable for high-resolution ambient applications with background RGM values. Possanzini et al. (26) made a substantial advance in denuder performance by developing an annular denuder

configuration that increased the collection efficiency per unit length by a factor of 30. The annular denuder is constructed with two coaxial tubes wherein airflow is directed through the annular space. Much higher flow rates can be achieved through the annular denuder as compared to a tubular denuder while still maintaining laminar flow and theoretical collection efficiencies $>99\%$.

Over the past 25 years, in almost all previous studies where denuders were used to measure gas-phase species, the denuders were chemically extracted and the resulting solutions subsequently analyzed (27, 28). Chemical extraction and analysis for RGM is time-consuming, generates hazardous waste, introduces high analytical blanks, and provides opportunity for contamination. We thought that thermal desorption of RGM from the KCl denuders was a possible alternative to chemical extraction because the compounds of interest (e.g., HgCl_2 , HgBr_2) have decomposition temperatures on the order of 300 °C while the melting point and boiling point of KCl is 771 and 1437 °C, respectively (29). We proceeded to design and construct quartz annular denuders that could be routinely desorbed at 500 °C to decompose collected RGM species to be quantified as Hg^0 .

Two quartz annular denuders were designed for RGM determinations, one for automated sampling (Figure 1a) and one for manual sampling (Figure 1b). The denuders differ only to the extent that the automated denuder is shaped to fit into its field sampling module (e.g., support posts are required to hold it securely in place and threads sized to accommodate its unique inlet and outlet configuration). The denuders and inlet systems were manufactured by URG Corporation (Chapel Hill, NC) to take advantage of their proprietary quartz etching and cross-linked Teflon coating procedures, respectively. Both denuder designs have a 25.4 cm active annular surface length with a 1 mm annular space. At a sampling flow rate of 10 lpm, the Reynolds numbers of both denuders are <400 , well within the laminar flow regime. The inner annulus tubes of the denuders have a small capillary vent to relieve air pressure during heating. The outer surface of the annulus and the inner surface of the outer tube are etched to provide additional surface area (Figure 2A). The etched quartz surface dramatically increases the denuder's capacity for the KCl coating solution and provides a uniform coating (Figure 2B). The unetched surface (Figure 2C) results in a sparse, nonuniform, and barely visible KCl coating (Figure 2D).

The denuder sampling inlet consists of an integrated elutriator/acceleration jet and an impactor/coupler (Figure 1b). Coarse particles $>2.5 \mu\text{m}$ are removed by aerodynamic impaction onto a glass impactor plate (30). The glass elutriator/acceleration jet has an extremely short residence time and is cross-linked Teflon-coated to minimize the loss of RGM. The impactor/coupler has an integrated Teflon seal ring and Teflon impactor support into which the removable glass impactor plate is installed. The automated denuder inlet also includes a cross-linked Teflon-coated zero air inlet junction and #25 thread coupler to facilitate the introduction of mercury-free air during the analysis cycle (Figure 1a).

Methods

Denuder Coating. The quartz annular denuders were cleaned, coated, and conditioned prior to RGM sampling. A new denuder was cleaned by rinsing thoroughly with (i) 10% reagent-grade nitric acid, (ii) deionized water (DIW) with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$, and (iii) laboratory-grade methanol, being careful not to introduce liquid into the annulus through the vent. The denuders were then allowed to air-dry in a class 100 laminar flow hood or dried with mercury-free air, generated using an activated carbon trap, in a denuder-drying

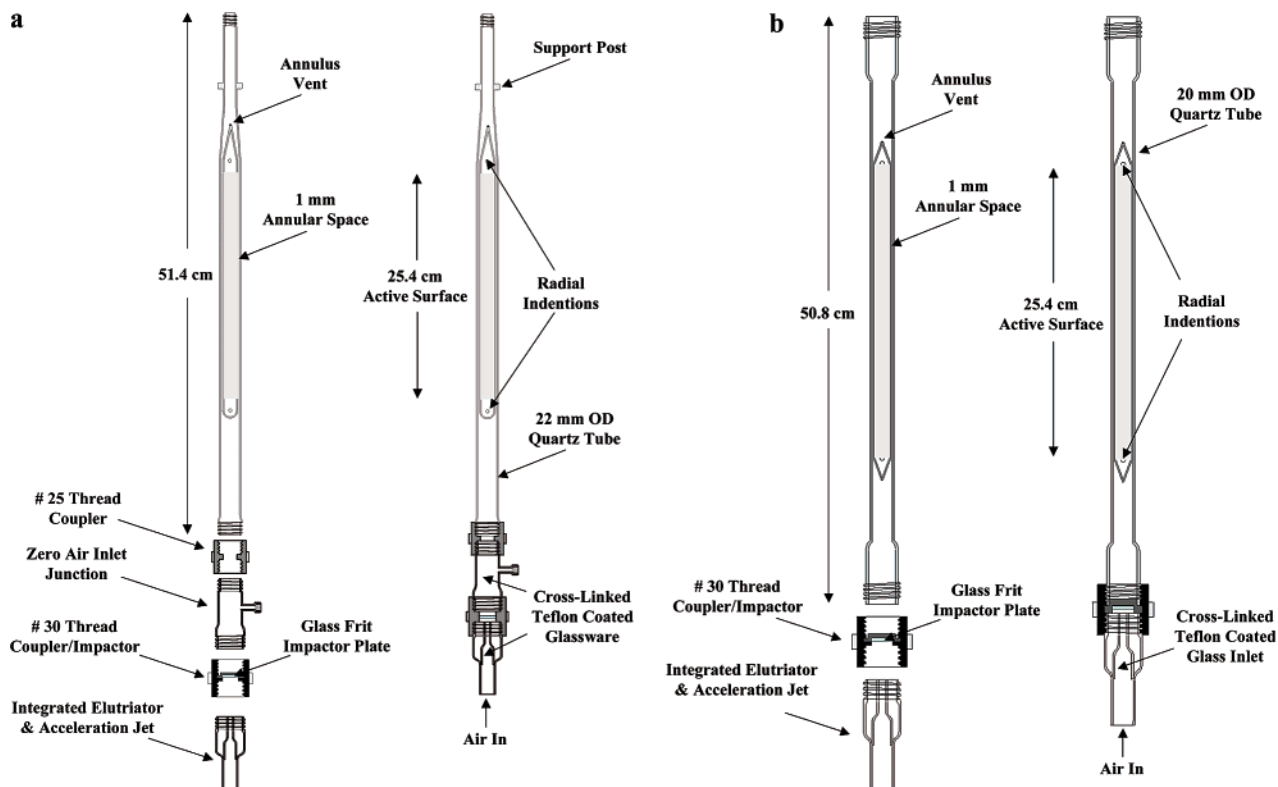


FIGURE 1. Diagrams of disassembled and assembled quartz annular denuder systems for (a) automated and (b) manual methods, respectively.

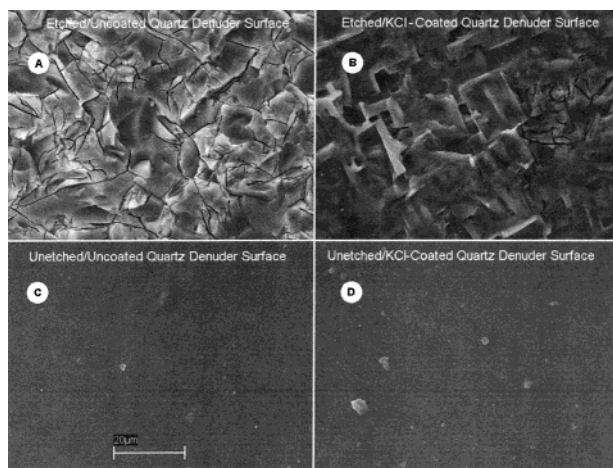


FIGURE 2. SEM micrographs showing the active collection surface of (A) etched and uncoated, (B) etched and coated, (C) unetched and uncoated, and (D) unetched and coated quartz denuder surfaces.

manifold. A denuder that had been previously coated was first thoroughly rinsed with DIW and then filled up with DIW to the radial indentions of the annulus for a 24-h soak. The denuders were stored vertically in ring stands making sure the entire active surface of the denuder was submerged in DIW. Following the 24-h soak, the denuders were cleaned as described previously.

The quartz denuders were coated with a 2.4 M aqueous KCl solution. The coating solution was prepared by dissolving 90 g of high purity KCl in DIW to produce a total volume of 500 mL. The subsaturated solution was found to produce a coating with an excellent collection capacity while preventing large crystal formation that can dislodge or cause particle impactation during sampling. The inlet side of the denuder to be coated was placed vertically into a small beaker of coating solution and supported using a ring stand. A vacuum line with an inline needle valve was connected to the exit side of

the denuder. The coating solution was drawn up the denuder to just above the active denuder surface, approximately 1–2 cm below the annulus vent. The coating solution was allowed to slowly drain back into the beaker, and the process was repeated 2 times. The denuder was then removed from the ring stand, and excess coating solution was shaken out. The inlet portion of the denuder (up to the active collection area) was rinsed of KCl coating solution by dipping the denuder into a beaker of DIW. The inlet surface was then dried with a particle-free wipe, and the denuder was installed vertically into a denuder-drying manifold. The denuders were dried with mercury-free air in a vertical orientation to ensure a uniform coating. If KCl crystals were observed outside of the active collection area, the denuder inlet was rinsed again.

Once the denuders were coated and dried, they were thermally conditioned to ensure that the KCl coating was cured in place and that any residual mercury was removed. The denuders were placed into a clamshell tube furnace (Lindberg/Blue M, model TF55035). Seals for both ends of the tube furnace heat zone were fabricated from folded quartz fiber sheets to ensure a tight seal between the oven and denuder. Bored #30 thread end caps with Teflon-clad silicone seal rings and glass inserts (fitted with heat shrink Teflon tubing) were used to couple both ends of the denuder to 0.64 cm o.d. Teflon tubing. Mercury-free air was then pulled through the denuder at 1.5 lpm while they were heated at 525 °C for 1 h. A coaxial cooling fan was positioned at each end of the tube furnace directed onto the exposed ends of the denuder to prevent excessive heat from damaging the threaded denuder end cap assemblies.

Manual Denuder Sampling. The manual sampling methodology was relatively inexpensive, simple, and portable. The required equipment consisted of only a temperature-regulated sampling case and volumetrically flow-controlled pump. The denuder field sampling case was designed to accommodate two complete manual sampling trains in a vertical orientation and to maintain the denuder sampling trains at 50 °C (Figure 3). The heating system inside the

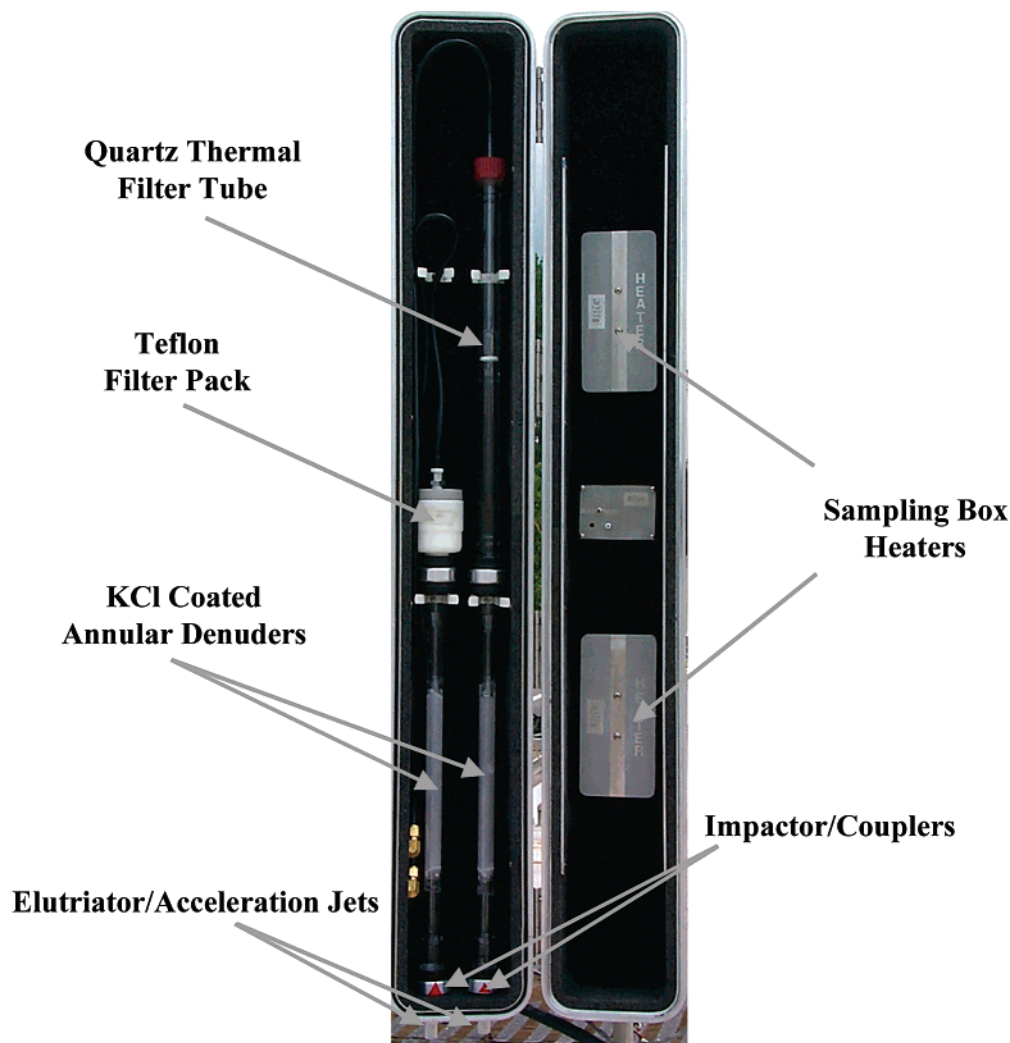


FIGURE 3. Photograph of manual denuder sample box highlighting key components (denuder heating sleeves not shown).

insulated box consisted of a pair of general radiant heaters mounted inside the case and a pair of electronic temperature-controlled (proportional, integral, and derivative PID) heating sleeves that were placed directly over the denuders to maintain 50 °C. The denuder heating sleeves were constructed of polypropylene pipe insulation lined with silicone heating tape. Maintaining the denuders and inlets well above ambient temperatures during sampling was critical to prevent hydrolysis of the KCl coating surface as well as ensure quantitative transport of RGM through the inlet. The volumetrically flow-controlled pump was set to maintain 10 lpm to ensure an impactor aerodynamic aerosol cut point of 2.5 μm . In this configuration, fine fraction (<2.5 μm) $\text{Hg}(\text{p})$ was collected downstream of the denuder onto a quartz fiber filter housed in either a 47 mm single stage Teflon filter pack or our custom 22 mm quartz thermal filter tube (URG Corporation). Field blanks were collected by assembling the denuder sampling trains, placing them in the sampling box for 2 min without the vacuum line attached, disassembling the sampling train, and transporting the denuders for analysis.

Manual Denuder Analysis. Manual denuders were thermally desorbed using a clamshell tube furnace and RGM was quantified as Hg^0 using a Tekran model 2537A vapor-phase mercury analyzer. The 2537A instrument utilizes two parallel gold matrix traps to preconcentrate Hg^0 that is subsequently thermally desorbed into a CVAFS analyzer (31). The 2537A instrument was configured to sample at 1.5 lpm for 5-min integrated samples.

A 2537A was optimized for manual denuder analysis by increasing the sensitivity of the instrument a factor of 2 (~8000 area units pg^{-1}) and incorporating a soda and lime trap into the sampling line. We occasionally observed that following the analysis of a denuder sample the 2537A response would drop up to 50%. We found that the 2537A gold trap collection efficiencies were significantly reduced (passivated) by a compound(s) collected by the denuder. After a number of subsequent thermal desorption cycles in mercury-free air, the gold traps would slowly return to normal. In response, we constructed traps using 12-cm lengths of acid-cleaned 1.27-cm diameter Teflon tubing filled with baked soda and lime (ACS-grade; EM Science, Gibbstown, NJ) held in place with baked quartz wool, similar to those used to protect gold matrix traps from acid gases during mercury analysis of precipitation (32) and particulate samples (33) oxidized using BrCl . The soda and lime traps were fitted with Teflon-reducing unions and installed in the sampling line just prior to the 2537A instrument inlet. The soda and lime traps were replaced on at least a weekly basis to prevent the absorption of Hg^0 that we observed with traps used for extended periods of time.

The manual denuder analysis procedure consisted of three steps and took 30 min. Once the denuder was placed in the tube furnace and the couplers secured, the purge step was initiated as the 2537A instrument pulled mercury-free air through the denuder (10 min). This provided one 2537A sample cycle to purge the ambient air from the denuder and

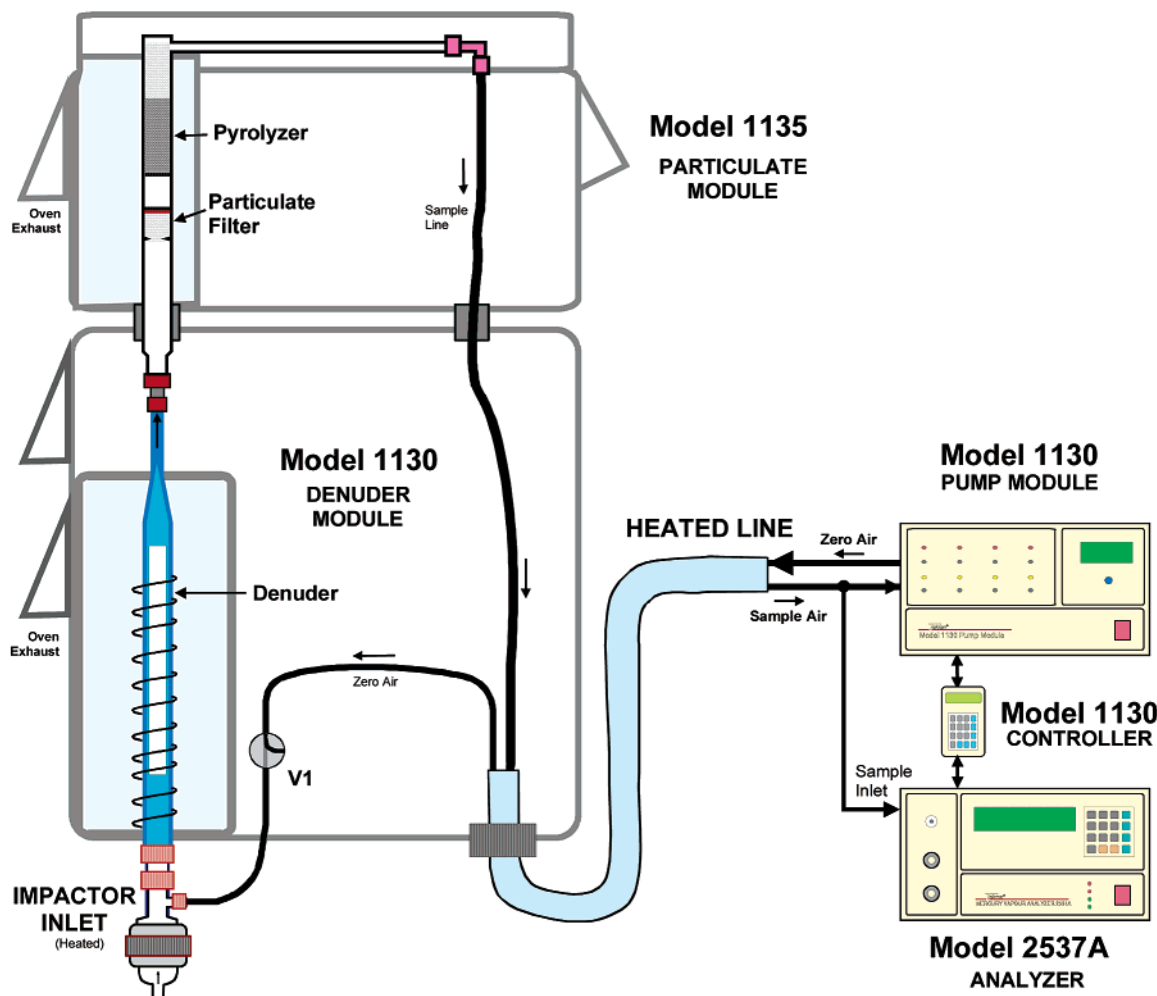


FIGURE 4. Schematic diagram of Tekran automated mercury speciation instrumentation showing the configuration of the model 1130 denuder module and the model 1135 particulate mercury unit.

one sample cycle to quantify the zero or background level to ensure no leaks in the system. The denuder was then rapidly heated to 500 °C for three sample cycles (15 min). Typically, ~90% of the mercury was liberated in the first heat cycle with the remaining 10% observed in the second and third heat cycles. The tube furnace was then turned off, opened, and ambient air from a coaxial cooling fan was directed onto the denuder for one sampling cycle.

We found that it was critical to keep both ends of the denuder relatively cool during the analysis procedure to prevent mercury emission from the coupler assemblies and Teflon sample tubing matrix. Proper seals between the furnace and denuder, coaxial cooling fans directed at the denuder ends, and use of recommended couplers (described previously under denuder coating) provided optimum results. Other types of couplers were tried (including machined solid Teflon) but were found to emit mercury during heating. Overheating the couplers or Teflon sampling line resulted in anomalously high blanks, poor precision, and erroneous data.

Automated Annular Denuder Sampling and Analysis. A fully automated system incorporating the KCl-coated annular denuder methodology was constructed by Tekran Inc. to provide semicontinuous measurements of Hg^0 , RGM, and fine fraction ($<2.5 \mu\text{m}$) $\text{Hg}(\text{p})$. The modularized system incorporated the Hg^0 analytical and data reduction capability of the Tekran 2537A, the Tekran model 1130 speciation unit for the determination of RGM, and the Tekran model 1135 unit for the determination of $\text{Hg}(\text{p})$ (Figure 4). The system was configured to avoid problems with RGM artifact forma-

tion on the $\text{Hg}(\text{p})$ filter by collecting RGM prior to the collection of $\text{Hg}(\text{p})$. The 1130 unit included a heated denuder sampling module, a heated umbilical sampling line, a pump module, and a controller module. The model 1130 controller module seamlessly integrated the analytical capabilities of the 2537A with the 1130/1135 modules. The system allowed the user full control over sample flow rates, sampling duration, desorption temperatures, and analysis timing parameters.

The automated speciation system was typically programmed to collect 1–2 h composite RGM and $\text{Hg}(\text{p})$ samples. During the sampling mode, the system pulled ambient air through the denuder and filter modules at 10 lpm while PID temperature controllers maintained the entire system at 50 °C. RGM was quantitatively collected onto the KCl-coated quartz annular denuder, $\text{Hg}(\text{p})$ was collected onto the quartz filter, and Hg^0 was passed through and was quantified by the 2537A (24 5-min Hg^0 determinations for each 2-h sampling period). The 2537A was configured to pull 1.25 lpm and the 1130 pump module to pull 8.75 lpm. The ambient air pulled through the system for the preconcentration of RGM and $\text{Hg}(\text{p})$ by the 1130 pump module is not needed for Hg^0 analysis and was vented directly to the atmosphere.

Following the 2-h sample period, the 1-h analysis cycle was initiated. The 1130 pump module ceased pulling ambient air and began to pump 6 lpm of zero air, generated using activated carbon traps, into the denuder inlet junction (Figure 1a). The 2537A continued to pull 1.25 lpm, flushing the system

for 15 min (the excess zero air is vented out the denuder inlet). The 1135 unit pyrolyzer oven was preheated to 800 °C for 5 min. The pyrolyzer was filled with quartz chips and was maintained at 800 °C through the analysis cycle to ensure complete decomposition of any mercury compounds eluted during subsequent steps (34). The 1135 filter (800 °C) and 1130 denuder (500 °C) were then sequentially desorbed for 15 min each, and Hg(p) and RGM were quantified as Hg⁰ by the 2537A, respectively. After the heating cycle, the entire system was cooled to 50 °C while being purged with zero air for 10 min before starting another 2-h denuder sampling period. The system was programmed so that the Hg⁰ determinations were reported in units of ng m⁻³ and the purge and heat cycles were reported in units of pg m⁻³. The RGM and Hg(p) concentrations were automatically corrected for the sampling flow rate of both the 2537A and the 1130 pump module. Final concentrations of RGM and Hg(p) were calculated by taking the sum of the three heat cycles for each analyte and subtracting 3 times the last zero air value prior to desorption (if detectable).

High-resolution mercury speciation results of the automated methodology provide the opportunity to explore the dynamic phenomenon that controls atmospheric mercury behavior. Having high-resolution speciated mercury results allowed for the development of a predictive model that incorporates physical and chemical parameters that occur at similar timescales to explain Hg⁰ depletion events observed in Barrow, AK (35). Automated mercury speciation data can also be useful for investigating source receptor relationships, monitoring industrial accidents or spills, and measuring flux.

Calibration of Tekran 2537A Analyzers. The Tekran 2537A CVAFS mercury analyzers used for manual and automated KCl-coated annular denuder method measurements were routinely calibrated using both the instruments internal Hg⁰ permeation tube and manual Hg⁰ injections. Tekran 2537A analyzers were calibrated using their internal permeation tubes on a daily basis during laboratory experiments and manual denuder analysis and on a weekly basis during routine automated analysis. The internal permeation tube (VICI Metronics, Santa Clara, CA) was maintained in an oven at 50 °C and continuously flushed with 30 mL min⁻¹ of ultrahigh purity grade argon to provide stable Hg⁰ output. The permeation rate (~1 pg s⁻¹) was initially calculated using a series of manual Hg⁰ injections and was recalibrated every 6 months. In addition, the perm tube calibrations were challenged on a monthly basis using manual Hg⁰ injected standard additions. If the permeation rate calibration and standard addition were off by more than 5%, then the permeation rate was immediately recalibrated.

Manual Hg⁰ injections were accomplished using a Tekran model 2505 mercury vapor primary calibration unit. Two to three milliliters of triple-distilled instrument-grade liquid elemental mercury (D.F. Goldsmith Chemical & Metal Corporation, Evanston, IL) was introduced into the calibration unit Teflon reservoir and sealed with a Teflon-clad silicone septa. The reservoir was encased in an insulated aluminum block equipped with a microprocessor-controlled thermoelectric cooler capable of maintaining precise temperature. The unit was equipped with two precision temperature sensors: one to monitor the block temperature and one to monitor the reservoir headspace temperature. Known volumes of mercury-saturated air were withdrawn from the reservoir headspace using a digital airtight syringe (Hamilton Company, Reno, NV) and injected into the Tekran 2537A analyzer injection port. The calibration unit reservoir temperature was set below ambient temperature (15 °C) to prevent condensation of mercury in the syringe. The mass of mercury delivered for each injection was calculated from the volume of mercury-saturated air and its vapor density at 15 °C.

Data Analysis. Data processing, descriptive statistics, and linear regression analysis was performed using SAS v.8.02 (SAS Institute, Cary, NC). The assumptions of the parametric procedures were examined using residual plots, skewness and kurtosis coefficients, the Shapiro–Wilk test, and the Brown–Forsythe test. Two-sided tests were used unless otherwise stated. A level of significance of $\alpha = 0.05$ was used for all statistical procedures.

Results and Discussion

Laboratory Evaluation. Automated and manual KCl-coated annular denuder methodologies were first evaluated in the laboratory to investigate the performance characteristics under controlled conditions with respect to accuracy, precision, breakthrough, and bias. To accomplish this evaluation, a custom-designed gas manifold system was constructed capable of delivering known low-level concentrations of both HgCl₂ (40–4000 pg m⁻³) and Hg⁰ (1–20 ng m⁻³) in various gas matrixes. Mercuric chloride was the RGM species chosen for our initial laboratory evaluation because it was determined to be thermodynamically favored in fossil fuel and municipal waste combustion emissions (22). While working with HgCl₂, it became immediately clear that it had a strong tendency to adhere to surfaces (e.g., it was extremely “sticky”). To generate reproducible and known pg m⁻³ concentrations of HgCl₂ in the gas-phase, all components of the glass manifold system were coated with highly cross-linked Teflon (URG Corporation), and the entire manifold was heated to 50 °C (Figure 5).

Several methods for the generation of HgCl₂ were attempted. The use of a capillary diffusion device with HgCl₂ dissolved in dodecane (C₁₂) was not pursued further because it was difficult to precisely control the capillary reservoir at a lower temperature than the heated manifold (necessary for the desired emission rate). A thick-walled (1.6 mm) FEP Teflon permeation tube was also tried but did not generate a sufficient RGM concentration to be measured. The HgCl₂ generation method that we chose because of simplicity, purity, and reproducibility was a thin walled permeation tube. We constructed our permeation tube using ~0.2 g of solid-phase mercury(II) chloride (PURATREM, 99.9995%; Strem Chemicals, Newburyport, MA) inserted into a thin-walled Teflon tubing (0.2 mm wall thickness, 1-cm long, PTFE heat-shrink tubing; Cole-Parmer, Vernon Hills, IL) with solid PTFE Teflon end plugs mounted on a 0.64 cm o.d. Teflon tube. The HgCl₂ source was inserted into a fitting in the sidearm of the manifold only when needed for each experiment to minimize the potential for adsorption of HgCl₂ to the manifold walls. The complete insertion of the HgCl₂ permeation tube into the heated manifold was necessary to prevent temperature gradients or changes. The concentration of the HgCl₂ in the gas stream was determined in real-time using a separate calibrated Tekran 2537A through a continuously heated KCl-coated manual annular denuder (500 °C). This real-time method of calibrating the manifold HgCl₂ concentration was independently confirmed using an integrated collection method on ion-exchange membranes, digestion and CVAFS quantification (15). To assess accuracy, precision and bias, the purity of the HgCl₂ in the manifold gas stream was also confirmed to have undetectable levels of Hg⁰. A constant temperature permeation tube, calibrated against a Tekran 2537A analyzer, generated the source of Hg⁰ introduced to the manifold. When needed, filtered ambient air or ultrapure-grade nitrogen was fed through a 6 cm i.d. × 45 cm cartridge filled with gold-coated glass beads and then a secondary fixed bed of gold-coated sand to remove all mercury compounds prior to introduction to the manifold (Figure 5).

Summarized in Table 1 are the results of several evaluation experiments of the KCl-coated annular denuder methodology. The results from the evaluation confirmed that the KCl-

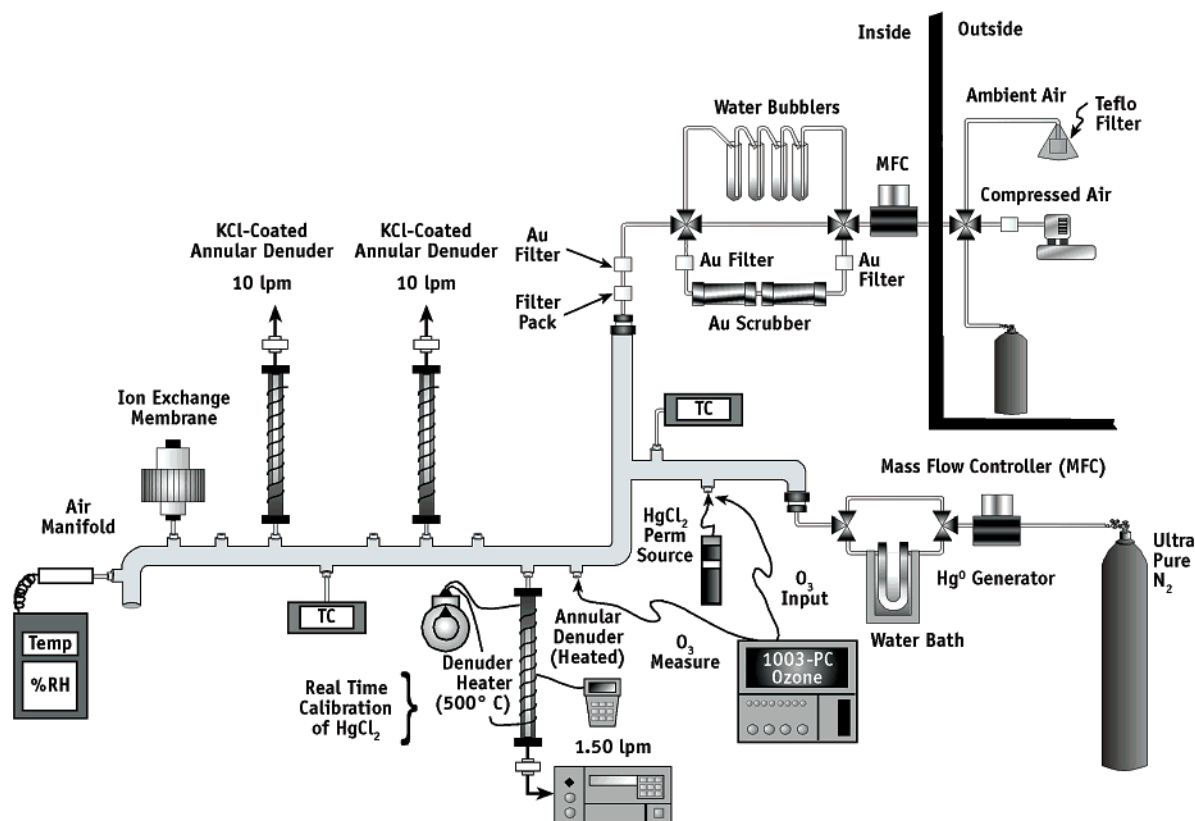


FIGURE 5. Schematic of the custom manifold system used for laboratory investigation of the KCl-coated annular denuder methodology.

TABLE 1. Summary of Laboratory Evaluation Experiments of KCl-Coated Annular Denuder Methodologies^a

experiment description	observations
precision—comparison of 2 Tekran 1130s in ambient air and HgCl ₂ spiked N ₂	(1) ambient air: range of 15–72 pg m ⁻³ $y = 1.16x + 2.1 \text{ pg m}^{-3}$, $r^2 = 0.997$, $n = 7$ (2) spiked HgCl ₂ : range of 0–600 pg m ⁻³ $y = 0.96x - 0.52 \text{ pg m}^{-3}$, $r^2 = 0.996$, $n = 39$
accuracy—comparison of the Tekran 1130 to measure RGM and a manual thermal converter denuder to measure real-time total mercury	HgCl ₂ spiked into N ₂ at 5–1500 pg m ⁻³ $\text{TCD} = 1.01\text{RGM} + 22.6 \text{ pg m}^{-3}$ $r^2 = 0.931$, $n = 17$
capture efficiency—KCl-coated annular denuder with ~1.5 ng m ⁻³ HgCl ₂ spiked ambient air over 24-h sample time period	>97%, $n = 2$
bias—inlet losses with spiked [HgCl ₂] = 1.6 ng m ⁻³	no significant losses

^a The relatively high concentrations of HgCl₂ and Hg⁰ used for the experiments were required to test the worst-case situation (urban air mass) and to ensure that potentially small biases could be detected.

coated annular denuder method was a viable choice and that further field-based method development should be conducted to confirm initial laboratory observations with respect to sensitivity, accuracy, precision, and bias. Also, the laboratory experiments with the KCl-coated annular denuder method clearly indicated its advantages over previous RGM methods.

Field Performance Characteristics. Data used to determine the performance characteristics of the manual and automated KCl-coated annular denuder methodologies described below were collected from February 1999 to April 2001 during six separate EPA field studies. The studies were conducted over a range of extreme conditions from the Florida Everglades in summer to the Arctic in winter and were collected over land, water, and from aircraft. We feel the results presented represent real world worst-case scenarios.

Our first set of experiments was conducted to compare the manual and automated KCl-coated annular denuder

sampling and analysis methodologies. Twenty-one collocated samples were collected in South Florida and Research Triangle Park, NC. A paired *t*-test for independent samples found no significant difference between the manual and automated methods ($p = 0.76$). A linear regression analysis found a significant relationship between the methods ($p < 0.0001$; $r^2 = 0.99$) and a nonsignificant intercept ($p = 0.89$; -0.14 pg m^{-3}). Although the manual and automated methodologies were identical in almost every aspect, it was prudent to establish equivalence.

The method detection limit (MDL) for RGM using the annular denuder methodology was found to be suitable for high-resolution determinations use in even remote areas. The mean \pm standard deviation of our field blanks ($n = 66$) was $2.2 \pm 1.2 \text{ pg}$. Table 2 presents the resulting MDLs (3σ) for sampling durations ranging from 1 to 12 h as $6.2\text{--}0.5 \text{ pg m}^{-3}$, respectively. Table 3 summarizes ambient RGM concentrations we measured at several locations in the United States using the manual denuder methodology. The data

TABLE 2. Method Detection Limits for RGM Using KCl-Coated Annular Denuders for Various Sample Durations

sample duration (h)	sample volume (m ³)	MDL (pg m ⁻³)
1	0.6	6.2
2	1.2	3.1
6	3.6	1.0
12	7.2	0.5

TABLE 3. Summary of RGM Concentrations at Locations in the U.S. Using Manual KCl-Coated Annular Denuders

site	N	mean (pg m ⁻³)	std dev (pg m ⁻³)	min (pg m ⁻³)	max (pg m ⁻³)
Baltimore, MD	30	23	26	5	139
Barrow, AK	46	24	22	1	97
Everglades, FL	45	15	12	3	54
Durham, NC	26	16	12	4	51

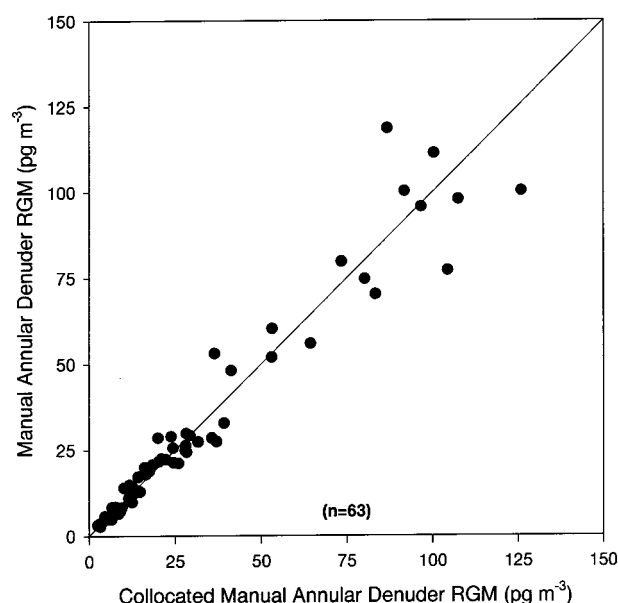


FIGURE 6. Collocated precision of manual denuders with 1:1 line during six EPA field studies (Feb 1999–April 2001).

show that sampling durations between 2 and 3 h were adequate to measure RGM even at the lowest observed concentrations (2–3 pg m⁻³).

The precision of the manual denuder method was determined by the collection of collocated samples ($n = 63$) to be $15.0 \pm 9.3\%$ (Figure 6). The relative precision between pairs of collocated denuder samples was better than that reported for ion-exchange filter packs ($\sim 20\%$; 15) and mist chambers ($\sim 20\%$; 14). The field collection efficiency of the denuders was determined by the collection of samples with two manual denuders in series. The field collection efficiency of the denuders was found to be a function of sampling duration. Samples that were collected for ≤ 5 h ($n = 17$) had an efficiency of 94%, samples that were collected between 5 and 12 h ($n = 15$) had an efficiency of 92%, and samples that were collected between 16 and 24 h ($n = 15$) had an average efficiency of 83%. Figure 7 shows that not all samples > 12 h had significant breakthrough; however, the probability for breakthrough increased. As a result, we do not recommend denuder sampling durations longer than 12 h.

RGM Artifact on Hg(p) Samples. After initial laboratory work demonstrated how “sticky” HgCl₂ was, we became

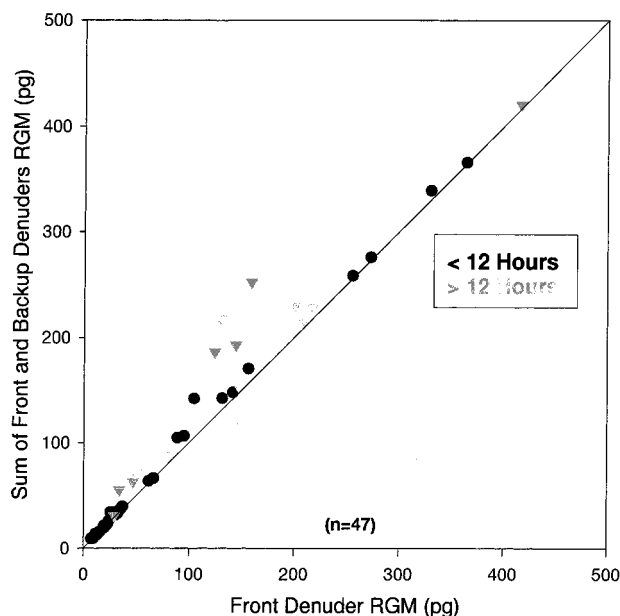


FIGURE 7. Relative RGM breakthrough for sampling durations < 12 h and > 12 h with 1:1 line during six EPA field studies (Feb 1999–April 2001).

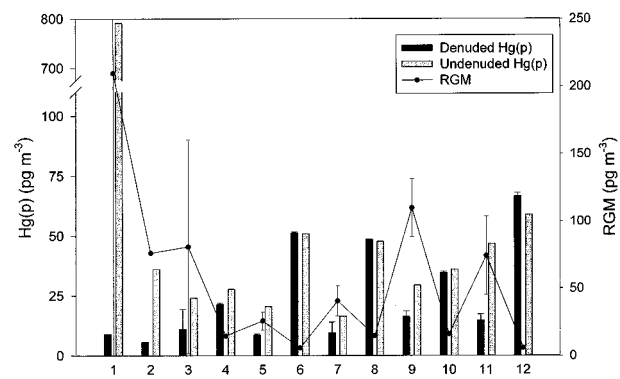


FIGURE 8. Denuded and collocated undenuded Hg(p) filter samples showing RGM artifact (Feb 19–24, 2000); error bars on RGM values denote standard deviation of sequential samples, and error bars on Hg(p) values denote replicate analysis uncertainty.

concerned that conventional filter sampling methodologies for Hg(p) (33, 36) were susceptible to artifact formation from ambient RGM species. We investigated this hypothesis by collecting 12 collocated pairs of 8–12 h integrated fine fraction ($< 2.5 \mu\text{m}$) Hg(p) samples onto 47 mm quartz fiber filters in the vicinity of a known anthropogenic source of RGM. One sample was collected in the conventional manner by pulling ambient air through a Teflon-coated size selective inlet directly onto the filter housed in a single-stage Teflon filter pack (URG). The collocated sample incorporated a KCl-coated annular denuder to remove RGM prior to Hg(p) collection onto the filter (Figure 3). The Hg(p) filters were subsequently analyzed by the University of Michigan Air Quality Laboratory using a nitric acid/microwave extraction procedure followed by CVAAS (33).

We found significant RGM artifact on quartz fiber filter samples collected for Hg(p) determination when KCl-coated annular denuders are not utilized (Kruskal–Wallis test; $p = 0.043$). Figure 8 plots the results of the Hg(p) comparison and the average RGM concentration during each sampling period. Further analysis revealed that whenever the RGM concentration exceeded 15 pg m^{-3} ($n = 8$), we observed significant artifact formation (Kruskal–Wallis test; $p = 0.003$), and that when the RGM concentration was $< 15 \text{ pg m}^{-3}$ (n

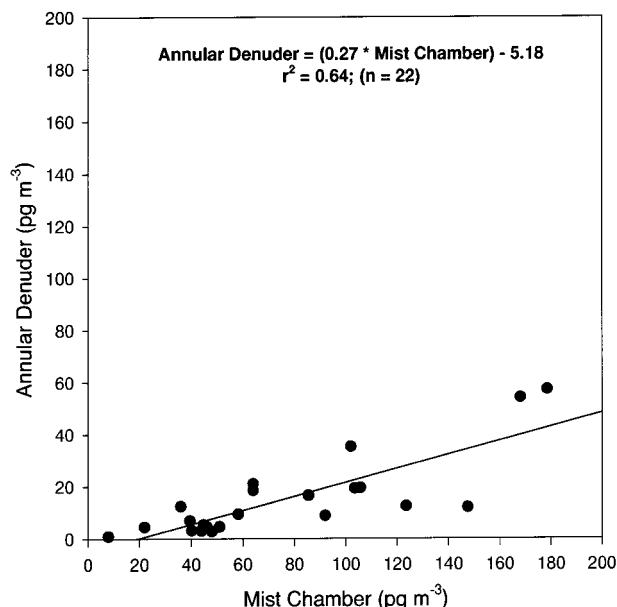


FIGURE 9. Comparison of denuders to refluxing mist chamber for RGM determination in South Florida (Feb 25–28, 1999, and June 21–26, 2000).

= 4), we observed no significant artifact (Kruskal–Wallis test; $p = 0.773$).

We also found that the artifact was not quantitative and could therefore not be subtracted or corrected. We did find some anecdotal evidence that suggests that the highest artifact formation was observed when higher RGM concentrations occurred near the end of the Hg(p) sampling period, suggesting that RGM may bleed off as additional lower concentration RGM air is pulled through the filter. During the daytime Hg(p) sampling periods (odd numbered observations in Figure 7), we stopped both Hg(p) samples to change the annular denuder every 2–4 h. As a result, each Hg(p) sampling period had 3–4 associated RGM sampling periods. The RGM concentration during Hg(p) sampling period 1 (210 pg m^{-3}) was the average of three sequential measurements (18, 26, and 662 pg m^{-3}). The resulting RGM artifact for sampling period 1 (undenuded Hg(p) – denuded Hg(p)) was extremely large, 782 pg m^{-3} . Conversely, the RGM concentration during sampling period 9 (110 pg m^{-3}) was the average of four sequential measurements of 107, 126, 131, and 84 pg m^{-3} , and the resulting artifact was only 13 pg m^{-3} . It should also be noted that sampling period 1 was the only sample where the total artifact was larger than the average RGM concentration, suggesting that the combination of RGM and Hg⁰ (that averaged 25.2 ng m^{-3} and got as high as 143 ng m^{-3} during the period) may have also contributed to the observed artifact.

Comparison of the Annular Denuder and Mist Chamber Methodologies. During two studies conducted in Southeast Florida (February 25–28, 1999, and June 21–26, 2000) we had the opportunity to run our annular denuders collocated with mist chambers run by researchers from Oak Ridge National Laboratory. Unlike results that were previously reported (37), our comparison found the mist chamber provided significantly higher RGM concentrations than the annular denuder ($p < 0.0001$; Figure 9). In fact, the mist chamber RGM results were, on average, a factor of 6.5 times higher. Additional research needs to be conducted to fully understand the observed difference between the annular denuder and mist chamber methodologies for RGM. Inter-comparison studies between the mist chamber and denuder methods are currently underway at ORNL and will be reported soon (38). The mist chamber methodology may have been

susceptible to positive artifact formation from (i) Hg(p) entrainment and (ii) aqueous oxidation of Hg⁰ to RGM in the HCl and NaCl scrubbing solution (14).

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