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APPENDIX V

Mercury Capture by Aerosol Transformation in Combustion Environments

MASTER

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INTRODUCTION

Mercury emissions from combustion sources have been a great concern^{1,2}. Unlike most other heavy metals that are emitted in particulate form, mercury has been reported to be released mainly in the elemental vapor phase³⁻⁶. Vapor phase elemental mercury is not effectively captured in typical air pollution control devices. Once emitted, mercury undergoes various biological processes in the atmosphere to form even more toxic organic mercury species such as methyl mercury^{5,7}. Due to its high toxicity, even trace amount of mercury poses severe adverse health effects and stringent regulation has been set for mercury emission^{8,9}.

To improve mercury capture, studies have been conducted to understand the behavior of mercury in combustion environments. In coal combustion, mercury is reported to be released primarily in elemental form in most cases^{2-4,9,10}. In waste incineration, a fraction of mercury is captured in gas washing devices such as scrubbers. It is proposed that chlorine in the waste reacts with mercury to form soluble mercury chloride^{1,6,11}. Thermodynamic equilibrium predictions also show the same trend^{12,13}. Fundamental reactions at high temperatures have also been investigated. It has been reported that the reaction with air is not important⁹. Oxidation is reported only with strong oxidants such as NO₂, HCl, Cl₂ or O₂ with activated carbon^{9,11,14}. Consequently, unless the gas stream contains these materials, mercury will remain in elemental form in the vapor phase. Research has been conducted in order to find new pathways to remove mercury from the gas stream. Sorbent materials are the ones that are studied most and sulfur impregnated activated carbon is found to be the most effective^{4,8,10,11,16}. However, the use of activated carbon is limited due to its low applicable temperature range, regeneration and slow adsorption rate.

While most current efforts are focused on the use of sorbent materials, it is possible to mechanically remove mercury from the gas stream by typical particulate control devices. The key is to transform mercury into the species that form particles, i.e., species with a lower saturation vapor pressure. Compared with mercury, mercury oxide has a lower vapor pressure which indicates a higher possibility of particle formation. Although it was reported that oxidation in the air was not important for mercury as discussed earlier⁹, certain literature reported that oxidation by oxygen occurred in the temperature range of 350 to 450 °C¹⁷. Below 350 °C, the rate is too slow. Above 450 °C, mercury oxide decomposes to release elemental mercury and oxygen. In addition, the residence time might be too short that oxidation in the air was not observed in previous studies. The objective of this study, therefore, is to investigate mercury oxidation in combustion environments by varying temperature and residence time, and to study the effect on the resultant particle size distribution.

EXPERIMENT

Apparatus and Materials

A flow reactor with real-time measurement of particle size distribution and composition analysis is used to study mercury oxidation and subsequent particle formation and growth in high temperature environments. Figure 1 shows the schematic of the experimental system. The alumina reactor tube (Coors Ceramic Company) is 91.44 cm long with an inner diameter of 2.54 cm. Compressed air is used as the carrier gas and is passed through HEPA filter (Balston Filter Products) to assure it is particle free. Mercury vapor is introduced into the system by passing air above liquid mercury contained in a gas washing bottle. The gas washing bottle is wrapped by a heating tape (Silicon Rubber, 4'×1/2", Thermolyne) and the temperature is controlled by adjusting the controller (Type 45500, Thermolyne). Another heating tape (Silicon Rubber, 8'×1/2", Thermolyne) is used for the Teflon tubing (from the exit

of the bottle to the entrance of the furnace) to minimize mercury condensation. The mercury vapor then undergoes reaction at an appropriate temperature range in the reactor. At the exit of the furnace, a well characterized cooling rate results in the possibility of particle formation. A glass fiber filter with Teflon coating (Type T60A20, Pallflex Products Corp.) is used downstream to collect particles for composition analyses. The gas stream is then passed through a series of sampling impingers to capture mercury species in vapor phase. The first sampling impinger that contains 0.1M HCl solution is used to determine the amount of soluble mercury species (i.e. HgO). The last three impingers that contain 4% KMnO₄ in 10% H₂SO₄ are used to determine the amount of elemental mercury²⁰. A tube with a 0.625 cm inner diameter and 130 cm in length is connected to the system after the tube exit to direct the sample particles to a Scanning Mobility Particle Sizer (Model 3934 SMPS, TSI Inc.) for real-time size distribution measurements.

Procedures and Measurement

Two sets of experiments were conducted. In Set 1, temperature was varied to determine the appropriate temperature range for oxidation in the air. The experimental conditions for this set are listed in Table 1. In Set 2, the flow rate was varied to study the effect of residence time. The experimental conditions for Set 2 are listed in Table 2. The mercury feed rate is determined by Cold Vapor Atomic Absorption Spectroscopy (CVAA). SMPS is used to measure the aerosol size distribution at the exit of the reactor which provides information on the mean particle size, number concentration, volume concentration and standard deviation. Measurements were made until the system had stabilized, and at least three measurements were averaged for each run. The particles collected on the filter were analyzed by X-ray diffraction (Siemens D5000) for composition. To determine the partition of mercury and mercury oxide in different phases, the filter was weighed and the concentration of the impinger solution was analyzed by CVAA.

RESULTS AND DISCUSSIONS

Temperature was varied from 410 °C to 1200 °C in Set 1 to investigate the appropriate temperature range for oxidation in the air. The residence times in the targeted temperature zone varied from 1.5 s (1200 °C) to 3.2 s (410 °C), which are similar to the residence time in previous study (1.5 s)⁹. No significant particle size distributions different from the background air were detected after the system had stabilized. Apparently, mercury oxidation did not occur at the temperature range studied in the given residence time. The result confirms the findings by previous studies⁹. However, an interesting feature was observed along the way of heating to the targeted temperature. The SMPS measurements showed significant amounts of particles when the furnace temperature reached 650 °C, and particle concentrations increased as the temperature increased during the heating process. Some typical particle size measurements under such circumstances are shown in Figure 2. The measured particle size distributions look similar to those of heavy metal species from combustion environments^{18,19}. That is, particles are formed by nucleation from vapor phase and then grow to the submicron range by condensation and coagulation. The particles collected on the filter were light yellow indicating that they were possibly HgO though not enough particles were collected for analysis by X-ray diffraction. However, no particles were observed after a certain period of time. As these particles were not observed during the heating process and only after the furnace temperature has reached 650 °C, these particles probably result from the vaporization of HgO that deposits on the alumina tube. The HgO is not directly formed by oxidation in the gas phase because no particles can be detected when the system has stabilized. Rather, the HgO is formed by the Hg that deposits on the alumina tube when the furnace temperature is still low but undergoes oxidation on the alumina tube during the heating process. Consequently, the

maximum time for mercury oxidation is the time needed to heat the furnace to the temperature at which particles begin to appear, which is approximately 90 minutes. However, 90 minutes is too long for to be practical in real combustion environments.

In Set 2, the residence time was increased by reducing the feed flow rate. The resultant residence times varied from 30.6 s (615 °C) to 45.8 s (320 °C), one order longer than those in Set 1. To assure that the particles are not from evaporation of mercury species from the wall of the tube, the alumina tube was heated to a higher temperature before each run. The measured mass flow rate of mercury species and their partitions are listed in Table 3. Figure 3 shows the measured particle size distributions at different temperatures. As shown in Figure 3, only minor amounts of particles were detected indicating that oxidation followed by aerosol formation was not important. If we compare the total particle volume concentration with the feed concentration, it is found that only less than 0.1% of the feed has been transformed into the aerosol phase. That oxidation is not important is further evidenced by the partition of Hg and Hg²⁺ (Table 3). Hg²⁺ is less than 4% of the total mercury and is even lesser for lower temperatures. Therefore, although oxidation is observed when the residence time is increased, the experimental results show that the oxidation rate is too slow and that capture of mercury by aerosol transformation resulting from oxidation is not feasible in practical systems.

As oxidation of mercury can not be the main mechanism to capture mercury vapor, alternative approaches have to be developed. One such approach is the use of sorbent materials as indicated earlier. Sorbent materials such as silica have been shown to be effective for certain toxic heavy metals, such as lead at high temperatures²¹. In a recent study, innovative vapor phase sorbent was shown to possess even greater capability for condensation of toxic metal vapors²². Currently, the use of vapor phase sorbents for mercury capture is being investigated.

CONCLUSIONS

Aerosol transformation of elemental mercury by oxidizing mercury in the air is investigated in this study by varying temperature and residence time. The experimental results show that mercury oxidation is not important at the temperature range and time scale studied. The rate of mercury oxidation is too slow that the capture of mercury vapor by transforming it into mercury oxide in aerosol phase is not practical in real systems. Studies are needed for alternative approaches to capture mercury vapor such as the use of sorbent materials.

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Table 1. Summary of the experimental conditions of Set 1

Furnace temp (°C)	Gas washing bottle temp (°C)	Flow rate @ 25 °C (lpm)
410, 430, 450, 480, 530, 580, 630, 660, 710, 730, 750, 780, 870, 1000, 1075, 1200	97	1.232

Table 2. Summary of the experimental conditions of Set 2

Exp #	Furnace temp (°C)	Gas washing bottle temp (°C)	Feed flow rate (lpm)	Dilution air flow rate (lpm)
1	615			
2	520			
3	425	97	0.1	2.0
4	320			

Table 3. Outlet mass flow rate of Hg species of Set 2

Exp #	rate (µg/min)		% of total	
	Hg	Hg ²⁺	Hg	Hg ²⁺
1	1.807	0.078	95.9	4.1
2	12.165	0.529	95.8	4.2
3	2.654	0.011	99.6	0.4
4	55.26	0.11	99.8	0.2

Inlet feed rate is 68.28 µg/min

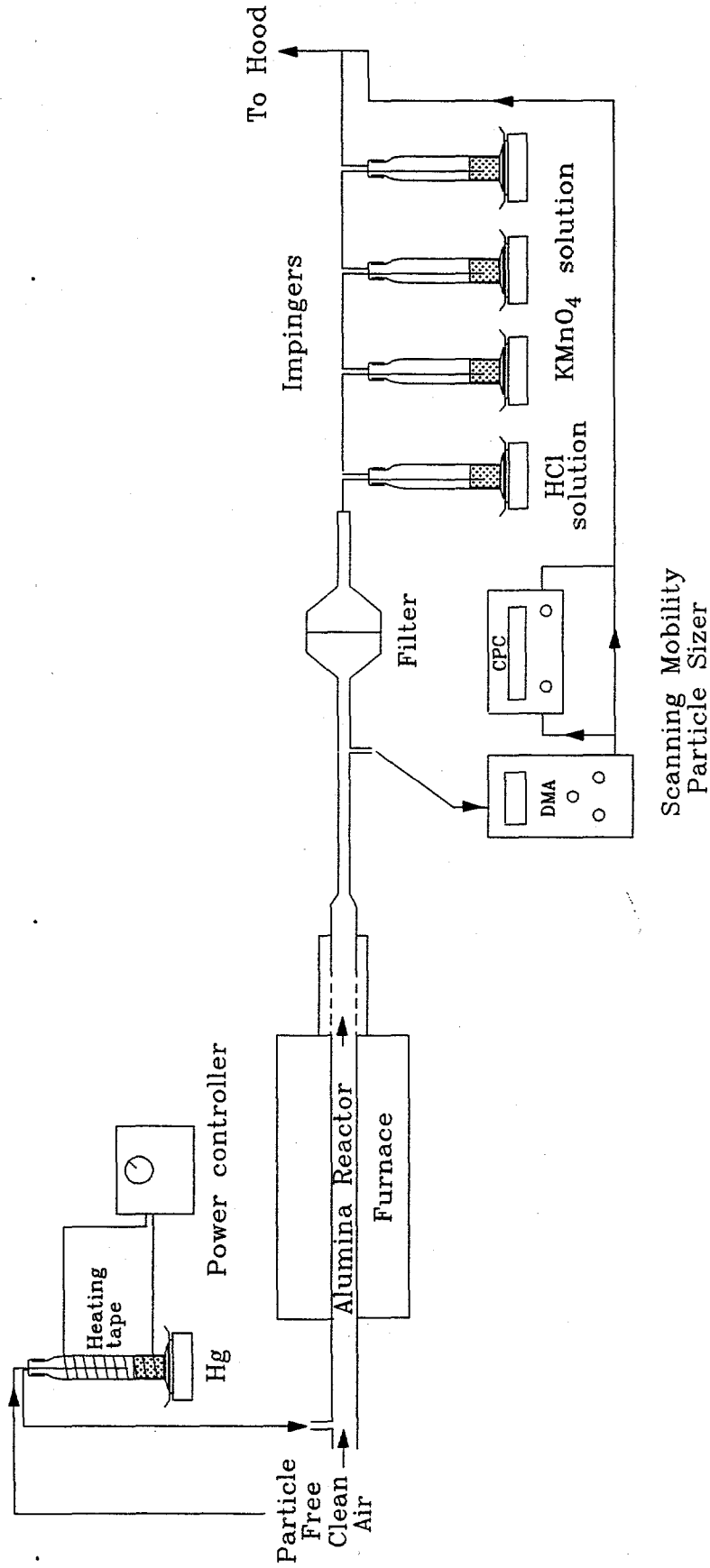


Figure 1. Schematic diagram of the experimental setup for understanding mercury transformation in high temperature environments

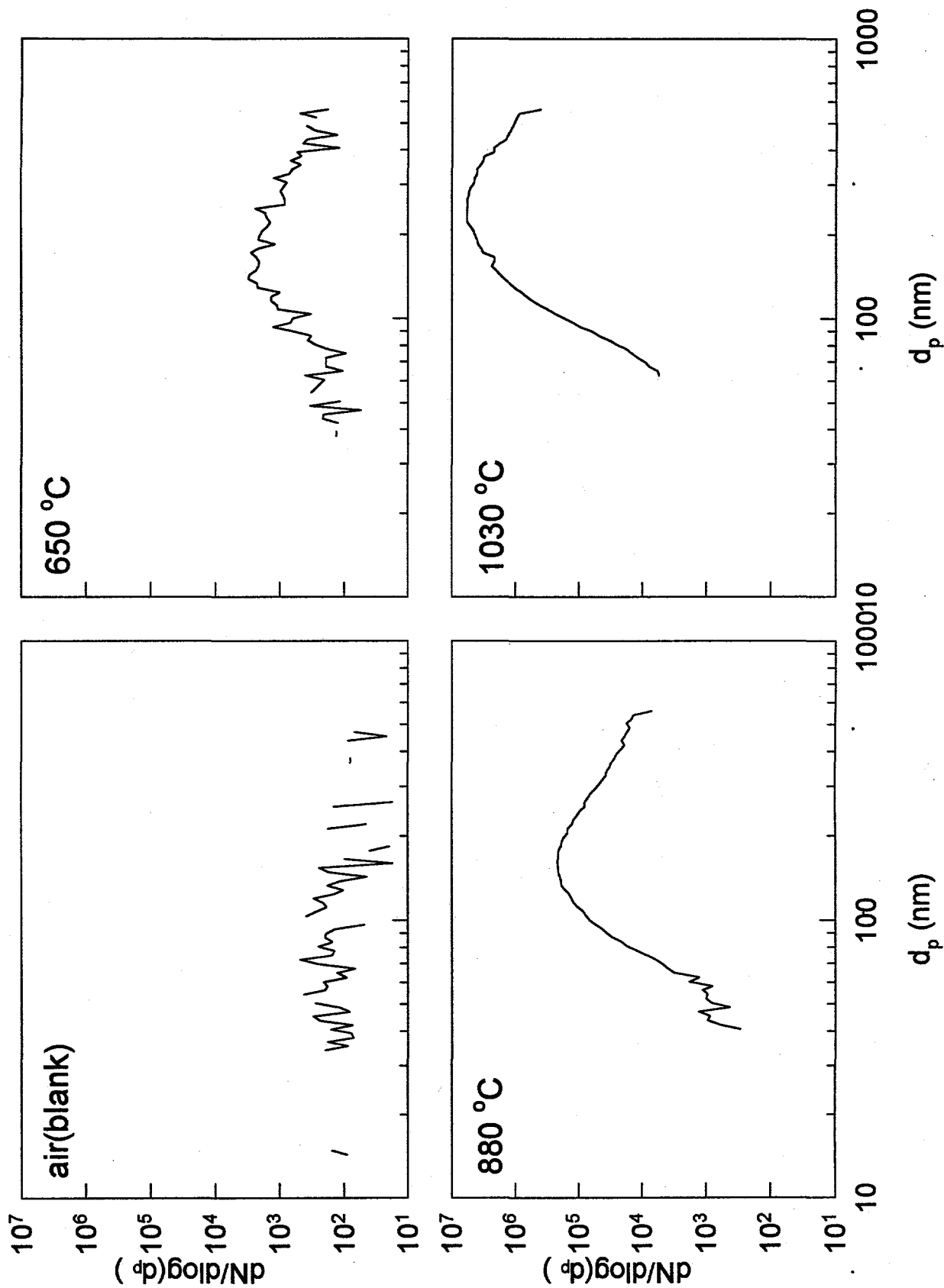


Figure 2. Measured particle size distributions of mercury species during the heating process

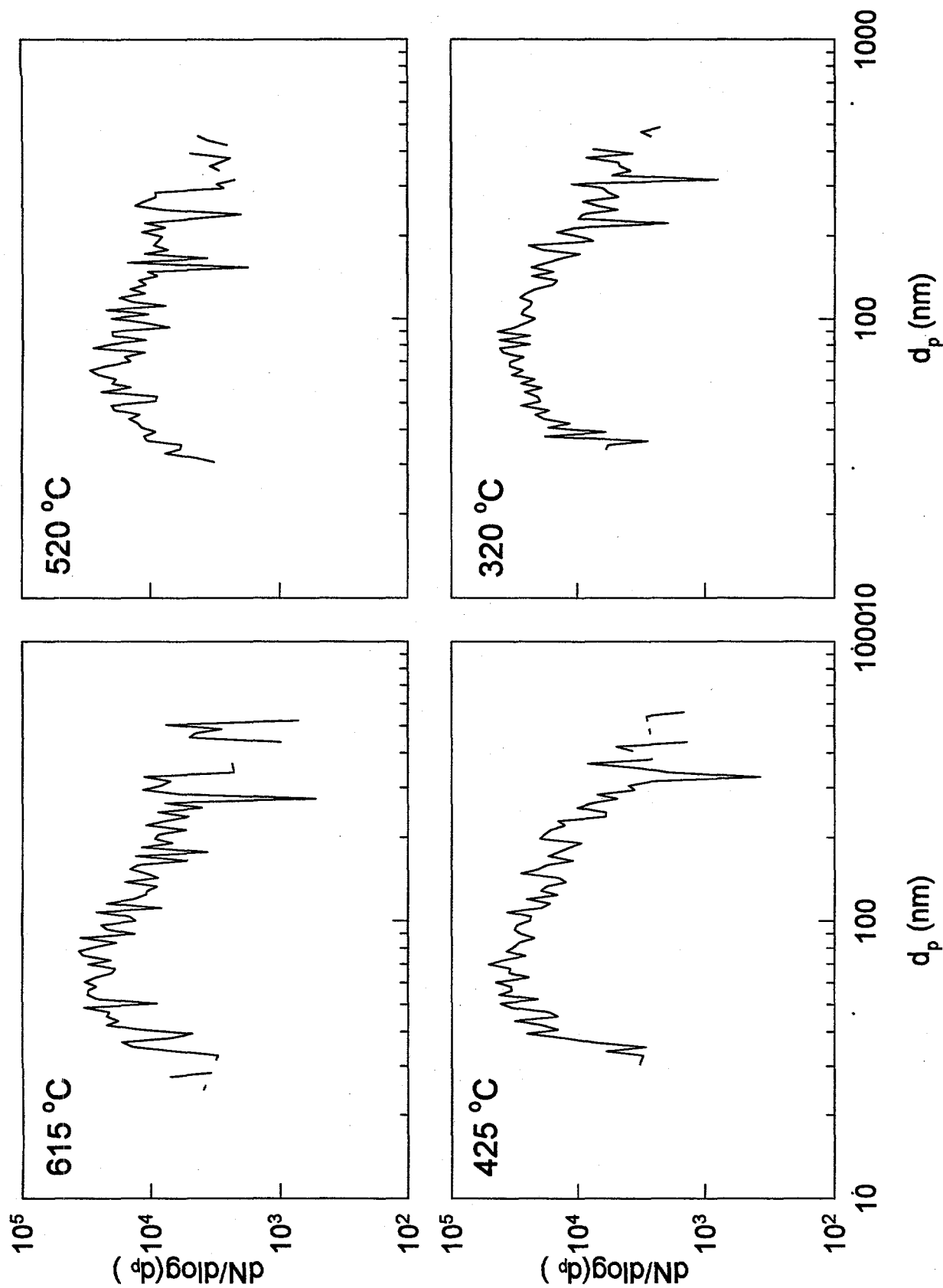


Figure 3. Measured particle size distributions of mercury species at different temperatures for long residence times