

Paper Number:

DOE/PC/92583-98/C0949

Title:

Optimization of Sampling Conditions to Minimize the Adverse Effect of Sulfur Dioxide on the Ability of the Ontario-Hydro Method to Accurately Distinguish the Chemical Forms of Mercury in Coal Flue Gas

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Contract Number:

DE-AC22-93-PC92583

Conference:

Advanced Coal-Based Power and Environmental Systems '97 Conference

Conference Location:

Pittsburgh, Pennsylvania

Conference Dates:

July 22 - 24, 1997

Conference Sponsor:

Federal Energy Technology Center - Morgantown and Pittsburgh

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**Optimization of Sampling Conditions to Minimize the
Adverse Effect of Sulfur Dioxide on the Ability of the
Ontario-Hydro Method to Accurately Distinguish the
Chemical Forms of Mercury in Coal Flue Gas**

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Background

As a consequence of findings from the Phase I Emissions Studies, the U. S. Department of Energy's Federal Energy Technology Center (DOE-FETC) has focused its efforts on identifying a sampling and analytical method to differentiate and quantify the chemical forms of mercury emitted from coal-fired electric utility boilers. DOE-FETC requested ATS to develop new methodologies for determining the chemical species of mercury in coal flue gas, either by the modification of existing ones or by the introduction of novel methods with the final validation of acceptable methods. Candidate methods must be robust enough to perform effectively in the presence of flue gas components such as SO₂, NO_x, HCl and fly ash. Under contract to DOE-FETC, ATS has performed both laboratory evaluations and pilot-scale studies of these methods.^{1,2,3,4}

Introduction

The goal of the work presented in this paper was the identification and quantification of various chemical forms of mercury in coal flue gas. To this end, bench-scale evaluations were carried out on the Ontario-Hydro Method to determine its capability to selectively isolate and retain various mercury species captured from flue gas streams containing moderate to high levels of sulfur dioxide (SO₂). Loss of mercury from the oxidized mercury capture solutions through chemical reduction by sulfur dioxide has been documented previously from both bench- and pilot-scale studies. Results from recent studies, giving further verification of this phenomenon with emphasis on optimization of sampling conditions to minimize this impediment to effective mercury speciation, are presented.

All speciation methods utilizing impinger trains were configured in a similar manner. The impingers immediately down-stream of the heated sampling probe and filter box contained solutions intended to capture oxidized (ionic) mercury while impingers further down-stream of these contained acidic potassium permanganate (KMnO₄). These latter solutions, having been shown by the EPA in their Method 101A validation studies to capture all forms of mercury, were utilized here to capture the remaining elemental mercury. The challenge was to develop, test and validate an oxidized mercury capture solution that would effectively capture and retain all of the oxidized mercury species while allowing 100% of the elemental mercury to pass through it and be captured down-stream in the KMnO₄ impinger solutions. A schematic of the impinger train utilized in the Ontario-Hydro Method is shown in Figure 1. For oxidized mercury capture, this method utilizes a 1.0 molar potassium chloride (KCl) impinger solution, which we have shown to be effective in its ability to retain mercuric chloride solution spikes given the appropriate sampling conditions.

ATS's approach to these method development studies has been to first test the existing methods under ideal laboratory conditions, with the philosophy that if the methods cannot perform as designed under ideal laboratory conditions, there is little chance that they would produce desired

performance results at plant site environments. In a similar spirit, ATS has pioneered “retention” studies. Since all potential speciation methods must meet three criteria: isolation, capture and retention of the distinct chemical forms of mercury, solutions that fail in laboratory tests to retain the solution spikes of mercury during the sampling of laboratory air cannot be expected to meet this criterion let alone the other two under the more severe field conditions. Moreover, selective capture of mercury is a meaningless consideration if retention ability cannot be confirmed.

The first step in evaluating the efficacy of oxidized or elemental mercury capture solutions of proposed mercury speciation trains is spiking the impinger containing the particular mercury species capture solution with a known amount of aqueous mercuric chloride. Sampling is then performed by drawing laboratory air with or without added flue gas components through a heated probe and filter box into the impinger train. If, and only if, the mercuric chloride spiked into the mercury capture solutions remained there during the course of the test, further testing of the solution’s ability to capture vapor phase mercury species capture studies is indicated.

In the initial stages of its mercury method developmental work, ATS has shown that the acidified permanganate (KMnO_4) solutions used in EPA Method 101A do indeed retain (100%) of the mercuric chloride spikes during the sampling of laboratory air.¹ (This is consistent with EPA’s determination that these solutions effectively capture all mercury species.) Furthermore, ATS was the first laboratory to report results from studies utilizing EPA Method 29 as a speciation method that showed varying degrees of migration of low level mercuric chloride spikes ($3.0 \mu\text{g}$) from the oxidized mercury capture solution (acidified hydrogen peroxide) to the acidified potassium permanganate.^{1,2,3} (A $3.0 \mu\text{g}$ solution spike corresponds to $1.0 \mu\text{g}/\text{Nm}^3$ flue gas concentration based on a total gas sample volume of $\sim 3 \text{ m}^3$.) Furthermore, additional evidence that EPA Method 29 would not speciate chemical forms of mercury came when Maskew and workers⁵ reported an almost even distribution of mercury between the peroxide and permanganate impingers for sampling performed at a pilot plant in which the flue gas was spiked with HgCl_2 . As a consequence of ATS's findings, DOE-FETC requested a "round robin" testing in which ATS and the 3 other laboratories (Research Triangle Institute, RTI; the University of North Dakota's Energy and Environmental Research Center, UNDEERC; and Radian Corporation) performed bench-scale air sampling tests using EPA Method 29 and following ATS's sampling and analytical protocol. The results from these tests varied widely among the 4 laboratories.² This inter-laboratory discrepancy with respect to the Method 29 results was resolved upon DOE-FETC’s request that ATS and UNDEERC perform identical, side-by-side, laboratory-scale experiments to determine the reasons for the conflicting results.³ These results indicated that ATS’s observations were correct and, ironically, occurred because their equipment and sampling conditions were more appropriate to actual field work than those employed by UNDEERC.

While these results demonstrated that EPA Method 29 may underestimate the oxidized mercury in flue gas, Laudal et. al.,⁶ in a review article sponsored by DOE and prepared for the Electric Power Research Institute, gave compelling evidence that the oxidized mercury capture solution (acidified hydrogen peroxide) may collect some fraction of the elemental mercury present in the flue gas thereby overestimating the oxidized mercury present.

Recently, DOE has recommended that ATS focus research on the more promising Ontario-Hydro Method. Initial results from studies carried out by ATS have shown that the potassium chloride (KCl) impinger solutions of Ontario-Hydro trains are capable of retaining mercury, added as mercuric chloride solution spikes, during the sampling of laboratory air^{1,2}. Results from recent studies,⁴ however, demonstrate a loss of mercury from the KCl impinger solutions and its subsequent recapture by the permanganate solutions if sulfur dioxide is present in the sampled air. These results and follow up studies on efforts to minimize this effect are presented in this paper.

Experimental

Reagents and Equipment

Every effort was made to avoid mercury contamination of the sampling and analytical systems. Chemicals used in this work were of analytical reagent grade quality with certified maximum mercury content. Deionized water and trace metal grade acids were used in preparing solutions. Glassware was cleaned following a lengthy procedure, developed by ATS, which included acid soaking and extensive rinsing to insure removal of mercury from impinger surfaces.

Standard solutions were prepared using class A volumetric glassware. Impinger contents were determined gravimetrically. An automatic pipette with certified precision and accuracy was used to spike mercury standard solutions into the desired impingers. Air sampling was performed using Nutech 2010 Stack Samplers. Mercury analyses were performed utilizing a Bacharach Model MAS-50B CVAAS Mercury Analyzer System. The mercury analyzer has a lower detection limit of 0.01 µg. Detection limits for individual and combined impinger solutions ranged from 0.01 to 0.30 µg depending upon sample dilution, as prescribed in the sampling train cleanup procedure, and the size of the aliquot taken for analysis required to carry out the analytical procedure.

Procedures

Whenever possible, EPA sampling and analytical protocol was followed exactly as stated for both the bench-scale tests and pilot-scale tests previously carried out. A full-size (6 ft) heated probe, followed by a quartz-fiber filter within a heated filter chamber (250⁰ F), was used in all experiments. In all the sampling runs performed in the laboratory, a total volume of 3.06 cubic meters of ambient laboratory air was collected over a period of approximately 3 hours unless otherwise specified. Filter weights, and the weights and volumes of the impingers and their contents were recorded before and after each sampling run. Likewise, the entire sampling train was leak checked before and after each run. In addition, temperatures and vacuum pressures were monitored and recorded every 30 minutes.

Upon completion of each sampling run, the train was disassembled, and the filter and impinger solutions were recovered following the appropriate EPA or other methodology. The impinger solutions were analyzed for mercury as described in EPA SW 846 Method 7470. Briefly, the

performance of this method involved reducing the mercury collected (in the mercuric form) to elemental mercury, which was then aerated and driven from the solution into an optical cell and measured by atomic absorption spectrophotometry. A five point curve was constructed in calibrating the instrument. Moreover, all procedures in the ATS Quality Assurance/Quality Control (QA/QC) Plan were followed during all sampling evaluation testing and during subsequent chemical analysis.

Experimental Plan

Laboratory-scale experiments were performed to determine the effect of sulfur dioxide on the ability of the Ontario-Hydro Method potassium chloride (KCl) impinger solutions to retain mercuric chloride spikes during train operation. Gas phase spiking of SO₂ into the laboratory air being sampled was achieved by passing controlled volumes of certified concentrations of SO₂ in N₂ directly into the sampling probe during testing. Tests were performed by adding either 15.0 or 25.0 µg of mercury as mercuric chloride to the first of the three impingers containing the KCl solution. (The mercury spike concentrations were based on expected concentrations of mercury in coal flue gas.) Then, the sampling train was assembled, leak-checked and laboratory air spiked with either 0, 1500 or 2200 ppmv of SO₂ was drawn through the sampling train. After sampling, the train was again leak-checked and the impinger solutions were recovered using the most currently accepted method.⁷ In this procedure, potassium permanganate replaces the previously used potassium dichromate in the treatment of the KCl solutions because the ensuing, more rapid chemical reaction insures that upon the development of the characteristic permanganate pink-purple color, all of the SO₂ has been consumed. Also, permanganate impinger solution treatment differs from the EPA Method 29 recovery procedure in that hydroxylamine hydrochloride is added directly to the impinger. This step eliminates the need to filter and treat large amounts of the brown manganese dioxide precipitate, which typically entrains most of the captured mercury. Thus, the KCl impinger solutions were treated immediately with a minimal amount of acidified KMnO₄ until a pink-purple color developed. The permanganate impinger solutions were first, treated with hydroxylamine hydrochloride to dissolve the manganese dioxide precipitate and to remove any permanganate remaining. Secondly, they were treated with a minimal amount of KMnO₄ to maintain an oxidizing solution and thereby prevent loss of mercury by its possible conversion to the less soluble and more volatile elemental form. Both KCl and permanganate impingers were rinsed with 8.0 N HCl to dissolve any brown deposits of manganese dioxide if they were evident.

Results and Discussion

Shown in Figure 2 is a bar graph with each bar representing the percentage of the of the mercuric chloride spiked into the first KCl impinger solution that remained after the completion of the experiment. In these experiments, 15 µg of mercury as mercuric chloride was chosen as the spike size, and the train was operated for a sampling time of 3 hours and at a sampling flow rate of 0.6

ft³/hr. In the first 3 experiments (left), no SO₂ was added to the sampled air; in the last 4 experiments (right), enough SO₂ was added to produce a concentration of 1500 ppm. The results were definitive with approximately 99±1% retention of the mercury spike when no SO₂ was added to the laboratory air and ~ 90 ±1 % in the case where the concentration of SO₂ was 1500 ppm in the air.

In order to investigate the effect of sampling flow rate and sampling time on mercury spike retention, experiments were performed in which these conditions were varied. Furthermore, a decision was made to increase the mercury spike from 15 to 25 µg since this would be more representative of a mid-range mercury containing coal. The results of these experiments are presented in Figure 3. A trend was apparent with percent retention decreasing as sample time varies from 1 to 3 hours and with percent retention increasing as sampling flow rate was decreased from 0.6 to 0.3 ft³/ hr.

To determine the effect of increased SO₂ concentration, experiments were carried out with 2200 ppm in the sampled air. All 8 trains sampled for 3 hours, 5 at the higher and 3 at the lower sampling flow rate. These results are shown in Figure 4. Clearly the effect of sampling flow rate shown here is consistent with that shown in the previous figure; however, no definitive effect from the increased SO₂ concentration is apparent from the data.

Concern over the effect of sulfur trioxide (SO₃) in the flue gas prompted a final series of experiments in which sulfuric acid (H₂SO₄) was added to the KCl impinger solution containing the mercury spike. The amount of H₂SO₄ added corresponded to the amount of SO₃ that would have been absorbed based on the assumption that SO₃ is always present with SO₂ and is found at approximately 1% of its concentration. Sampling flow rate and time were varied in these experiments. Shown in Figure 5 are the results. Again, the effect of varying sampling flow rate and sampling time shown here is consistent with that shown in Figure 3; however, no definitive effect from the presence of the H₂SO₄ is apparent from the data.

Conclusions

This laboratory-scale study has lead to the following specific conclusions:

- The presence of SO₂ in the sampled air reduces mercury spike retention.
- Reducing sampling time increases mercury spike retention.
- Reducing sampling flow rate increases mercury spike retention.
- Increasing SO₂ concentration from 1500 to 2200 ppm has little effect on mercury spike retention.

- The presence of H₂SO₄ in impinger solutions to simulate SO₃ in the flue gas has no apparent effect on mercury spike retention.

These conclusions provide the basis for optimizing sampling conditions to minimize the effect of SO₂ on the operation of Ontario-Hydro Method sampling trains thus making continued work toward final validation of the methodology now possible.

In general, experimental studies conducted by ATS on methods proposed for differentiating and quantifying the various chemical forms of mercury emitted from coal-fired boilers have given insight into the physical and chemical processes taking place within the various sampling systems and will lead to the validation of a reliable and robust mercury speciation technique.

Future Work

These findings demand further developmental studies for final validation of the Ontario-Hydro Method. Effective retention of oxidized mercury by the KCl impinger solutions has been demonstrated. The next step is to carry out studies to determine the ability of the method to selectively capture vapor phase mercury species. Further testing and optimization of the Ontario-Hydro Method will be carried out by ATS and UNDEERC personnel.

Acknowledgments

ATS wishes to acknowledge DOE Grant No. DE-AC22-93PC92583 which provided funding for this project. ATS also wishes to acknowledge Mr. Tom Brown and Mr. Rich Hargis of FETC; Mr. Dennis Laudal of UNDEERC and Mr. Keith Curtis of Ontario Hydro Technologies for their helpful input.

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Figure 1:

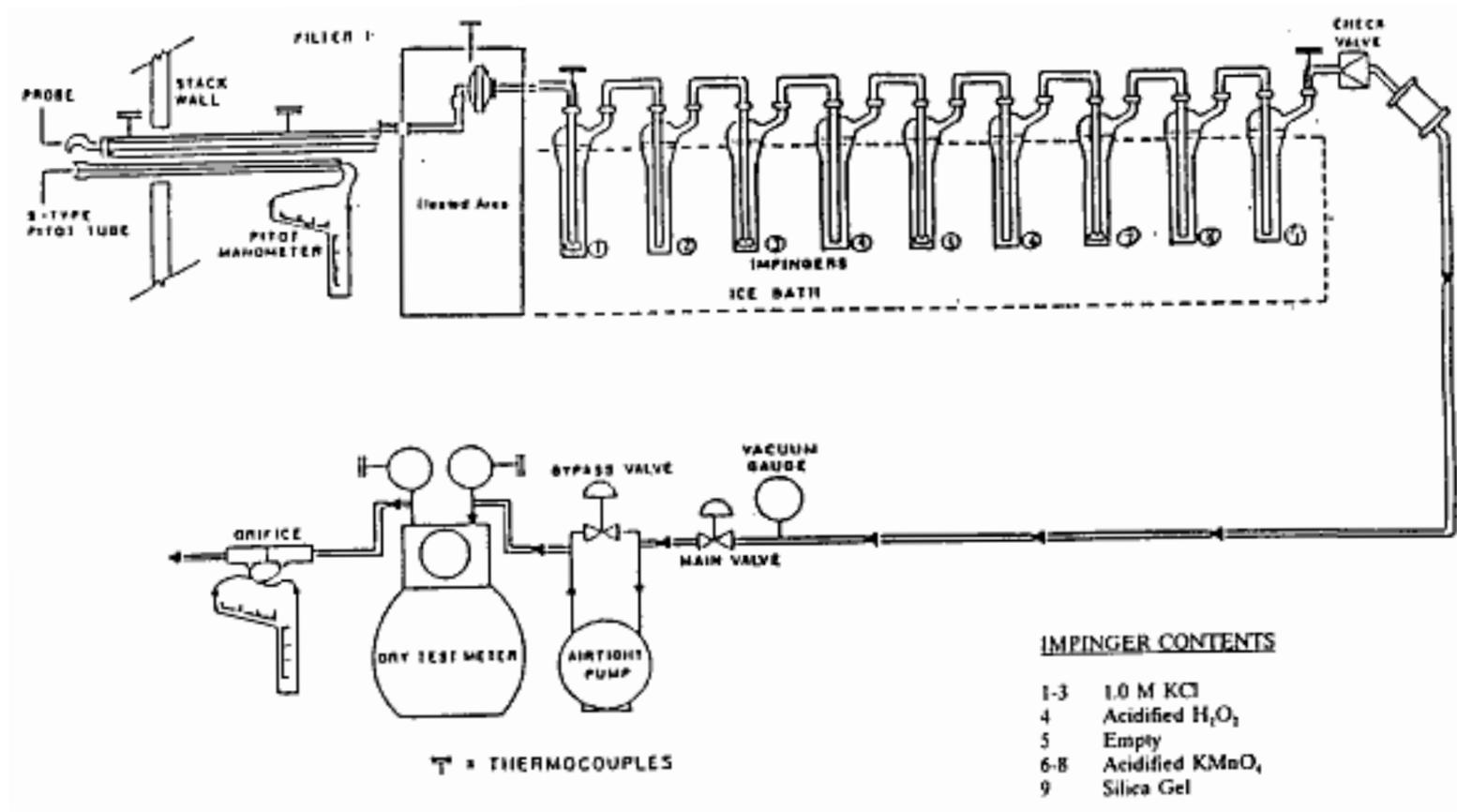


Figure 2:

Mercury Spike Retention (%) with and without SO₂

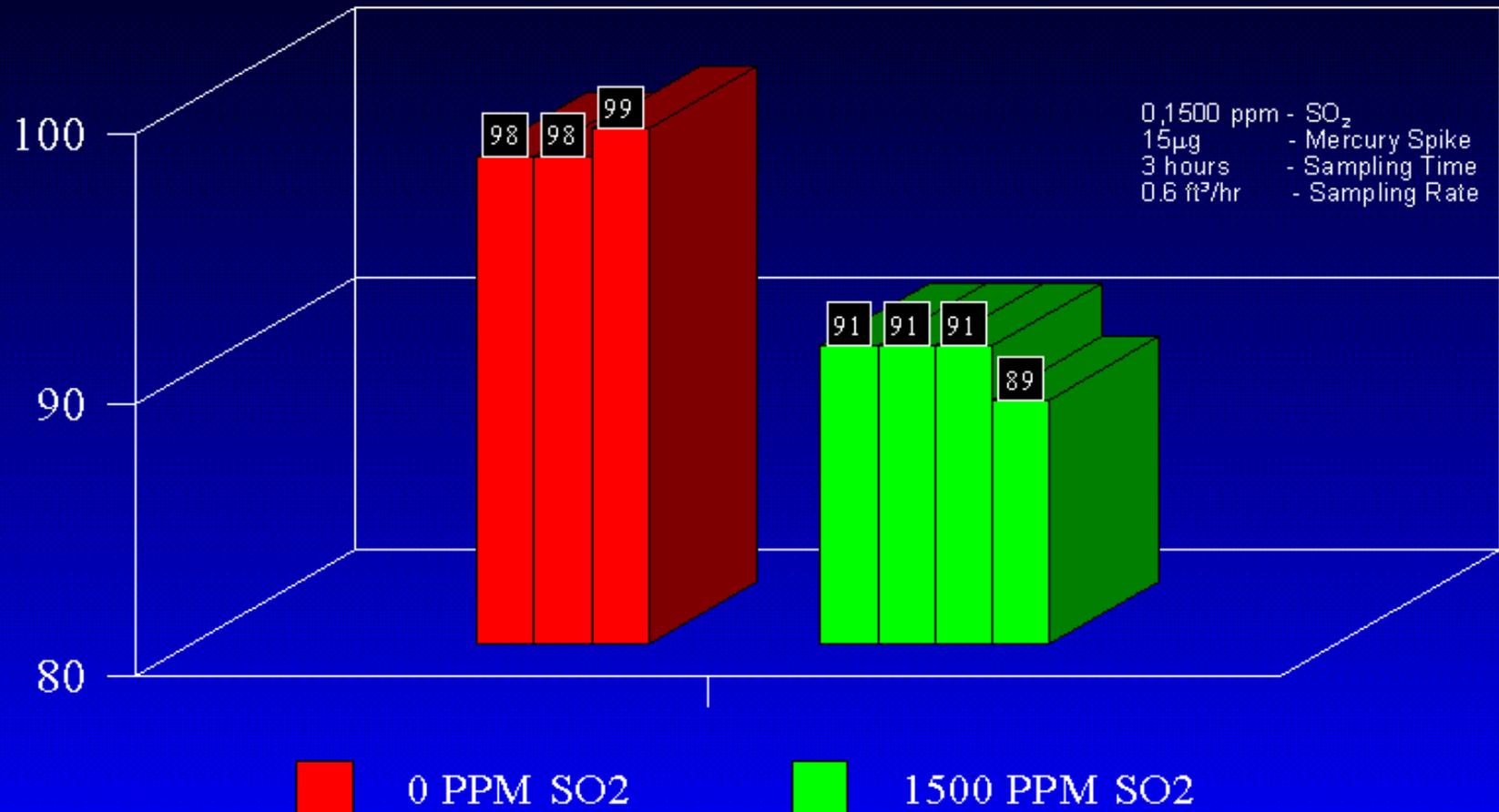


Figure 3:

Mercury Spike Retention (%) with SO₂ at 1500 PPM

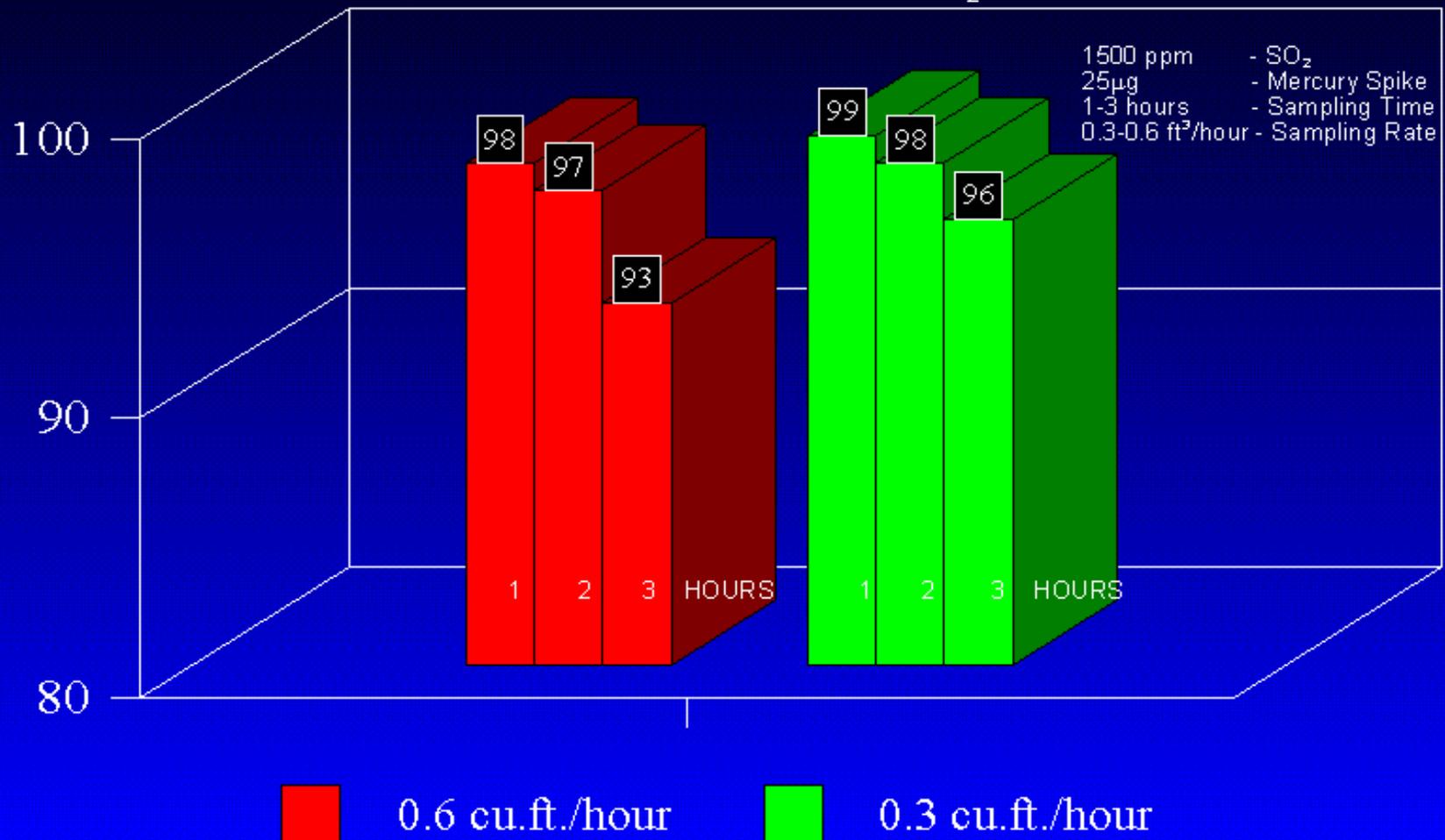


Figure 4: Mercury Spike Retention (%) with SO₂ at 2200 PPM

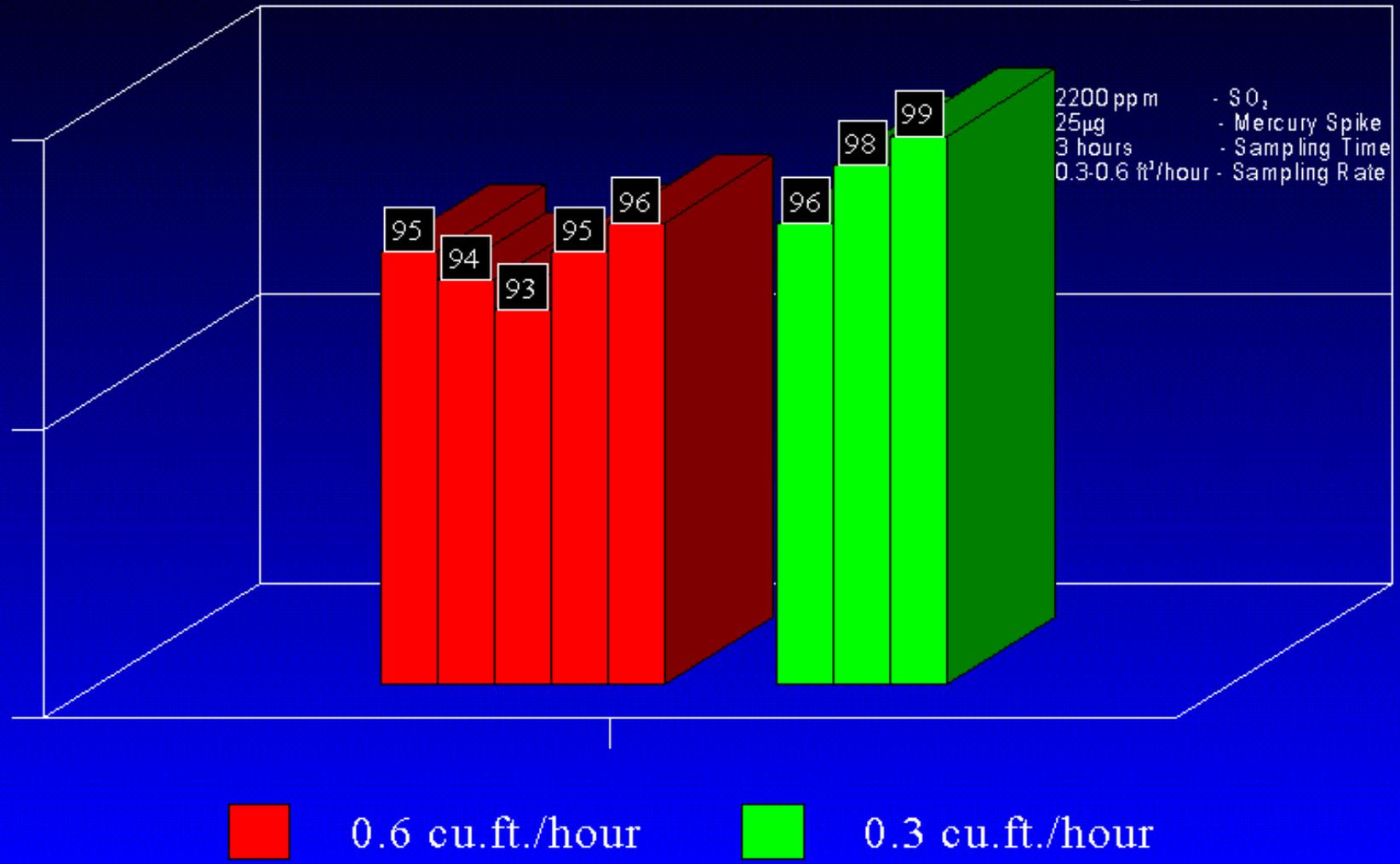


Figure 5:

Mercury Spike Retention (%) with Simulated SO₃ Sampling

