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ACTIVE CLEANING TECHNIQUE FOR REMOVING CONTAMINATION FROM OPTICAL SURFACES IN SPACE

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PREPARED FOR
GEORGE C. MARSHALL SPACE FLIGHT CENTER
MARSHALL SPACE FLIGHT CENTER
ALABAMA 35812

BY

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1.0 SUMMARY

This report describes the work accomplished under NASA Contract NAS8-26385. The overall objective of this contract was to develop an active cleaning technique (ACT) for removing contaminants from optical surfaces in space. This effort has concentrated on the feasibility of using plasma exposure as a means of in-situ cleaning.

Since the first year's effort has been documented previously, this report only summarizes the results of that effort and concentrates on the work accomplished since that time. The major work accomplished includes: (1) development of an in-situ reflectometer for use in conjunction with the contaminant film deposition/cleaning facility; (2) completion of Apollo Telescope Mount (ATM) filter treatment experiments to assess the effects of plasma exposure on the UV transmittance; (3) attempts to correlate the atomic oxygen flux with cleaning rate; (4) completion of in-situ butadien contamination/plasma cleaning/UV reflectance measurement experiments; (5) carbon cleaning experiments using various gases; (6) completion of silicone contamination/cleaning experiments; and (7) experiments conducted at low chamber pressures to determine cleaning rate distribution and contamination of surfaces adjacent to those being cleaned.

The major results of these experiments are: (1) all gases used produced similar plasma cleaning effects; (2) in-situ UV reflectance measurements failed to show any large effects of exposing samples to ambient conditions; (3) UV reflectance of mirrors contaminated with silicones could only be partially restored; (4) plasma cleaning at low chamber pressures is possible with proper design; (5) at low chamber pressures the region of plasma cleaning corresponds to the region of a visible plume; and (6) an aluminum-grid coating on carbon-coated surfaces appears to inhibit carbon removal.

It is recommended that plasma tube development be continued and further performance tests be conducted with a suitable plasma tube configuration. It is also recommended that an investigation be made to determine the mechanism responsible for the plasma cleaning phenomena.

2.0 INTRODUCTION

The need for developing an in-situ or active cleaning technique (ACT) for use in both space and vacuum chambers is apparent. Manned spacecraft have experienced numerous contamination problems including deposition of volatile organic compounds onto windows, and light scattering from particulate contaminants surrounding the spacecraft. Sources of this contamination include outgassing of organic compounds, waste and water dumps, rocket plumes, and leakage from the life support system. It is believed that contaminant film deposition has also occurred on unmanned spacecraft surfaces. Data from a reflectometer experiment on the ATS-3 spacecraft (Reference 1) has indicated rather severe degradation on reflective surfaces, which may be the result of contaminant film deposition. Also, the TV camera mirror from the Surveyor III spacecraft which resided on the moon for 2-1/2 years was covered with a diffuse coating--presumably the result of contaminant film deposition. Contamination on an unmanned spacecraft has been verified with quartz-crystal thin film monitors on OGO-6 (Reference 2). A recent review of the spacecraft contamination problem has been published in Reference 3.

Contamination can also occur during spacecraft testing in high vacuum chambers. An example of this was the extreme-UV solar spectroheliometer experiment for the Apollo Telescope Mount (ATM) vehicle. A film of back-streamed diffusion pump oil was apparently deposited on surfaces during thermal/vacuum testing (Reference 4). Another example of contaminant film deposition during environmental testing is discussed in Reference 5. In those experiments it was shown that an extremely stable organic film could be deposited onto telescope mirror surfaces during irradiation with low energy protons in a relatively clean vacuum environment.

Based on existing knowledge, contamination problems anticipated for future spacecraft include: (1) deposition of non-volatile substances onto optical components, sensing elements, and temperature control surfaces; (2) particulate and gaseous contamination near the spacecraft (resulting in light scattering and absorption); and (3) chemical contamination which can interfere with upper atmosphere studies, analysis of interplanetary or planetary matter, and material processing experiments. It is anticipated that contamination effects can be reduced by changes in design,

materials, operating procedures, and possibly control techniques. The use of more sensitive surfaces and longer term missions will, however, offset these improvements. Thus, the need exists for developing an ACT for space use.

Experiments reported in Reference 5 have shown that exposure to a plasma, containing atomic oxygen or combinations of other reactive gases, is an effective means of removing hydrocarbon contaminant films from optical surfaces in a vacuum. The detailed mechanisms of this cleaning process are not known.

The objective of the present program (NASA Contract NAS8-26385) was to develop an ACT for removing contaminants from optical surfaces in space. This contracted effort has concentrated on establishing the feasibility of using a reactive gas plasma for in-situ cleaning. (A companion contract, NASA Contract NAS8-28270, is aimed at development of a laboratory demonstration model ACT device incorporating both reactive gas plasma and ion sputtering cleaning techniques.) The work accomplished during the first year of the present program (described in detail in Reference 6) included: (1) development of a facility for depositing contaminant films and performing plasma cleaning experiments; (2) completion of plasma cleaning experiments on hydrocarbon contaminant films; (3) completion of experiments to determine the effects of an oxygen plasma on selected uncontaminated optical surfaces; (4) completion of thermal cleaning experiments on selected optical surfaces; and (5) initiation of plasma cleaning experiments on silicone contaminant films. These experiments resulted in the following conclusions:

(1) Thermal cleaning experiments showed that the cleaning phenomenon observed on optical surfaces during oxygen plasma exposure does not result from thermal effects.

(2) Exposure to oxygen plasma successfully removed polymerized butadiene contamination from the following surfaces: (a) mirrors coated with 1/2 λ MgF_2/Al, 3/4 λ MgF_2/Al, gold, and platinum; (b) gratings coated with 1/2 λ MgF_2/Al and platinum; (c) fused silica optical flats; (d) silvered FEP Teflon.

(3) Exposure to oxygen plasma further degraded butadiene contaminated thermal control paint samples (ITT Research Institute's S-13g and Z-93). Synergistic

effects were indicated as a result of an experiment in which pristine paint samples were exposed to an oxygen plasma. It was shown that oxygen plasma without butadiene contamination would not produce degradation.

(4) Exposure to oxygen plasma successfully removed polymerized methane contamination from 3/4 λ MgF_2/Al-coated mirrors.

(5) Exposure to oxygen plasma successfully removed ethylene glycol contamination from 1/2 λ MgF_2/Al-coated mirrors.

(6) Combinations of oxygen and hydrogen plasma exposures could not remove silicone contamination from 1/2 λ MgF_2/Al-coated mirrors. A chlorine plasma removed the silicone film in selected areas but also caused pin hole formation in the reflective aluminum film.

(7) Short-duration (∿ 15 min.) exposure to an oxygen plasma produced no degradation on a pristine 3/4 λ MgF_2/Al-coated mirror.

The work documented in this report is based primarily on the recommendations made after the first year's effort (Reference 6). The following sections include descriptions of the preparation of an in-situ ultraviolet reflectometer/monochromator and the results of in-situ contamination/cleaning experiments, the results of further cleaning experiments on silicone films, oxygen flux/cleaning rate correlation results, cleaning rate distribution experiments and the contamination of surfaces adjacent to those being cleaned.

3.0 EXPERIMENTAL APPARATUS

3.1 Contaminant Film Deposition/Cleaning Facility

Figure 1 shows the contaminant film deposition/cleaning facility developed during the first phase of this contract. The details of this facility are described in Reference 6. A contaminant vapor source, proton accelerator, ultraviolet light source, residual gas analyzer and a plasma generator system are incorporated in the facility. The proton accelerator and residual gas analyzer were not used in the experiments described in this report. Also, only a single plasma tube was used instead of the three plasma tubes shown in Figure 1. Figure 2 shows the plasma tube configuration used in all experiments except those described in Section 4.6. The plasma tube consists of a 10 mm ID outer quartz tube, a 4 mm ID inner quartz tube and diametrically opposed tungsten wire electrodes in the annulus. The radio frequency (r.f.) power was supplied with a 13.6 MHz power supply. The plasma tube was normally operated at a nominal upstream pressure of 4 torr which produces an oxygen flow rate of about 50 STD cc/min. The resultant vacuum chamber pressure at this flow rate is in the 10^{-3} - 10^{-2} torr range.

Under these conditions the plasma discharge results in what may be called the 'ignited plume' mode of operation. The plasma discharge occurs both in the plasma tube and in a localized plume ('ignited plume') extending beyond the downstream end of the plasma tube. In this mode of operation, there is also a 'chamber discharge' phenomenon (i.e., a glow throughout the vacuum chamber). Section 4.6 describes the operation of a modified plasma tube configuration at low chamber pressures (10^{-5} - 10^{-4} torr range) where the 'chamber discharge' phenomenon does not occur.

The contamination source used in the experiments was either 1, 3 butadiene or outgas products of silicone compounds which were placed in a heated tube connected to the contamination inlet port. The following section (3.2) describes the addition of an ultraviolet reflectometer/monochromator to the facility. This allows in-situ reflectance measurements of samples involved in the contamination/cleaning experiments.

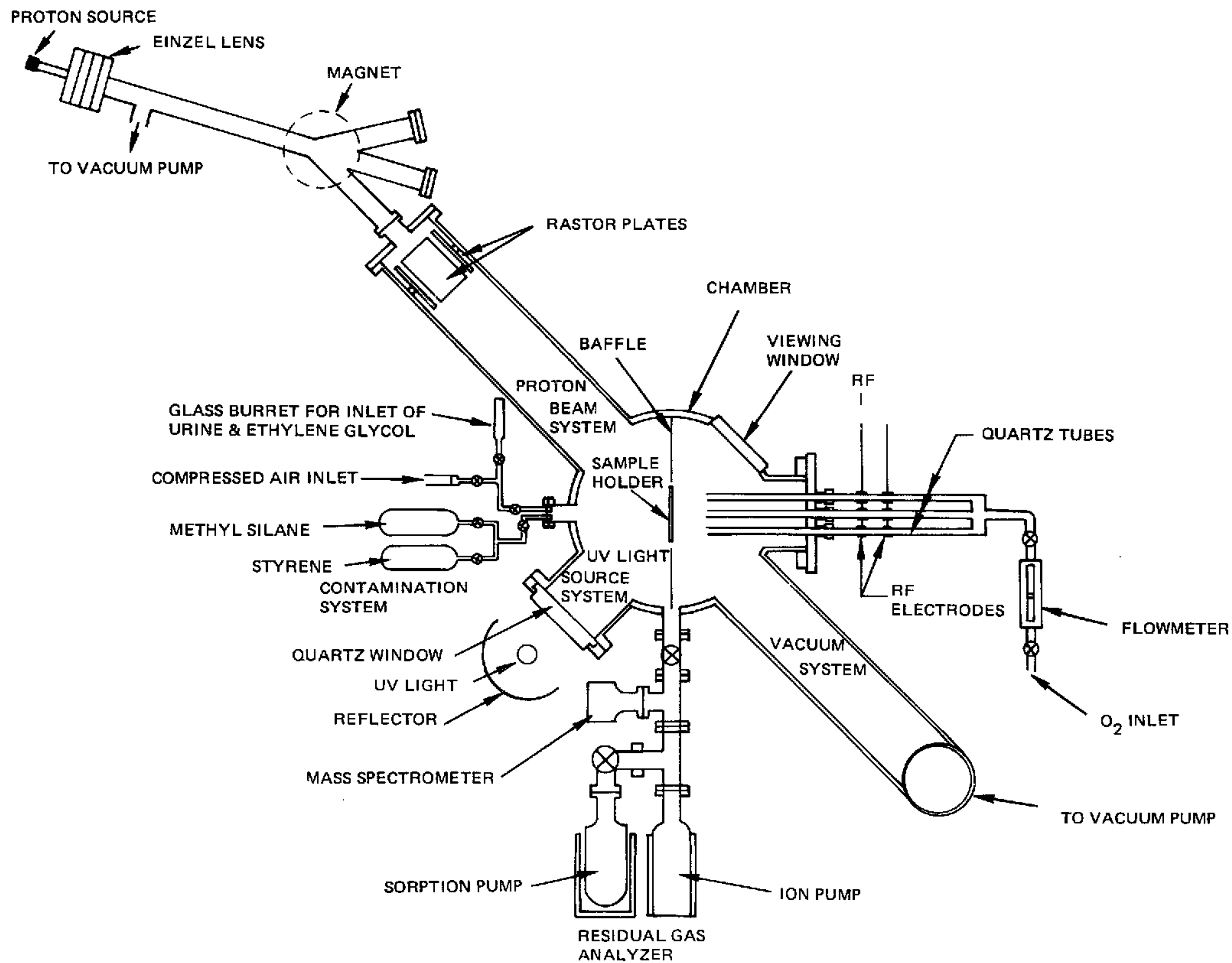

Figure 1: CONTAMINANT FILM DEPOSITION/CLEANING FACILITY

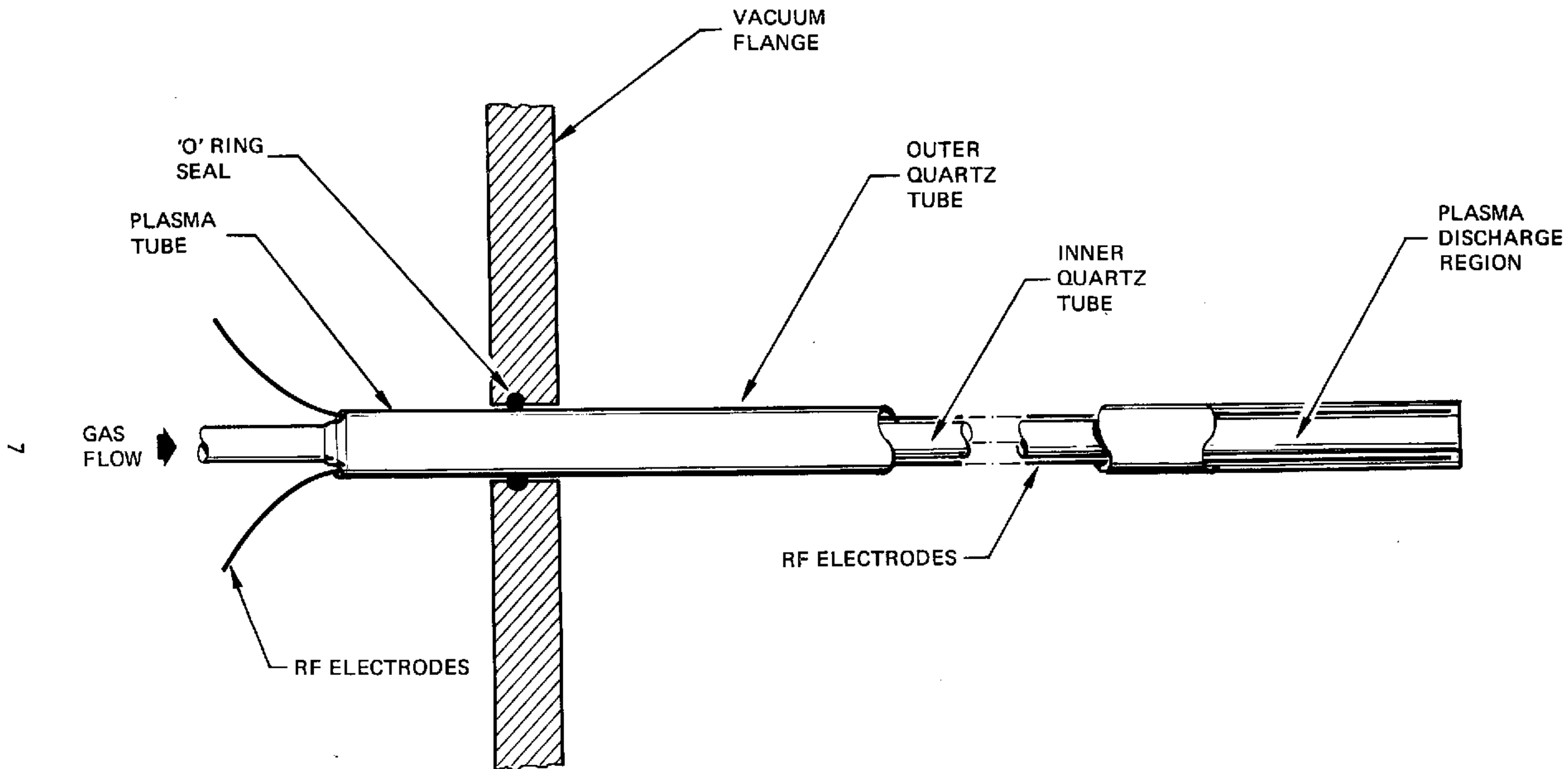

Figure 2: PLASMA TUBE CONFIGURATION

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3.2 In-Site Ultraviolet Reflectometer/Monochromator

An ultraviolet reflectometer was prepared which could be used in conjunction with the existing plasma cleaning/contamination facility. This instrument allows reflectance measurements to be made before and after contaminant deposition and plasma cleaning, without exposing specimens to ambient pressure. In prior experiments (Reference 6) specimens had to be transferred in air to the ultraviolet reflectometer, thus introducing possible chemical and optical changes in the contaminant films.

A schematic of the in-situ ultraviolet reflectometer and plasma cleaning chamber is shown in Figure 3. The reflectometer facility is located immediately below the existing plasma cleaning chamber. Specimens can be either contaminated or plasma-exposed, and then transferred with a translational/rotational probe to the reflectometer chamber. A gate valve separates the two chambers during contamination and cleaning operations to protect the reflectometer optics. The reflectometer and associated ultraviolet monochromator are commercially available equipment*, although the reflectometer was modified slightly to allow insertion of a specimen with the transfer probe. Also, special electronics were fabricated to (1) control the voltage applied to the measurement photomultiplier (PM) detector based on output from a reference PM tube, and (2) to measure the current output from the measurement PM tube. Both the plasma chamber and the reflectometer/monochromator are evacuated with liquid-nitrogen-trapped diffusion pumps. A photograph of the plasma cleaning chamber, monochromator and reflectometer is shown in Figure 4.

Figure 5 shows a photograph of the apparatus used for transferring the specimen. The specimen transfer probe is actuated with a rack/pinion gear drive mounted on the top of the plasma cleaning chamber. Test specimens (5.08 x 5.08 cm sq) are mounted in a fixture which is attached to the end of the transfer probe with a flexible connector. The specimen mounting fixture is designed such that it locks into optical alignment when inserted into the reflectometer chamber, and clamps to the temperature-controlled copper plate when located in the plasma cleaning chamber.

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*McPherson Instrument Co., Acton, Massachusetts
Monochromator Model 218
Reflectometer Model 655SS

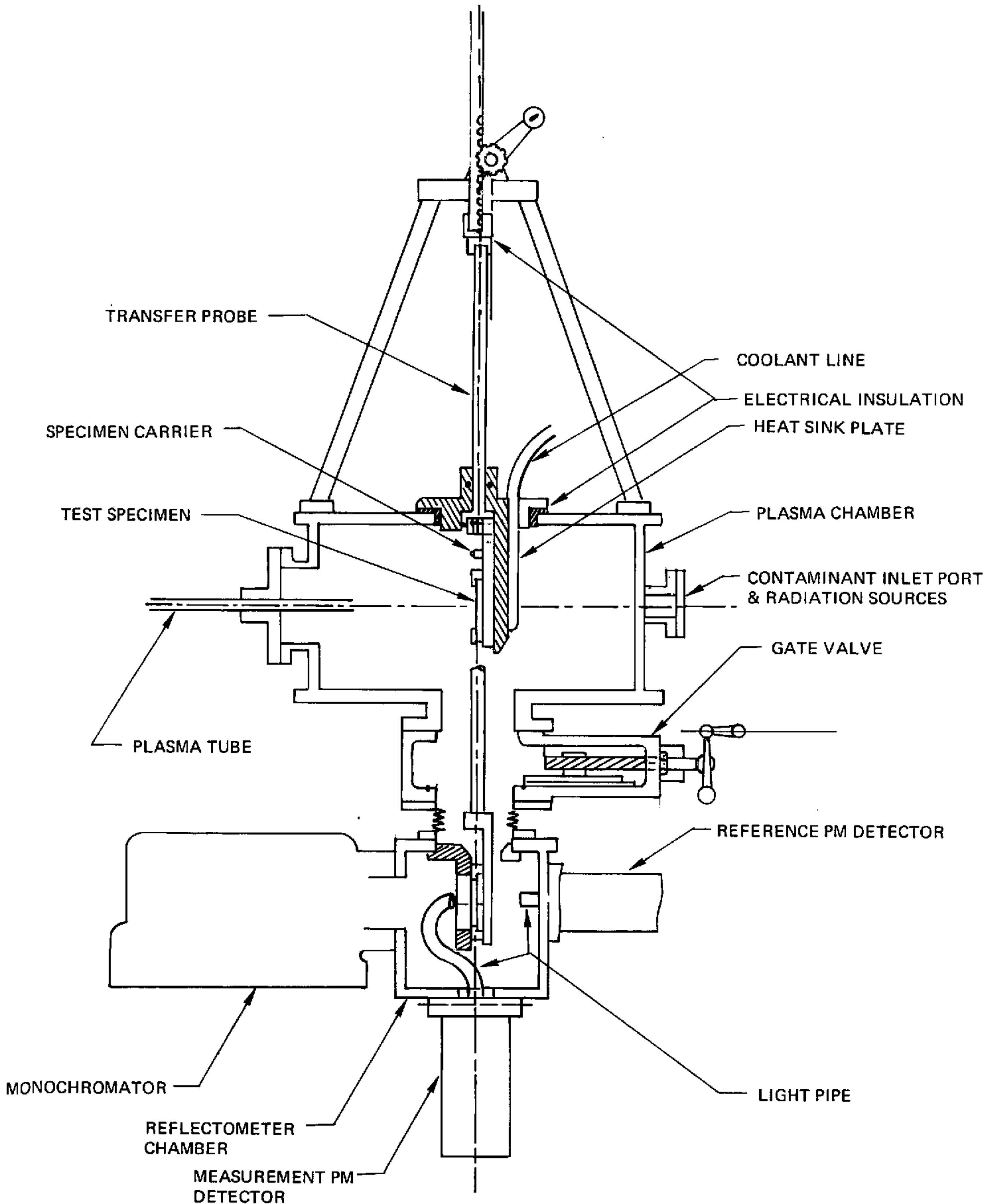

Figure 3: SCHEMATIC OF IN-SITU UV REFLECTOMETER

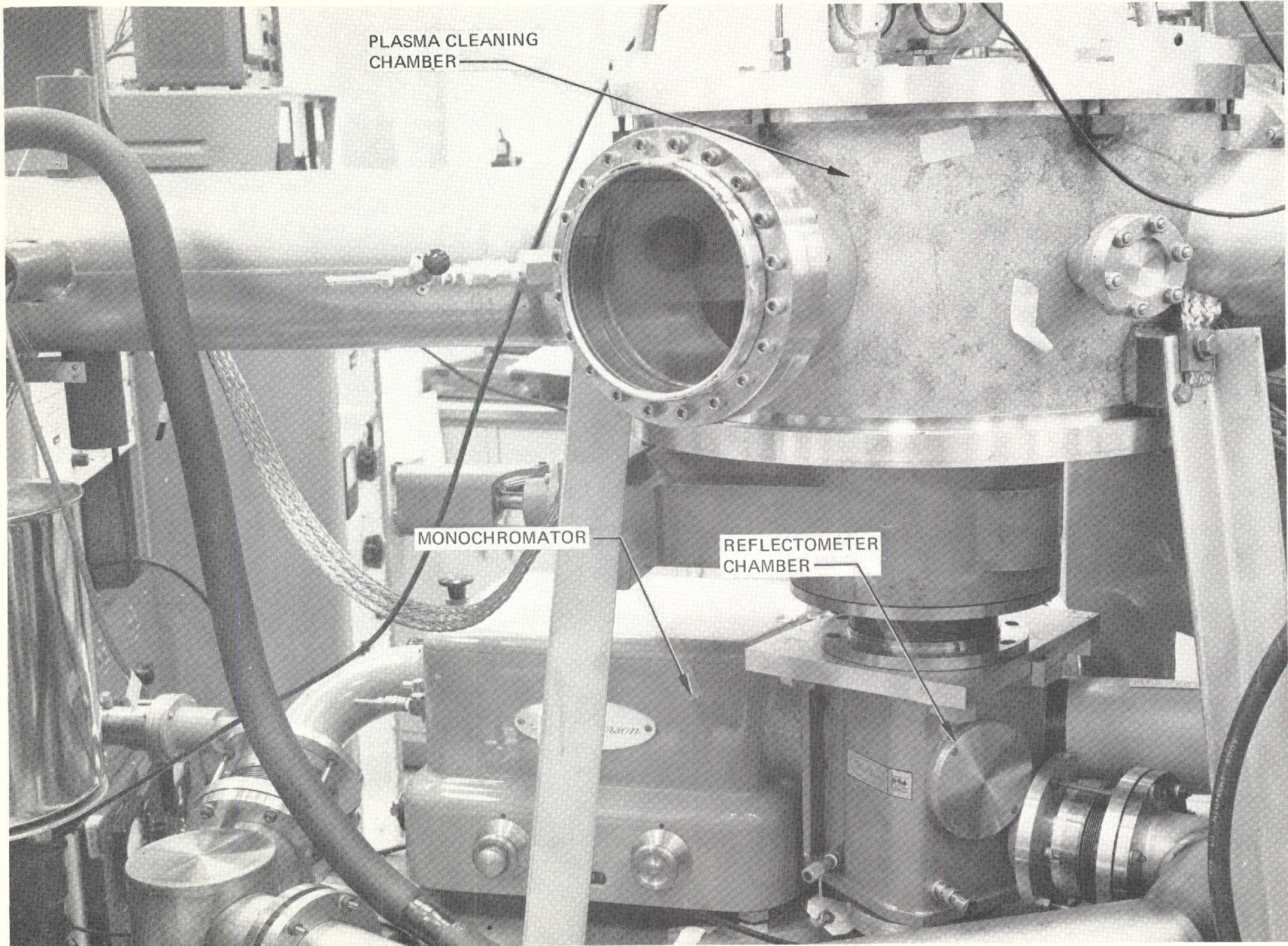

Figure 4: PLASMA CLEANING FACILITY

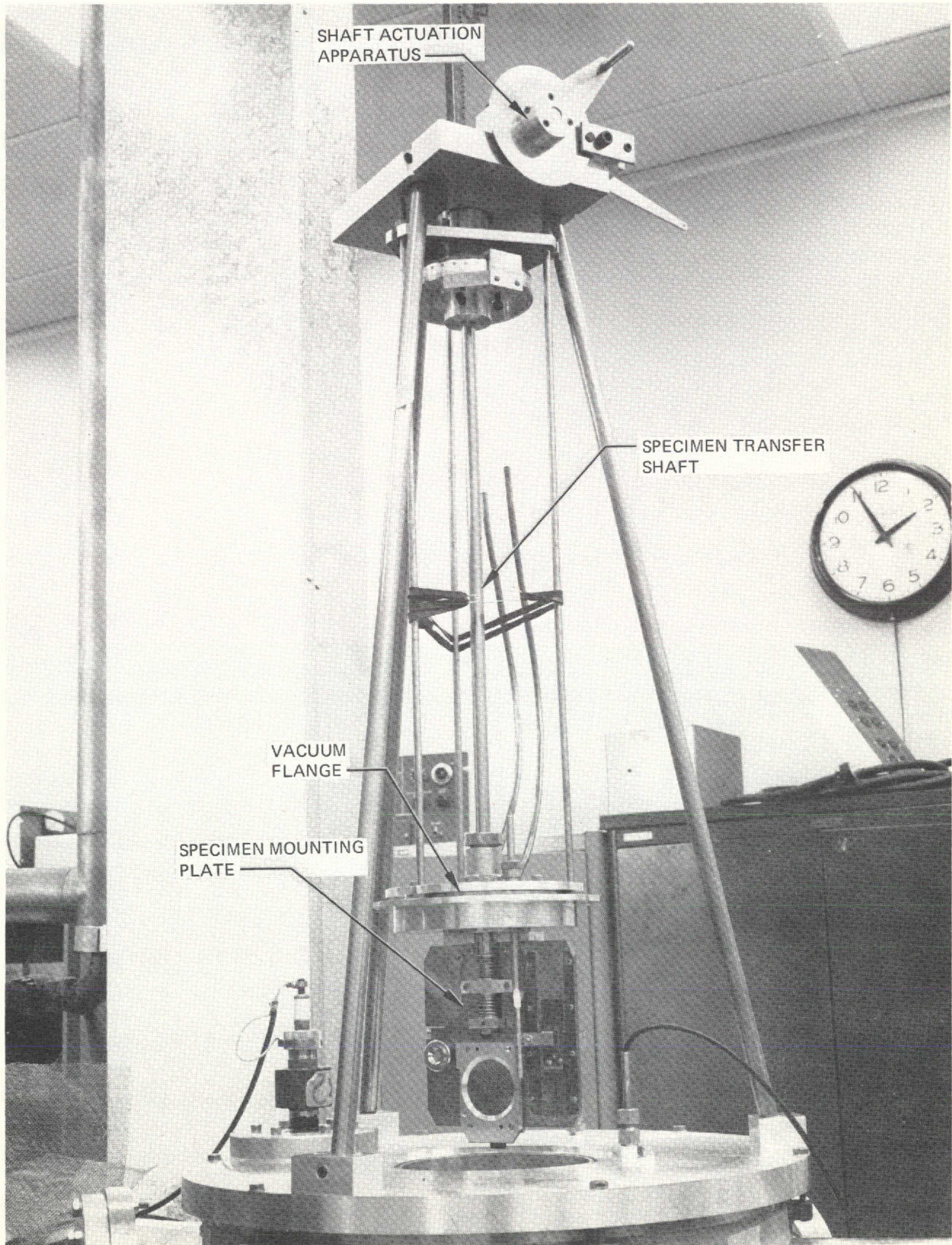

Figure 5: APPARATUS USED FOR TRANSFERRING SPECIMEN FROM PLASMA CLEANING CHAMBER TO REFLECTOMETER

The specimen mounting fixture and heat-sink plate are designed such that they can be retracted from the plasma chamber by upward linear motion of the transfer probe. Also, they can be rotated 360 degrees (with respect to the probe axis), and are electrically isolated from the chamber. Withdrawal of the entire assembly from the chamber facilitates installation of specimens. The rotational feature of the specimen mounting apparatus allows it to be oriented towards the plasma generation tube, the contaminant inlet port, and ultraviolet or proton radiation sources. The capability to electrically isolate specimens from the chamber may be useful for future contamination and cleaning experiments.

A detailed view of the specimen mounting plate and associated hardware is shown in Figure 6. The mirror specimen is mounted in a fixture which is located at the lower center of the plate. The mirror fixture locks onto the copper mounting plate when the transfer shaft is in its upper position, and releases from the plate when the shaft is lowered. A quartz crystal monitor (QCM) is mounted on the plate at the left side of the specimen. An interferometer reference mirror (IFM) for contaminant film thickness measurements is mounted at the right side of the specimen. A thin brass cover can be moved along the surface of the IFM to protect contaminated or cleaned areas from additional plasma exposure. The cover is actuated with a translational/rotational shaft which passes through a vacuum seal in the plasma chamber wall.

Details of the reflectometer optical system are shown in Figure 7. A conventional Hinteregger gas discharge lamp is used as the light source for the monochromator. As shown in the figure, light from the entrance slit is collimated and directed to the grating. Reflected light from the grating illuminates a second concave mirror and is focussed on the exit slit. The grating is ruled with 600 lines/mm, blazed at 150 nm wavelength, and employs an aluminum reflective coating which is overcoated with MgF_2. Light entering the reflectometer chamber is reflected by an oscillating mirror to the reference PM detector and the measuring PM detector. Both detectors utilize a sodium-salicylate-coated light pipe to transmit radiation from the chamber to the PM tube cathode. The measuring detector has a rotatable U-shaped light pipe such that it can view either the reflected light from a mirror specimen or the light incident on the specimen. The latter measurement is made by removing the mirror from the light path and orienting the light pipe to view direct light

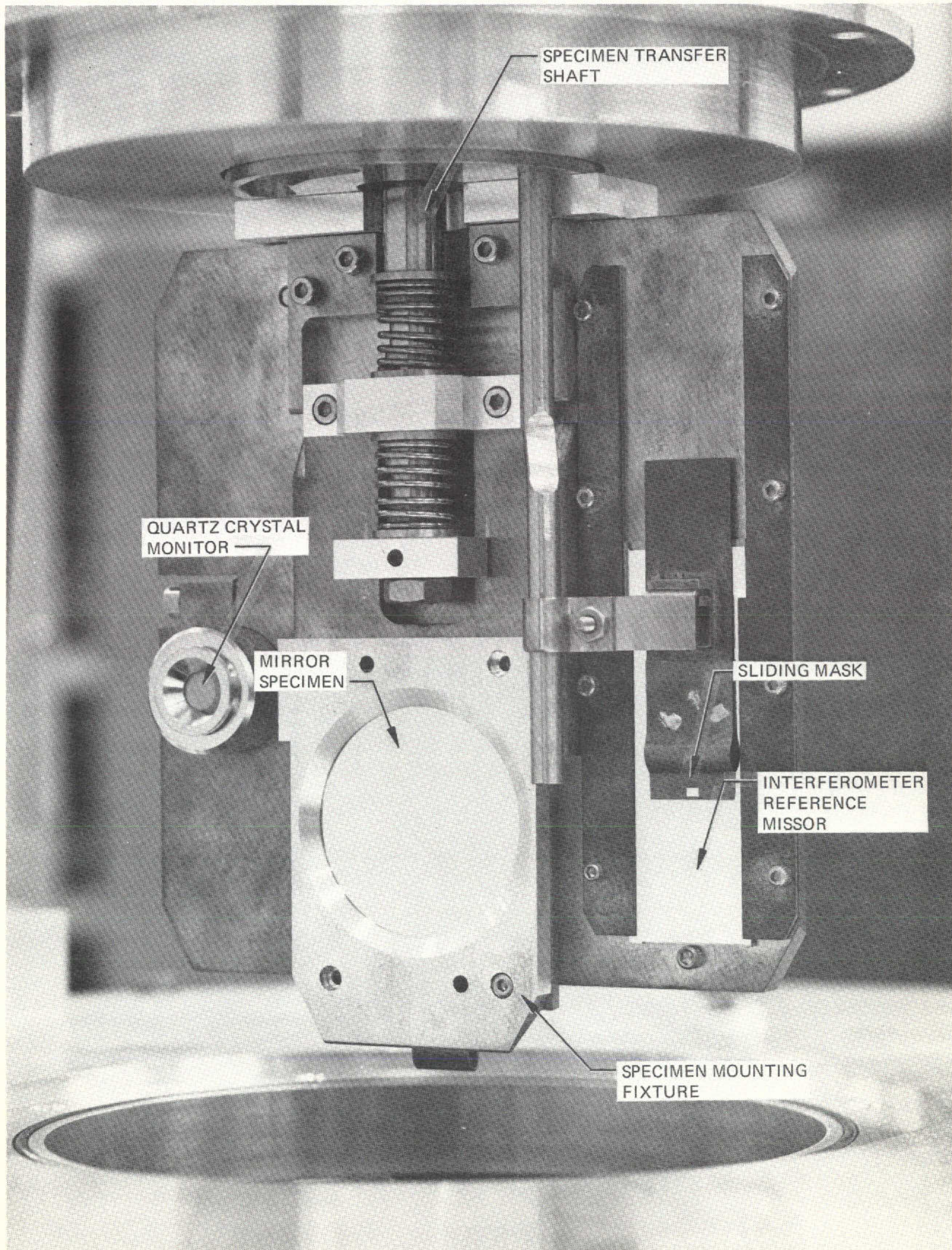

Figure 6: SPECIMEN MOUNTING PLATE

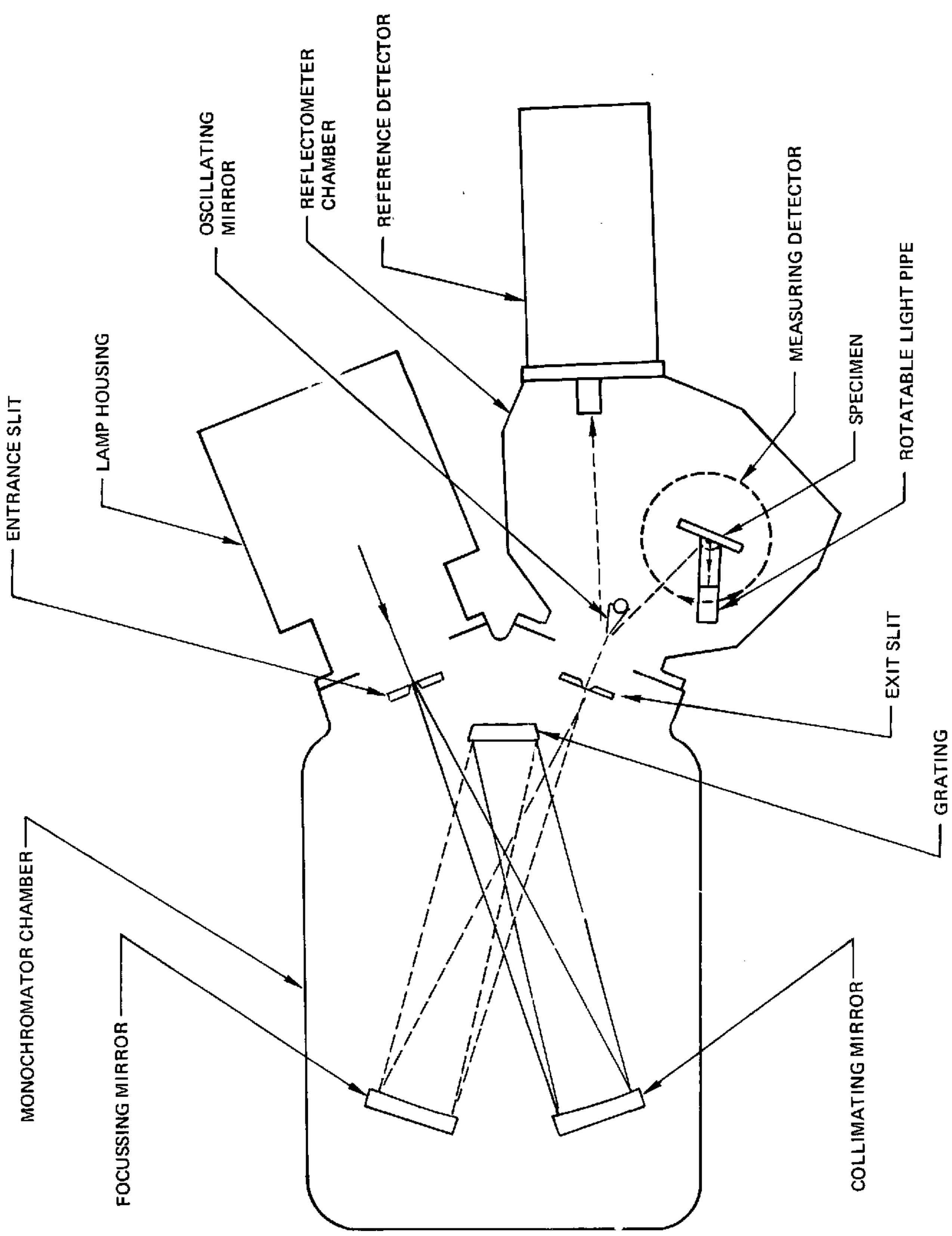

Figure 7: *LIGHT PATH SCHEMATIC FOR IN-SITU ULTRAVIOLET REFLECTOMETER*

from the oscillating mirror. Reflectance is determined by ratioing outputs of the PM tube in the "reflected" and "incident light" positions. Variations that may occur in the monochromator light output while the two readings are being taken are compensated by changes in voltage applied to the measurement PM tube. As mentioned earlier, an electronic feedback control system is used whereby the output of the reference PM tube is used to control the voltage on both the reference and measurement PM tubes. In essence, the voltage required to maintain constant current output on the reference PM tube is applied to the measurement tube.

For purposes of this program, the angle of light incidence on the test specimen was set at 24 degrees from normal. The angle of incidence can be changed by rotating the alignment fixture in the reflectometer chamber. Transmittance measurements can also be made with the reflectometer, however, the specimen holding fixture on the transfer probe would have to be modified to allow light to pass through it.

Prior to conducting in-situ contamination/cleaning experiments, ultraviolet reflectometer checkout tests were conducted to establish wavelength operating range, reproducibility and accuracy. The reflectance of a gold-coated mirror was measured at three wavelengths and compared to data taken with a different reflectometer. The agreement between data from the two reflectometers was good. The wavelength range capability for the grating was initially established to be between 120 and 240 nanometers (nm). Scattered light was held responsible for the lower limit and second-order effects for the upper limit. Second-order radiation is light of one-half the wavelength at which the monochromator is set to operate. Reproducibility of the in-situ system was found to be excellent. Repeated UV reflectance scans of a pristine MgF_2 overcoated Al mirror yielded data with reproducibility within 1 percent. This data, in comparison with reflectance data from a different reflectometer for the same mirror taken a year earlier, was lower by as much as 11 percent. This discrepancy may be due to erroneous reflectance data or, more likely, changes in optical properties of the mirror caused by contamination during storage.

To extend the long wavelength measurement capability of the reflectometer, a sapphire-window manual deployment mechanism was installed in the monochromator. The deployment of the sapphire window is actuated external to the monochromator by means of a sealed shaft. By deploying the sapphire window to intercept the light

beam emerging from the entrance slit, the shorter wavelengths are eliminated from the beam. This extends the long wavelength measurement capability to 300 nm by eliminating the second-order radiation.

4.0 EXPERIMENTAL RESULTS

4.1 ATM Filter Treatment Experiments

Plasma treatment experiments were conducted on aluminum filters of the type used in an OSO-7 spacecraft experiment and planned for use in an ATM solar scanning experiment. These filters consist of a vacuum deposited aluminum membrane (3.3 cm sq) supported on a fine wire grid. They are designed to transmit radiation in the 17 to 80 nm wavelength region, and reject (reflect or absorb) radiation in the region beyond about 80 nm. The filter treatment experiments developed out of earlier exploratory work, in conjunction with the Naval Research Laboratory (Washington), which was aimed at determining the cause of degradation of an extreme-UV solar scanning experiment on an OSO spacecraft. Since it was postulated that the aluminum filters may be oxidizing in space, the filters were exposed to an oxygen plasma in an attempt to verify this degradation mechanism. Surprisingly, it was found that the transmittance (at 30.4 and 58.4 nm) of the filters increased. It was then postulated that the "as prepared" filters were contaminated and the plasma was removing this contamination. One source of contamination was thought to be residual fluorescein (a parting agent used in the manufacture of the filters). Subsequently the present contract was expanded to include (1) determining whether residual fluorescein was, in fact, the cause of degradation of OSO filters, and (2) determining an optimum plasma exposure-time for maximizing the transmittance of filters.

The ATM filter treatment experiments involved exposure of several filters to an oxygen plasma, and one filter to an argon plasma. Transmittance measurements at a wavelength of 58.4 nm were made before and immediately after each plasma exposure. The measurement facility used was a Boeing-fabricated reflectometer (modified to measure transmittance) and an associated McPherson Model No. 225 monochromator.

The first set of filters (No.'s 5 and 6) were treated with a series of oxygen plasma exposures. Each filter had half of its surface area purposely coated with a layer of fluorescein, 7 nm thick on No. 5 and 15 nm on No. 6. These thicknesses of fluorescein were assumed to be relatively large compared with any residual fluorescein resulting from the manufacturing process. Therefore, if the plasma was in fact removing residual fluorescein, the presence of additional fluorescein on half

of each filter should significantly retard the increase in transmittance. The transmittance data are presented in Table 1 and in Figure 8. Figure 8 shows the percent change in transmittance ($\frac{\Delta T}{T}$ x 100) vs accumulated plasma exposure time for the uncoated portions of filter No.'s 5 and 6.

TABLE 1: TRANSMITTANCE DATA FOR FLUORESCEIN-COATED ALUMINUM FILTERS EXPOSED TO AN OXYGEN PLASMA

	FILTER NO. 5		FILTER NO. 6	
	Uncoated Portion	Coated Portion (~7 nm)	Uncoated Portion	Coated Portion (~15 nm)
Initial Measurement	13.0%	10.5	12.3	7.0
After 120 sec oxygen plasma exposure	17.5	18.3	17.5	18.0
After additional 900 sec plasma exposure	21.0	--	21.0	--
Remeasurement after ~68 hrs in ambient air	19.2	--	--	--
Measurement after additional 3260 sec plasma exposure	20.0	--	21.0	--
Remeasurement after ~77 hrs in ambient air	18.5	--	19.5	--

As noted in the table, the initial transmittance of fluorescein-coated areas was substantially lower than the uncoated portions. After an oxygen plasma exposure of 120 sec, the transmittance of both portions of each filter increased to essentially the same value (17.5 to 18.3 percent). The fact that coated portions of the filters differed in initial transmittance, but had equivalent transmittance after the first plasma exposure, indicates removal of fluorescein. After an additional 900 sec exposure, the transmittance of both filters continued to increase (see Figure 8). It therefore appears unlikely that the removal of residual fluorescein is alone responsible for the increase in transmittance.

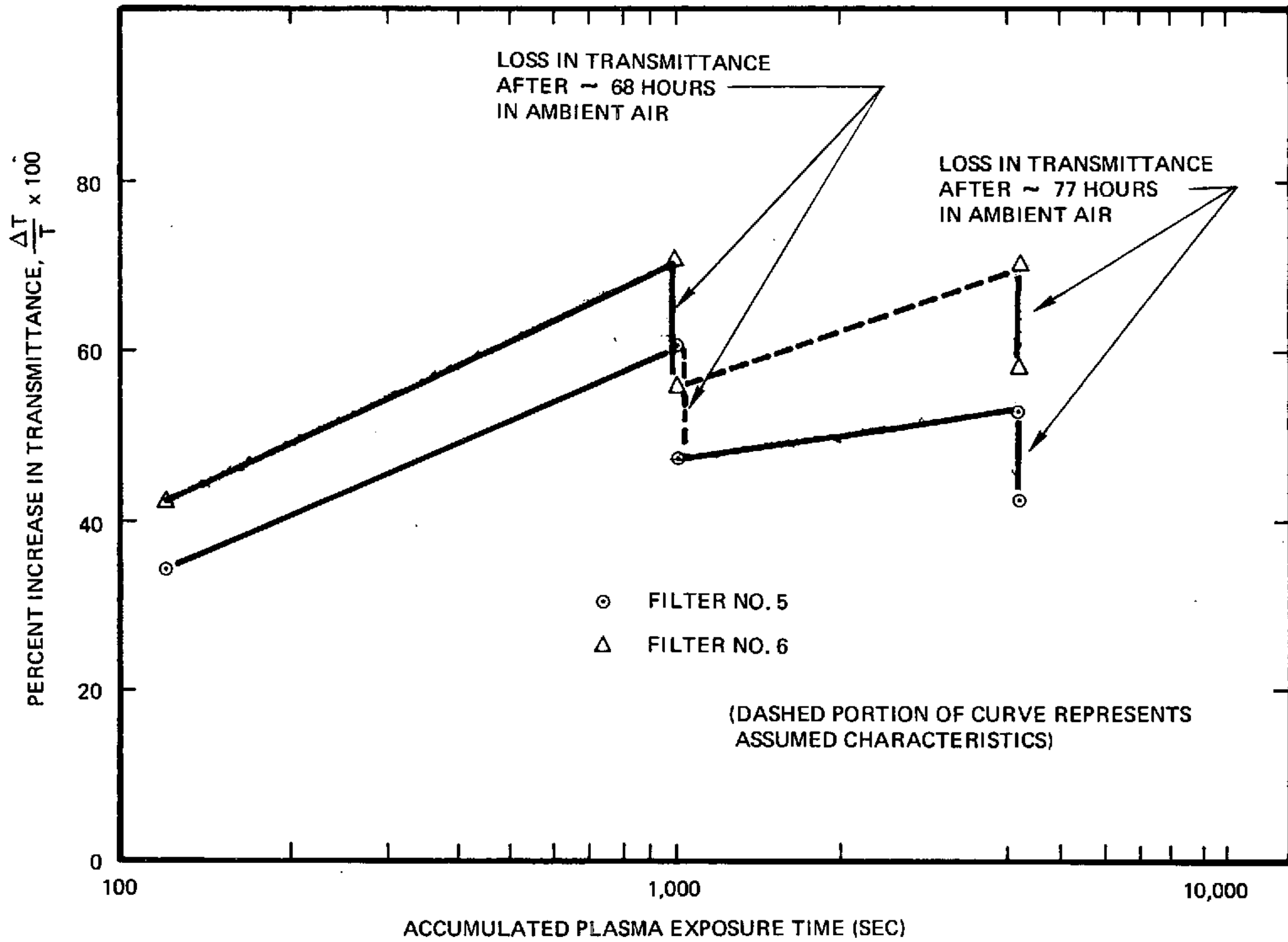

Figure 8: THE EFFECT OF OXYGEN PLASMA EXPOSURE AND AMBIENT AIR EXPOSURE ON ATM FILTER NOS. 5 AND 6

After about 68 hours in ambient air, filter No. 5 was remeasured and a slight loss in transmittance was observed (Figure 8). Subsequently, filter No.'s 5 and 6 were exposed for an additional 2360 secs in an oxygen plasma. The transmittance of filter No. 5 once again increased, but only slightly. Remeasurement after a period of about 77 hours in ambient air again showed a slight decrease in the transmittance of each filter (Figure 8). It must be concluded that exposure to ambient air following treatment will produce a slight decrease in transmittance of aluminum filters.

The second set of filters, No.'s 1 and 9, were involved in a series of oxygen plasma exposures to determine an optimum exposure time for producing maximum transmittance. Filter No. 9 was shielded with a 4.2 cm sq aluminum plate, located 2.54 cm from the filter surface. It was anticipated that this shield would protect the specimen from radiation produced in the plasma discharge, while allowing impingement of active species. Data on filter No.'s 1 and 9 are presented in Table 2 as well as in Figure 9. As shown in Figure 9, there is an optimum exposure time of about 2000 secs for both the shielded and unshielded filters. Although the shielded filter (No. 9) exhibits a lower rate of transmittance increase initially, it reaches a slightly higher maximum (49 vs 44 percent). In general, the results of this experiment indicate that radiation produced in the plasma discharge is not the primary cause of observed increases in filter transmittance during plasma treatment.

TABLE 2: TRANSMITTANCE DATA FOR ALUMINUM FILTERS EXPOSED TO AN OXYGEN PLASMA

	Filter No. 1	(Shielded) Filter No. 9
Initial measurement	21.0%	21.5
After 15 secs oxygen plasma exposure	23.0	22.0
After additional 30 secs	25.5	24.0
After additional 75 secs	27.0	27.0
After additional 300 secs	28.7	29.5
After additional 1,380 secs	30.2	32.0
After additional 5,400 secs	28.5	30.5
After additional 10,800 secs	25.0	28.7

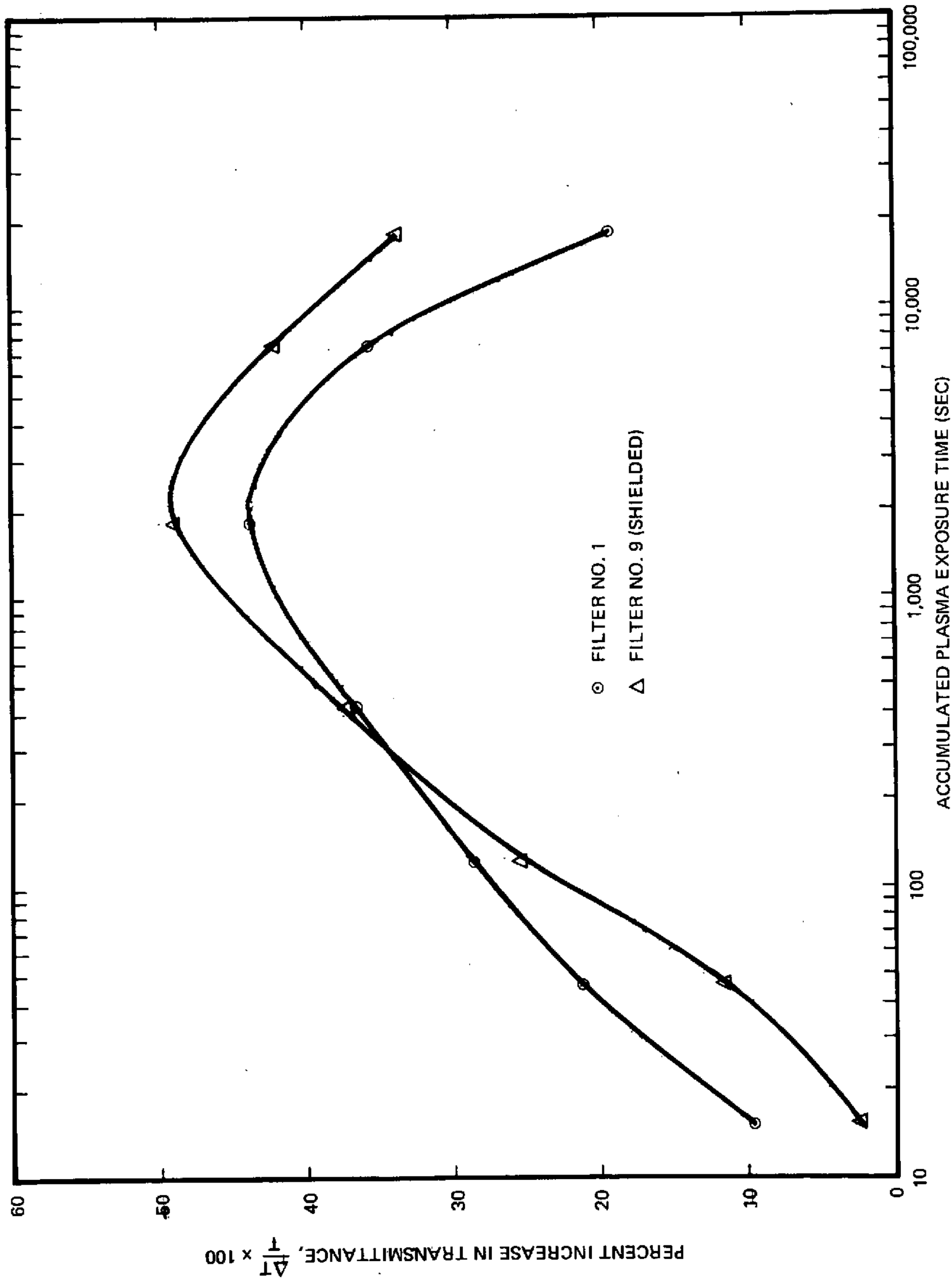

Figure 9: *THE EFFECT OF OXYGEN PLASMA EXPOSURE ON UNSHIELDED AND SHIELDED ATM FILTER NOS. 1 AND 9*

Filter No. 7 was exposed to a low-temperature argon plasma to determine whether the increased transmittance effect is unique to reactive gas plasma exposure (e.g., oxygen). The argon plasma exposure of 2,440 secs (similar to the optimum exposure time for the oxygen plasma) produced a 32 percent increase in transmittance. Consequently it must be concluded that the reactive-gas cleaning principle, available in an oxygen plasma but not in an argon plasma, is not necessary to produce the desired effect. Subsequent to these experiments it was also found that: the presence of atomic oxygen is not sufficient for cleaning carbon (Reference 7); an argon plasma is as effective as an oxygen plasma in removing a butadiene contaminant film (Section 4.3.3); helium, hydrogen and oxygen plasmas are equally effective in removing carbon (Section 4.4); and, helium, hydrogen and oxygen plasmas all have an effect on a silicone contaminant film (Section 4.5).

4.2 Atomic Oxygen Flux/Cleaning Rate Correlation

At the beginning of the contracted effort it was believed that the plasma cleaning mechanism was the reaction, of atomic oxygen with the contaminant film, forming volatile products. This led to the contractual requirement of determining the correlation between cleaning rate and atomic oxygen flux. This correlation, along with that between plasma tube operating conditions and atomic oxygen flux generated, would then define the requirements for plasma cleaning. A more direct correlation would be that between the plasma tube operating conditions and the plasma cleaning rate. However, with the exception of those experiments conducted at the end of the program (Section 4.6), all of the experiments were conducted under conditions which resulted in a plasma discharge throughout the vacuum chamber. In this mode of operation the plasma cleaning is not directly related to the discharge in the plasma tube. The companion contract (NAS 8-28270) includes the development of a plasma tube that operates at low chamber pressures where the 'chamber discharge' does not occur.

Based on the assumption that atomic oxygen was responsible for cleaning, the development of an atomic-oxygen-flux probe was initiated under the present contract and continued under the companion contract. The probe development was based on the measurement of heating caused by atomic oxygen recombination on a catalytic surface. Reference 7 documents the probe development and problems that led to termination of the development effort. The oxidation rate of silver was then used (assuming the silver oxidation to be caused by atomic oxygen) to determine the

lower bound on the atomic oxygen flux. Results of experiments in the companion contract showed that the plasma tubes (operating in a high vacuum environment without a visible plume) produced silver oxidation but did not produce any measurable contaminant cleaning. Consequently, it was concluded that there is no significant correlation between atomic oxygen flux and plasma cleaning rate (see Reference 7).

4.3 Butadiene Contamination/Cleaning Experiments

4.3.1 MgF_2 Overcoated Al Mirror Experiments

In-situ contamination/cleaning experiments were conducted on two MgF_2 overcoated Al mirrors (MgF 39 and MgF 56). Prior to the contamination/cleaning experiments, MgF 39 (a 1/2λ MgF_2-overcoated Al mirror) was involved in the previously discussed (Section 3.2) check-out tests performed on the in-situ reflectometer. Specular reflectance data for MgF 39 is presented in Figure 10. This mirror specimen, together with a quartz cyrstal (QCM) and an interferometer reference mirror, (IFM) were exposed to 1-3 butadiene gas at a pressure of 4 torr in the presence of UV radiation for 918 minutes. The resulting reflectance degradation, as much as 90 percent at some wavelengths, was comparable to the degradation observed for MgF 48 which was contaminated for 1096 minutes (Reference 6, Figure 25, p. 40). Measurement of the contaminant film by interferometry indicated a deposited thickness of about 250 nm. The QCM response to the contaminant deposition is shown in Figure 11. The overall frequency change during contamination was 650 Hz. The deposition rate appeared nearly linear (about 42 Hz/hour) following an initial period (about 20 mins.) of negligible deposition. The mirror, QCM, and IFM were then treated to a series of oxygen plasma exposures (see Table 3). Plasma operating conditions were similar for all exposures (see Table 4). The first three plasma exposures successively reduced the UV reflectance at shorter wavelengths and increased the reflectance at longer wavelengths (see Figure 10). The wavelength range of increasing reflectance successively extended into shorter wavelength regions. The fourth plasma exposure substantially improved the reflectance of MgF 39 throughout the entire region. The fifth and sixth exposures increased the reflectance to within 3 percent of the initial value at 220 nm. At shorter wavelengths the remaining degradation was as much as 53 percent. Further plasma exposures successively decreased the UV reflectance in the wavelength region from 120 to 150 nm while not

significantly affecting the reflectance above 150 nm. As a result of the apparent degradation by over-cleaning, plasma treatment was ceased after the tenth exposure.

TABLE 3

Exposure No.	Time (min)	Cumulative Time (min)
1	21	21
2	20	41
3	30	71
4	50	121
5	33	154
6	20	174
7	30	204
8	30	234
9	35	269
10	72	341

TABLE 4

Oxygen flow. . . . . 50 Std cc/min
Upstream pressure (reservior). . . . . 4.0 torr
Downstream pressure (chamber). . . . . 1.0×10^{-3} torr
Radiofrequency power . . . . 15 Watts

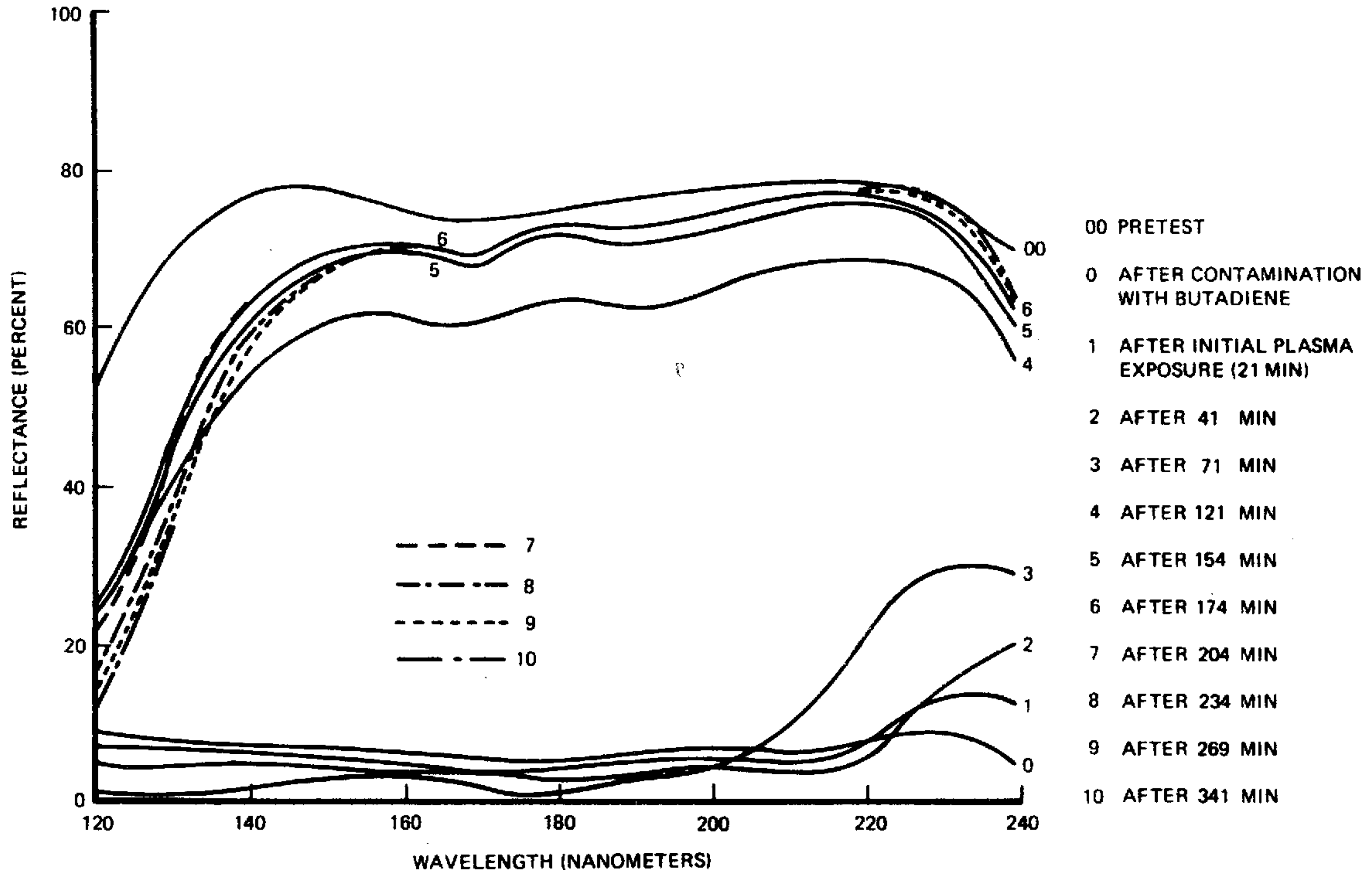

Figure 10: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA EXPOSURE ON REFLECTANCE OF 1/2λ – Mg F_2/Al – COATED MIRROR (NO Mg F-39)

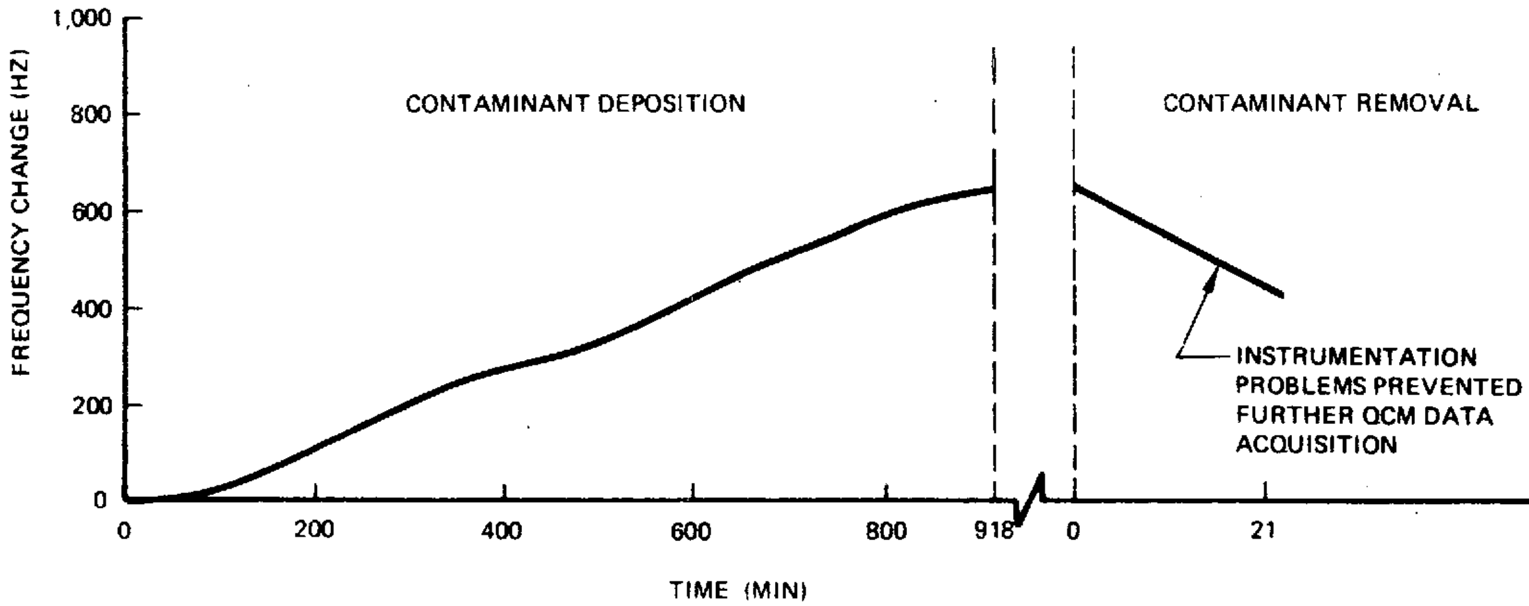

Figure 11: QCM RESPONSE TO BUTADIENE CONTAMINATION AND OXYGEN PLASMA EXPOSURE

A similar set of experiments was conducted with a second $1/2\lambda$ - MgF_2/Al coated UV reflecting mirror (MgF 56). Spectral reflectance data for this mirror is shown in Figure 12. The initial measurement of this mirror indicated higher reflectance in the region from 120 to 140 nm, and otherwise similar reflectance in comparison with MgF 39. MgF 56 with its companion QCM and IFM were then contaminated in the presence of 1 - 3 butadiene gas (chamber pressure about 4.0 torr) and UV radiation for 320 minutes. The resulting degradation in reflectance (as much as 75 percent) was less than the degradation observed with MgF 39. The QCM recorded a frequency change of 200 Hz. Interferometry indicated a deposited film thickness of about 30 nm. MgF 56 with QCM and IFM were then treated in a series of six plasma exposures of 3 minutes each. Plasma operating conditions were the same as before except the r.f. power was set to 30 watts. Reflectance measurements indicated a trend observed previously with MgF 39 whereby restoration occurred first in the longer wavelength region and, with successive exposures, extended into the shorter region. Following the first two plasma exposures, reflectance maxima and minima in the shorter wavelength regions (120 to 200 nm) were observed to shift their wavelength position. This is an expected interference phenomenon observed with small changes in the thickness of initially thin films. Following the sixth plasma exposure, a total exposure time of 18 minutes, the initial reflectance of MgF 56 had been totally restored within the wavelength region from 120 to 240 nm.

In general, correlation of cleaning rate data between MgF 39 and MgF 56 was inhibited by: (1) the lack of QCM data due to instrumentation problems; and (2) the lack of IFM data for some test conditions where contaminant film surface roughness made interferometric measurements impossible. Both MgF 39 and MgF 56 were contaminated under identical conditions, with MgF 39 having a greater exposure time by almost a factor of 3. The QCM responded comparably with a frequency change greater for MgF 39 by a factor of 3.25. Measurement by interferometry, however, indicated that a film thickness of 250 nm had been deposited on MgF 39 and only 30 nm was deposited on MgF 56; a factor of 8.25 difference.

4.3.2 Monochromator Optics Contamination and Refurbishment

Following the second series of contamination/cleaning experiments involving MgF 56, it was discovered that the McPherson Model 218 monochromator optics had become contaminated. This contamination apparently occurred when air accidentally bled

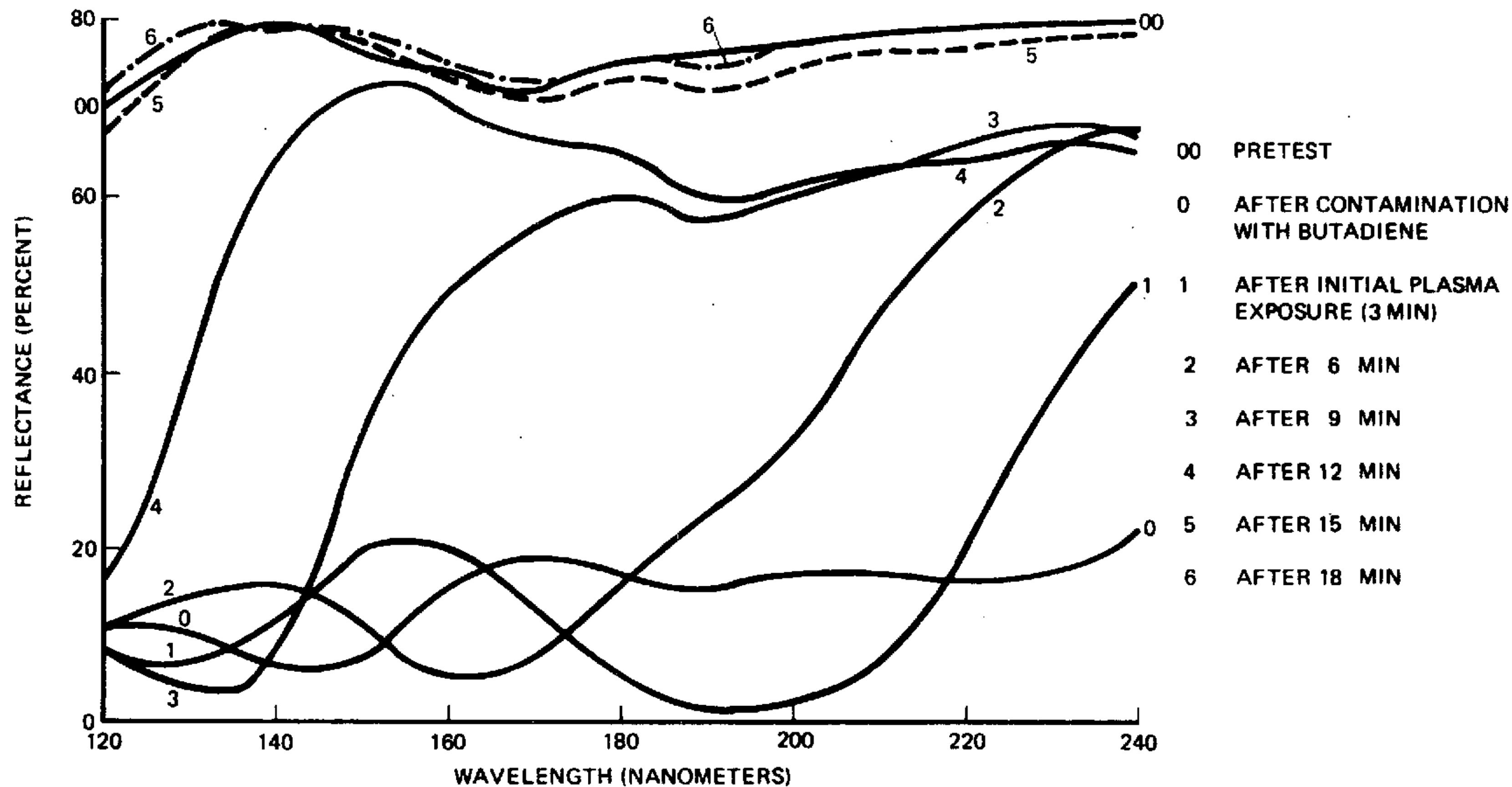

Figure 12: EFFECT OF BUTADIENE CONTAMINATION AND PLASMA EXPOSURE ON REFLECTANCE OF 1/2λ – Mg F_2/Al – COATED MIRROR (NO Mg F-56)

into the system during operation. Efforts to remove the contamination by chemical means (application and removal of collodion films) resulted in further visual degradation (scattering). Treatment of the contaminated grating and mirrors in both oxygen and hydrogen bromide plasmas produced no visible improvement. Efforts were also directed at understanding the degradation phenomenon. Patches of reflective film were removed from a mirror and examined both visually and with a scanning electron microscope. It was noted that the diffuse appearance was only present on the exposed side of the film. A scanning electron-beam photomicrograph of the exposed surface of the reflective coating revealed several regions (about 5 microns in diameter) typified by a crater-like impression in the center of numerous blister-like formations of similar size (about 0.3 microns). It is possible that these formations were the cause of the observed light scattering. The mirrors and grating were then returned to McPherson Instruments, Inc. where they were recoated with Al and MgF_2. These fresh coatings substantially increased the spectral output of the UV monochromator. Unfortunately, the output of the system degraded again in several hours of running time. Wavelength conversion surfaces (sodium salicylate) on the photomultipliers were then examined. One surface appeared to have lost part of the sodium salicylate coating. Both conversion surfaces were subsequently recoated, and the system performance remeasured. Results showed a slight increase in spectral output from the monochromator.

A plasma cleaning device was then fabricated and installed in the monochromator as shown in Figure 13. The quartz plasma tube assembly and a viewing window were both installed in the monochromator cover plate. An O-ring seal was used for the plasma tube to facilitate rotation to each of the three optical surfaces. During normal operation of the monochromator the plasma tube is removed and a suitable sealing plate is installed in its location.

The plasma tube operation was checked with the grating removed and the two mirrors covered with aluminum foil. The limited capacity of the mechanical pump, which backs the diffusion pump on the monochromater, did not allow the plasma tube pressure to be set high enough (about 4 torr) to initiate a discharge in the tube. However, a discharge was initiated throughout the monochromator (chamber discharge) when the system pressure reached about 10^{-2} torr. Subsequent plasma cleaning of

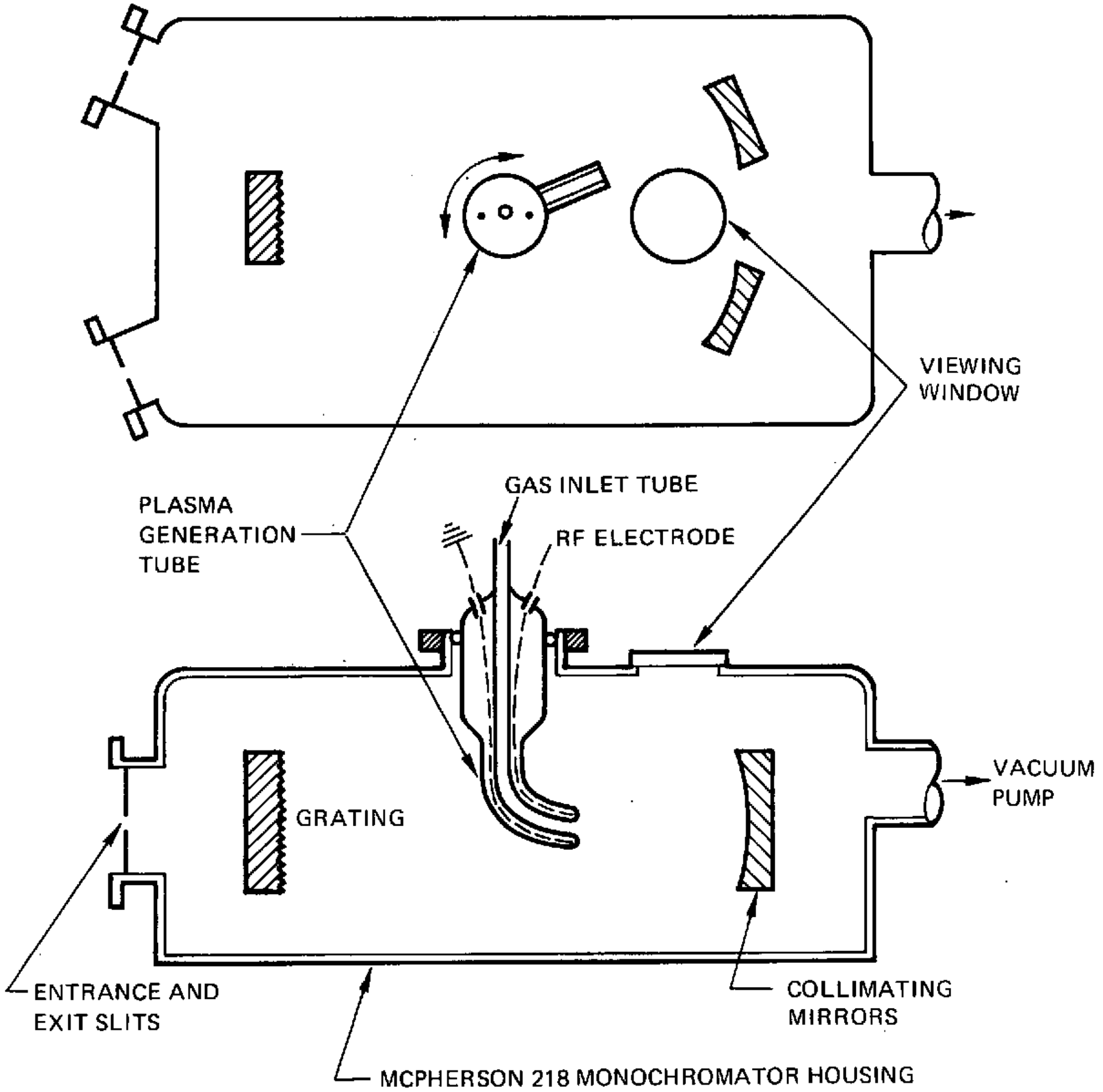

Figure 13: SCHEMATIC SHOWING INSTALLATION OF PLASMA CLEANING DEVICE IN McPHERSON 218 MONOCHROMATOR

the monochromator mirrors and grating utilized this chamber discharge with a system pressure of 1.5 - 2.0 x 10^{-2} torr and a peak to peak r.f. voltage of 2000 volts.

Figure 14 shows the effects of recoating the solium salicylate wavelength conversion surfaces and plasma cleaning the optical surfaces. This figure shows the spectral output of the monochromator optics as a function of wavelength. The spectral output is given in terms of $\log_{10}$ (I/I_o) where I_o is the light intensity at zeroth order (i.e., mirror like reflection from the grating) and I is the intensity at a given wavelength. The recoating of the wavelength conversion surfaces improved the performance considerably at wavelengths above 130 nm, however, little improvement occurred at shorter wavelength. Plasma cleaning improved the performance throughout the spectrum with the greatest improvement occurring at a wavelength of about 120 nm. Each cleaning consisted of a plasma exposure of 15 minutes. Initially the grating was removed and the second mirror covered with aluminum foil while the first was left exposed. The spectral response was then measured and the process repeated for the second mirror exposure. The grating was cleaned in place while the mirrors were covered. Finally the mirrors and grating were simultaneously exposed to the plasma. As can be seen from Figure 14 only a slight improvement in performance was gained by this exposure. Another 15 minute plasma exposure of the mirrors and grating failed to show any further increase in the monochromator performance.

4.3.3 Gold and Platinum Coated Mirror Experiments

The in-situ contamination/cleaning experiments were continued using gold and platinum coated mirrors. These experiments utilized two gold coated mirrors and one platinum coated mirror. The mirrors were contaminated by exposure to UV radiation in a 1,3 butadiene environment, and subsequently exposed to argon and oxygen plasmas. In addition to the plasma cleaning effects, the effects of extended periods (at vacuum and ambient conditions) on the contaminant films were investigated.

Table 5 gives the 'log of events' for gold coated mirror sample Au6. Figures 15 and 16 show the reflectance data for this sample. The primary objective of this

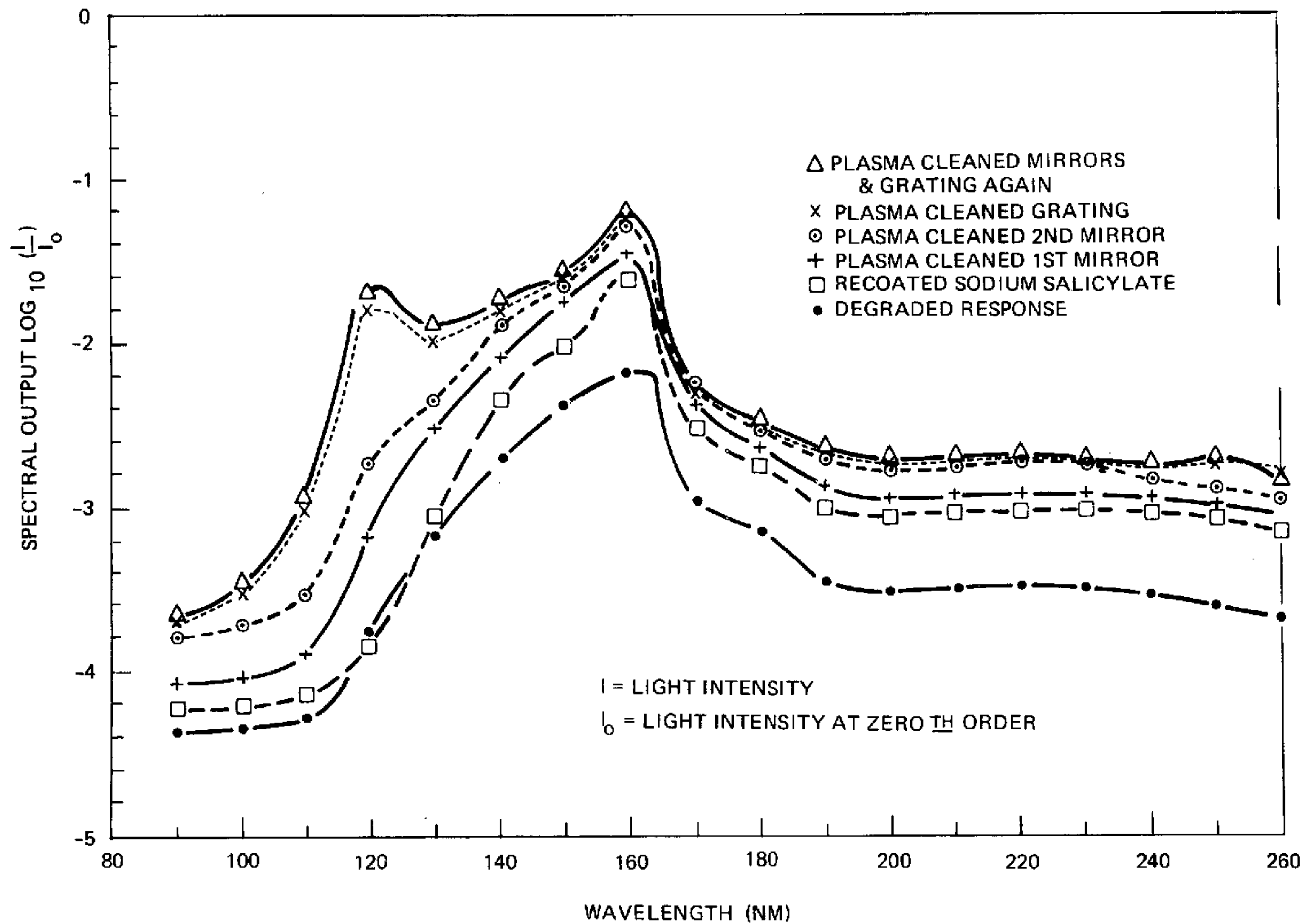

Figure 14: UV MONOCHROMATOR OUTPUT

TABLE 5: LOG OF EVENTS FOR GOLD COATED MIRROR - Au6

EVENT	COMMENT
Contamination	
Exposed to UV radiation at 4 torr 1,3 butadiene for 100 minutes	QCM response indicated film deposition of about 5 x 10^{-6} gm/cm^2. UV reflectance degraded by more than factor of 3.
Sample 'let up to air' for one hour	No change in UV reflectance.
Argon Plasma Exposures 1st exposure 7.5 minutes 2nd exposure 5. minutes 3rd exposure 22.5 minutes	Chamber pressure 5 x 10^{-3} torr, plasma tube pressure 4 torr, RF power 18 watts, RF voltage 2000 volts, peak to peak. 'Ignited plume' mode of operation. All exposures increased the UV reflectance.
Oxygen Plasma Exposure 1st exposure 7.5 minutes 2nd exposure 15. minutes 3rd exposure 15. minutes 4th exposure 10. minutes	Chamber pressure 6 x 10^{-3} torr, plasma tube pressure 6 torr, RF power 35 watts, RF voltage 2500 volts peak to peak. 'Ignited plume' mode of operation. First three exposures significantly increased UV reflectance. Fourth exposure gave no further increase. UV reflectance not completely restored.
Sample left under vacuum for 3 days	Chamber pressure rose from about 10^{-5} torr to 3.5 torr in 3 days. UV reflectance slightly degraded at shorter wavelengths.
Plasma Cleaned Monochromator Optics	20 minutes oxygen plasma exposure. UV reflectance measurements showed some differences, from previous values, below 140 nm.
Oxygen Plasma Exposure	15 minute exposure produced small increase in reflectance.

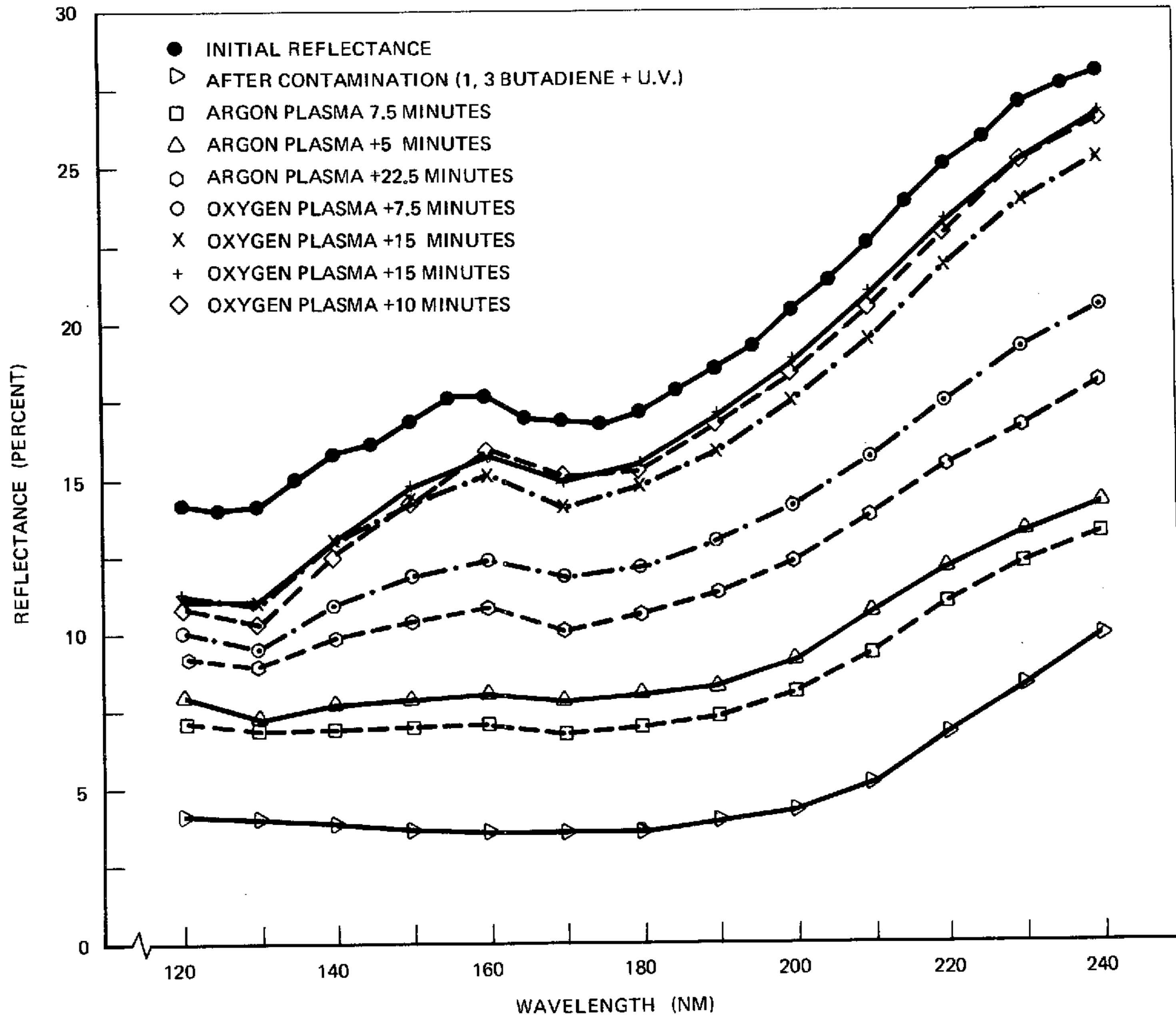

Figure 15: REFLECTANCE DATA FOR GOLD COATED MIRROR Au 6

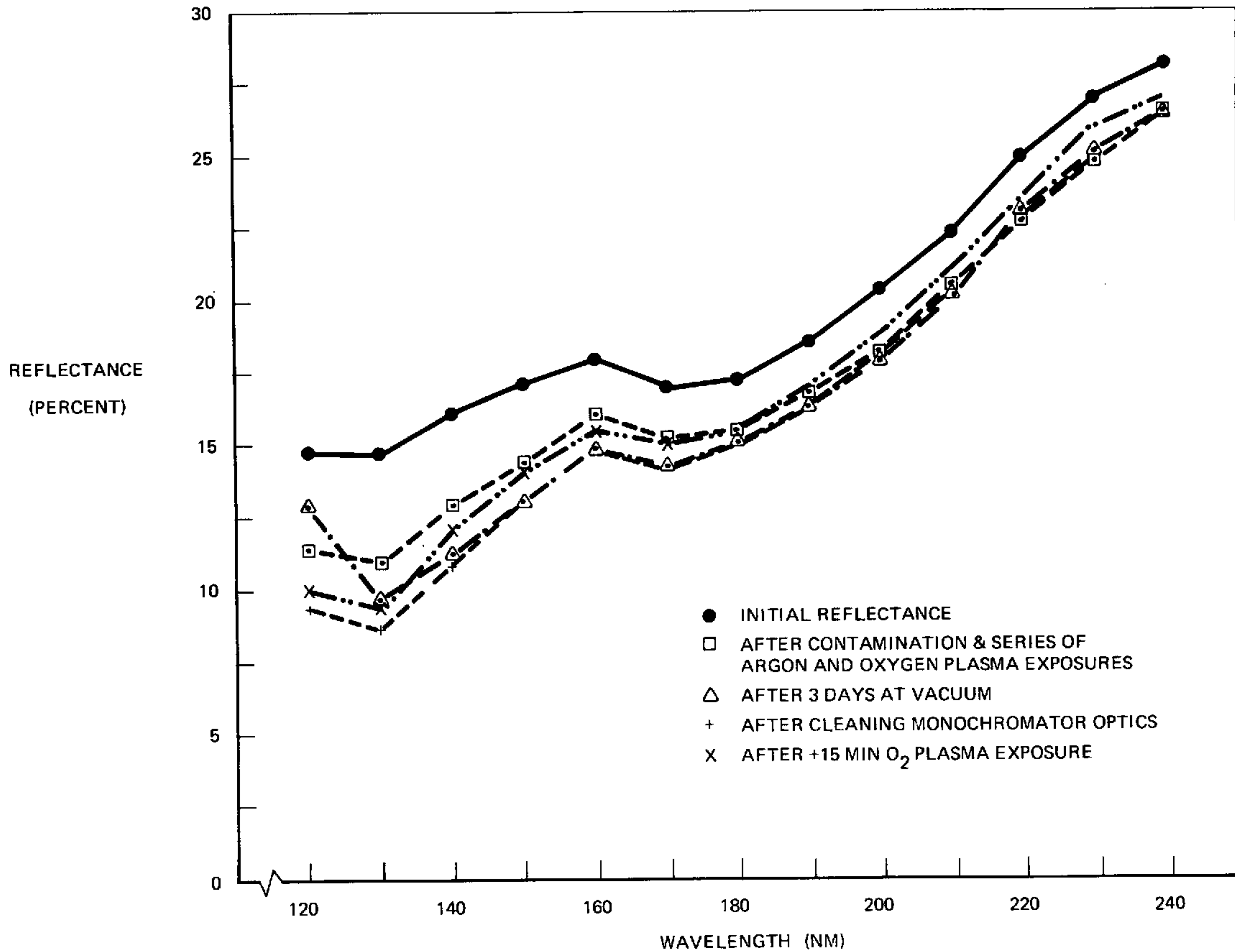

Figure 16: REFLECTANCE DATA FOR GOLD COATED MIRROR Au 6

experiment was to determine the effect of exposure to an argon plasma. Figure 15 shows that the argon plasma removes the contaminant film. Instead of continuing the argon plasma exposures it was decided to see if an oxygen plasma would clean more rapidly. The data in Figure 15 do not indicate any apparent differences in cleaning rate. Since the reflectance was not completely restored, the question is raised as to whether or not the order of exposure (in this case argon first and then oxygen) affects the contaminant cleaning. Data for this sample show that a short term (one hour) exposure to ambient air does not change the contaminant film effects on the UV reflectance. A slight degradation of UV reflectance occurred during an extended period (3 days) under vacuum (see Figure 16). The data in Figure 16 also show that monochromator optics degradation influences the reflectance data measurements in the 120 to 140 nm wavelength region.

In order to see if the order of plasma exposure (argon or oxygen first) affects the contaminant film cleaning, experiments were conducted using a second gold coated mirror (Au7). Table 6 gives the 'log of events' and Figures 17-19 show the reflectance data for sample Au7. Figure 17 shows that the UV reflectance was nearly restored using two oxygen plasma exposures and that an additional exposure using an argon plasma had little effect on the reflectance. Since the UV reflectance of Au7 was more completely restored using an oxygen plasma than that of Au6 using first argon and then oxygen plasmas, Au7 was recontaminated to see if argon would be as effective as oxygen in plasma cleaning.

Figure 18 shows that a 15 minute argon plasma exposure restored the UV reflectance to that prior to recontamination. These data indicate that there is little difference between argon and oxygen plasma cleaning. If the cleaning phenomenon is, as has been thought, due to the chemical reaction between the plasma and the contaminant film resulting in volatile products, then it seems reasonable to expect much more effective cleaning with oxygen than with argon. Since this does not occur, the cleaning phenomenon must be related to the interaction of excited atoms in the plasma with the contaminant film and/or ion sputtering of the contaminant film. Figure 18 also shows that the UV reflectance of the sample degraded after it had been exposed to air while the vacuum chamber quartz UV window was being cleaned. This degradation might have been caused by contamination from the solvents (ethanol and methylethylketone) used in cleaning the window.

TABLE 7: LOG OF EVENTS FOR GOLD COATED MIRROR - Au7

EVENT	COMMENT
Contamination	
Exposed to UV radiation at 4-6 torr 1,3 butadiene for 78 minutes	QCM response indicated film deposition of about $1.7x10^{-6}$ gm/cm^2.
Continued exposure for additional 18 minutes after leaving at vacuum overnight.	Total contaminant film deposition of about $2.2x10^{-6}$ gm/cm^2. UV reflectance degraded by more than factor of 2.
Oxygen Plasma Exposures	
1st exposure 7.5 minutes 2nd exposure 22.5 minutes	UV reflectance nearly restored by these exposures.
Argon Plasma Exposure	15 minutes exposure produced little change in reflectance.
Contamination	
Exposed to UV radiation at 4 torr 1,3 butadiene for 100 minutes.	QCM indicated film deposition of about $1.8x10^{-6}$ gm/cm^2. UV reflectance degraded.
Argon Plasma Exposure	15 minute exposure restored UV reflectance to that prior to recontamination.
Let Chamber 'up to air' and cleaned quartz UV window	UV reflectance degraded slightly.
Contamination	
Exposed to UV radiation at 4 torr 1,3 butadiene for 30 minutes	QCM response showed slow contamination rate (film deposition of only about $0.2x10^{-6}$ gm/cm^2). UV reflectance showed very little degradation.
Let up to air and recleaned window. Exposure for additional 99 minutes	QCM showed total film deposition of about $2.9x10^{-6}$ gm/cm^2. UV reflectance degraded by more than factor of 2.5.
Exposed sample to ambient air for 20 hours.	UV reflectance remained unchanged.
Argon Plasma Exposures	
1st exposure 22.5 minutes 2nd exposure 22.5 minutes	First exposure nearly restored UV reflectance. Second exposure caused significant degradation.
17 hours under vacuum	UV reflectance degraded slightly.
Oxygen Plasma Exposure	25 minute exposure produced further degradation.

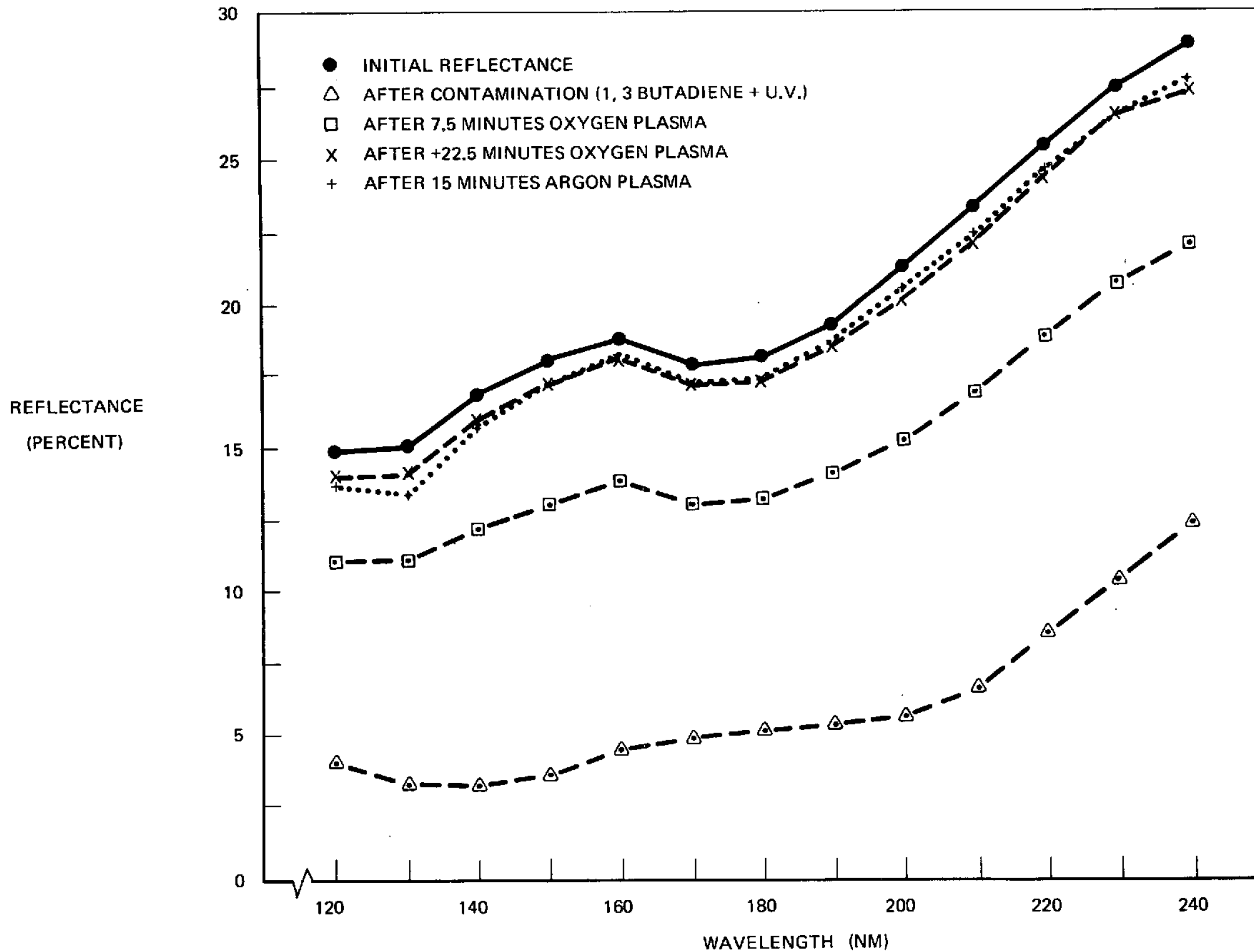

Figure 17: REFLECTANCE DATA FOR GOLD COATED MIRROR Au 7

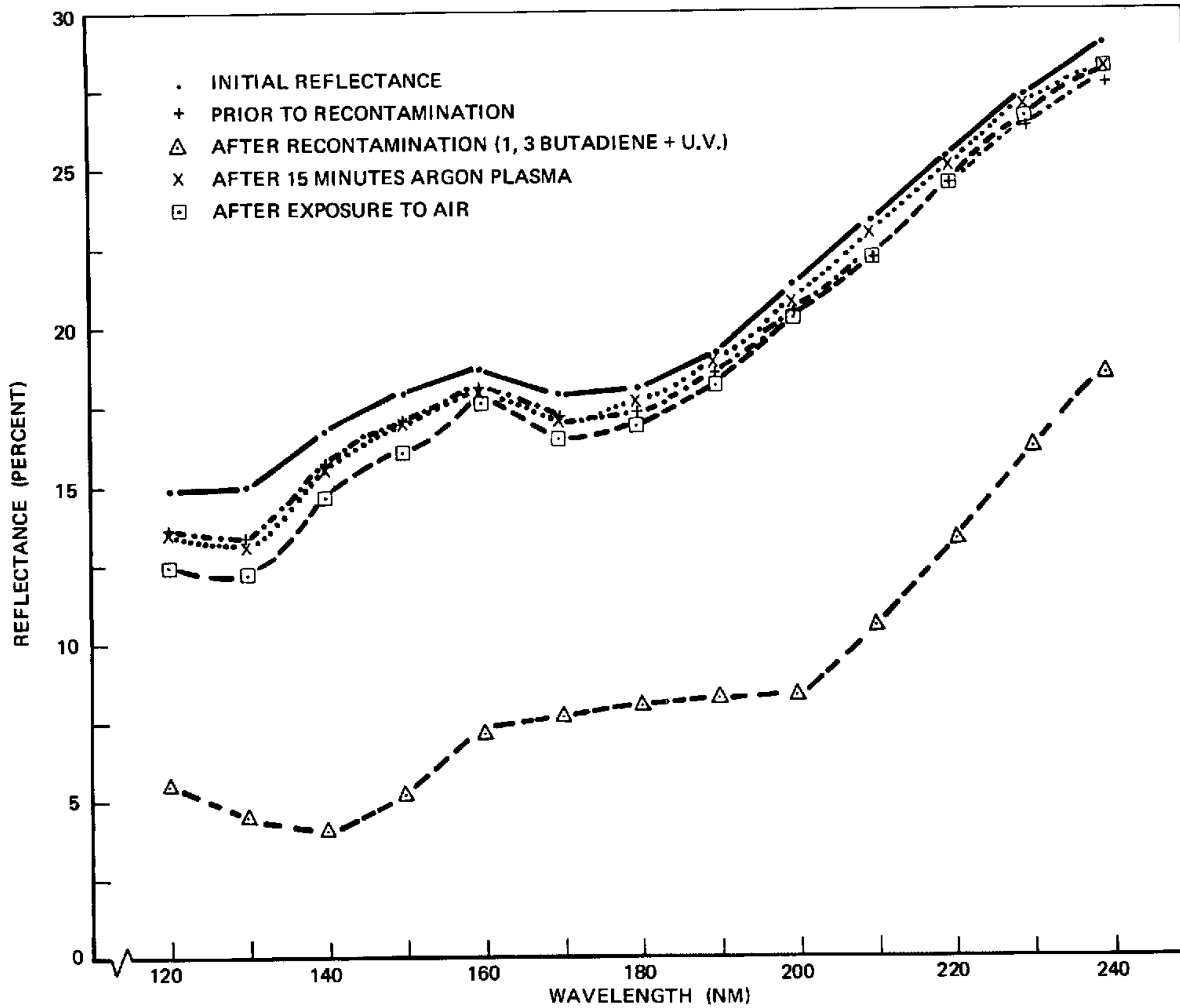

Figure 18: REFLECTANCE DATA FOR GOLD COATED MIRROR Au 7

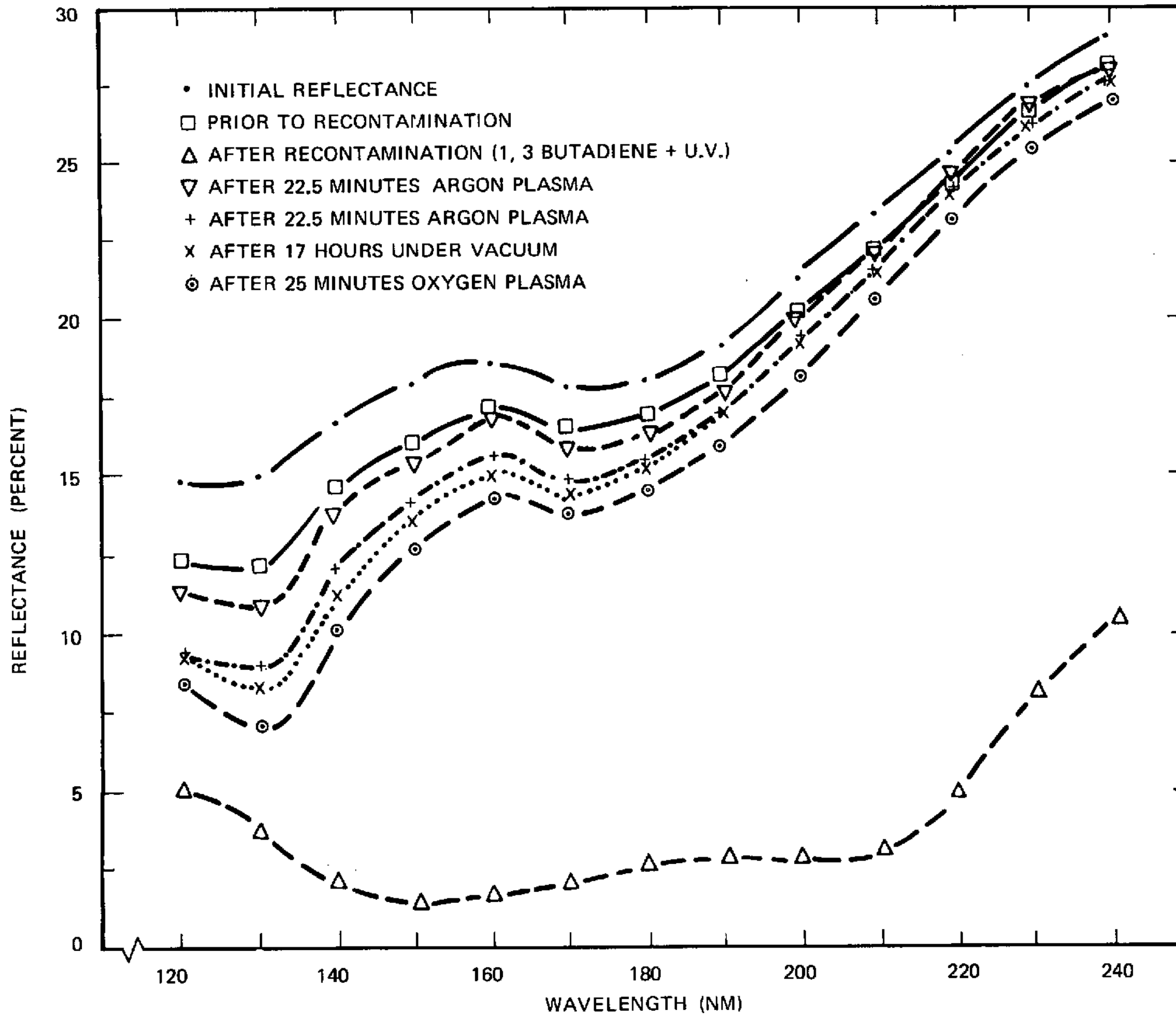

Figure 19: REFLECTANCE DATA FOR GOLD COATED MIRROR Au 7

Following the argon plasma cleaning, sample Au7 was recontaminated and exposed to ambient air for 20 hours. This ambient air exposure had no measurable effect on the degraded UV reflectance of the sample. Figure 19 shows that a 22.5 minute argon plasma exposure nearly restored the UV reflectance to that prior to recontamination. However, an additional 22.5 minute argon plasma exposure produced degradation in the reflectance. Leaving the sample exposed to vacuum for 17 hours resulted in slight further reflectance degradation. This result is consistent with that observed for sample Au6. Apparently contaminants from the closed-off vacuum system deposit on the cooled sample to some degree. An additional 25 minute exposure to an oxygen plasma produced further reflectance degradation. The results of the final plasma exposures indicates 'over cleaning' of the sample.

Table 7 gives the 'log of events' for the experiment using platinum coated mirror Pt 14. The reflectance data for this sample are shown in Figures 20 and 21. Figure 20 shows that the degradation, produced by the butadiene contaminant film, was almost eliminated with a single 7.5 minute oxygen plasma exposure. A second exposure increased the reflectance beyond that prior to contamination. A third exposure produced little effect. The sample was then contaminated again and left under vacuum, with the vacuum system closed-off for 65 hours. Figure 21 shows the amount of degradation still present after this extended period under vacuum. The degree of degradation is less than that shown in Figure 20. Some of the contaminant film may have been removed by the extended period under vacuum, however, it should be noted that the initial contamination produced a film six times thicker than that produced in the recontamination. Consequently, the primary reason for the differences in degree of degradation is probably the amount of contaminant film deposited rather than the effects of the extended vacuum exposure. A 7.5 minute oxygen plasma exposure essentially restored the reflectance to its value prior to recontamination. A second exposure produced little change in the reflectance. However, after plasma cleaning the monochromator optics, a remeasurement of the reflectance showed slight degradation in the 120-150 nm wavelength region. This again indicates that the degradation of the monochromator optics influences the reflectance measurements in the shorter wavelength region.

TABLE 7: LOG OF EVENTS FOR PLATINUM MIRROR - Pt 14

EVENT	COMMENT
Contamination	
Exposed to UV radiation at 5 torr 1,3 butadiene for 100 minutes	QCM response indicated film deposition of about 3.2×10^{-6} gm/cm^2. UV reflectance degraded by more than factor 2.
Oxygen Plasma Exposures	
1st exposure 7.5 minutes 2nd exposure 7.5 minutes 3rd exposure 7.5 minutes	First exposure nearly restored UV reflectance. Second exposure restored reflectance beyond original. Third exposure caused very little change.
Contamination	
Exposed to UV radiation at 5 torr 1,3 butadiene for 60 minutes	QCM response indicated film deposition of about 0.5×10^{-6} gm/cm^2.
Left at vacuum for 65 hours	Chamber pressure rose to 5 torr.
Oxygen Plasma Exposures	
1st exposure 7.5 minutes 2nd exposure 7.5 minutes	First exposure restored reflectance to that prior to recontamination. Second exposure produced little change.
Plasma Cleaned Monochromator Optics	15 minute oxygen plasma exposure. UV reflectance slightly below previous measurement.

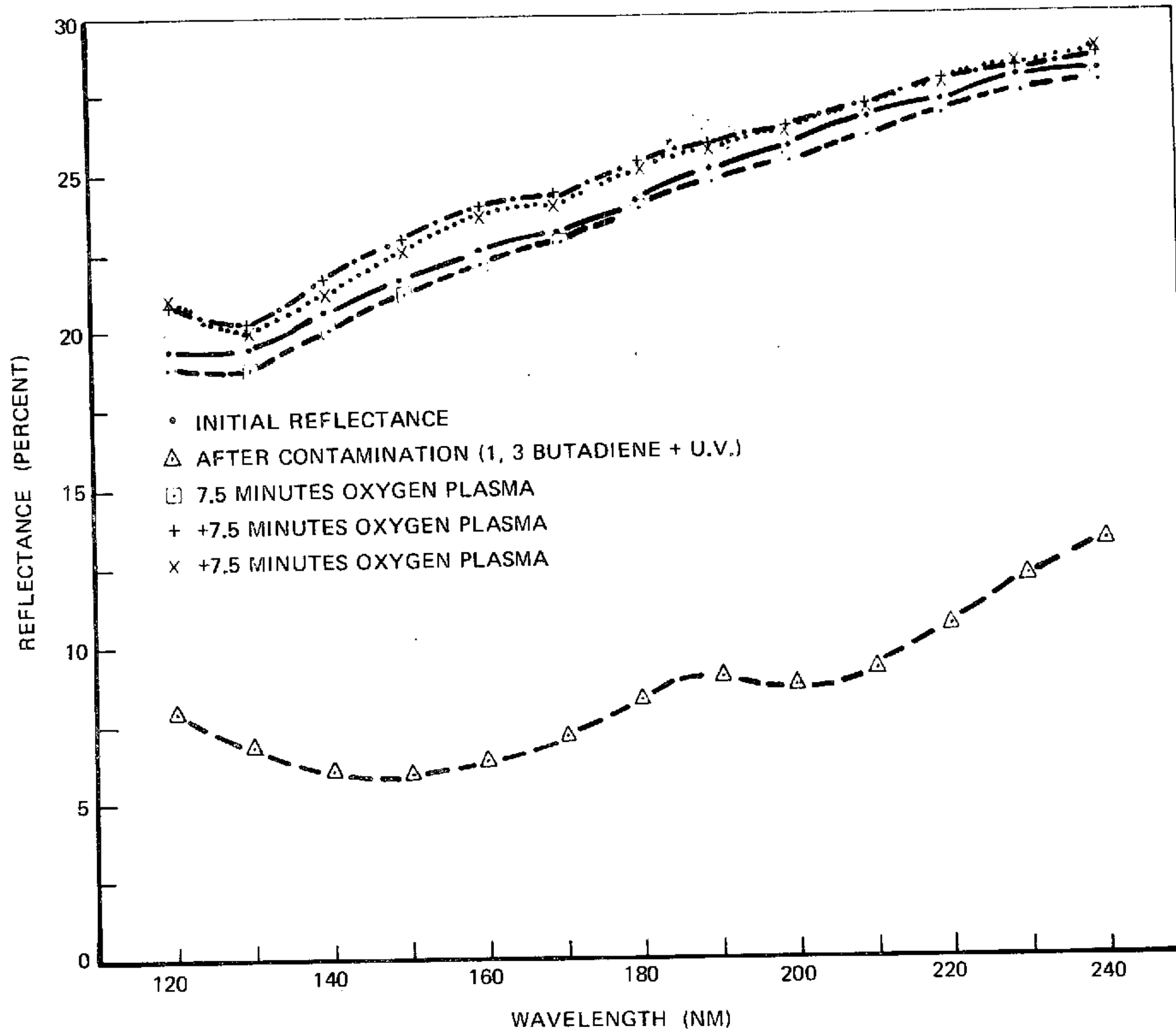

Figure 20: REFLECTANCE DATA FOR PLATINUM COATED MIRROR Pt 14

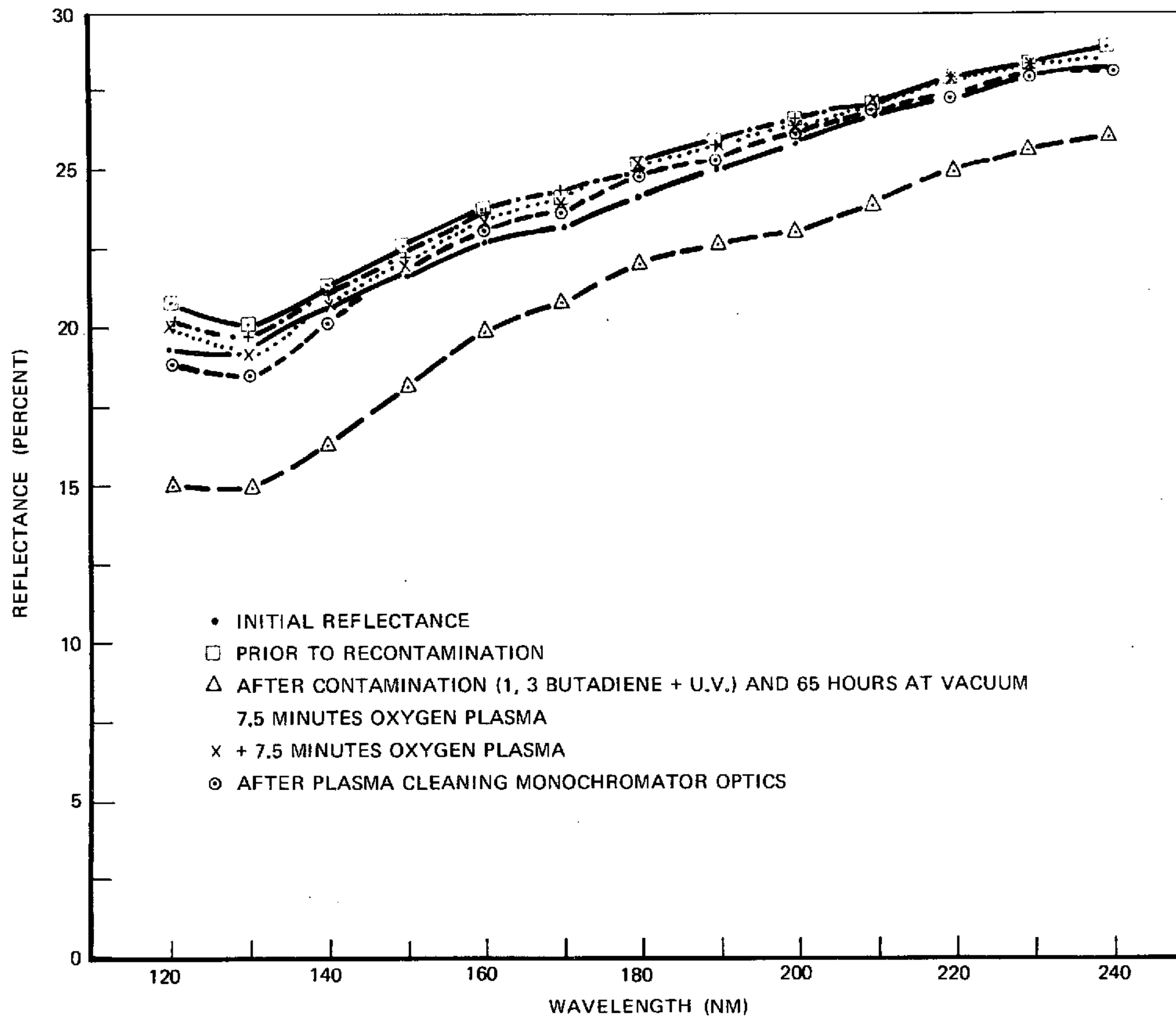

Figure 21: REFLECTANCE DATA FOR PLATINUM COATED MIRROR Pt 14

4.4 Carbon Cleaning Experiments

The experiments discussed in the preceding section showed argon to be as effective as oxygen in plasma cleaning butadiene contaminant films. Subsequently experiments were conducted to see if plasma cleaning of carbon deposits would be affected by the type of gas used. These experiments used a Quartz Crystal Microbalance (QCM). The quartz crystal was coated with gold which was in turn overcoated with about 20 nm of vacuum deposited carbon.

Figure 22 shows the effects of plasma exposure on the frequency of the QCM. A reduction in the QCM frequency indicates a removal of mass from the crystal (removal of 1 microgram/cm^2 changes the frequency by about 50 Hertz). All plasma exposures used the 'ignited plume' mode of operation. The initial series of tests used helium, oxygen and hydrogen plasmas. Figure 22 (top dashed curves) indicates that oxygen and hydrogen are about equally effective in removing carbon. Helium appeared to be less effective. To verify this result a second series of tests were made using helium and oxygen. Figure 22 (bottom solid curves) indicates that helium is as effective as oxygen in removing the carbon. The final plasma exposure, using oxygen, removed the remaining carbon from the QCM. These results show that helium, oxygen and hydrogen plasmas are about equally effective in removing carbon.

4.5 Silicone Cleaning Experiments

The mirrors used in these experiments were contaminated with outgassed products of silicone compounds (RTV3116 and RTV602). The silicone compounds were heated in a chamber contamination inlet port. This heating produced outgassed products which condensed on the mirror surface. The contaminant film deposition was monitored using a gold coated QCM. In the initial experiment, the QCM was contaminated with the outgassed products from RTV3116. The QCM response indicated a contaminant film deposition of about 1.8×10^{-6} gm/cm^2. The QCM was subsequently exposed to oxygen, argon and hydrogen plasmas. The QCM response during these exposures gave no indication of contaminant film removal. Consequently it was decided to contaminate MgF_2/Al mirrors and use the UV reflectance data to assess the effects of plasma exposure.

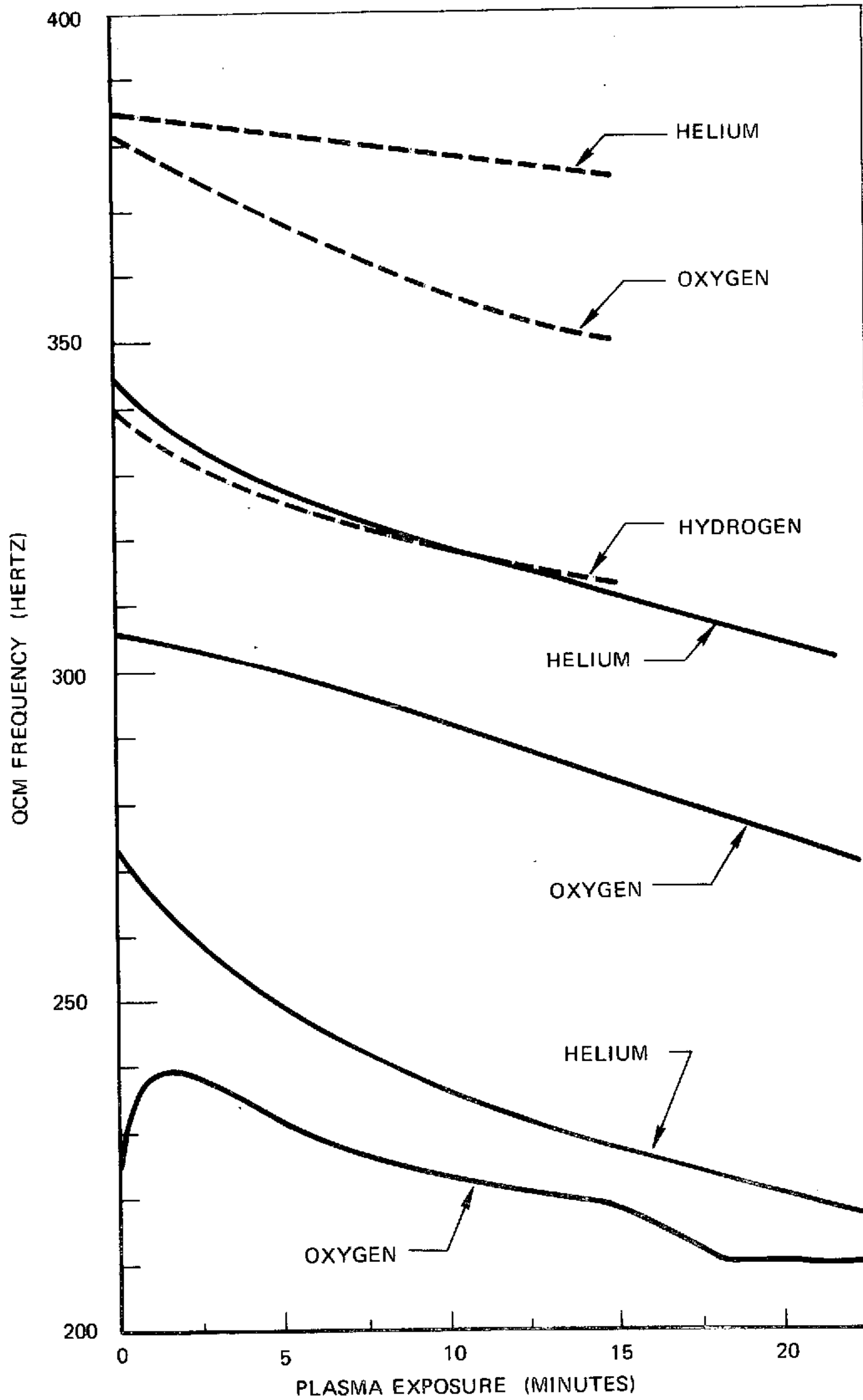

Figure 22: PLASMA CLEANING OF CARBON COATED QCM

The first MgF_2/Al mirror (MgF 113) was exposed to the outgas products of RTV3116 for 24 minutes. The QCM response indicated a contaminant film deposition of about $2x10^{-6}$ gm/cm^2. The UV reflectance of the sample was severely degraded in the 120-140 nm wavelength region and was increased in the 180-240 nm wavelength region (Figure 23 shows the reflectance data for sample MgF 113). As shown in Figure 23, some of the contaminant film appears to have evaporated during a 17 hour period under vacuum. The sample was then subjected to a series of helium plasma exposures (the first for 20 minutes, then four of 30 minutes each). These exposures increased the reflectance at the shorter wavelengths and decreased it at the longer wavelengths (see Figure 23). The restoration at the shorter wavelengths appeared to be limited, whereas, the degradation at the longer wavelengths appeared to be progressive. A subsequent 15 minute exposure to an oxygen plasma (results not shown in Figure 23) resulted in very little change in reflectance except for a slight degradation in the 120-140 nm wavelength region.

A second MgF_2/Al mirror (MgF 114) was exposed to the outgas products of RTV3116 for 30 minutes. The QCM response indicated a contaminant film deposition of about $1.5x10^{-6}$ gm/cm^2. The effects of the contaminant film on the UV reflectance are similar to those observed for sample MgF 113 (see Figure 24). The data in Figure 24 also indicate that some of the contaminant film evaporated, as before, during a 19 hour exposure to vacuum. This sample was subjected to a series of hydrogen plasma exposures of 7.5, 10, 12 and 7.5 minutes. As with the helium plasma exposures of MgF 113, the hydrogen plasma exposures increased the reflectance of MgF 114 at the shorter wavelengths and decreased it at the longer wavelengths. However, the hydrogen plasma produced more restoration at the shorter wavelengths and less degradation at the longer wavelengths, than the helium plasma. Subsequent to this series of plasma exposures the sample was left under vacuum for 18 hours and then subjected to three additional plasma exposures (12 minutes using hydrogen, 9 minutes using oxygen and 7.5 minutes using helium). Figure 25 shows the reflectance data for these cases. The hydrogen plasma exposure resulted in a slight improvement at the shorter wavelengths and slight degradation at the longer wavelengths. The oxygen plasma exposure resulted in slight further degradation. The helium plasma exposure produced a significant further degradation of the reflectance.

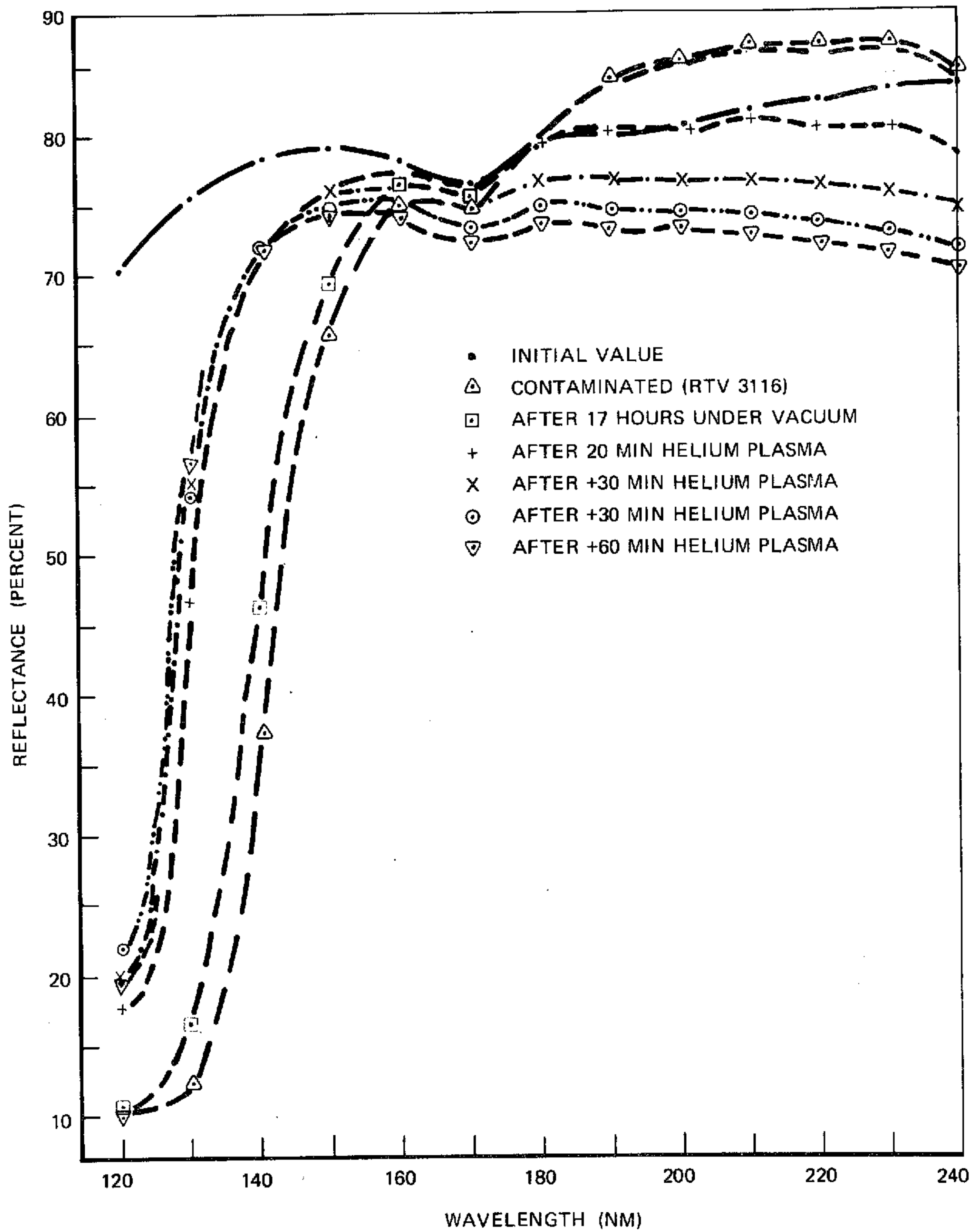

Figure 23: REFLECTANCE DATA FOR Mg F_2/Al MIRROR Mg F113

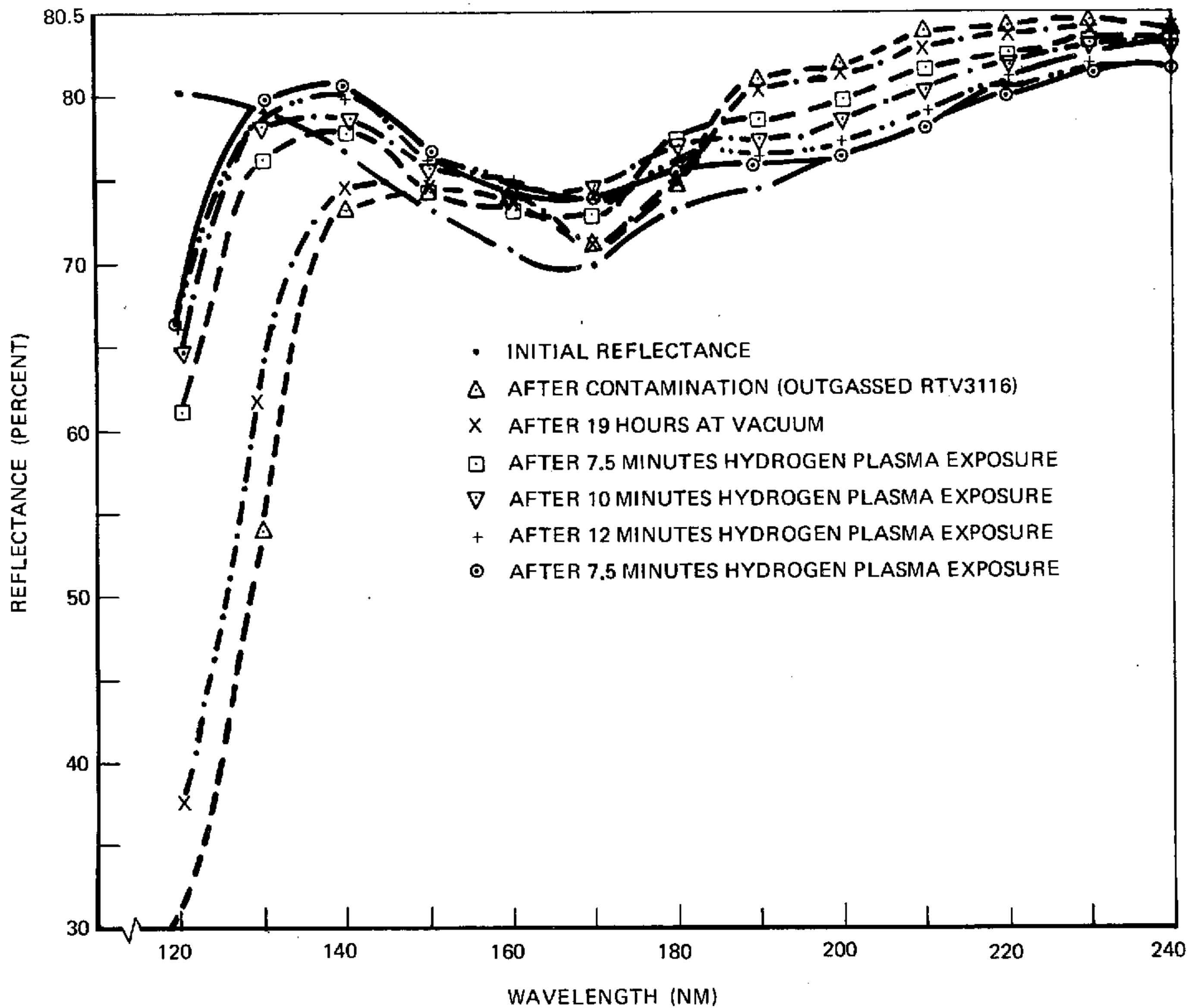

Figure 24: REFLECTANCE DATA FOR Mg F_2/Al MIRROR Mg F114

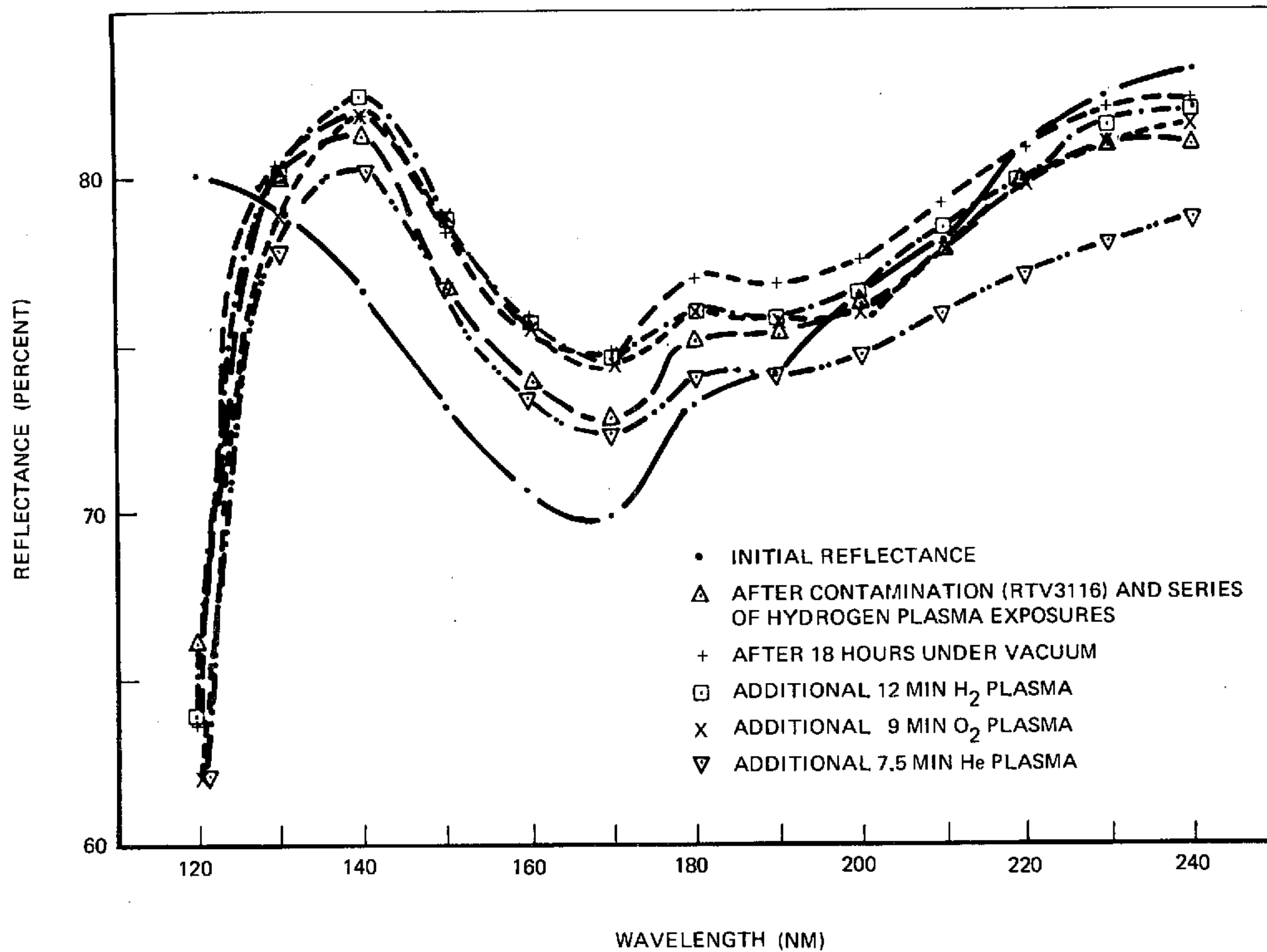

Figure 25: REFLECTANCE DATA FOR MgF_2/Al MIRROR Mg F114

These initial experiments showed that the UV reflectance of MgF_2/Al coated mirrors, contaminated with the outgas products from RTV3116, could be partially restored using helium and hydrogen plasmas. Further experiments were conducted using the outgas products of RTV602 to contaminate MgF_2/Al coated mirrors. The silicone compounds in RTV602 are similar to those in S-13 white paint (a spacecraft coating). These experiments utilized a sapphire window in the in-situ monochromator to extend the reflectance measurements to 300 nm. Two mirrors were used in these tests. The first mirror MgF 116 was exposed to the RTV602 outgas products for 27 minutes. The QCM response indicated a contaminant film deposition of about $2.2x10^{-6}gm/cm^2$. During this exposure a gold coated glass slide was also contaminated. This slide was placed in the chamber contamination inlet port so that a thick contaminant film would result. Subsequent infrared analysis of this film revealed the presence of dimethylsiloxane. Subsequent to contamination, sample MgF 116 was exposed to UV radiation for 30 minutes. This exposure produced some restoration of the reflectance. (The reflectance data for MgF 116 are shown in Figures 26 and 27 for the 120-170 nm and 160-300 nm wavelength regions, respectively). The sample was then subjected to a series of hydrogen plasma exposures. Figure 26 shows that these exposures produced a significant restoration of the reflectance at shorter wavelengths, and Figure 27 shows a progressive degradation at the longer wavelengths. Two additional hydrogen plasma exposures totaling 52.5 minutes produced little change in the shorter wavelengths and slight further degradation at the longer wavelengths. (Thes data are not shown in Figures 26 and 27).

The second mirror MgF 117 was first exposed to the outgas products of RTV602 for 75 minutes with a resultant indicated film deposition of only about $0.8x10^{-6}gm/cm^2$. A subsequent reflectance measurement revealed negligible contamination. During this initial contamination attempt the chamber pressure was about 10^{-3} torr. At first this pressure was attributed to outgassing effects, however, a system leak was discovered later. After sealing the leak, the sample contamination procedure was repeated. A 30 minute exposure then resulted in a total indicated film deposition of about $3x10^{-6}gm/cm^2$. The sample was then exposed to a series of oxygen plasma exposures. Figures 28 and 29 show the reflectance data for mirror MgF 117 in the 120-170 nm and 160-300 nm wavelength regions, respectively. The degraded reflectance, prior to plasma exposure, shows minimums at about 122, 127 and 132 nm,

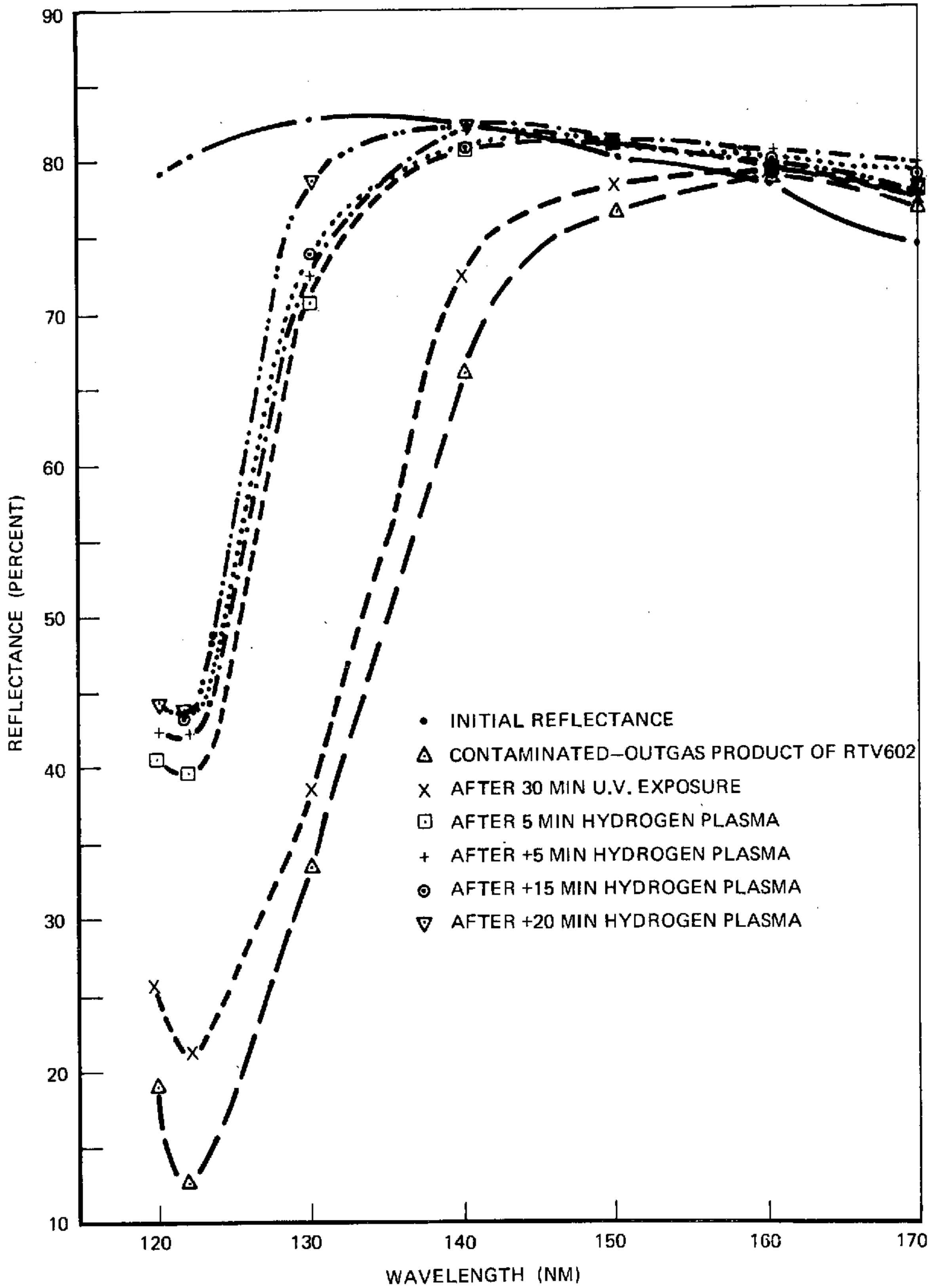

Figure 26: REFLECTANCE DATA FOR Mg F_2/Al MIRROR Mg F116

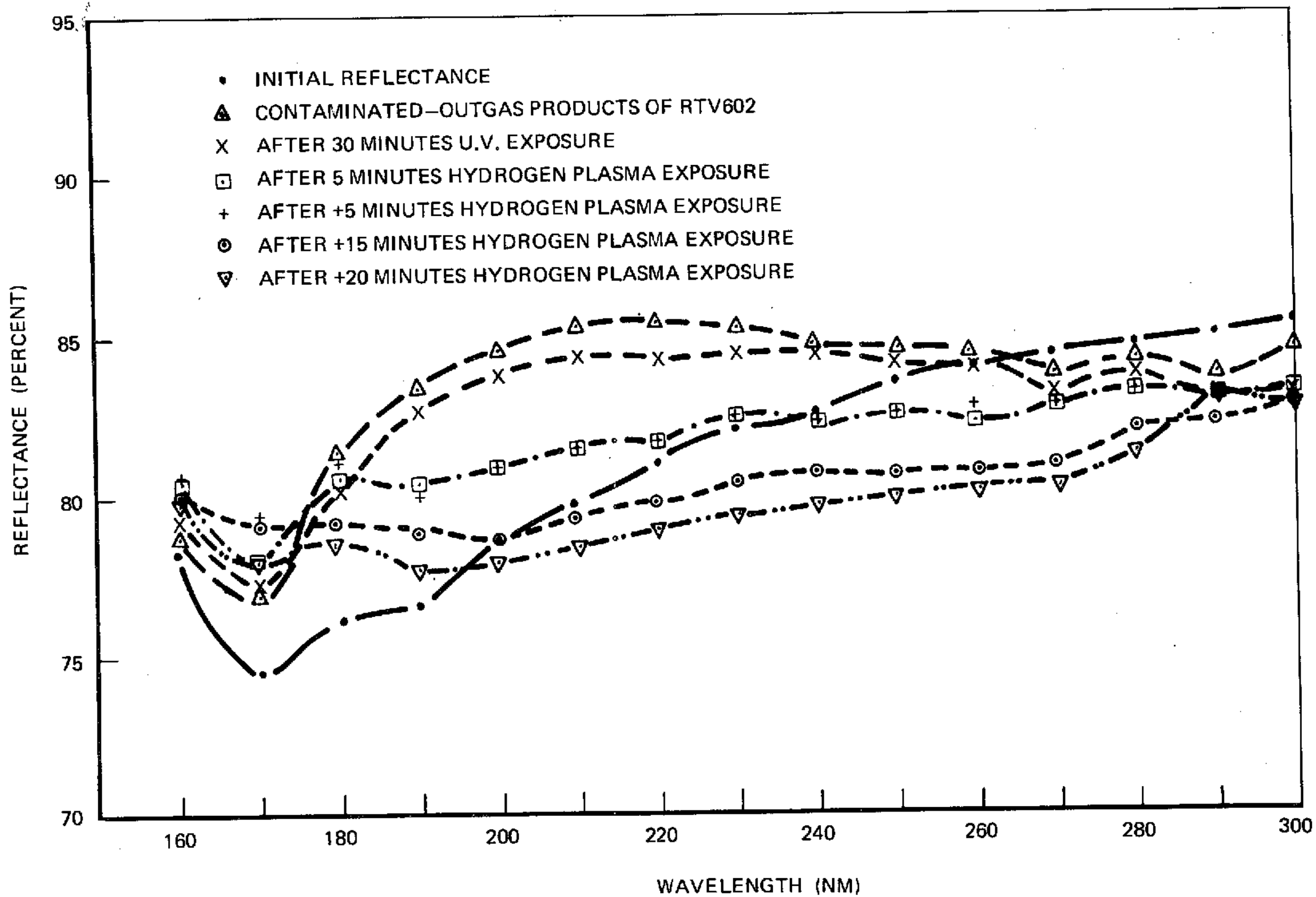

Figure 27: REFLECTANCE DATA FOR MgF_2/Al MIRROR Mg F116

whereas, that for MgF 116 showed only the 122 nm minimum. This difference might be explained by the fact that, after contamination, MgF 116 was left under vacuum and then let up to air prior to the reflectance measurement; or that MgF 117 had a somewhat thicker contaminant film. Figure 28 shows that the minimums at 127 and 132 nm were removed by oxygen plasma exposure, however, the restoration at 122 nm was much less than that obtained for MgF 116 using hydrogen plasma exposure. The data shown in Figure 28 also show that the reflectance at the shorter wavelengths is initially increased and then progressively degrades with continued exposure to an oxygen plasma. Figure 29 shows somewhat the opposite effect at the longer wavelengths.

These silicone contamination experiments all show that a contaminant film deposition on MgF_2/Al mirrors on the order of $2x10^{-6}$ gm/cm^2, produced a strong absorption band in the 120-130 nm wavelength region and increased the reflectance at the longer wavelengths (170-300 nm). Helium, hydrogen and oxygen plasma exposures all resulted in some restoration of the reflectance at the shorter wavelengths, however, hydrogen appeared to give the best results. After contamination, plasma exposure degraded the reflectance at the longer wavelengths, with helium plasma exposure producing the most severe degradation.

4.6 Experiments Conducted at Low Chamber Pressures

4.6.1 Plasma Tube Development

The plasma cleaning experiments described earlier in this report were conducted at vacuum chamber pressures in the 10^{-3} to 10^{-2} torr range with a 'chamber discharge' phenomena present. This 'chamber discharge' appears to produce more or less uniform plasma cleaning throughout the vacuum chamber away from the plasma tube outlet. Plasma cleaning is, however, enhanced in the ignited plume region near the plasma tube outlet. Consequently, experiments to determine cleaning rate distribution and contamination of surfaces adjacent to those being cleaned, would be meaningless unless they could be conducted at low chamber pressures where the 'chamber discharge' does not occur.

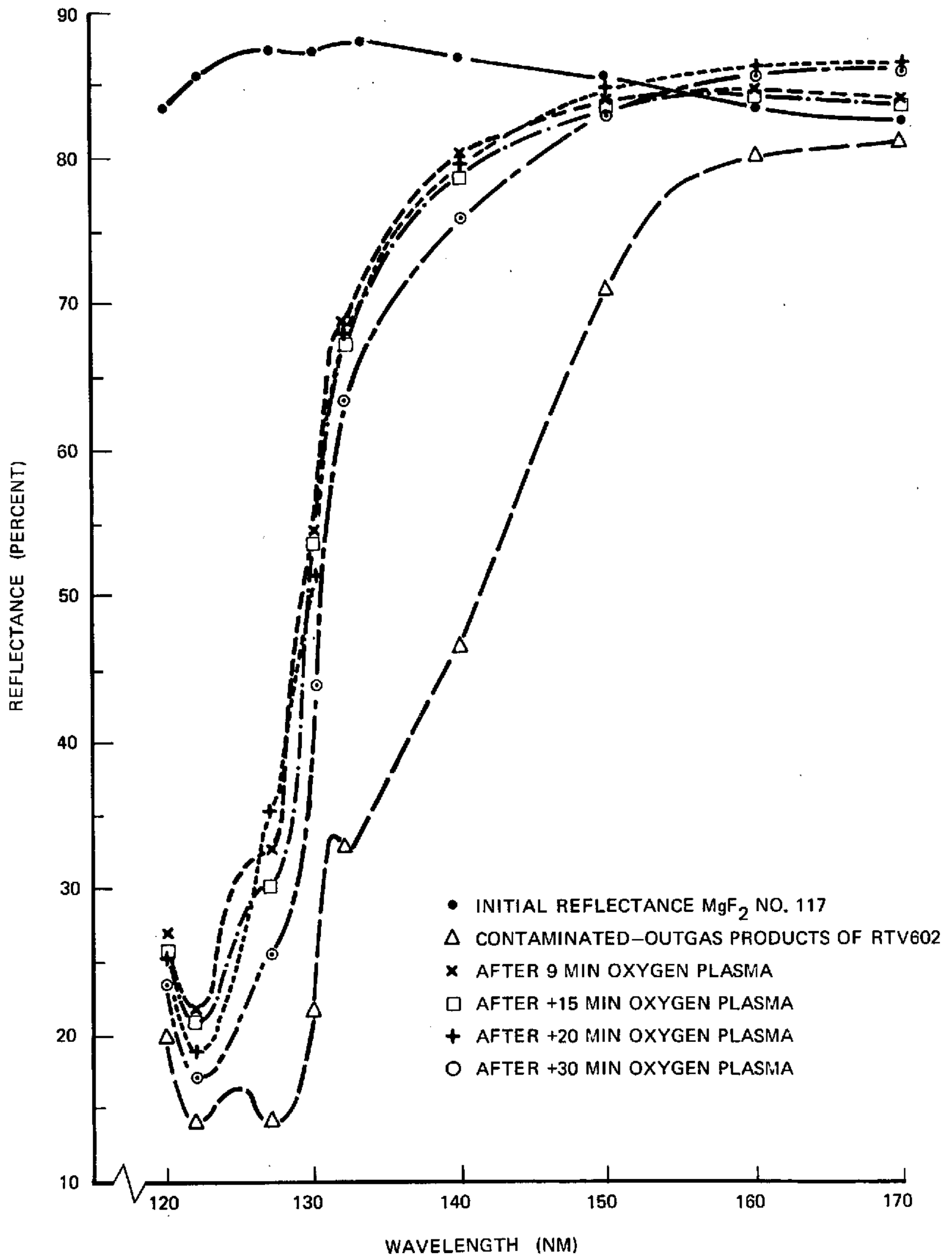

Figure 28: REFLECTANCE DATA FOR Mg F_2/Al MIRROR Mg F117

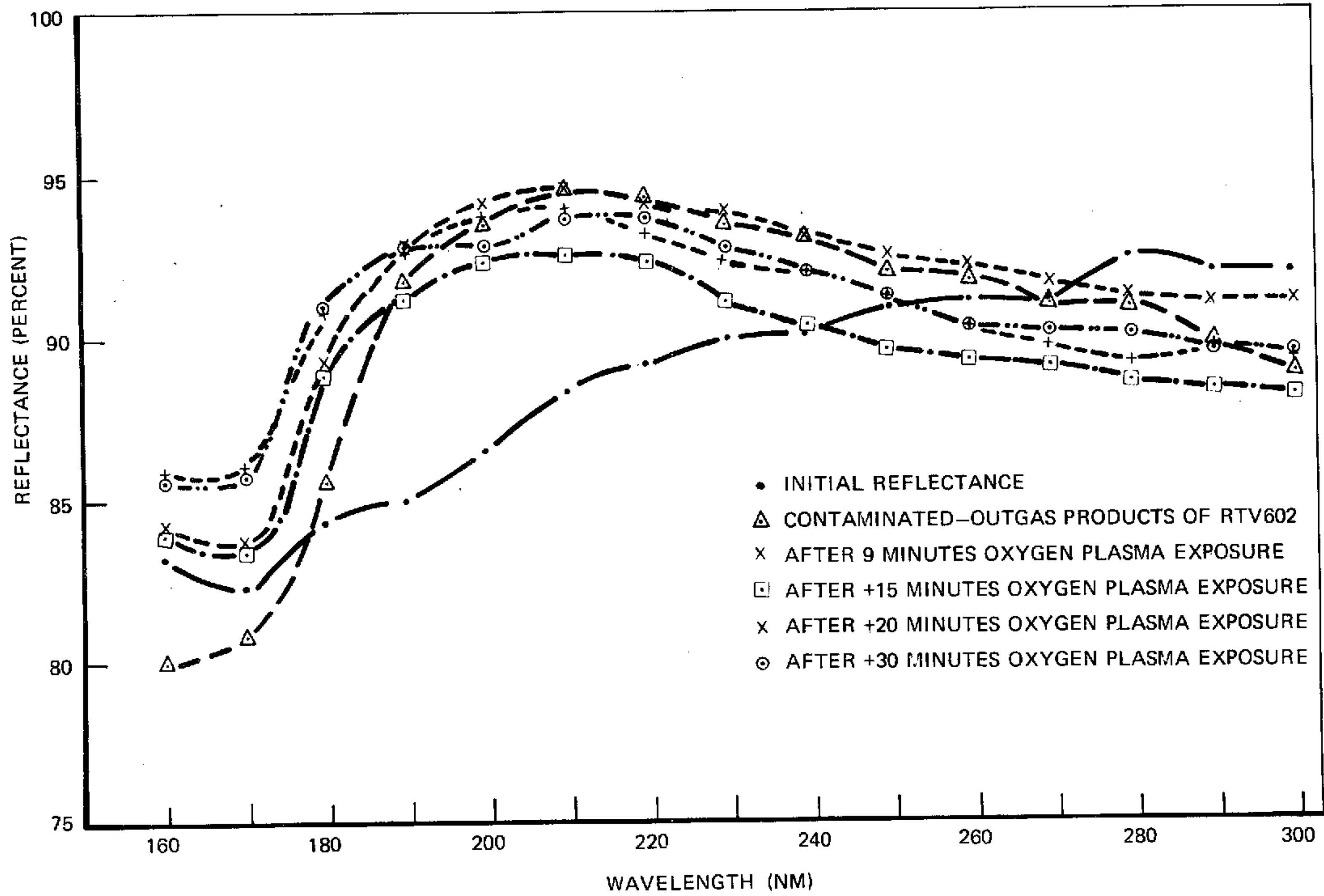

Figure 29: REFLECTANCE DATA FOR Mg F_2/Al MIRROR Mg F117)

The development of a plasma tube that would operate at low chamber pressures (10^{-5} to 10^{-4} torr) is covered under companion Contract NAS8-28270. The initial plasma tube developed under that contract (Reference 7) produced atomic oxygen (based on silver oxidation) at low chamber pressures, however, it did not produce plasma cleaning effects. Continuation of the plasma tube development effort revealed that a visible plume (i.e., a localized, glowing, conical shaped region extending beyond the plasma tube into the vacuum chamber) could be produced at low chamber pressures if the plasma discharge extended to the downstream end of the plasma tube. It was also found that plasma cleaning occurred within the region of the visible plume. Preliminary experiments were conducted, using a prototype plasma tube, to determine whether contamination occurs on surfaces adjacent to those being cleaned, and the cleaning rate distribution. Figure 30 shows the prototype plasma tube configuration used in these experiments. A 4 mm ID quartz tube with axial electrodes was used as the plasma tube. The r.f. power was brought into the chamber through a separate passthrough and the electrodes leads were connected using soft solder.

4.6.2 Cleaning Rate Distribution

In order to determine the approximate cleaning rate using the prototype plasma tube, a cleaning test was conducted using a carbon-coated QCM. The QCM was mounted on a rod such that it could be translated axially or rotated through the visible plume. The conditions for this test were chamber pressure of 4.5×10^{-5} torr, upstream oxygen pressure of 0.7 torr, and r.f. power set at 210 watts forward and 110 watts reflected. (It was not possible to zero the reflected power with the existing impedance matching network.) The results of this test showed that carbon removal occurred when the QCM was located in the visible plume and did not occur with the QCM outside the plume. The carbon removal rate varied with axial distance from the plasma tube outlet. Table 8 shows this measured variation.

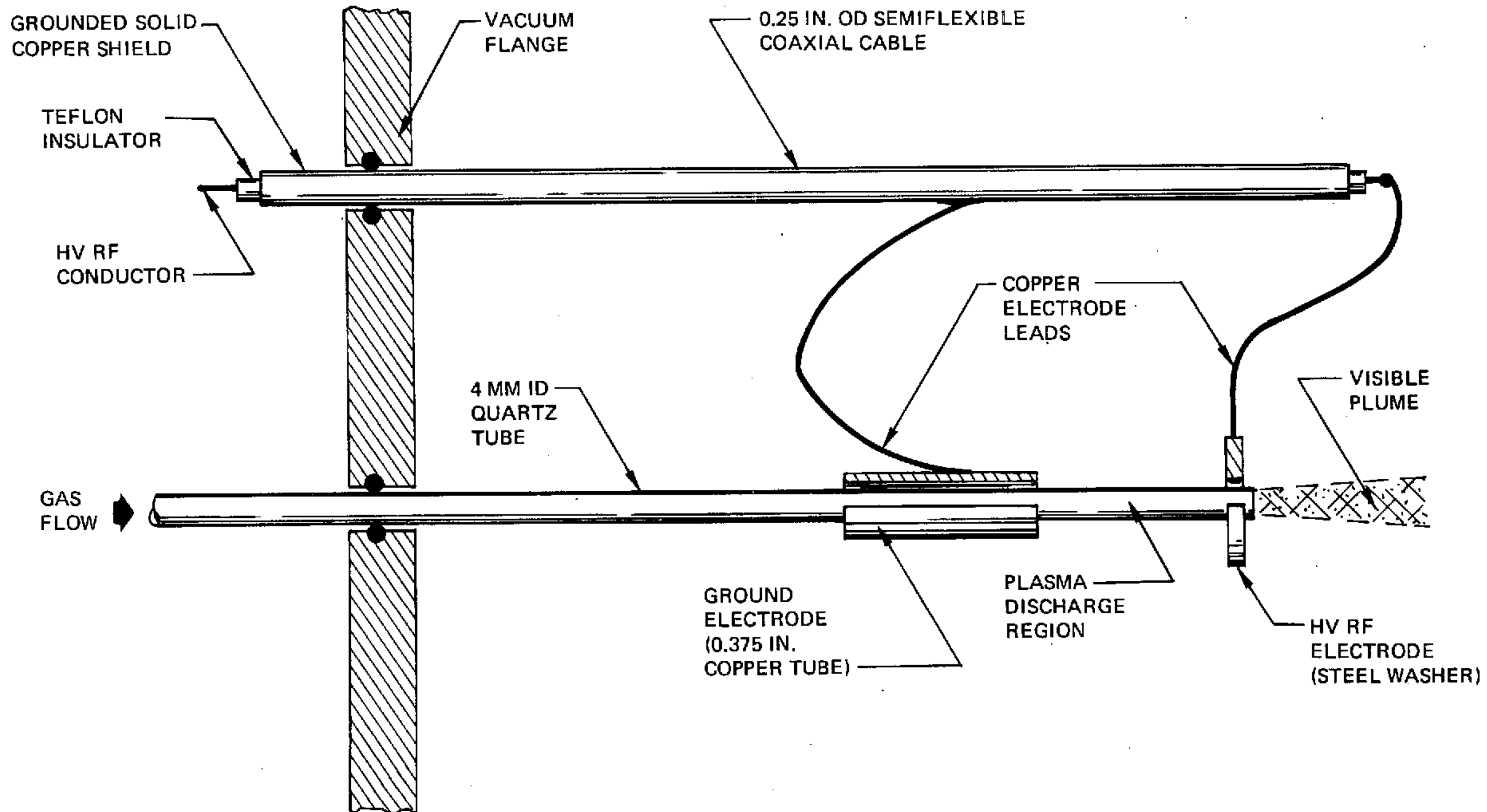

Figure 30: PROTOTYPE PLASMA TUBE CONFIGURATION

TABLE 8: CARBON REMOVAL RATE

DISTANCE FROM PLASMA TUBE (cm)	*CARBON REMOVAL RATE (gm/cm^2-min.)
1.25	2.7×10^{-6}
2.5	1.3×10^{-6}
3.75	0.9×10^{-6}
5.0	0.4×10^{-6}

A test to measure the radial extent of carbon removal was conducted using a glass slide coated with 100 nm of vacuum deposited carbon. Initially this slide was positioned perpendicular to the plasma tube axis at about 5 cm from the tube outlet. A plasma exposure of 20 minutes (test conditions similar to the QCM tests) resulted in removal of carbon in a spot about 1 cm in diameter. The clean spot was not symmetrical (i.e., not circular) due to the asymmetry in the visible plume. A modification to the electrode lead wire routing resulted in a more symmetric plume and the same slide was exposed for an additional 30 minutes at a distance of about 11 cm. This exposure resulted in slight additional carbon removal from the slide.

Based on these results further experiments were conducted to determine the cleaning rate distribution in a plane perpendicular to the plasma tube axis. These experiments used interferometry measurements to determine the amount of carbon removal from the slide. The initial test used a glass slide that was overcoated with about 130 nm of vacuum deposited carbon. Prior to testing, a grid network of aluminum (about 67 nm thick) was vacuum deposited over the carbon. The slide was then exposed to the plasma for 20 minutes at 11 cm from the plasma tube. The approximate operating conditions for the exposure were chamber pressure 4×10^{-5} torr, upstream oxygen pressure of 0.5 torr, and r.f. power at 165 watts forward and 75 watts reflected. After exposure, another aluminum grid network, overlapping the first, was vacuum deposited onto the sample to provide steps for the interferometry measurements. These measurements indicated carbon removal of up to about 15 nm,

*These results must be considered tentative since the QCM was not accurately positioned with respect to the visible plume centerline.

however, no pattern of cleaning was apparent. A new slide was then prepared with 260 nm of vacuum deposited carbon and aluminum strips (60 nm thick) vacuum deposited onto the carbon. This slide was exposed for 2.5 hours at about 11 cm from the plasma tube under the following operating conditions; chamber pressure $4x10^{-5}$ torr, upstream oxygen pressure 0.65 torr, and r.f. power at 100 watts forward and 60 watts reflected. After vacuum depositing aluminum cross-strips on the slide, interferometry measurements indicated carbon removal of up to about 16 nm but no definite cleaning pattern was apparent. This slide was then positioned closer to the plasma tube (about 5 cm distance) and exposed for 30 minutes under the following conditions; chamber pressure $6x10^{-5}$ torr, upstream oxygen pressure 0.72 torr, and r.f. power at 150 watts forward and 70 watts reflected. Post-test interferometry measurements indicated carbon removal of up to 65 nm with a definite pattern of removal. An area of the slide, about 2 cm diameter, showed significantly greater carbon removal than that for the remaining area. Figure 31 shows the cleaning rate distribution obtained by averaging the interferometry measurements at equal distances from the apparent center of the cleaned area. The rms deviations in the measurements are also shown in Figure 31. These deviations give an indication of the accuracy of the cleaning rate distribution determination.

Comparison of carbon removal rates, on aluminum-strip-coated and uncoated specimens, shows that the vacuum deposited aluminum grid apparently inhibits the rate of carbon removal. The uncoated specimen lost about 100 nm of carbon coating in a 20 minute exposure; whereas, less than 65 nm was removed from the specimen with the aluminum-grid-coating in 30 minutes of exposure. The interferometry measurements also show little carbon removal adjacent to the aluminum and increased carbon removal as the distance from the aluminum is increased. (Figure 31 data were based on the maximum carbon removal in each segment of the grid network.) Therefore, the method used to determine the cleaning rate distribution may not give accurate results. Even though this method may not give the absolute cleaning rate for an undisturbed surface, it may accurately give the relative cleaning rate distribution.

It was also noted in the carbon-cleaning experiments that the visible plume geometry is dependent on the plasma tube configuration, the r.f. electrode geometry, r.f. frequency and power, and the plasma tube pressure. Consequently, the cleaning rate distribution results should be considered preliminary and further investigation of plume geometry is recommended.

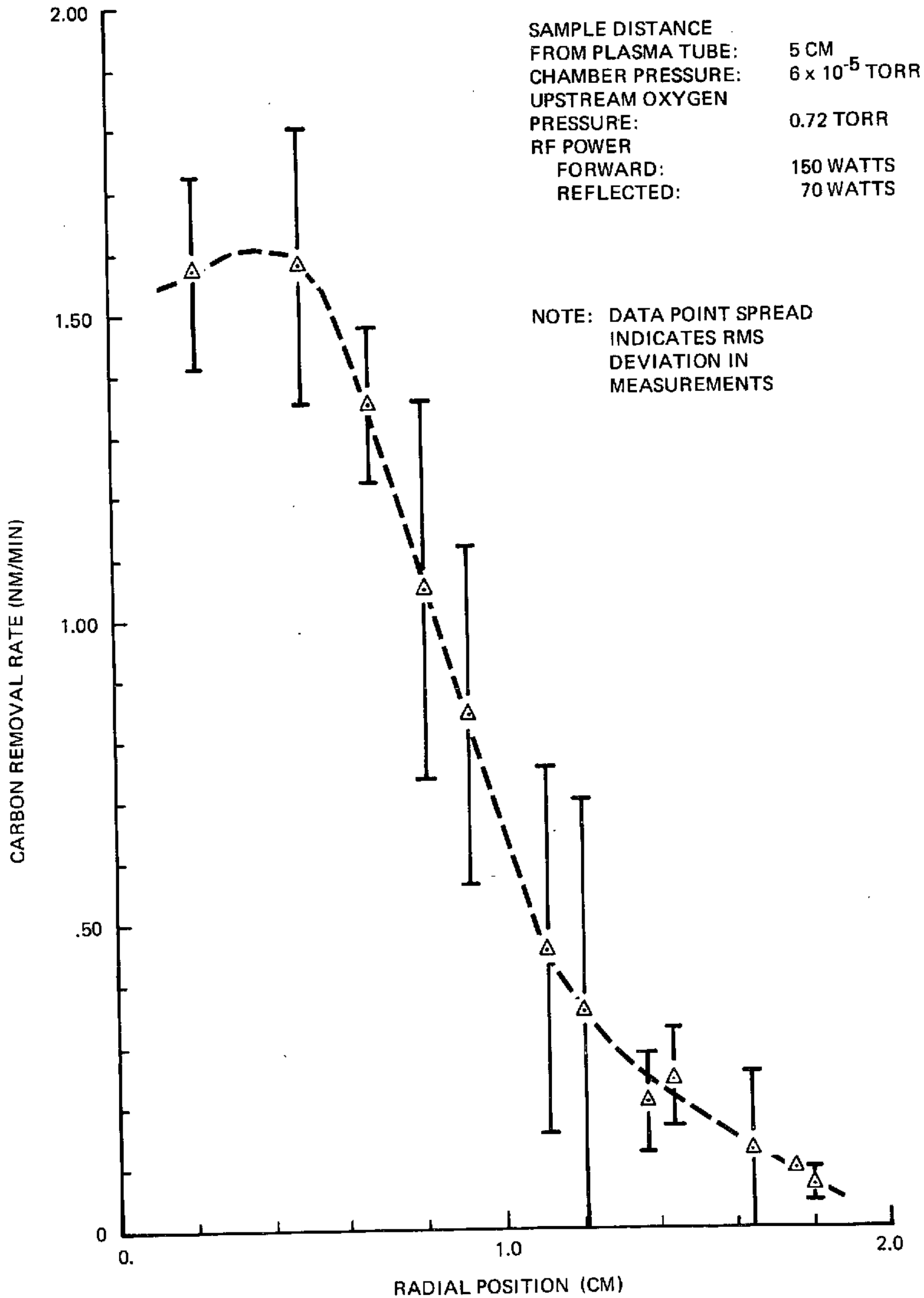

Figure 31: CLEANING RATE DISTRIBUTION

4.6.3 Contamination of Adjacent Surfaces

An experiment was conducted, using the prototype plasma tube configuration shown in Figure 30, to determine whether contamination occurs on a surface adjacent to one being cleaned. Two MgF_2/Al mirrors were used in this experiment (MgF 57 and MgF 118). Mirror MgF 118 was installed in the sample holder and its initial reflectance measured with the in-situ reflectometer/monochromator. Mirror MgF 118 was then removed and mirror MgF 57 installed in the sample holder and its initial reflectance measured. Mirror MgF 57 was then contaminated by exposure to UV radiation, in a 1, 3 butadiene environment, for 133 minutes. The QCM response indicated a contaminant film deposition of about 3.2×10^{-6} gm/cm^2. The reflectance was remeasured, the system let up to air, and mirror MgF 118 was installed adjacent to MgF 57. One edge of mirror MgF 118 was placed adjacent to an edge of MgF 57 and positioned such that there was an angle of about 120° between the mirror surfaces. Mirror MgF 57 was centered normal to the plasma tube axis at a distance of about 11 cm. This placement allowed the visible plume to impinge on MgF 57 but not on MgF 118.

Mirror MgF 57 was cleaned in a series of plasma exposures of 30, 40 and 50 minutes duration. The operating conditions for these exposures were; chamber pressure 4×10^{-5} torr, upstream oxygen pressure 0.65 torr, and r.f. power at 130 watts forward and 80 watts reflected. Figure 32 shows the reflectance data for MgF 57. The first two exposures increased the reflectance and the final exposure produced a slight decrease in reflectance. After completing the plasma exposures, the system was let up to air and the reflectance of mirror MgF 118 was remeasured. Figure 33 shows the reflectance data for MgF 118. These data indicate that MgF 118 was contaminated during the plasma cleaning of the adjacent mirror. However, there exists uncertainty as to whether or not the contamination of MgF 118 was caused by the contaminant cleaning of the adjacent surface. In the experimental set-up mirror MgF 118 was in close proximity to the end of the semi-flexible coaxial cable (see Figure 30). When the plasma tube was in operation considerable heat was generated in the r.f. leads due to the impedance mismatch in the prototype system. This heating may have caused outgassing of the exposed teflon insulation and/or the soft solder connections used for the electrode leads. This outgassing would also explain the failure of the plasma to completely restore the reflectance of mirror MgF 57.

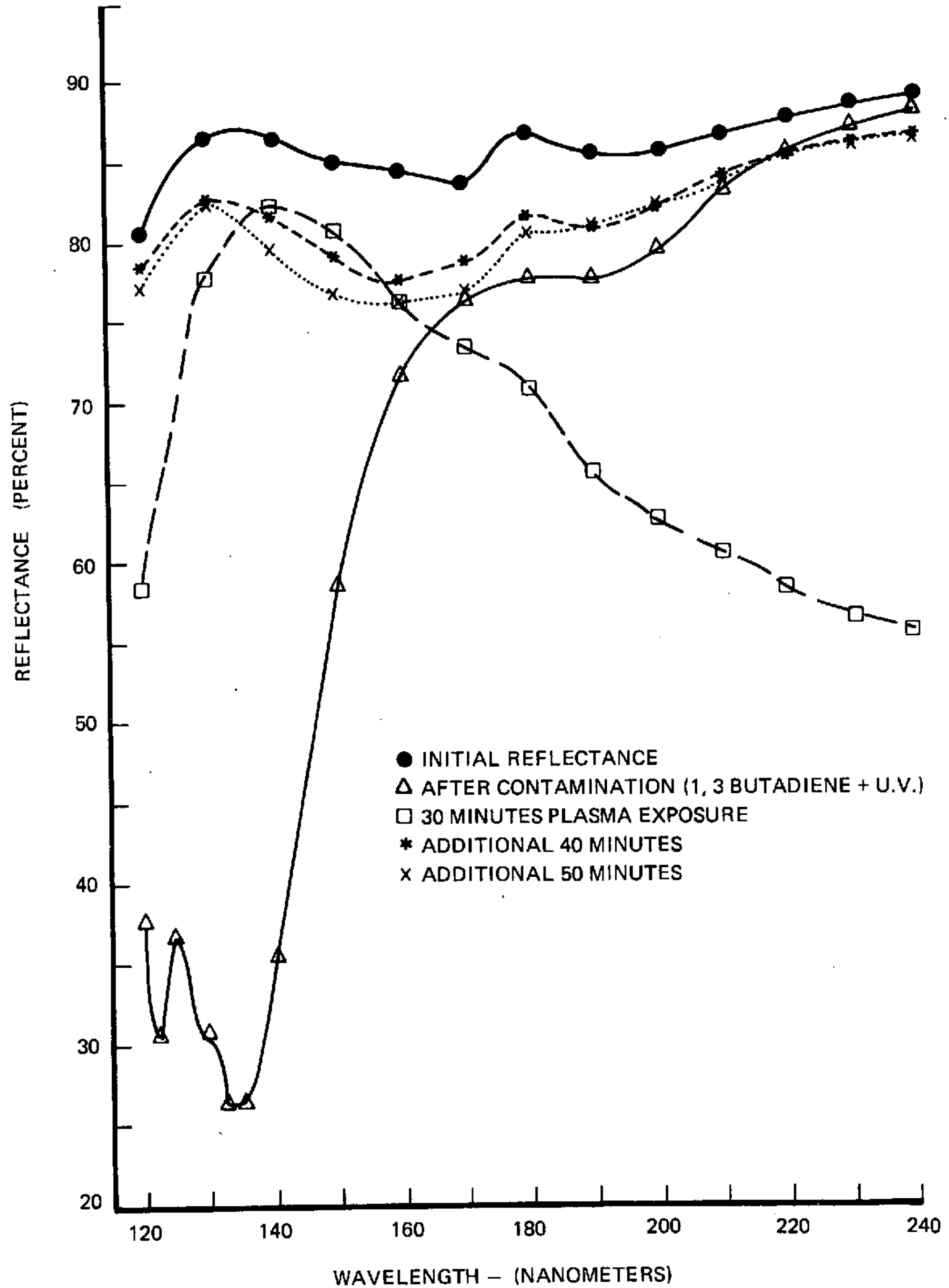

Figure 32: REFLECTANCE DATA FOR MgF_2/Al MIRROR Mg F57

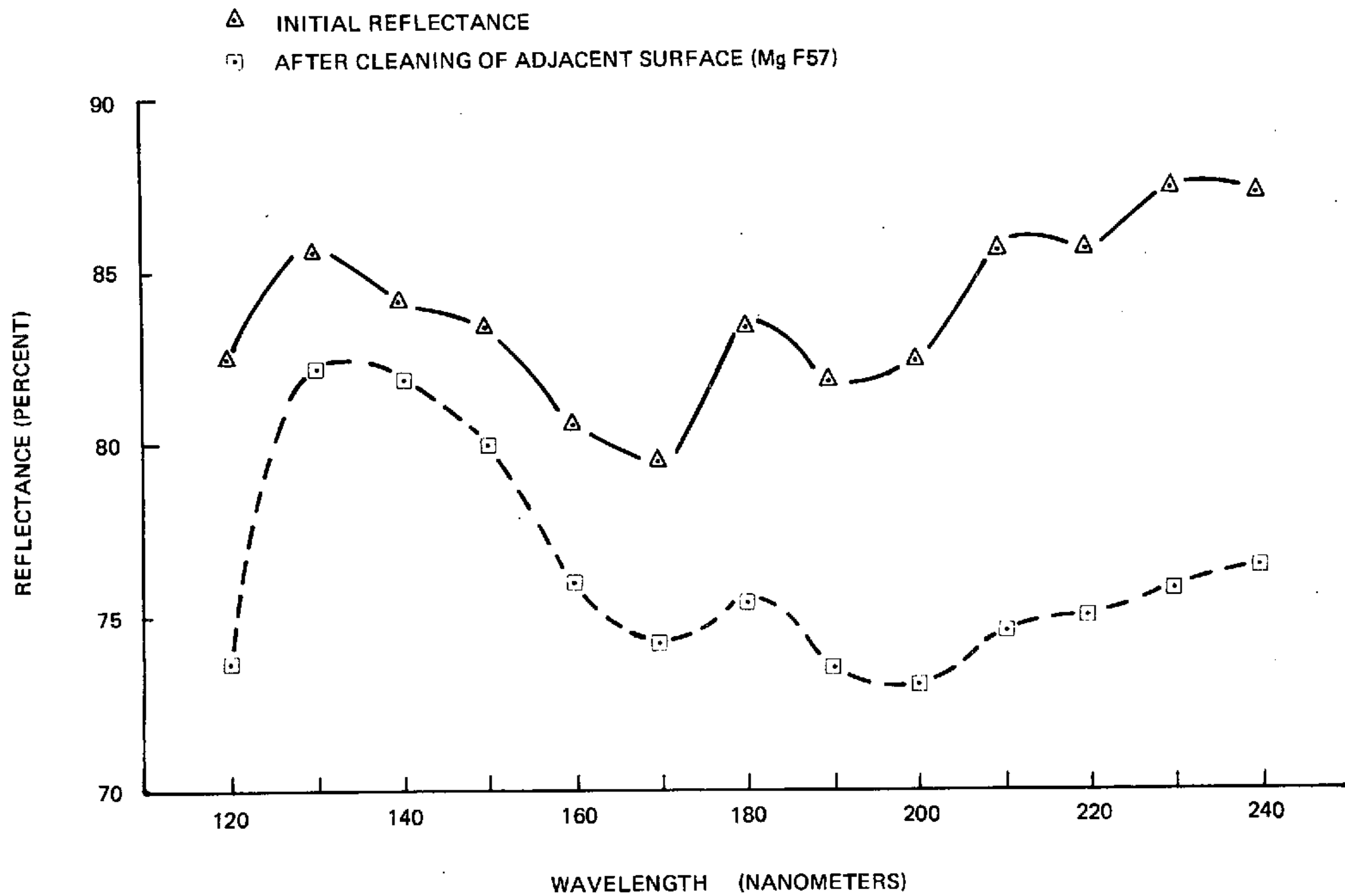

Figure 33: REFLECTANCE DATA FOR Mg F_2/Al MIRROR Mg F118

A definitive experiment on the contamination of adjacent surfaces should be conducted using the plasma tube being developed under companion Contract NAS8-28270. This plasma tube will have the r.f. electrode system shielded from the vacuum environment thus eliminating this source of contamination.

5.0 CONCLUSIONS AND RECOMMENDATIONS

In addition to the conclusions reached during the first years effort, the following conclusions have resulted from the experiments discussed in this report:

A. ATM Filter Treatment (Filter, consisting of vacuum deposited aluminum on a fine wire grid, designed to transmit in the 17-80 nm wavelength region).

(1) Both oxygen and argon plasma exposure increased filter transmittance.

(2) There is an optimum exposure period which maximizes the filter transmittance.

(3) An extended period at ambient conditions following plasma treatment, decreases the filter transmittance.

B. Atomic Oxygen Flux/Cleaning Rate Correlation.

There is no measurable correlation between the atomic oxygen flux and plasma cleaning rate. Atomic oxygen is apparently not a significant factor in the cleaning mechanism.

C. In-Situ Butadiene Contamination/Cleaning Experiments.

(1) Exposure to ambient conditions, between contamination and cleaning, is not a very significant factor in the experiments to establish feasibility of an ACT for space applications.

(a) Extended period at vacuum or exposure to ambient conditions resulted in slight UV reflectance degradation of a cleaned surface.

(b) Extended period at vacuum or exposure to ambient conditions had no apparent effect on the butadiene contaminant film or subsequent plasma cleaning.

(2) An argon plasma cleans the butadiene contaminant film as effectively as an oxygen plasma.

(3) Restoration of UV reflectance is less complete for surfaces with thicker contaminant films. This may be due to either residual uncleanable contaminant or to an 'overcleaning effect' from the longer plasma exposures required to remove the thicker film.

D. Carbon Cleaning Experiments.

Oxygen, hydrogen and helium plasma exposures are about equally effective in removal of vacuum deposited carbon.

E. Silicone Contamination/Cleaning Experiments.

(1) Silicone contaminant (dimethylsiloxane), about 2×10^{-6} gm/cm^2 on MgF_2/Al mirrors, produces severe reflectance degradation in the 120 to 130 nm wavelength range. Reflectance is increased in the 170 to 300 nm wavelength region.

(2) The reflectance at shorter wavelengths was partially restored with helium, oxygen and hydrogen plasma exposure. Oxygen produced the least restoration and hydrogen the greatest.

(3) Plasma exposure (helium, oxygen and hydrogen) decreased the reflectance of contaminated mirrors at the longer wavelengths. Helium plasma exposure produced the most degradation.

(4) Extended periods in vacuum appeared to result in some removal of the silicone contaminant. Exposure to UV radiation also produced some contaminant removal.

F. Experiments at Low Chamber Pressures.

(1) Proper plasma tube design will allow the active cleaning species to be produced at low chamber pressures. A prototype plasma tube was operated at chamber pressures of 10^{-5} to 10^{-4} torr with operation independent of chamber pressure. The plasma cleaning region corresponds to the region of a visible plume.

(2) The cleaning rate distribution was measured showing a cleaning region of about 2 cm diameter at a distance of 5 cm from the prototype plasma tube. A vacuum deposited aluminum grid, overcoated on a vacuum deposited carbon layer, appeared to inhibit the rate of carbon removal.

(3) Preliminary results showed that an adjacent surface was contaminated during plasma cleaning of a butadiene contaminant film. However, the contaminant source was probably the exposed r.f. electrode system, on the prototype plasma tube, rather than the contaminant film removal.

Based on results of this research, it is recommended that development of a plasma tube, for low flow rate and low chamber pressure operation, be continued. This development should be aimed at:

(1) Determination of operational characteristics. The r.f. voltage and power requirements should be determined as function of plasma tube/r.f. electrode geometry, r.f. frequency, and gas flow rate. The 'visible plume' character (geometry and brightness) should be observed as the system parameters are varied. This observation would serve as an indicator of the cleaning effectiveness.

(2) Quantitative determination of the cleaning rate distribution for various sets of operating conditions.

(3) Correlating the cleaning rate with plasma tube operating conditions.

The experiment, to determine the contamination of surfaces adjacent to those being cleaned, should be repeated with the possibility of extraneous contamination being

eliminated. It is also recommended that an investigation be made to determine the plasma cleaning mechanism. This determination might provide an explanation of the 'overcleaning effect', show the limitations on the type of contaminants that can be cleaned, and possibly provide guidelines as to the type of gas and operational mode required for different contaminants.

6.0 REFERENCES

1. Heaney, J. B.: "Results from the ATS-3 Reflectometer Experiment." AIAA Paper No. 69-644 presented at the 4th Thermophysics Conference, San Francisco, California, June 1969.

2. McKeown, D. and W. E. Corbin: "Removal of Surface Contamination by Plasma Sputtering." AIAA Paper No. 71-475 presented at the 6th Thermophysics Conference, Tullahoma, Tenn., April 1971.

3. Cothran, C. A., M. McCargo and S. A. Greenberg: "A Survey of Contamination of Spacecraft Surfaces," AIAA Paper No. 71-475 presented at the 6th Thermophysics Conference, Tullahoma, Tenn., April 1971.

4. Private Communication with Dr. G. Timothy, Harvard College Observatory, Cambridge, Mass., April 1971.

5. Gillette, R. B. and B. A. Kenyon: Applied Optics 10, 3 (1971).

6. Gillette, R. B., W. D. Beverly and G. A. Cruz: "Active Cleaning Technique for Removing Contamination from Optical Surfaces in Space." Annual Report No. 1, Contract NAS8-26385, March 1972.

7. Shannon, R. L. and R. B. Gillette: "Active Cleaning Technique Device," Design Study Summary Report, Contract NAS8-28270, D180-15454-1, March 1973.