EPA-600/4-77-040
August 1977

Environmental Monitoring Series

SULFUR DIOXIDE BUBBLER TEMPERATURE STUDY

Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

SULFUR DIOXIDE BUBBLER TEMPERATURE STUDY

By

Barry E. Martin
Field Studies Section
Environmental Monitoring and Support Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

The instability of sulfur dioxide collected in the absorbing reagent specified by the Federal Register Method[1] has been shown to result in substantial errors at ambient temperatures above 21°C (70°F) by several investigators.

A series of temperature controlled studies was designed by the Field Studies Section, Environmental Monitoring Branch, to determine the temperature characteristics of the typical Indoor and All Weather Five-Gas® Samplers used to collect 24 hour integrated samples of sulfur dioxide from ambient air. These studies included tests to determine the temperature inside the samplers using 32°C (90°F) thermal heating strips. The results of these tests suggest that the temperature maintained in both samplers is elevated enough to cause decay of SO_2 collected by the Federal Reference Method. Several methods were investigated to control the temperature of the sulfur dioxide absorbing reagent, potassium tetrachloromercurate, before, during and after sampling. A small commercially available refrigerator was evaluated as an inexpensive method of controlling the absorbing reagent temperature. With certain modifications, the refrigerator was found to be an acceptable method of maintaining the necessary temperature control during sampling. A thermoelectric cooler was also evaluated and found to be acceptable. As the result of this investigation, a contract was funded to develop an acceptable prototype thermoelectric cooler which could be incorporated into the existing All Weather

Five-Gas Sampler® to maintain the temperature control of 12±5°C during various atmospheric temperature ranges. Two companies responded to the invitation to bid. Evaluations were performed on these thermoelectric systems and data show that the systems will control the temperature of the absorbing solution within the acceptable range.

A method of controlling the temperature of the collected solution during shipping was also investigated. A styrofoam shipping container using a eutectic mixture for cooling was evaluated. It was found a 21°C temperature was maintained in the sulfur dioxide - tetrachloromercurate solution for a period of 50 hours at ambient temperatures up to 50°C.

CONTENTS

Abstract iii
Figures vi
Tables vii
Acknowledgement viii

1. Introduction 1
2. Conclusions 3
3. Results and Discussion 5

References 22

FIGURES

Number		Page
1	Temperature inside SO_2 samplers under varied temperatures	6
2	Effects of ambient conditions on the temperature inside all weather sampler	7
3	Temperature inside an indoor sampler using standard $32^{o}C$ heater under varied temperatures	8
4	Modified refrigerator system	11
5	Modified Bendix permeation chamber system	12
6	Effects of chamber temperature variations on TCM solution temperature using Bendix permeation chamber	13
7	Hilton Industries Model 2125 Sampling Train Assembly	15
8	RAC Sampling Train Assembly	15
9	Effects of constant temperature of $50^{o}C$ on TCM solution stored in a Trans Temp Cool Pak	19
10	Effects of time on the TCM solution temperature stored in a Trans Temp Cool Pak exposed to variable high temperature	20

TABLES

Number		Page
I	Effects of time and temperature on collected SO_2	9
II	Temperature of TCM solution during ambient sampling	17

ACKNOWLEDGEMENT

The author would like to express appreciation to Joel Vernon Daughtridge for his assistance in the testing of the SO_2 samplers and thermoelectric temperature controlled systems.

SECTION 1

INTRODUCTION

The dichlorosulfito-mercurate (SO_2-TCM) solutions collected by the Federal Reference Method[1] have been shown to be unstable during storage at temperatures above 21°C (70°F)[2,3]. Since there is a stability problem with the collected SO_2-TCM solutions at elevated temperatures, the SO_2 collected by the potassium tetrachloromercurate (TCM) may be decaying prior to analysis during sampling and storage, indicating SO_2 concentrations lower than those actually collected. Based on a temperature-time decay table developed by the Quality Assurance Branch of the Environmental Monitoring and Support Laboratory (QAB/EMSL), a minimum temperature decay range of 12°C±5°C was selected as the desirable TCM solution sampling temperature. Temperature studies were performed to characterize elevated temperatures that SO_2 - TCM solutions might be exposed to before, during, and after ambient air sampling. Studies were also designed to develop a temperature controlled sampling system which will maintain the desired temperature of 12°C±5°C in temperature ranges expected during summer months.

To perform these evaluation studies, two commercially available sampling shelters were utilized. One design consisted of a thermostated compartment in which the five-gas sampling system is housed. The sampling pump system is a separate component and is not housed in the shelter. This sampler is designed for indoor use. It is commonly referred to as the Indoor Five-Gas Sampler. The second design consists of an All Weather shelter which houses a temperature controlled Five-gas sampler in one section and the sampling pump in a separate ventilated section. This sampler is designed for use outdoors and is referred to as the All Weather Five-Gas Sampler.

SECTION 2

CONCLUSIONS

The results of the tests on the typical Indoor and All Weather Five-Gas Samplers indicate that at ambient temperatures above 20°C, the temperature inside the samplers was elevated enough to cause decay of collected SO_2, when the Federal Reference Method (FRM) is used. Data show that it is necessary to control temperature inside both samplers (Indoor and All-Weather) to limit decay of the SO_2 collected by the FRM. The results from testing new prototype systems to control the temperature show that several units adequately maintain the TCM solution temperature below the temperature at which decay of collected SO_2 occurs. These devices may be as simple as a small properly modified refrigerator or as sophisticated as a special thermoelectrical control to maintain the solution temperature. A means of controlling the TCM solution temperature during sampling and storage must be implemented immediately to insure good quality data collected by the Federal Reference Method at sites where the TCM bubbler would be exposed to elevated temperatures above 25°C.

SECTION 3

RESULTS AND DISCUSSION

The environmental chamber used to obtain test temperatures was Model B5-67M manufactured by Forma Scientific, Inc. This chamber maintains a desired temperature at ± 0.3°C with a uniformity of ±0.5°C over the range of 0°C to 50°C. All of the temperatures monitored in this study were measured using Yellow Springs Instrument Company (YSI) 700 series thermilinear (linear thermistors) probes. These probes are teflon coated which allowed them to be inserted in the SO_2 sampling solution without affecting their performance. YSI Sostman Series 740A thermivolt signal conditioners were used to convert the signal from the probe into a linear temperature analog millivolt signal. These units cover a temperature span from 0°C to 100°C with a system accuracy of ±0.4°C including the probes. The YSI systems were verified using an ASTM thermometer prior to initiation of the study. The output of the signal conditioners was monitored using a Model 680 Hewlett Packard recorder to provide a continuous record of the temperatures being measured.

Initially, tests were conducted to determine if a potential temperature problem existed in the Indoor and the All-Weather 5-gas samplers. For this test, the temperature probes were not placed in the sampler solution, but were located at the approximate position of the SO_2 bubbler. Both types of samplers equipped with the standard 32°C heater were placed in the temperature controlled environmental chamber. The Indoor sampler was not sampling during this temperature check. The All-Weather sampler has a built-in sampling pump which acts as a source of heat. Therefore, during this temperature check, the All-Weather sampler was sampling the environmental chamber air at a flowrate of 200 cm^3/min. Fifty (50) ml of water was substituted for the TCM solution in the SO_2 bubbler in both samplers. After the initial stabilization period, the temperature inside both samplers remained constant for 24 hours. Figure 1 is a plot of the chamber temperature versus the temperature inside the SO_2 samplers. Figure 1 indicates that the temperature inside the All-Weather sampler is one to six degrees higher than the temperature inside the Indoor sampler under similar conditions. This difference is attributable to the heat generated by the sampling pump.

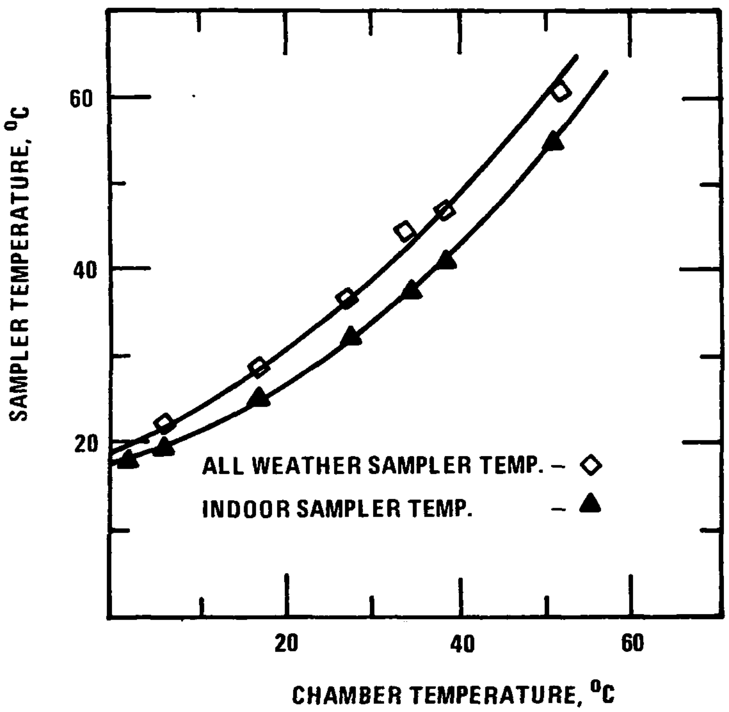

Figure 1. Temperature inside SO_2 samplers under varied temperatures.

Another temperature check was performed on the All-Weather sampler equipped with the 32°C heater strip under actual sampling conditions for ambient SO_2 at the Environmental Research Center, Research Triangle Park, N.C. During the test, the ambient temperature monitored varied from -3°C to 20°C. For this ambient temperature range, the 32°C heater strip controlled the temperature inside the sampler from 9° to 30°C. Figure 2 is a plot of the ambient temperature versus the temperature inside the sampler. The wide scatter observed on the graph suggests that the temperature inside the sampler is affected by external meteorological conditions such as wind speed and wind direction. At an ambient temperature of 20°C, the temperature inside the All Weather sampler reached 30°C.

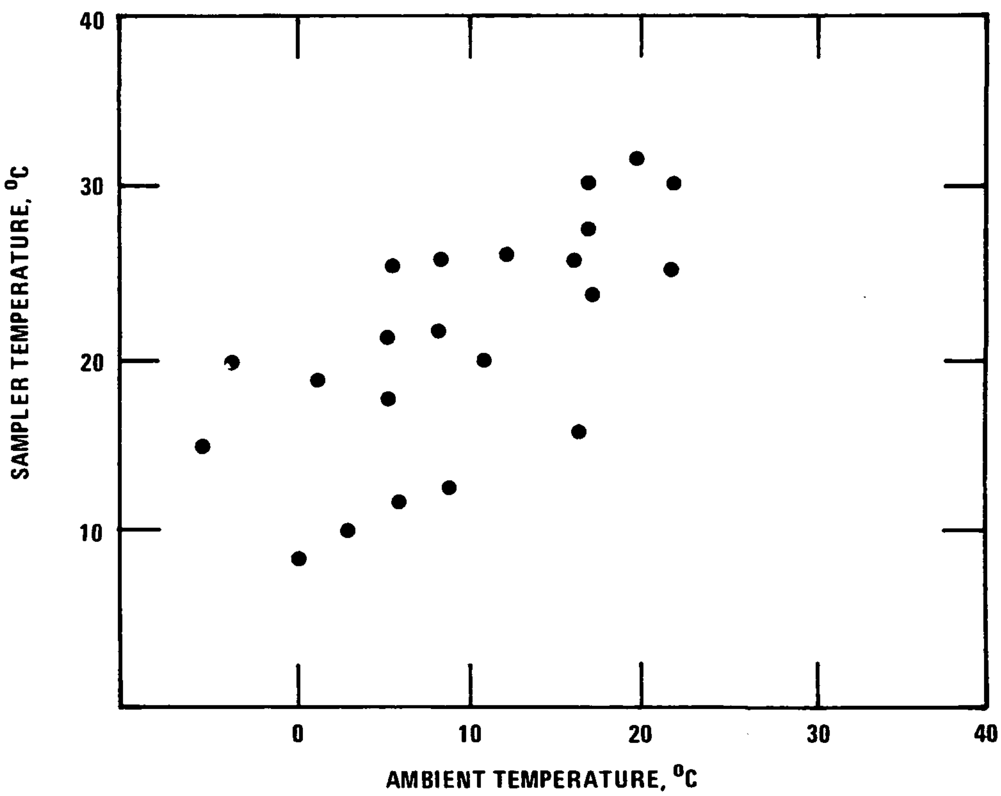

Figure 2. Effects of ambient conditions on the temperature inside all weather sampler.

A further study was performed to determine the temperature in the Indoor sampler equipped with the 32°C heater strip under various chamber temperatures. Figure 3 is a plot of the environmental chamber temperature versus the TCM solution temperature. Data showed that if the Indoor sampler is used with the 32°C heater strip operational, decay of SO_2 in the TCM absorbing solution occurs when ambient temperatures are in excess of 8°C.

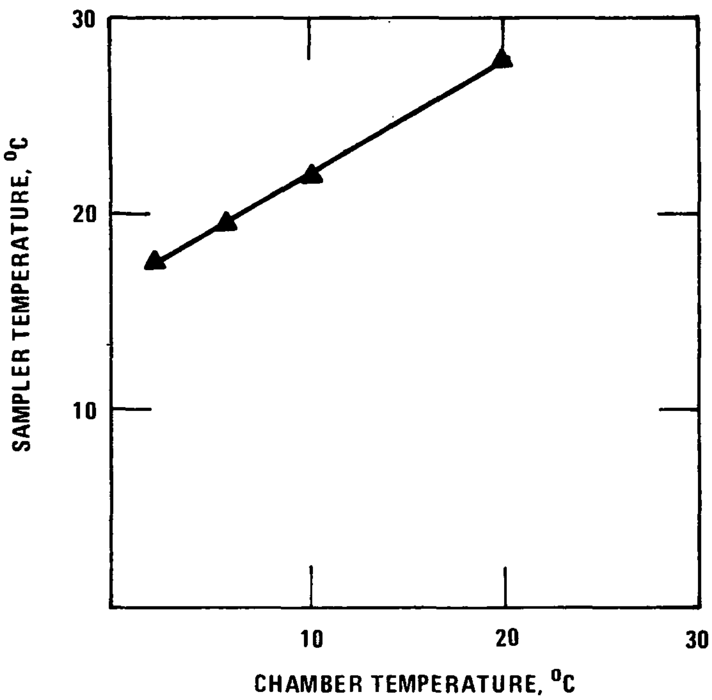

Figure 3. Temperature inside an indoor sampler using standard 32°C heater under varied temperatures.

The Quality Assurance Branch (QAB) supplied the Field Studies Section (FSS) with a temperature-time decay table for SO_2 collected by the Federal Reference Method. See Table I. Table I shows the percent SO_2 remaining in the TCM solution after exposure to various temperatures. From this table, a minimum temperature decay range of 12°C ± 5°C was selected by the Field Studies Section (FSS) as the desirable TCM solution sampling temperature. Since there is decay of the collected SO_2 at elevated temperatures, a means of controlling the TCM temperature within the desired range during sampling and shipping is needed.

TABLE I. EFFECTS OF TIME AND TEMPERATURE ON COLLECTED SO_2

			% SO_2 REMAINING						
		At End	Days After Sampling						
°C	°F	Of sampling	1	2	3	4	5	6	7
5	41	99.9	99.8	99.8	99.8	99.7	99.7	99.6	99.6
10	50	99.9	99.8	99.7	99.6	99.5	99.4	93.5	99.2
15	59	99.8	99.4	99.0	98.6	98.2	97.8	97.4	97.0
20	68	99.6	98.7	97.8	96.9	96.1	95.2	94.3	93.5
25	77	98.9	96.7	94.4	92.2	90.2	88.1	86.1	84.2
30	86	97.4	92.2	87.4	82.8	78.5	74.3	70.4	66.7
35	95	95.1	84.0	74.1	65.5	57.9	51.3	45.2	39.9
40	104	87.6	66.8	50.8	38.7	29.5	22.5	17.2	13.0
45	113	75.3	41.4	22.7	12.5	6.9	3.8	1.9	1.1
50	122	56.3	15.6	4.3	1.2	0.9	0.1	0	0

One method of controlling the TCM solution temperature during sampling was the use of a small commercially available 1.5 ft^3 refrigerator (Sanyo Model SR 4801). The only required modification to this refrigerator was the drilling of two 1/4" holes in the back of the refrigerator for the sample and exhaust lines. The results indicate that the small refrigerator is capable of maintaining 12°C±5°C at ambient temperatures of 25°C to 50°C. However, if the ambient temperature is below 20°C, it will be necessary to install a small strip heater in the refrigerator to keep the temperature inside the refrigerator above 7°C.

Due to the cool temperature maintained by the refrigerator, water condensed in the sample inlet lines and in the bubblers. This condensation will be a problem in sampling on high relative humidity days. Therefore, a study was conducted using a sample stream saturated with water to determine the amount of condensation in the sample inlet lines and in the bubbler. Using an uninsulated sample inlet line, enough water condensed in the sample line inside the refrigerator to stop the sample flow and to increase the total volume of solution at the end of sampling to 52 ml. Since water is added to the TCM solution under high relative humidity conditions, it may be necessary to use less than 50 ml of the TCM solutions. Using a sample inlet line insulated with standard water pipe insulation, only a few drops of moisture were evident in the sample inlet line. To prevent any accumulation of moisture, the sample inlet line inside the refrigerator should be wrapped with heater tape. The voltage to the heater tape should be adjusted so that the temperature of the sample inlet line is near the average ambient temperature. Under these conditions, water condensation in the sample inlet line should not occur or at least be minimized and not interfere with the collection of SO_2 in the bubblers. Figure 4 is a diagram of this system. A small refrigerator such as the one used in this experiment could be used as an inexpensive means of maintaining sub-ambient temperatures during the hot summer months. If necessary, as many as five bubblers could be installed in the refrigerator.

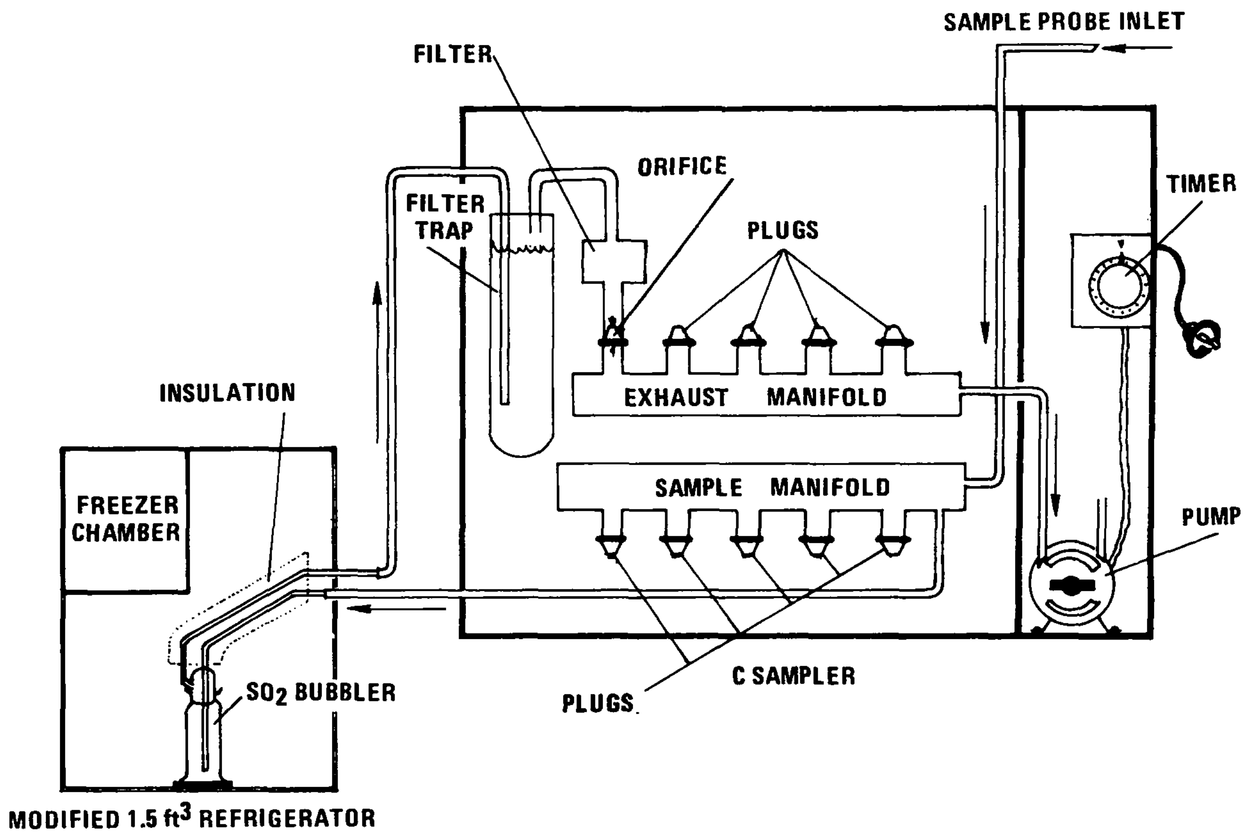

Figure 4. Modified refrigerator system.

Another device investigated to determine the feasibility of controlling the temperature of the TCM solution at sub-ambient levels was the permeation chamber utilized in the Bendix Calibrator Model 8851. For this test, a sample flow rate of 200 cm^3/min was used. The temperature probe was placed in the TCM solution. The Bendix permeation chamber was then placed in the temperature controlled environmental chamber and the chamber temperature was varied. These results indicate that this thermoelectrically controlled permeation chamber is capable of maintaining a temperature cool enough to limit SO_2 decay in the TCM solution during sampling. These thermoelectric permeation chambers and controllers are expensive and therefore may not be practical for field use. Figure 5 is a diagram of this experimental set-up.

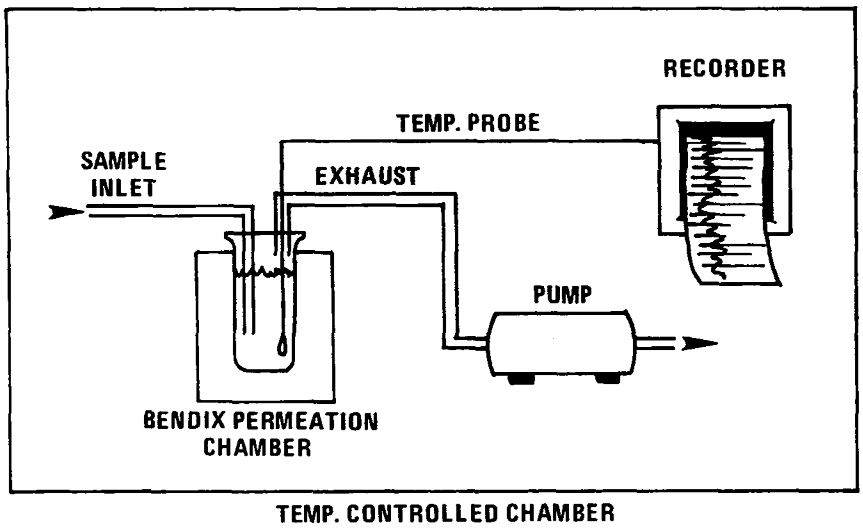

Figure 5. Modified Bendix permeation chamber system.

Figure 6 is a plot of the chamber temperature versus the TCM solution temperature using the Bendix permeation chamber.

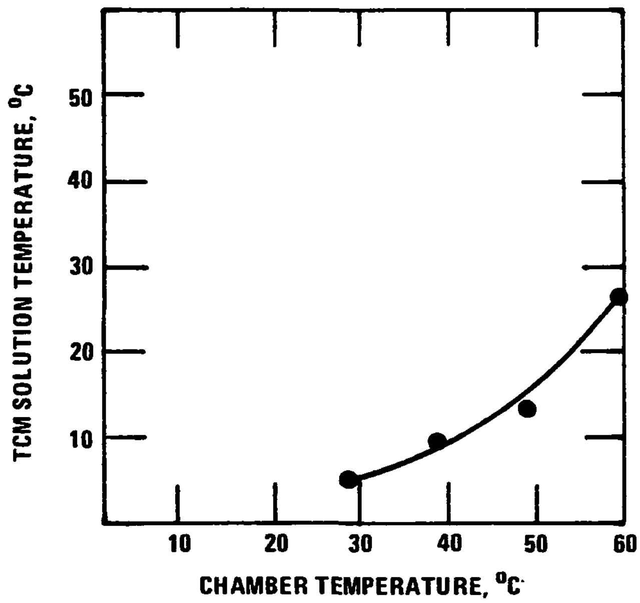

Figure 6. Effects of chamber temperature variations on TCM solution temperature using Bendix permeation chamber.

Research Appliance Corporation (RAC) and Hilton Industries were contracted to build prototype thermoelectric temperature controlled holders for the SO_2 bubbler train. Ideally, these temperature controlled systems should maintain the TCM bubbler solution temperature at 12°C ± 5°C for an ambient temperature range of 0°C - 50°C. Hilton Industries manufactured a prototype thermoelectric temperature controlled holder which controlled the temperature of only one sample holder and which restricts the total number of possible samples to two. This unit could be installed in the existing sample train of either the Indoor or All-Weather sampler. The addition of this controller to either sampler requires modifications to the sampler box for ventilation of the thermoelectric cooler. This can be accomplished by cutting a 5 inch diameter hole in the inner wall of the All Weather sampler or cutting a 5 inch diameter hole in an external wall of the Indoor sampler. During testing in the environmental chamber, this unit did not meet the original purchase specifications of 12°C ± 5°C over a temperature range of 0°C -50°C. After several modifications by the manufacturer, the unit met the purchase specifications when tested in the environmental chamber and would maintain the desired temperature range. This unit (Model 1125) is presently available from Hilton Industries for $300.

Hilton Industries also manufactured a prototype thermoelectric temperature controlled dual sample holder (Model 2125) that replaced the existing sampling train holder and controlled the temperature in both sampling cells to 12°C ± 5°C. Ventilation for the unit must be provided as described for the Model 1125. On the actual test run in our laboratory, the prototype of this model did not meet the purchase specifications and had to be modified by the manufacturer. Since modifications, this unit has undergone extensive testing and will control the TCM solution temperature in both bubblers to 12°C ± 5°C for an ambient temperature range of 0°C - 50°C. The Model 2125 is presently available from Hilton Industries for $320. Figure 7 is a picture of the Hilton Industries Model 2125 thermoelectric sampling train assembly.

RAC manufactured a prototype three gas sampler to replace the five-gas samplers. This unit underwent similar temperature testing in the environmental chamber as did the Hilton units. The actual TCM solution temperature showed more variance than was observed in the Hilton units, but remained within the purchase specifications. The unit controls only the TCM bubbler and not the remaining two bubblers. The temperature of the solution inside the nontemperature controlled bubblers which is heated to 25°C ± 5°C by a thermostated heater ranged from 25°C at 0°C environmental chamber temperature

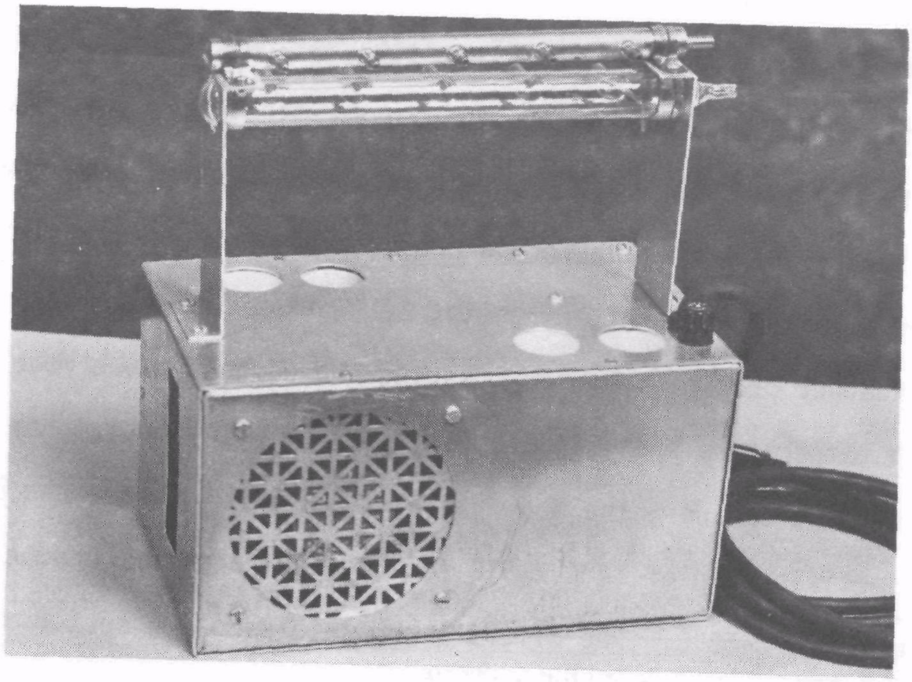

Figure 7. Hilton Industries Model 2125 Sampling Train Assembly.

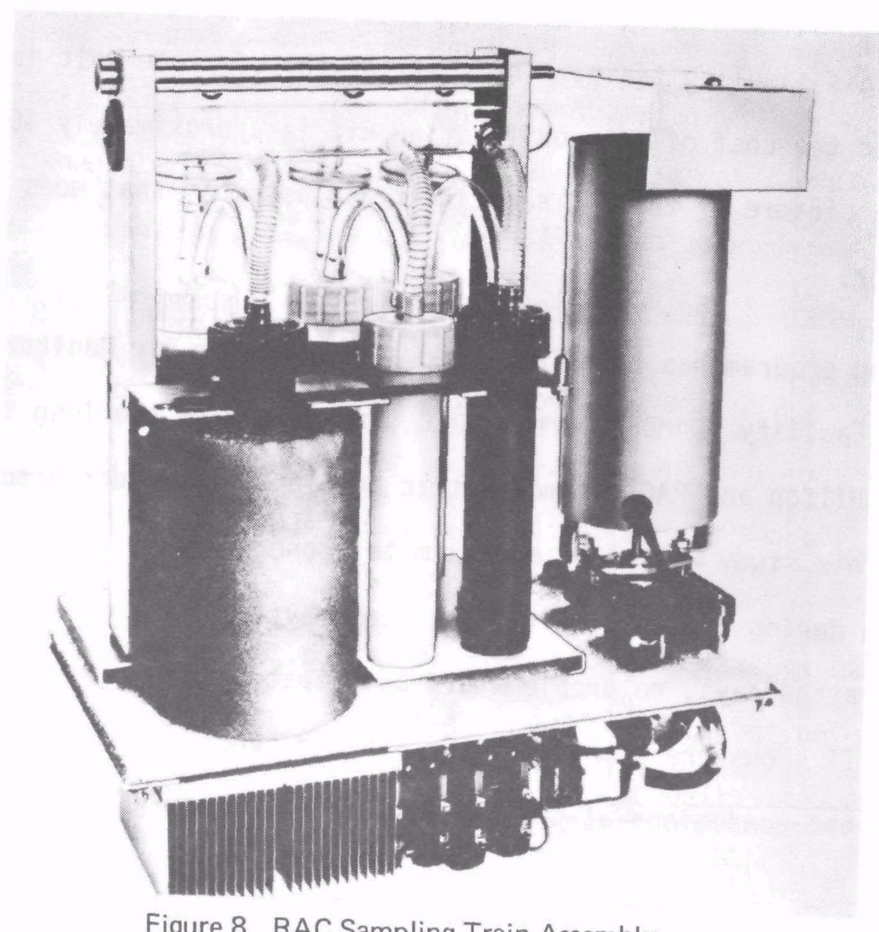

Figure 8. RAC Sampling Train Assembly.

to 63°C at 50°C environmental chamber temperature. At ambient temperatures above 25°C, the temperature inside the non-temperature controlled bubblers is determined by the ambient temperature. During testing, this unit developed an electrical problem and subsequently blew several fuses. RAC was informed of this and modifications were made in the production line model to eliminate any recurrence of this problem. After receipt of two RAC thermostatically controlled All-Weather production units, testing showed that these models did not meet the high temperature specifications. However, after additional modifications by the manufacturer, the modified production models met the original temperature specification of 12°C ± 5°C for the environmental chamber temperature range of 0°C-50°C. RAC offers a complete sampling system and a modification kit to convert existing units. A complete unit consists of the temperature controlled shelter, 3 gas sampling train, pump and necessary supplies. The modification kit consists of a new temperature controlled shelter and 3 gas sampling train. The cost for the complete unit is approximately $800 and the cost of the modification kit is approximately $600. See Figure 8 for a picture of the RAC sampling train assembly that goes in the All Weather sampler.

A sampling program has been initiated at the Durham Air Monitoring and Demonstration Facility (DAMDF) Durham, N.C., to determine the long term durability of the Hilton and RAC thermoelectric bubbler units under actual sampling conditions. This study will last approximately one year. Since no major problems arose during the initial tests on each system, which ran for approximately 60 operating days, no problems are anticipated during this durability study. Table II shows the temperature inside the bubblers during an actual run under ambient conditions at the DAMDF. The RAC unit tested is the prototype and not the latest production model. The production model is now being tested under ambient conditions. The temperatures measured under ambient conditions for the thermoelectric holders are slightly higher than those taken in the environmental chamber tests. This difference may be caused by the effect of ambient conditions on the signal conditioners used to convert the signal to millivolts. The signal cable was not of sufficient length to allow the conditioners to be placed in a temperature controlled facility. However, the temperatures measured were controlled at low enough levels to sufficiently reduce decay of collected SO_2.

TABLE II. TEMPERATURE OF TCM SOLUTION DURING AMBIENT SAMPLING

Hour	Ambient Temp, °C	Hilton Bubbler Temp, °C		RAC Bubbler Temp, °C	
		1	2	1	2
15		20	18	11	
16	4	20	19	11	28
17	3	20	19	11	27
18	1	20	19	12	26
19	-1	20	19	12	26
20	-2	20	18	12	25
21	-3	19	18	12	24
22	-3	19	18	12	24
23	-4	19	18	12	23
24	-4	19	18	15	23
1	-5	19	18	18	23
2	-5	19	18	18	22
3	-6	19	19	18	22
4	-6	19	19	17	22
5	-6	19	19	17	22
6	-6	19	19	17	22
7	-4	19	19	18	22
8	-2	20	19	19	23
9	1	20	19	20	23
10	1	20	19	21	24
11	-1	20	19	20	24
12	0	20	19	19	23
13	0	20	19	19	23
14	1	20	19	19	23

A test was conducted to determine the maximum length of time that the SO_2 bubbler solution could spend in transit from a field site in a Trans Temp Cool Pak shipping container. Two of the Trans Temp Cool Paks (eutectic mixtures) were charged in a freezer for at least 24 hours. The Cool Paks were then placed in a Trans Temp shipping container. An SO_2 bubbler filled with TCM solution was also placed in the Trans Temp shipping container. This shipping container was then placed in a 50^oC (122^oF) environmental chamber. The temperature of the TCM solution was monitored. Figure 9 is a plot showing time versus temperature using the Trans Temp Cool Pak shipping container. Within one (1) hour, the temperature of the TCM solution was below 0^oC. After 24 hours, the TCM solution temperature had risen to 8^oC. At the end of 50 hours, the solution temperature was 21^oC (70^oF).

A second test similar to the above was run varying the chamber temperature from 25^oC to 40^oC. This temperature range was chosen to determine the maximum length of time that the TCM bubblers could spend in transit under variable elevated temperature conditions. Figure 10, is a plot showing time versus temperature using the Trans Temp Cool Pak shipping container. Under the specific conditions outlined in Figure 10, the TCM solution temperature reached 21^oC (70^oF) in 62 hours. Obviously, if the chamber temperature was maintained at a lower temperature, the solution temperature would remain below 21^oC for a longer time.

The 3M Company manufactures a time/temperature tag ("Monitormark") which can be used as an indication of the maximum temperature to which a sample was exposed during transit. These tags can be purchased for certain specified time/temperature ranges and are available for as little as $0.25 each when purchased in large quantities. The "Monitormark" tags could be used as a

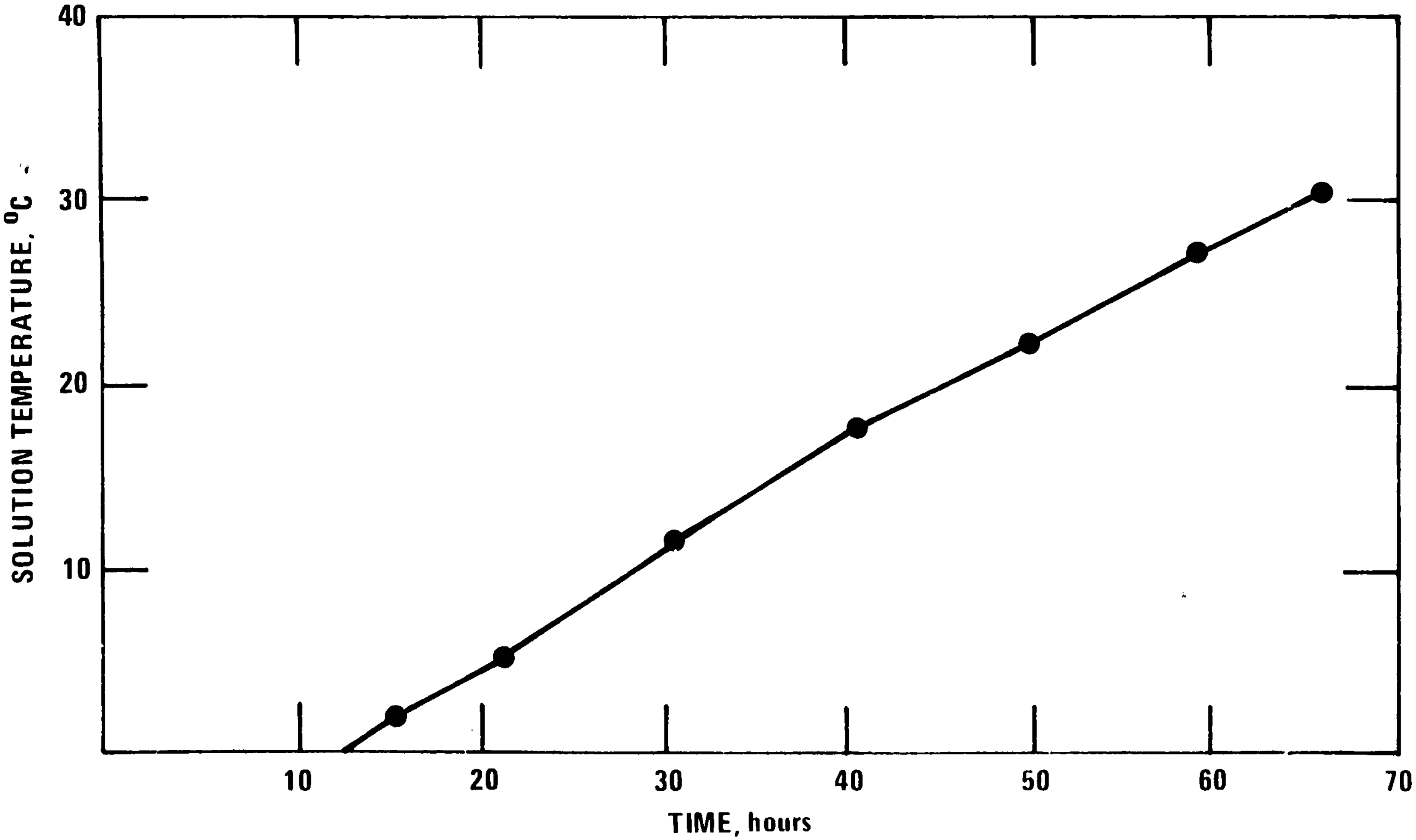

Figure 9. Effects of constant temperature of 50° C on TCM solution stored in a Trans Temp Cool Pak.

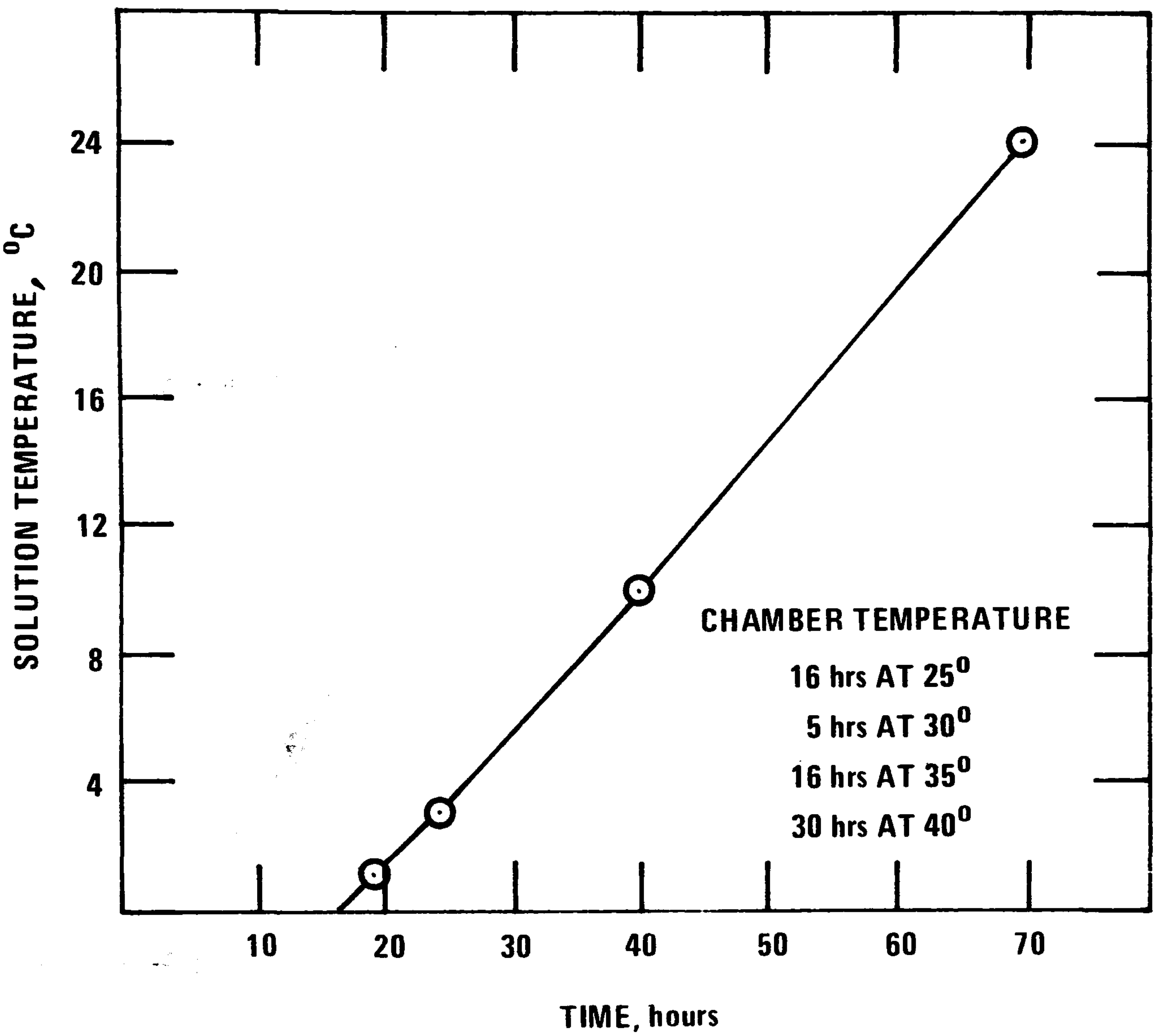

Figure 10. Effects of time on the TCM solution temperature stored in a Trans Temp Cool Pak exposed to variable high temperature.

quality assurance measure during shipping. These "Monitormark" tags were not evaluated during this project. However, several sample tags were obtained and sent to the Rockwell International Corporation, Newbury Park, California for evaluation. The results of their evaluation are not available at present.

REFERENCES

1. Title 40 - Protection of Environment, National Primary and Secondary Ambient Air Standards, Appendix A - Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method). Federal Register 36 (228): 22385 - 22388, Nov. 25, 1971.

2. Fuerst, R. G., Scaringelli, F. P., Margeson, J. H., "Effect of Temperature on Stability of Sulfur Dioxide Collected by the Federal Reference Method", EPA - 600/4-76-024, May, 1976.

3. Scaringelli, F. P., L. Elfers, D. Norris, and S. Hochheiser, Anal. Chem. 42: (14): 1818-1820, December, 1970.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/4-77-040	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE SULFUR DIOXIDE BUBBLER TEMPERATURE STUDY		5. REPORT DATE August 1977 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Barry E. Martin		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT NO. 1AD606 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency Office of Research and Development, EMSL Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED Inhouse 14. SPONSORING AGENCY CODE EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This paper describes a series of temperature-controlled studies designed to determine the temperature characteristics of several thermostated systems used to collect sulfur dioxide from the ambient air by the EPA Federal Reference Method.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 31
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (9-73)