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A PLASMA FURNACE FOR ASHING MICRO-SAMPLES OF PARTICULATE MATTER

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A PLASMA FURNACE FOR ASHING MICRO-SAMPLES OF PARTICULATE MATTER

by

W.K. Boyd* and R.K. Jeffrey**

ABSTRACT

This report describes a low-temperature, radio-frequency (R-F) ashing technique used in the preparation and concentration of combustible samples prior to chemical analysis and microscopic examination.

Samples are placed in a plasma reactor through which oxygen is passed. The R-F field within the reactor converts the molecular oxygen into an active species, i.e. atomic oxygen. Low-temperature oxidation results with the consequent removal of carbon, hydrogen and nitrogen as volatile oxides, and the retention of most metallic ions.

This technique has been successfully used for the past year to effectively destroy organic matrix in combustible samples without excessive loss of mineral content and to improve analyses based on atomic absorption, emission spectroscopy and conventional 'wet' methods.

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Direction des mines
Bulletin technique TB 136

FOUR À PLASMA POUR L'INCINÉRATION D'ÉCHANTILLONS MICROSCOPIQUES DE MATIÈRE PARTICULAIRE

par

W.K. Boyd* et R.K. Jeffrey**

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RÉSUMÉ

Le présent rapport décrit une technique d'incinération à basse température, par radiofréquence (RF), utilisée dans la préparation et la concentration d'échantillons combustibles avant l'analyse chimique et l'examen au microscope.

Les échantillons sont placés dans un réacteur à plasma à travers lequel on fait circuler de l'oxygène. Le champ de radiofréquence dans le réacteur converti l'oxygène moléculaire en une espèce active, à savoir, l'oxygène atomique. Il se produit alors une oxydation à basse température qui entraine l'élimination du carbone, de l'hydrogène et de l'azote sous forme d'oxydes volatils, et la rétention de la majeure partie des ions métalliques.

Cette technique est employée avec succès depuis un an pour détruire complètement la matrice organique des échantillons combustibles sans perte trop importante des minéraux qu'ils renferment, et pour améliorer les techniques d'analyse basée sur la spectroscopie d'absorption ou d'émission atomique et les méthodes classiques par voie humide.

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Analysis of the elemental composition of powdery substances generally requires intense ashing of the material in order to convert the elements of interest into a form susceptible to common analytical techniques. Ashing is usually an oxidation process, involving conversion of the carbon and hydrogen of an organic matter in the sample to carbon dioxide and water. Oxidation procedures have traditionally been classified into two categories: wet ashing, which makes use of liquid oxidizing agents such as sulphuric or perchloric acids, and dry ashing, which usually implies high temperature combustion of the organic constituents using either air or oxygen. Both methods, however, include inherent sources of error. These are:

1. formation and loss of volatile metallic compounds during ashing; (sodium, iron and vanadium are appreciably volatized when organic samples containing porphyrin compounds are heated.)
2. contamination from the reagents or the air used to oxidize the sample;
3. cross contamination when more than one sample is ashed;
4. mechanical losses from decrepitation, fire and explosion, and entrainment of finely divided particulate matter in hot convection currents around the ashing crucible;
5. destruction of mineral and physical substructure;
6. undesirable reactions with sample containers; and
7. non-uniformity in the degree of combustible burn-off.

The use of a gaseous plasma to oxidize organic dust constituents in a low-temperature radio frequency (RF) furnace has recently gained wide acceptance because such systems effectively eliminate all of the aforementioned sources of error(1).

An evaluation of available instruments for low-temperature RF ashing established that the plasma furnace and console designed by International Plasma Corporation (IPC) provided the flexibility, reproducibility, and reliability required to satisfactorily and quickly dry-ash micro-samples of dust.

This report describes (a) the components and operation of the IPC model 1003 B plasma machine, (b) the effectiveness and application of this system to micro-analytical techniques, and (c) the procedure and results of several experiments using powdered charcoal and combustion residues.

THEORY

Low-temperature oxygen plasma ashing is based upon the chemical reaction between reactive species in the gas plasma and solid, powdery material, i.e., atomic oxygen, the gaseous species, enters into chemical reaction and forms compounds. Fission of the oxygen molecules by the RF field generated within the reactor chambers is essentially homolytic in nature:

$$O_2 \xrightarrow{\text{RF energy}} O^- + O^-$$

Carbon and hydrogen readily combine in the plasma to form oxidation products, which results mainly in the loss of water and oxides of carbon.

Optimal control of RF power and oxygen flow to the reactors maintains a moderately low temperature of the sample during the ashing process.

PLASMA FURNACE SYSTEM

The IPC 1003 B system, shown in Figure 1, contains three major inter-connected components:

1. a model PM 105 Generator Control Console,
2. a model PM 504 B Process Treatment Console, and
3. a Vacuum Pump.

PM 105 Generator Control Console

The PM 105 Generator Control Console comprises a 300-watt RF generator along with two precision metering systems to monitor both RF power levels and the pressure in the plasma reactors. The control panel, schematically illustrated in Figure 2, consists of four modules of switches which are conveniently grouped and readily identified by inspection of the panel from left to right. The modules are as follows:

1. POWER consists of:
   (a) a Power ON/OFF switch;
   (b) an "ON" green indicator light;
   (c) a built-in automatic drop-out magnetic breaker to protect the console from overload.

2. RF POWER consisting of:
   (d) a "READY" amber light, which comes on three minutes after the main power (AC-117 volts) has been turned on, and indicates that operation may proceed. This three-minute delay enables a warm-up period during which the radial-beam, ceramic, power tetrode reaches its correct emission temperature;

(e) an "OPER" red light;

(f) an RF "OPER/STBY" switch (red-covered toggle switch) to energize RF power system;

(g) a CHANNEL SELECTOR (A/B) switch which allows a second treatment console to be plugged into and operated from the PM 105.

3. RF METER which includes:

(h) an RF rotary range selector allowing a choice of 0 to 5, 0 to 50, or 0 to 300 watts to be induced through the generator;

(i) an "FWD/REFL" switch used for converter tuning in conjunction with the matching knobs of the PM 304 Converter Plug-In.

4. POWER ADJUST consisting of:

(j) an RF range switch used in conjunction with rotary range selector (h). The LOW position is for 0 to 5 watts while the HIGH position is for 0 to 50 and 0 to 300 watts.

(k) an RF power level dial having a range of 0 to 100 for setting the output power desired;

(l) a vacuum meter; and

(m) a wattmeter which indicates power output level as dialed by the RF power knob (K).

PM 504 B Process Treatment Console

The Process Treatment Console consists of three subcomponents.

A. PM 404 Vacuum Plug-In

The PM 404 Vacuum Plug-In provides complete control of all the vacuum process parameters through simple manipulation of five valve controls located on the front panel of the treatment console, as schematically illustrated in Figure 2. The controls include:

1. an ON/OFF gas switch to initiate the input of oxygen to the reactor chambers:
2. a gas flow needle valve to control the flow rate of oxygen entering the reactor chambers; and

three vacuum process control switches which are designated:

3. "PURGE" to vent the entire system when ON (up position). This restores the reactor chambers to atmospheric pressure by opening a solenoid valve which in turn allows ambient air to enter the chambers by means of a 1/4-in.-ID tube.
4. "FAST" for a rapid evacuation of the reactor chambers; and
5. "SLOW" to facilitate a more gradual evacuation of the reactor chambers.

B. PM 304 Converter Plug-In

The PM 304 Converter Plug-In is a manually operated converter to provide reproducibility of treatment process parameters by means of:

6. a "FINE" matching knob; and
7. a "COURSE" matching knob which provides direct digital dialing to tune the RF power. This procedure is discussed further under the PM 105 "FWD/REFL" section.

C. PM 204 Reactor

As schematically illustrated in Figure 3, the PM 204 Reactor consists of the following components:

8. Two reactor chambers of 3 x 7-in. long quartz tube, sealed at one end, are horizontally mounted in the PM 504 chassis. Each reactor chamber is separately coupled to a 11 1/2 x 2-in.-ID metal vacuum manifold and a 1/4-in.-ID gas supply inlet by 1 1/2- and 1/2-in.-OD quartz tubing respectively. All glass to metal components are coupled by means of silicone rubber sleeves to facilitate the removal of the chambers for cleaning purposes. Located externally, adjacent to, and partially enclosing each reactor chamber are two RF grids shaped to match the curvature of the reactor chamber and mounted in opposing positions to each other;

9. a 10 x 4 x 1/4-in. quartz glass door, gasketed with silicone rubber O-rings, locks and vacuum-seals the receiving ends of the two reactor chambers during ashing operations;

10. an outer protector door, tinted to protect the operator from exposure to RF radiation, is manually locked into position when the system is in operation. A mini-switch automatically trips the RF power source in the event the protector door is opened during operation.

Figure 4 schematically illustrates the electrical cable and gas tubing connections between the PM 105 Generator Control Console and the PM 504 B Process Treatment Console.

Vacuum Pump

The system is served by a 1/3-hp, belt-driven Edwards 150 high-vacuum pump having a minimum rating of 150 ℓ/min at zero pressure and 0.1 Torr under operating conditions. The pump inlet is connected to the vacuum manifold in the PM 504 B chassis by means of a thick-walled 2-in.-OD tygon tube. A built-in bypass gate valve on the pump permits: (a) controlled evacuation and purging of the vacuum system in the furnace during operations, and (b) purging of the high-vacuum pump oil with ambient air after shutdown. The pump outlet exhausts through a glass oil trap into a fume hood located above the furnace.

Figure 5 is a schematic line-diagram illustrating the essential components of the complete vacuum-pressure system.

OPERATING PROCEDURES

Plasma Initiation

Prior to energizing the plasma furnace, it is important that the panel switches on the PM 504 B and PM 105 units of the furnace be in the following positions:

PM 504 B
(from left to right)

Gas ON/OFF switch	OFF
Gas flow valve	closed (clockwise deadstop)
Purge switch	OFF (down position)
Fast vacuum switch	OFF (down position)
Slow vacuum switch	OFF (down position)
Fine matching knob	full to right (clockwise)
coarse matching knob	near 5

PM 105
(from left to right)

Power ON/OFF switch	OFF
RF OPER/STBY switch	STBY
Channel selector (A/B) switch	A
RF rotary selector range selector	300
FWD/REFL switch	FWD
RF range switch (HIGH/LOW)	HIGH
RF power level dial	0

The following steps are to be followed in order to energize the plasma system:

1. Turn power ON/OFF switch to ON.
2. Turn the vacuum pump ON (bypass valve fully open).
3. Open the valve on oxygen tank and regulate 10 psig to the system.
4. Allow three-minute warm-up until the READY amber light comes on.
5. Close the inner seal (quartz) door and seat it securely against the silicone O-rings.
6. Close the outer RF protector door and lock it.
7. Close the bypass valve on the vacuum pump.
8. Turn the fast vacuum switch to ON (up position).
9. Allow the system to pump down to the lowest reading (about 8) on vacuum-meter logging scale.
10. Turn the gas ON/OFF switch to ON.
11. Regulate the requisite flow of oxygen to the reactor chambers by turning the gas flow valve counter-clockwise. Refer to the flow-rate/pressure curve, Figure 6, for calibrated vacuum meter logging scale reading vs. O_2 flow (cc/min). (Figure 7 schematically illustrates the flow system for calibrating the vacuum system).

12. Lift the RF OPER/STBY switch to OPER: the red light should now come on.

13. Regulate the RF power (requisite Forward with minimum Reflected) by the RF Power Level Dial in the following manner:

    advance the RF Power Level Dial, observing the forward and reflected powers using the FWD/REFL switch on the power meter. Until the plasma is initiated (which is readily observed by the glow emitted from the reactor chambers) the forward and reflected powers will be approximately the same. As the power is advanced to the point where the reflected power reaches between 200 and 300 watts, the plasma will suddenly become initiated. The reflected power will then fall to only a few watts and the forward power will rise to approximately 300 watts.

14. Tune the converter in the following manner:

    When the plasma has been initiated, switch the FWD/REFL switch to the REFL position and note the reading. Then slowly change the matching controls (FINE and COURSE) on the PM 504 B and note how the reflected power rises and falls. Note also how the forward power rises and falls. By varying the two controls alternately, it will be found that a minimum value of reflected power can be achieved. The optimum settings for the converter tuning controls will result in minimum reflected power. The value of these optimum settings will depend upon the type of gas used, the system pressure, and the RF power level.

NOTE: Ideally the converter tuning controls should always be set for minimum reflected power. Where the conditions within the plasma change with time it may be convenient to change the controls during the process. This need not cause concern as long as, during the process, the reflected power remains substantially lower than the forward power. (Reflected = 0.05 Forward)

Ashing Procedure

The following is a step-by-step procedure for the dry ashing of -200 mesh-micro-samples. This procedure, which is employed when ashing powdered coal, fly ash, pulverized scale deposits, incineration products, and air pollution dust samples, permits the operation of the machine with negligible loss of sample due to sudden pressure changes in the reactor tubes as a result of evacuation, plasma induction, and removal of samples from the machine.

A. Initial Start-Up

NOTE: Panel switches on the PM 504 B and PM 105 modules must be in position as described under the heading "plasma initiation".

1. Turn OFF the overhead fumehood.
2. Turn ON the plasma furnace using the power ON/OFF switch (the green light should now be ON).
3. Turn ON the vacuum pump with the bypass valve fully opened.

NOTE: ca 3 minutes after the power ON/OFF switch has been turned on, the amber light will illuminate automatically. This three-minute delay is provided to allow the radial-beam ceramic tetrode to reach its correct emission temperature before operation. DO NOT APPLY ANY RF POWER TO THE SYSTEM UNTIL THE AMBER LIGHT COMES ON.

4. Carefully place sample(s) in the reactor chamber(s) using the specially designed trays (as shown in Figure 8).
5. Close and seal the inner quartz door on the silicone O-rings.
6. Close the outer RF protector door.
7. Turn the "SLOW" Switch to ON and then slowly close the pump bypass valve.
8. Allow the system to pump down to 50 on the vacuum meter logging scale.
9. Turn the "FAST" vacuum switch to ON.
10. Turn the "SLOW" vacuum switch to OFF.
11. Allow the system to evacuate and stabilize. After 20 minutes note the final reading on the vacuum meter logging scale.
12. With the gas flow valve <u>completely</u> closed (clockwise dead-stop) turn the gas ON/OFF switch ON.
13. <u>Slowly</u> regulate oxygen into the system via the gas flow valve until the desired flow is obtained. (See calibrated flow graph, Figure 5).
14. Turn the RF OPER/STBY switch to OPER (red light should now be on) and adjust to the desired level by means of the RF power level dial. (Refer to the section entitled "Plasma Initiation" for matching and tuning procedure).

B. Downtime Between Sets of Samples

In order to minimize operating procedures between sets of samples and to reproduce optimum ashing conditions, the following routine should be carried out:

1. Turn the RF OPER/STBY switch to STBY (the red light should now be off).
2. Open the bypass valve on vacuum pump.
3. Turn the "SLOW" vacuum switch to ON (up position).
4. Turn the "FAST" vacuum switch to OFF (down position).
5. When the vacuum meter logging scale reads 70, turn the "PURGE" switch ON (up position).
6. Turn the "SLOW" vacuum switch OFF (down position).
7. Turn the gas ON/OFF switch to OFF and close the gas flow valve by turning it clockwise to deadstop.
8. Open the outer RF protector door and allow the inner quartz door to slowly "pop" to atmospheric pressure.
9. Turn the "PURGE" switch to OFF (down position).
10. Turn the overhead fume hood OFF.
11. Remove the ashed sample(s) and replace with a new set.
12. Repeat steps 5 to 13, detailed under the section entitled "Initial Start-Up".
13. Turn the RF OPER/STBY switch to OPER.

C. Shutdown at End of Day

1. Turn off the RF power by
   i) returning the RF power level dial to "0",
   ii) placing the RF OPER/STBY switch to STBY (red light should now be off).

2. Open the bypass valve on the vacuum pump.
3. Turn the "SLOW" vacuum switch to ON (up position).
4. Turn the "FAST" vacuum switch to OFF (down position).
5. When the vacuum meter logging scale reads ca 70, turn the "PURGE" switch to ON (up position).
6. Turn the "SLOW" vacuum switch to OFF (down position).
7. Turn the gas ON/OFF switch to OFF, and close the gas flow valve (clockwise deadstop).
8. Open the outer RF protector door.
9. Turn the "PURGE" switch OFF (down position).
10. Allow the inner quartz door to slowly "pop" under atmospheric pressure.
11. Remove the samples.
12. Close the inner quartz and outer RF doors.
13. Drain oxygen lines by closing the tank valve and bypassing the gas flow into the fume hood.
14. Purge the vacuum pump, i.e., allow ambient air to enter the pump, by opening the bypass valve, for at least 15 minutes.
15. Turn the power ON/OFF switch to OFF.

MAINTENANCE PROCEDURES

The IPC 1003 B system requires occasional maintenance and when this is necessary, the following steps should be used:

Removal and Cleaning of the Reactor Chambers

1. Remove the ball joint clamp which attaches the reactor stem to the rear manifold.
2. Slowly pull the reactor chamber forward with one hand.
3. Slip off the rubber inlet hose with the other hand.
4. The inlet now becomes free of the inlet tubing. Tip the reactor downward.

5. Slide the reactor chamber out of the machine (chassis).
6. Clean the tubes with an acetone-damped cloth.
7. The tubes are replaced by reversing the above procedure.

Cleaning of Quartz Doors and Silicone Rubber O-Rings

This procedure merely involves slipping the O-rings off the tube flange and washing them with soap and water. This should be done daily to ensure a good vacuum seal with the doors. It is also advisable to clean the inner quartz door with soap and water to ensure clean surfaces and good vacuums.

Oil Purging

After a series of samples have been treated, the bypass valve on the ES-150 vacuum pump should be left open, and the pump should be operated for approximately thirty minutes. This is to purge the pump-oil of any contaminants resulting from the ashing process.

Periodically the pump oil becomes rancid or contaminated. If the oil becomes 'clouded' or darker than usual, it should be changed.

CONCLUSIONS

Optimum conditions for ashing -200-mesh powdered material were determined following exhaustive experiments. The ashing rates, as shown in Figure 9, are computed to be those for the entire machine based upon the measured values of the samples. This allows correlation between the oxygen flow, which is evenly distributed over the two RF reactor chambers, and the RF power, which is the total input power to both chambers.

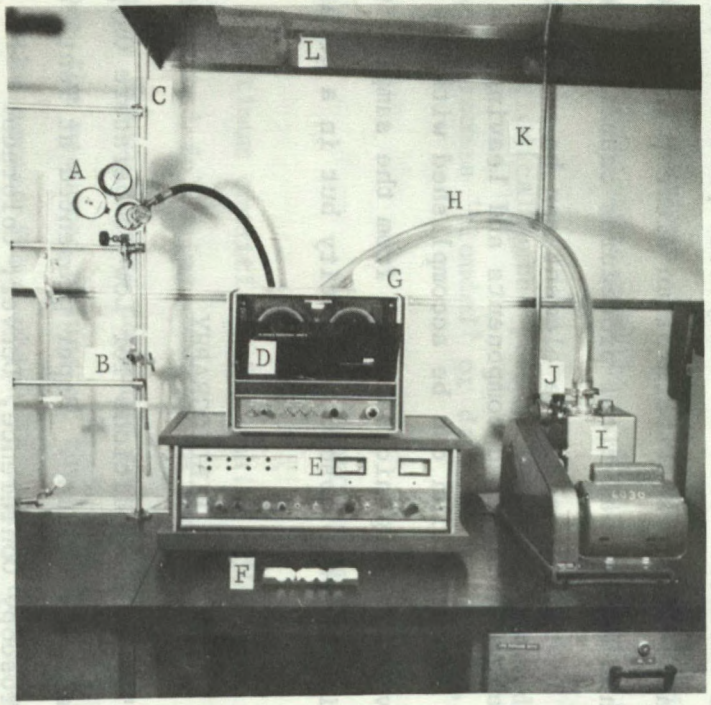
In reviewing these results, it immediately becomes clear that, for a given level of power, the ashing rate increases with the addition of more oxygen until such time that more oxygen is being added than there is power to totally excite it, i.e., the addition of more oxygen at a given RF power level does not further enhance the oxidation rate. For most practical purposes, the maximum O_2 flow rate (cc/min) should be equal to the RF power (watts), i.e., a 1:1 ratio. The fastest ashing condition was found to be the 300 cc/min O_2 at 300 watts of RF power (as shown in Figure 10).

As a result of repeated experiments carried out to determine the weight loss, if any, silica dishes were found to be extremely stable under all operating conditions and, thereby, judged adequate as sample containers.

In conclusion, when the content of a trace amount of an element must be determined, it is essential that an analytical procedure of sufficient sensitivity be found. Often, so little of an element is present in such small percentages that known analytical procedures cannot detect it in micro-sized samples. In these cases, the element can be measured if it can be concentrated by removing unwanted components and leaving the desired components intact. This concentration can be accomplished with the RF gas plasma reactor. By removing the organic material from the sample, the desired element is left in the same absolute quantity but in a greater percentage.

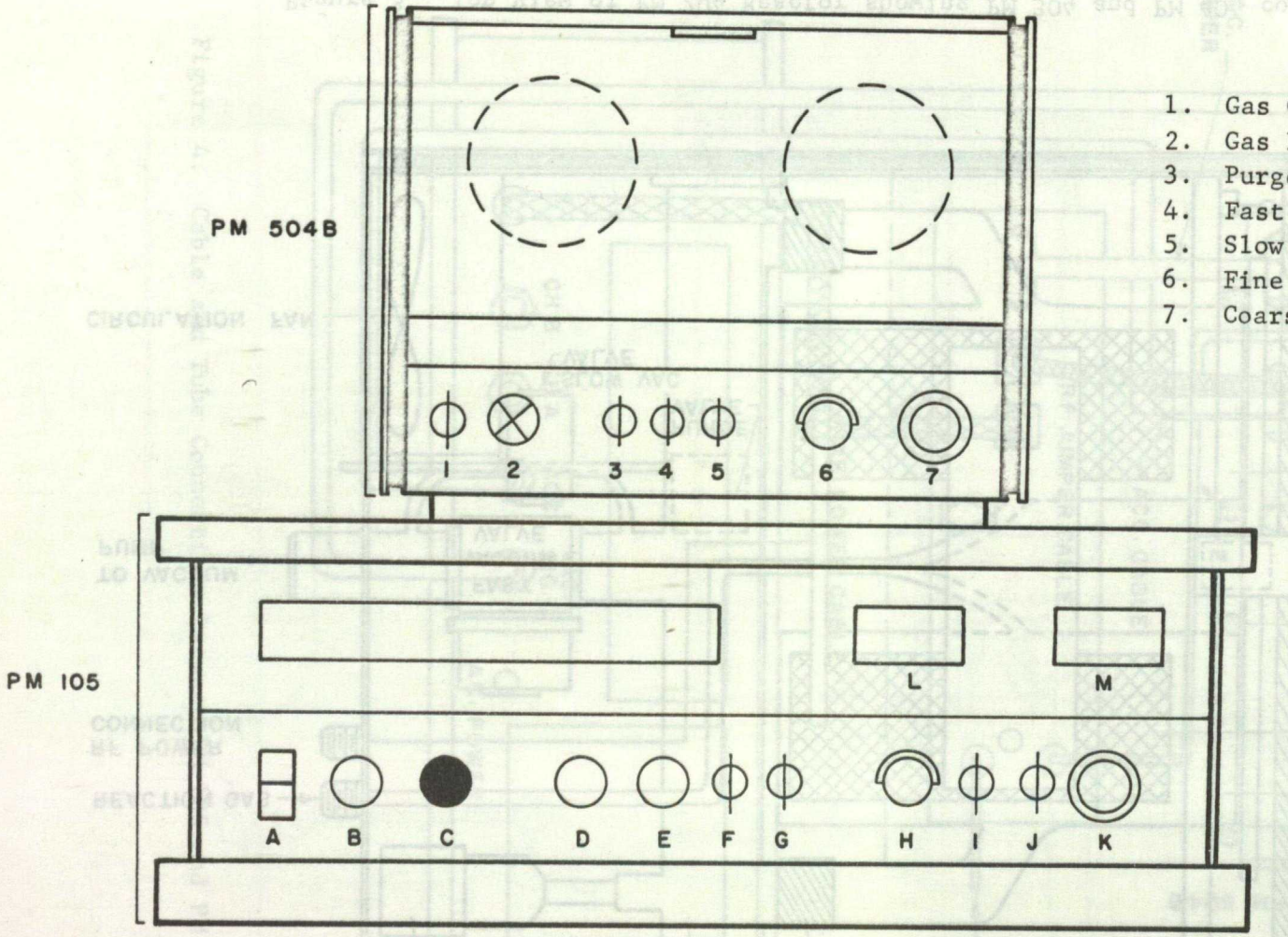
BIBLIOGRAPHY

1. Bersin, Richard L , "Optimum Conditions for Low-Temperature Oxygen-Plasma Ashing of Organic Materials". Paper presented at Tenth Annual Rocky Mountain Spectroscopy Conference, Denver, Colorado.



A. Secondary Oxygen Regulator
B. O_2 Inlet-line Bleed Valve
C. O_2 Bleed Exhaust
D. PM 504B Process Treatment Console
E. PM 105 Generator Control Console
F. Tray of Ashing Crucibles
G. Manual Timer Clock
H. Tygon Vacuum Hose
I. Vacuum Pump
J. Pump Bypass Valve
K. System Exhaust
L. Fumehood

Figure 1. Plasma furnace and control console



1. Gas ON/OFF Switch
2. Gas Flow Valve
3. Purge Switch
4. Fast Vacuum Switch
5. Slow Vacuum Switch
6. Fine Matching Knob
7. Coarse Matching Knob

A. Power ON/OFF Switch
B. "ON" Green Light
C. Reset Button
D. "READY" Amber Light
E. "OPER" Red Light
F. RF OPER/STBY Switch
G. Channel Selector (A/B)
H. RF Rotary Range Selector
I. FWD/REFL Switch
J. RF Range Switch
K. RF Power Level Dial
L. Vacuum Meter
M. Wattmeter

Figure 2. PM 105 Generator and PM 504B Treatment Control Consoles.

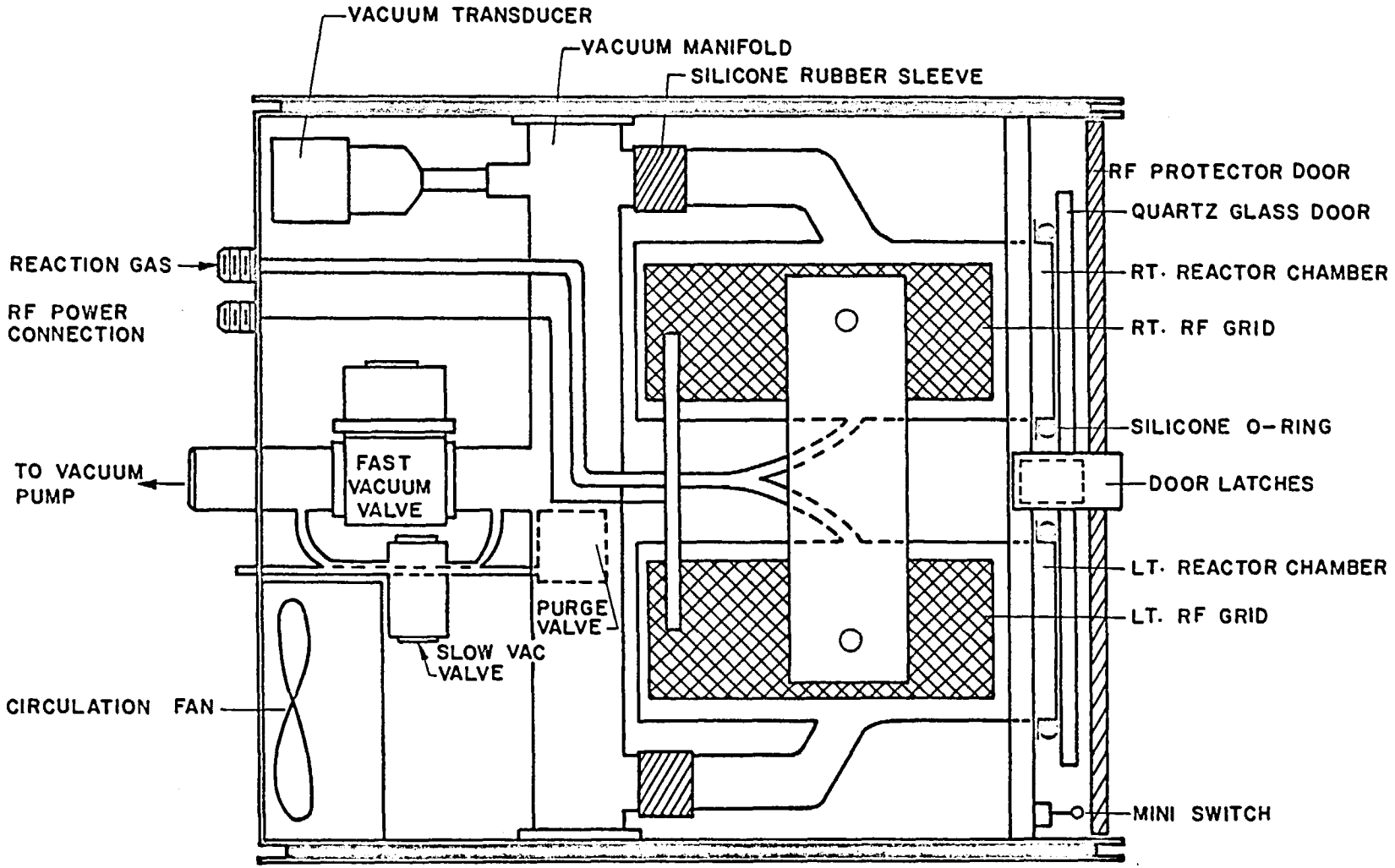


Figure 3. Top view of PM 204 Reactor showing PM 304 and PM 404 components.

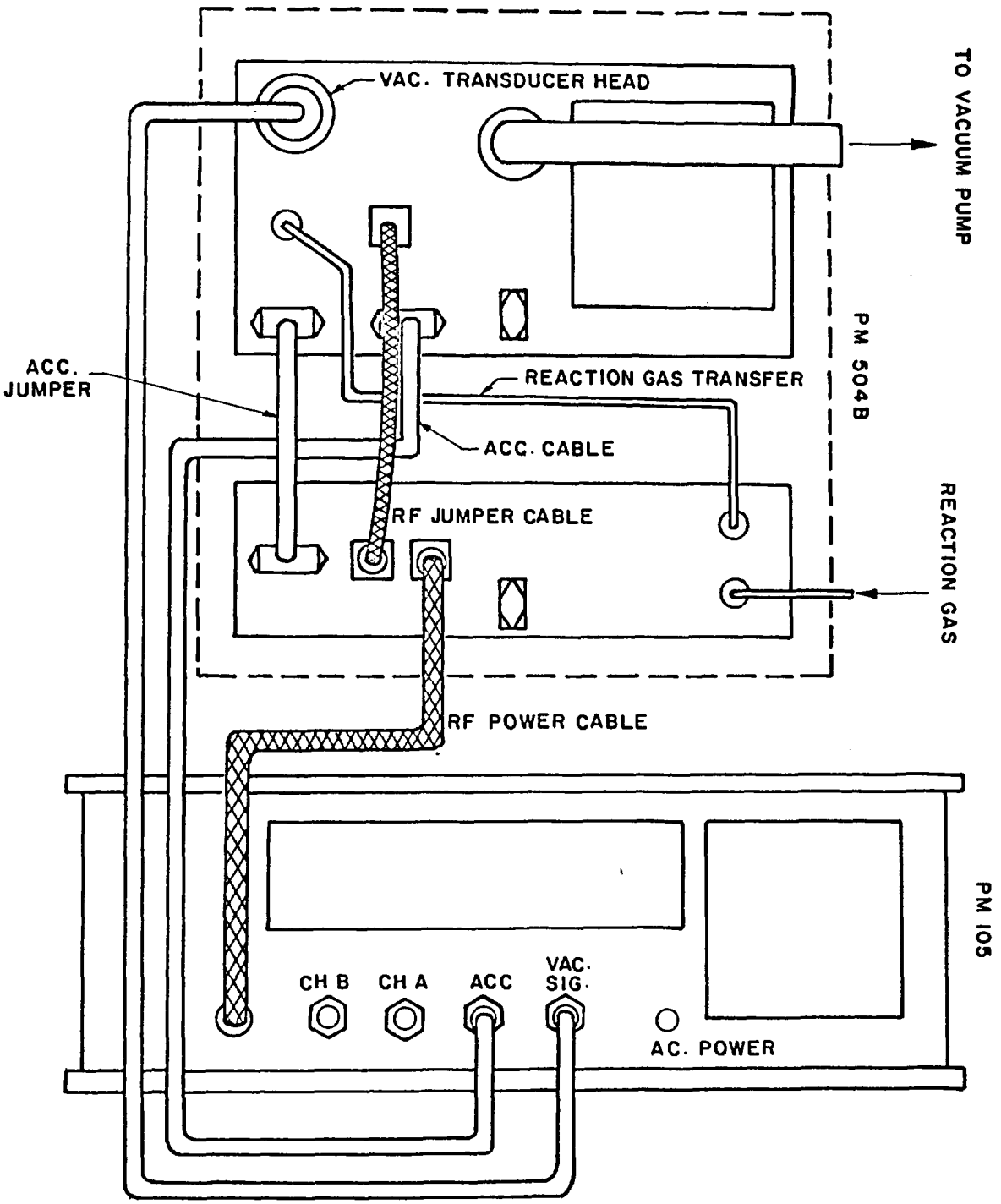


Figure 4. Cable and Tube Connections between PM 105 and PM 504 B.

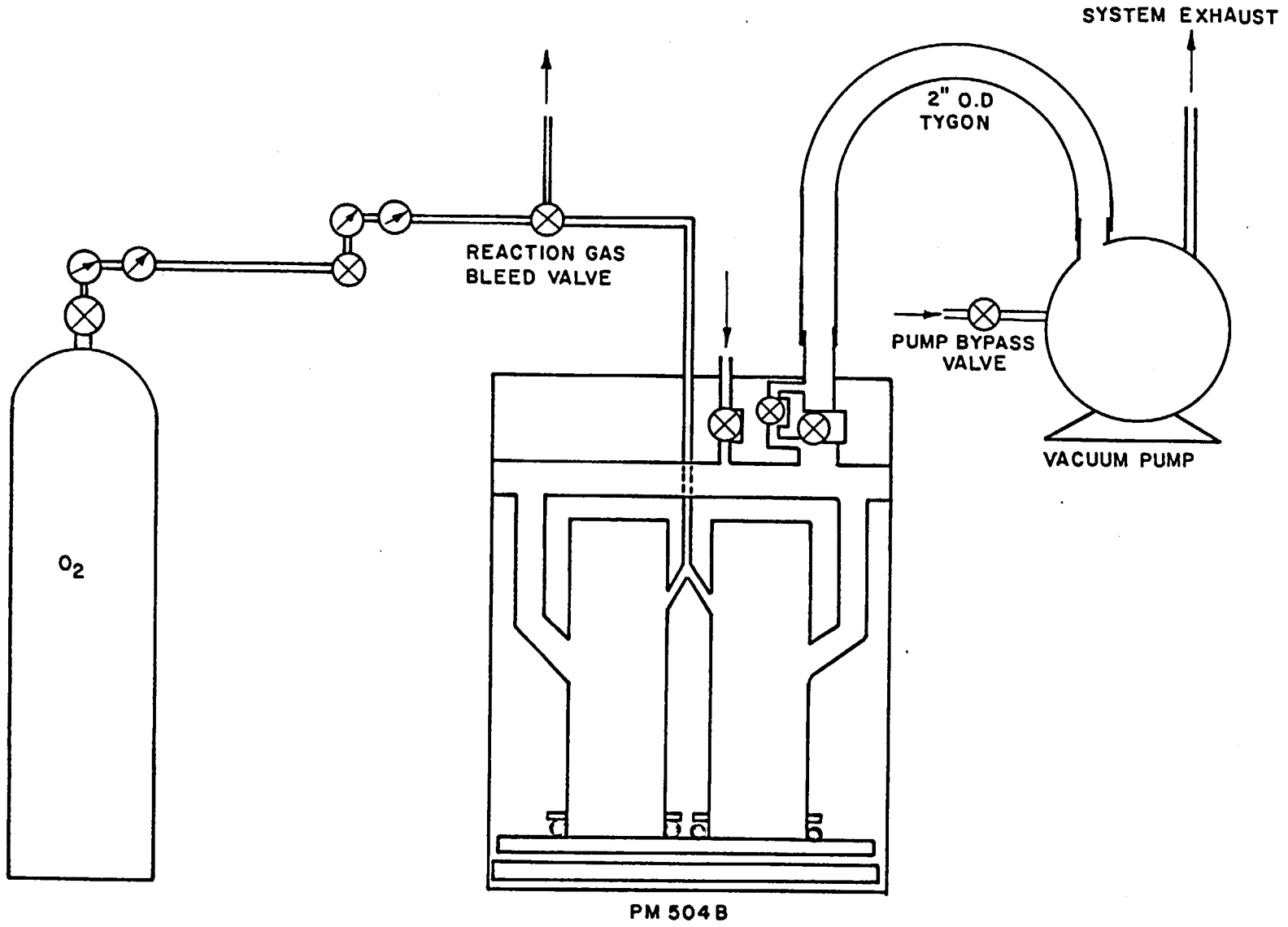


Figure 5. Flow Diagram (not showing PM 105 Generator Control Console)

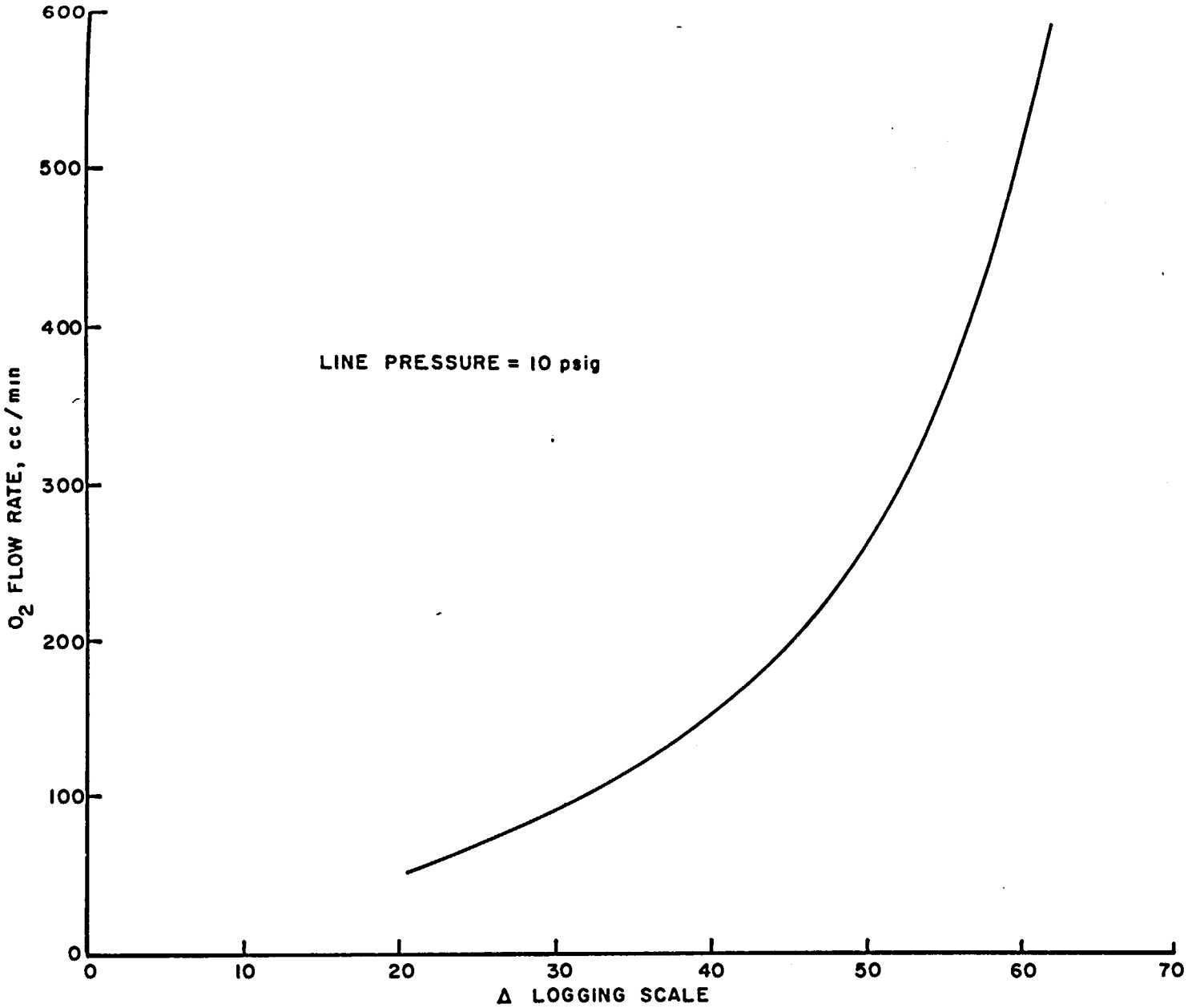


Figure 6. Calibrated O_2 Flow Curve.

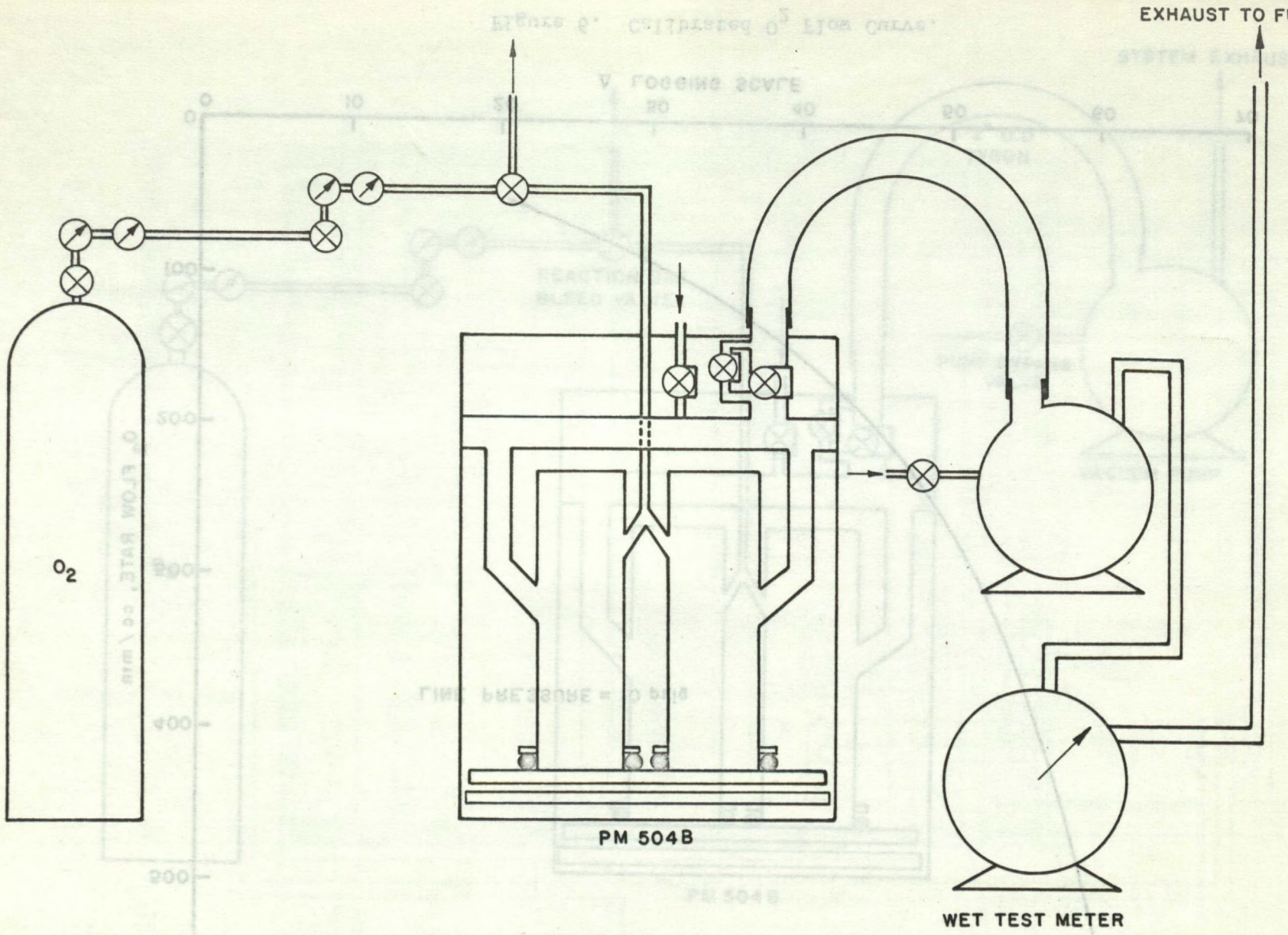
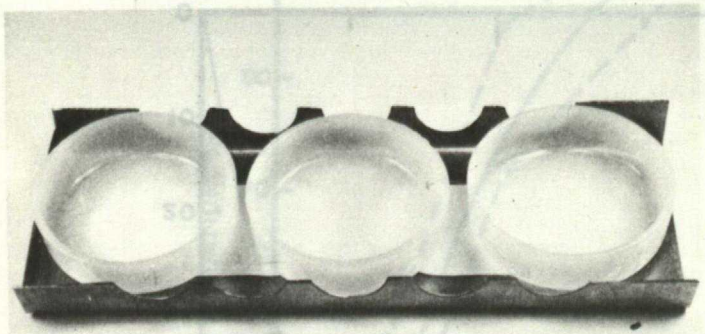
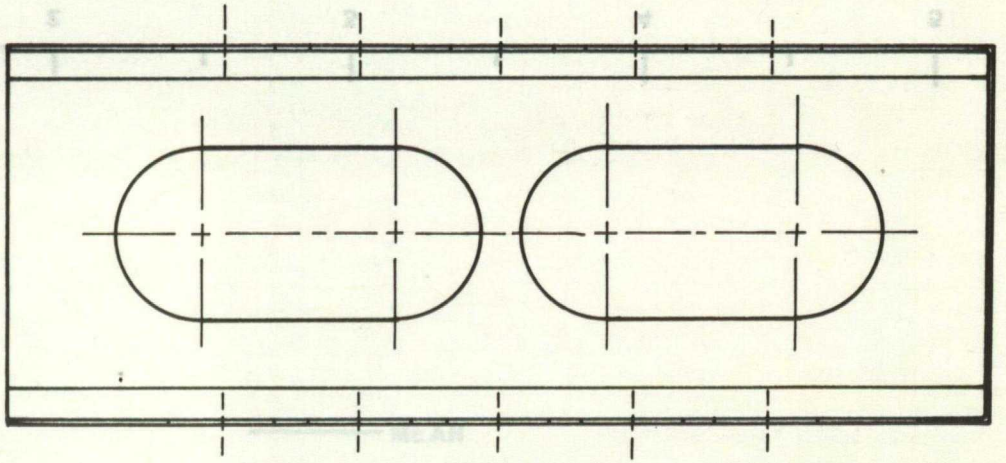
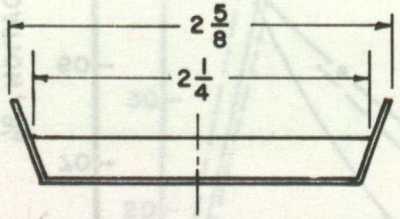


Figure 7. Flow System for Calibrating Oxygen Flow.

MATERIAL — 28 ga STAINLESS STEEL NO. 316







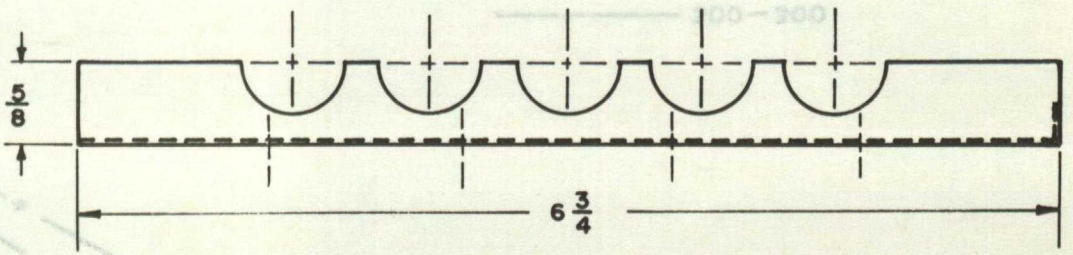


Figure 8. Silica sample dishes and tray.

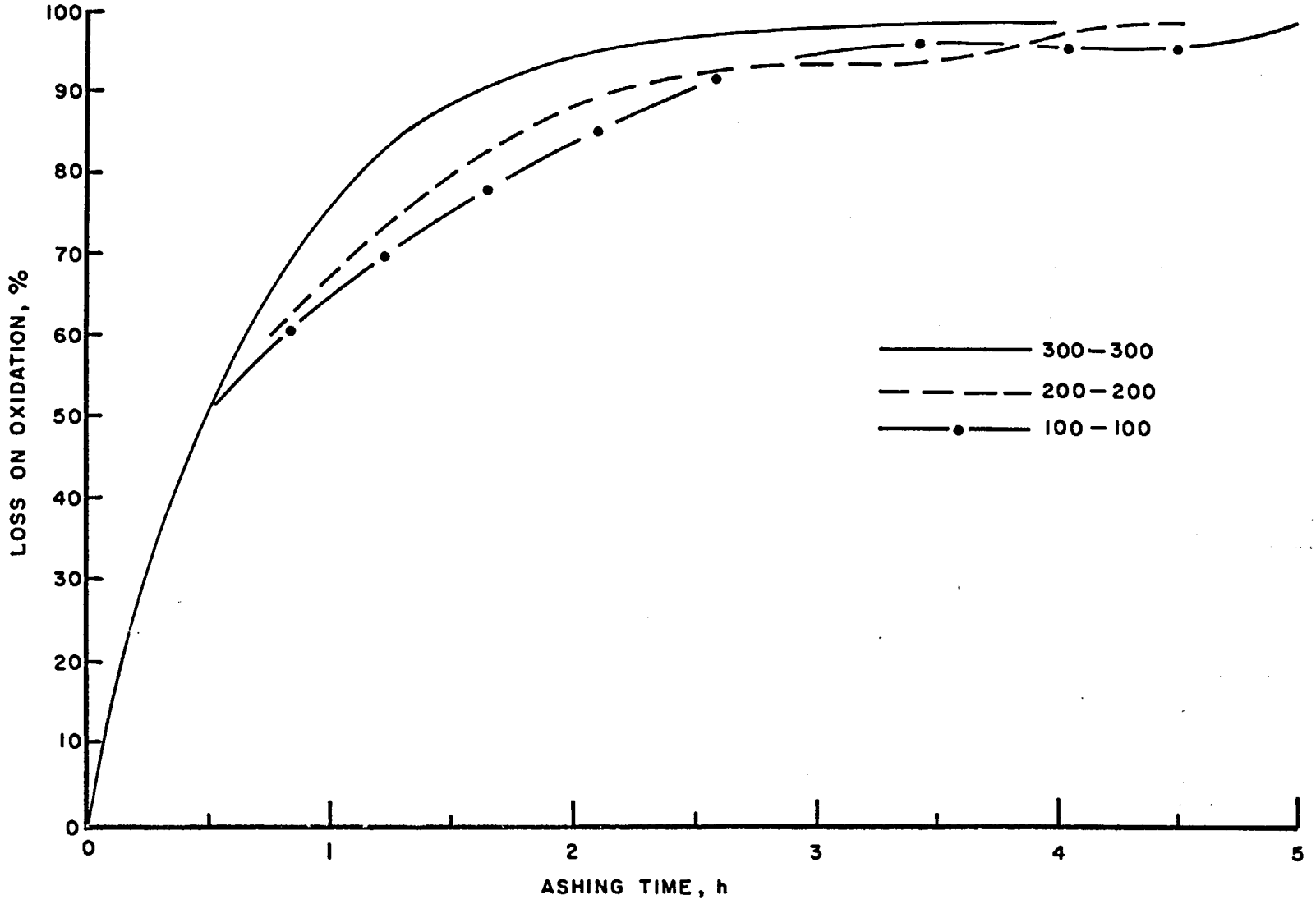


Figure 9. Comparison of three sets of 1:1 (watts:cc/min) ashing parameters.

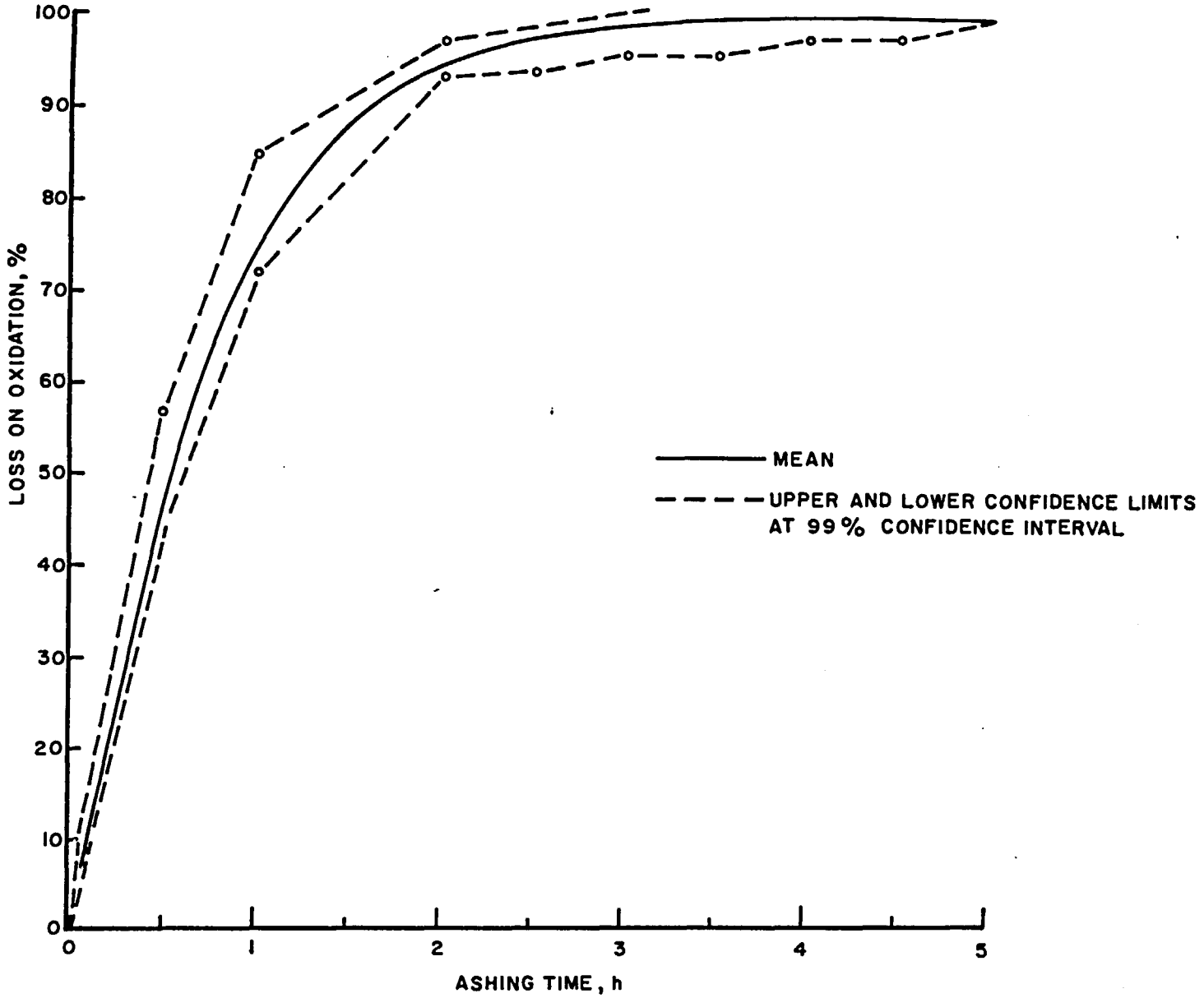


Figure 10. Oxidation curve at practical conditions.
RF = 300 watts, 0_2 = 300 cc/min