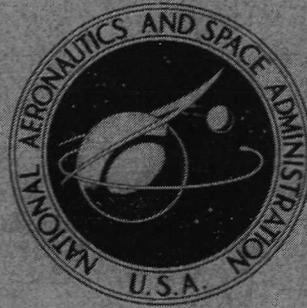


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POTASSIUM PERMANGANATE FOR
MERCURY VAPOR ENVIRONMENTAL CONTROL

by David E. Kuivinen
Lewis Research Center
Cleveland, Ohio 44135

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16. Abstract Potassium permanganate (KMnO ₄) has been evaluated for application in removing mercury vapor from exhaust air systems. The KMnO ₄ may be used in water solution with a liquid spray scrubber system or as a solid adsorber bed material when impregnated onto a zeolite. Air samples contaminated with as much as 112 mg/m ³ of mercury have been scrubbed to 0.06 mg/m ³ with the KMnO ₄ impregnated zeolite (molecular sieve material). The water spray solution of permanganate was also found to be as effective as the impregnated zeolite. The KMnO ₄ impregnated zeolite has been applied as a solid adsorber material to (1) a hardware decontamination system, (2) a model incinerator, and (3) a high vacuum chamber for ion engine testing with mercury as the propellant. A liquid scrubber system has also been applied in an incinerator system. Based on the results of these experiments, it is concluded that the use of KMnO ₄ can be an effective method for controlling noxious mercury vapor.			
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POTASSIUM PERMANGANATE FOR MERCURY VAPOR ENVIRONMENTAL CONTROL

by David E. Kuivinen

Lewis Research Center

SUMMARY

Mercury vapor in exhaust emissions can be effectively controlled by potassium permanganate, a strong oxidizer. The potassium permanganate may be added to water and used in a conventional spray scrubber system, or it may be impregnated in a zeolite material and used as a solid adsorber material in a packed filter bed. In experimental studies of these applications, both the solid material and the liquid spray systems were virtually 99 percent efficient for mercury vapor removal.

The impregnated zeolite (molecular sieves) has been applied successfully to research exhaust systems using mercury, a mercury decontamination system, and an incinerator. A water spray scrubber using a solution of potassium permanganate has also proven to be successful when applied to the incinerator. Mercury contaminated software, rags, protective clothing, and paper may be safely burned without releasing toxic mercury vapor to the atmosphere.

INTRODUCTION

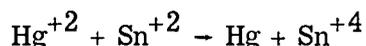
The discovery of excessively high levels of mercury in fish resulted in the closing of Lake St. Clair to commercial fishing on March 24, 1970, by the Canadian Department of Fisheries. The closing of Lake St. Clair and the subsequent commercial fishing ban placed on Lake Erie by the State of Ohio has dramatized the continuing hazard of mercury poisoning. The general public has as a result become more aware of mercury and its compounds as potential health hazards. Contaminated food is one source of accidental mercury poisoning; however, other sources may be mercury contaminated water and air.

The public is also exposed to mercury because of its use in various medicines (merthiolate, mercurochrome, diuretics), dental amalgams (fillings), clinical and household thermometers, electrical switches, fluorescent lamps, flashlight batteries, and pesticides. Laboratory personnel encounter the use of mercury in manometers,

McLeod vacuum gages, mercury vacuum diffusion pumps, amalgamation processes, and many laboratory chemicals. Industrial processes, such as chlor-alkali production, pesticide and herbicide production, and many other processes, generate waste mercury that finds its way into waste water systems and exhaust air stacks. Because mercury vapor is considered toxic, the American Conference of Governmental Industrial Hygienists (ACGIH) has established the Threshold Limit Value (TLV) at 0.05 milligram per cubic meter of air (ref. 1) for an 8-hour exposure.

NASA's Lewis Research Center has a continuing concern for the safe control of research exhaust emissions that may contain mercury vapor. This Center has pioneered research on electric rocket engines that use mercury as a propellant (e.g., the electron bombardment ion engine). Ion thruster research and other programs using mercury must control the safe release of mercury vapor through conventional exhaust systems. Improved methods for the control of mercury vapor are under study at the Center to protect personnel and the public from exposure to the vapor.

This report will discuss the application of potassium permanganate (KMnO_4) as a material for controlling mercury vapor from exhaust systems. The Federal Water Quality Administration (ref. 2) suggested the use of KMnO_4 in a water/acid solution to scrub mercury from the exhaust of an atomic absorption spectrophotometer used in the analysis of water samples for mercury. A bubbler type of scrubber (containing the KMnO_4 solution) was added to the exhaust of the instrument as a safety feature to protect the analyst from the toxic vapor. The analytical procedure for detecting mercury in water samples creates mercury vapor by relying on the reduction of the bivalent Hg^{+2} to elemental Hg using stannous sulfate as the reducing agent. This reduction is shown in the following equation:



The free mercury is aspirated from the reduced solution into an air stream and carried into the spectrophotometer where it is detected. The exhaust gas containing the mercury is passed through the bubbler scrubber to remove it from the gas. In order to verify that the scrubber solution actually worked to remove mercury vapor, the bubbler was placed upstream of the spectrophotometer. No mercury was detected from purposely mercury seeded water samples as the solution absorbed the mercury before it reached the instrument. The $\text{KMnO}_4/\text{H}_2\text{SO}_4$ solution was considered worthy of a larger scale investigation in a pilot study program. The pilot program consisted of testing KMnO_4 in different matrix materials to find more convenient forms for control applications. The materials considered in the pilot tests were (1) $\text{KMnO}_4/\text{H}_2\text{SO}_4$ in water solution, (2) crystalline KMnO_4 , and (3) KMnO_4 treated molecular sieve zeolite. If the materials were found capable of removing large concentrations of mercury, they were then

tested in a scrubber section connected to the exhaust of an incinerator. Mercury contaminated software, such as rags, paper, and protective clothing, was burned in the incinerator. The resulting mercury vapor was passed through the scrubber with the other exhaust products to remove the mercury. This report covers both the pilot program and the incinerator test program with quantitative results taken from the incinerator tests. Included in these results are samples taken from a prototype solid adsorber filter bed used in a mercury ion engine test facility.

MATERIALS

Potassium Permanganate Scrubber Solution

A sufficient amount of technical grade potassium permanganate (KMnO_4) was dissolved in warm water to make approximately a 0.2 percent by weight solution (2 g/liter). This concentration is not critical. However, care must be taken to avoid coming into direct contact with KMnO_4 because it is a powerful oxidizer. Rubber gloves, face shield, and protective clothing should be worn when handling the material, both as dry crystals and in water solution.

Potassium Permanganate Impregnated Zeolite

A sufficient amount of technical grade KMnO_4 was dissolved in warm water to make a 0.5 percent solution by weight (5 g/liter). Carefully add 3.2- or 1.6-millimeter (1/8- or 1/16-in.) pellets of 5A or 13X molecular sieve material to the KMnO_4 solution to absorb the KMnO_4 into the pellets. This was accomplished by using a wire screen basket to contain the pellets. The pellets were soaked for about 5 minutes and then removed from the solution. The pellets were transferred to an open pan and oven dried at 378 K over night. The quantity of material prepared was determined by the size of the filter bed needed. Much heat was evolved when the dry pellets were added to the solution; therefore, one should wear protective clothing, a face shield, and gloves. It was necessary to wear a particulate filter mask when sieving the dried pellets to remove any permanganate fines that may have been created in the process. The material was then packed into a filter. A 9.16-centimeter (4-in.) bed depth was a convenient depth for this material. It was necessary to sandwich the treated zeolite between two 2.54-centimeter (1-in.) layers of untreated molecular sieves to prevent KMnO_4 bleeding.

APPARATUS

Atomic Absorption Spectrophotometer

An atomic absorption (AA) spectrophotometer was used for the detection of mercury vapor in the laboratory evaluation of the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ bubbler scrubber (figs. 1 and 2). It was subsequently used also in the pilot test program evaluation of the various forms of KMnO_4 studied. In the analysis of water samples for mercury, a conventional AA spectrophotometer was modified to accept a gas absorption cell (100 mm long by 10 mm in diam, with quartz windows). The cell was placed in the optical light path of the spectrophotometer. The inlet of the cell was connected to a 100-milliliter sample bottle which has a sintered Pyrex aspirator tube. The sample bottle was connected to a flowmeter (0 to 2500 cm^3/min) and a compressed air cylinder. The outlet of the cell was connected to a bubbler scrubber containing a solution of KMnO_4 and H_2SO_4 (fig. 1).

The spectrophotometer was used as a mercury vapor detector when elemental mercury (either obtained from a reduced water solution or as free Hg) is carried by air to the absorption cell where the mercury vapor absorbs ultraviolet (UV) radiation from a mercury hollow cathode lamp. The absorption is measured by a photomultiplier adjusted to the 253.7-nanometer wavelength of mercury. The amount of mercury present is proportional to the UV radiation absorbed. The flow rate of compressed air used for aspiration of the samples was 1000 cubic meters per minute. The instrument had a sensitivity for mercury at 0.05 milligram per cubic meter.

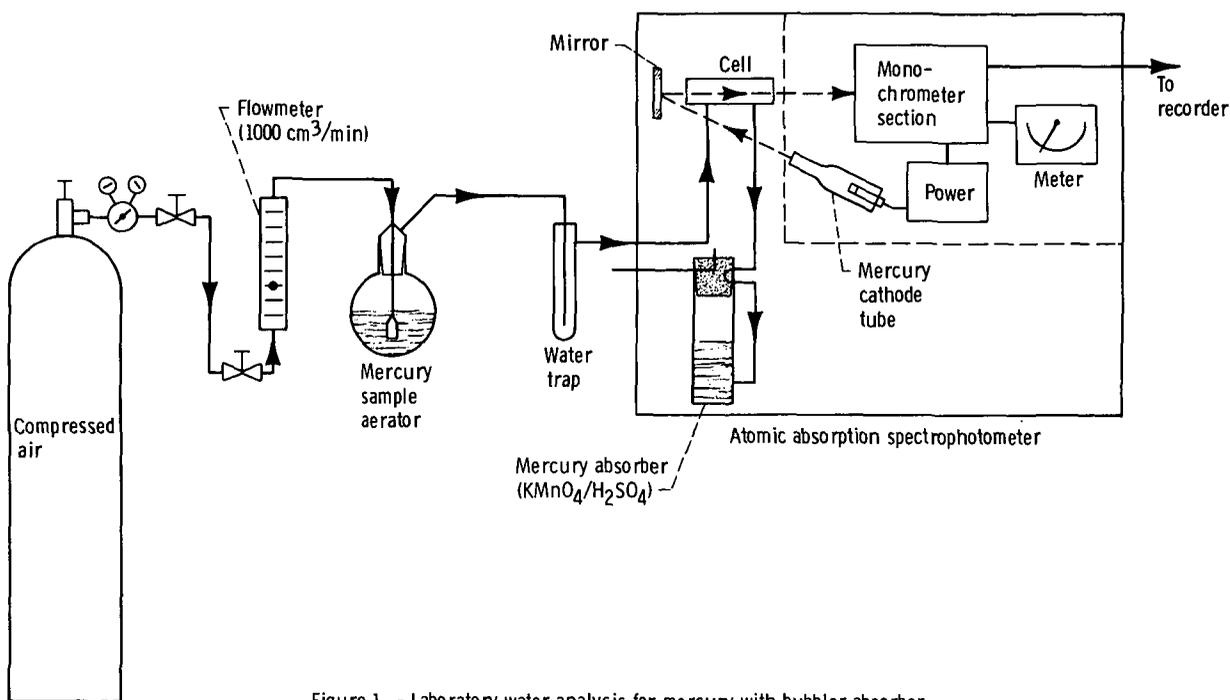


Figure 1. - Laboratory water analysis for mercury with bubbler absorber.

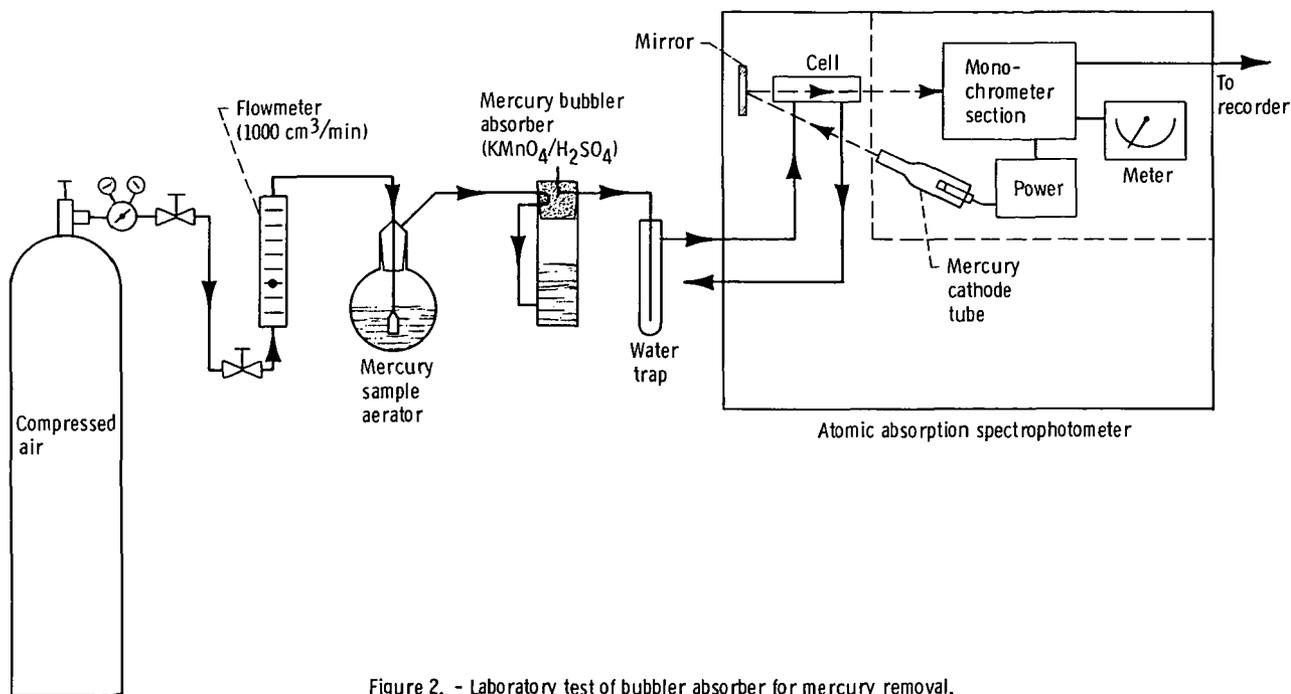


Figure 2. - Laboratory test of bubbler absorber for mercury removal.

Mercury Analyzer System

The Coleman Mercury Analyzer (Model MAS50) was used for the analysis of air samples taken from the incinerator test program and the research exhaust systems. The Coleman instrument was used because of its convenience of being portable. The instrument consists of a closed-loop circulating air system (with pump), a gas absorption cell (150-mm long), an ultraviolet (UV) mercury vapor lamp light source, and a UV sensitive phototube (253.7 mm). The range of the instrument is 0 to 9 micrograms of mercury with a 0.01-microgram sensitivity. Mercury is reduced from a water solution with stannous chloride and is aspirated into the air stream. Its UV absorption is measured by the phototube as it enters the cell. Air samples are passed through a 100-milliliter volume of $\text{KMnO}_4/\text{H}_2\text{SO}_4\text{-HNO}_3$ treated water to collect the mercury. The sampling system is described in the next section. Air samples of 1-liter size were used for the analysis.

Air Sampler System

The air sample system was used for taking samples of combustion air from the incinerator test program and from a mercury engine test facility. The air sampler sys-

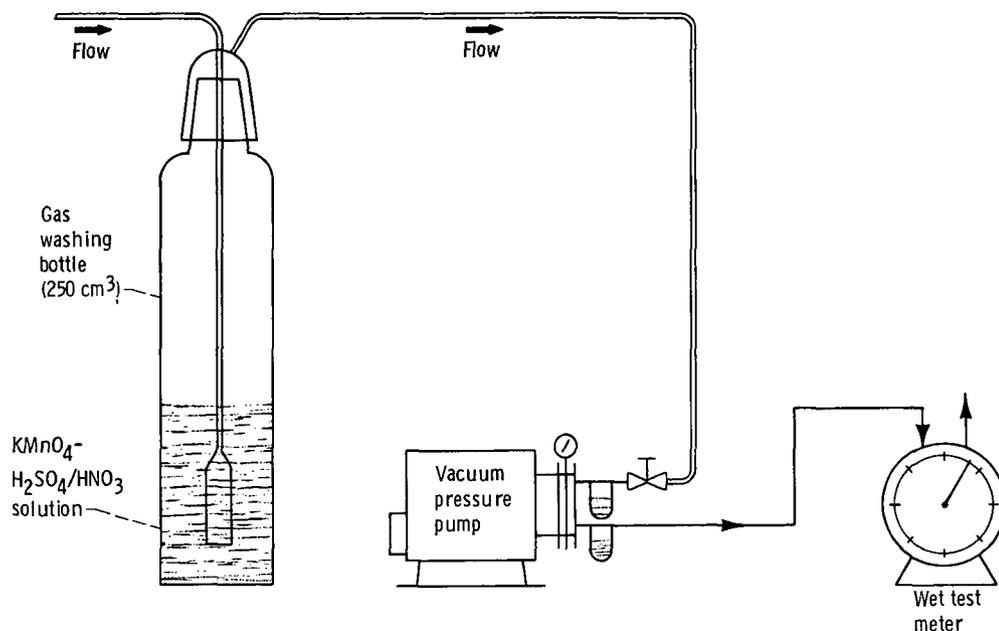


Figure 3. - Mercury sampler system.

tem (fig. 3) consisted of a 250-milliliter gas washing bottle (with fritted aspirator tube) connected in series with a pressure-vacuum pump and a wet test meter for measuring the volume of sample gas taken. The gas washing bottle contained an absorbant solution made up of 100 milliliters of distilled water, 5 milliliters each of 35 percent nitric acid and 50 percent sulfuric acid, and 4 drops of 5 percent KMnO_4 solution. One-liter samples of air were convenient for analytical purposes.

TEST PROCEDURE

The test programs conducted for the evaluation of KMnO_4 as a material for controlling mercury vapor are described in two sections: first, the pilot test program and, second, the incinerator test program.

Pilot Test Program

The pilot program, in general, consisted of seeding compressed air samples with mercury vapor and then passing the contaminated air through the absorbing material and analyzing the effluent for mercury. The absorbing materials studied in the pilot test program were (1) KMnO_4 in H_2SO_4 solution, (2) KMnO_4 crystals, and (3) KMnO_4 treated molecular sieve zeolite. Figure 4 shows a compressed air cylinder connected in series

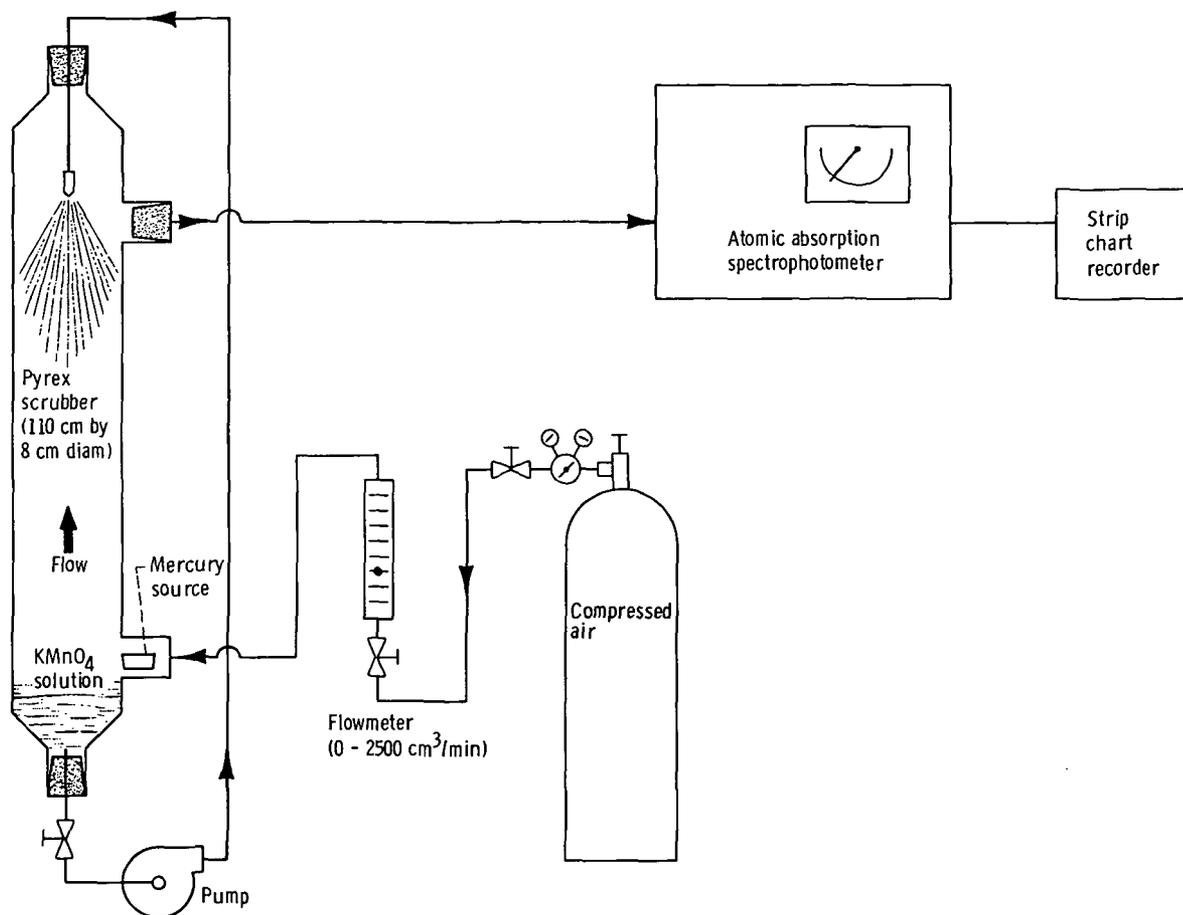


Figure 4. - Pilot program liquid scrubber.

with a flowmeter (0 to 2500 cm³/min.) and a pilot scrubber (Pyrex glass) which contained the KMnO₄/H₂SO₄ scrubber solution. The outlet of the scrubber was connected to the atomic absorption spectrophotometer which was used for the detection of mercury. A laboratory size water pump circulated the absorbing solution through the scrubber through a spray nozzle at 0.045 cubic meter per minute (12 gas/min). A piece of copper metal was heavily coated with mercury and placed at the inlet of the scrubber. The compressed air picked up the mercury from the piece of copper and carried the now contaminated air through the KMnO₄/H₂SO₄ spray and to the AA spectrophotometer for analysis. The flow rate of air that was used throughout the test programs was 1000 cubic centimeters per minute.

The experiments using the KMnO₄ crystals and impregnated zeolite used the same basic system, however, with some minor changes. First, the mercury source was moved to the outlet of the scrubber, for convenience only. The KMnO₄ solution was drained from the scrubber, and the system was rinsed with water to remove any residual KMnO₄ solution and dried. A Pyrex glass bulb (150 mm long by 50 mm in diam) was

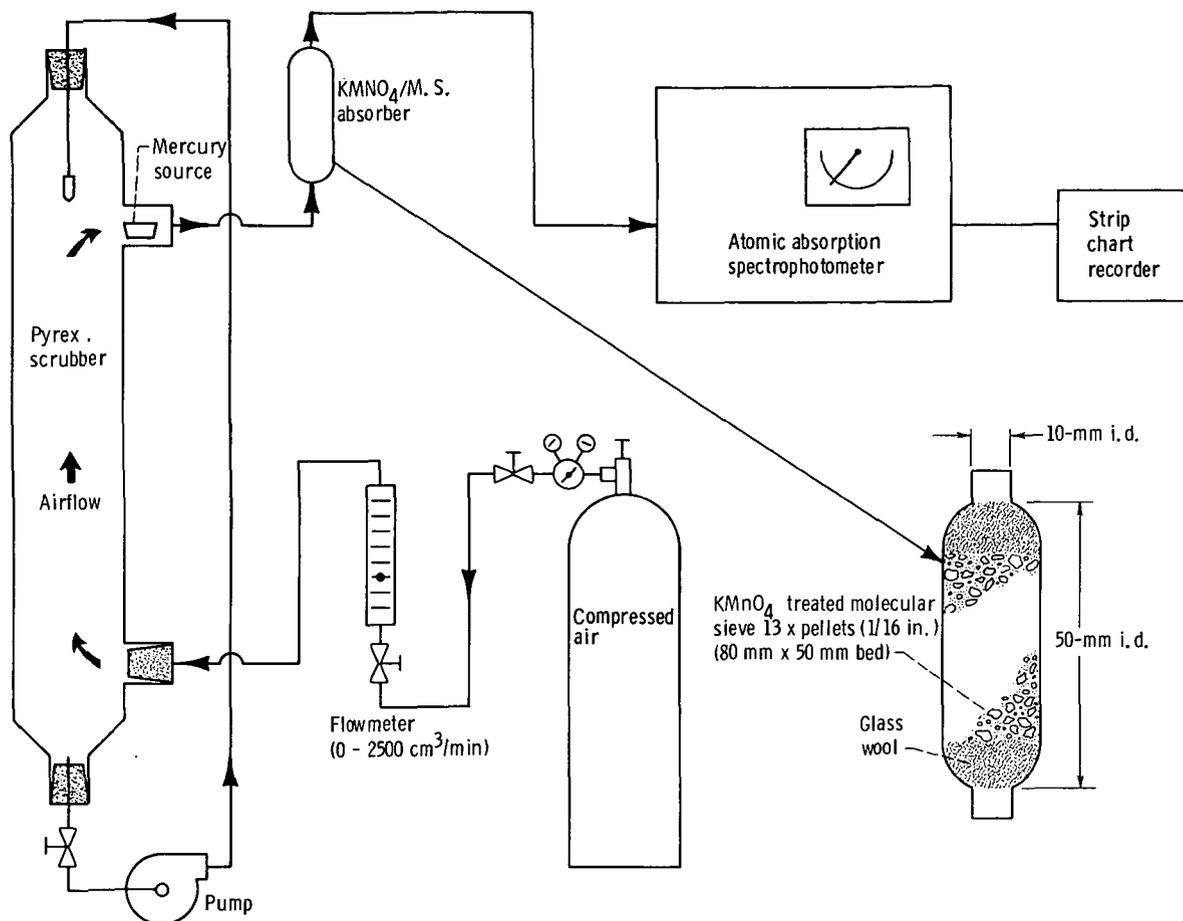


Figure 5. - Pilot program solid adsorber.

packed with KMnO_4 impregnated molecular sieve pellets (supported at both ends with glass wool). The solid adsorber bed was placed downstream of the mercury source (fig. 5) and ahead of the spectrophotometer. The crystalline KMnO_4 experiments were conducted in the same manner as the zeolite, except that a gas washing bottle (packed with KMnO_4 crystals) was substituted for the zeolite bed. The mercury content was measured before and after the scrubber. When the liquid scrubber was used, the influent gas analyses were made by turning off the water spray system. In testing the solid packed scrubbers, the influent samples were taken before the adsorbers were placed in the flow system.

Incinerator Test Program

The incinerator test program was conducted for the purpose of evaluating the feasibility of using permanganate to scrub mercury from combustion products. The purpose

of the incinerator was to burn paper, rags, and protective clothing which had become contaminated with mercury. The mercury-laden combustion products would be vented through the scrubber, removing mercury and particulates. The test program consisted of evaluating a spray system using 0.2 percent KMnO_4 solution and a solid filter bed packed with KMnO_4 impregnated molecular sieve zeolite.

The "incinerator" was fabricated from a 55-gallon barrel (fig. 6) with a grating for the support of the combustible materials and an open bottom for natural draft. The incinerator's exhaust flue was vented to the scrubber.

The scrubber section was also constructed from a 55-gallon barrel that acted as a spray plenum. The plenum was vented through a 30.6-centimeter exhaust duct that housed the filter bed and water demister. The filter bed (10.15 cm deep by 30.6 cm in diam) was packed with ceramic saddles, and the water demister (also 10.15 cm deep) was packed with stainless-steel wool. The scrubber's spray system was a closed loop that had a separate tank for both a sump and mixing tank. Spray nozzles were located

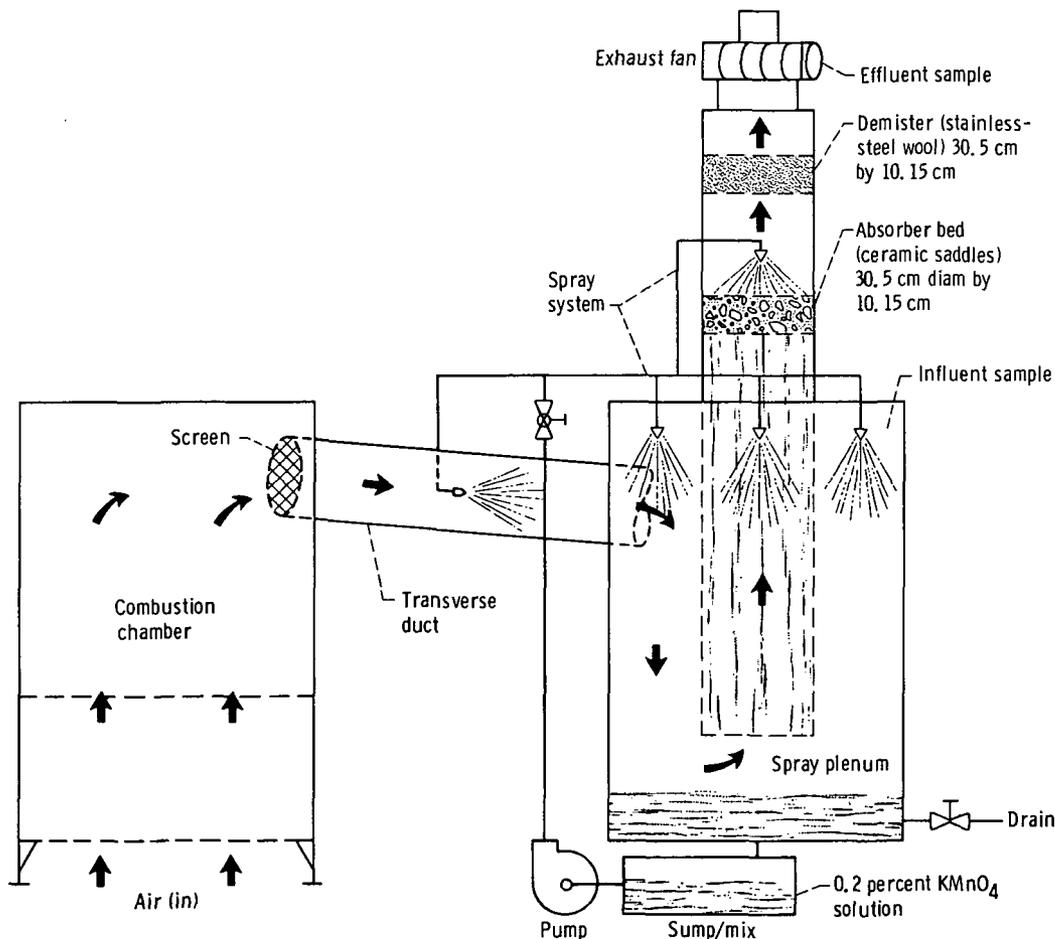


Figure 6. - Incinerator-liquid scrubber assembly.

circumferentially around the base of the exhaust duct on top of the plenum, within the transverse duct, and between the demister and absorber bed. The spray system was used for cooling the combustion products and absorbing the mercury vapor.

The incinerator scrubber system was evaluated by vaporizing mercury in the combustion unit by use of a propane torch directed onto a small can that contained mercury. Mercury contaminated rags and paper were also burned in the incinerator to evaluate the scrubber.

The KMnO_4 impregnated molecular sieve material was evaluated by using the same basic system, with only minor changes (fig. 7). First, all of the spray nozzles were removed with the exception of the spray within the transverse duct, which was then connected to the public water supply. The water pump and mixing tank were also removed. The scrubber plenum acted only as a collection tank for the cooling water. Second, the demister and the absorber sections were interchanged in position. The ceramic material was replaced with dry impregnated zeolite. The system was tested in the same manner as the liquid system using vaporized mercury from a heated source and with combustible materials.

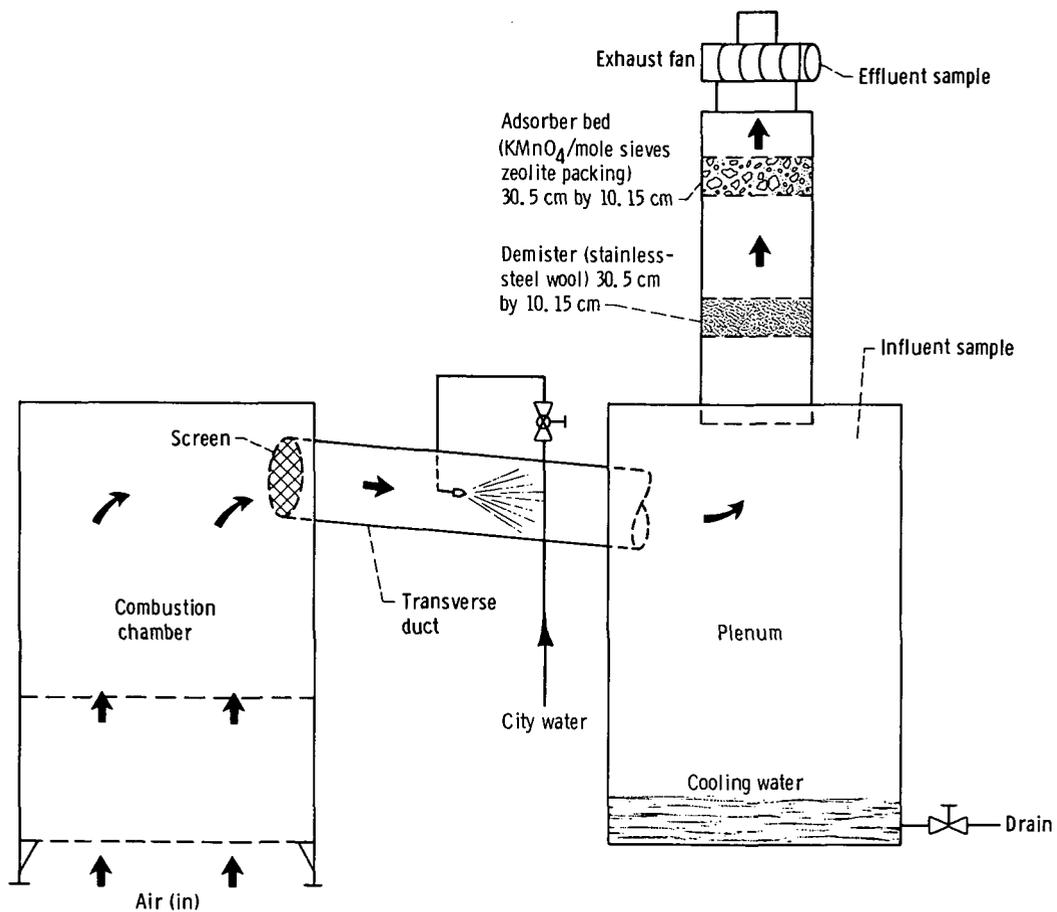


Figure 7. - Incinerator-solid adsorber assembly.

The sampling procedures used for the two incinerator test programs consisted of sampling the effluent gases at the exhaust fan, and the influent samples at the scrubber barrel section through a top penetration. The samples were taken by use of the gas sampling system described in the APPARATUS section of this report and analyzed by use of the Coleman Mercury Analyzer. One-liter samples were convenient for the analyses.

RESULTS AND DISCUSSION

The three mercury absorbing systems tested in the pilot study program were evaluated to determine overall effectiveness. The concentration of mercury vapor was estimated to be 20 milligrams per cubic meter. A quantitative measurement was not made on the mercury saturated air sample because the atomic absorption spectrophotometer gave an OFF scale reading when exposed to the saturated air. The lower detection limit, however, for the instrument was 0.05 milligram per cubic meter. When each material was tested, no mercury was detected in the effluent air samples, indicating an apparent absolute absorption. Because the results were simply "go" or "no go," they do not appear in the tables.

One problem occurred in the use of sulfuric acid (H_2SO_4) with the water solution of $KMnO_4$. Excessive corrosion was noted in the liquid pump and the spray nozzle, and both were made of mild steel. The water solution was retested without the use of the acid and was found to be just as effective in removing mercury.

The success of these simple tests led to further investigation using the $KMnO_4$ system with an incinerator equipped with a scrubber section. A prototype filter bed packed with $KMnO_4$ impregnated zeolite was also tested in a field application. Crystalline $KMnO_4$ was not further evaluated in the larger scale tests because it presented hazards in handling and was unsafe for any incinerator application.

The results of the incinerator test program using the treated zeolite adsorber are found in table I. The concentration of mercury vapor and the effluent results were made by using the portable Coleman Mercury Analyzer with the mercury sampler shown in figure 3. The mercury vapor was absorbed in a solution of $KMnO_4$ treated with nitric and sulfuric acids. It was found that the plastic sample tubing gave background concentrations of mercury when only clean air passed through the sampler system. These results are subtracted from the effluent results to give the actual mercury found in the effluent gases (see table I). The apparent mercury found in these background samples was attributed to solvent volatiles coming from uncured plastic tubing. Purging for 5 to 10 minutes with clean air would often clean up the tubing. The results of the solid zeolite material showed that mercury levels from an average of 55 milligrams per

TABLE I. - PERMANGANATE IMPREGNATED ZEOLITE FOR
MERCURY VAPOR REMOVAL INCINERATOR TESTS

Mercury taken, mg/m ³	Mercury from zeolite effluent, mg/m ³	Mercury back-ground tygon, mg/m ³	Effluent mercury, mg/m ³
60	2.2	1.3	0.9
55	.7	.6	0
55	.8	.6	.2
55	1.8	1.5	.3
55	2.7	1.5	1.2
^a 112	^a .06	---	^a .06

^aThese samples were taken from research system containing several hundred pounds of mercury.

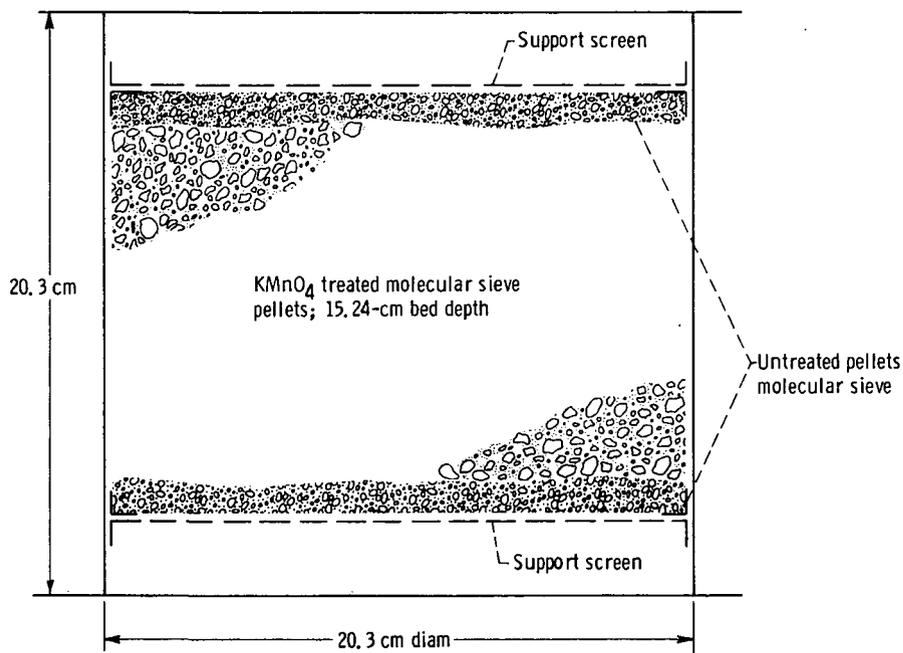


Figure 8. - Potassium permanganate (KMnO_4) treated molecular sieve pellets.

cubic meter were reduced to 1.2 milligrams per cubic meter and less.

The results of samples taken from a mercury test facility that had a treated zeolite prototype scrubber were included in table I. The mercury saturated air system contained 112 milligrams per cubic meter, and the adsorber reduced the level to 0.06 milligram per cubic meter. Rubber tubing was used for sampling this system, and no background concentrations were found. These samples were determined by the AA spectrophotometer. The filter was 15.25 centimeters deep by 20.3 centimeters in diameter (fig. 8).

The results of using $KMnO_4$ in the water spray scrubber for the incinerator program are shown in table II. Mercury levels from about 50 milligrams per cubic meter were reduced to 0.10 milligram per cubic meter or less with lower background levels found as a result of 10-minute purges taken between samples.

TABLE II. - PERMANGANATE TREATED SCRUBBER WATER
FOR MERCURY REMOVAL INCINERATOR TESTS

Mercury taken, mg/m ³	Mercury from scrubber effluent, mg/m ³	Mercury background tygon, mg/m ³	Effluent mercury, mg/m ³
50	0.02	----	0.02
50	.1	0.05	.05
50	.15	.05	.10
15	0	0	0

CONCLUDING REMARKS

These tests prove that potassium permanganate can be an effective material for use in removing mercury vapor from contaminated air sources. Perhaps the water spray scrubber is more efficient than the solid material; however, it may require more problems in handling and result in subsequent secondary treatment of mercury contaminated water. Relevant engineering parameters, that is, pressure drop, breakthrough capacities, and useful life were not evaluated in this testing program. The author also recognizes that the solid and liquid scrubbers used in the incinerator program were not sized or designed for maximum effectiveness, but were merely used for determining permanganate feasibility.

In subsequent applications, a potassium permanganate zeolite adsorber has been used effectively on scrubbing the exhaust air of a hardware decontamination system

used for cleaning mercury contaminated parts. A spray scrubber has been applied to a clothes dryer used to volatilize mercury from clothing and cleanup rags so that they may be reused. These applications have proven that toxic mercury vapor can be removed from air systems by using potassium permanganate.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, May 18, 1972,
113-26.

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