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GAS MASK CANISTER TESTS AGAINST RADIOACTIVE SULFUR DIOXIDE

By

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GAS MASK CANISTER TESTS AGAINST RADIOACTIVE SULFUR DIOXIDE

Report by J W Thomas

Work done by R G Orrison
J W Thomas
R L Quinn

September 2 1952

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ABSTRACT

The object of this work was to investigate the application of radioactive gases to gas mask canister testing Sulfur 35 was selected as the test isotope to avoid shielding problems, and was used to prepare sulfur dioxide in curie amounts The influent and effluent sulfur dioxide gas concentrations were measured with a flow type ionization chamber equipped with vibrating reed electrometer and recorder

An ultra sensitive test was developed Penetrations as low as 10^{3} μg/l may be estimated Results of several high activity trial runs showed almost immediate penetration of the gas in very small quantities Several interesting applications of the flow ionization chamber to canister testing are discussed

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GAS MASK CANISTER TESTS AGAINST RADIOACTIVE SULFUR DIOXIDE

Introduction

As the use of radioactive material increases information on the protection afforded by gas mask canisters against radioactive gases will be needed It is true that this information can probably be obtained from data on the performance of canisters against inert (non-radioactive) gases but there are several reasons for developing tests using radioactive materials Ordinary canister tests against inert gases are not designed to detect the very low penetrations permissible with high activity radioactive gases hence the results of inert canister tests are not directly applicable However, it can be inferred from canister charcoal bed sorption theory that the gas penetrating the canister prior to the breakpoint is much less than the amount detectable by inert test The use of radioactive gases will provide the high sensitivity required and will also permit the use of continuous recording instruments to determine gas concentrations There is also the remote possibility that radioactivity itself will affect the sorption process

Sulfur 35 was selected as the test isotope This is a pure beta emitter consequently, shielding problems are negligible Sulfur 35 is available at a reasonable price in carrier free form (40,000 curies per gram) The half life of 87 days allows ample time for experiments without serious long-term decontamination problems

The sulfur 35 was converted to sulfur dioxide for use in the canister tests This procedure is described in Appendix I

Apparatus and Procedure

A conception of a good $S^{35}O_2$ canister testing apparatus is shown in Figure 1 The more complicated equipment actually used in the test de-

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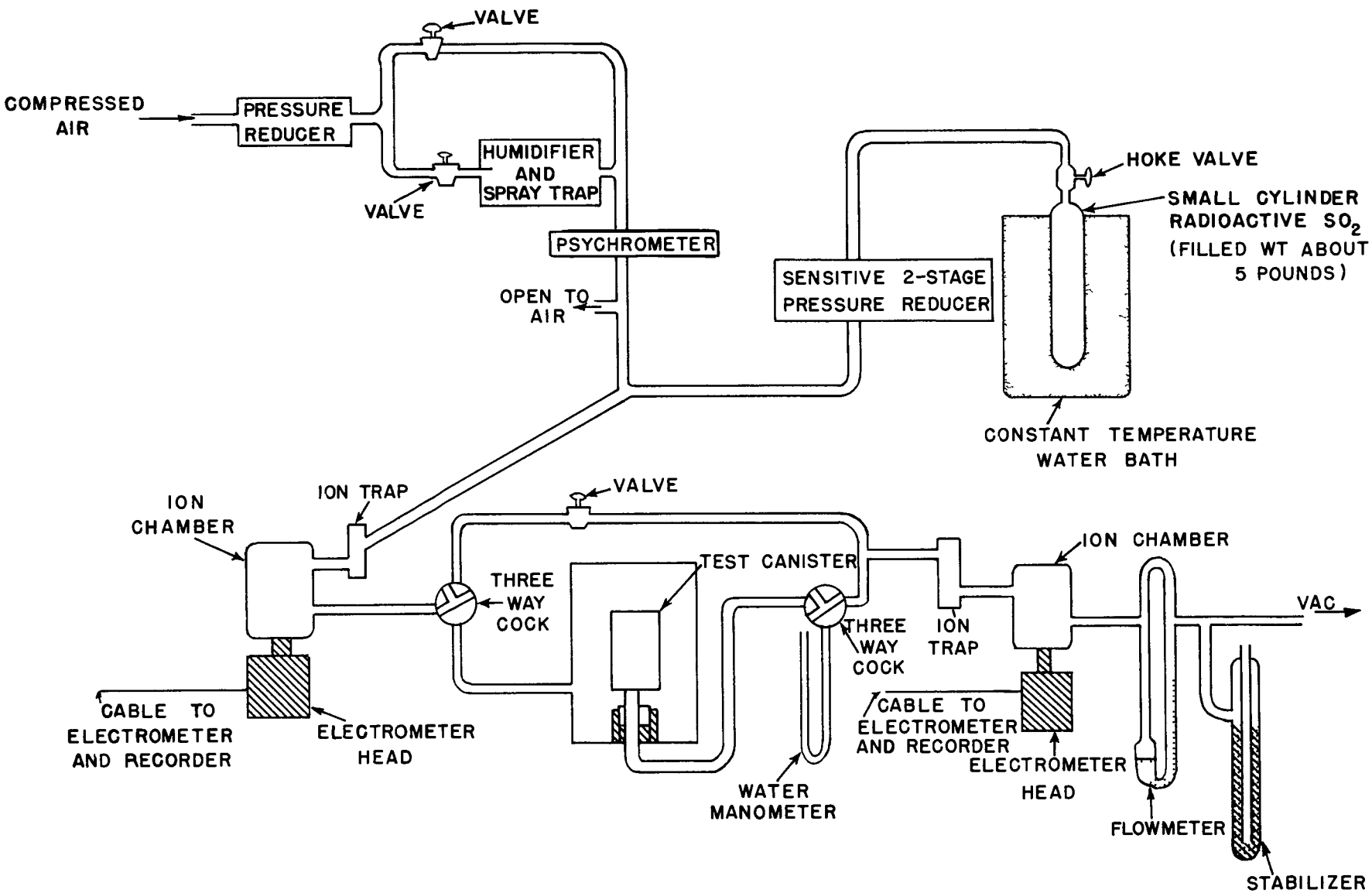

FIGURE 1 CANISTER TESTING APPARATUS

velopment work is described in the quarterly reports [1] [2] [3] [4] Since the ionization chamber-electrometer was found very reliable and sensitive the auxiliary sampling systems etc , of the experimental apparatus are not needed and apparatus of Figure 1 is recommended

It is necessary to avoid wasting valuable radioactive gas For this reason the usual water stabilizer on the SO_2 gas line was replaced by a pressure regulator This regulator should be a sensitive two-stage type The operation of the influent and effluent ionization chambers, with ion traps, for determination of gas concentrations is described fully in other reports [5,6]

The operating procedure is essentially as follows The test canister is mounted in the chamber and the canister inlet closed A vacuum of about 25 cm of water is drawn on the canister and part of the line by means of a three-way cock The cock is closed to connect the canister and manometer and the rate of rise of the leak testing manometer noted The rate of leakage is calculated with sufficient accuracy by the formula $L = V\frac{\Delta P}{\Delta T}$ where L is the leakage in ml/min, V the volume of canister and line in liters, and $\frac{\Delta P}{\Delta T}$ is the pressure drop in cm of water per minute This equation applies directly, without a proportionality constant, since atmospheric pressure is roughly 1000 cm of water

After elimination of leaks, air of the humidity desired is passed through the system, usually at 32 l/ min to establish the pressure drop through the canister line The air stream is alternately switched between the canister line and the bypass line and the resistance compensating value adjusted so that the pressure drop is equal in both lines This condition is obtained when there is no difference in the main flowmeter reading for either path, and allows the flow to be switched between the canister and bypass line without any adjustment of the vacuum water stabilizer

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1 Protective Equipment Evaluation Program - Quarterly Progress Report, ORNL Y-605 January - March 1950

2 Protective Equipment Evaluation Program - Quarterly Progress Report, ORNL, Y-638, April - June 1950

3 Protective Equipment Evaluation Program - Quarterly Progress Report, ORNL, Y-687, July - September 1950

4 Protective Equipment Evaluation Program - Quarterly Progress Report, ORNL, Y-724 October - December 1950

5 Quinn, R L "A Flow-Type Ionization Chamber For Measurement of Activity in Low Energy Beta Emitting Gases," ORNL Y-791, Aug 1, 1951

6 Thomas J W and R L Quinn, "Calibration of a Flow Ionization Chamber with Radioactive Sulfur Dioxide," ORNL, Y-793 Aug 20, 1951

The flow is made to pass through the bypass line and the pressure regulator on the SO_2 line opened to establish the gas concentration The pressure regulator is adjusted so that the influent ion chamber registers the desired concentration A three-way cock is switched to the canister line, starting the test The effluent ion chamber rends the penetration of the canister After the breakpoint has been reached the increasing penetration may be followed by changing the ion chamber sensitivity This is done by changing the millivolt range of the electrometer and/or introducing a lower resistance into the electrometer circuit by means of the turret type switch provided

Results

The operation of the apparatus was demonstrated by a number of test runs Figure 2 shows the determination of the sorption-desorption characteristics of a M10A1 canister Figures 3 and 4 show tests at relatively high activities of SO_2 The canister effluent concentrations given are approximate since at the time of the test an accurate calibration of the ionization chamber-electrometer had not been made However the values given are considered reliable to within 25-50% For Figure 3 the canister penetration in the first 10 minutes of test, obtained by rough integration of the curve was less than 1 μg SO_2 For Figure 4 the corresponding figure was less than 3 μg SO_2

Discussion

Figure 2 shows the test method to be well adapted to study of sorption-desorption phenomena The first peak in the figure represents a total desorption of less than 0 02 grams of SO_2 After the effluent concentration had dropped to a steady value it was possible to introduce about 2 grams more of SO_2 into the canister before the effluent concentration again began to rise The second peak represents a desorption of about 0 1 g SO_2 Again after the effluent concentration had dropped, it was possible to introduce about 2 grams of SO_2 before the rise These results show that some slow process is occurring on or within the individual charcoal granules After this process has occurred, the surface of the granule is free to pick up new SO_2 molecules

Figures 3 and 4 show $S^{35}O_2$ penetrating the M11 canisters within several minutes of the start of the test The breakpoint of the canisters on inert gas, using the Thomas Autometer[7] to detect the effluent is about 20 minutes The

7 This instrument, designed to measure SO_2 continuously in a flowing gas stream is manufactured and sold by the Leeds and Northrup Co 3901 Stenton Ave , Philadelphia, Pa

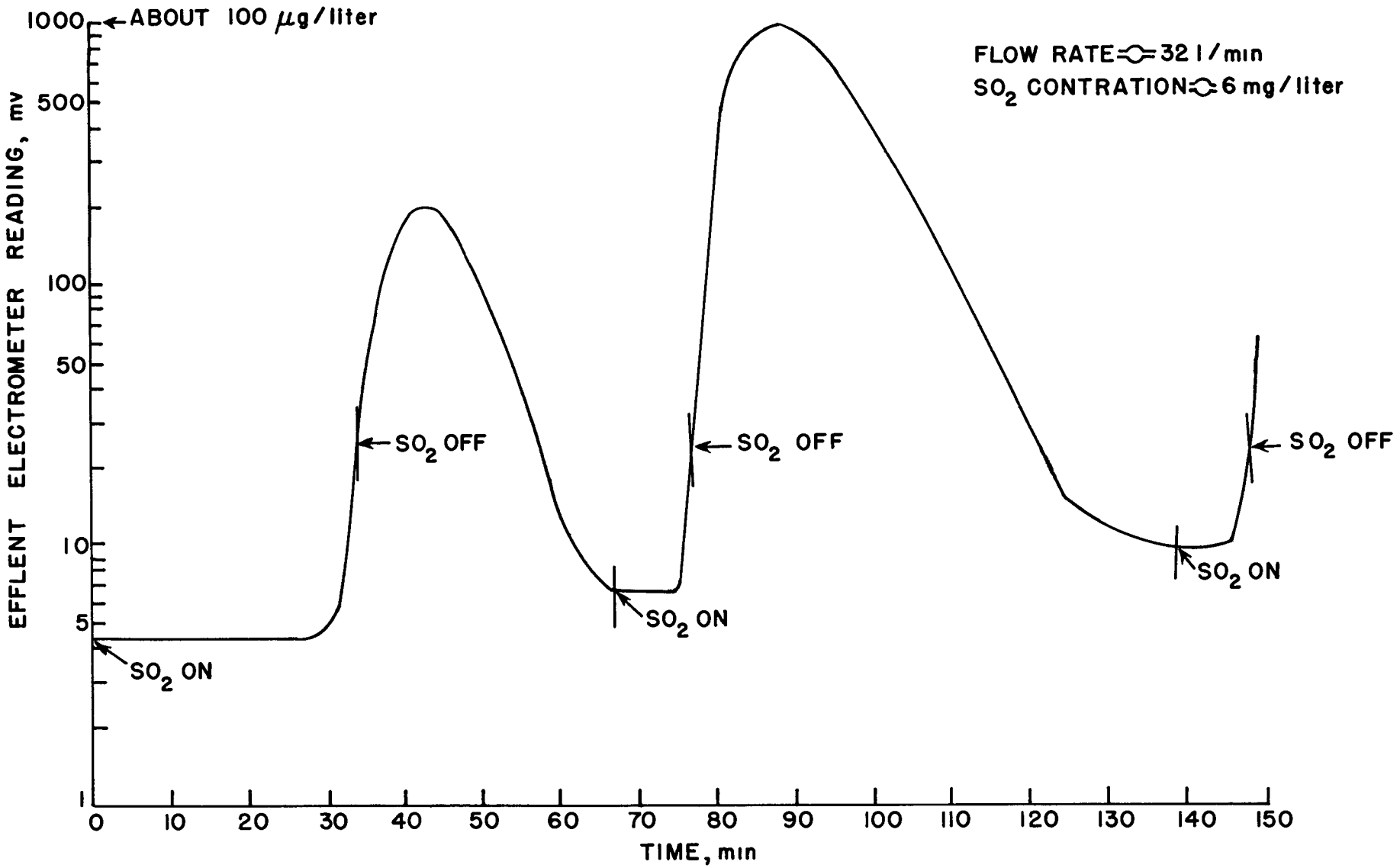

FIGURE 2 SORPTION AND DESORPTION IN A M10AI CANISTER

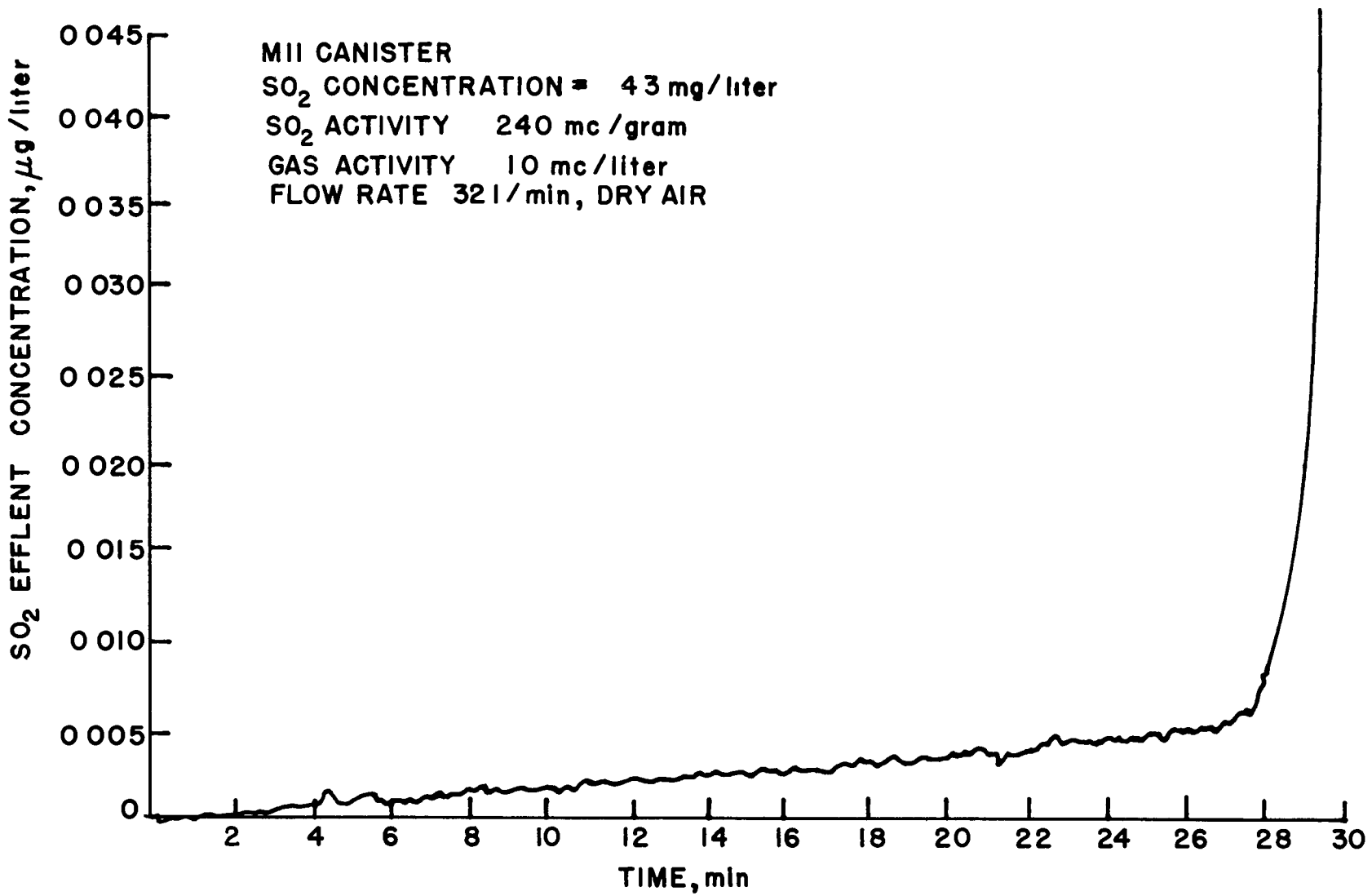

FIGURE 3 TEST OF MII CANISTER

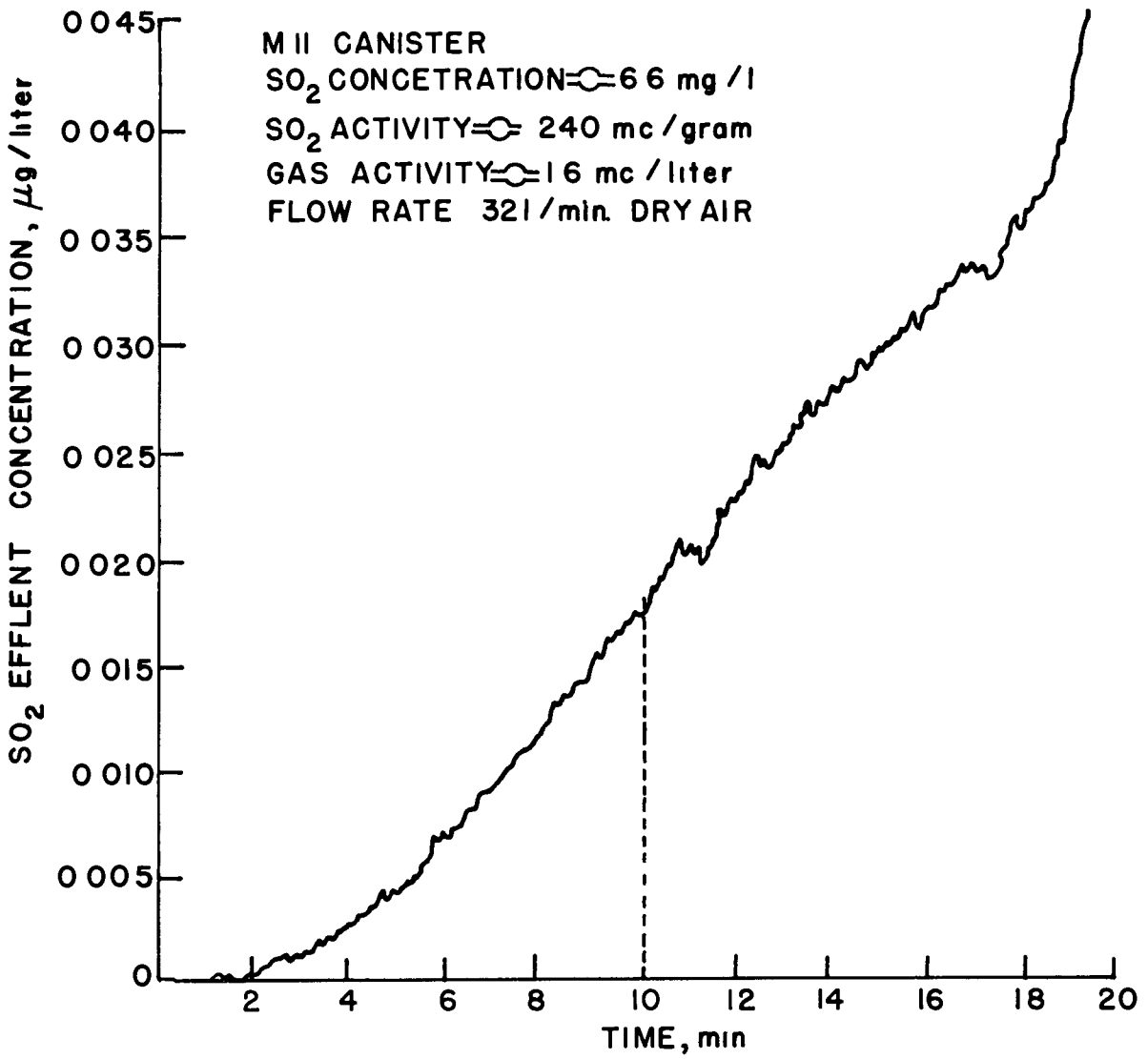

FIGURE 4 TEST OF MII CANISTER

apparent early penetration of the radioactive gas is attributed to the extremely high sensitivity of the test There is also a possibility that this penetration was due to leaks and is not related to the canister performance However, in either case, it may be stated that the canister efficiency is over 99 998% for the first 20 minutes of the test

The flow ionization chamber used in this work, offers several interesting possibilities in development of new techniques of canister testing The ionization chamber basically detects ionized air Air ions have an appreciable half-life This was demonstrated by pulling room air across a piece of uranium metal and then through four feet of saran tubing into the ionization chamber This caused a high reading of the electrometer, and when the metal was removed from in front of the tube, the reading dropped back to normal It was further shown that a gas mask canister would remove the ions Presumably a defective canister would allow penetration of ionized air It may therefore be possible to use ionized air as a test agent for filter paper and/or charcoal beds This may allow a rapid, inexpensive test without injuring the item tested in any way The value of the test of course would have to be determined experimentally

Another possible application of the flow ionization chamber is its use to determine if a canister previously used in radioactive gases or aerosols is still serviceable This would be done by passing room air into the canister and thence through the ionization chamber If the chamber shows the presence of ions, then it is evident that either (1) a radioactive gas or aerosol is penetrating the canister or (2) the sorbed radioactive gas has penetrated sufficiently far in the charcoal bed so that the ions produced by its radiation penetrate the remaining charcoal layer A gamma emitter sorbed in the canister would cause complications but these probably could be overcome by proper testing technique It may therefore be possible to develop a rational procedure for accepting or rejecting canisters which have been used in radiological work This procedure if successful, would have the important advantage of detecting an approaching canister breakdown before the actual breakdown occurs

Conclusions

A canister test method applicable to tests with radioactive sulfur dioxide and other radioactive gases has been developed Penetrations as low as 10^{3} μg/liter may be estimated

The M11 canister was found to be over 99 998% efficient against radioactive sulfur dioxide, 1 millicurie per liter

Recommendations

It is recommended that (1) a study be made of the application of ionized air to charcoal bed or filter testing, (2) the possibility of using the flow ionization chamber in radiological work to detect approaching canister breakdown be investigated

APPENDIX I

PREPARATION OF RADIOACTIVE SULFUR DIOXIDE

Flow Diagram

A flow diagram of the apparatus is shown in Figure 5 Air at about 2 liters per minute is dried and passed into the burner producing SO_2 and a small amount of SO_3 The aerosol canister shown is made by the Chemical Corps and consists of two layers of Type 6 paper in series This canister together with the ice-water bath traps out SO_3 from the SO_2 air gas stream [8] To condense out the sulfur dioxide two cold traps are used The first contains chloroform at its freezing point, -63°C The second contains freon-12 at about -130°C The $CHCl_3$ bath is prepared by cooling about 3 liters of $CHCl_3$ with liquid nitrogen This is continued until roughly 25% of the $CHCl_3$ has frozen The resulting chloroform ice is soft and does not tend to break the pyrex condenser (bulb 50 ml capacity) immersed in the bath Freon-12 CCl_2F_2 for the second bath may be obtained from a standard commercial cylinder Gas from the cylinder is passed into the bottom of a 4-liter Dewar filled to the top with lumps of dry ice This liquifies some of the gas (b p - 28°C) The dry ice may now be removed and the freon cooled to -130°C with liquid nitrogen The second SO_2 condenser used in this bath has a capacity of about 500 ml The "M10A1" canister shown is a standard type made by the Chemical Corps It is used to prevent radioactive SO_2 from entering the vacuum system The SO_2 cylinder used for storing the gas is a commercial type [9] A small Hoke value was connected to the top of the cylinder A mercury manometer is provided for observing pressure changes when transferring SO_2 from the condensers to the cylinder

Burner

The burner detail is shown in Figure 6 This is made entirely of Pyrex except for the quartz mantle The mantle is about 25 cm long and 5 cm in diameter and is wrapped with 20 ft of Nicrome V wire The total resistance of the wire is about 30 ohms At 120 volts the heating wire gives an output of about 500 watts To provide insulation the outside of the mantle was wrapped with Fiberglass The vaporizer which fits inside the mantle has a capacity of about 4 grams of sulfur

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8 Thomas, J W "Filtration of SO_3 Gas Molecules by Type 6 Paper," ORNL-Y-685 November 9 1950

9 "Lecture Bottle" made by Matheson Co East Rutherford N Y This cylinder is made to hold one pound of SO_2

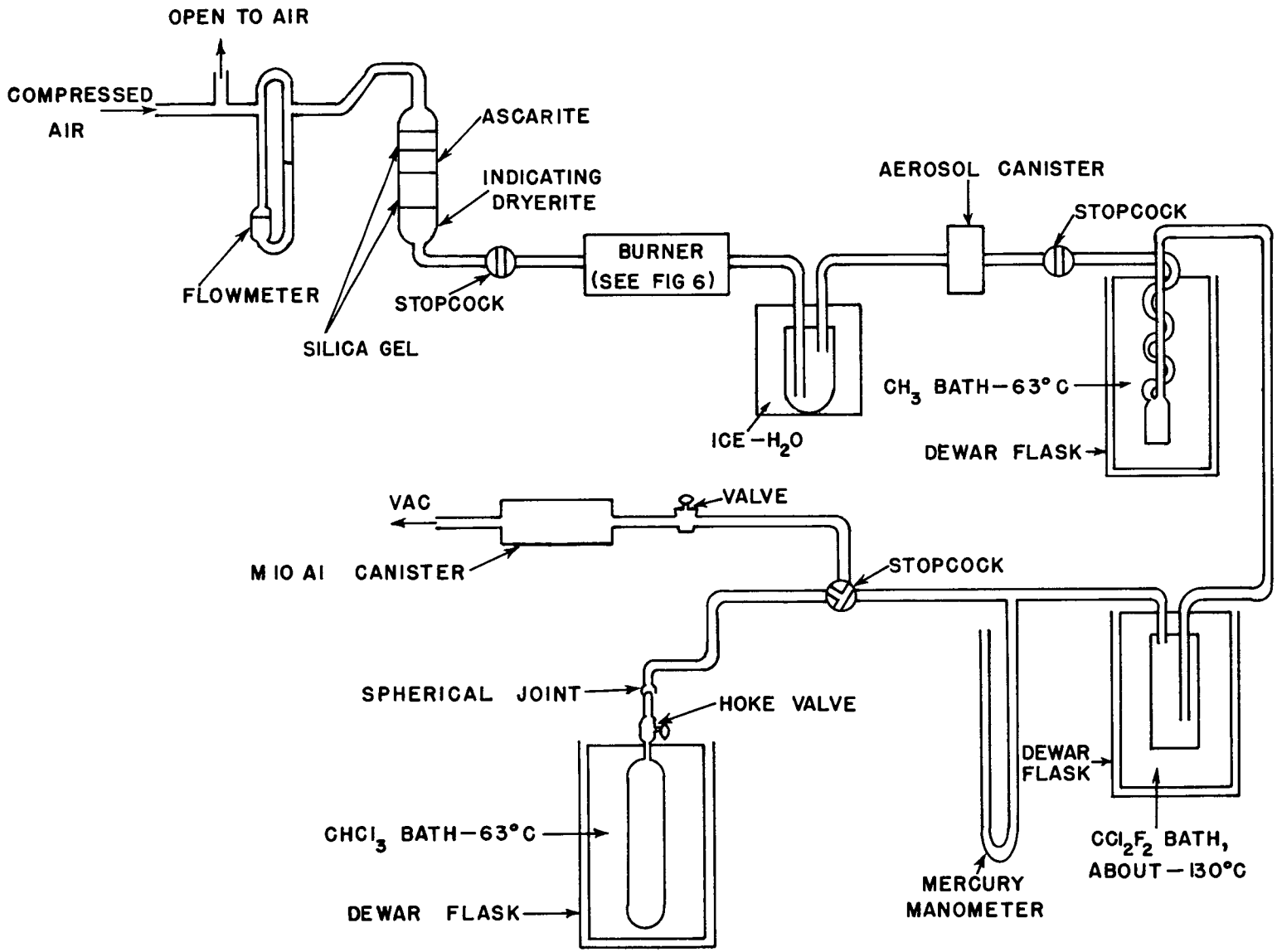

FIGURE 5 FLOW DIAGRAM, SO_2 APPARATUS

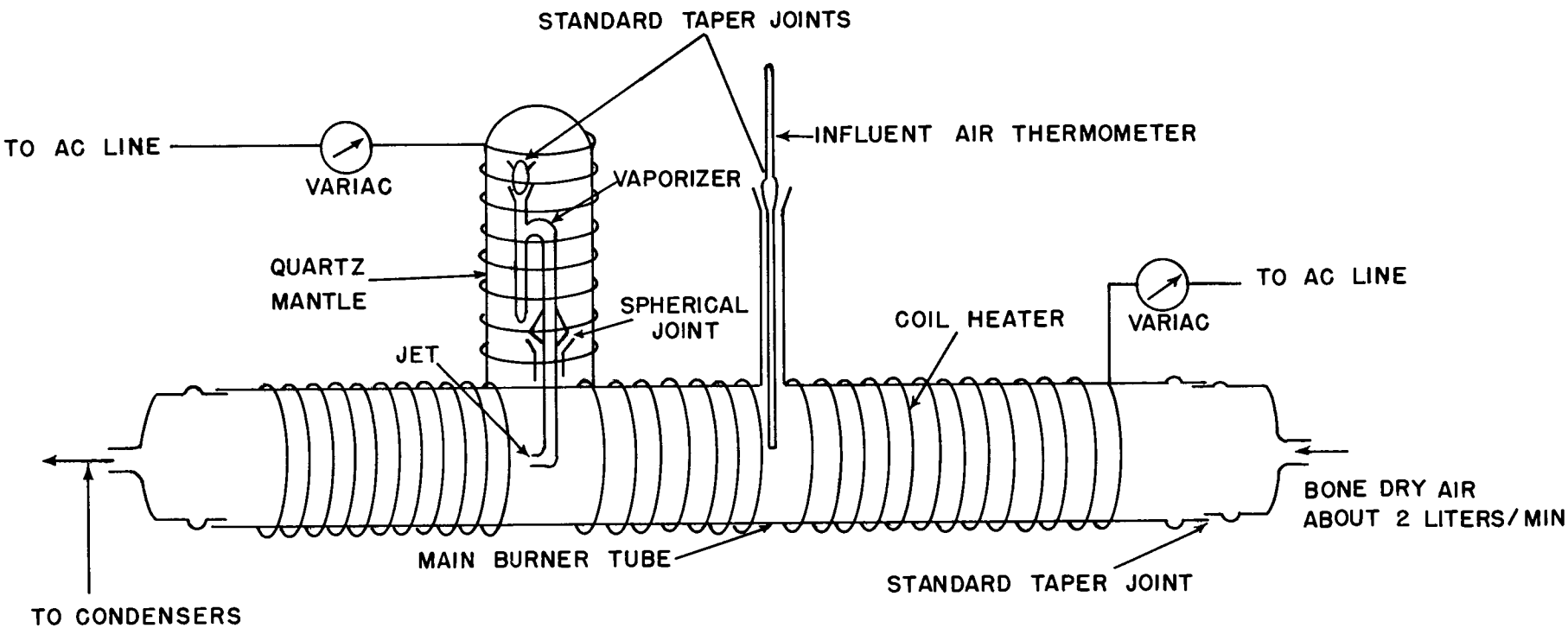

FIGURE 6 SULPHUR BURNER DETAIL

The main burner tube was also wrapped with Nichrome wire and covered with Fiberglass insulation The wattage was not measured but was probably about 500 watts at 120 volts The length of the main burner tube between the tapered joints was 40 cm, 5 cm diameter

Procedure

Before starting a run the vaporizer is filled with 2 to 4 grams of radioactive sulfur and the entire apparatus swept out with dry air The cooling baths are brought to operating temperature, and the main burner tube heaters turned on so that the influent air at 2 liter/min attains a temperature of about 300°C The three-way stopcock is of course turned so the flow is through the protective canister to the vacuum line

To start the run the variac controlling the mantle is turned up at a slow rate about 5 volts per minute until a flame of burning sulfur vapor is observed at the jet of the vaporizer The mantle variac is controlled to keep this flaming jet about 2-3 cm long After 20 or 30 minutes all of the sulfur is burned and the stopcock between the condensers and aerosol canister is closed The three-way stopcock is turned to connect the cylinder with the condensers and a vacuum of about 450 mm Hg draw on the system to allow for subsequent expansion of air in the condensers The cooling baths are removed from the condensers allowing SO_2 to distill over into the cylinder The rate of transfer of SO_2 is controlled by observing the mercury manometer, and recooling the condensers momentarily if necessary Toward the end of the process liquid nitrogen is poured over the cylinder and the condensers immersed in hot water to drive over practically all of the SO_2 in the condensers

Efficiency of Process

The efficiency of the burning process alone was determined by absorbing the effluent in iodine solution instead of condensing and storing the gas in a cylinder Two bubblers were used to absorb the gas The first contained 200 ml of 1N iodine and the second 100 of 0 01N sodium thiosulfate The thiosulfate bubbler absorbs any iodine volatilized by the iodine bubbler The charge to the burner vaporizer was 3 05 grams of sulfur The theoretical yield of sulfur dioxide was therefore 6 10 grams The yield as determined by titration of the iodine solution was 5 81 grams an efficiency of 95% for the burning process alone

During transfer of the gas from the condensers to the cylinder a small amount of air is trapped in the cylinder Analysis of the contents of several cylinders by iodine absorption showed that the gas contained therein was about 95% SO_2

During the preparation of radioactive SO_2 of high activity (about 300 mc/gram of SO_2) the efficiency of the entire procedure was estimated The charge to the burner was 3 84 grams of sulfur The weight gain of the cylinder was 7 68 grams a gross yield of 87 7% Assuming 95% purity, as had been obtained previously the true yield of SO_2 was about 83% of theoretical

Discussion

Several difficulties were encountered in the development of the procedure given here The chief difficulty was the formation and escape of unburned sulfur aerosol This usually occurs unless the incoming air is heated somewhat above the ignition point of sulfur 250°C Also, it is obviously necessary to maintain an excess of air in the burning area The pyrex vaporizer tended to melt out of shape and the use of quartz would be desirable In the condensation of the sulfur dioxide a very small amount of water vapor will give trouble If the air stream is not bone dry condensation and freezing of water will occur in the 6 mm I D coils of the first SO_2 condenser perhaps causing a stoppage of the air flow However proper operation of the apparatus of Figures 1 and 2 virtually eliminates these difficulties and an overall yield of 80-85% is readily obtained

Recently H R Bronstein of this laboratory has designed another sulfur burning apparatus designed to use oxygen from a cylinder instead of air and operated at a much slower burning rate with smaller condensers This apparatus has been operated to give yields over 95% but the procedure requires a longer operating time

If any more work is to be done it is recommended that (1) the burner be made entirely of quartz (2) oxygen be used instead of air (3) the flow rate be reduced (4) smaller condensers be used