Developing Laboratory Test Facilities to Evaluate Carbon Based Materials to Control Mercury Emissions

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ABSTRACT

Changes in carbon technology and new applications for the technology have led to the development of a research and testing facility which can be used to evaluate new carbons and formulations quickly, and at a relatively low cost. Märker Umwelttechnik GmbH has developed a testing facility that simulates the thin layer of adsorbent on a fabric filter through which a simulated flue gas can be passed. A novel development in this flue gas simulation system is the use of mercuric chloride ($HgCl_2$) instead of elemental mercury (Hg°). Most research into mercury adsorption has been conducted using elemental mercury while in most municipal waste combustors (MWCs), $HgCl_2$ makes up about 85% of the total mercury emissions.

This paper discusses the development of the test facility and describes how it is used to develop new adsorption products. A comparison of laboratory test results to actual field testing will be presented to illustrate the value of this system.

INTRODUCTION

Regulatory requirements for the control of mercury emissions are becoming ever more stringent and their implementation more speedy. In light of this fact and in response to its need to provide both timely and cost effective service its clients needs, Märker Umwelttechnik GmbH (Märker) set out to develop a testing facility to simulate the thin layer of carbon or Sorbalit® on a fabric filter. This test facility has enhanced Märker's ability to promptly and economically evaluate product formulations by replicating the actual operating conditions in the field. Typical conditions simulated include flue gas concentrations of moisture and HCl, gas temperature and fabric filter materials and layer thickness.

Because of mercury's great volatility and the variety of its binding forms, the process of controlling mercury and its compounds is a difficult one. Due to their high vapor pressures even at low temperatures, mercury and its compounds are present in the flue gas mainly as gas phase materials. Also, depending upon the quantity of chloride in the stack gas, the flue gas components, the combustion process and the operating conditions of the plant, mercury may be present in a variety of forms in the flue gas. In passage through the gas path of a plant, conversion reactions between individual species can and do take place. In addition to its elementary form, mercury is emitted mostly as $HgCl_2$ and other mercury compounds such as mercury sulfide or mercury oxide may also be present albeit to a much smaller degree. Further, mercury bound as $HgCl_2$ predominates in the flue gas of most waste combustion processes such as MWCs, MWIs and HWIs where the $HgCl_2$ component of the mercury emissions can be as much as 85% to 95% of the total. Typically for fossil fuel fired boilers, mercury bound as $HgCl_2$ is 50% or less in the flue gas.

Historically, most researchers have evaluated carbon adsorption on the basis of elemental mercury removal which Märker scientists did not believe would provide representative results of actual field conditions. Since elemental mercury by virtue of its smaller molecular size (~3.6Å) is not as easily adsorbed as $HgCl_2$ (~5.4Å) or $HgSO_4$ (~5.3Å), projections of mercury removal requirements for waste incineration processes based on the assumption that elemental mercury needed to be removed would overestimate the carbon requirement. Since open hearth coke (HOK) which is a residual coke material with a reduced surface area than activated carbon costs about DM 590/tonne ($360/ton) and activated carbon depending on activation method and impregnation method, costs from DM 1700 - DM 14,000 /tonne ($1,000 - $8,500/ton) such an assumption was both expensive and wasteful.

Therefore, Märker concluded that to determine representative total mercury emissions and removal efficiencies both in the field and in the laboratory, it is generally both sufficient and representative to detect only the $HgCl_2$ component. Further, the increase in regulatory activity with regard to acid gases and heavy metals in general and to mercury emissions specifically, increased client urgency for Märker to develop product formulations which were both effective in controlling emissions and yet economically attractive. In response to this urgent client need for optimized product formulations, and in light of the high costs and time frames associated with field testing, Märker designed a test facility specifically geared to generating mercury laden test gases and simulating field conditions so that various product formulations could be easily, effectively, and inexpensively evaluated.

TEST FACILITY DESCRIPTION

Reference test gases are essential for determining the adsorbtivity of a product formulation. The mercury test gases now available in pressure cylinders are characterized by good stability, but in some cases the indicated concentrations differ considerably from actual values. To ensure high test gas quality, a test gas generator system has been developed for accurately generating mercury in the form of $HgCl_2$. The principle of gas diffusion, in which a carrier gas (N_2 & O_2 mixture) controlled by a mass-flow regulator is conducted through a temperature-controlled gas cell, is used for this purpose. A test gas with a reference mercury content can be generated in the Märker laboratory test facility at constant conditions (temperature, volumetric flow).

The laboratory test setup allows a known quantity of mercury, as $HgCl_2$ to be passed through the substance to be tested (typically activated carbon or Sorbalit®) within a given time and the residual content of mercury exiting the test material can then analytically determined. This procedure allows conclusions concerning the adsorbtivity of individual substances to be drawn.

The laboratory test setup is designed with the following components:

- Test Gas Station: This consists of a 40 liter test gas cylinder filled with a mixture of nitrogen and 10% oxygen.
- Gas metering: The metering is performed using a Tylan instrument which operates on the basis of the thermal conductivity of gases.
- Hg metering: The metering is performed by using a hose pump to aspirate a solution of $HgCl_2$ from a glass container into a U-tube evaporator thru a Teflon tube immersed in the solution. The glass container is set onto a laboratory scale. The hose pump is set at about 0.2 g/min. The quantity of $HgCl_2$ is determined with precision by means of the difference in the laboratory scale readings at the beginning and end of a test.

- U-Tube Evaporator: This serves to evaporate the $HgCl_2$ solution, mix it with the test gas, and introduce the gas mixture into the reactor. The evaporator consists of a glass U-tube in an electrically heated oven which operates at a temperature of 640 °C. Test gas from the test gas station is heated in the first part of the U-tube and mixed with the $HgCl_2$ solution in the second part using glass wool or glass beads to facilitate evaporation of the $HgCl_2$ solution and mixing of the gases. All connections are made with standard laboratory connections.

- Adaptor: This is a glass tube wrapped in heating tape and connects the evaporator outlet to the inlet of the reaction tube via ground glass tapered joints.

- Reactor: It consists of heated enclosure which contains a reaction tube containing the substance being tested (e.g. activated carbon or Sorbalit®). The reactor chamber is heated and maintained at the desired temperature. The test substance is contained within the reactor tube as a one (1) cm thick layer imbedded between layers of densely packed quartz wool. Figure 1 is a sketch of the reactor tube which illustrates the main components. Figure 2 is a photo of the reactor tube set into the heated enclosure.

- End piece: It is attached to the reactor via a ground glass tapered joint and provides an interconnection to the adsorption bottle and is equipped with a thermowell for the insertion of a thermocouple positioned as closely as possible to the test substance layer.

- Adsorption bottle: This contains 40 ml of 10% HNO_3. The gases from the reactor are passed through the HNO_3 solution to precipitate Hg from the test gas stream.

- Gas meter: The precise test gas volume through the system is determined using a calibrated gas meter. Test gas flow is readily determined using a stop watch in conjunction with the meter readings.

Figure 3 is a photo of the test system. The $HgCl_2$ solution is aspirated by means of a gas pump and fed into the evaporator through a Teflon nozzle and mixed in a layer of glass wool or glass beads. In the evaporator, the $HgCl_2$ solution is evaporated, introduced and thoroughly mixed into the hot test gas upstream of the reactor. In the reactor, the mercury-laden test gas flows through the layer of the substance by which the mercury is adsorbed. The test gas stream containing the unadsorbed mercury is then directed into the HNO_3 solution in the adsorption bottle to precipitate mercury from the gas stream. The mercury content of this solution is determined and compared with the initial value. The degree of mercury removal by the test substance can then be calculated.

TEST PROCEDURE

Prior to testing, the reaction tube is loaded with a densely packed layer of quartz wool about three (3) cm long. Then 250 mg of the test substance together with two (2) grams of quartz sand are weighed into the reaction tube and are mixed and compressed into a dense structure using quartz wool in the tube.

The system is then prepared for the test as follows:

- The evaporator is turned on and temperature set and maintained at 640°C.
- The end piece is attached to the reaction tube which contains the previously charged test substance and a thermocouple is inserted via a thermowell fitted into the end piece.
- The adsorption bottle containing 40 ml of 10% HNO_3 is attached to the end piece.
- Prior to starting up the reactor, the cooling water supply to the reactor infrared oven must be turned on.
- The reactor infrared oven is turned on and the reactor is heated to the desired temperature (typically, 180 - 300°C). In addition for heating, the test gas feed to the gas cylinder at the main valve must be opened and set to a pressure of 1 bar.
- The test gas flow is set at 1.8 l/m using the Tylan instrument.
- When the reactor has reached the desired temperature, the test gas flow is turned off again
- The fixed setting for the $HgCl_2$ solution is about 0.2 g/m. The actual quantity pumped is precisely determined by scale reading which is set to "zero", the $HgCl_2$ solution container is set up on the scale, and the Teflon tube is connected to the hose pump.
- At the end of these preparations, the gas meter and the scale readings are noted and the values recorded.
- The Teflon nozzle is then introduced into the evaporator and the test is begun. To start a test, the test gas feed must be opened and the pump turned on.
- The duration of a test is ten (10) minutes.
- During the test, the temperature of the adaptor must be kept at 100°C and the reaction temperature constant.
- Values are logged every two (2) minutes.
- If condensation appears in the evaporator or in the adaptor, it should be removed with a hot air blower.

When the test is over;

- The pump and test gas are turned off and the Teflon nozzle is removed from the evaporator.
- The scale and the gas meter readings are noted and recorded in the test log.

- The adsorption bottle with the hose is pulled off and the frit and the hose are rinsed. The rinsing are transferred to a 100-ml measuring cylinder and the quantities noted and recorded. The rinsing are then places in a 250-ml sample bottle and labeled.
- Lastly, the reaction tube is removed from the reactor and cleaned.

As stated previously, the amount of $HgCl_2$ into the reactor is determined by weight difference of the $HgCl_2$ solution container. However, this value is confirmed for all tests by running a blank sample (i.e. with an empty reactor tube) and measuring the $HgCl_2$ concentration as though the reactor tube had been charged with reagent.

NEW PRODUCT DEVELOPMENT

The Märker test facility has greatly improved the evaluation and development process for new Sorbalit® /Sorbalime™ products by reducing both testing time and cost factors while markedly improving the reliability of the test results. Previous to Märker's development of the test facility, the most reliable source of data was gathered from the full-scale testing of a new application. Typically (and obviously), the full-scale testing method was not only very expensive by any economic measure in terms of labor and time but in that the information gathered could not be considered either typical or reproducible. The result was that the final product material was ultimately developed by the "fine tuning" of intermediate product formulations.

The development of product formulations involves variations in product carbon content, sulfur content, and product type as well as the use of a whole range of carbon sources (e.g. coconut shell, wood, coal etc.) and suppliers (e.g. Calgon and Norit). In addition, new applications requiring mercury removal continually surface which require an expeditious response by Märker from both marketing and regulatory reasons.

As a result of these pressing needs, the Märker analytical department set out to define and refine a laboratory scale analytical methodology in the new product developmental cycle rather than being required to continually "fine tune" each new product formulation on a full scale until it was optimized.

COMPARISON OF LABORATORY AND FIELD TESTING RESULTS

Table 1 is illustrative of the test results gathered using the test facility. As shown in the table, an initial test is run using a blank tube (containing no substance) to confirm that the system has been properly set up and that the reference values are as indicated.

Test 1 was performed on a test substance consisting of a 250 gram sample of Sorbalit® containing 5% open-hearth carbon. An average (over three test runs) of 6.8 micrograms (μg) of mercury (as $HgCl_2$) were passed through the test substance using the 90% nitrogen/10% oxygen carrier test gas. The average mercury (as

$HgCl_2$) exiting the test substance over the three test runs was 0.27 micrograms (μg) yielding a collection efficiency of 96.0% for the test.

Test 2 was performed on a test substance consisting of a 250 gram sample of ground up pellets of hydrated lime mixed with 5% activated carbon, 0.5% sulfur and 5% Bentonite. An average (over three test runs) of 6.8 micrograms (μg) of mercury (as $HgCl_2$) were passed through the test substance using the 90% nitrogen / 10% oxygen carrier test gas. The average mercury (as $HgCl_2$) exiting the test substance over the three test runs was 0.20 micrograms (μg) yielding an apparent collection efficiency of 97.1% for the test.

Test 3 was performed on a test substance consisting of a 125 gram sample of Sorbalit® containing 7.5% open-hearth carbon and 10% Portland cement. An average (over four test runs) of 4.02 micrograms (μg) of mercury (as $HgCl_2$) were passed through the test substance using the 90% nitrogen / 10% oxygen carrier test gas. The average mercury (as $HgCl_2$) exiting the test substance over the four test runs was 1.48 micrograms (μg) yielding an apparent collection efficiency of 63.3% for the test.

The table illustrates the variations in the test substance type and quantity as well as the mercury quantity and concentration which can be inexpensively, expeditiously simulated, and reproduced in the test facility thus enhancing Märker's ability to economically and reliably optimize its products to its clients' needs.

Since the test facility is a recent addition to Märker's technical services department, laboratory testing comparisons to field tests are limited. However, Märker has performed both laboratory and field tests for a MWC in WI Geiselbullach. The results are as follows:

Location	Operating Temperature, °C	Hg Total Quantity In $\mu g/m^3$	Hg Total Quantity Out $\mu g/m^3$	% Hg Removal
Test Facility	180	300	45	85.0%
WI Geiselbullach	200	260	13	95.0%

CONCLUSIONS

In response to regulatory requirements for the control of mercury emissions which created urgency on the part of Märker's client industries, Märker designed a testing facility to simulate the thin layer of sorbent on a fabric filter has enhanced its ability to promptly and economically evaluate product formulations in response to both its internal needs and to clients demands. Testing to date using this facility confirms that mercury laden test gases can be synthesized to simulate almost any client application. As a result, we can now quickly and economically evaluate various product formulations geared to the simultaneous control of mercury and other pollutant emissions such as HCl.

Major savings in terms of both cost and time, together with test results which are more reliable and representative are the hallmark for the use of the Märker test facility. The typical cost for performing a test in the Märker test facility is in the range of $600 - $1,000 per sample while the cost of performing mercury tests in the field is in excess of $10,000.

Test results of various formulations have provided valuable information concerning the effectiveness of using open-hearth carbon, activated carbon, Portland cement, Bentonite and various sulfur compounds. The test facility's ability to test these product formulations and vary the amounts as well as the types of additives has enhanced client confidence in Märker's products to provide them with effective emissions control coupled with quantifiable cost savings.

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Table 1. Sorbalit® Research Test Data

Test No.	Reaction Conditions (Adsorbent Weight, mg)	Adsorbent	Reactor Temp °C	HgCl$_2$ Solution			Hg Total Quantity In μg	Hg Total Quantity Out μg	% Hg Removal
				Hg Content μg/g	HCl Content mg/g	Solution Metered g			
B1	Empty Tube	None	180	1.7	125	4	6.8	6.7	
B2	Empty Tube	None	180	1.7	125	4	6.8	6.8	
1A	250	Sorbalit® with 5% HOK 95% Ca(OH)$_2$	180	1.7	125	4	6.8	0.49	92.8%
1B	250		180	1.7	125	4	6.8	0.19	97.2%
1C	250		180	1.7	125	4	6.8	0.13	98.1%
Average Test 1			180	1.7	125	4	6.8	0.27	96.0%
2A	250	Dravo pellets: 5% Carbon 0.5% Sulfur 5% Bentonite 89.5% Ca(OH)$_2$	180	1.7	125	4	6.8	0.32	95.3%
2B	250		180	1.7	125	4	6.8	0.14	97.9%
2C	250		180	1.7	125	4	6.8	0.13	98.1%
Average Test 2			180	1.7	125	4	6.8	0.20	97.1%
3A	125	Sorbalit® pellets: 7.5% HOK 10% Portland 82.5% Ca(OH)$_2$	180	2.1	125	2.002	4.20	1.70	59.6%
3B	128		180	2.1	125	1.656	3.48	1.30	62.6%
3C	124		180	2.1	125	2.001	4.20	1.50	64.3%
3D	125		180	2.1	125	2.001	4.20	1.40	66.7%
Average Test 3			180	2.1	125	1.915	4.02	1.48	63.3%

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1B	250		180	1.7	125	4	6.8	0.19	97.2%
1C	250		180	1.7	125	4	6.8	0.13	98.1%
Average Test 1			180	1.7	125	4	6.8	0.27	96.0%
2A	250	Dravo pellets: 5% Carbon 0.5% Sulfur 5% Bentonite 89.5% $Ca(OH)_2$	180	1.7	125	4	6.8	0.32	95.3%
2B	250		180	1.7	125	4	6.8	0.14	97.9%
2C	250		180	1.7	125	4	6.8	0.13	98.1%
Average Test 2			180	1.7	125	4	6.8	0.20	97.1%
3A	125	Sorbalit® pellets: 7.5% HOK 10% Portland 82.5% $Ca(OH)_2$	180	2.1	125	2.002	4.20	1.70	59.6%
3B	128		180	2.1	125	1.656	3.48	1.30	62.6%
3C	124		180	2.1	125	2.001	4.20	1.50	64.3%
3D	125		180	2.1	125	2.001	4.20	1.40	66.7%
Average Test 3			180	2.1	125	1.915	4.02	1.48	63.3%

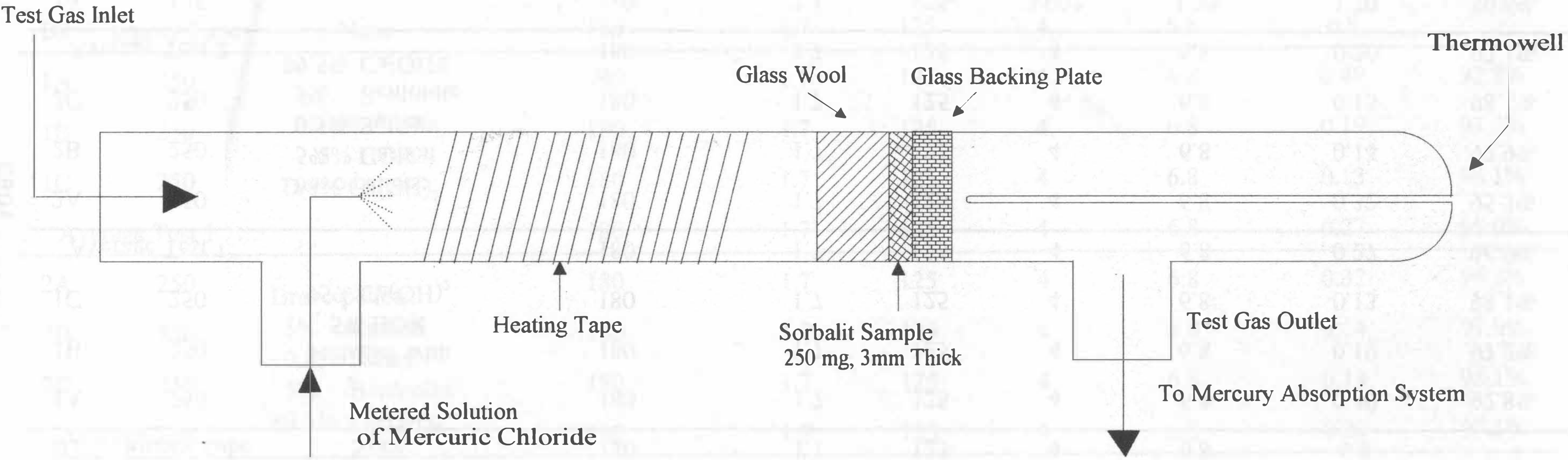

Figure 1. Sketch of Märker's reaction tube assembly.

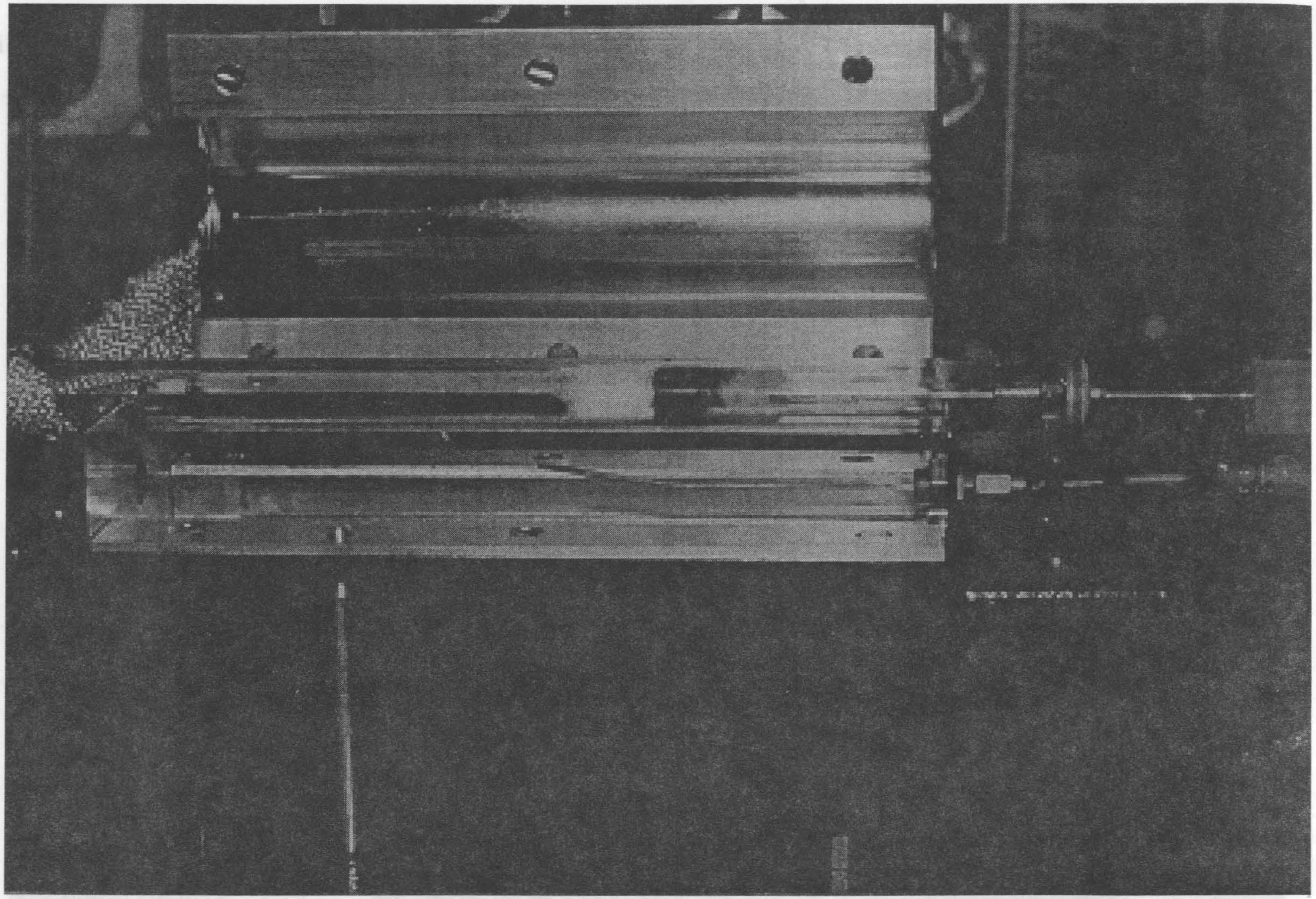

Figure 2. Reactor tube and oven

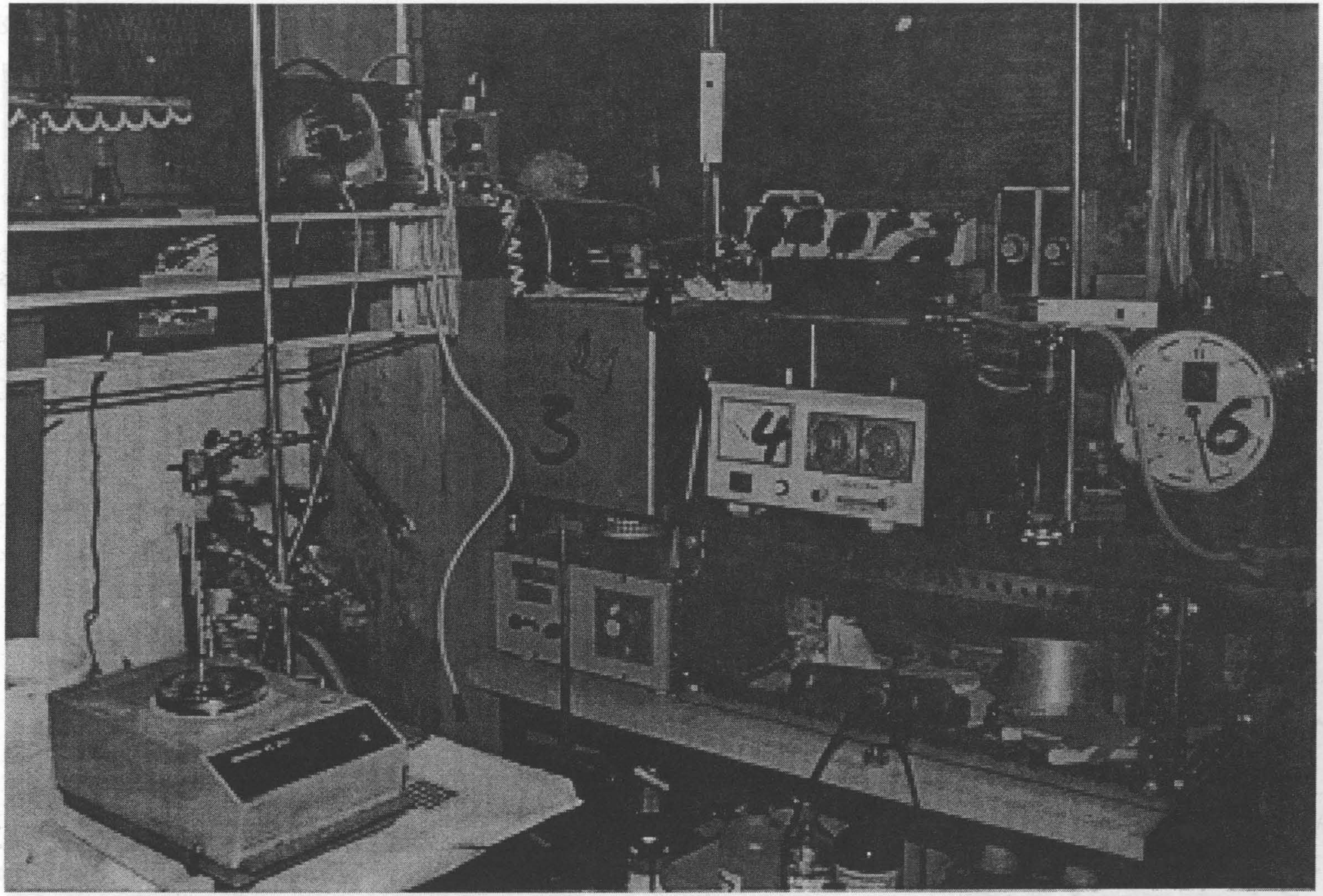

Figure 3. Märker's mercury testing system