AN INSTRUMENT FOR GRAVIMETRIC CALIBRATION
OF FLOW DEVICES WITH CORROSIVE GASES

C. J. Remenyik
James O. Hylton

Oak Ridge National Laboratory*
P. O. Box 2008
Oak Ridge, TN 37831-6007
615-574-6315

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AN INSTRUMENT FOR GRAVIMETRIC CALIBRATION OF FLOW DEVICES WITH CORROSIVE GASES

Carl J. Remenyik
Adjunct R&D Participant II
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6007

James O. Hylton
Sensors & Metrology Group Leader
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6007

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ABSTRACT
An instrument was developed for the calibration of mass flow controllers primarily used in the production of semiconductor wafers. Almost all other types of such calibrators require measurement of temperature, pressure and volume. This instrument measures the weight of gas collected in a container and makes measuring those thermodynamic variables unnecessary. The need to measure the weight of the gas container is eliminated by submerging it in a liquid (presently water) and balancing its weight with the force of buoyancy. The accuracy of this Gravimetric Calibrator is unaffected by the pressure and temperature of the gas. The Calibrator can also measure reactive, corrosive, and non-ideal gases. The container remains connected to the process by a torsion capillary, and a load cell measures the changing gas weight continuously throughout the measuring process. A prototype was designed for gas flows ranging from 1 sccm of hydrogen to 10,000 sccm of tungsten hexafluoride, constructed, tested, and used to calibrate flow devices. Experience with the prototype and results are presented, and plans for further developments are discussed. Design of a version for the flow range from 0.1 sccm to 100 sccm is in progress.

REASONS FOR DEVELOPING THE GRAVIMETRIC CALIBRATOR
Chemical vapor deposition is one of the techniques applied in the production of semiconductor wafers. Some of the gases used in these processes are highly reactive or toxic and must be administered in very small and precise quantities. Instruments widely used for this purpose are Thermal Mass Flow Controllers. In the following paragraphs, devices most frequently used to calibrate Mass Flow Controllers are described. A large number of these calibrators determine the rate of mass flow indirectly from measurements of temperature, pressure, and volume using the equation of state for ideal gases. There are several types:

1. One discharges the process gas from a pressure cylinder the inside volume of which has been measured. For a mass flow measurement, the initial pressure and temperature inside the cylinder are measured. After
the gas has flown for a measured length of time, the final pressure and temperature are measured. The values permit calculation of the mean rate of gas flow between the initial and final times. The cylinder must be sufficiently strong to prevent significant change in the inside volume due to the pressure change.

2. In the instruments of a second type, the volume is variable. The lower end of a vertical cylinder is closed except for a gas inlet. The upper end is open. A flat insert is fitted to the cylinder such that it can freely slide up and down inside the cylinder like a piston. The gap between the insert and the cylinder wall is closed by a liquid seal, usually mercury. The liquid seal doesn't hinder the motion of the insert. The vertical position of the insert is determined by some method that may be visual if the cylinder is transparent, it may use electric contacts, or resistance, time of flight measurement of ultrasonic signals, laser interferometry, or other processes. During a measurement, gas enters the cylinder and pushes the insert upward. Displacement of the insert, time, inside pressure and temperature are measured. The inside cross sectional area of the cylinder must be known. With these pieces of information, a mean rate of gas flow can be calculated.

3. A third method, the Bell Prover, is a variant of the second in which the cylinder, or bell, is turned upside down; its open lower end is submerged in a liquid, and it floats freely on the liquid. The process gas is ducted into the cylinder from below through the liquid. As the gas enters the cylinder during a measurement, the cylinder rises, and the level of the liquid surface remains unchanged. The same quantities are measured as in the previous case, with the exception that the position of the cylinder replaces the position of the insert.

4. There are several methods that exploit dynamic effects of gas flows. They utilize devices like the venturi tube, orifice meter, turbine meter. They require, besides time or frequency, pressure and temperature weight of discharged gases and thus also their mass. In the process, a pressure cylinder is weighed with its gas content. Then the cylinder is connected to the calibration system, and a measurement is performed during which gas is discharged from the cylinder. After the measurement, the cylinder is separated from the system and weighed again. The difference in weight and the length of time of the run give the mean mass flow rate during the run. This method may be operated also in such a manner that gas is being collected in a cylinder that is initially evacuated.

All of the above methods are subject to limitations that prevent them either from achieving the required accuracy or from being used at all under the required conditions. The first three instrument types require the measurement of pressure, temperature, and volume, reducing the accuracy of the calibration cumulatively by the errors of each of these measurements. Further uncertainty is introduced into the calibration by adsorption or absorption at the cylinder walls. Through these processes, gas molecules are removed from the gaseous phase within the cylinder, distorting the pressure and temperature readings. Also, those instruments in which the gas comes in contact with liquid seals, or others liquid barriers, cannot be used when the gas is strongly reactive. For the calculation of the mass flow rate, the gas constant of the gas or gas mixture involved has to be determined.

For those instruments that involve dynamic effects of the gas flows for measuring mass flow rates, the flow processes are complex and make the relationships between pressures, temperatures, gas properties and mass flow rates so complicated that the mass flow rates cannot be calculated from the measured quantities. Therefore, the instruments have to be calibrated with one of the other methods, and they have to be calibrated separately for each gas or gas mixture used. Thus, their accuracies cannot be greater that those of the instruments used for their calibration.
The last category of instruments mentioned above are gravimetric types. The cylinders used to discharge or collect gases have to be strong enough to withstand the operating pressure differences inside and outside the cylinders, and, therefore, they are heavy. The accuracy of balances with which such heavy cylinders can be weighed is adequate only if the weight of the discharged or collected gas is sufficiently large. At the flow rates occurring in the production of semiconductor wafers, this requirement necessitates calibration runs that last many hours, or even days, and then they yield only the average mass flow rate of the entire run. The procedure is further prolonged because the cylinder has to be disconnected from the system for each weighing, and the pipes communicating with the cylinder have to be purged before the connection to the cylinder may be opened if the process gas is toxic or reactive.

The gravimetric Calibrator discussed in the following section was developed to eliminate the most restrictive limitations of the instruments mentioned above.

**DESIGN OF THE GRAVIMETRIC CALIBRATOR**

The Gravimetric Calibrator measures the mass of a quantity of gas collected in or discharged from a receptacle, or it determines the mass flow rate. It achieves this by measuring the weight of the gas. Figure 1 shows a schematic diagram of the instrument.

![Gravimetric Calibrator Schematic Diagram](image)
The receptacle is a long cylindrical container submerged in water with its long axis horizontal. Its weight is adjusted so that it takes a force of a few grams to prevent it from sinking when it is evacuated. The receptacle is supported at two points along a horizontal axis that is perpendicular to the long axis, and it goes through the centroid of the internal cavity of the receptacle. When there is any amount of gas inside the receptacle, the center of mass of this body of gas coincides with the centroid. Thus, this configuration insures that any gas inside the receptacle is supported through it's center of mass. The significance of this will be explained later. The receptacle is connected to the gas flow system through a capillary tube (Fig. 2). This capillary tube is horizontal and parallel to the transversal axis of the receptacle. In this arrangement, the capillary is subjected to torsion when the receptacle centroid moves up or down. The receptacle is suspended from a load cell.

If the receptacle is evacuated, the indication of the load cell recorded, and the gas is permitted to stream in, the load cell indicates a change in load; but this is not the weight of the entering gas alone, because the changing pressure inside the receptacle changes the receptacle's dimensions and that changes the buoyancy force. In order to eliminate this effect, the receptacle was placed inside a shell with a small gap between them. If the gap contained air or some other gas, the changing volume of the receptacle would change the pressure inside the gap, and the outside shell would respond by changing its volume. The volume changes of the receptacle are decoupled from the shell if the gap is evacuated, but that solution raised a concern. If there is a leak, the gap would eventually fill up undetected with a gas or water vapor, and the receptacle's volume changes would again affect the shell and the buoyancy force without any possibility for the user of the instrument to become aware that the measurements are no longer correct. The problem was solved by venting the gap to the atmosphere through a capillary tube. This modification insures that the pressure inside the gap is always atmospheric and the shell volume does not change. However, there is still
a source of error. When the receptacle volume or the barometric pressure changes, air flows in or out of the gap, changing the weight of the gas contained in the shell-receptacle assembly. But this error is much smaller than the maximum allowable according to the design accuracy of the instrument, even when the rapidity of the barometric pressure change is the greatest that any weather conditions can produce. (Tornadoes are a possible exception.)

An error is caused by the connecting capillary tube. When the receptacle is in some general position, the capillary is strained in an unknown way and exerts a force on the receptacle and thus affects the load cell indication. If the receptacle does not move, this force is constant and has no effect on the measurement. The changing gas weight, however, changes the deformation of the load cell and the suspension mechanism resulting in a vertical displacement of the receptacle and consequently also in a change in this force. This force change is proportional to the change in the gas weight. The error can be calculated or determined by calibration to make corrections, but it may be ignored because the capillary is designed so that the force in question is four to five orders of magnitude smaller than the weight of the gas.

The location of the receptacle suspension has to be measured carefully. If the line of action of the load cell reaction goes through the mass center of the gas, the entire gas weight acts on the load cell. If the mass center is between the capillary and the suspension, the weight of the gas is distributed between the capillary and the load cell, and the load cell indication is less than the weight. If the mass center is farther away from the capillary than the suspension, the indication is more than the gas weight. This deviation is again proportional to the gas weight; it can be calculated from the dimensions of the receptacle or determined by calibration, and a calibration factor can be calculated if the deviations are too large to be ignored. This is not a flaw in the instrument, and special applications may make it preferable to locate the suspension deliberately off the mass center.

RESULTS AND PLANNED DEVELOPMENTS

A prototype instrument was built, and it is in use. It has a receptacle with a 20-liter capacity. It can handle a range extending from 1 sccm of hydrogen (Molecular Weight 2) to 10,000 sccm of tungsten hexafluoride (Molecular Weight 298). Tests were performed with nitrogen. Individual flow rate measurements lasted from less than a minute to several minutes. For flow rates of about 100 sccm and higher, the accuracy was about 0.5%. At smaller flow rates, the accuracy is increasingly less, which probably indicates that the present instrument is too large for these small flow rates.

The water tank in which the receptacle is submerged turned out to be a source of unnecessary disturbance. It was available from an earlier project when this instrument was built. Its dimensions are approximately 30cm high, 30cm wide and 200cm long, and it requires too much water to fill. The existing temperature controls are not capable of keeping the water temperature sufficiently steady and uniform. As a consequence, random convection currents arise and disturb the instrument's operation. This seems to be the reason why the accuracy is not substantially better than 0.5%.

Current plans call for an instrument designed for flows between 0.1 sccm and 100 sccm. The temperature control of the liquid will be designed with particular care, and the liquid may be other than water.