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Environmental Assessment of Coal- and Oil-firing in a Controlled Industrial Boiler; Volume III. Comprehensive Assessment and Appendices

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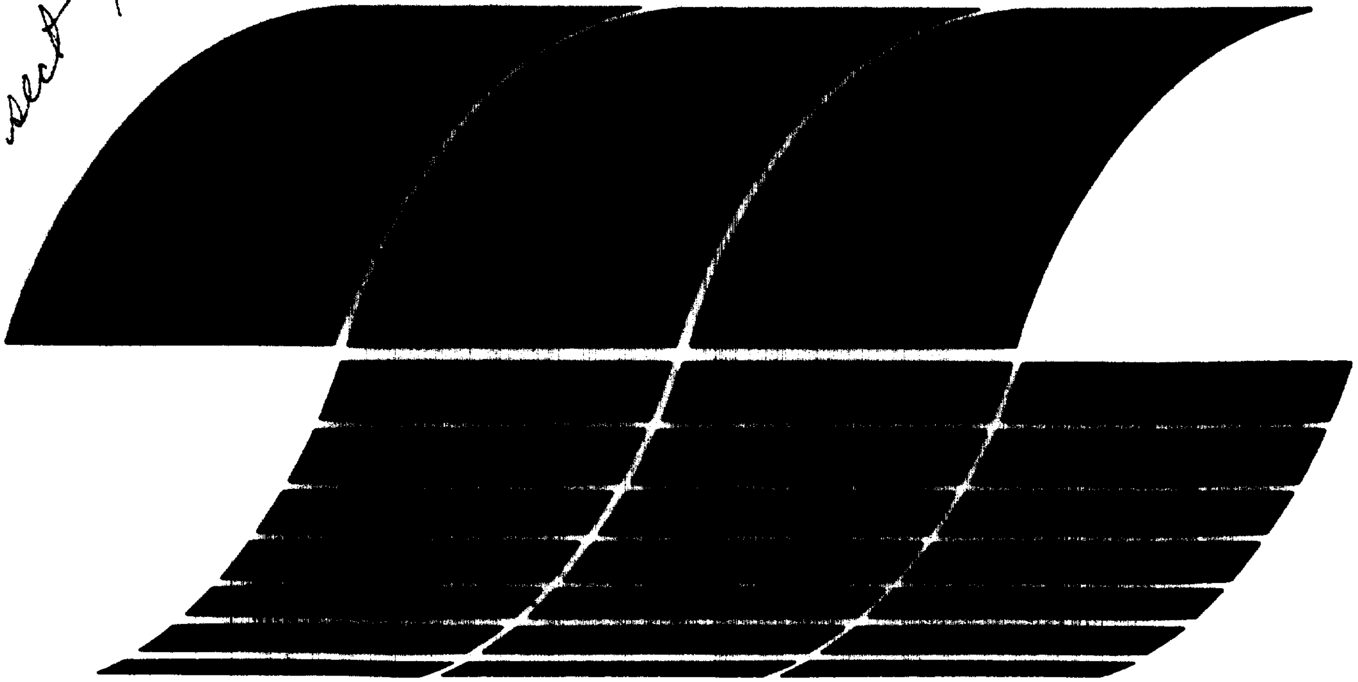

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Environmental Assessment of Coal- and Oil-firing in a Controlled Industrial Boiler;
Volume III. Comprehensive Assessment and Appendices

by

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Office of Research and Development
Washington, DC 20460

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ABSTRACT

The report gives results of a comparative multimedia assessment of coal versus oil firing in a controlled industrial boiler. Relative environmental, energy, economic, and societal impacts were identified. Comprehensive sampling and analyses of gaseous, liquid, and solid emissions from the boiler and its control equipment were conducted to identify criteria pollutants and other species. Major conclusions include: (1) while the quantity of particulates from oil firing is considerably less than from coal firing, the particles are generally smaller and more difficult to remove, and the concentration of particulates in the treated flue gas from oil firing exceeded that from coal firing. (2) NO_x and CO emissions during coal firing were about triple those during oil firing. (3) Sulfate emissions from the boiler during coal firing were about triple those during oil firing; however, at the outlet of the control equipment, sulfate concentrations were essentially identical. (4) Most trace element emissions (except vanadium, cadmium, lead, cobalt, nickel, and copper) were higher during coal firing. (5) Oil firing produces cadmium burdens in vegetation approaching levels which are injurious to man; coal firing may produce molybdenum levels which are injurious to cattle. (6) The assessment generally supports the national energy plan for increased use of coal by projecting that the environmental insult from controlled coal firing is not significantly different from that from oil firing.

This report was submitted in fulfillment of Contract Number 68-02-2613, Task 8 by TRW Environmental Engineering Division under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from October 24, 1977 to May 5, 1978, and work was completed as of May 5, 1978.

CONTENTS

Appendices

LIST OF ABBREVIATIONS

acm/min -- Actual Cubic Meters Per Minute
ACFM -- Actual Cubic Feet Per Minute
DSCM -- Dry Standard Cubic Meters
ESCA -- Electron Spectroscopy for Chemical Analyses
FGD -- Flue Gas Desulfurization
ICPOES -- Inductively Coupled Plasma Optical Emission Spectroscopy
MATE -- Minimum Acute Toxicity Effluent
NAAQS -- National Ambient Air Quality Standards
NSPS -- New Source Performance Standards
SSMS -- Spark Source Mass Spectrometry
TSP -- Total Suspended Particulate

ACKNOWLEDGMENTS

The cooperation of the Firestone Tire and Rubber Company and FMC is gratefully acknowledged. We are particularly indebted to Gary Wansley of Firestone and Carl Legatski of FMC, without whose cooperation this assessment could not have been completed.

SECTION I

INTRODUCTION

A comparative multimedia assessment of coal-firing and oil-firing in an industrial boiler was conducted. Extensive sampling and analysis of all major gaseous, liquid, and solid emissions and effluents was done. The test boiler was a dual fuel 10 MW equivalent unit that is capable of burning both coal and oil. During the tests conducted for this study the boiler burned either exclusively coal or oil, although it can burn both fuels simultaneously if required. The boiler is equipped with a pilot double-alkali flue gas desulfurization (FGD) unit designed to treat approximately 30% of the total flue gas, approximately 3 MW equivalent. During the tests, however, the FGD was processing only about 10-15% (13% average) of the total when coal was fired and 23-30% (25% average) when oil was burned. This corresponds to approximately 1.5 MW and 2.5 MW, respectively. Because the FGD was operating at less than design capacity, there is some question about the typicalness of the test results. That is, the pilot unit may have been performing better than the full size commercial version will.

The assessment consists of several parts. First, comprehensive emissions assessments of each fuel were conducted. These assessments consist of detailed examinations of gaseous, liquid and solid emissions and effluents considering both pre- and post-scrubber emissions for each fuel. That is, the emissions to all three media were determined for the case where no FGD was present and for the case where an FGD capable of scrubbing 100% of the flue gas was present. The comprehensive emissions assessment also consisted of an examination of the effects and efficiencies of the scrubber for both fuels.

These comprehensive emissions assessments were used to develop a comparative emissions assessment. This assessment examines the differences in the quantities and character of the emissions resulting from the combustion of each fuel. In this case the primary emphasis was on the emissions and effluents resulting from the burning of each fuel where 100% scrubbing capacity was available. This part of the project was concerned with determining the emissions resulting from each fuel with emission controls in place. Of special concern was the cross-media impacts of each fuel.

On the basis of the emissions assessments a comparative environmental, societal and energy impact assessment was developed. The emphasis here was on the relative impacts of each fuel assuming full flue gas desulfurization. The uncertainties inherent in these types of analyses dictated that the differences rather than the absolute magnitude of these impacts be considered.

The report consists of three volumes. Volume I is an executive summary which summarizes the major results and conclusions of the study. Volume II presents the comparative assessments. Included are a description of the test setting, the comparative emissions assessment, and the comparative environmental, societal and energy impact assessment. This volume, Volume III, contains the comprehensive assessments and appendices and includes detailed descriptions of the test site, the test protocol and a detailed presentation of data.

SECTION 2

SUMMARY AND CONCLUSIONS

A comparative assessment of coal and oil firing in a controlled industrial boiler was conducted. The comprehensive emissions assessments for each fuel were used to develop a comparative emissions assessment. On the basis of the emissions assessment a comparative environmental assessment was developed.

The following is a list of the major conclusions resulting from the comprehensive coal and comprehensive oil assessments;

COMPREHENSIVE COAL ASSESSMENT

- Uncontrolled emissions of criteria pollutants generally corresponded well with values reported in AP-42. Although NO_x emissions were slightly higher than the average AP-42 value, they appear to be within the normal range for similar industrial units.

- NO_x reductions varying from approximately 0 to 24 percent were measured across the scrubber. However, the magnitude of NO_x reductions could not be correlated to changes in variables monitored during the test period (i.e., temperature, gas flow rate, liquid/gas ratio, boiler load, etc.). For this reason, it is considered feasible that observed NO_x reductions are a sampling phenomenon, perhaps related to leaks in the sample train.

- Sulfur dioxide removal data indicated an average scrubber efficiency of 97 percent. Controlled SO_2 emissions were 36.3 ng/J (0.08 pounds/MM Btu) which is less than either existing or proposed NSPS limitations for utility boilers.

- Mass balance data indicate that the multiclone unit upstream of the scrubber was removing little or no fly ash during the test period. The scrubber was found to remove 99.4 percent of the inlet particulate removal.

- Although the removal efficiency for total particulates is high, there appears to be a net increase in emission rates across the scrubber for particulates less than 3 μm in size. This net increase can be attributed to the poor removal efficiency of the scrubber for fine particulates, and to the sodium bisulfate ($NaHSO_4$) and calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2H_2O$) particulates generated by the scrubber. Both $NaHSO_4$ and $CaSO_3 \cdot 1/2H_2O$ have been identified at the scrubber outlet but not at the inlet.

- The relatively poor removal efficiency (approximately 30%) for SO_3 across the scrubber is an indication that SO_3 is either present as very fine aerosols in the scrubber inlet, or is converted to very fine aerosols as the flue gas stream is rapidly cooled inside the scrubber.

- The overall removal efficiency for trace elements across the scrubber is 99.5 percent. Of the 22 major trace elements, 18 exceed their MATE values at the scrubber inlet and four at the scrubber outlet. The four trace elements in the scrubber flue gas that pose a potential hazard are arsenic, chromium, iron, and nickel. In addition, the emission concentration of beryllium at the scrubber outlet is equal to its MATE value.

- The relative removal efficiency for trace elements across the scrubber can be explained by enrichment theory. In general, trace elements that occur as element vapors or form volatile compounds at furnace temperatures are more concentrated in the smaller particulates, as a result of subsequent condensation and surface adsorption. These are the same trace elements that are removed less efficiently by the scrubber.

- ESCA analysis has shown that while there may be higher surface concentration of sulfur containing compounds in the particulates emitted from the scrubber, most of the sulfur containing compounds are probably present as solid sulfates and sulfites. Thus, it is conceivable that sulfuric acid vapor is condensed and deposited on the particulates emitted, whereas sodium bisulfate and calcium sulfite hemihydrate are emitted as fine, solid particulates.

- The overall sulfur balance indicates that over 92 percent of the fuel sulfur is emitted as SO_2, less than 1 percent of the fuel sulfur is emitted as SO_3, and approximately 3 percent of the fuel sulfur is emitted as $SO_4^{=}$.

- Total organic emissions were generally less than 6 ng/J (0.01 pound/MM Btu) and these emissions appear to be primarily C_1 to C_6 hydrocarbons and hydrocarbons heavier than C_{16}. While uncontrolled emission rates for C_7 to C_{16} and higher hydrocarbons are low, emissions of these organics were further reduced by 90 to 100 percent in the scrubber unit.

- No polycyclic organic material (POM) were detected in either scrubber inlet or outlet samples drawn during the test period. Total organic emissions were sufficiently low that attempts to identify specific compounds resulted only in identification of substances normally associated with laboratory analyses and sampling equipment.

- The combined wastewater stream generated from the boiler operation apparently does not pose an environmental hazard since the discharge concentrations of inorganics and organics are all well below their MATE values.

- The scrubber cake produced during coal firing contained 29% coal fly ash. With the exception of boron, trace element concentrations in the scrubber cake far exceeded their MATE values. Because the trace elements may leach from the disposed scrubber cake, these solid wastes must be disposed of in specially designed landfills.

- Mass balance closure for most of the trace elements have been found to be in the 75 to 107 percent range. This closure instills confidence on the validity of the sampling and analysis data for trace elements.

COMPREHENSIVE OIL ASSESSMENT

- Uncontrolled emissions of criteria pollutants do not generally correspond with emission factors from AP-42. NO_x emissions were nearly 23% lower than the AP-42 emission factor, although they appear to be within the normal range for similar industrial units. CO emissions were nearly 63% lower than the AP-42 emission factor. SO_2 and total hydrocarbons corresponded well with their respective AP-42 emission factors. Particulate emissions, in the absence of coal ash contamination, are approximately twice the value tabulated in AP-42.

- Sulfur dioxide removal data indicated an average scrubber efficiency of 97%. Controlled SO_2 emissions were 26.8 ng/J 90.06 lb/MM Btu) which is less than either existing or proposed NSPS limitations for utility boilers.

- Particulate removal data indicate that, on the average, scrubber efficiency was 84% during the test period. However, based on particulate catches essentially free of coal ash contamination, the scrubber efficiency was approximately 75% for oil-firing particulates.

- Organic emissions were generally less than 5 ng/J (0.01 lb/MM Btu) and appear to be composed primarily of C_1 to C_6 hydrocarbons and organics heavier than C_{16}. Approximately 88 and 83% of the C_7 to C_{16} and higher than C_{16} organics, respectively, were removed by the scrubber.

- The organic compounds identified in the gas samples were generally not representative of combustion-generated organic materials, but were compounds associated with materials used in the sampling equipment and in various analytical procedures. This again confirms the low level of organic emissions.

- Polycyclic organic material (POM) was not found in the scrubber inlet or outlet at detection limits of 0.3 $\mu g/m^3$. MATE values for most POM's are greater than this detection limit. However, since the MATE values for at least two POM compounds - benzo(a)-pyrene and dibenz(a,h)anthracene - are less than 0.3 $\mu g/m^3$, additional GC/MS analyzes at higher sensitivity would be required to conclusively preclude the presence of all POM's at MATE levels.

- When emissions are uncontrolled, 90 to 92% of the sulfur in the fuel feed is emitted as SO_2, less than 1% as SO_3, and 1.5% as $SO_4^=$.

- SO_2 is efficiently removed by the scrubber (97 to 98% efficiency). The SO_3 removal efficiency (28 to 29%) suggests that SO_3 is associated with fine particulates or aerosols. $SO_4^=$ is about 60% removed by the scrubber, and so is probably associated with the larger particulates.

- Of the 22 major trace elements analyzed in the flue gas stream, 11 exceeded their MATE values at the scrubber inlet while only 5 exceeded MATE values at the scrubber outlet. These 5 elements are arsenic, cadmium, chromium, nickel and vanadium. With the exception of chromium, elements exceeding their MATE values at the scrubber outlet were removed from the flue gas stream with efficiencies lower than the overall average removal efficiency of 87%.

- Beryllium emissions were 0.001 mg/m^3 after scrubbing this corresponds to half the MATE value for this element. At this emission concentration, the National Standard for Hazardous Air Pollutants limitation of 10 grams beryllium per day would only be exceeded by boilers of 100 MW capacity or greater.

- The combined wastewater stream from the boiler operation apparently does not pose an environmental hazard, since the discharge concentrations of organics are all well below their MATE values.

- Mass balance closure for 10 of the 20 trace elements analyzed is between 50 and 136%. Poorer mass balance closure was obtained for the remainder of trace elements due to the extremely low element concentrations and/or contamination of the scrubber recycle solution by coal firing components.

- The scrubber cake produced contains about 1% oil flyash. With the exception of antimony, boron, molybdenum and zinc, trace element concentrations in the scrubber cake exceeded their health based MATE values. All ecology based MATE values were exceeded by trace element concentration. Because the trace elements may leach from the disposed scrubber cake, these solid wastes must be disposed of in specially designed landfills.

SECTION 3
PLANT DESCRIPTION

The host for this assessment was the Pottstown, Pennsylvania plant of the Firestone Tire and Rubber Company. Boiler number 4, one of four used to supply process and heating steam to the plant, was used in the assessment. The boiler burns either coal or oil and has a pilot FMC double alkali flue gas desulfurization system designed to treat approximately one-third of the boiler flue gas.

The excellent cooperation and assistance by the Firestone Tire and Rubber Company and FMC was invaluable in performing this assessment.

GENERAL SETTING

Pottstown is situated 64 kilometers (40 miles) northwest of Philadelphia along the Schuylkill River. (See Figure 3-1.) The Firestone Tire and Rubber Company plant layout is shown in Figure 3-2.

Steam Plant

The steam plant consists of four separate boilers which supply process and heating steam to the entire facility. Boiler Numbers 3, 4, and 5, operate at a fairly constant rate of 45,000 kg/hr (100,000 lb/hr) of steam. Process steam demand is relatively steady, since the plant operates 24 hours per day, seven days per week. Fluctuations in heating load are satisfied by either boosting steam generation rates on these boilers or by operating Boiler No. 1. The steam generation rate of Boiler No. 1 varies from zero to approximately 22,700 kg/hr (50,000 lb/hr) of steam.

Boiler Number 4 was chosen for this assessment because it has a pilot scale flue gas desulfurization system and a dual fuel capability.

BOILER DESCRIPTION

Boiler No. 4 is a Type P-22 EL, integral furnace, once through Babcock and Wilcox unit. (See Table 3-1 for boiler specification data and Figure 3-3 for a schematic of the boiler and associated equipment.) When it was installed in 1958, the boiler was designed as a coal-fired unit but was converted to fire either coal or oil in 1967. The changeover from one fuel to the other can be accomplished in less than thirty minutes.

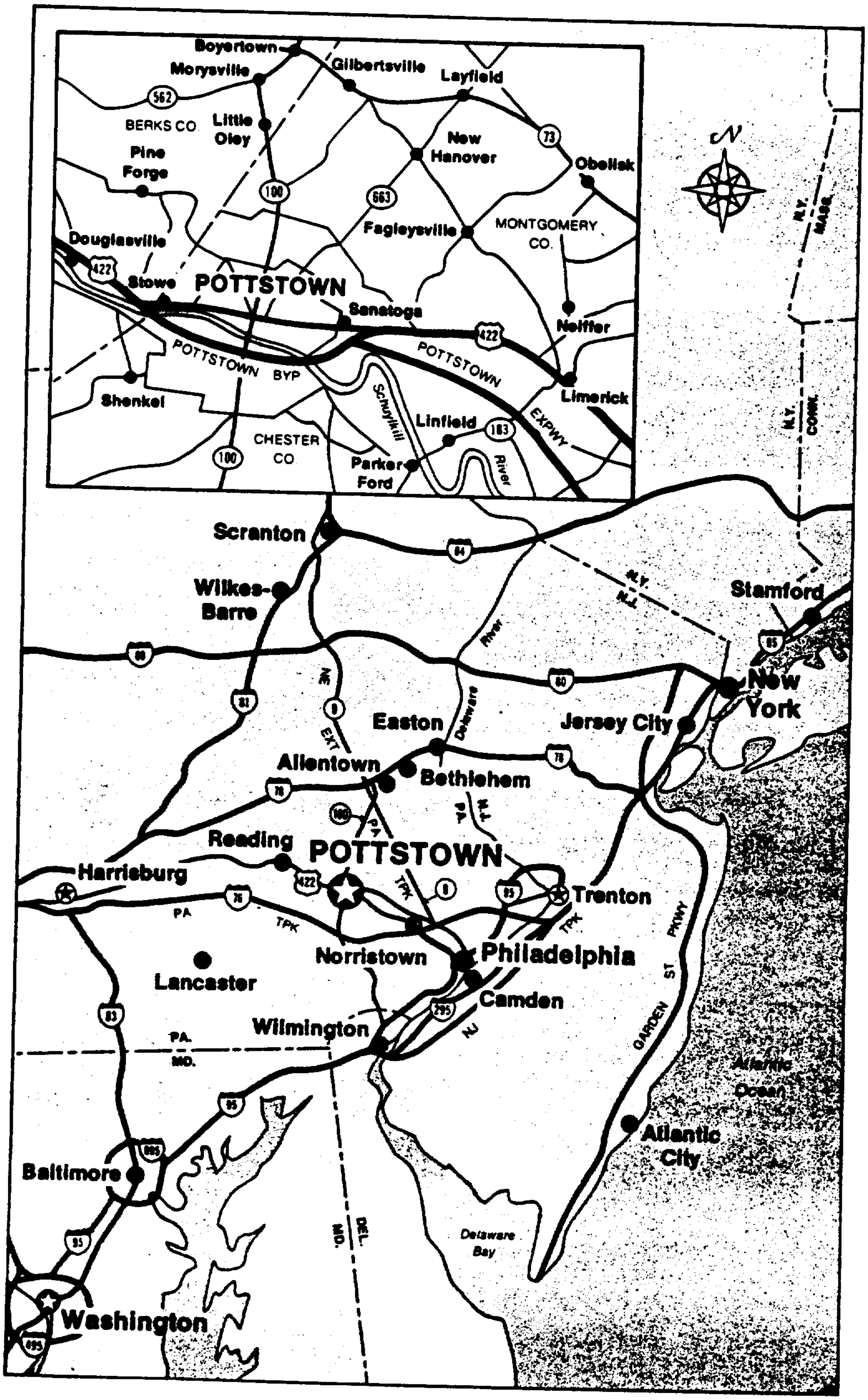


Figure 3-1. Location of Pottstown, Pennsylvania

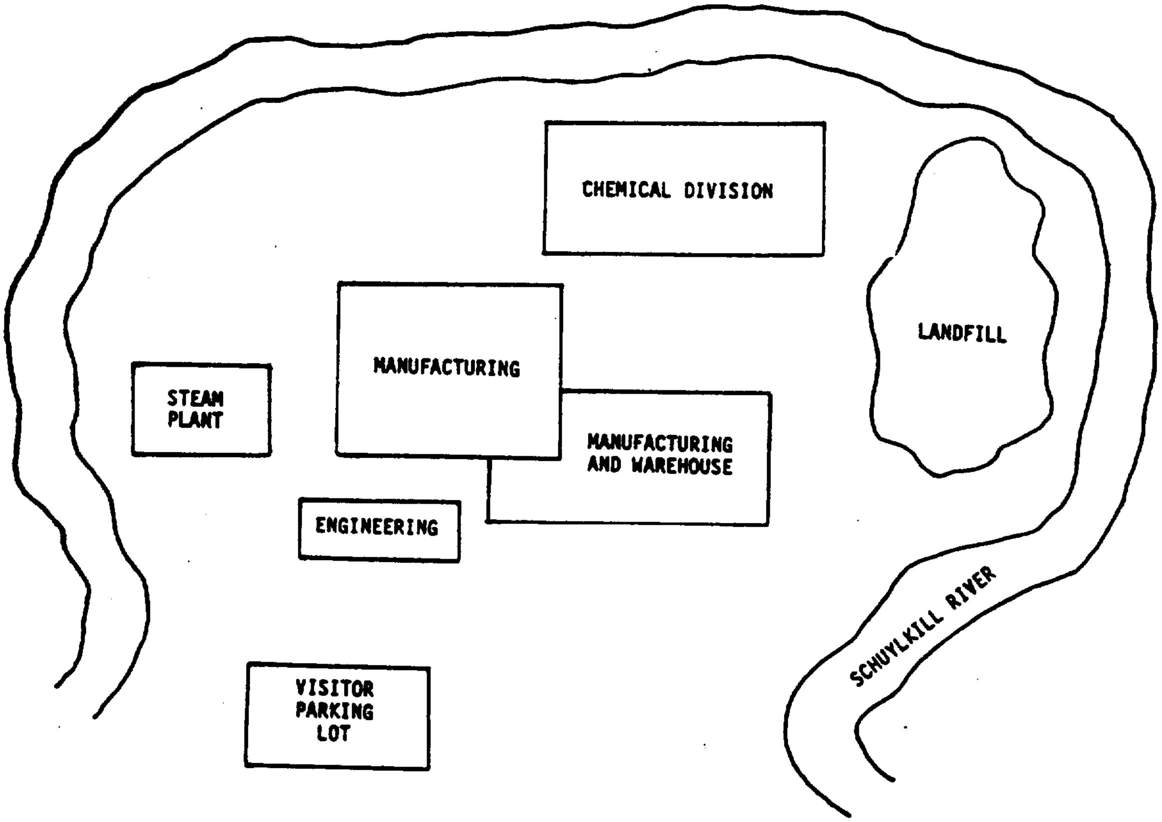


Figure 3-2. Industrial site plant layout.

TABLE 3-1. BOILER NUMBER 4 DESIGN DATA

Boiler Type:	Oil/Pulverized coal; face fired; integral furnace; dry bottom.
Manufacturer:	Babcock and Wilcox, Type P-22 EL
Type of burner:	Circular conical
Number of burners:	3
Burner arrangement:	Triangular, one face
Air Preheater:	yes
Fuel:	Number 6 fuel oil; High volatile bituminous coal, Class II, Group 2, of ASTM D388
Design steam rate:	45,000 kg/hr (100,000 lb/hr); 1.4 mPa (190 psi); at approximately 193°C (380°F).
Use:	Process steam.

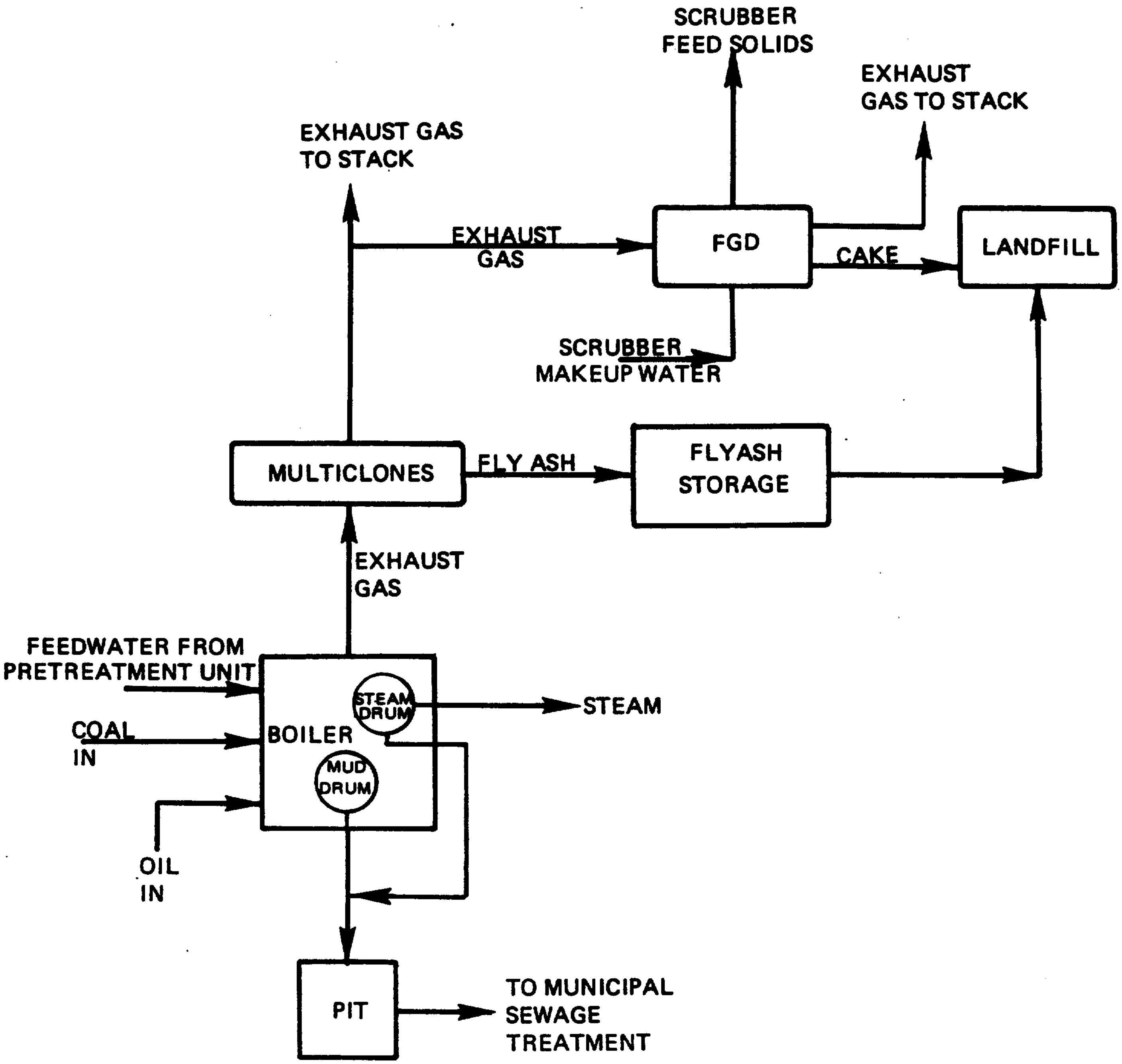


Figure 3-3. Boiler system schematic.

The two fuels are usually not burned simultaneously except when converting from oil to coal firing. The coal is ignited by continuing oil firing until a stable coal flame is obtained. Oil is fired simultaneously with coal to maintain acceptable steam generation rates when coal with a low heat content is burned.

The boiler was designed to burn either Number 6 fuel oil or a high volatile eastern bituminous coal. The boiler does not presently have fuel oil specifications. Therefore, sulfur and heat content vary with supplier. Analysis data for the fuel oil burned during testing can be found in Section 6. The coal burned is required to meet Class II, Group 2 of ASTM D388. Normally Pennsylvania coal is used. However, coal purchased from a mine in Kentucky was burned during the 1978 coal strike. Analysis data for the coal burned during testing can be found in Section 5. The fuel handling systems are shown in Figures 3-4 and 3-5 for coal and oil, respectively.

An air preheater is located in the flue gas plenum directly downstream of the boiler. This gas to gas heat exchange recovers approximately 4.2 gigajoules/hr (4 million BTU/hr) when the boiler is operating at full load. This represents a potential annual savings of 907,000 kg (1000 tons) of coal, or 5500 barrels of oil.

Tables 3-2 and 3-3 present data on the monthly fuel consumption and steam generation during 1976 and 1977, respectively.

The boiler is scheduled to operate 45 weeks per year on a 24-hour-per day, 7-day-per-week basis.

The following maintenance is scheduled:

- Continuous surface blow-down of the steam drum to control alkalinity and solids is maintained;
- Once per shift each end of the mud drum is blown down;
- Soot is blown once per shift;
- Bottom ash is removed from the unit once per day.

Table 3-4 presents data on the number of days that boiler No. 4 was off-line during 1976 and 1977. Coal use, oil use, and the off-line schedule are compared for 1976 and 1977 in Figures 3-6 and 3-7. An overhaul in July 1977 accounts for part of this off-line schedule.

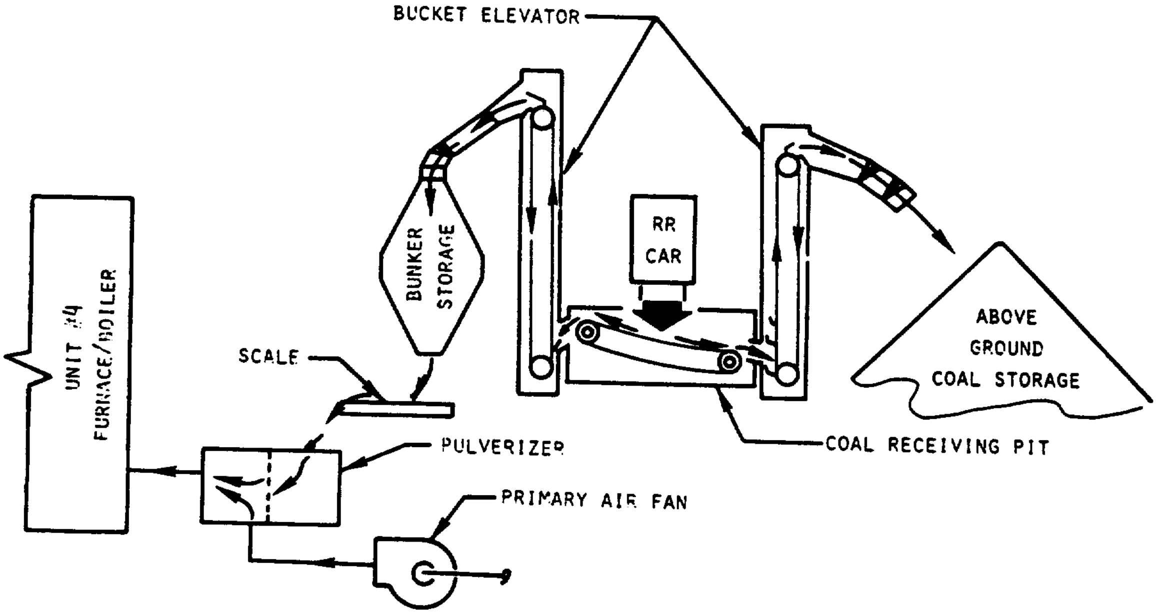


Figure 3-4. Coal handling flow diagram.

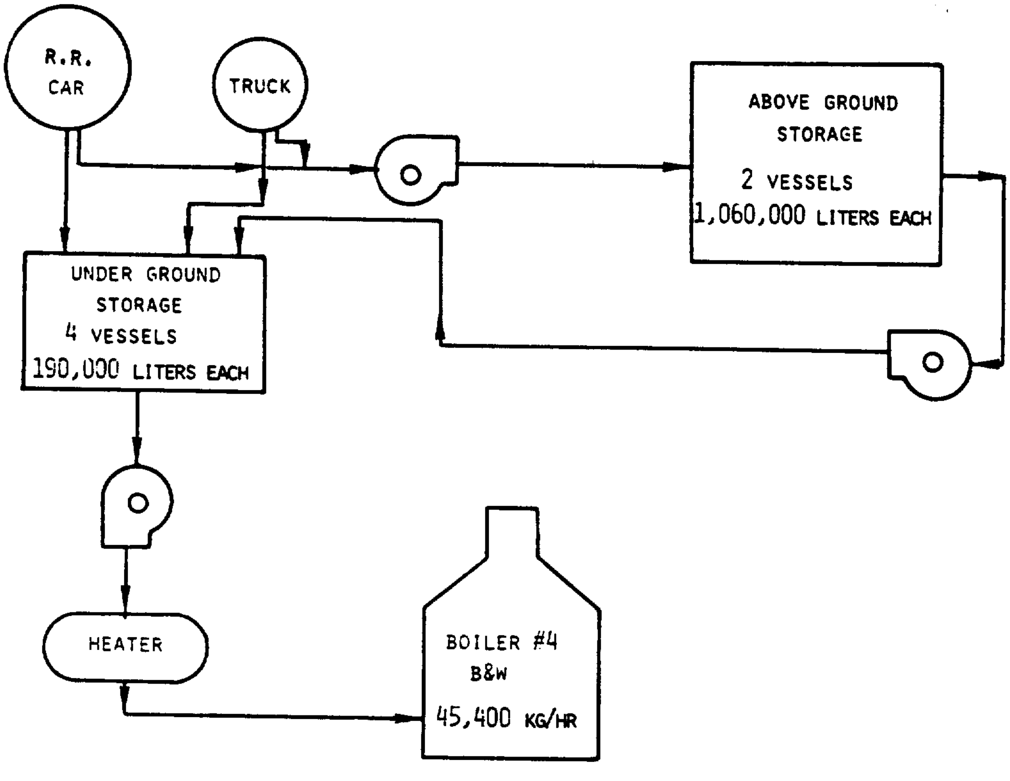


Figure 3-5. Fuel oil distribution to boiler number 4.

TABLE 3-2. 1976 STEAM GENERATION AND FUEL CONSUMPTION DATA FOR BOILER NUMBER 4

Month	Total steam generated by unit	Steam generated by coal firing	Steam generated by oil firing	Coal Used to fire unit	Oil used to fire unit
	Pounds	Pounds	Pounds	Pounds/Month	Pounds/Month
JANUARY	63,191,120	NONE	63,191,120	NONE	479,630
FEBRUARY	56,731,849	NONE	56,731,849	NONE	426,064
MARCH	59,284,346	NONE	59,284,346	NONE	437,432
APRIL	65,082,129	NONE	65,082,129	NONE	481,852
MAY	54,663,247	NONE	54,663,247	NONE	408,942
JUNE	24,615,374	NONE	24,615,374	NONE	181,786
JULY	64,379,436	NONE	64,379,436	NONE	478,111
AUGUST	32,185,973	NONE	32,185,973	NONE	487,381
SEPTEMBER	17,249,137	NONE	17,249,137	NONE	125,047
OCTOBER	67,981,950	45,367,432	22,614,518	3,809,400	165,614
NOVEMBER	61,173,241	58,149,635	3,023,606	5,183,440	23,822
DECEMBER	70,591,100	67,407,612	3,183,488	5,733,500	23,408

TABLE 3-3. 1977 STEAM GENERATION AND FUEL CONSUMPTION DATA FOR BOILER NUMBER 4

Month	Total steam generated by unit	Steam generated by coal firing	Steam generated by oil firing	Coal used to fire unit	Oil used to fire unit
	Pounds	Pounds	Pounds	Pounds/Month	Pounds/Month
JANUARY	64,436,850	54,930,366	9,506,484	4,831,180	70,554
FEBRUARY	63,787,500	55,383,646	8,403,854	4,892,600	17,053
MARCH	61,963,231	54,338,243	7,624,988	4,886,200	12,165
APRIL	61,350,362	58,033,817	3,316,545	4,875,820	24,567
MAY	69,071,439	53,378,917	15,692,522	4,710,700	118,251
JUNE	67,044,394	60,757,611	6,286,783	5,038,420	46,492
JULY	12,301,200	10,634,135	1,667,065	810,840	11,703
AUGUST	48,932,444	41,596,830	7,335,614	3,458,880	59,448
SEPTEMBER	65,526,263	60,504,449	5,021,814	5,488,900	37,758
OCTOBER	72,127,226	50,656,817	21,470,409	4,176,380	160,074
NOVEMBER	54,799,650	43,500,403	11,299,247	3,690,860	84,153
*DECEMBER	-	-	-	-	-

*At the time that this table was developed no information was available for December 1977.

TABLE 3-4. NUMBER OF DAYS THAT BOILER WAS OFF-LINE FROM 1 JANUARY 1976 TO NOVEMBER 1977

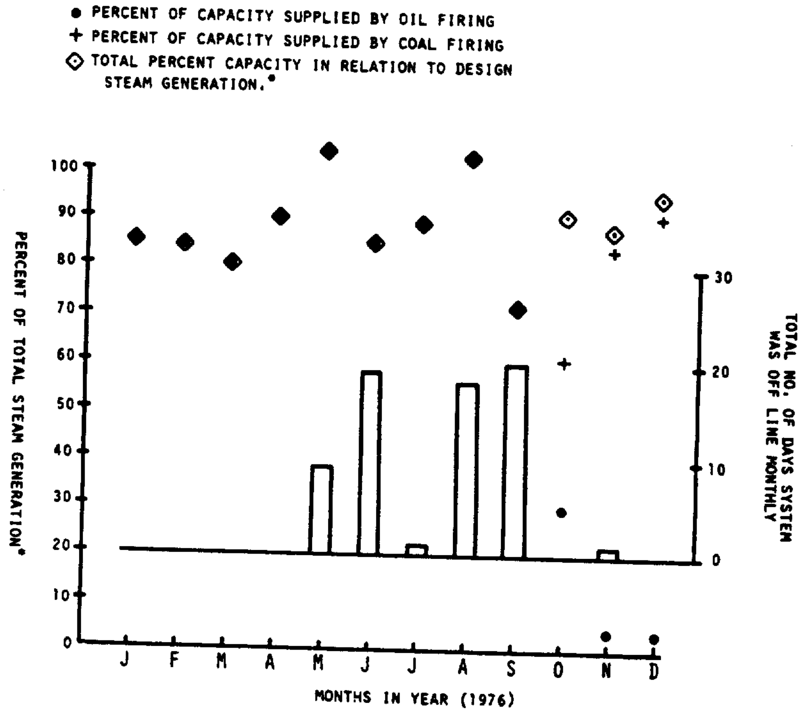
Month	No. of days off-line	
	1976	1977
JANUARY	--	--
FEBRUARY	--	--
MARCH	--	3
APRIL	--	2
MAY	9	--
JUNE	19	--
JULY	1	23
AUGUST	18	8
SEPTEMBER	20	1
OCTOBER	--	--
NOVEMBER	1	6
DECEMBER	--	*
Total	68	45

Exhaust gas cleaning

The flue gases are treated by an air pollution system which consists of multiclone units and a pilot FGD unit. The multiclones are the primary particulate control device. All of the flue gas passes through the multiclones after which the steam is split and two-thirds of the flue gas is ducted to the stack. The other one-third is ducted to the pilot FGD system which removes SO_2 and additional particulates. There are no NO_x controls on the system.

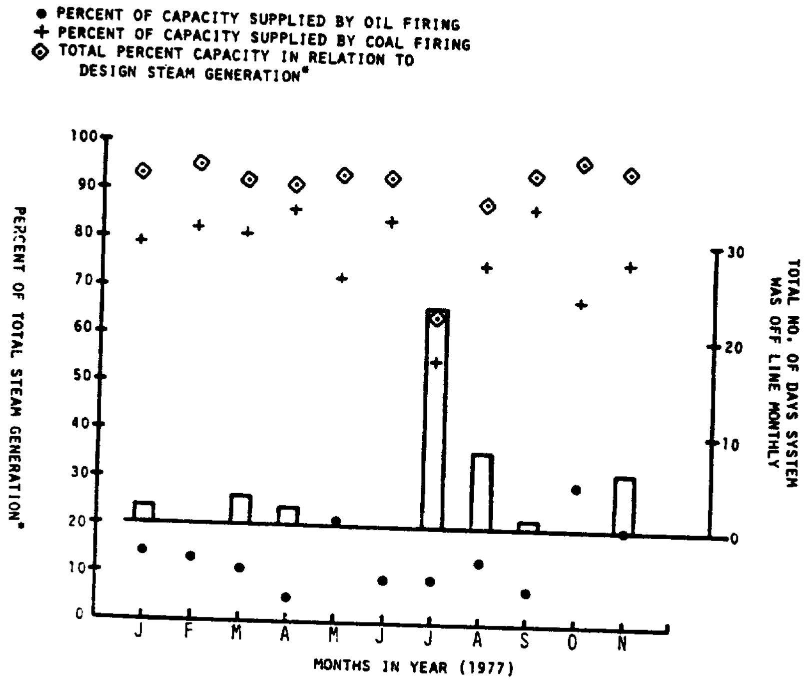
Multiclone Unit

The collection efficiency of the multiclone varies as a function of the particle size distribution and grain loading. Typically, multiclones remove 90 percent of those particles with diameters of 10μ and greater, and 50 to 80 percent of those particles with diameters of 3μ and greater. The



*ASSUMING 100,000 LBS/HR AS 100% STEAM GENERATION

Figure 3-6. Comparison of fuel use and off-line schedule for 1976.



*ASSUMING 100,000 LBS/HR AS 100% STEAM GENERATION

Figure 3-7. Comparison of fuel use and off-line schedule for 1977.

collection efficiency of multiclones drops off rapidly for particles less than 3μ diameter.

The fly-ash is periodically collected and transported to an on-site landfill for final disposal.

Flue Gas Desulfurization System

The flue gas desulfurization (FGD) system was designed and manufactured by FMC Corporation. The FGD system is a pilot unit designed to handle 280 acm/min (10,000 ACFM) of flue gas, which is approximately one-third of the volume of the flue gas from the boiler. The pilot plant was placed on-line in January of 1975.

Figure 3-8 is the basic flow diagram of the FMC FGD system as it is applied at this site.

The flue gas (stream 1) is withdrawn downstream of the boiler on the exit side of the multiclone dust collectors. Fly-ash loading at the scrubber inlet is substantially higher during coal-firing than during oil-firing. To accommodate the wide variation in fly-ash loading the FGD system was designed to operate with or without fly-ash, and can be operated without any mechanical changes on either fuel.

Upon entering the FGD unit the flue gases are contacted with a slightly acidic scrubbing solution (stream 4) which removes SO_2 and particulates. The SO_2 and particulates are removed at the scrubber throat and carried away in the scrubbing solution. The process utilizes a sodium sulfite-sodium bisulfite solution as the absorbent. The basic reaction for SO_2 removal is:

$$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2NaHSO_3$$

A bleed stream (stream 5) of the scrubbing solution is removed from the system at a rate which keeps the pH of the solution in an acceptable range. The bleed stream is reacted with calcium hydroxide in a short retention time, agitated vessel to regenerate the sodium sulfite. The basic chemistry of sodium sulfite regeneration process is:

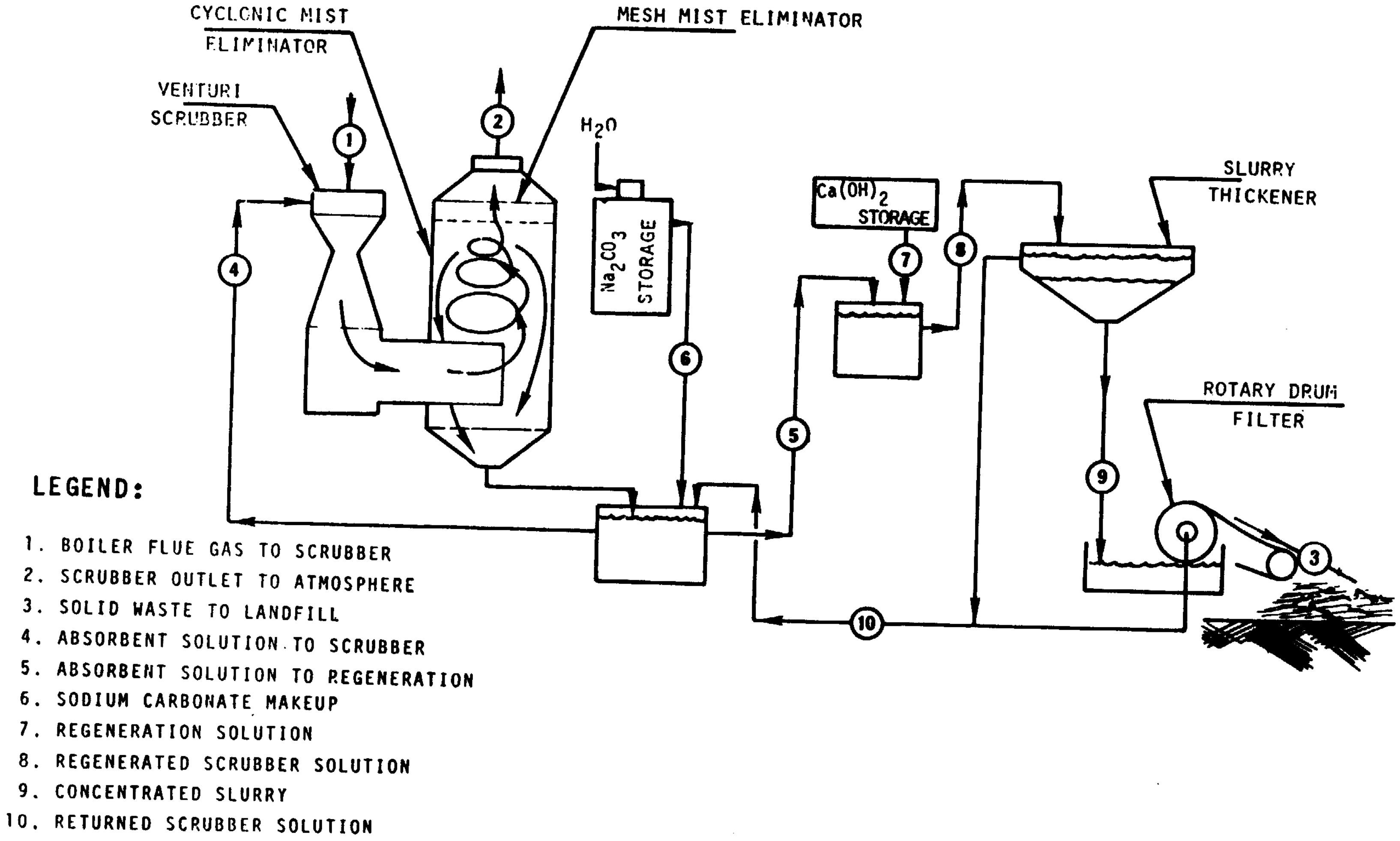


Figure 3-8. FMC unit at the industrial facility.

$$2NaHSO_3 + Ca(CH)_2 \longrightarrow CaSO_3 \bullet 2H_2O + 1\text{-}1/2H_2O + Na_2SO_3$$

The slurry of precipitated sulfur compounds (stream 8) is concentrated and pumped to a rotary drum filter where the essentially clear liquid and solid waste products are separated. The clear liquid (stream 10) is returned to the system for further utilization. The solid wastes, in the form of filter cake containing 40 percent (by weight) water, (stream 3) are removed from the rotary drum filter and conveyed to a storage bin to await transportation to the dump site. Because of the heavy particulate loading, more filter cake is produced during coal firing than during oil firing.

The on-site landfill, which is the final disposal facility for all of the solid waste generated at the facility, has several test wells from which samples are collected every three months and sent to an independent laboratory for analysis. Monthly tests are conducted by plant personnel to monitor sodium and specific conductivity. With permission of the Pennsylvania Department of Environmental Resources, this site is being used as an experimental disposal area for the filter cake from the FMC unit.

Boiler Water Pretreatment

Water is brought in from the nearby Schuylkill River and treated by a pretreatment facility to make it acceptable as boiler feedwater. The water treatment process is made up of three stages; a precipitator stage, a hot softening stage, and a filtration stage.

On exiting the filtration stage, the treated water is piped to a storage vessel where it is mixed with condensate returned from the boiler.

Liquid wastes are generated by the water pretreatment plant at a relatively constant rate independent of the fuel being used in the boiler. The major constituents of the effluent are compounds of calcium and magnesium. The effluent is sent to a collection pit, mixed with acid water from the resin plant and blow-down from the boilers, and then disposed of directly into the municipal sewage system.

Boiler Blowdown

There are two blowdown sources in the boiler system, the steam drum and the mud drum. There is a continuous blowdown from the steam drum which keeps the level of suspended solids in the boiler feedwater within an acceptable range. Tests of the steam drum blowdown effluent are made every four hours and adjustments to blowdown rate are made accordingly. The mud drum is blown once per shift.

The effluent from both blowdowns is sent to the same pit that collects effluent from the water pretreatment unit.

Cooling Water

Approximately 150-190 l/min (40 to 50 gpm) of water from the boiler feedwater storage tank is used in a once-through cooling system. This water is composed of approximately 50 percent condensate return and 50 percent make-up water. After use, it is also sent directly to the municipal sewage system.

SECTION 4

TEST DESCRIPTION

Multi-media emission tests were conducted on Boiler No. 4 of the Firestone plant from 27 September through 8 October, 1977. Gaseous, liquid and solid emissions were sampled during coal and oil firing to obtain data for the assessment. Flue gas sampling was conducted before and after the scrubber to determine which pollutants are removed or modified by the control device.

Emissions were characterized using EPA's phased approach. This approach utilizes two levels of sampling and analysis (Level 1 and Level 2). Level 1 procedures are accurate within a factor of about 3. They provide preliminary assessment data and identify problem areas and information gaps. Based on these data a site specific Level 2 sampling and analysis plan is developed. Level 2 provides more accurate and detailed information to confirm and expand on the information gathered in Level 1. The methods and procedures used for Level 1 are documented in the manual, "Combustion Source Assessment Methods and Procedures Manual for Sampling and Analysis", September 1977. The Level 2 methods and procedures include "state-of-the-art" techniques adapted to the needs of this site. They are described in Volume III Appendices B and C.

Normally all Level 1 samples are analyzed and evaluated before moving to Level 2. Because of the program time constraints, the Level 1 and Level 2 samples were obtained during the same test period. However, analysis of the samples did proceed in a phased manner except where sample degradation was of concern. In that case Level 2 analysis was performed on the samples prior to Level 1 completion.

TESTS AND FIELD ANALYSES

The industrial boiler assessment tests were conducted on the solid, liquid and gaseous effluent streams and the fuel. Tests were conducted during both coal and oil firing. Figure 4-1, the system schematic for boiler No. 4, and desulfurization unit, shows the sampling locations. Parameters sampled during coal and oil firing at each location are summarized in Table 4-1. The table also identifies the sampling and analysis methods used.

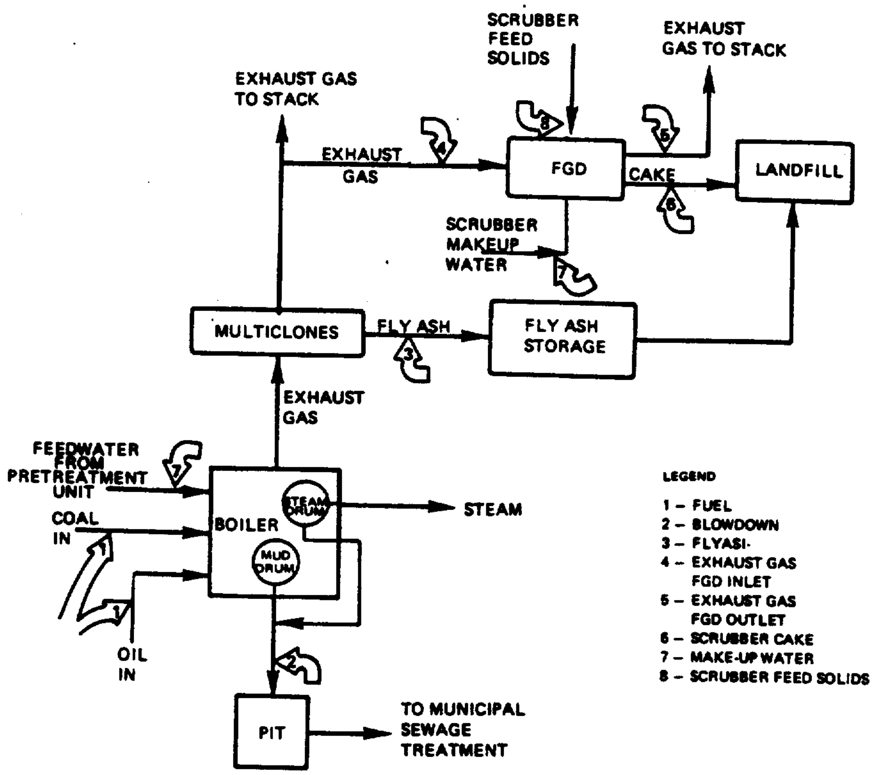


Figure 4-1. Boiler system schematic and sampling locations.

Gaseous Effluents

The boiler flue gas was sampled at the inlet and the outlet of the pilot flue gas desulfurization unit. Integrated bag samples were taken at both points during each test. On-site analyses of CO_2, O_2, N_2 and C_1-C_6 organics were conducted. Continuous monitors were used to analyze CO, NO/NO_x, SO_2 and total hydrocarbons (as CH_4). Figure 4-2 is a schematic of the continuous monitor setup. A Thermal Electron Corporation (TECO) gas conditioner was used to remove condensate and particulate from the gas sample. The instruments used are specified in Table 4-1.

Isokinetic sampling was performed at each location during all tests using four different sampling trains (gaseous streams only).

The Source Assessment Sampling System (SASS) was used to collect Level 1 gaseous and particulate emission samples at the scrubber inlet and outlet. The SASS train is illustrated in Figure 4-3. The train consists of a heated probe, three cyclones and a filter in a heated oven. The cyclones were used only during the coal inlet tests. During the other tests the

TABLE 4-1. PARAMETERS SAMPLED FOR COAL AND OIL FIRING

Location	Parameter	Sampling Method	Analysis
1	FUEL (coal & oil)	Grab	
	C, H, N, S, ash, moisture, heating value		Ultimate (lab)
	Inorganics		Level II (lab)
2	COMBINED BLOWDOWN	Composite dipper	On-site HACH kit
	Alkalinity/acidity pH conductivity hardness TSS nitrate sulfate sulfite phosphate ammonia nitrogen		
	organics		Level 1 & 2 (lab)
3	FLYASH	Composite grab	
	inorganics		Level 1 & 2 (lab)
	organics		Level 1 & 2 (lab)
4&5	FLUE GAS (inlet & outlet)		
	CO	Continuous, Beckman Model 865 Grab (bag)	Direct reading GC (TCD) on site
	CO_2	Grab (bag)	GC (TCD) on site
	$NO/NO_2/NO_x$	Continuous, TECO Model 10A	Direct reading
	N_2,O_2	Grab (bag)	GC (TCD) on site
	SO_2	Continuous, TECO Model 41	Direct reading
	SO_2/SO_3 H_2SO_4,HCl, HF, particulate sulfate,	Goksoyr-Ross	Level 2 (lab)
	total hydrocarbons (as CH_4)	Continuous, Beckman Model 400	Direct reading
	C_1 - C_6 organics	Grab (bag) SASS	GC (FID) on site Level 1 (lab)
	particulate & vapor	Method 5	Level 2 (lab)
	particulate sizing	Anderson impactor SASS	Level 1 Level 2
6	SCRUBBER CAKE	Composite grab	
	inorganics		Level 1 & 2 (lab)
	organics		Level 1 & 2 (lab)
7	BOILER & SCRUBBER MAKEUP WATER	Top grab	
	organics		Level 1 (lab)
	inorganics		Not required
8	SCRUBBER MAKEUP SOLIDS	Grab	Not required

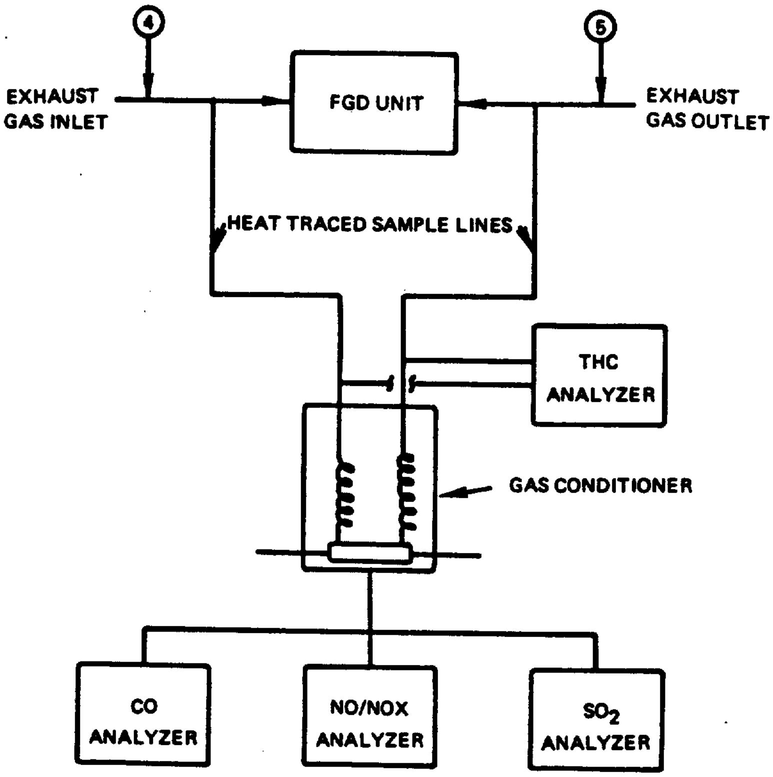


Figure 4-2. Flue gas continuous monitor setup.

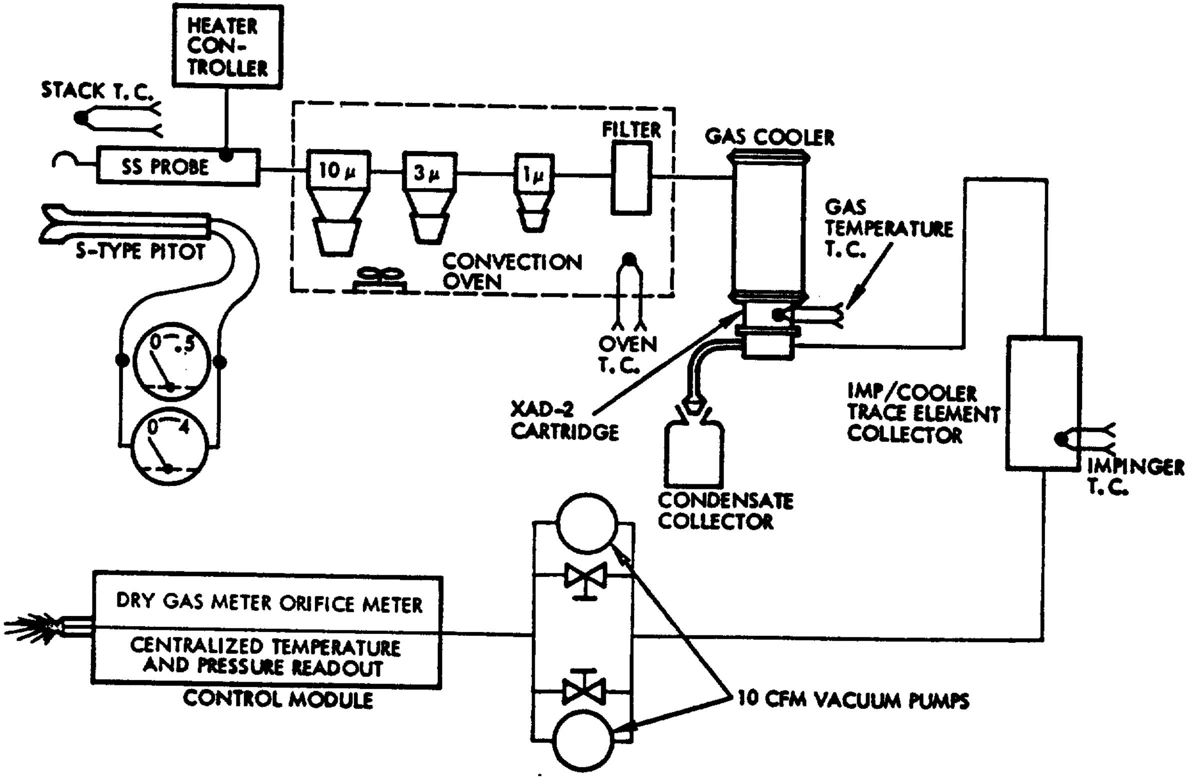


Figure 4-3. Source assessment sampling system (SASS) schematic.

particulate loadings were too low for the cyclones to work effectively. The remainder of the system consists of a gas conditioning system, an XAD-2 polymer absorbent trap and a series of impingers. The polymer traps gaseous organics and some inorganics and the impingers collect the remaining inorganics. All sample contact surfaces are Type 316 stainless steel, teflon, or glass. The train was run for 6 to 8 hours until a minimum of 30 cubic meters of gas had been collected.

Previous sampling and analysis experience had indicated that SASS train materials may contaminate certain organic and inorganic samples. The combination is of concern only when the pollutant is present at a concentration that is near the detection limit of the Level 2 methods. To avoid that possibility all-glass sampling trains were used to collect Level 2 samples. Method 5 sampling trains were modified as shown in Figure 4-4 for organics and Figure 4-5 for inorganics. Both trains sampled approximately 10 cubic meters of flue gas during a 6 to 8 hour test run.

A controlled condensate train (Goksoyr-Ross), as shown in Figure 4-6, was used at each location to obtain samples for SO_2, SO_3 (as H_2SO_4), particulate sulfate, HCl and HF.

During Level 2 test runs, Anderson cascade impactors were used to obtain particulate samples by particle size fraction. A pre-separating 10μ cyclone was used up-stream of the impactor on the inlet side.

Liquid Effluents

The combined boiler blowdown was sampled using the composite dipper method and boiler and scrubber makeup water were sampled by the top grab method. The samples were analyzed as shown in Table 4-1. In addition, each sample was extracted with methylene chloride and the extracts returned to the lab for further analysis.

Solid Effluents

Composite samples of the flyash and scrubber filter cake were collected per Level 1 procedures and returned to the lab for analysis. Grab samples of the scrubber feed solids were also obtained.

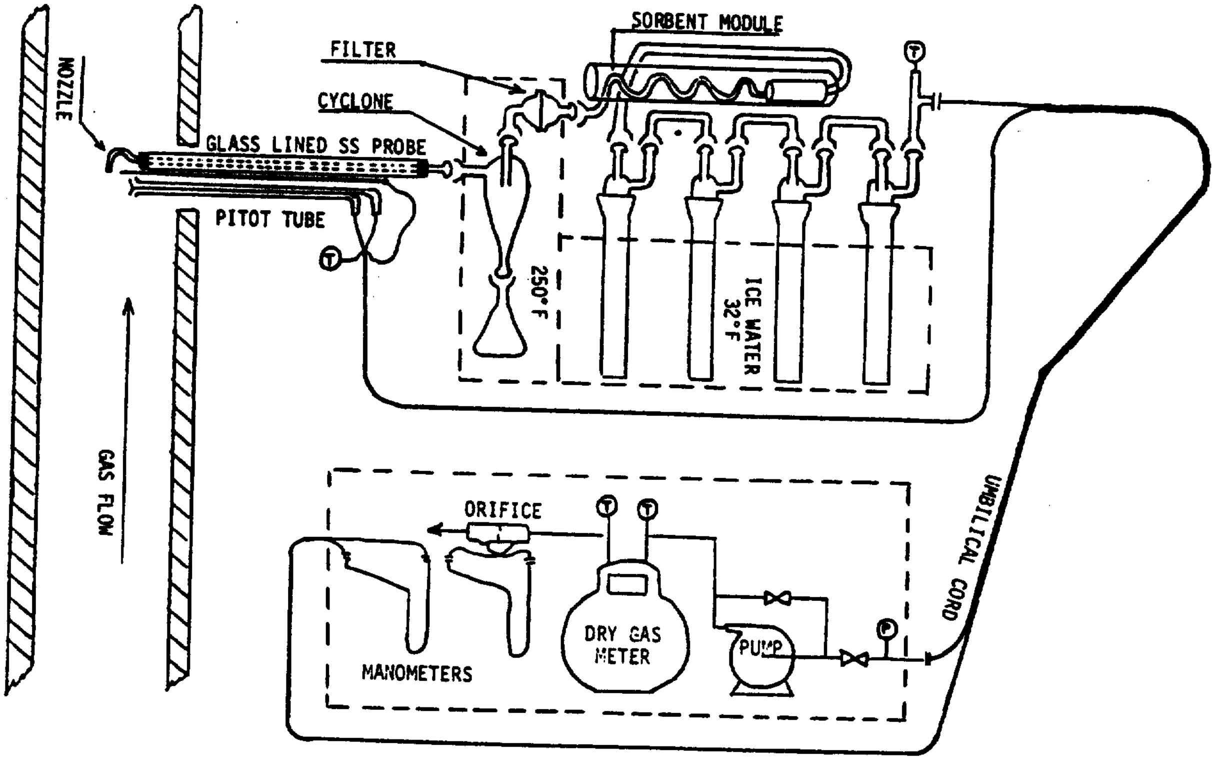


Figure 4-4. Organic sampling train.

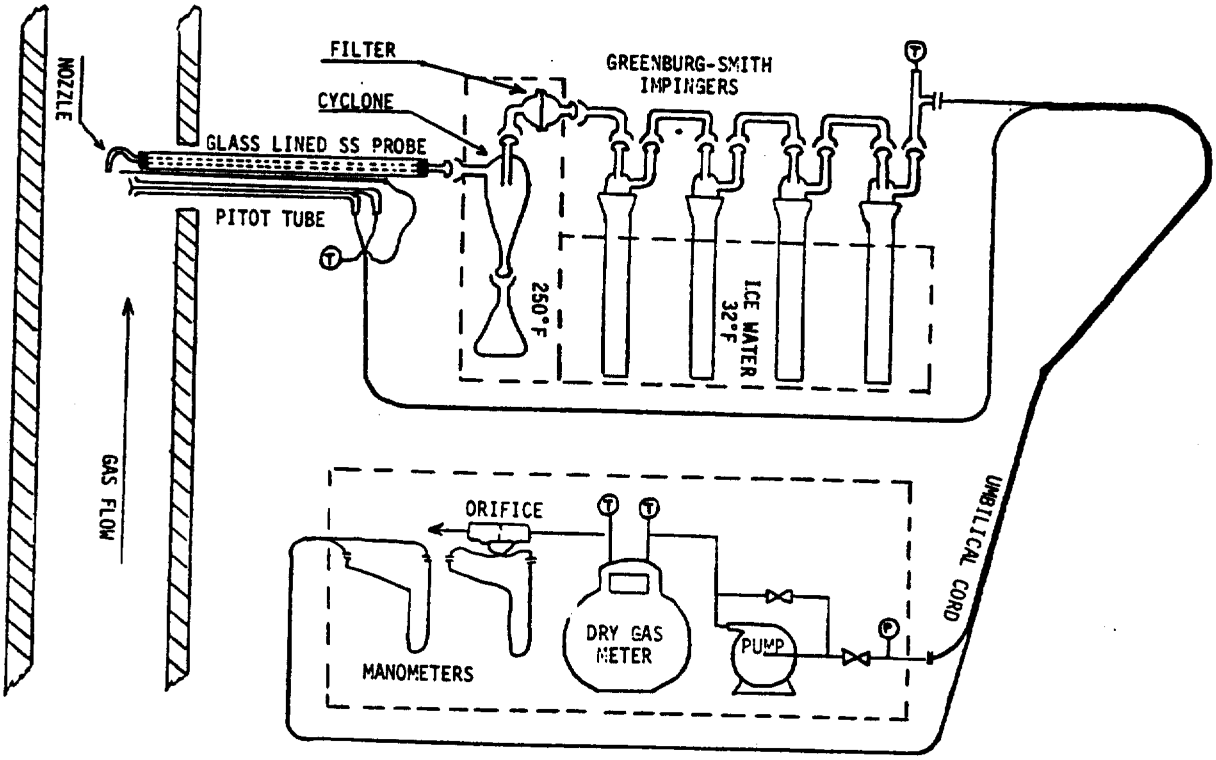


Figure 4-5. Inorganic sampling train.

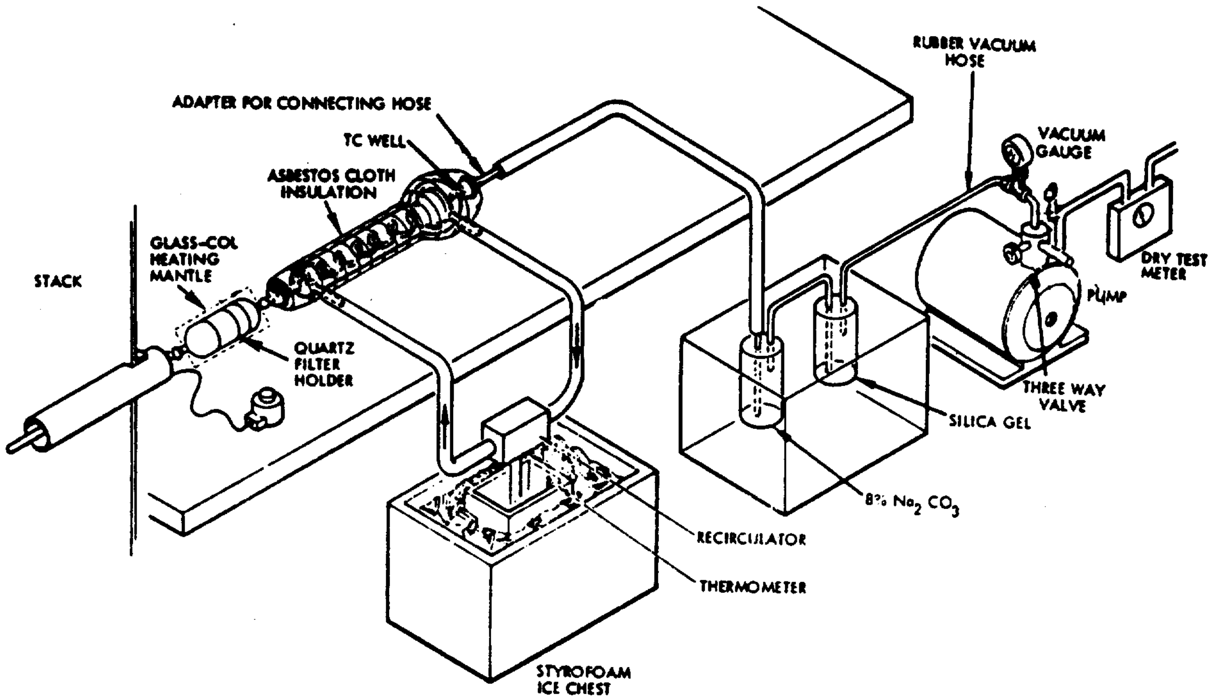


Figure 4-6. Controlled condensation train.

LABORATORY ANALYSES

The samples identified in Table 4-2 were returned to the laboratory for analysis. The Level 1 analysis scheme for particulates and gases from the SASS train is shown in Figure 4-7. The Level 1 analysis scheme for solids, slurries and liquids is shown in Figure 4-8. Detailed analysis procedures can be found in the manual "Combustion Source Assessment Methods and Procedures Manual for Sampling and Analysis," September 1977.

The Level 2 inorganic liquid sample analysis scheme is shown in figure 4-9 with the inorganic solids analysis scheme shown in Figure 4-10. The analysis scheme for the controlled condensate train is presented in Figure 4-11. A discussion of the specific procedures used for this program and their results can be found in Volume III Appendix C.

The Level 2 analysis scheme for organic SASS and modified Method 5 components is shown in Figure 4-12. The analysis scheme for organic aqueous samples is shown in Figure 4-13. A discussion of the specific procedures and results for this program can be found in Volume III Appendix C.

TABLE 4-2. SUMMARY OF SAMPLES SENT TO LABORATORY FOR ANALYSIS

SASS Train

Probe rinse
Cyclone catch
Filter
Resin
Resin Condensate
Impinger solutions

Controlled Condensation

Probe rinse
Filter
Impinger solutions

Inorganic and Organic Trains

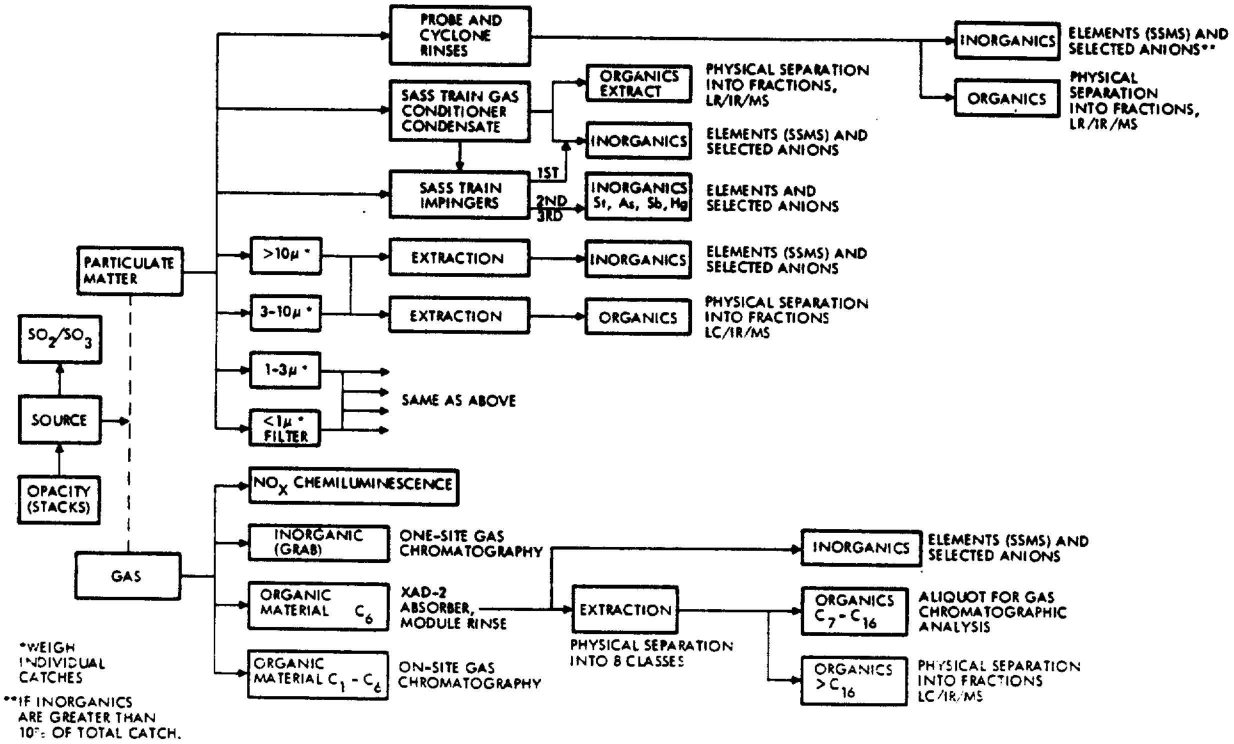
Probe rinse
Cyclone catch
Filter
Impinger solution

Liquid Samples

Neat
Extracts

Solid Samples

As found



*WEIGH INDIVIDUAL CATCHES

**IF INORGANICS ARE GREATER THAN 10% OF TOTAL CATCH.

Figure 4-7. Basic level 1 sampling and analytical scheme for particulates and gases.

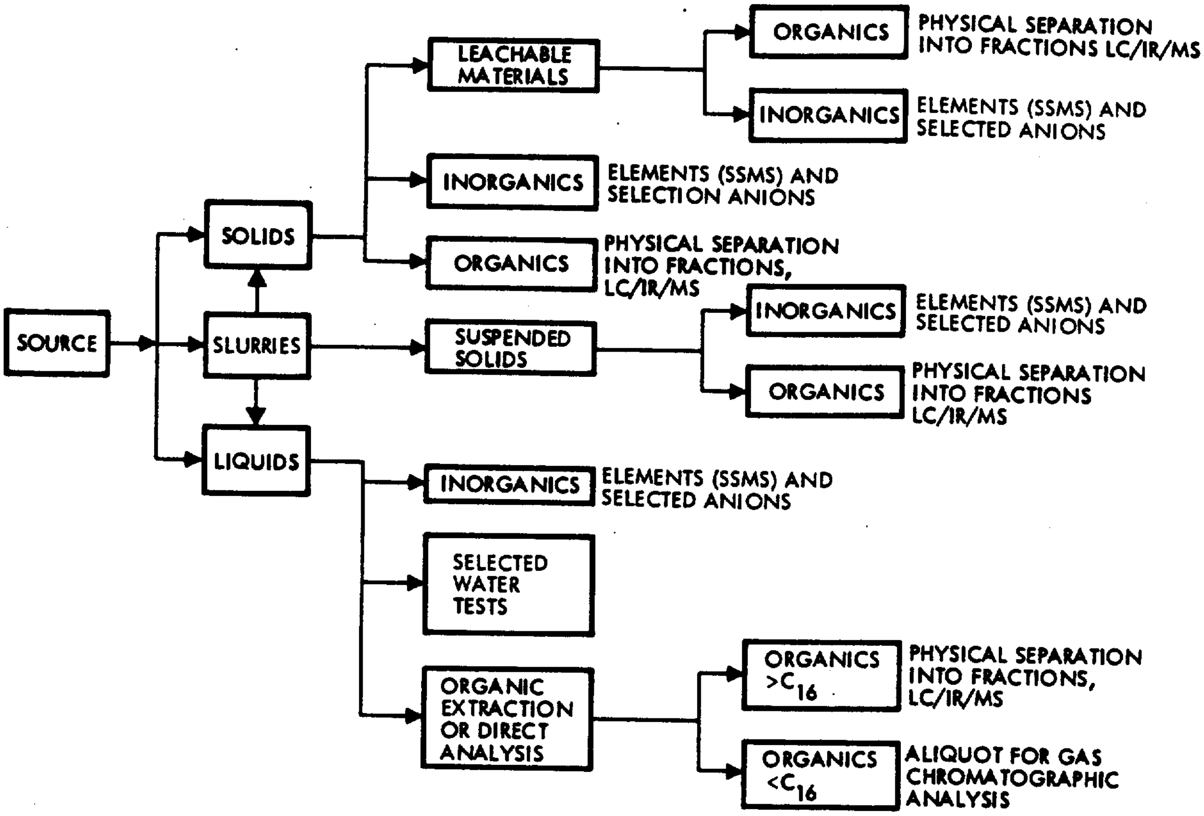


Figure 4-8. Basic level 1 sampling and analytical scheme for solids, slurries and liquids.

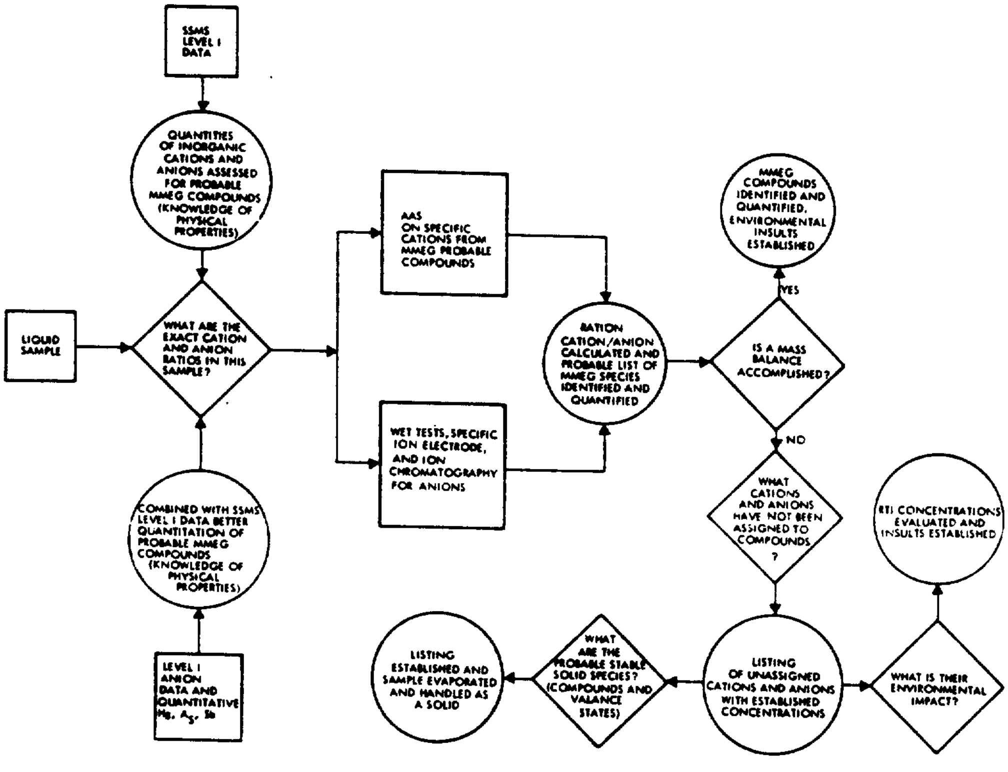


Figure 4-9. Level 2 inorganic liquid sample analysis scheme.

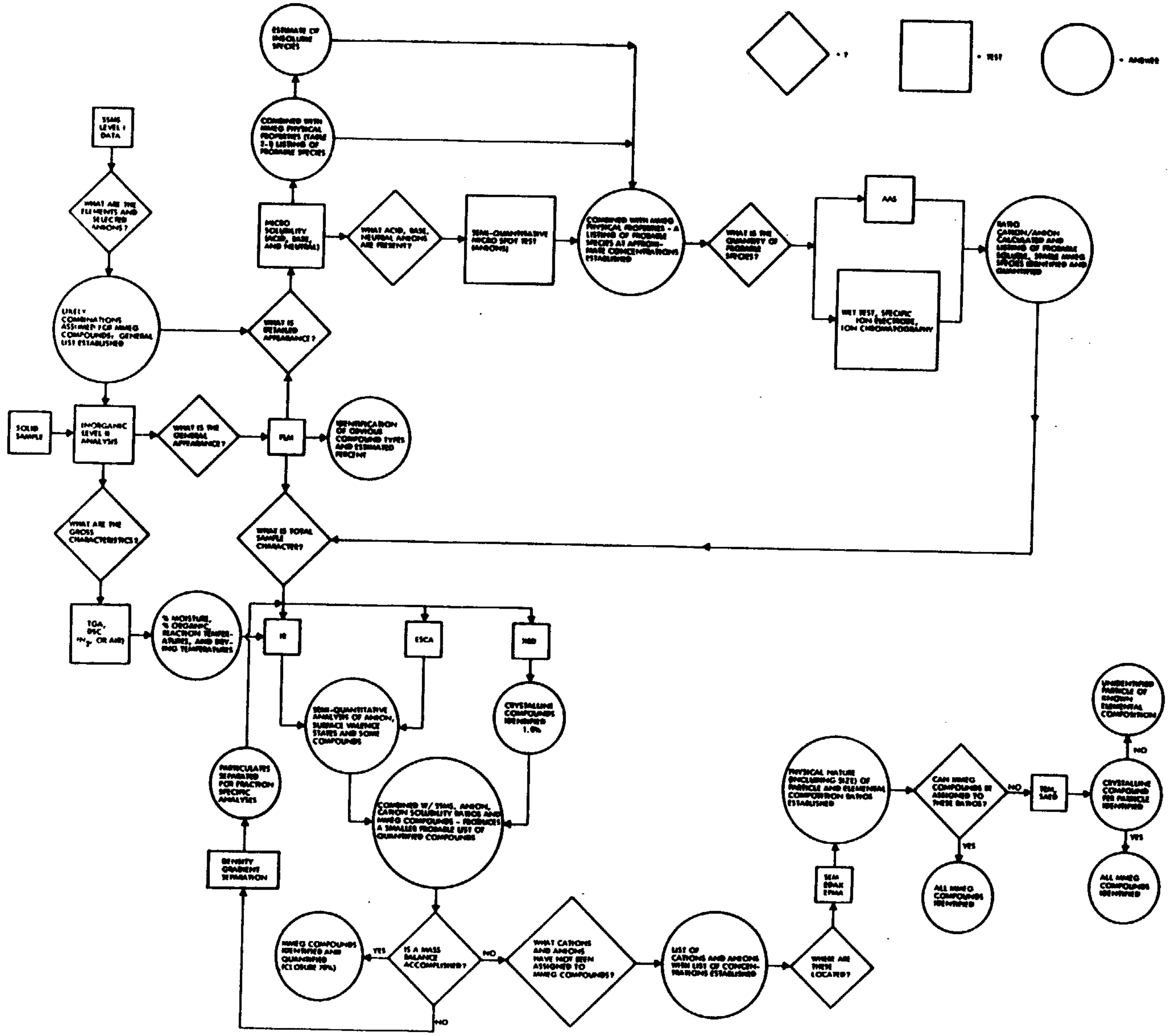


Figure 4-10. Level 2 inorganic solids analysis scheme.

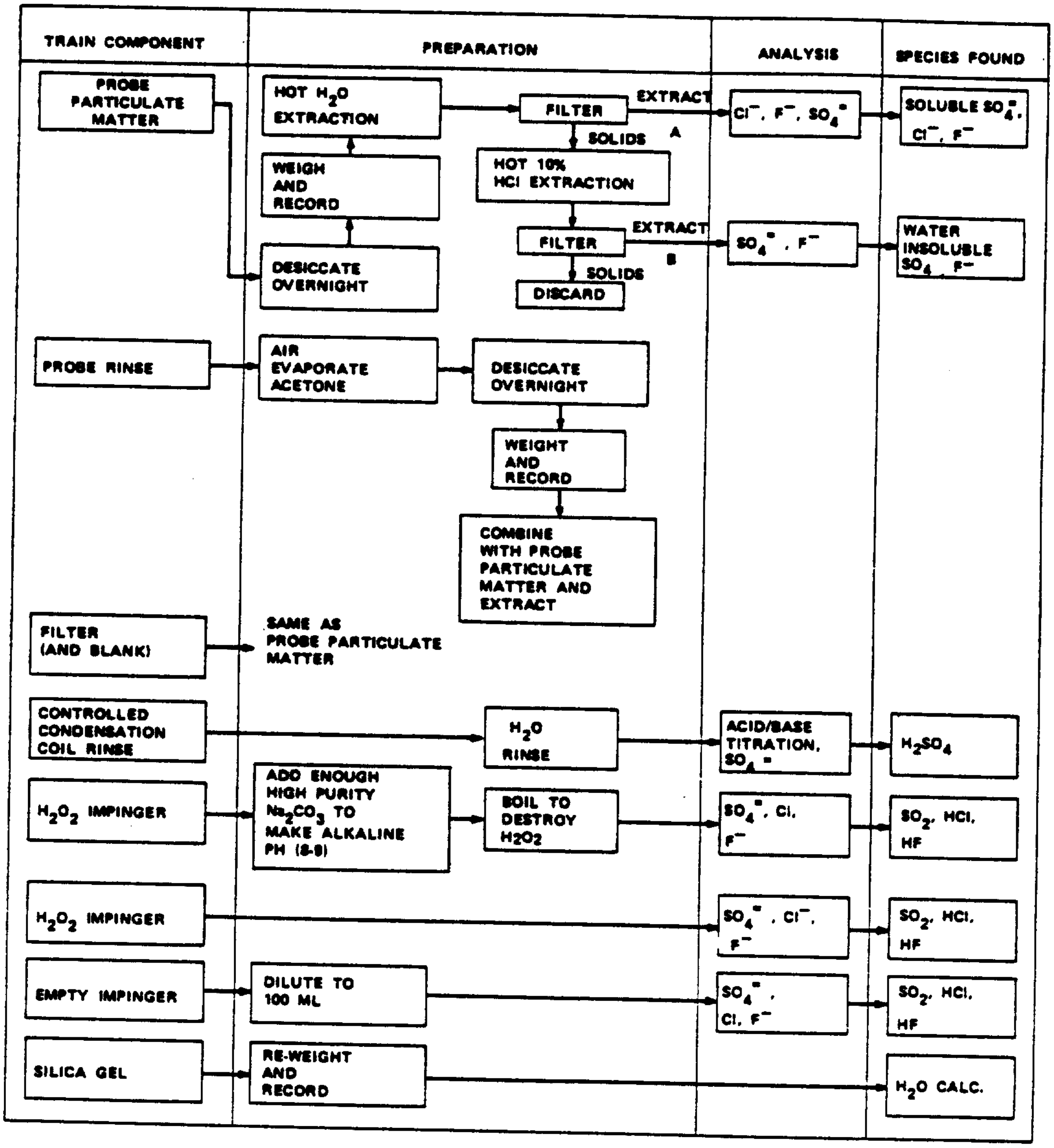
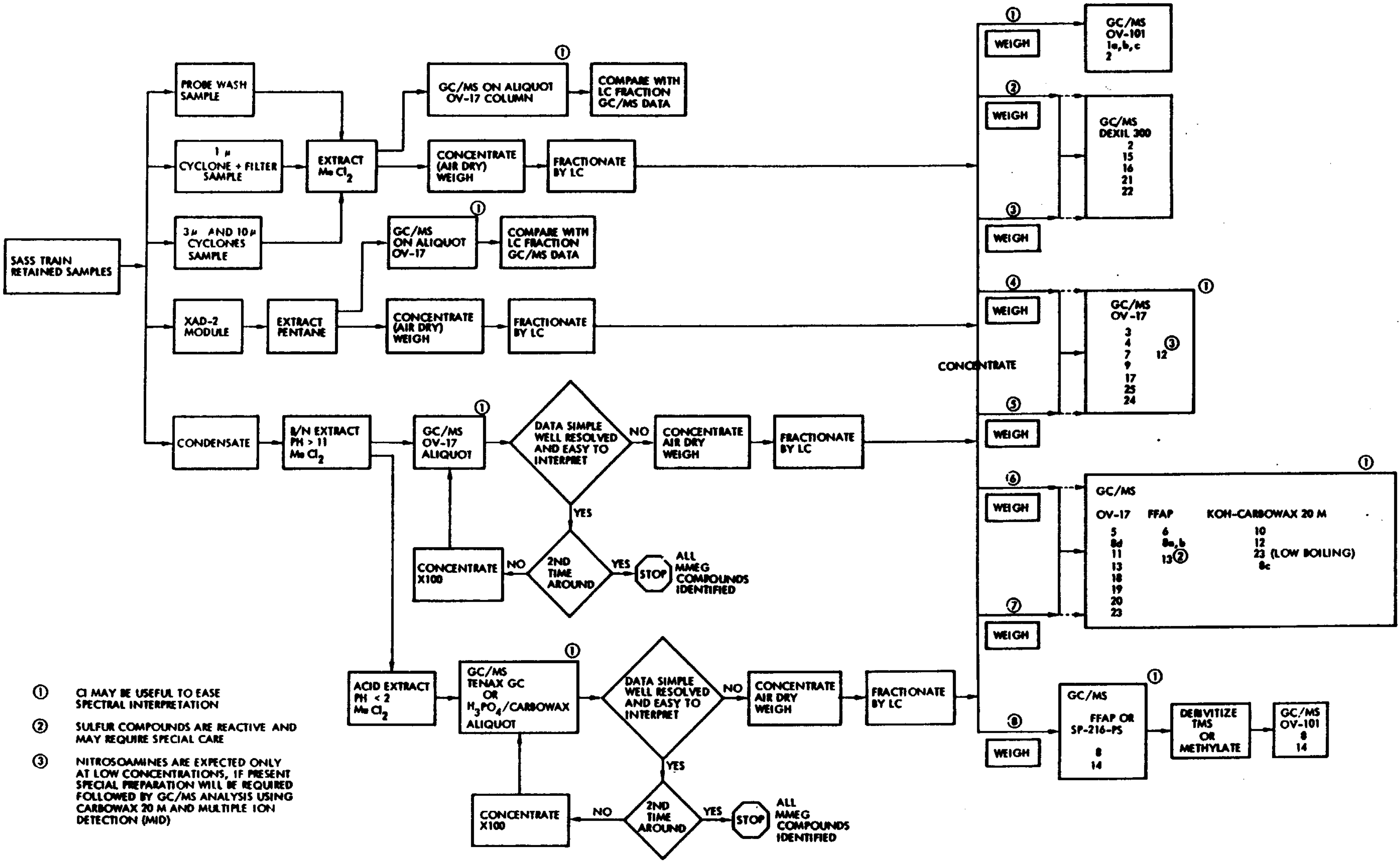


Figure 4-11. Analysis scheme for controlled condensate train components.

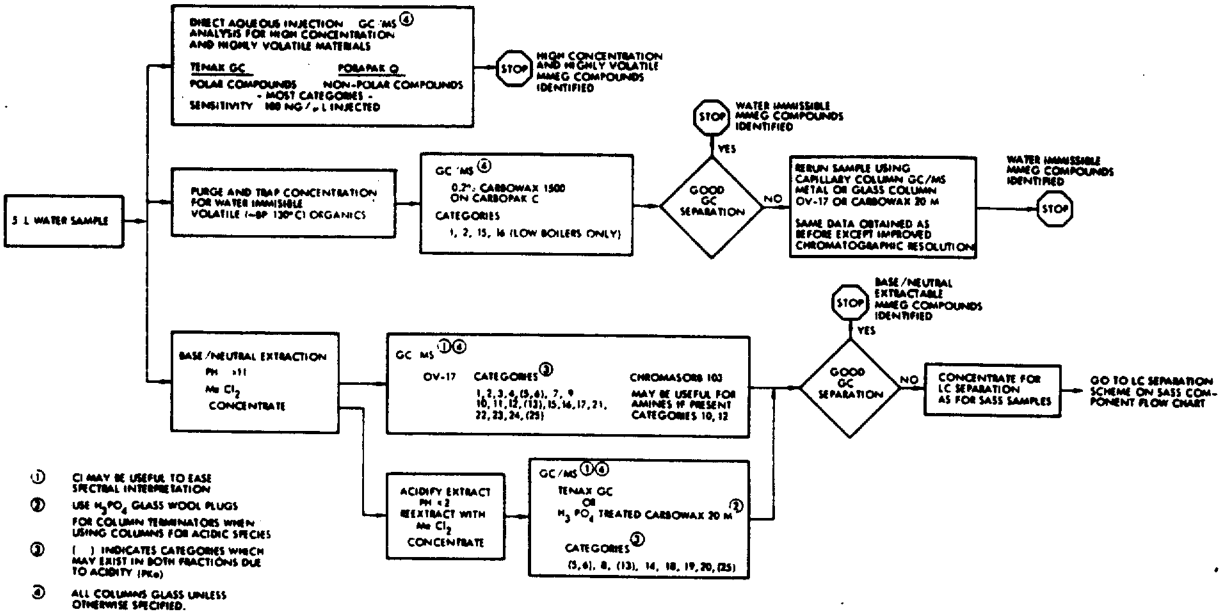


① CI MAY BE USEFUL TO EASE SPECTRAL INTERPRETATION

② SULFUR COMPOUNDS ARE REACTIVE AND MAY REQUIRE SPECIAL CARE

③ NITROSOAMINES ARE EXPECTED ONLY AT LOW CONCENTRATIONS, IF PRESENT SPECIAL PREPARATION WILL BE REQUIRED FOLLOWED BY GC/MS ANALYSIS USING CARBOWAX 20 M AND MULTIPLE ION DETECTION (MID)

Figure 4-12. General logic flow chart for level 2 organic SASS component analysis.



① CI MAY BE USEFUL TO EASE SPECTRAL INTERPRETATION

② USE H_3PO_4 GLASS WOOL PLUGS FOR COLUMN TERMINATORS WHEN USING COLUMNS FOR ACIDIC SPECIES

③ ( ) INDICATES CATEGORIES WHICH MAY EXIST IN BOTH FRACTIONS DUE TO ACIDITY (PKa)

④ ALL COLUMNS GLASS UNLESS OTHERWISE SPECIFIED.

Figure 4-13. General logic flow chart for level 2 organic aqueous samples.

SECTION 5

COMPREHENSIVE ASSESSMENT OF COAL FIRING CASE FOR AN INDUSTRIAL BOILER

This section provides a comprehensive multimedia assessment of emissions/effluents associated with a coal-fired industrial boiler equipped with an FGD system. Data from Level I/Level II sampling and analyses are utilized to quantitatively determine emissions in gas, solid and liquid waste streams and to evaluate performance of pollution control equipment in use during coal firing. Waste stream pollutant concentrations are compared with Minimum Acute Toxicity Effluent (MATE) values, where appropriate, to provide an indication of risk to public health and ecology. Simplified air quality models are used to determine the relative ground level air quality resulting from both uncontrolled and controlled emissions.

TEST CONDITIONS

Five tests were performed with a coal-fired industrial boiler generating from 34,000 to 44,200 kg steam per hour (75,000 to 97,500 pounds per hour) which corresponds to between 75 and 97% of full load operation for the unit tested. Specific test conditions are summarized in Table 5-1. Tabulated fuel feed rates are the nominal feed rates maintained during each test. Assuming a constant thermal efficiency of 90%, steam production data and coal analyses indicate that nominal fuel feed rates are accurate to within approximately 13%. Oxygen concentrations provided in Table 5-1 were measured in flue gas samples drawn from the inlet of the system's wet scrubber unit. Due to air leakage into upstream ducting operating at sub-atmospheric pressure and possible air leakage into the flue gas bag sampling system, tabulated data are not representative of furnace gas concentrations. During normal operation, the concentration of oxygen in the furnace after combustion is between 3 and 4% which corresponds to an excess air input of 16 to 23% during coal firing. Excess air estimates presented in Table 5-1 were computed assuming a mean oxygen concentration of 3.5% in the furnace and utilizing fuel analyses data.

Test data relating to scrubber throughput and loading, and total flue gas generation rates are presented in Table 5-2. Measured flow rates

TABLE 5-1. SUMMARY OF TEST CONDITIONS - COAL FIRING

Test No.	Steam Production Rate kg steam/hr	Steam Production Rate lbs. steam/hr	% of Maximum Load	Nominal Coal Feed Rate, kg/hr	% O_2 at Scrubber Inlet*	Estimated % Excess Air to Furnace†
200	39,700	87,500	87.5	3629	7.8	20
201-1	44,200	97,500	97.5	3629	8.2	20
201-2	43,100	95,000	95.0	3629	8.4	20
201-3	34,000	75,000	75.0	3175	8.3	20
201-4	40,800	90,000	90.0	3629	6.7	20

* Due to air leaks in ducting upstream of the scrubber inlet, tabulated O_2 values are not representative of combustion zone O_2 concentrations. Combustion zone O_2 concentrations normally range from 3 to 4% for this unit.

† % excess air is estimated to be $100 \times \frac{O_2 - CO/2}{0.264\ N_2 - (O_2 - CO/2)}$
where:
O_2 was assumed to be 3.5% and other species concentrations are computed from fuel analyses.

TABLE 5-2. FRACTION OF FLUE GAS PROCESSED BY THE SCRUBBER DURING COAL COMBUSTION

Test No.	Flow Rate at Scrubber Inlet, dscm/min*	% of Design Load	Total Flue Gas Flow Rate, dscm/min*	Fraction of Total Flue Gas Processed by the Scrubber
200	99	56	754	0.13
201-1	91	51	761	0.12
201-2	89	50	798	0.11
201-3	98	55	684	0.14
201-4	102	58	706	0.14
Average	96	54	741	0.13

* Dry standard cubic meters per minute (dscm/min).

through the scrubber inlet expressed as dry standard cubic meters per minute (dscm/min) and percentage of design scrubber loading are presented in the first two columns. For discussion in this report, standard temperature and pressure are defined as 20°C and one atmosphere pressure, respectively. Although the scrubber was designed for a capacity of approximately 177 dscm/min (6,250 dscfm), it is a manually controlled variable venturi type unit capable of processing a substantial range of loadings. A loading of 90 to 102 dscm/min (51 to 57% of design loading) was maintained during testing, rather than full loading, because failure of the multiclone particulate removal unit upstream of the scrubber resulted in high solids loading at the scrubber and unacceptably high scrubber cake production rates. The scrubber is a pilot unit and, as such, was not sized to process the total flue gas output of the furnace. Typical inlet and outlet gas temperatures for the scrubber unit were 300°F and 125°F, respectively. Total flue gas flow rates presented in the table were computed from coal analyses, coal feed rate data and flue gas analyses utilizing the following expression:

$$n_{FG} = \frac{4.762\ (n_C + n_S) + .9405\ n_H - 3.762\ n_{O_2}}{1 - 4.762\ (O_2/100)}$$

where: n_{FG} = gm moles of dry effluent/gm of fuel.

n_j = gm moles of element j in fuel per gm of fuel.

O_2 = volumetric O_2 concentration in percent.

As indicated in Table 5-2, the flue gas slip stream drawn for scrubber processing ranged from 11 to 14% of the total flue gas generated.

A high volatile bituminous feed coal was utilized for all coal-fired tests. Ultimate analyses of feed coal samples obtained during each of the five tests performed are presented in Table 5-3. These data indicate an essentially constant feed coal composition during the five days of testing. Average coal moisture and ash contents were 7.15 and 9.90 % w/w, respectively. Mean coal sulfur, nitrogen and chlorine contents were 1.64, 0.92, and 0.12 % w/w, respectively. An average coal heat content of 29,485 kJ/kg (12,683 Btu/pound) was determined. Additional analyses were performed on feed coal samples from test 201-1 to determine concentrations of 17 trace

TABLE 5-3. SUMMARY OF ULTIMATE COAL ANALYSES

Weight %	Test Number						
	200	201-1	201-2	201-3	201-4	Average	σ*
Moisture	8.44	7.37	6.54	7.18	6.23	7.15	0.86
Carbon	71.69	70.62	73.30	71.94	72.97	72.10	1.07
Hydrogen	4.33	4.18	4.31	4.27	4.30	4.28	0.06
Nitrogen	0.86	1.00	0.88	0.87	0.98	0.92	0.07
Chlorine	0.10	0.10	0.12	0.13	0.15	0.12	0.02
Sulfur	1.64	2.00	1.38	1.68	1.50	1.64	0.23
Ash	8.94	11.19	9.41	9.85	10.09	9.90	0.85
Oxygen	4.00	3.54	4.06	4.08	3.78	3.89	0.23
kJ/kg	29,263	28,872	29,997	29,419	29,874	29,485	459

* σ = One standard deviation.

elements (Ca, Mg, Sb, As, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, V, Zn, Se, Sr, and Zr) and 2 minor elements (Fe and Al). The method employed for analysis of these elements was inductively coupled plasma optical emission spectroscopy (ICPOES) which is generally considered to be more accurate than spark source mass spectrometry (SSMS). However, a single feed coal sample from test 200 was analyzed for the trace elements boron and beryllium by SSMS, and for mercury by cold vapor analysis. These data are presented in Table 5-4. Considering the uniformity of feed coal ultimate analyses obtained during the test period, it appears reasonable to assume that tabulated trace and minor element analyses are typical of the coal fired during the five day test period. Although analyses of other coal samples from the same source (mine or cleaning plant) are not available for direct comparison, analyses of most trace and minor elements presented in Table 5-4 appear to be consistent with concentration limits typifying Appalachian and Eastern Interior Basin coals. No coal strontium analyses were found for comparison. Trace elements present in somewhat higher concentrations than are indicated to be typical by the limited published data are antimony, arsenic, cobalt, copper, molybdenum, and zirconium. However,

TABLE 5-4. CONCENTRATION OF MAJOR TRACE ELEMENTS IN COAL-TEST 201-1

Element	µg/g Coal				Reference
	Sample A	Sample B	Average	Typical Range†	
Ca	820	720	770	0 - 1600	2,4
Mg	400	300	350	0 - 959	2,4
Sb	80	90	85	0.2 - 8.9	2
As	140	133	137	0.5 - 93	1,2
B	-	-	2.4*	4 - 115	1,3
Cd	3	4	3.5	0.1 - 65	2
Cr	49	47	48	4 - 144	1,3
Co	102	152	127	0.5 - 43	1,2
Cu	98	46	72	3 - 61	1,2
Fe	10,750	13,750	12,250	0.3 - 40,000	2,4
Pb	77	95	85	4 - 218	1,2
Mn	13	11	12	6 - 181	2
Mo	238	348	293	0.4 - 30	1,2
Ni	23	51	37	2 - 80	1,2
V	49	44	47	2 - 147	1,2,3
Zn	48	64	56	6 - 5,350	2
Se	68	77	73	0.4 - 74	2,3
Sr	72	64	68	NO DATA	
Al	15,900	12,100	14,000	0.4 - 40,700	2,4
Zr	325	215	270	8 - 133	2
Be	-	-	2.3*	0.6 - 4.1	1
Hg	-	-	0.14‡	0.07 - 0.49	1

* Boron and beryllium analysis were performed by SSMS on a feed coal sample from test 200.

† Typical range for Appalachian and Eastern Interior Basin coals.

‡ Mercury was determined by cold vapor analysis of a coal sample from test 200.

the significance of these higher concentrations is not apparent due to the limited quantity of published data and the complete absence of source specific data.

STACK EMISSIONS

As discussed previously, the wet scrubber unit processed from 11 to 14% of the total generated flue gas. Flue gas analyses were performed on samples drawn from the scrubber inlet and outlet. Results of these analyses were utilized to estimate total boiler emissions on the basis of 100% of the flue gas being treated by a scrubber. That is, it was assumed that additional scrubber modules could be added to the system such that the total flue gas output would be processed with a mean scrubber efficiency identical to that obtained using the pilot scrubber. All emissions data presented in the following sections are based on this assumption.

Criteria Pollutants

Federal New Source Performance Standards (NSPS) currently in effect define allowable NO_x (as NO_2), SO_2, and total particulate emission rates from utility boilers having 25 MW or greater output. Existing NSPS limitations on NO_x emissions from coal fired units are 300 ng/J (0.70 lb/MM Btu) although a proposed standard of 200 ng/J (0.50 lb/MM Btu) maximum emissions and 65% reduction of uncontrolled emissions is under consideration. Proposed NO_x standards are based on boiler emission levels achievable with proper excess air control and staged combustion. The NSPS limitation on SO_2 emissions for coal fired units is 520 ng/J (1.20 lb/MM Btu). Potential standards based on SO_2 emission levels achievable through flue gas desulfurization (FGD) would impose the further requirement for 90% reduction of uncontrolled emissions from sources producing more than 85 ng/J (0.20 lb/MM Btu). The NSPS limitations for total particulates is currently 43 ng/J (0.10 lb/MM Btu). A proposed particulate standard of 13 ng/J (0.03 lb/MM Btu) maximum emissions and 99% reduction of uncontrolled emissions is being considered. Proposed particulate standards are based on emission levels achievable with electrostatic precipitators (ESP) and baghouses. Federal NSPS do not currently address either CO or total hydrocarbons.

Similar standards relating to industrial boilers have not been promulgated to date. Therefore, criteria pollutant emission data presented in this section will be discussed in the context of the existing and proposed Federal NSPS for utility boilers.

As mentioned previously, 5 coal-fired tests were performed on the Firestone industrial boiler. Criteria pollutant concentrations were generally measured at frequent intervals during each test and averaged to obtain the mean concentration for the test. The 5-test averages of criteria pollutant emissions data are presented in Tables 5-5 through 5-8. Average emissions data from the individual tests are presented in Tables 5-9 and 5-10. Additionally, the 5-test averages of scrubber inlet data are presented in Table 5-11 for comparison with the EPA AP-42 emission factors for uncontrolled sources. The data are discussed by specific compound in the ensuing sub-sections.

Nitrogen Oxides

Mean NO_x emissions measured during the testing period were 421 ng/J (0.98 lb/MM Btu) prior to FGD contacting. Full load NO_x emissions were approximately 491 ng/J (1.14 lb/MM Btu) at the scrubber inlet. This emission rate is somewhat higher than the average uncontrolled emission rate of 343 ng/J (0.80 lb/MM Btu) tabulated in AP-42 for bituminous coal fired, dry bottom, 10 MW industrial boilers. However, examination of published industrial boiler data indicates that NO_x emissions measured during the test period are not at variance with typical ranges of NO_x emissions (Reference 5). The average measured NO_x emission rate after FGD was 372 ng/J (0.87 lb/MM Btu) which is nearly 25% higher than the current NSPS limitation of 300 ng/J. As indicated by data presented in Tables 5-1 and 5-9, NO_x data varied with boiler load, as expected. Test 201-3 was performed at the lowest boiler load (75% of full load) and, therefore, resulted in the lowest NO_x emissions measured. Indeed, the average NO_x emission rate measured at the scrubber outlet during test 201-3 was 259 ng/J (0.60 lb/MM Btu) which is lower than the current NSPS limitation.

NO_x data generally indicate a reduction of NO_x emissions across the scrubber during the test period. Measured NO_x data obtained during test 201-2 are presented in Figure 5-1 to display typical fluctuations in NO_x

TABLE 5-5. CRITERIA POLLUTANT EMISSIONS FOR A COAL-FIRED INDUSTRIAL BOILER IN CONCENTRATION UNITS (5 TEST AVERAGE)

Pollutant	mg/Nm^3 (Grain/SCF)	
	Before Scrubber	After Scrubber
NO_x (as NO_2)	992 (0.43)	880 (0.38)
CO	37 (0.02)	34 (0.01)
SO_2	2600 (1.14)	90 (0.04)
Organics (as CH_4)	14 (0.01)	15 (0.01)
Total Particulates	7100 (3.10)	45 (0.02)

TABLE 5-6. CRITERIA POLLUTANT EMISSIONS FOR A COAL-FIRED INDUSTRIAL BOILER IN TEMPORAL UNITS (5 TEST AVERAGE)

Pollutant	kg/hr (lb/hr)	
	Before Scrubber	After Scrubber
NO_x (as NO_2)	44.3 (97.7)	39.2 (86.4)
CO	1.66 (3.66)	1.50 (3.31)
SO_2	117 (258)	3.80 (8.38)
Organics (as CH_4)	0.59 (1.30)	0.65 (1.43)
Total Particulates	315 (694)	1.99 (4.39)

TABLE 5-7. CRITERIA POLLUTANT EMISSIONS FOR A COAL-FIRED INDUSTRIAL BOILER IN THERMAL UNITS (5 TEST AVERAGE)

Pollutant	ng/J (lb/MM Btu)	
	Before Scrubber	After Scrubber
NO_x (as NO_2)	421 (0.98)	372 (0.87)
CO	15.9 (0.04)	14.3 (0.03)
SO_2	1112 (2.59)	36.3 (0.08)
Organics (as CH_4)	5.79 (0.01)	6.29 (0.01)
Total Particulates	2951 (6.86)	18.6 (0.04)

TABLE 5-8. CRITERIA POLLUTANT EMISSIONS FOR A COAL-FIRED INDUSTRIAL BOILER IN PRODUCTION RATE UNITS (5 TEST AVERAGE)

Pollutant	mg/kg steam (lb/1000 lb steam)	
	Before Scrubber	After Scrubber
NO_x (as NO_2)	1089 (1.09)	962 (0.96)
CO	41.2 (0.04)	37.1 (0.04)
SO_2	2883 (2.88)	93.8 (0.09)
Organics (as CH_4)	15.4 (0.01)	16.7 (0.02)
Total Particulates	7570 (7.57)	47.6 (0.05)

TABLE 5-9. SUMMARY OF CRITERIA POLLUTANT EMISSIONS-COAL FIRING

Test No.	ng/J (lb/MM Btu)							
	NO_x (as NO_2)	CO	SO_2	HC* (as CH_4)	C_1 - C_6 Organics	C_7 - C_{16} Organics	Organics Higher Than C_{16}	Total Particulates
200 Inlet	417 (0.97)	20.7 (0.05)	1009 (2.35)	3.79 (0.01)	<5.49 (<0.01)	0.34 (0.00)	2.28 (0.01)	2361 (5.49)
200 Outlet	367 (0.85)	18.5 (0.04)	25.4 (0.06)	4.22 (0.01)	<5.49 (<0.01)	0.27 (0.00)	0.33 (0.00)	14.3 (0.03)
201-1 Inlet	491 (1.14)	16.5 (0.04)	1284 (2.99)	4.35 (0.01)	<5.65 (<0.01)			3122 (7.26)
201-1 Outlet	457 (1.06)	15.7 (0.04)	39.0 (0.09)	5.22 (0.01)	<5.65 (<0.01)			20.9 (0.05)
201-2 Inlet	455 (1.06)	17.7 (0.04)	1295 (3.01)	0.88 (0.00)	<5.75 (<0.01)			
201-2 Outlet	358 (8.33)	15.9 (0.04)	35.5 (0.08)	1.33 (0.00)	<5.75 (<0.01)			
201-3 Inlet	330 (0.77)	16.2 (0.04)	1028 (2.39)	10.9 (0.03)	<5.69 (<0.01)			
201-3 Outlet	258 (0.60)	12.7 (0.03)	31.8 (0.07)	10.9 (0.03)	<5.69 (<0.01)			
201-4 Inlet	409 (0.95)	8.56 (0.02)	942 (2.19)	8.95 (0.02)	<5.06 (<0.01)			3370 (7.84)
201-4 Outlet	420 (0.98)	8.95 (0.02)	49.7 (0.12)	9.73 (0.02)	<5.06 (<0.01)			20.6 (0.05)
Average Inlet	421 (0.98)	15.9 (0.04)	1112 (2.59)	5.79 (0.01)	<5.53 (<0.01)	0.34 (0.00)	2.28 (0.01)	2951 (6.86)
Average Outlet	372 (0.87)	14.3 (0.03)	36.3 (0.08)	6.29 (0.01)	<5.53 (<0.01)	0.27 (0.00)	0.33 (0.00)	18.6 (0.04)

* Total hydrocarbons as determined by flame ionization detection (FID) analysis.

TABLE 5-10. SUMMARY OF CRITERIA POLLUTANT EMISSIONS - COAL FIRING

Test No.	kg/hr							
	NO_x (as NO_2)	CO	SO_2	HC (as CH_4)	C_1 - C_6 Organics	C_7 - C_{16} Organics	High Molecular Weight Organics	Total Particulates
200 Inlet	45	2.2	106	0.40	<0.59	0.04	0.25	248
200 Outlet	39	2.2	3.0	0.56	<0.59	0.001	0.004	1.7
201-1 Inlet	51	1.7	134	0.45	<0.60	--	--	324
201-1 Outlet	46	1.6	3.9	0.53	<0.60	--	--	2.1
201-2 Inlet	49	1.9	139	0.09	<0.62	--	--	--
201-2 Outlet	40	1.8	3.9	0.15	<0.62	--	--	--
201-3 Inlet	30	1.5	97	0.97	<0.53	--	--	--
201-3 Outlet	23	1.1	2.7	1.01	<0.53	--	--	--
201-4 Inlet	44	0.9	100	0.96	<0.55	--	--	362
201-4 Outlet	46	0.9	5.2	1.00	<0.55	--	--	2.1
Average Inlet	44	1.6	115	0.58	<0.57	0.04	0.25	311
Average Outlet	39	1.5	3.7	0.64	<0.57	0.001	0.004	2.0

TABLE 5-11. COMPARISON OF CRITERIA POLLUTANT EMISSIONS WITH EMISSION FACTORS FOR UNCONTROLLED BOILERS

Pollutant	ng/J (lb/MM Btu)			
	Test Data Before Scrubber		Average Emission Factors for Uncontrolled Sources*	
NO_x (as NO_2 at full load)	491	(1.14)	343	(0.80)
CO	15.9	(0.04)	19	(0.04)
SO_2	1112	(2.59)	1189	(2.77)
Organics	5.79	(0.01)	5.72	(0.01)
Total Particulates	2951	(6.86)	3212	(7.47)

* Factors are computed from AP-42 values using the national average bituminous coal higher heating value of 11,263 Btu/lb (Reference 6).

levels observed during an eight hour test. Average NO_x removals were computed for each test by integrating the area between plots of scrubber inlet and outlet concentrations versus time and averaging the total area with respect to time. Time integrated NO_x removal data are presented in Table 5-12. The slight increase in NO_x emissions measured during test 201-4 results from a single outlying scrubber outlet data point in a group of data which otherwise corresponds well with inlet data. Thus, the apparent increase is considered not to be significant. Otherwise, these data indicate that average NO_x removals across the scrubber ranged from 6 to 24%.

Although NO_x removal in both wet and dry FGD systems has been reported in the literature, no information is available regarding the chemistry of such occurrences (References 7 & 8). It is feasible that some degree of NO_x removal may be effected by dissolution of NO_2 in the slightly acidic scrubber solution. However, it should be noted that data presented in Table 5-12 do not indicate a correlation between the extent of NO_x removal and scrubber inlet NO_x concentration. And, as mentioned previously, inlet and outlet gas temperatures and flow rates in the scrubber unit were essentially identical for all tests. Thus, the extent of NO_x removal cannot be correlated to variables monitored during testing. Further, as indicated by data in Table 5-9, NO_x removal trends are paralleled by CO removal trends. These

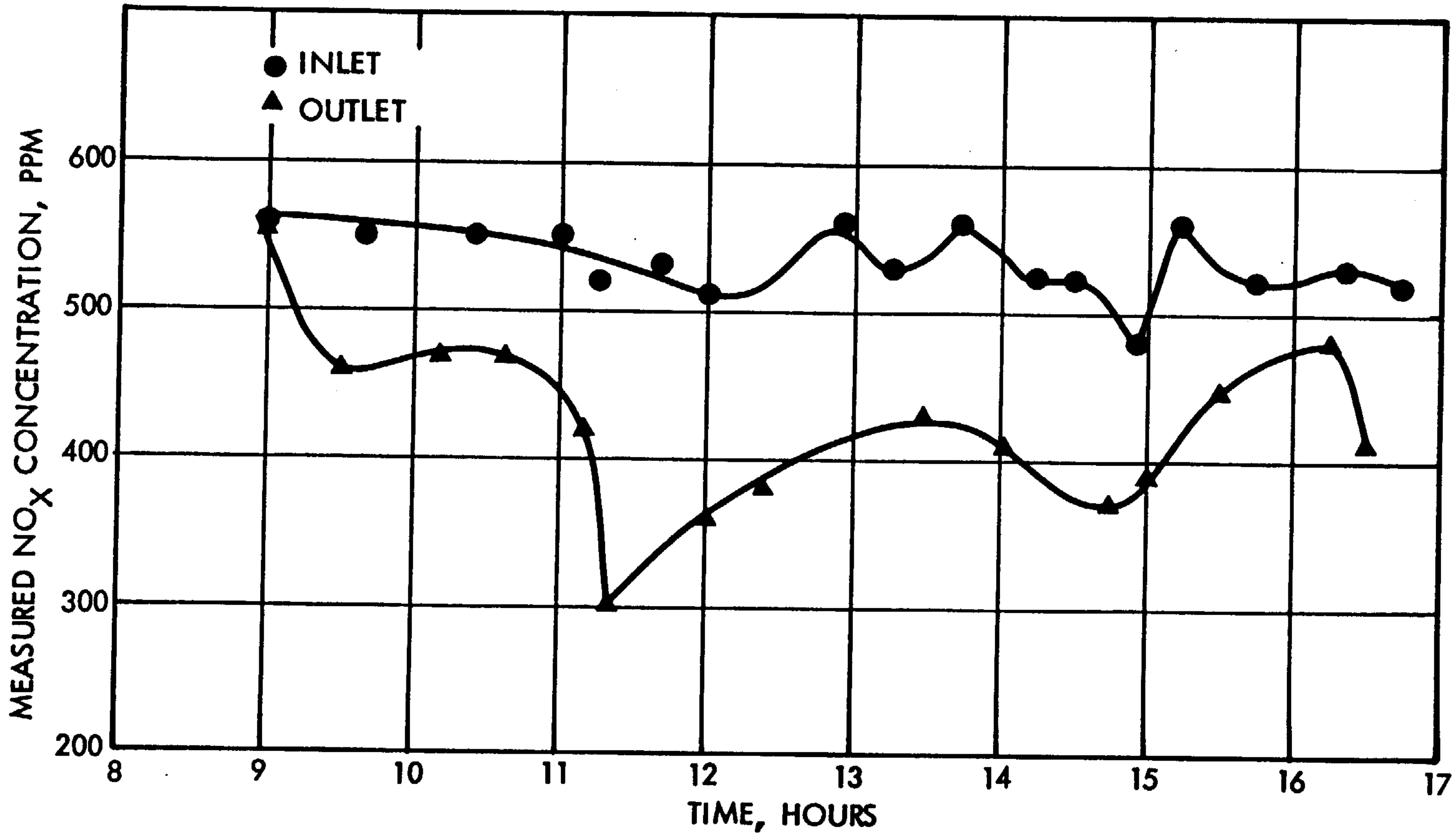


Figure 5-1. NO_X Concentration Profiles Measured at Scrubber Inlet and Outlet During Test 201-2.

TABLE 5-12. SUMMARY OF NO_x REDUCTION DATA

Test No.	Average NO_x As NO_2 ng/J (ppm) Inlet	Average NO_x As NO_2 ng/J (ppm) Outlet	Average NO_x Removal by Integration Method* ng/J (ppm)	Average NO_x Removal by Integration Method* %
200	417 (515)	367 (456)	37 (46)	8.9
201-1	491 (591)	457 (551)	28 (34)	5.7
201-2	455 (539)	358 (424)	93 (110)	20.3
201-3	330 (395)	258 (309)	79 (95)	24.0
201-4	409 (547)	420 (564)	Not Significant	

* The area between plots of inlet and outlet NO_x concentrations vs time was integrated and averaged with respect to time to yield average removals.

observations may indicate that measured NO_x (and CO) removal is actually a sampling phenomenon, perhaps related to small air leaks in the sampling train and subsequent dilution of the sample gas prior to analysis.

Carbon Monoxide

Carbon monoxide emission rates in the flue gas stream were measured to be 15.9 ng/J (0.04 lb/MM Btu). Measured CO emission rates correspond well with the value reported in AP-42, namely 19 ng/J (0.04 lb/MM Btu). A slight reduction in CO emissions was observed after scrubbing in most tests with an average reduction of 10% being measured. However, the significance of measured CO emission reductions at such low concentrations is questionable due to low analytical sensitivity (approximately 7% at these CO levels) and, as discussed for NO_x data, data trends and lack of correlation may indicate a sampling phenomenon.

Sulfur Dioxide

Average SO_2 emission rates prior to scrubbing were measured to be 1112 ng/J (2.59 lb/MM Btu). Measured uncontrolled SO_2 emission rates compare favorably with the value of 1189 ng/J (2.77 lb/MM Btu) reported in AP-42. Average SO_2 emission rates measured after scrubbing were 36.3 ng/J (0.08 lb/MM Btu) which corresponds to a mean scrubber efficiency of 96.7%. Thus, SO_2 emissions after FGD were substantially lower than either existing or proposed NSPS limitations.

Hydrocarbons

Emissions of organic material measured as methane were found to be 5.79 ng/J (0.01 lb/MM Btu), on the average, prior to scrubbing. Measured total organic emissions compare well with the tabulated AP-42 value of 5.72 ng/J (0.01 lb/MM Btu). It should be noted that, during these tests, the flue gas analyzed was processed by a gas conditioner. Therefore, higher molecular weight organics may have been condensed or scrubbed from the flue gas prior to flame ionization detection (FID) analysis. As will be discussed subsequently, total hydrocarbon emissions measured by FID analysis of the scrubber inlet gas may be low by approximately 30%. The slight increase in hydrocarbons across the scrubber, although statistically insignificant with respect to mean hydrocarbon values due to concentration fluctuations during testing, has statistical significance with respect to available real time inlet and outlet data pairs. That is, based on available inlet and outlet data pairs (measured not more than 30 minutes apart), outlet samples are biased high with respect to inlet samples. The magnitude of the bias is approximately 5 ppm (∿1.5 ng/J) at the excess oxygen levels measured. The cause of the observed bias is not known at the present time. However, data from recent tests will be available to determine whether data bias is related to gas sampling techniques. The possibility of bias arising from moisture interference, improper FID calibration or variable sample gas flow rate has been evaluated and subsequently discarded.

In addition to FID analyses, gas chromatograph analyses were performed on limited bag samples of flue gas and sample catches from the Level I (SASS) train. Gravimetric analyses were also performed on Level I samples to quantify high molecular weight organics. Bag samples were collected over a 30 to 45 minute period, one sample per test, and utilized to determine C_1 to C_6 organics. The SASS train contacts approximately 30 cubic meters of flue gas which were drawn isokinetically during the test. Analysis of SASS train samples provides quantitative measurement of C_7 to C_{16} organics by GC and organics higher than C_{16} by gravimetric methods.

Analytical results for scrubber outlet SASS train XAD-2 resin samples were not available due to sample handling problems. However, data from coal-fired utility boilers were utilized to obtain an average ratio of resin adsorbed organics to all other organics collected by the SASS train. These ratios were used in conjunction with data from the scrubber outlet probe rinse, resin module rinse, particulate organics and other organic catches from the SASS train to estimate the resin catch. Calculated outlet organic data from the C_7 to C_{16} and higher than C_{16} organic fractions are considered to be accurate to within a factor of three to four.

Data from FID, GC and gravimetric analysis indicate 28 to 60% of the scrubber inlet organics are heavier than C_{16} with the balance being composed primarily of C_1 to C_6 hydrocarbons. Scrubber outlet hydrocarbons appear to consist almost entirely of C_1 to C_6 hydrocarbons due to removal of organics higher than C_7 (21% removal of C_7 to C_{16} fraction and 85% removal of the $>C_{16}$ fraction). It is interesting to note that while removal of organics higher than C_7 is apparently 2.02 ng/J, no decrease in total hydrocarbons by FID analysis was observed. This may indicate that the FID was analyzing only the C_1 to C_6 fraction and that heavier fractions were removed by the gas conditioner. Under the assumption that FID data reflect the C_1 to C_6 fraction only, total hydrocarbon emissions would be approximately 8.4 ng/J (0.02 lb/MM Btu) or approximately 45% higher than indicated by FID. Scrubber inlet hydrocarbons would then consist of 27% organics higher than C_{16} with the balance being the C_1 to C_6 fraction. Again, scrubber outlet hydrocarbons would consist primarily of the C_1 to C_6 fraction.

Total Particulates

Average emission rates of total particulates prior to scrubbing were 2951 ng/J (6.86 lb/MM Btu). A mass balance of the coal ash indicates that approximately 75%* of the total ash was present in the flue gas at the scrubber inlet. These data indicated that the multiclone unit located upstream of the scrubber was removing little or no particulate material. This observation was subsequently verified by site operators who noted that the multiclone unit was subject to mechanical failure during the test period. Hence, particulate loadings measured at the scrubber inlet appear to be representative of uncontrolled emissions. Mean particulate loadings measured at the scrubber inlet are approximately 8% lower than the value of 3212 ng/J (7.47 lb/MM Btu) presented in AP-42. Particulate emissions after scrubbing were 18.6 ng/J (0.04 lb/MM Btu) which corresponds to 99.4% particulate removal efficiency in the scrubber. It is evident from these data that the scrubber is an effective particulate control device which does not appear to require auxiliary mechanical collectors. Controlled particulate emissions are well below the existing NSPS limitation of 43 ng/J (0.10 lb/MM Btu) although they are slightly higher than the proposed limitation of 13 ng/J (0.03 lb/MM Btu).

Particulate Size Distribution

The particulate size distributions for the scrubber inlet and outlet were determined using two different methods. For the high particulate loading at the scrubber inlet, the fractions of particulates in each size range were determined optically using polarized light microscopy (PLM) and are expressed in terms of number percent (i.e., the number of particles in each size range). For the lower particulate loadings at the scrubber outlet, the fractions of particulates in each size range were determined using an Anderson cascade impactor. The cascade impactor determines weight percent in each size range. Different sizing methods were used because the particulate concentration at the scrubber inlet was too high and caused problems in the interpretation of the cascade impactor data.

An estimate of the scrubber inlet particulate size distribution by number is presented in Table 5-13. However, PLM size data are based on particle diameter and a number distribution, and cannot be directly

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* As shown in Table 5-21, approximately 10-20% of the particulates at the scrubber inlet is oil soot which is a system residual from previous oil firing.

TABLE 5-13. APPROXIMATE SCRUBBER INLET PARTICULATE SIZE DISTRIBUTION FOR COAL FIRING (PLM) - TEST 201-1

Particle Diameter Size Range, Microns	Approximate Numerical %
<1	6
1 - 3	26
3 - 10	40
>10	28

compared with the cascade impactor size data, which are based on aerodynamic diameter and a weight distribution. The PLM particulate size data have, therefore, been converted to aerodynamic diameter and weight distribution basis, by assuming that particulates of different size have the same density (refer to Table 5-14). This is a reasonable assumption because the major components of the particulates generated from coal combustion, the aluminosilicates and the iron oxides, are known to partition equally among small and large particulates. With the constant density assumption, the weight distribution in each size range would be proportional to the product of the number distribution and the particulate volume representing the size range. The particulate volume was calculated based on the geometric mean diameter for the size range.

In Table 5-14, the scrubber inlet particulate size distribution by weight, as estimated from the PLM size distribution by number, is presented along with the scrubber outlet particulate size distribution determined using the Anderson cascade impactor. The data presented show a significant change in the particulate size distribution before and after scrubbing, as the larger particulates are effectively removed in the venturi scrubber. The emission rates of the particulates in each size fraction before and after scrubbing are presented in Table 5-15. These again show that the removal efficiency for particulates in the 3 - 10 μm range is 97.9%, and the removal efficiency for particulates larger than 10 μm is more than 99.9%. It is also interesting to note that for particulates less than 3 μm

TABLE 5-14. SCRUBBER INLET AND OUTLET PARTICULATE SIZE DISTRIBUTION BY WEIGHT FOR COAL FIRING - TEST 201-1

Aerodynamic Diameter Size, Range, Microns	Weight %	
	Scrubber Inlet	Scrubber Outlet
< 1	0.0017	62
1-3	0.041	30
3-10	2.24	7
>10	97.7	1

TABLE 5-15. EMISSION RATES OF PARTICULATES FOR A COAL-FIRED BOILER IN TEMPORAL UNITS - TEST 201-1

Aerodynamic Diameter Size Range, Microns	kg/hr		Removal Efficiency
	Scrubber Inlet	Scrubber Outlet	
<1	0.0055	1.30	< 0
1-3	0.13	0.63	< 0
3-10	7.3	0.15	97.9
>10	316.5	0.021	>99.9
Total	324.0	2.10	99.3

in size, there is a net increase in emission rates across the scrubber. This net increase indicates that the venturi scrubber is probably not effective in removing the fine particulates present in the flue gas, and that fine particulates may be generated within the scrubber. Based on the analysis of SO_3 and $SO_4^=$ emission data, it has been estimated that up to 40% of the fine particulate emissions at the scrubber outlet could be contributed by scrubber generated $NaHSO_4$. The remaining portion of the net increase in fine particulates across the scrubber can probably be attributed to the uncertainties associated with the assumptions used in converting PLM number size distribution data to weight size distribution, and to calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) particulates generated by the scrubber.

Sulfur Compounds: SO_2, SO_3, $SO_4^=$

The Goksoyr-Ross controlled condensation system was used to determine SO_3 emissions for tests 201-1 and 201-4. As shown in Table 5-16, less than 1% of the fuel sulfur is emitted as SO_3. The overall sulfur balance indicates that over 94% of the sulfur input in the fuel is emitted as SO_2, SO_3 or sulfate ($SO_4^=$) in the flue gas. The remainder of the sulfur is associated with the bottom ash or may be unaccounted for. The scrubber, in addition to removing 95 to 97% of the SO_2, also removes 32 to 33% of the SO_3 and 88% of the $SO_4^=$. The relatively poor removal efficiency for SO_3 is an indication that SO_3 is either present as very fine aerosols in the scrubber inlet, or is converted to very fine aerosols as the flue gas stream is rapidly cooled inside the scrubber. The higher removal efficiency for $SO_4^=$ is an indication that most of the $SO_4^=$ in the scrubber inlet is present as metallic sulfates in particulates larger than 3 μm in size.

The 3 to 5% of the SO_2 and 67 to 68% of the SO_3 that are not removed pass through the scrubber. For $SO_4^=$, however, a more complex process occurs. At the scrubber inlet 24% of the sulfates is water soluble and 76% is acid soluble (15% HNO_3). At the outlet the values are 97% and 3% respectively (These data are summarized in Table 5-17). This is an indication that the combustion generated sulfates are not simply passing through the scrubber.

TABLE 5-16. SO_2, SO_3 AND $SO_4^=$ EMISSIONS FROM COAL FIRING

Pollutant	Concentration mg/m^3	Mass emission rate g/hr	Thermal emission rate ng/J	Production emission rate mg/kg steam	% of fuel sulfur found in flue gas	Removal efficiency* %
SO_2						
201-1 Inlet	2,970	134,000	1,280	3,030	92	
201-1 Outlet	90.0	3,950	37.8	89.3	2.7	97
201-4 Inlet	2,420	102,000	937	2,490	94	
201-4 Outlet	130	5,180	47.8	127	4.8	95
SO_3						
201-1 Inlet	16.9	764	7.3	17.3	0.42	
201-1 Outlet	11.7	513	4.9	11.6	0.28	33
201-4 Inlet	12.6	527	4.9	13.0	0.39	
201-4 Outlet	9.0	359	3.3	8.8	0.26	32
$SO_4^=$						
201-1 Inlet	154.1	6,950	66.3	157	3.2	
201-1 Outlet	19.1	838	8.00	19.0	0.39	88‡
Total						
201-1 Inlet	-	-	-	-	95 †	
201-1 Outlet	-	-	-	-	3.4†	-
201-4 Inlet	-	-	-	-	94 †	
201-4 Outlet	-	-	-	-	5.1†	-

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[*] Calculated from mass emission rate.

[†] As all three sulfur species.

[‡] This removal is actually a net removal since the scrubber both removes and generates sulfates.

TABLE 5-17. SUMMARY OF SULFATE EMISSIONS DURING COAL FIRING - TEST 201-1

	mg/m^3	
	Inlet	Outlet
Water soluble	36.7 (24%)	18.6 (97%)
Acid soluble	117.4 (76%)	0.5 (3 %)
Total	154.1	19.1

Because of the possibility that the $SO_4^=$ emissions from coal combustion may be modified by the scrubbing process, an analysis effort to determine the nature of $SO_4^=$ emissions was initiated. Both the Fourier Transform IR (FTIR) analysis and the X-Ray Diffraction (XRD) analysis have confirmed the presence of sodium bisulfate ($NaHSO_4$) in the scrubber outlet, but not in the scrubber inlet. This is positive proof that sulfates, as the result of oxidation of sodium bisulfite ($NaHSO_3$) and sodium sulfite (Na_2SO_3), are generated within the scrubber and emitted in the scrubber effluent gas. Also, tests on boilers with flue gas concentrations of 400 to 8,000 ppm SO_2 have shown that there is no correlation between initial SO_2 concentration and the net sulfate formation rate (Ref. 9). This implies that the scrubber has a minimum sulfate emission rate that is virtually unaffected by inlet SO_2 concentration.

Based on the above findings, it is believed that $NaHSO_4$ emissions from the scrubber are on the order of 5 mg/m^3 (the difference between total outlet sulfate and H_2SO_4 emissions was determined as SO_3). Furthermore, if one assumes that only a small fraction of the SO_3 was collected on the filter as H_2SO_4 because of the high filter temperature (175°C), then the scrubber contribution could be as high as 19 mg/m^3, or 0.8 kg/hr for test 201-1. As discussed in the previous section, this amount of scrubber generated $NaHSO_4$ could account for 40% of the fine particulate (3 μm) emissions at the scrubber outlet.

Inorganics

The emission concentrations for 22 major trace elements at the scrubber inlet and outlet are presented in Table 5-18. To assess the hazard potential of these emissions, the emission concentrations are compared with the Minimum Acute Toxicity Effluent (MATE) values. The MATE values are emission level goals developed under the direction of EPA, and can be considered as concentrations of pollutants in undiluted emission streams that will not adversely affect those persons or ecological systems exposed for short periods of time (Ref. 10). MATE values for air derived from human health considerations are used as the basis for comparison here.

As shown in Table 5-18, of the trace elements presented, 18 exceed their MATE values at the scrubber inlet and 4 at the scrubber outlet. The four trace elements in the scrubber effluent that pose a potential hazard are arsenic, chromium, iron and nickel. The MATE value for arsenic is extremely low because arsenic is a cumulative poison producing long-term chronic effects in humans, and the MATE values for chromium and nickel are extremely low due to considerations for potential human carcinogenicity. The established Threshold Limit Values (TLV's) for arsenic, chromium and nickel are 0.5, 0.5 and 0.1 mg/m^3, respectively. If the TLV's are used as the basis for comparison, the emission concentrations for arsenic, chromium and nickel are all less than their respective TLV's and would be considered less hazardous. Additionally, it may be noted that the emission concentration of beryllium at the scrubber outlet is equal to its MATE value. At this emission concentration, the total beryllium emissions from boilers greater than 50 MW in capacity would amount to more than 10 grams per day and exceed the National Emission Standard for Hazardous Air Pollutants.

In Table 5-19, the emission factors and the mass emission rates for the 22 major trace elements at the scrubber inlet and outlet are presented. The mass emission rates were used to calculate the removal efficiency for these trace elements by the scrubber. The overall removal efficiency for these trace elements is approximately 99.5%. As indicated in Table 5-19, however, some of the trace elements are not being removed as effectively as others.

TABLE 5-18. EMISSION CONCENTRATIONS OF TRACE ELEMENTS DURING COAL-FIRING TEST 201-1

Trace Element	Scrubber Inlet mg/m^3	Scrubber Outlet mg/m^3	MATE Value mg/m^3	Degree of Hazard†	
				Scrubber Inlet	Scrubber Outlet
Be*	0.1	0.002	0.002	50	1.0
Hg‡	0.011	0.005	0.05	0.22	0.10
Ca	74	0.036	16	4.6	0.002
Mg	19	0.011	6.0	3.2	0.002
Sb	3.7	0.025	0.050	74	0.5
As	7.8	0.22	0.002	3900	110
B*	0.2	0.03	3.1	0.07	0.01
Cd	0.47	0.0010	0.010	47	0.1
Cr	2.6	0.13	0.001	2600	130
Co	3.6	0.012	0.050	72	0.24
Cu	9.6	0.020	0.20	48	0.10
Fe	450	2.4	1.0	450	2.4
Pb	8.5	0.021	0.15	57	0.14
Mn	0.78	0.015	5.0	0.16	0.003
Mo	10	0.027	5.0	2.0	0.005
Ni	1.4	0.063	0.015	93	4.2
V	3.1	0.058	0.50	6.2	0.12
Zn	2.3	0.048	4.0	0.58	0.012
Se	3.2	0.099	0.200	16	0.50
Sr	11	0.058	3.1	3.5	0.019
Al	480	2.6	5.2	92	0.5
Zr	1.6	0.018	5.0	0.32	0.004
Total	1100	6.2			

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* Approximate values as determined by Spark Source Mass Spectrometry (SSMS). The other values presented are determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) analysis.

† Degree of hazard is defined as the ratio of the discharge concentration to the MATE valve.

‡ Mercury was determined by cold vapor analysis of SASS train samples taken during test 200.

TABLE 5-19. EMISSION FACTORS AND MASS EMISSION RATES OF TRACE ELEMENTS DURING COAL-FIRING TEST 201-1

Trace Element	Emission Factor, ng/J		Emission Rate, g/hr		Removal Efficiency %	Enrichment Factor
	Scrubber Inlet	Scrubber Outlet	Scrubber Inlet	Scrubber Outlet		
Be*	0.04	0.001	5	0.09	98	3.7
Hg†	0.08	0.037	0.50	0.23	55	84
Ca	32	0.015	3300	1.6	99	0.09
Mg	8.2	0.0046	860	0.48	99	0.11
Sb	1.6	0.010	170	1.1	99	1.2
As	3.4	0.092	350	9.7	97	5.3
B*	0.1	0.01	10	1.2	88	2.1
Cd	0.20	0.00042	21	0.044	99	0.4
Cr	1.1	0.054	120	5.7	95	9.5
Co	1.6	0.0050	160	0.53	99	0.6
Cu	4.1	0.0084	430	0.88	99	0.4
Fe	190	1.0	20,000	110	99	0.99
Pb	3.7	0.0088	380	0.92	99	0.5
Mn	0.34	0.0063	35	0.68	98	3.4
Mo	4.3	0.026	450	1.2	99	0.5
Ni	0.60	0.026	61	2.8	95	8.6
V	1.3	0.024	140	2.5	98	3.6
Zn	0.99	0.020	100	2.1	98	3.9
Se	1.4	0.041	140	4.3	97	5.8
Sr	4.7	0.024	500	2.5	99	0.9
Al	210	1.1	22,000	110	99	1.0
Zr	0.69	0.0075	72	0.79	99	2.1
Total	470	2.6	50,000	270	99	

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* Approximate values as determined by SSMS. The other values were determined by ICPOES analysis.

† Mercury was determined by cold vapor analysis of SASS train samples taken during test 200.

To better understand the removal efficiency of the individual trace elements, the enrichment factor for each trace element across the scrubber has been computed. The enrichment factor is defined here as the ratio of the concentrations of trace element to aluminum in the scrubber outlet, divided by the corresponding ratio in the scrubber inlet. Aluminum is selected as the reference material because it has been known to partition equally among particulates of different size*. The enrichment factors presented in Table 5-19 show that beryllium, mercury, antimony, arsenic, boron, chromium, manganese, nickel, vanadium, zinc, selenium and zirconium are enriched across the scrubber. The enrichment observed is due primarily to the partitioning of trace elements as a function of particulate size, and the greater collection efficiency of the scrubber for the large size particulates. It may also be noted that many of the trace elements that show an enrichment trend, such as mercury, selenium and arsenic, either occur as element vapors or form volatile oxides and halides at furnance temperatures. Condensation and surface adsorption of the more volatile elements or their oxides and halides downstream of the furnace could, therefore, result in higher concentrations of these trace elements on smaller particulates.

To gain better insight into the nature of the particulates generated from coal combustion, the Electron Spectroscopy for Chemical Analysis (ESCA) technique was used to determine the surface and subsurface concentrations of elements in the particulates. The main use of ESCA, however, was in the study of the sulfur depth profile of sulfur containing compounds in the particulates. The ESCA results, expressed as normalized atom percent, are presented in Table 5-20. For particulates at the scrubber inlet, comparison of the 201-1 cyclone with the 201-1 filter results shows similar sulfur surface content. The sharp drop in S atom percent after etching of the scrubber inlet filter sample, on the other hand, indicates that some surface coating of the particulates occurred.

Assuming that the bulk of the particulate is homogeneous with respect to aluminosilicates, the thickness of the surface coating can be most

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* Silicon, iron, and scandium have also been used by other investigators as the reference element in the computation of enrichment factors. Notice that iron has no enrichment in this study while silicon and scandium were not measured.

TABLE 5-20. DEPTH PROFILE ANALYSIS OF COAL PARTICULATE WITH CONCENTRATIONS EXPRESSED AS NORMALIZED ATOM PERCENT* - TEST 201-1

		O	Na	S	Si	Al	Fe	Cl	P	V	Ca	C	K
Inlet	Level II cyclone catch	57	4	11	6	7	2	2	1				
	Level II filter catch	56	2.4	11.5	14.1	8	1.4	1.5	1.2		2		
	Level II filter catch; 76 Å	54.2	2.1	4.0	17.9	12.6	2.1	1.3	2.2	1.0	2.7		
Outlet	Level II filter catch	45.7	5.5	13.2	7.1	2.2		1.2	1.1	0.7	1.3	14.9	7.1
	Level II filter catch; 75 Å	48	7.4	11.5	9.0	5.2	1.2	1.1	1.1		1.1	12.1	1.8
	Level II filter catch; 150 Å	48.3	9.1	10.0	10.1	7.7	1.2	1.2	1.2			10.0	1.2
	Level II filter catch; 300 Å	48.3	8.8	8.0	10.6	9.6	2.1	1.0	1.2	0.5		8.0	1.8
	Level II filter catch; 500 Å	47.9	7.3	6.7	10.8	13	1.7	1.2	1.1		1.2	8.1	1.1
	Level II filter catch; 700 Å	47	7.3	6.1	11.6	11.0	2.3	0.9	1.5	0.5	1.0	8.8	1.6

* The atom percent of the 12 elements presented here adds up to 100 percent. Other elements present in the cyclone and filter catches were not studied in ESCA. Hence, the atom percents in this table are normalized atom percents and not absolute atom percents.

readily estimated by considering the concentration of coating elements relative to the concentration of aluminum or silicon. The relative concentration may be plotted as a function of penetration to enable graphical estimation of coating thickness. Aluminum is selected as the reference element here rather than silicon because the ESCA analyses were run directly on the filter and the silicon content of the filter would interfere with the interpretation of data.

Depth profiles for six major elements in the scrubber outlet particulates are depicted graphically in Figure 5-2. These profiles show that sulfur and carbon are more concentrated near the surface than deeper inside the particles. Both the sulfur and the carbon curves, however, level off after ∿275 Å. Hence, the thickness of the deposited layer of sulfur and carbon appears to be approximately 275 Å. For sulfur, these data indicate that while there may be higher surface concentration of sulfur containing compounds in the particulates emitted from the scrubber, some of these compounds are probably deposited on particles composed of solid sulfate or sulfite. This would be the case if sulfuric acid condensed on the sodium bisulfate ($NaHSO_4$) or calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) particles that have been found to be present. For carbon, the depth profile data indicate that a fraction of the carbon, either oil soot*, or as a carbon containing compound (such as carbonate or bicarbonate), could be deposited on the surface of the fine particulates emitted. The leveling off of the carbon curve, however, indicates that another fraction could be emitted as solid oil soot particles or solid carbonate/bicarbonate particles. The depth profile for iron, vanadium, chlorine, and calcium is reasonably flat and indicates that the relative concentrations of these elements remain approximately constant.

The approximate composition of the particulates at the scrubber inlet and outlet has also been investigated using PLM analysis. The estimated weight percentages of the major components of the particulates are

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* Oil soot deposited in the duct-work downstream of the boiler during oil-firing.

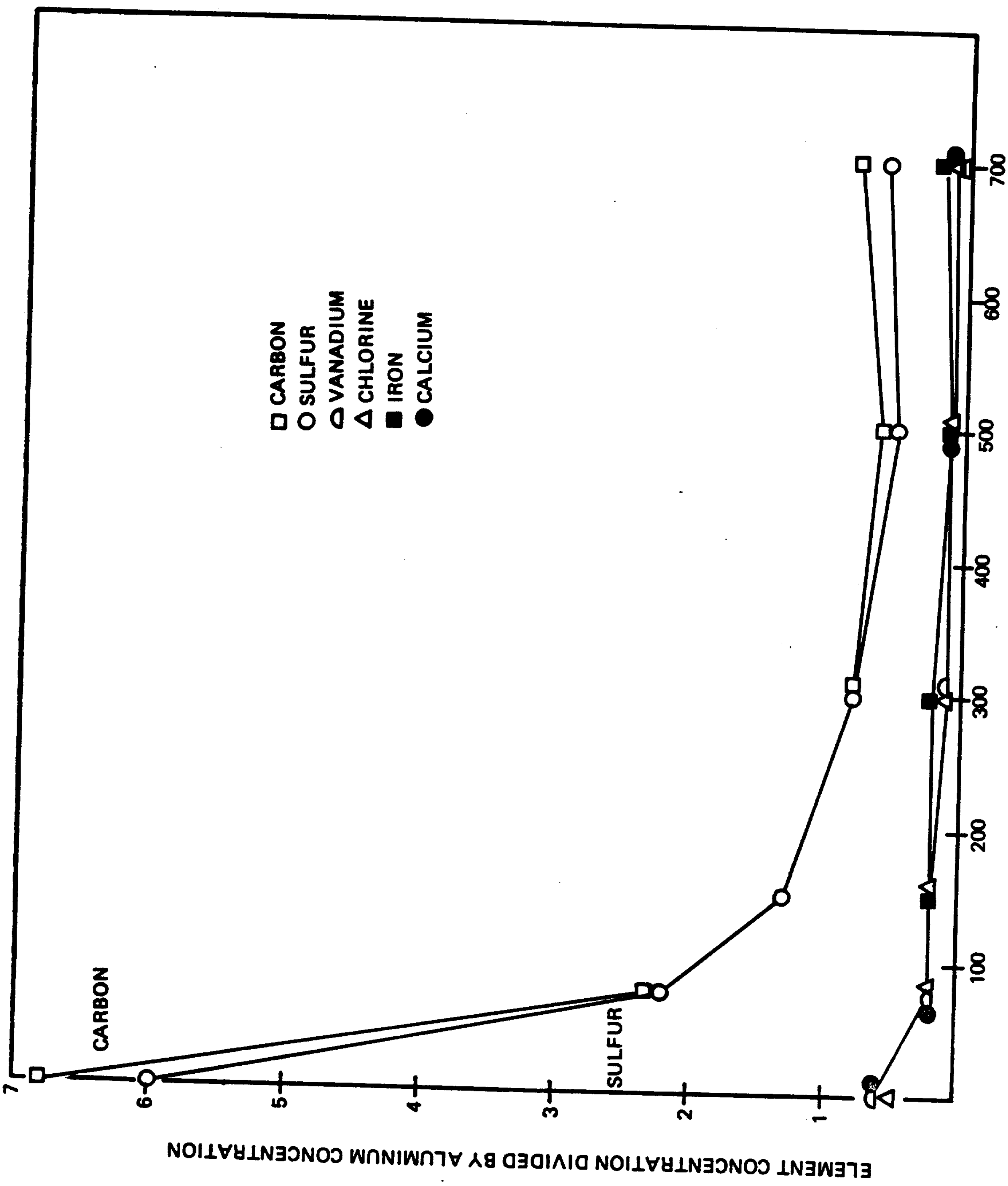

Figure 5-2. Depth profile analysis of outlet coal particulate - Test 201-1.

presented in Table 5-21. It may be noted that a substantial fraction of the particulates at both the scrubber inlet and outlet is composed of oil soot. The increase in the weight percent of oil soot in the particulates across the scrubber is consistent with the results of ESCA analysis, as discussed in the previous section. Both the PLM analysis and the ESCA analysis have shown that oil soot could be emitted as fine, solid particulates. The calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) and the unknown sulfate identified at the scrubber outlet are mostly generated by the scrubber[†]. As discussed previously, the unknown sulfates may be composed primarily of sulfuric acid and sodium bisulfate.

TABLE 5-21. MAJOR COAL PARTICULATE COMPONENTS - TEST 201-1

Component	Approximate weight % Inlet	Outlet
Ash*		
Fused	15-30	-
Unfused	50-65	-
Minerals		
Fe_2O_3	1-5	15-25
Fe_3O_4 (magnetite)	10-15	-
SiO_2	< 2	-
$CaCO_3$	-	1-5
Oil soot†	10-20	25-40
Coke	< 2	-
$CaSO_3.1/2\ H_2O$ and Unknown sulfate	-	50-65

* Iron-aluminum silicates.

† See text for discussion.

[†] Strictly speaking, $CaSO_3 \cdot 1/2\ H_2O$ is formed in the regeneration of Na_2SO_3 and a fraction of it is carried over with the regenerated Na_2SO_3 into the scrubber.

Chloride, Fluoride, and Nitrate Emissions

Emissions data for chloride (Cl^-), fluoride (F^-), and nitrate emissions (NO_3^-) are presented in Table 5-22. Chlorides and fluorides are removed with high degrees of efficiency, at greater than 99% and greater than 85%, respectively. These are to be expected because the overall removal efficiency of the trace element cations with which these anions may be associated is greater than 99%. The removal efficienty for nitrates cannot be determined because the nitrate emissions at both the scrubber inlet and outlet are expressed as "less than" values.

Organics

Four methods of analyses were utilized in determining flue gas organic loadings. Continuous FID analyses were performed to determine total organic concentrations assuming all carbon to be present as methane. A field chromatograph was employed to analyze concentrations of organics in the range of C_1 to C_6 hydrocarbons and a laboratory chromatograph was used in determining hydrocarbons in the C_7 - C_{16} boiling range. Gas chromatography was applied to bag samples of gas collected over a 30-45 minute period. Higher molecular weight organics were determined gravimetrically from residues of solvent rinses and extracts.

For C_7 - C_{16} organics, the subscripted carbon number refers to a boiling range rather than a specific molecular structure. For example, the C_8 designation refers to compounds boiling in the range of approximately 110 to 140°C while normal octane boils at 125.7°C. The approximate boiling ranges corresponding to each carbon are presented in Table 5-23.

TABLE 5-22. CHLORIDE, FLUORIDE, AND NITRATE EMISSIONS FROM COAL FIRING - TEST 201-1

	Inlet*		Outlet*		Removal Efficiency
	mg/m^3	ng/J	mg/m^3	ng/J	
Chloride (Cl^-)	10.9	4.7	<0.009	<0.004	>99
Fluoride (F^-)	0.51	0.22	<0.076	<0.03	>86
Nitrate (NO_3^-)	<1.1	<0.48	<0.58	<0.25	-

* Mass as the ion.

TABLE 5-23. APPROXIMATE BOILING RANGES CORRESPONDING TO EACH CARBON NUMBER

Carbon Number	Approximate Boiling Range	Carbon Number	Approximate Boiling Range
C_1	-160 to -100°C	C_9	140 to 160°C
C_2	-100 to - 50°C	C_{10}	160 to 180°C
C_3	- 50 to 0°C	C_{11}	180 to 200°C
C_4	0 to 30°C	C_{12}	200 to 220°C
C_5	30 to 60°C	C_{13}	220 to 240°C
C_6	60 to 90°C	C_{14}	240 to 260°C
C_7	90 to 110°C	C_{15}	260 to 280°C
C_8	110 to 140°C	C_{16}	280 to 300°C

Results of organic determinations made during test 200 are summarized in Table 5-24. Total organics determined as methane by FID show a slight increase across the scrubber. However, as mentioned previously, this increase can not be explained with available data. Total hydrocarbon analyses appear to correspond well with GC and gravimetric hydrocarbon analyses. These data indicate that, although uncontrolled total organic emissions are low, organics which are produced consist primarily of light hydrocarbons in the C_1 to C_6 range and hydrocarbons heavier than C_{16}. Also, concentrations of hydrocarbons higher than C_{16} appear to decrease by more than 80% across the scrubber. It should be noted that analytical results for the outlet resin samples from the SASS train were not available, so these were calculated using data from ten coal fired boiler tests which used similar sampling trains, and assuming the proportion of organic material in the resin sample to the rest of the organics trapped in the sampling train to be constant. These calculated values are good to a factor of 3 to 4.

A quantitative analysis of the C_7 to C_{16} organic fraction from test 200 indicates that organic material was present for all boiling ranges with the exception of the C_7 and C_{11} fractions which were present at concentrations lower than 0.4 $\mu g/m^3$ (limit of detection). Measured concentrations at the scrubber inlet ranged from 21 to 215 $\mu g/m^3$. The highest

TABLE 5-24. COMPARISON OF ORGANIC MEASUREMENT METHODS DURING COAL FIRING - TEST 200

Method	Organic Concentration mg/m^3 Inlet	Organic Concentration mg/m^3 Outlet	% Change
Total as CH_4 (FID)	9	11	Not Significant
C_1 - C_6 (GC)	$\leq$12.7*	$\leq$12.7*	-
C_7 - C_{16} (GC)	0.81	0.652	-20
C_{16} (Gravimetric)	5.4	0.788	-85

*These values represent the detection limit of the instrument used.

concentrations were found in the C_8, C_{12}, C_{13} and C_{16} fractions which had 215, 130, 128 and 121 μg/m^3, respectively.

Organic materials collected by the XAD-2 resin during sampling of the test 200 scrubber inlet gas were separated by liquid chromatography (LC) and the fractions were subsequently analyzed by infrared spectroscopy (IR) per standard Level 1 procedures. Only resin extracts and resin module rinse samples were submitted for LC/IR analyses since the organic contents of other samples were too low for such treatment. Results of sample analyses (not corrected for resin blank species contents) and blank analyses are presented in Table 5-25. Many of the compound categories found in the sample are also present in the blank, although in most instances blank contributions appear to be minor. The presence of silicones and esters in the sample is most probably characteristics of the sampling system (i.e., lubricants and resin interference) rather than the source.

An attempt was made to identify the specific compounds that made up the total organic emissions. Table 5-26 summarizes the organics that were identified. None of the identified compounds is directly associated with combustion. They are, however, representative of the types of compounds that are used in the manufacture of the sample bags, XAD-2 resin and the

TABLE 5-25. SUMMARY OF THE INFRARED ANALYSIS OF ORGANICS PRODUCED DURING COAL COMBUSTION - TEST 200 INLET (NOT CORRECTED FOR BLANK)

Total Organics, mg/m^3	LC1*		LC2		LC3		LC4		LC5		LC6		LC7		Total	
	Sample	Blank	Sample	Blank	Sample	Blank	Sample	Blank	Sample	Blank	Sample	Blank	Sample	Blank	Sample	Blank
	0.14	0.02	--	-	0.06	0.03	0.12	0.01	0.37	0.02	0.95	0.10	0.06	-	1.70	0.18
Category	Intensity†															
Aliphatic Hydrocarbons	XM	XM			XM	XM	Xm			Xm				Xm		
Aromatic Hydrocarbons	XM	XM			XM	XM	XM		Xm	Xm				Xm		
Chlorinated Hydrocarbons											Om					
Silicones					Xm		Xm			Xm						
Heterocyclic Sulfur Compounds							Xm		Xm							
Thiocarbonyl Compounds							Xm									
Nitro Compounds							XM		Xm	Om				Om		
Ethers			N/A				XM									
Esthers							XM		XM	XM	XM	XM	XM	XM		
Amides						Xm					Xm		Om	Om		
Alcohols											Xm		Xm			
Glycols												XM		XM		
Phenols							Xm						OM			
Carboxylic Acids							Xm				XM	XM	XM	XM		
Silicates						Xm										

* LC fractionation was performed per standard Level 1 analytical procedures.

† O = At least one species suspected present
X = At least one species present
M = Material type accounts for 50% of the sample
m = Material type accounts for 10% of the sample

TABLE 5-26. ORGANIC COMPOUNDS IDENTIFIED IN THE FLUE GAS DURING COAL FIRING*

Compound Name	μg/m³ 201-2 In	μg/m³ 201-2 Out	μg/m³ 201-3 In	μg/m³ 201-3 Out
Propionaldehyde	170	380	54	-
Ethyl-n-butyl ether	2000	1500	910	1500
Hydrocarbon (C_6H_{14})	-	-	380	-
Chloropropanol	-	-	-	3.9
Unidentified Alcohol	-	4.0	-	-
Ketone (MW 140)	3.9	-	6.9	-
Methyl substituted aromatic	1.7	-	-	-

* As discussed in the text, these compounds are not considered to be directly associated with combustion.

solvents used in the analysis. This finding is consistent with both GC and FID analyses indicating very low organic emissions during testing.

Polycyclic Organic Material

Polycyclic organic material (POM) was not found in either the scrubber inlet or outlet samples at detection limits of 0.3 μg/m³. This observation is consistent with the findings to date from the EPA sponsored project "Emissions Assessment of Conventional Combustion Sources". However, two POM compounds for which MATE values are below 0.3 μg/m³ are benzo(a)pyrene and dibenz(a,h)anthracene. The MATE values for benzo(a)pyrene and dibenz(a,h)anthracene are 0.02 μg/m³ and 0.09 μg/m³, respectively. While available data indicate that many POM compounds are not present at significant concentrations during coal firing, additional analyses at higher GC/MS sensitivity would be required to conclusively preclude the presence of all POMs at significant concentrations.

Scrubber Efficiency

Flue gas analyses indicate that scrubber processing removes a significant percentage of input sulfur oxides (SO_2, SO_3 and particulate $SO_4^=$), total particulates and organics of the C_7 class and higher. Scrubber removal efficiency data for these flue gas components are presented in Table 5-27. As discussed in the criteria pollutants section, the significance of data indicating NO_x and CO removal appears to be somewhat questionable. Therefore, these components are not included in this discussion.

Average removal efficiencies have been discussed previously. However, it is important to note that it is the C_7 hydrocarbons and higher hydrocarbons which are removed with 77% efficiency. These fractions comprise 32 to 69% of the total generated organics. Hence, based on the total generated organics, a removal efficiency of 25 to 53% was obtained.

TABLE 5-27. SCRUBBER EFFICIENCY DURING COAL FIRING

Test Number	% Removal				
	SO_2	SO_3	$SO_4^=$*	Total Particulates	C_7 and higher Organics
200	97	--	--	99	77
201-1	97	33	88	99	--
201-2	97	--	--	--	--
201-3	97	--	--	--	--
201-4	95	32	--	99	--
Average	97	32	88†	99	77†

* This removal rate is actually a net change rate. As described earlier the scrubber both removes and generates sulfates.

† One data point only.

It is not known for certain by what process organics are removed with such a high degree of efficiency. There are, however, at least three possible mechanisms:

- Dissolution - Some organics are partially water soluble. These compounds could be removed by dissolving in the slurry.
- Condensation - High boiling organics could condense and be removed as "particulate".
- Sorption - Some organics could adsorb on particulates.

One or any combination of these mechanisms may account for the high removal efficiencies.

LIQUID WASTE

As discussed in Section 3, only one significant waste water stream is produced. The stream is a combination of water treatment waste, boiler blowdown, and acid waste water from elsewhere in the plant. The quality of this combined stream is such that it is acceptable for disposal into the municipal sewer system. Liquid streams from the scrubber operation are passed to the thickener and recirculated to the scrubber after the filtration step. There is no direct wastewater discharge from the scrubber operation, as the process is designed to dispose of all of the water that enters its system through evaporation and moisture entrained in the scrubber cake.

Because several streams are mixed together, it is not possible to accurately determine what part of the effluent is attributable to the boiler. However, the flow rate of the combined stream is approximately 10,000 liters/hr (40 gallons/min).

Water Quality Parameters

Table 5-28 summarizes the waste water parameters for the combined waste water stream. Note that these values do not represent water produced solely by the boiler but also include process waste.

Inorganics - Combined Waste Water Stream

Table 5-29 shows discharges of the major inorganics in the combined stream as determined by SSMS analyses (note that these are accurate only to within a factor of about 3). None of these elements exceeds its MATE value based on human health considerations. However, based on the uncertainty in SSMS analysis, cobolt, cadmium, nickel and copper may exceed their MATE values based on ecological considerations.

TABLE 5-28. COMBINED STREAM WASTE WATER PARAMETERS - COAL FIRING

Parameter	Test 200	Test 201-1	Test 201-2	Test 201-3	Test 201-4	Average
pH	7.9	7.5	8.2	8.0	7.3	7.8
Hardness, mg/l (as $CaCO_3$)	210	158	135	145	100	150
Alkalinity, mg/l (as $CaCO_3$)	115	125	130	125	145	128
Cyanide, mg/l	0	0	0	0	0	0

TABLE 5-29. WASTE WATER INORGANICS FOR COAL FIRING

Trace Element	mg/l	g/hr*	MATE Value, mg/l		Degree of Hazard	
			Health	Ecology	Health	Ecology
Be	<0.001	<0.01	0.030	0.055	<0.033	<0.018
F	0.8	8	38	--	0.021	--
V	0.003	0.03	2.5	0.15	0.0012	0.02
Cr	0.002	0.02	0.25	0.25	0.008	0.008
Co	0.1	1	0.75	0.25	0.13	0.40
Ni	0.005	0.05	0.23	0.010	0.022	0.50
Cu	0.02	0.2	5.0	0.050	0.004	0.40
Sr	0.5	5	46	--	0.011	--
Cd	<0.001	<0.01	0.050	0.001	<0.02	<1.0
Sb	<0.001	<0.01	7.5	0.20	<0.0001	<0.005
Pb	0.01	0.1	0.250	0.050	0.04	0.20

* Flow rate of 10,000 liters per hour, combined waste water.

Organics - Combined Waste Water Stream

Table 5-30 summarizes the concentrations of C_7 - C_{16} organics in the combined stream. High molecular weight organics ($>C_{16}$) were present at a concentration of 0.21 mg/liter, but are probably attributable to process wastes generated at the manufacturing site. As a basis for comparison, the water MATE values for alkanes, alkenes, and alkynes are in the 500 to 14,000 mg/liter range based on human health considerations, and in the 1.0 to 100 mg/liter range based on ecological considerations. The discharge concentrations of organics are all well within these MATE values.

TABLE 5-30. SUMMARY OF C_7 - C_{16} ORGANICS IN THE WASTE WATER - COAL FIRING

Carbon Number	mg/l	Carbon Number	mg/l
C_7	ND	C_{13}	ND
C_8	ND	C_{14}	0.1
C_9	ND	C_{15}	0.1
C_{10}	0.1	C_{16}	ND
C_{11}	ND		
C_{12}	0.1	Total C_7 - C_{16}	0.4

ND means none detected.

SOLID WASTE

Three solid waste streams are produced by the system:

- Bottom ash;
- Fly ash;
- Scrubber cake.

Table 5-31 shows the approximate quantities of bottom ash and scrubber cake that were produced. Only small quantities of fly ash were produced during the test period due to the malfunctioning of the multiclone.

TABLE 5-31. SOLID WASTE PRODUCTION RATES - COAL FIRING

Test	Bottom Ash		Scrubber Cake†	
	kg/hr*	μg/J	kg/hr	μg/J
200	∿80	∿0.75	1100	10.2
201-1	∿80	∿0.76	1100	10.5
201-2	∿80	∿0.73	1200	11.0
201-3	∿80	∿0.86	850	9.1
201-4	∿80	∿0.74	840	7.8

* 15 tons a week

† Scaled up to represent scrubbing of 100% of the flue gas for boiler number 4.

The scrubber cake produced after filtration has the appearance of a clayey silt. Its grain size is quite uniform and characteristic of silty soils, but its behavior closely resembles a clay in many respects. As obtained from the vacuum filter, the scrubber cake consists of small lumps and appears to be relatively dry; in actuality, however, the water content generally ranges from about 30 to 50%.

If it is assumed that calcium sulfite hemihydrate ($CaSO_3.1/2\ H_2O$) is formed from SO_2 scrubbing and Na_2SO_3 regeneration, then the mass balance in Table 5-32 shows that the scrubber cake is composed of 28.5% coal fly ash and 23.8% $CaSO_3.1/2\ H_2O$. However, if the multiclone had been functioning properly during the test period, more fly ash would be removed upstream of the scrubber and the fly ash content of the scrubber cake would be lowered proportionally. The amount of scrubber cake produced could be reduced to 600-750 kg/hr on wet basis, assuming approximately 60 to 80% multiclone efficiency.

TABLE 5-32. SCRUBBER CAKE MASS BALANCE FOR COAL FIRING - TEST 201-1

Component	Contribution to Scrubber Cake kg/hr	Weight %
Fly Ash Removed by Scrubber	324	29.5
$CaSO_3 \cdot 1/2\ H_2O$ Formed from SO_2 Scrubbing and Na_2SO_3 Regeneration	262	23.8
$CaSO_4$, $CaCO_3$, Na_2SO_4, $Ca(OH)_2$, $NaHSO_3$ and Na_2SO_3 Losses (estimated)	10-85	0.9-7.7
Water	429-504	39-46
Total	1100	100

Although the scrubber cake material is composed predominately of relatively insoluble solids (calcium sulfite, calcium sulfate, and some calcium carbonate), the intersititial water does contain soluble residues of lime, sulfate, sulfite and chloride salts. Trace elements in the fly ash may also leach from the disposed scrubber cake and are of special concern. The concentrations of 20 trace elements in the scrubber cake are presented in Table 5-33. Here it may be noted that with the exception of boron, the trace element concentrations in the scrubber cake have far exceeded the MATE values for solids. This is the result of reducing a large volume of low concentration pollutants to a smaller volume of concentrated pollutants. The degree of hazard for the trace elements in the scrubber cake is sufficiently high to warrent the disposal of these solid wastes in specially designed landfills.

TABLE 5-33. INORGANIC CONTENT OF SCRUBBER CAKE FROM COAL-FIRING (DRY BASIS) - TEST 201-1

Element	Concentration µg/g	MATE Value, µg/g		Degree of Hazard	
		Health	Ecology	Health	Ecology
Ca	60,715	480	32	126	1,897
Mg	1,458	180	174	8.1	8.4
Sb	315	15	0.4	21	788
As	532	0.5	0.1	1,064	5,320
B	88	93	50	0.9	1.8
Cd	13	0.1	0.002	130	6,500
Cr	141	0.5	0.5	282	282
Co	424	1.5	0.5	283	848
Cu	112	10	0.1	11	1,120
Fe	47,241	3.0	0.5	15,738	94,482
Pb	297	0.5	0.1	594	2,970
Mn	51	0.5	0.2	102	255
Mo	1,117	150	14	7.4	80
Ni	114	0.45	0.02	253	5,700
V	195	5.0	0.3	39	650
Zn	282	50	0.2	5.6	1,410
Se	256	0.10	0.05	2,560	5,120
Sr	642	92	--	7.0	--
Al	45,310	160	2.0	283	22,655
Zr	106	15	--	7.1	--
Total	159,409				

The concentrations of 20 trace elements present in fly ash are presented in Table 5-34. Again, in almost every case, the trace element concentration in the fly ash has far exceeded its MATE value for solids. Trace element concentrations in the bottom ash would be similar to those of the fly ash, except that the more volatile elements and the elements that form volatile compounds would be more enriched in the fly ash. Thus, the concentrations of arsenic, antimony, boron, chromium, manganese, nickel, vanadium, zinc, selenium and zirconium would all be lower in the bottom ash.

An overall mass balance for the 20 trace elements has been performed and the results are summarized in Table 5-35. The percent of trace element in the coal feed that could be located in the effluent streams (scrubber cake, scrubber effluent gas, bottom ash and fly ash) is used as a measure of mass balance closure. With the exception of boron, copper, strontium and zirconium, the closure of mass balance for the trace elements has been found to be good. This is an indication of the reliability and accuracy of sampling and analysis data for trace element and flow rate measurements.

The scrubber cake was also analyzed for organics but none were detected. This is to be expected since the concentration of organics in the flue gas stream was extremely low.

ANNUAL EMISSIONS

Table 5-36 presents an estimate of the annual emissions of the major pollutants for the controlled and uncontrolled case. It was assumed that the boiler operates at 100% load, 87% of the year (7560 hours/years), and that coal is the only fuel burned.

TABLE 5-34. INORGANIC CONTENT OF FLY ASH FROM COAL-FIRING - TEST 201-1

Element	Concentration μg/g	MATE Value, μg/g		Degree of Hazard	
		Health	Ecology	Health	Ecology
Ca	378	480	32	0.8	12
Mg	2,478	180	174	14	14
Sb	438	15	0.4	29	1,095
As	1,015	0.5	0.1	2,030	10,150
B	20	93	50	0.2	0.4
Cd	18	0.1	0.002	180	9,000
Cr	434	0.5	0.5	868	868
Co	408	1.5	0.5	272	816
Cu	320	10	0.1	32	3,200
Fe	129,330	3.0	0.5	43,110	258,660
Pb	438	0.5	0.1	876	4,380
Mn	121	0.5	0.2	242	605
Mo	1,288	150	14	9	92
Ni	165	0.45	0.02	367	8,250
V	376	5.0	0.3	75	1,253
Zn	179	5.0	0.2	36	895
Se	378	0.10	0.05	3,780	7,560
Sr	728	92	--	8	--
Al	109,450	160	2.0	684	54,725
Zr	187	15	--	12	--
Total	248,149				

TABLE 5-35. MASS BALANCE ON TRACE ELEMENTS - TEST 201-1

Element	Coal Feed g/hr	Scrubber Cake g/hr	Scrubber Effluent Gas g/hr	Bottom and Fly Ash* g/hr	Percent Recovery†
Ca	2,794	40,072	1.6	30	‡
Mg	1,270	962	0.5	198	91
Sb	308	208	1.1	35	79
As	497	351	9.7	81	89
B	8.7	58	1.2	1.6	700
Cd	12.7	8.6	0.04	1.4	79
Cr	174	93	5.7	35	77
Co	461	280	0.53	33	68
Cu	261	74	0.88	26	39
Fe	44,455	31,179	110	10,346	94
Pb	308	196	0.92	35	75
Mn	44	34	0.68	9.7	100
Mo	1,063	737	1.2	103	79
Ni	134	75	2.8	13	68
V	171	151	2.5	30	107
Zn	203	186	2.1	14	100
Se	265	169	4.3	30	77
Sr	247	424	2.5	58	196
Al	50,806	29,905	110	8,756	76
Zr	980	70	0.79	15	9

* For mass balance calculations, bottom ash has been assumed to have the same trace element concentrations as fly ash. This is an approximate assumption, as some trace elements are enriched in the fly ash.

† Percent recovery is defined as 100 times the ratio of the sum of the emissions for a trace element to the trace element in the coal feed.

‡ Percent recovery for calcium is not calculated because most of the calcium in the scrubber cake is from the lime slurry.

TABLE 5-36. ANNUAL EMISSIONS - COAL FIRING*

Pollutant		kg/year		% Difference
		Scrubber Inlet	Scrubber Outlet	
Gaseous	NO_x (as NO_2)	500,810	442,520	-12
	SO_2	1,127,300	36,800	-97
	SO_3	6,184	4,157	-33
	SO_4	67,214	8,110	-88
	CO	16,119	14,497	-10
	Organics (as CH_4)	5,870	6,377	+ 9
	$C_1 - C_6$ Organics	<5,606†	<5,606†	—
	$C_7 - C_{16}$ Organics	345	274	-21
	High Molecular Weight Organics	2,311	335	-86
	Total Particulates	2,991,700	18,856	-99
	0 — 1μ		11,691	—
	1 — 3μ		5,657	—
	3 — 10μ		1,320	—
	>10μ		188	—
		M^3/year		
Liquid	Blowdown/wastewater	~76,000	~76,000	0
	Cooling water	~86,000	~86,000	0
		kg/year		
Solid	Bottom ash	~778,600	~778,600	0
	Fly ash (mechanical separator)‡	~1,800,000	~1,800,000	0
	Scrubber cake ‡	0	8,054,100	—

* Assuming 100% load, 45 weeks/year (7,560 hours/year).

† These values represent the detection limit of the instrument used.

‡ Assuming that the mechanical separator is operating properly.

AIR QUALITY ASSESSMENT - COAL FIRING

Simplified air quality models were used to determine the relative ground level air quality resulting from uncontrolled and controlled emissions. The ambient air quality values are approximate only. The emphasis should be placed on the relative values for each case as opposed to their absolute values.

Worst case weather conditions and typical weather conditions were considered. The worst case was assumed to be plume trapping. An equation proposed by Bierly and Hewson [11] was used with the following assumptions: inversion height 100 meters, wind speed 1.0 meter/second, D class stability (neutrally stable) in the mixing layer, and effective stack height of 50 m (164 ft). The typical case was assumed to correspond to the standard Gaussian convective diffusion equation, [12]. The following conditions were used: wind speed 4.0 meters/second and D class stability. These conditions could reasonably be expected to occur almost anywhere in the country. Typical does not mean average. It was assumed that all species were inert. No photochemical reactions were considered. (See Appendix A for details.)

Figures 5-3 through 5-10 present plots of approximate ground level ambient air quality as a function of distance directly downwind from a single 10 MW equivalent source. Data for NO_x, CO, SO_2 and particulates are presented. The purpose of these figures is not to attempt to accurately predict air quality but to compare the effects of controlled and uncontrolled emissions under an arbitrary but realistic set of meteorological conditions. It is implicit in this approach that each set of meteorological conditions remains constant for a sufficient length of time for the ambient air quality to reach steady state conditions at each distance.

Table 5-38 presents a summary of the federal ambient air quality standards for each pollutant. The standards are also shown on each plot.

Keeping in mind the caveats mentioned above, several observations can be made:

- The NO_x standard is exceeded under both weather conditions. Since the scrubber does not remove significant amounts of NO_x, there is no substantial difference between the controlled and uncontrolled cases. (The boiler has no NO_x controls.)

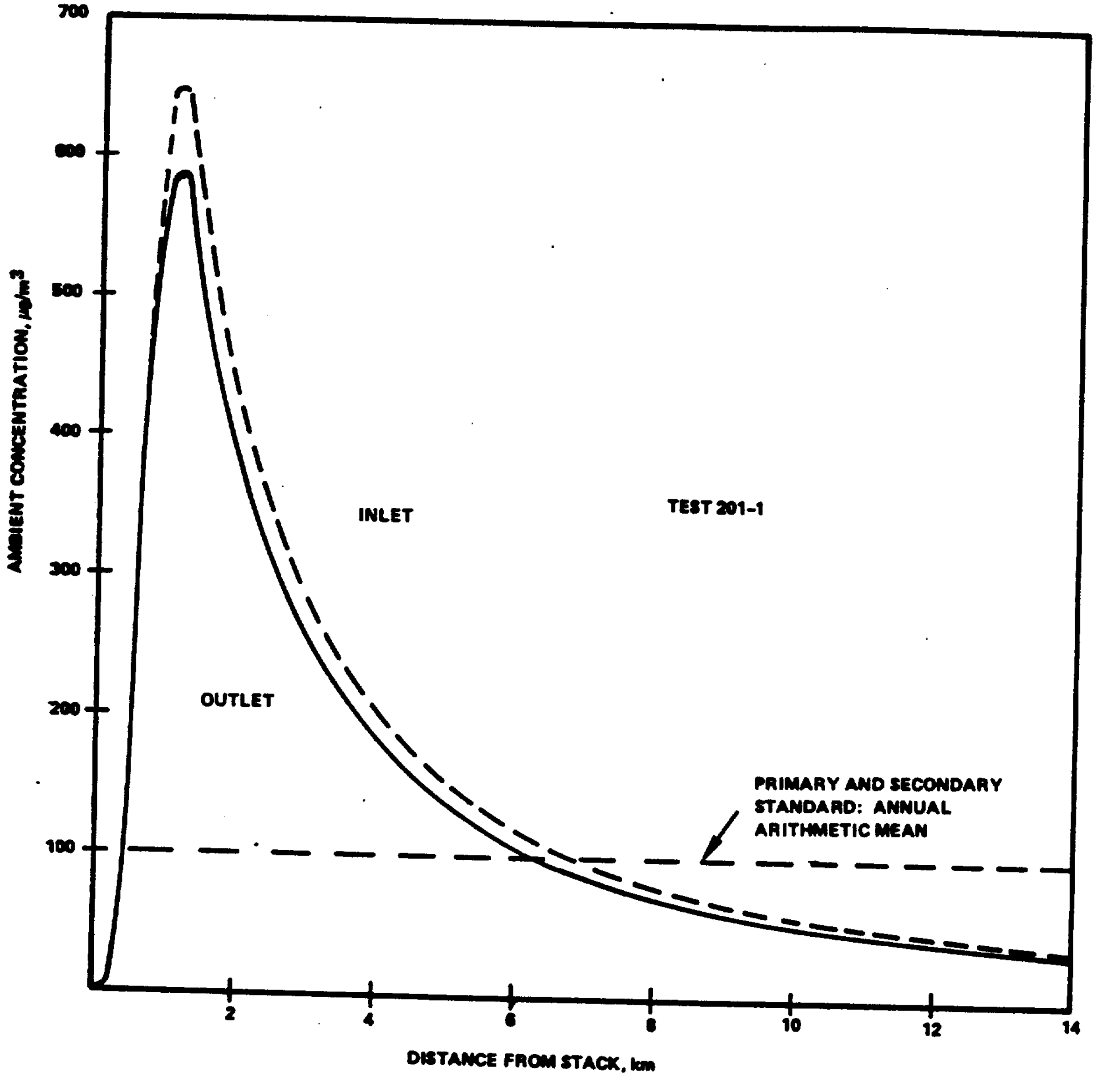

Figure 5-3. Relative NO_x air quality under worst case weather conditions - coal firing.

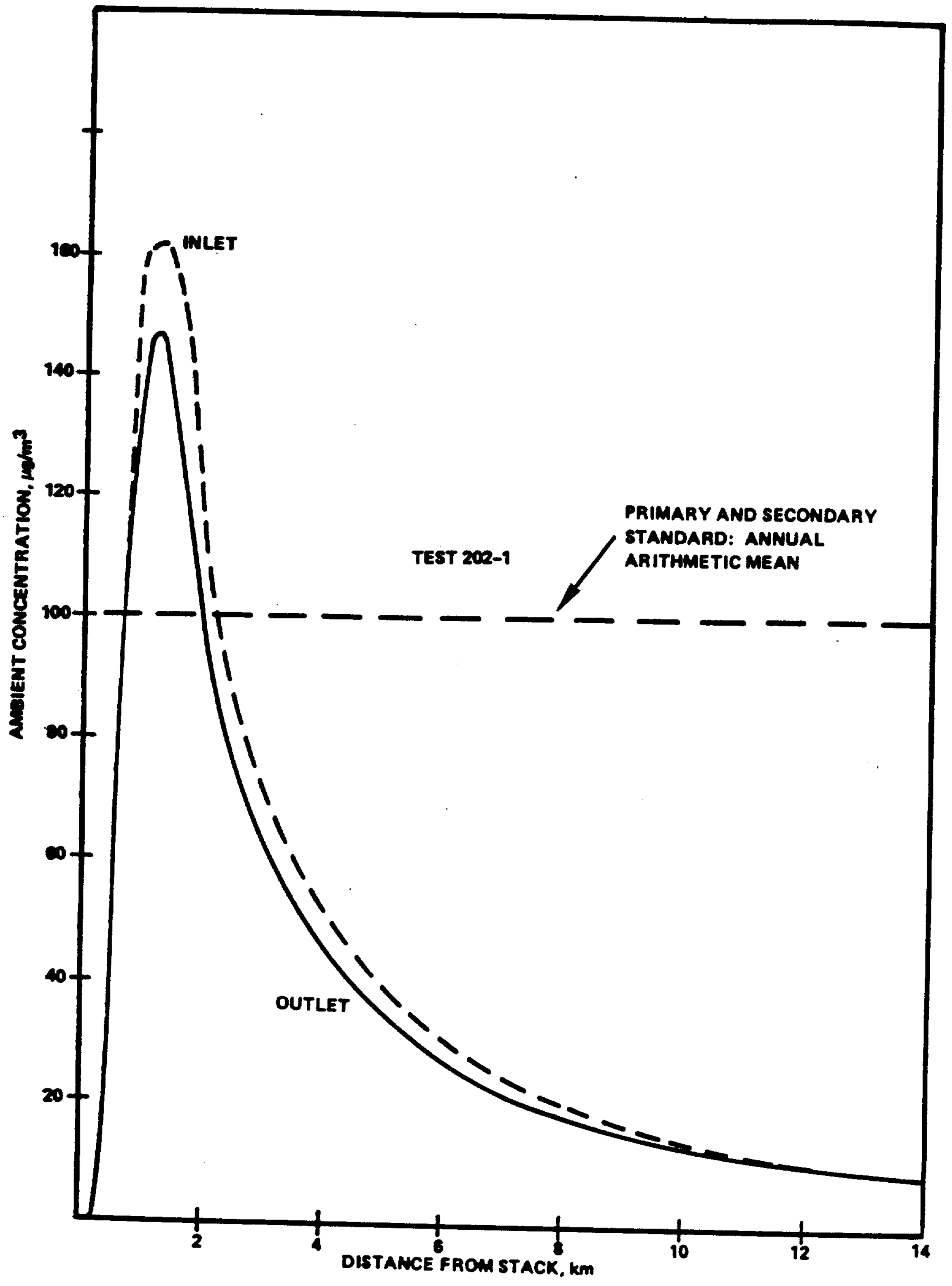

Figure 5-4. Relative NO_x air quality under typical weather conditions - coal firing.

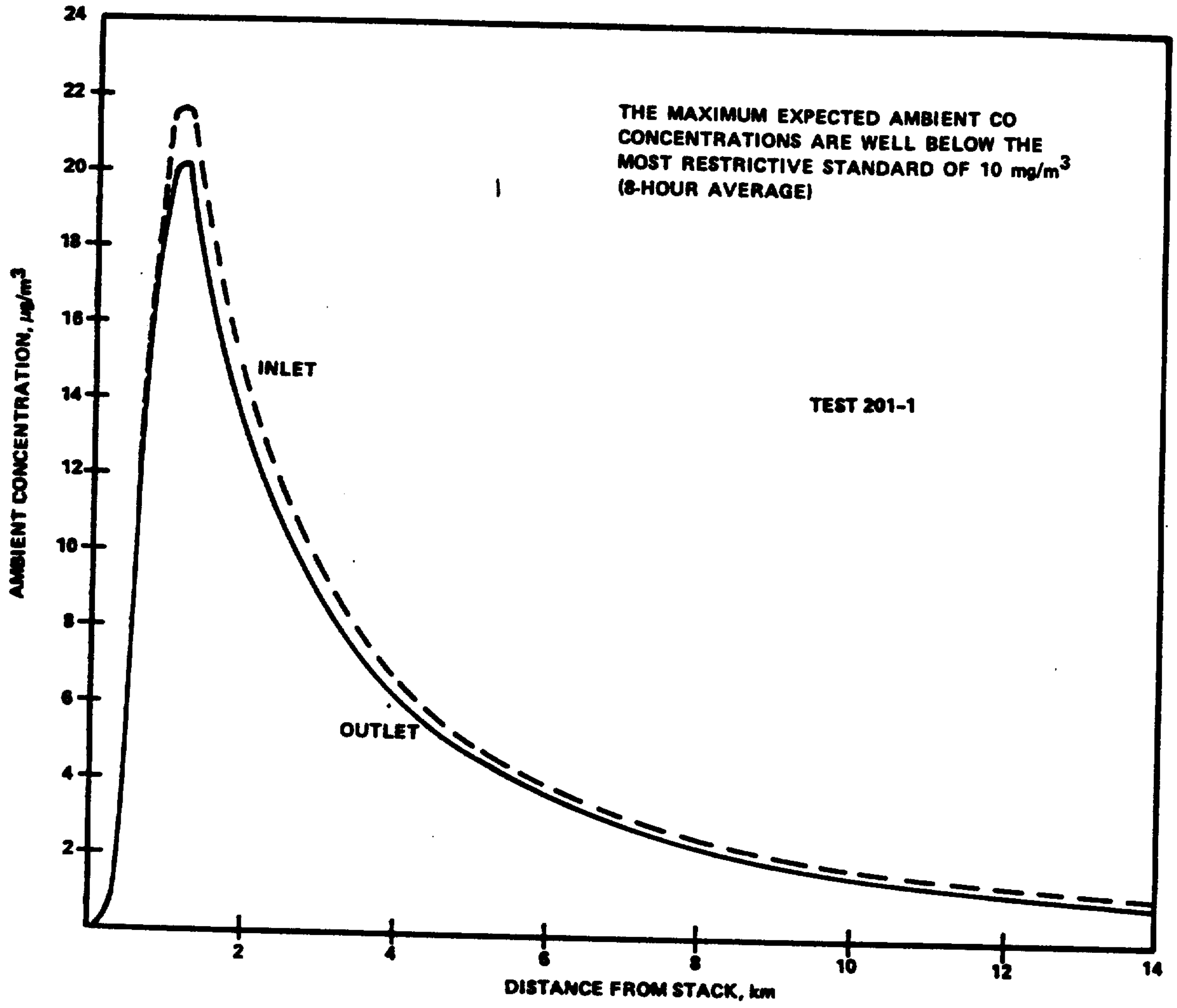

Figure 5-5. Relative CO air quality under worst case weather conditions - coal firing.

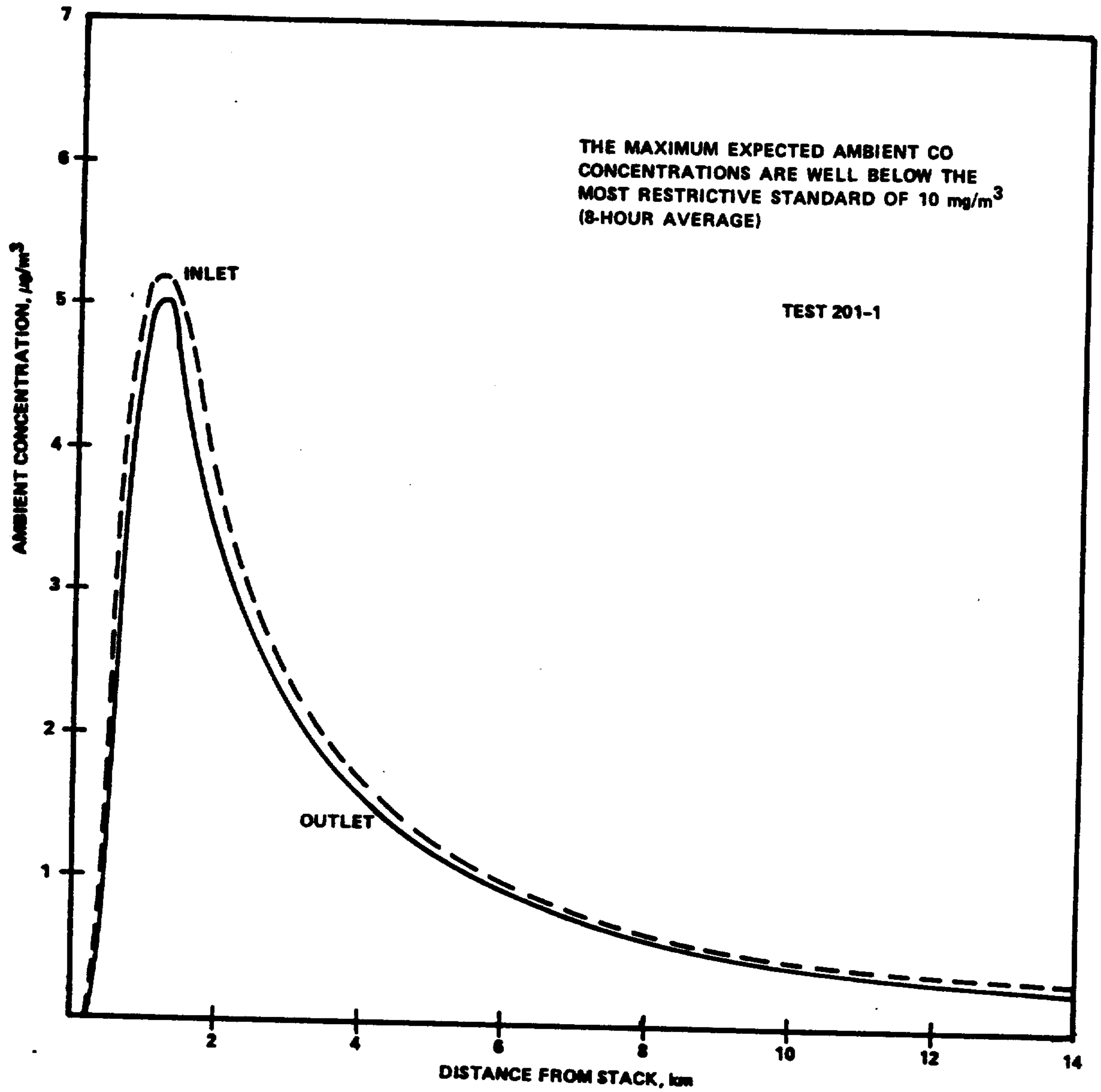

Figure 5-6. Relative CO air quality under typical weather conditions - coal firing.

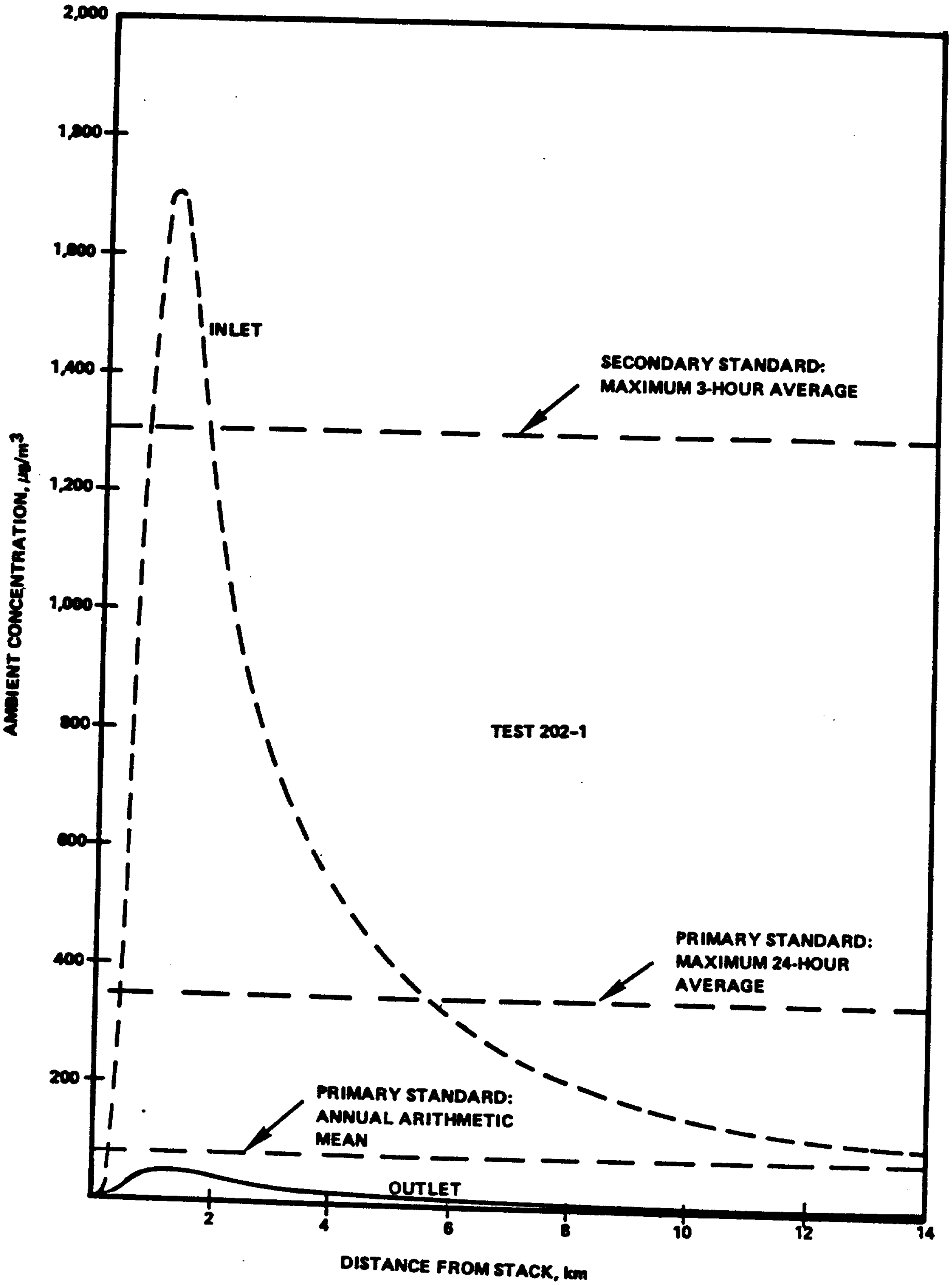

Figure 5-7. Relative SO_2 air quality under worst case weather conditions - coal firing.

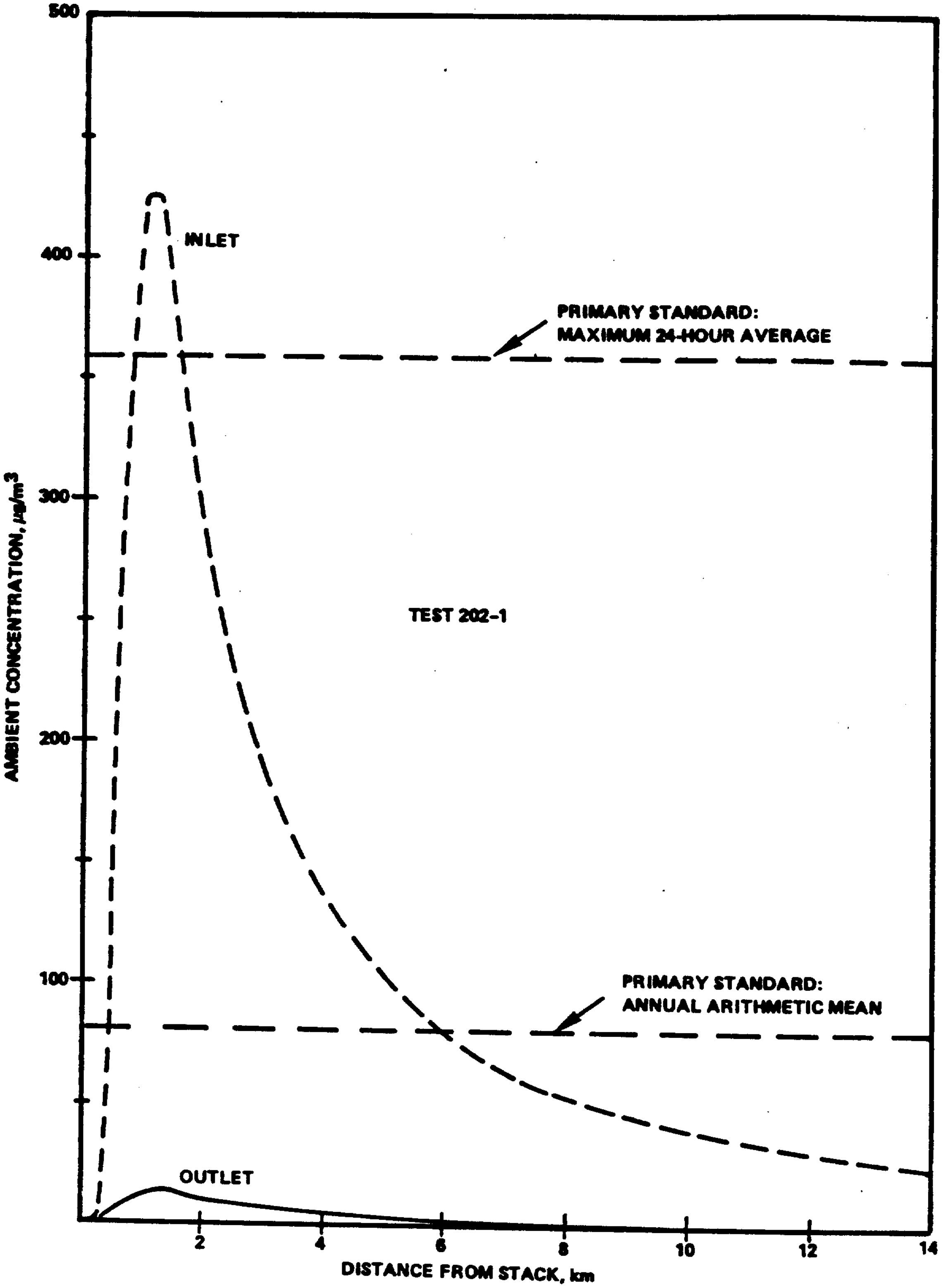

Figure 5-8. Relative SO_2 air quality under typical weather conditions - coal firing.

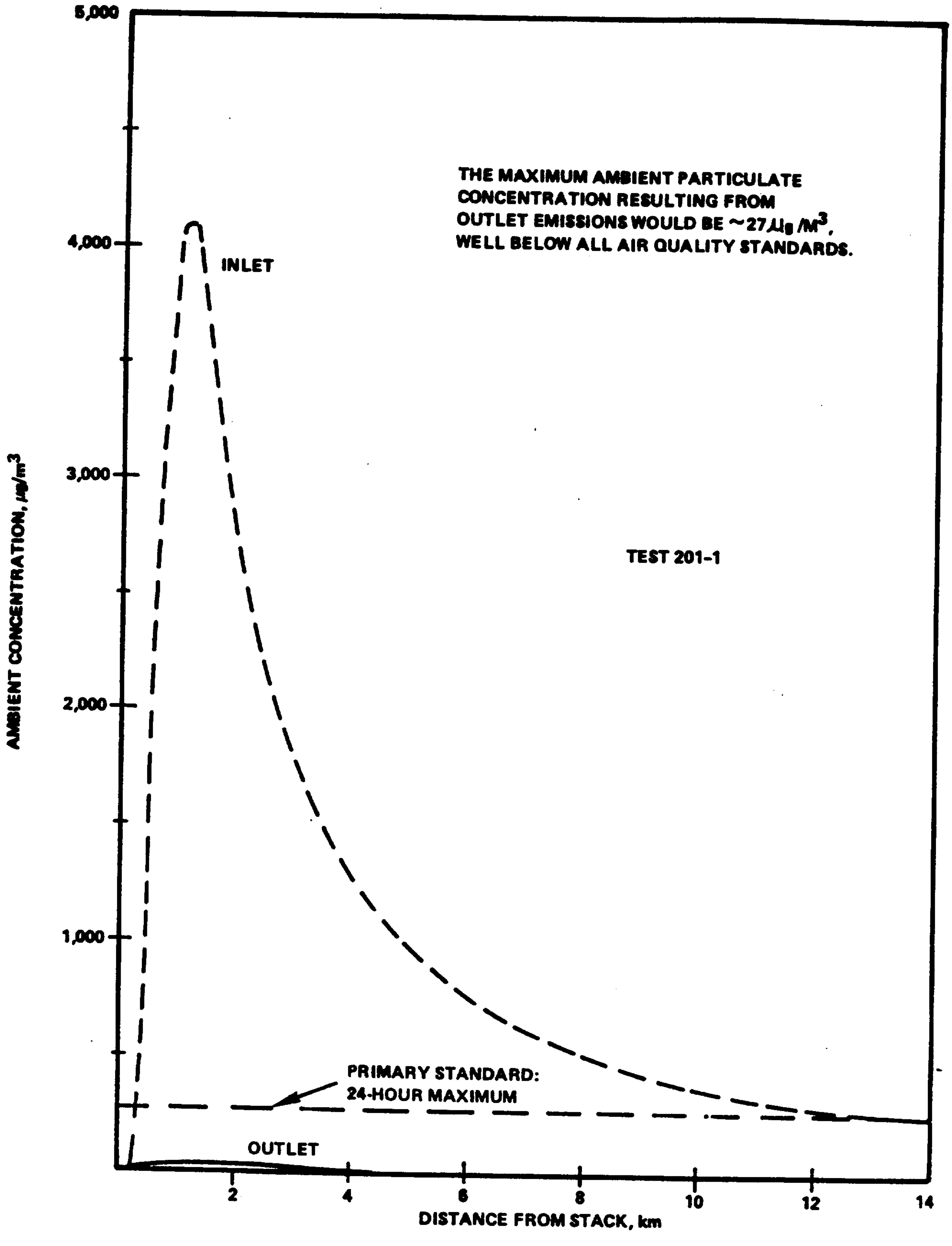

Figure 5-9. Relative particulate air quality under worst case weather conditions - coal firing.

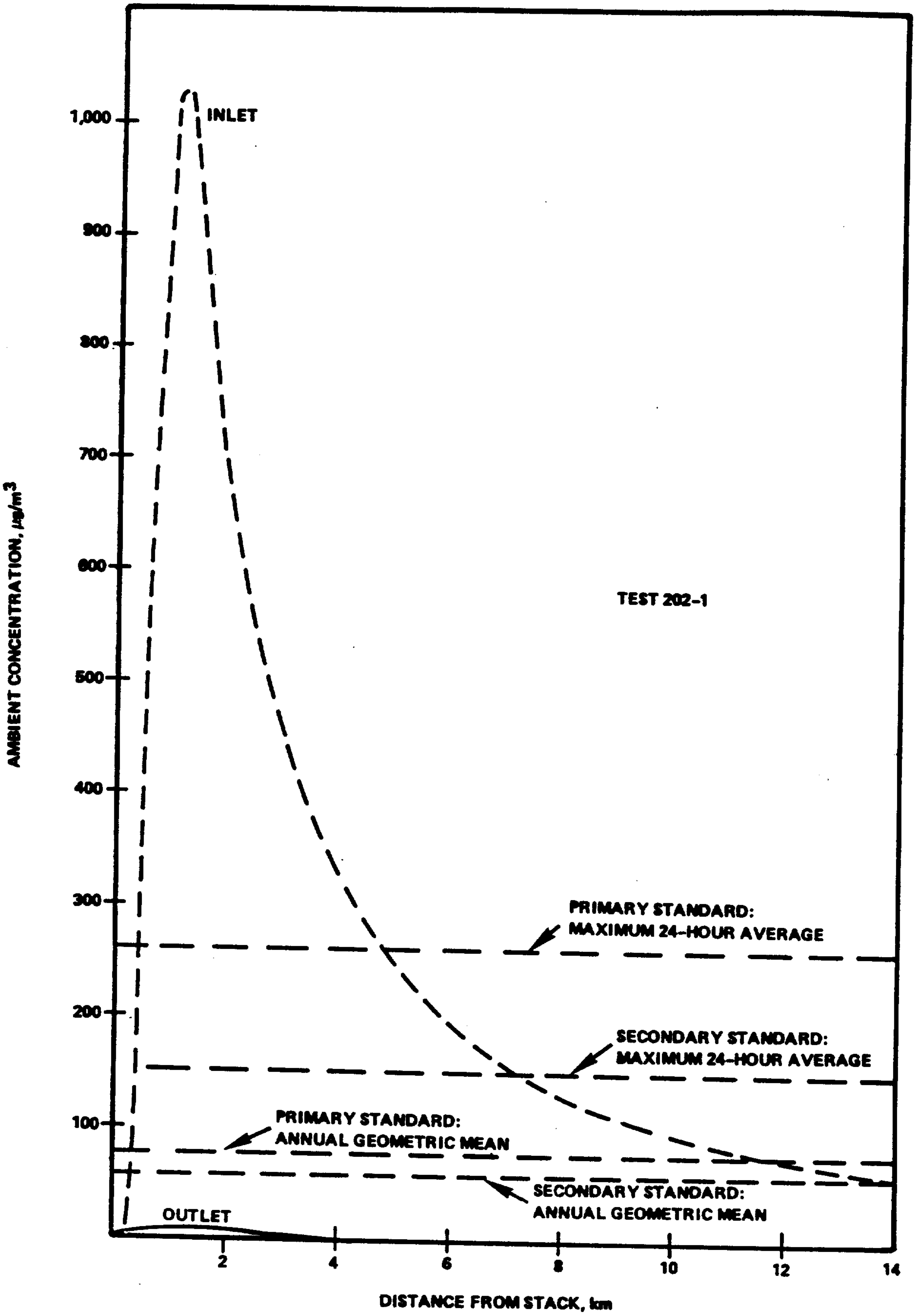

Figure 5-10. Relative particulate air quality under typical weather conditions-coal firing.

- CO standards are not exceeded under any conditions. The most restrictive standard is 10 mg/m^3 (10,000 μg/m^3) and the maximum predicted level is only about 0.2% of this value. As with NO_x there is no substantial difference between the cases based on scrubber inlet and outlet data.

- All primary SO_2 standards are exceeded under both weather conditions for uncontrolled emissions. For controlled emissions no standard is exceeded under either weather condition.

- All particuate standards are exceeded under both weather conditions for uncontrolled emissions. For controlled emissions no standard is exceeded.

TABLE 5-37. NATIONAL AMBIENT AIR QUALITY STANDARDS FOR CRITERIA POLLUTANTS

Pollutant	Pollutant standard Primary*	Secondary†
Nitrogen dioxide	100 μg/m^3(0.05 ppm) annual arithmetic mean.	Same as primary
Carbon monoxide	10 mg/m^3 (9 ppm) maximum 8-hour average; 40 mg/m^3 (35 ppm) maximum 1-hour average.	Same as primary
Sulfur dioxide	80 μg/m^3(0.03 ppm) annual arithmetic mean: 365 μg/m^3 (0.14 ppm) maximum 24-hr average.	1300 μg/m^3 (0.05 ppm) maximum 3-hour average
Total suspended Particulate	75 μg/m^3 annual geometric mean: 260 μg/m maximum 24-hr average.	60 μg/m^3 annual geometric mean: 150 μg/m^3 maximum 24-hr average.

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*Primary, necessary to protect the public health.

† Secondary, necessary to protect the public welfare.

CONCLUSIONS - COAL FIRING IN A 10 MW INDUSTRIAL BOILER WITH FGD

1) Uncontrolled emissions of criteria pollutants generally corresponded well with values reported in AP-42. Although NO_x emissions were slightly higher than the average AP-42 value, they appear to be within the normal range for similar industrial units.

2) NO_x reductions varying from approximately 0 to 24 percent were measured across the scrubber. However, the magnitude of NO_x reductions could not be correlated to changes in variables monitored during the test period (i.e., temperature, gas flow rate, boiler load, etc.). For this reason, it is considered feasible that observed NO_x reductions are a sampling phenomenon, perhaps related to leaks in the sample train.

3) Sulfur dioxide removal data indicated an average scrubber efficiency of 97 percent. Controlled SO_2 emissions were 36.3 ng/J (0.08 pounds/MM Btu) which is less than either existing or proposed NSPS limitations for utility boilers.

4) Mass balance data indicate that the multiclone unit upstream of the scrubber was removing little or no fly ash during the test period. Under the resulting near full fly ash loading, the scrubber removed 99.4 percent of the inlet particulates.

5) Although the removal efficiency for total particulates is high, there appears to be a net increase in emission rates across the scrubber for particulates less than 3 μm in size. This net increase can be attributed to the poor removal efficiency of the scrubber for fine particulates, and to the sodium bisulfate ($NaHSO_4$) and calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2H_2O$) particulates generated by the scrubber. Both $NaHSO_4$ and $CaSO_3 \cdot 1/2H_2O$ have been identified at the scrubber outlet but not at the inlet.

6) The relatively poor removal efficiency (approximately 30%) for SO_3 across the scrubber is an indication that SO_3 is either present as very fine aerosols in the scrubber inlet, or is converted to very fine aerosols as the flue gas stream is rapidly cooled inside the scrubber.

7) The overall removal efficiency for trace elements across the scrubber is 99.5 percent. Of the 22 major trace elements, 18 exceed their MATE values at the scrubber inlet and four at the scrubber outlet. The four trace elements in the scrubber effluent that pose a potential hazard are arsenic, chromium, iron, and nickel. In addition, the emission concentration of beryllium at the scrubber outlet is equal to its MATE value. The National Emission Standard for Hazardous Air Pollutants limitation of 10 grams beryllium per day would not be exceeded except by boilers of 50 MW capacity or greater at this concentration.

8) The relative removal efficiency for trace elements across the scrubber can be explained by enrichment theory. In general, trace elements that occur as element vapors or form volatile compounds at furnace temperatures are more concentrated in the smaller particulates, as a result of subsequent condensation and surface adsorption. These are the same trace elements that are removed less efficiently by the scrubber.

9) ESCA analysis has shown that while there may be higher surface concentration of sulfur containing compounds in the particulates emitted from the scrubber, most of the sulfur containing compounds are probably present as solid sulfates and sulfites. Thus, it is conceivable that sulfuric acid vapor is condensed and deposited on the particulates emitted, whereas sodium bisulfate and calcium sulfite hemihydrate are emitted as fine, solid particulates.

10) The overall sulfur balance indicates that over 92 percent of the fuel sulfur is emitted as SO_2, less than 1 percent of the fuel sulfur is emitted as SO_3, and approximately 3 percent of the fuel sulfur is emitted as $SO_4^{=}$.

11) Total organic emissions were generally less than 9 ng/J (0.02 pound/MM Btu) and these emissions appear to be primarily C_1 to C_6 hydrocarbons and hydrocarbons heavier than C_{16}. While uncontrolled emission rates for C_7 to C_{16} and higher hydrocarbons are low, emissions of these organics were further reduced by 21% and 85%, respectively, in the scrubber unit.

12) Polycyclic organic material (POM) was not found in the scrubber inlet or outlet at detection limits of 0.3 $\mu g/m^3$. MATE valves for most POM's are greater than this detection limit. However, since the MATE values for at least two POM compounds - benzo(a)pyrene and dibenz(a,h)anthracene - are less than 0.3 $\mu g/m^3$, additional GC/MS analyses at higher sensitivity would be required to conclusively preclude the presence of all POM's at MATE levels.

13) The combined wastewater stream generated from the boiler operation apparently does not pose an environmental hazard, since the discharge concentrations of most inorganics and organics are all well below their MATE values. However, based on the uncertainty in SSMS analyses, cobalt, cadmium, nickel and copper may exceed their MATE values based on ecological considerations.

14) The scrubber cake produced contains a significant amount of coal fly ash. With the exception of boron, trace element concentrations in the scrubber cake exceeded their health MATE values. All ecology MATE values were exceeded. Because the trace elements may leach from the disposed scrubber cake,

these solid wastes must be disposed of in specially designed landfills.

15) Mass balance closure for most of the trace elements have been found to be in the 75 to 107 percent range. This closure instills confidence on the validity of the sampling and analysis data for trace elements.

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SECTION 6
COMPREHENSIVE ASSESSMENT OF OIL FIRING CASE FOR AN INDUSTRIAL BOILER

This section provides a comprehensive multimedia assessment of emissions/effluents associated with an oil-fired industrial boiler equipped with an FGD system. Data from Level I/Level II sampling and analyses are utilized to quantitatively determine emissions in gas, solid and liquid waste streams and to evaluate performance of pollution control equipment in use during oil firing. Waste stream pollutant concentrations are compared with Minimum Acute Toxicity Effluent (MATE) values, where appropriate, to provide an indication of risk to public health and ecology. Simplified air quality models are used to determine the relative ground level air quality resulting from both uncontrolled and controlled emissions.

TEST CONDITIONS

Five oil-fired tests were performed on the industrial boiler at the Firestone facility. Unit loadings ranged from 31,800 to 45,400 kg steam per hour (70,000 to 100,000 pounds per hour) which corresponds to between 70 and 100% of full load operation for this boiler. Specific test conditions are presented in Table 6-1. Tabulated fuel feed rates are nominal, although oil analysis and steam production data indicate that they are accurate to within 3% if a 90% thermal efficiency is assumed. Oxygen concentrations presented in Table 6-1 were measured in flue gas samples drawn from the inlet of the scrubber unit. Due to air leaks into upstream ducting operating at sub-atmospheric pressure and the possibility of air leaks in the sampling train, tabulated oxygen concentrations are not generally representative of concentrations at the furnace outlet. During normal operation, oxygen concentrations in the furnace after combustion range from 3 to 4% which corresponds to an excess air input of 17 to 25% for oil firing. Estimated excess air levels presented in Table 6-1 were computed assuming an average oxygen concentration of 3.5% in the furnace and utilizing fuel analyses data.

Test data relating to flue gas flow rates and scrubber loading are summarized in Table 6-2. Flue gas flow rates through the scrubber were

TABLE 6-1. SUMMARY OF TEST CONDITIONS - OIL FIRING

Test No.	Steam Production Rate		% of Maximum Load	Nominal Oil Feed Rate, Gal/hr	% O_2 at Scrubber Inlet*	Estimated % Excess Air to Furnace+
	kg Steam/hr	lb Steam/hr				
202-1	45,400	100,000	100	900	5.8	21
202-2	45,400	100,000	100	900	6.3	21
202-3	44,200	97,500	97.5	880	6.1	21
202-4	42,200	93,000	93.0	805	4.0	21
203	31,800	70,000	70.0	600	Not Measured	21

*Due to air leaks in ducting upstream of the scrubber inlet, tabulated O_2 values are not representative of combustion zone O_2 concentrations. Combustion zone O_2 concentrations normally range from 3 to 4% for this unit.

+% excess air is estimated to be $100 \times \frac{O_2 - CO/2}{0.264\ N_2 - (O_2 - CO/2)}$, where O_2 was assumed to be 3.5% and other species concentrations were computed from fuel analyses.

TABLE 6-2. FRACTION OF FLUE GAS PROCESSED BY SCRUBBER DURING OIL COMBUSTION

Test No.	Flow Rate at Scrubber Inlet,* dscm/min	% of Design Load	Total Flue Gas Flow Rate,* dscm/min	Fraction Processed by the Scrubber
202-1	193	109.0	824	0.24
202-2	192	108.5	850	0.23
202-3	189	107.8	818	0.23
202-4	155	87.6	657	0.24
203	171	96.6	537	0.32
Average	180	101.9	737	0.25

*Dry standard cubic meters per minute (dscm/min).

155 to 193 dry standard cubic meters per minute (dscm/min) which corresponds to between 88 and 109% of full design loading. As discussed in Section 5, the scrubber is a pilot unit which does not process the entire flue gas output of the furnace. From 23 to 32% of the total flue gas was processed through the scrubber during oil-firing tests.

Ultimate analyses of fuel oil samples for the five oil fired tests are presented in Table 6-3. The fuel composition was essentially constant during testing. Additional analyses were performed on fuel samples from test 202-4 to determine concentrations of 22 trace elements (Ca, Mg, Sb, As, B, Cd, Cr, Co, Cu, Pb, Mn, Mo, Ni, V, Zn, Se, Sr, Fe, Al, Be, Hg and Zr). These data are presented in Table 6-4. The method employed for analysis of most of these elements was Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) which is generally considered to be more accurate than Spark Source Mass Spectrometry (SSMS).

TABLE 6-3. SUMMARY OF ULTIMATE OIL ANALYSES

Weight %	202-1	202-2	202-3	202-4	203	Average	σ[*]
Carbon	85.96	85.83	86.54	86.77	86.29	86.28	0.39
Hydrogen	10.95	10.88	10.95	10.92	10.89	10.92	0.03
Nitrogen	0.31	0.34	0.42	0.30	0.42	0.36	0.06
Sulfur	2.08	1.95	1.97	1.97	1.85	1.96	0.08
Ash	0.02	0.02	0.02	0.01	0.02	0.02	0.004
Oxygen	0.68	0.98	0.10	0.03	0.53	0.46	0.40
kJ/kg	-	-	-	-	-	40,741[+]	-

[*] σ = One standard deviation.

[+] The heat content of the oil burned is nearly constant at this value; individual values were not available.

TABLE 6-4. CONCENTRATION OF MAJOR TRACE ELEMENTS IN OIL (TEST 202-4)

Element	ppm in Fuel Oil	Typical Range[*]	Reference
Ca	5.50	No Data	
Mg	<0.4	No Data	
Sb	0.03[†]	0.002-0.8	1
As	2.0[‡]	0.0006-1.1	1
B	<0.15	No Data	
Cd	<3.5	No Data	
Cr	2.2	0.002-0.02	1
Co	<1.25	No Data	
Cu	1.40	No Data	
Fe	12.3	0.003-14	1,2
Pb	2.6[†]	No Data	
Mn	0.4[†]	0.001-6	1
Mo	2.9[†]	<0.1-1.5	1
Ni	16.0	14-68	3
V	36.5	15-590	3
Zn	3.0	No Data	
Se	0.7[†]	0.03-1	1
Sr	0.23	No Data	
Al	3.5	No Data	
Zr	<0.05	No Data	
Be	<0.05[**]	No Data	
Hg	0.09[††]	0.02-30	1

[*] Except for V and Ni, these ranges are for U.S. and foreign crude oils. Ranges of V and Ni concentrations are for fuel oils.

[†] Values were calculated from concentrations at the scrubber inlet when ICPOES analysis provided upper limit data only.

[‡] Arsenic concentration calculated from concentration at the scrubber inlet (see text).

[**] Performed by SSMS on a feed oil sample from test 203.

[††] Performed by cold vapor analysis on a feed oil sample from test 203.

However, oil beryllium was analyzed by SSMS on a sample from test 203, and mercury was analyzed using cold vapor analysis on the same sample. Several of the oil trace elements were below the ICPOES detection limit. Approximate values for these elements were calculated from the concentrations found at the scrubber inlet, assuming that essentially all of the oil trace elements reach the scrubber. As no bottom ash was generated during oil firing, this assumption should be valid. The value for arsenic presented in the table, 2 ppm, was also calculated because the value obtained from ICPOES analysis, 45 ppm, appeared to be unreasonable compared to both the SSMS value (0.1 ppm) and the typical ranges found in the literature.

Considering the uniformity of fuel oil ultimate analyses obtained during the test period, it appears reasonable to assume that tabulated trace element analyses are typical of the oil-fired during the five day test period. Listed for comparison are typical concentration ranges for nickle and vanadium in fuel oils, and other trace element concentrations in U.S. and foreign crude oils. The crude oil values should be used for rough comparison. Analyses of most trace elements for which typical values are available appear to be consistent with the crude oil values. Arsenic and molybdenum values are on the high side, and chromium is quite a bit higher than the typical crude oil values. However, the significance of these higher concentrations is not apparent due to the limited quantity of published data and the complete absence of source specific data.

STACK EMISSIONS

As discussed previously, the scrubber unit processed 23 to 32% of the total flue gas generated during oil firing. However, under the assumptions specified in Section 5, mass emission rate data presented in the ensuing sections are reflective of full stream loadings at the scrubber inlet and outlet.

Criteria Pollutants

Current NSPS define allowable emission rates of NO_x (as NO_2), SO_2 and total particulates from utility boilers having 25 MW or greater output. Existing NSPS for limitation of NO_x emissions from oil-fired units is 129 ng/J (0.30 lb/MM Btu) and proposed standards would impose the further requirement for 65% reduction of uncontrolled emissions. The current NSPS limitation on SO_2 emissions from oil-fired boilers is 344 ng/J (0.80 lb/MM Btu). Potential standards could impose further requirements for up to 90% reduction of uncontrolled SO_2 emissions. The existing NSPS limitation on particulate emissions is 43 ng/J (0.10 lb/MM Btu) and proposed standards would reduce this limit to 13 ng/J (0.03 lb/MM Btu). Current federal NSPS do not address either CO or total hydrocarbon emissions.

Because similar standards for industrial boilers have not been promulgated to date, criteria pollutant emissions data presented in this section will be discussed in the context of existing and proposed federal NSPS for utility boilers.

As mentioned previously, 5 oil-fired tests were performed on the Firestone industrial boiler. Criteria pollutant concentrations were generally measured at frequent intervals during each test and averaged to obtain the mean concentration for the test. The 5-test averages of criteria pollutant emissions data are presented in Tables 6-5 through 6-8. Average emissions data from the individual tests are presented in Tables 6-9 and 6-10. Additionally, the 5-test averages of scrubber inlet data are presented in Table 6-11 for comparison with the EPA AP-42 emission factors for uncontrolled sources. The data are discussed by specific compound in the ensuing sub-sections.

TABLE 6-5. CRITERIA POLLUTANT EMISSIONS FOR AN OIL-FIRED INDUSTRIAL BOILER IN CONCENTRATION UNITS (5 TEST AVERAGE)

Pollutant	mg/Nm^3 (Grain/SCF) Before Scrubber		After Scrubber	
NO_x (as NO_2)	467	(0.20)	450	(0.20)
CO	15.3	(0.01)	14.9	(0.01)
SO_2	2763	(1.21)	74.3	(0.03)
Organics (as CH_4)	6.81	(0.00)	7.47	(0.00)
Total Particulates	317	(0.14)	50.7	(0.02)

TABLE 6-6. CRITERIA POLLUTANT EMISSIONS FOR AN OIL-FIRED INDUSTRIAL BOILER IN TEMPORAL UNITS (5 TEST AVERAGE)

Pollutant	kg/hr (lb/hr) Before Scrubber		After Scrubber	
NO_x (as NO_2)	22.2	(48.9)	21.4	(47.2)
CO	0.71	(1.58)	0.69	(1.52)
SO_2	130.7	(288)	3.55	(7.83)
Organics (as CH_4)	0.34	(0.75)	0.36	(0.79)
Total Particulates	14.8	(32.5)	2.28	(5.03)

TABLE 6-7. CRITERIA POLLUTANT EMISSIONS FOR AN OIL-FIRED INDUSTRIAL BOILER IN THERMAL UNITS (5 TEST AVERAGE)

Pollutant	ng/J (lb/MM Btu) Before Scrubber		ng/J (lb/MM Btu) After Scrubber	
NO_x (as NO_2)	168	(0.39)	161	(0.37)
CO	5.47	(0.01)	5.31	(0.01)
SO_2	993	(2.31)	26.8	(0.06)
Organics (as CH_4)	2.49	(0.01)	2.74	(0.01)
Total Particulates	113	(0.26)	17.6	(0.04)

TABLE 6-8. CRITERIA POLLUTANT EMISSIONS FOR AN OIL-FIRED INDUSTRIAL BOILER IN PRODUCTION RATE UNITS (5 TEST AVERAGE)

Pollutant	mg/Kg Steam (lb/1000 lb. steam) Before Scrubber		mg/Kg Steam (lb/1000 lb. steam) After Scrubber	
NO_x (as NO_2)	499	(0.50)	482	(0.48)
CO	16.1	(0.02)	15.5	(0.01)
SO_2	2945	(2.95)	79.7	(0.08)
Organics (as CH_4)	7.62	(0.01)	7.99	(0.01)
Total Particulates	331	(0.33)	51.6	(0.05)

TABLE 6-9. SUMMARY OF CRITERIA POLLUTANT EMISSIONS - OIL FIRING

Test No.	ng/J (lb/MM Btu)							
	NO_x	CO	SO_2	HC† (as CH_4)	C_1 - C_6 Organics	C_7 - C_{16} Organics	Organics Higher Than C_{16}	Total Particulates
202-1 Inlet	175 (0.41)	5.08 (0.01)	938 (2.18)	2.84 (0.01)	<4.63 (< 0.01)	--	--	166 (0.39)
202-1 Outlet	166 (0.39)	4.70 (0.01)	32.1 (0.07)	3.20 (0.01)	<4.63 (< 0.01)	--	--	20.2 (0.05)
202-2 Inlet	175 (0.41)	5.30 (0.01)	1075 (2.50)	4.61 (0.01)	<4.79 (< 0.01)	--	--	--
202-2 Outlet	165 (0.38)	5.03 (0.01)	29.2 (0.07)	5.01 (0.01)	<4.79 (< 0.01)	--	--	--
202-3 Inlet	181 (0.42)	6.22 (0.01)	1085 (2.52)	1.71 (0.00)	<4.73 (< 0.01)	--	--	--
202-3 Outlet	177 (0.41)	5.92 (0.01)	26.7 (0.06)	1.98 (0.01)	<4.73 (< 0.01)	--	--	--
202-4 Inlet	141 (0.33)	5.30 (0.01)	874 (2.03)	0.82 (0.00)	<4.14 (< 0.01)	--	--	59.0 (0.14)
202-4 Outlet	138 (0.32)	5.60 (0.01)	19.2 (0.04)	0.76 (0.00)	<4.14 (< 0.01)	--	--	15.0 (0.03)
203 Inlet*	--	--	--	--	--	0.17 (0.00)	2.61 (0.01)	--
203 Outlet*	--	--	--	--	--	0.02 (0.00)	0.43 (0.00)	--
Average Inlet	168 (0.39)	5.47 (0.01)	993 (2.31)	2.49 (0.01)	<4.57 (< 0.01)	0.17 (0.00)	2.61 (0.01)	113 (0.26)
Average Outlet	161 (0.37)	5.31 (0.01)	26.8 (0.06)	2.74 (0.01)	<4.57 (< 0.01)	0.02 (0.00)	0.43 (0.00)	17.6 (0.04)

[*] Emission factors were computed assuming an O_2 concentration of 5.5%, the average concentration for test 202.

[†] Total hydrocarbons as determined by FID.

TABLE 6-10. SUMMARY OF CRITERIA POLLUTANT EMISSIONS - OIL FIRING

Test No.	kg/hr							
	NO_x	CO	SO_2	HC (as CH_4)	C_1 - C_6 Organics	C_7 - C_{16} Organics	Organics Higher Than C_{16}	Total Particulates
202-1 Inlet	23.7	0.69	128	0.39	< 0.63	--	--	22.4
202-1 Outlet	22.7	0.64	4.35	0.45	< 0.63	--	--	2.74
202-2 Inlet	24.0	0.71	146	0.61	< 0.64	--	--	--
202-2 Outlet	22.4	0.66	3.98	0.66	< 0.64	--	--	--
202-3 Inlet	24.1	0.83	143	0.25	< 0.62	--	--	--
202-3 Outlet	23.6	0.78	3.53	0.25	< 0.62	--	--	--
202-4 Inlet	16.9	0.63	106	0.12	< 0.50	--	--	7.13
202-4 Outlet	16.9	0.67	2.33	0.08	< 0.50	--	--	1.82
203 Inlet	--	--	--	--	--	0.02	0.25	--
203 Outlet	--	--	--	--	--	0.00	0.04	--
Average Inlet	22.2	0.71	131	0.34	< 0.60	0.02	0.25	14.8
Average Outlet	21.4	0.69	3.55	0.36	< 0.60	0.00	0.04	2.28

TABLE 6-11. COMPARISON OF CRITERIA POLLUTANT EMISSIONS WITH EMISSION FACTORS FOR UNCONTROLLED BOILERS

Pollutant	ng/J (lb/MM Btu) Test Data Before Scrubber		ng/J (lb/MM Btu) Average Emission Factors for Uncontrolled Sources*	
NO_x (as NO_2 at full load)	175	(0.41)	217	(0.51)
CO	5.47	(0.01)	14.7	(0.03)
SO_2	993	(2.31)	904	(2.10)
Organics (as CH_4)	2.49	(0.01)	2.94	(0.01)
Total Particulates	113	(0.26)	29.4	(0.07)

*Factors are computed from EPA AP-42 values using the national average oil heating value of 146,285 Btu/gal (Reference 4).

Nitrogen Oxides

Average NO_x emissions measured during oil-firing were 168 ng/J (0.39 lb/MM Btu) prior to FGD processing. Full load NO_x emissions were 175 ng/J (0.41 lb/MM Btu) prior to FGD processing. This emission rate is approximately 19% lower than the tabulated AP-42 emission factor of 217 ng/J (0.51 lb/MM Btu) for 10 MW oil-fired industrial boilers. However, available published data indicate that the measured uncontrolled NO_x emission rate is well within the range typical of oil-fired industrial boilers (Reference 5). Average NO_x emissions after FGD were 161 ng/J (0.37 lb/MM Btu) which is 23% higher than the current NSPS limitation of 129 ng/J (0.30 lb/MM Btu). As indicated in Table 6-9, NO_x emissions decreased upon decreasing the boiler load from 100 to 93%, as expected. However, comparison of full load NO_x emission rates with 97.5% loading data (175 ng/J at full load versus 181 ng/J at 97.5% loading) indicates slight data scatter which appears to be on the order of 10 ng/J.

Data presented in Table 6-9 indicate NO_x reduction across the scrubber for all oil-fired tests; the magnitude of measured average reduction is from 2 to 6%. However, the larger NO_x reductions of 5 and 6% measured during tests 202-1 and 202-2 are reflective, at least in part, of a small air leak which was discovered in the sampling line to the scrubber outlet. This leakage problem, associated with a faulty coupling, was rectified prior to tests 202-3 and 202-4. Data from the latter tests indicate NO_x reductions of approximately 2%. Hence, NO_x removal during this test period appears to be approximately 2% as indicated by tests 202-3 and 202-4 rather than the somewhat higher value indicated by tests 202-1 and 202-2.

Carbon Monoxide

Emission rates of CO prior to FGD were 5.47 ng/J (0.01 lb/MM Btu). This measured average CO emission rate is nearly 63% lower than the AP-42 value of 14.7 ng/J (0.03 lb/MM Btu) for uncontrolled oil-fired industrial boilers. Average CO emissions after FGD processing were 5.31 ng/J (0.01 lb/MM Btu). Although average CO emission data indicate a 3% reduction across the scrubber, data from the tests which were not subject to known problems with the sampling train (tests 202-3 and 202-4) indicate a 6% increase to a 5% reduction across the scrubber. Further, at these low CO concentrations, analytical sensitivity is approximately 15% of the measured value. Therefore, the slight reduction in CO measured across the scrubber is considered to be of little significance.

Sulfur Dioxide

Average SO_2 emissions prior to scrubbing were 993 ng/J (2.31 lb/MM Btu). Measured SO_2 emissions compare well with the AP-42 value of 904 ng/J (2.10 lb/MM Btu) for uncontrolled oil-fired industrial boilers. Average SO_2 emissions after scrubbing were 26.8 ng/J (0.06 lb/MM Btu) which corresponds to 97% FGD efficiency. The controlled SO_2 emission rate of 26.8 ng/J is substantially lower than either the existing NSPS limitation of 344 ng/J (0.80 lb/MM Btu) or potential standards requiring up to 90% reduction.

Hydrocarbons

Emissions of hydrocarbons measured as methane were, on the average, 2.49 ng/J (0.01 lb/MM Btu) prior to scrubbing. The measured uncontrolled hydrocarbon emission appears to compare well with the AP-42 average value of 2.94 ng/J (0.01 lb/MM Btu) for uncontrolled oil-fired industrial boilers. However, it should be noted that, during these tests, flue gas samples were processed through a gas conditioner prior to FID analysis. Therefore, higher molecular weight organics may have been scrubbed or condensed from the sample gas slipstream prior to analysis. As will be subsequently discussed, total hydrocarbon emissions measured by FID analysis of the scrubber inlet gas may be low by a factor of 2 to 3. Emission data obtained after flue gas scrubbing generally indicate a slight increase of hydrocarbons across the scrubber unit; the magnitude of this increase is 0.25 ng/J or approximately 10%, on the average. However, examination of all real time scrubber inlet and outlet data pairs (obtained not more than 30 minutes apart) measured during the test period indicates that the difference between scrubber inlet and outlet hydrocarbon analyses is statistically insignificant. Similar treatment of the individual tests indicated that a statistically significant bias between scrubber inlet and outlet hydrocarbon analyses existed for only one of the four tests performed, namely test 202-2. Therefore, these data appear to indicate that hydrocarbon analyses measured by FID at the scrubber inlet and outlet do not differ significantly.

In addition to FID hydrocarbon analyses, gas chromatograph analyses were performed on limited bag samples of the flue gas and sample catches from the Level I sampling (SASS) train. Gravimetric analyses were also performed on Level I samples to quantify high molecular weight organics. Each bag sample was collected over an interval of 30 to 45 minutes, with a single sample being collected per test. These samples were utilized to measure C_1 to C_6 hydrocarbons. The SASS train contacts approximately 30 cubic meters of flue gas which were drawn isokinetically during the test. Analysis of SASS train samples provides quantitative measurement of organic compounds higher than C_7.

Analytical results for scrubber outlet SASS train XAD-2 resin samples were not available due to sample handling problems. However, data from oil-fired utility boilers were utilized to obtain an average ratio of resin adsorbed organics to all other organics collected by the SASS train for each fuel. These ratios were used in conjunction with data from the scrubber outlet probe rinse, resin module rinse, particulate organics and other organic catches from the SASS train to estimate the resin catch. Calculated outlet organic data from the C_7 to C_{16} and higher than C_{16} organic fractions are considered to be accurate to within a factor of two to three. Average chromatograph and gravimetric hydrocarbon analyses indicate that 35 to 94% of the scrubber inlet hydrocarbons are higher than C_{16} with the balance being composed primarily of C_1 to C_6 organics. Organics in the scrubber outlet consist of 9 to 16% hydrocarbons higher than C_{16} and, again, the balance is primarily C_1 to C_6 organics. These data indicate that 88% of the C_7 to C_{16} organics and 83% of the organics higher than C_{16} are removed by the scrubber. This corresponds to removal of 2.33 ng/J organic material which is in conflict with FID total organic data indicating no organic removal. These data may indicate that the FID was analyzing only the C_1 to C_6 fraction and that heavier fractions were removed by the gas conditioner prior to analysis. Under the assumption that FID data reflect the C_1 to C_6 fraction only, the data would indicate that 49% of the scrubber inlet hydrocarbons are higher than C_{16} with the balance being composed primarily of C_1 to C_6 organics. The scrubber outlet organics would consist primarily of C_1 to C_6 organics with 13% organics higher than C_{16}. Further, the total hydrocarbon emissions, although still low, would increase by a factor of 2 to 3.

Total Particulates

Average emission rates of total particulates at the scrubber inlet were 113 ng/J (0.26 lb/MM Btu). As discussed in Section 5, these emissions approximate uncontrolled emissions owing to multiclone malfunction during the test period. This uncontrolled emission rate is nearly a factor of four greater than the AP-42 value of 29.4 ng/J (0.07 lb/MM Btu). Data presented in Table 6-9 indicate that particulate emissions prior to scrubbing were substantially greater during test 202-1 than during test 202-4, indicating that coal ash from previous tests may have been emitted during early oil-firing tests. If particulate data from test 202-4 are assumed to be representative of oil-firing emissions, the particulate emission rate of 59 ng/J (0.14 lb/MM Btu) measured at the scrubber inlet exceeds the AP-42 value by a factor of two. This assumption appears to be valid since PLM data indicate that particulates from Test 202-4 are composed primarily of oil soot and sulfate compounds (refer to the Inorganic subsection for analysis).

Total particulate emissions after scrubbing were 17.6 ng/J (0.04 lb/MM Btu), on the average. This controlled emission rate corresponds to a scrubber particulate removal efficiency of 84%. However, based on the particulate catch known to be free of coal ash contamination, the scrubber efficiency appears to be approximately 75% for oil-firing particulates. Particulate emissions after scrubbing are well below existing NSPS standards of 43 ng/J (0.10 lb/MM Btu) although they are slightly higher than the proposed limitation of 13 ng/J (0.03 lb/MM Btu).

Particulate Size Distribution

Size distributions of oil-firing particulates at the scrubber inlet and outlet were determined with an Anderson cascade impactor. Attempts at additional size distribution determinations by PLM proved unsuccessful due to the agglomerating nature of oil soot, a major component of oil-fired particulates. As discussed previously, particulates from early oil-firing tests (such as Test 202-1) collected prior to scrubbing appear to contain residual particulate from coal fired tests. Since coal particulate is generally coarser than oil particulate, contaminated oil particulate would probably appear to be somewhat coarser than pure oil particulate samples. Impactor data for test 202-1 are summarized in Table 6-12. The substantial difference between scrubber inlet and outlet size distributions indicates that larger particulates are removed with greater efficiency than small particulates. Emission rate data and removal efficiencies are presented in Table 6-13. These data show that particulates larger than 3 microns in diameter are removed with greater efficiency than smaller particles.

TABLE 6-12. PARTICULATE SIZE DISTRIBUTION BY WEIGHT - TEST 202-1

Aerodynamic Diameter Size Range, Microns	Weight %	
	Scrubber Inlet	Scrubber Outlet
<1	20	83
1 - 3	1	12
3 - 10	74	5
>10	5	0

TABLE 6-13. EMISSION RATES OF PARTICULATES FOR AN OIL-FIRED BOILER IN TEMPORAL UNITS - TEST 202-1

Aerodynamic Diameter Size Range, Microns	kg/hr		Removal Efficiency
	Scrubber Inlet	Scrubber Outlet	
<1	4.48	2.27	49.2
1 - 3	0.22	0.33	<0
3 - 10	16.6	0.14	97.4
>10	1.12	0.00	100
Total	22.4	2.74	87.8

Sulfur Compounds: SO_2, SO_3, and $SO_4^=$

SO_2 was monitored continuously using a pulsed fluorescent analyzer. SO_3 was determined as H_2SO_4 using the Goksoyr-Ross controlled condensation system, and $SO_4^=$ was determined by anion analysis of the particulate extracts from the Method 5 sampling train. A summary of these analytical results is presented in Table 6-14. As can be seen from the sulfur balance, 90 to 92% of the input sulfur is emitted as SO_2 when emissions are uncontrolled. The removal efficiency for SO_2 is high: 97 to 98%. 28 to 29% of the SO_3 was also removed by the scrubber. This low efficiency shows that SO_3 is not associated with larger particulates, which are efficiently scrubbed, but probably as fine liquid aerosols. Using similar reasoning, the higher $SO_4^=$ removal efficiency indicates that $SO_4^=$ is more likely than SO_3 to be associated with larger particulates.

Table 6-15 shows the breakdown of the sulfate emissions into the water and acid soluble fractions before and after the scrubber. While both types of sulfates were removed by the scrubber, the fraction of water soluble sulfates increased from 56 to 88%. One explanation is that the acid soluble fraction is more efficiently removed than the water soluble fraction. This cannot be checked by comparing the removal efficiencies of the major element cations (Table 6-17) as a function of the solubility of their sulfates because the types of sulfates present are not known. A second explanation may be that the water and acid soluble fractions are removed with comparable efficiency, and that the scrubber contributes small quantities of water soluble sulfate to the gas stream passing through. Because of this possibility, an analysis effort utilizing Fourier Transform Infrared Analysis (FTIR) and X-ray diffraction analysis was initiated to determine the nature of $SO_4^=$ emissions. For the dual alkali system, possible sulfate species would be $CaSO_4$ and $Ca(HSO_4)_2$ from the scrubber regeneration step, $NaHSO_4$ and Na_2SO_4 from oxidation of $NaHSO_3$ and Na_2SO_3. Calcium sulfate and bisulfate are ruled out because of the low calcium concentration at the outlet (70 $\mu g/m^3$; see Table 6-16). Fourier transform infrared analysis showed the presence of $NaHSO_4$ at both the inlet and outlet of the scrubber, but x-ray diffraction results indicated that $NaHSO_4$ made up less than 1% of the

TABLE 6-14. SO_2, SO_3, AND $SO_4^=$ EMISSIONS FROM OIL FIRING

Pollutant	Concentration mg/m^3	Mass Emission Rate g/hr	Thermal Emission Rate ng/J	Production Emission Rate mg/kg steam	% of Fuel Sulfur Found in Flue Gas	Removal Efficiency %
SO_2						
202-1 Inlet	2582	127,500	940	2811	92	
202-1 Outlet	88.5	4,371	32.2	96.4	3	97
202-4 Inlet	2689.2	106,060	874	2514	90	
202-4 Outlet	59.2	2,335	19.2	55.4	2	98
SO_3						
202-1 Inlet	20.6	1,017	7.50	22.4	0.59	
202-1 Outlet	14.6	721	5.31	15.9	0.42	29
202-4 Inlet	25.8	1,018	8.39	24.1	0.69	
202-4 Outlet	18.6	734	6.05	17.4	0.50	28
$SO_4^=$						
202-4 Inlet	70.4	2,776	22.9	65.8	1.58	
202-4 Outlet	28.0	1,140	9.10	26.2	0.63	60
Total						
202-1 Inlet					93	
202-1 Outlet					3.6	
202-4 Inlet					93	
202-4 Outlet					3.1	

TABLE 6-15. SUMMARY OF SULFATE EMISSIONS DURING OIL-FIRING - TEST 202-4*

	mg/m^3	
	Inlet	Outlet
Water Soluble	39.7 (56%)	24.5 (88%)
Acid Soluble	30.7 (44%)	3.5 (12%)
Total	70.4	28.0

*See Appendix C, Table 15, for details.

particulate matter in the gas stream, whereas sulfates accounted for 40% of the particulate matter at the inlet and 60% at the outlet. It is possible that scrubber generated Na_2SO_4 caused the change in sulfate solubilities, but this has not been confirmed.

Inorganics

Concentrations of 22 major trace elements present in the flue gas at the scrubber inlet and outlet are presented in Table 6-16. MATE values [6] for these elements are also presented for comparison. As discussed in Section 5, tabulated MATE values represent air stream concentrations which are not considered to adversely affect human health upon short term exposure.

Of the 22 elements analyzed, 11 exceed their respective MATE values at the scrubber inlet and 5 exceed their MATE values at the scrubber outlet. The 5 elements exceeding their MATE values at the scrubber outlet are arsenic, cadmium, chromium, nickel and vanadium. The MATE value for arsenic is extremely low because arsenic is a cumulative poison producing chronic effects in humans. MATE values for nickel and chromium are extremely low due to considerations for potential human carcinogenicity. Similarly, the low MATE value for cadmium results from considerations of potential carcinogenic, oncogenic and teratogenic effects upon humans. The MATE value for

TABLE 6-16. EMISSION CONCENTRATIONS OF TRACE ELEMENTS DURING OIL-FIRING TEST 202-4

Element	Scrubber Inlet mg/m^3	Scrubber Outlet mg/m^3	MATE Value mg/m^3	Degree of Hazard[‡]	
				Scrubber Inlet	Scrubber Outlet
Be[*]	<0.001	0.001	0.002	<0.50	0.50
Hg[†]	0.0016	0.0002	0.05	0.032	0.004
Ca	0.41	0.070	16	0.026	0.004
Mg	0.31	0.030	6.0	0.052	0.005
Sb	0.062	0.006	0.050	1.24	0.120
As	0.15	0.030	0.002	75.0	15.0
B	0.53	0.039	3.1	0.171	0.013
Cd	0.28	0.066	0.010	28.0	6.60
Cr	0.17	0.018	0.001	170	18.0
Co	0.10	0.012	0.050	2.0	0.24
Cu	0.54	0.007	0.20	2.70	0.035
Fe	4.8	0.28	1.0	4.8	0.28
Pb	0.20	0.013	0.15	1.333	0.087
Mn	0.03	0.004	5.0	0.006	0.001
Mo	0.22	0.025	5.0	0.044	0.005
Ni	1.1	0.20	0.015	73.3	13.33
V	2.7	0.82	0.50	5.40	1.640
Zn	0.61	0.065	4.0	0.153	0.016
Se	0.050	0.006	0.200	0.25	0.03
Sr	0.043	0.001	3.1	0.014	0.0003
Al	5.7	0.48	5.2	1.096	0.092
Zr	0.015	0.001	5.0	0.003	0.0002
Total	18	2.5			

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[*] Beryllium was determined by Spark Source Mass Spectrometry (SSMS). The other values, with the exception of mercury, are determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) analysis.

[†] Mercury was determined by cold vapor analysis of SASS train samples taken during test 203.

[‡] Degree of hazard is defined as the ratio of the discharge concentration to the MATE value.

vanadium is comparatively higher since vanadium has been associated with eye and bronchial irritation without indication of chronic effects. Emissions of arsenic and chromium after scrubbing are below their TLV's which are each 0.5 mg/m^3. Hence, if the TLV's were used as the basis for comparison, emissions of arsenic and chromium would be considered less hazardous. Emissions of cadmium, nickel and vanadium after scrubbing exceed their TLV values of 0.05, 0.1 and 0.5 mg/m^3, respectively, in addition to exceeding their respective MATE values.

Beryllium emissions were measured to be 0.001 mg/m^3 after scrubbing; this corresponds to half the MATE value for this element. At this emission concentration, the National Standard for Hazardous Air Pollutants limitation of 10 grams beryllium per day would only be exceeded by boilers of 100 MW capacity or greater.

Emission factors and mass emission rates for the 22 elements analyzed are presented in Table 6-17. Also presented in the table are scrubber removal efficiencies for each element. An overall removal efficiency of 87% was obtained for these elements although several elements were removed with less efficiency, namely calcium, arsenic, cadmium, nickel, and vanadium. It is interesting to note that, with the exception of chromium, all elements which exceeded their MATE values at the scrubber outlet were removed with lower than average efficiency during scrubbing.

Enrichment factors across the scrubber have been computed for each element and are presented in the last column of Table 6-17. The enrichment factor is defined as the ratio of the concentrations of trace element to aluminum at the scrubber outlet divided by the corresponding ratio at the scrubber inlet. As discussed in Section 5, aluminum is selected as the reference material because it has been known to partition equally among particulates of different sizes. Tabulated enrichment factors indicate that all elements analyzed are enriched across the scrubber with the exception of boron, copper, iron, lead, strontium and zirconium. The observed enrichment is principally due to the partitioning of trace

TABLE 6-17. EMISSION FACTORS AND MASS EMISSION RATES OF TRACE ELEMENTS DURING OIL-FIRING TEST 202-4

Element	Emission Factor, ng/J		Emission Rate, g/hr		Removal Efficiency %	Enrichment Factor
	Scrubber Inlet	Scrubber Outlet	Scrubber Inlet	Scrubber Outlet		
Be*	<0.0003	0.0003	<0.04	0.04	Unknown	>11.9
Hg†	0.0006	0.0001	0.05	0.006	87	1.48
Ca	0.13	0.022	16	2.7	83	2.03
Mg	0.10	0.0094	12	1.1	91	1.15
Sb	0.02	0.0019	2.5	0.23	91	1.15
As	0.049	0.0094	5.9	1.1	81	2.37
B	0.17	0.012	21	1.5	93	0.87
Cd	0.091	0.021	11	2.5	77	2.80
Cr	0.055	0.0057	6.7	0.69	90	1.26
Co	0.033	0.0038	3.9	0.46	89	1.43
Cu	0.18	0.002	21	0.27	99	0.15
Fe	1.6	0.088	190	11	95	0.69
Pb	0.065	0.0041	7.9	0.50	94	0.77
Mn	0.010	0.0013	1.2	0.15	87	1.58
Mo	0.072	0.0079	8.7	0.95	89	1.35
Ni	0.36	0.063	43	7.7	83	2.16
V	0.88	0.26	110	31	71	3.61
Zn	0.20	0.02	24	2.5	90	1.27
Se	0.016	0.002	2.0	0.23	87	1.43
Sr	0.014	0.0003	1.7	0.038	98	0.28
Al	1.9	0.15	220	18	92	1.0
Zr	0.0049	0.0003	0.59	0.038	94	0.79
Total	6.0	0.78	710	96	87	

---

*Beryllium was determined by SSMS. The other elements, except mercury, were determined by ICPOES.

†Mercury was determined by cold vapor analysis of SASS train samples taken during test 203.

elements as a function of particulate size, and the greater collection efficiency of the scrubber for the large size particulates. It may also be noted that many of the trace elements that show enrichment, such as selenium, arsenic and mercury, either occur as elemental vapors or form volatile compounds at furnace temperatures. Condensation and surface adsorption of the more volatile elements or their compounds downstream of the furnace could, therefore, result in higher concentrationf of these elements on smaller particulates.

ESCA analyses were performed on particulates from oil firing to determine surface and subsurface elemental concentrations. The ESCA results are presented in Table 6-18 as normalized atom percentages for each particulate catch and penetration depth. Scrubber inlet data indicate that coarser particulate matter collected by the cyclone differs somewhat from finer particulates collected on the filter. The principal difference is the higher carbon and lower silica contents of the coarser particulate. It is interesting to note that the filter catch particulates from the scrubber inlet and outlet yielded very similar ESCA analyses both at the particle surface and at 76 Å penetration. Elements which appear to be enriched on the surface include sulfur, phosphorous and carbon. On the other hand, vanadium and the typical ash components aluminum and silicon appear to be more concentrated on the bulk of the particulate matter.

The composition of particulates at the scrubber inlet and outlet during Test 202-4 has also been determined by PLM analysis. Estimated weight percentages of particulate components are presented in Table 6-19. Particulates at the scrubber inlet are composed primarily of oil soot, various sulfate/sulfite compounds and fused ash while outlet particulate is composed largely of sulfates and sulfites. Sulfate data presented previously indicate that scrubber inlet particulates contain approximately 40% sulfate ion. Hence, the PLM estimate for $CaSO_3 \cdot 1/2\ H_2O$ and unknown sulfates weight percentages of 20 to 39% appears to be somewhat low. Further, the $CaSO_3 \cdot 1/2\ H_2O$ would appear to be present only as a minor constituent. This may indicate that the tabulated inlet weight percentage of oil soot, the most

TABLE 6-18. DEPTH PROFILE ANALYSIS OF OIL PARTICULATE WITH CONCENTRATIONS EXPRESSED AS NORMALIZED ATOM PERCENT* - TEST 202-4

	O	Na	S	Si	Al	Fe	Cl	P	V	Ca	C	K
Inlet												
Level II Cyclone Catch	38.5	3.2	12.9	2.6	2.3		1.4	0.6	1.2		37.4	
Level II Filter Catch	48.6	4.2	10.7	11.8	3.1		1.3	1.5	1.7		17.2	
Level II Filter Catch; 76Å	46.3	4.7	6.5	17.1	3.3	0.8	1.4	1.1	3.3	0.9	12.9	1.7
Outlet												
Level II Filter Catch	45.5	5.7	9.7	14.6	3.4	1.3	2.3	1.6	1.7		14.1	
Level II Filter Catch; 76Å	53.5	3.2	6.8	22.0	4.0		1.3	1.0	2.0		6.2	

* The atom percent of the twelve elements presented here adds up to 100 percent. Other elements present in the cyclone and filter catches were not studied in ESCA. Hence, the atom percents in this table are normalized atom percents and not absolute atom percents.

TABLE 6-19. MAJOR COAL PARTICULATE COMPONENTS - TEST 202-4

Component	Approximate Weight % Inlet	 Outlet
Ash*		
Fused	13 - 23	--
Unfused	1 - 4	--
Minerals		
Fe_2O_3	< 1	8 - 16
Fe_3O_4 (magnetite)	< 1	--
$CaCO_3$	≤ 3	--
Oil Soot	43 - 57	2 - 8
$CaSO_3 \cdot 1/2\ H_2O$ and Unknown Sulfate	20 - 39	80 - 90

*Iron-aluminum silicates.

difficult particulate component to quantify, is high with respect to the true particulate composition. Similarly, sulfate data indicate that outlet particulates are approximately 63% sulfate ion. Assuming that sulfate ions are combined with calcium or sodium, outlet particulates may consist of up to 92% sulfate compounds. Hence, $CaSO_3 \cdot 1/2\ H_2O$, if present in either the scrubber inlet or outlet, appears to be a minor constituent of particulates generated during oil-firing.

Chloride, Fluoride, and Nitrate Emissions

The results of anion analysis on extracts of particulate matter collected at the inlet and outlet of the scrubber are presented in Table 6-20. The fluoride removal efficiency is high, 89%, as would be expected, since the overall removal efficiency of the trace element cations is also high, 87%. The lower removal efficiencies for chlorides and nitrates, 52% and 57%, respectively, suggest that these anions may be associated with the finer particulate matter which is not efficiently removed by the scrubber.

TABLE 6-20. CHLORIDE, FLUORIDE, AND NITRATE EMISSIONS FROM OIL FIRING - TEST 202-4

	Inlet*		Outlet*		Removal Efficiency, %
	mg/m^3	ng/J	mg/m^3	ng/J	
Chloride (Cl^-)	0.46-0.47	0.15	0.22 -0.23	0.072-0.075	52
Fluoride (F^-)	0.054	0.017	0.006-0.008	0.002-0.003	89
Nitrate (NO_3^-)	0.24	0.076	0.102	0.033	57

*Mass as the ion.

Organics

Organics in the gaseous effluent stream were analyzed using both Level 1 (Test 203) and Level 2 (Tests 202-1 through 202-4) procedures. Samples were taken using the SASS train in Test 203 and were analyzed by gas chromatography for total chromatographable organics (GC/TCO), by gravimetry, by infrared absorption spectroscopy (IR), and by low resolution mass spectrometry (LRMS). GC/TCO analysis yields values for organics in the C_7 to C_{16} range, a value for the total concentration of high molecular weight organics is determined gravimetrically, IR analysis of the residues from the gravimetric determination identifies the classes of compounds present in the high molecular weight fraction, and LRMS on sample fractions separated by liquid chromatography (LC) provided further identification information. The subscripted carbon numbers refer to boiling ranges of organic mixtures; these are presented in Table 5-23.

In Tests 202-1 through 202-4, three types of samples were taken. The gas stream was continuously monitored with a flame ionization detector (FID) for total organics, expressed as CH_4; gas bag samples were taken for analysis of the C_1 to C_6 organics; and samples from a modified Method 5 sampling train (with an XAD-2 resin module) and from gas bags were analyzed for identification of volatiles using gas chromatography/mass spectrometry (GC/MS).

Table 6-21 summarizes the organic concentrations by category. As mentioned previously, the apparent increase in total organics across the scrubber is not statistically significant. Any C_1 to C_6 organics were present at sufficiently low concentrations that they were not detected. The C_7 to C_{16} fraction was removed with 85% efficiency, and higher molecular weight organics with 83% efficiency. In the range of C_7 and above, the concentration of higher molecular weight organics was much greater than the concentration of volatiles.

TABLE 6-21. COMPARISON OF ORGANIC MEASUREMENT METHODS

Test	Method	Organic Concentration mg/m^3 Inlet	Organic Concentration mg/m^3 Outlet	% Change
202-1	Total as CH_4 (continuous FID)	8	9	Not Significant
202-1	C_1 - C_6 (GC on bag samples)	≤12.7	≤12.7	---
203	C_7 - C_{16} (GC on SASS train samples)	0.469	0.07*	85%
203	$>C_{16}$ (Gravimetric on SASS train samples)	7.27	1.2*	83%

*The values for the XAD-2 resin fraction were calculated using data obtained from similar sampling trains on four oil-fired boilers.

Results of IR analysis on the fractionated scrubber inlet XAD-2 resin extract from SASS train samples are presented in Table 6-22. Other SASS train samples contained insufficient organic material to warrant IR analysis. It is apparent that the blank contained many organic materials released by the XAD-2 resin. This was a source of difficulty in interpreting analytical results, especially because the amount of resin-generated material seemed to vary from sample to sample. The two classes of compounds analyzed by IR which were not also found in the blank are heterocyclic sulfur compounds and sulfonic acids. LRMS identified the heterocyclic sulfur compound as dibenzothiophene, which is probably a reaction product of SO_2 and organic material from combustion or from the resin. Likewise the sulfonic acid may be an SO_2 reaction product, or it may be contamination from a cleaning agent.

Table 6-23 presents results of the GC/MS analysis. Only those compounds are listed which were not present in blank samples. None of these compounds would be directly associated with combustion. Several are, however, associated with lubricants, material used in the manufacture of gas bags, and solvents used for cleaning test apparatus. These results agree with the GC/TCO, gravimetric, and FID data indicating low organic emissions.

Polycyclic Organic Material

Polycyclic organic material (POM) was not found in either the scrubber inlet or outlet samples at detection limits of 0.3 $\mu g/m^3$. This observation is consistent with the findings to date from the EPA sponsored project "Emissions Assessment of Conventional Combustion Sources". However, two POM compounds for which MATE values are below 0.3 $\mu g/m^3$ are benzo(a)pyrene and dibenz(a,h)anthracene. The MATE values for benzo(a)pyrene and dibenz(a,h)anthracene are 0.02 $\mu g/m^3$ and 0.09 $\mu g/m^3$, respectively. While available data indicate that many POM compounds are not present at concentrations greater than or equal to their MATE value during oil firing, additional analyses at higher GC/MS sensitivity would be required to conclusively preclude the presence of all POMs at concentrations above their MATE values.

TABLE 6-22. SUMMARY OF THE INFRARED ANALYSIS OF ORGANICS FROM OIL COMBUSTION - TEST 203, INLET

Total Organics, mg/m^3	LC Fraction														Total	
	LC1 Sample/Blank		LC2* Sample/Blank		LC3 Sample/Blank		LC4 Sample/Blank*		LC5 Sample/Blank		LC6 Sample/Blank		LC7 Sample/Blank		Sample/Blank	
	0.09	0.02			0.05	0.03	0.03	0.01	0.04	0.02	0.28	0.10	0.02		0.51	0.18
Category	Intensity															
Aliphatic Hydrocarbons	XM	XM			XM	XM			Xm	Xm	Xm			Xm		
Aromatic Hydrocarbons	Xm	Xm			XM	XM	Xm		Xm	Xm	Xm			Xm		
Silicones									Xm	Xm	Xm					
Heterocyclic Sulfur Compounds									Xm		Xm		Xm			
Nitro Compounds									Om	Om			Om	Om		
Esters						Xm	XM		XM	XM	XM	XM	XM	Xm		
Amides													OM	Om		
Glycols											XM	XM	XM	XM		
Carboxylic Acids											XM	XM	XM	XM		
Sulfonic Acids													XM			
Silicates						XM										

*Not analyzed.

O = At least one species suspected present
X = At least one species present

M = Major component
m = Minor component

TABLE 6-23. ORGANIC COMPOUNDS IDENTIFIED BY GC/MS IN FLUE GAS DURING OIL FIRING

Compound	Concentration, µg/m^3			
	202-2		202-3	
	Inlet	Outlet	Inlet	Outlet
Propionaldehyde	200	---	142	---
Nitromethane	---	---	63	---
Ethyl-n-butyl Ether	1700	---	1000	---
Ethyl Acetate	---	---	---	2300
4-methyl-3-pentene-2-one	---	570	350	28
Octanol	---	---	45	---
Ketone (MW 138)	---	---	20	---
Ketone (MW 140)	14	---	---	---
Phthalic Anhydride	---	---	29	---
Amyl Benzoate	---	1.6	---	---
Glycerol Triacetate	---	---	42	---

Scrubber Efficiency

Flue gas analyses indicate that scrubber processing removes significant percentages of flue gas sulfur oxides (SO_2, SO_3 and $SO_4^=$), total particulates and organics of the C_7 class and higher. Scrubber removal efficiency data for these flue gas components are summarized in Table 6-24. The average removal efficiencies have been discussed in previous subsections. However, it is important to note that it is the C_7 and higher hydrocarbons which are removed with 84% efficiency. These fractions comprise 38 to 96% (the most accurate estimate appears to be 53%) of the organics measured at the scrubber inlet. Hence, based on the total organics generated, a 32 to 84% removal efficiency was obtained.

TABLE 6-24. SCRUBBER EFFICIENCY DURING OIL FIRING

Test Number	% Removal				
	SO_2	SO_3	$SO_4^{=}$*	Total Particulates	C_7 and Higher Organics
202-1	97	29	--	88	--
202-2	97	--	--	--	--
202-3	97	--	--	--	--
202-4	98	28	60	75	--
203	--	--	--	--	84
Average	97	29	60†	82	84†

*This removal rate is actually a net change rate. As described earlier, the scrubber removes and, possibly, generates sulfates.

†Only one data point.

It is not known for certain by what process organics are removed with such a high degree of efficiency. There are, however, at least three possible mechanisms:

- Dissolution - Some organics are partially water soluble. These compounds could be removed by dissolving in the slurry.
- Condensation - High boiling organics could condense and be removed as "particulate".
- Sorption - Some organics could adsorb on particulates.

One or any combination of these mechanisms may account for the high removal efficiencies.

LIQUID WASTE

As discussed previously, only one significant waste water stream is produced. The stream is a combination of water treatment waste, boiler blowdown, and acid waste water from elsewhere in the manufacturing plant. The quality of this combined stream is such that it is acceptable for disposal into the municipal sewer system. Liquid streams from the scrubber operation are passed to the thickener and recirculated to the scrubber after the filtration step. There is no direct wastewater discharge from the scrubber operation, as the process is designed to dispose of all of the water that enters its system through evaporation and moisture entrained in the scrubber cake.

Because several streams are mixed together, it is not possible to accurately determine what part of the effluent is attributable to the boiler. However, the flow rate of the combined stream is approximately 10,000 liters/hr (40 gallons/min).

Water Quality Parameters

Table 6-25 summarizes the waste water parameters for the combined waste water stream. Note that these values do not represent water produced solely by the boiler but also include process waste.

TABLE 6-25. COMBINED STREAM WASTE WATER PARAMETERS - OIL FIRING

Parameter	Test 202-1	Test 202-2	Test 202-3	Test 202-4	Test 203	Average
pH	7.5	6.5	7.5	6.5	6.9	7.0 ± 0.5
Hardness, mg/l (as $CaCO_3$)	105	140	155	150	110	132 ± 23
Alkalinity, mg/l (as $CaCO_3$)	135	65	120	50	140	102 ± 42
Cyanide, mg/l	0	0	0	0	0	0

Inorganics - Combined Waste Water Stream

Analyses of major inorganic cations in the combined waste water stream are presented in Table 6-26. These data are based on the SSMS technique which is accurate to within a factor of approximately 3. Of the eleven elements analyzed, none exceeds its MATE value based on health considerations while only nickel and copper may exceed their respective MATE values based on ecological considerations.

Organics - Combined Waste Water

Concentrations of C_7 to C_{16} organics measured in the combined waste water stream are summarized in Table 6-27. The only fractions analyzed to contain even low concentrations of organics were the C_{10}, C_{14} and C_{15} fractions, and these were each below 0.1 mg/liter. Higher molecular weight organics were not detected. Thus, the total quantity of organics measured in the combined waste water stream was less than 0.3 mg/liter. As a basis for comparison, the water MATE values for alkanes, alkenes and alkynes are in the 500 to 14,000 mg/liter range based on human health considerations and in the 1.0 to 100 mg/l range based on ecological considerations. Discharge concentrations of organics in the combined waste water stream are well within these MATE values.

TABLE 6-26. WASTE WATER INORGANICS - OIL FIRING

Element	mg/l	g/hr*	MATE Value, mg/l Health	MATE Value, mg/l Ecology	Degree of Hazard Health	Degree of Hazard Ecology
Be	<0.001	<0.01	0.030	0.055	0.033	0.018
F	4	40	38.0	--	0.1	--
V	0.002	0.02	2.50	0.150	0.001	0.013
Cr	0.02	0.02	0.250	0.250	0.08	0.08
Co	0.007	0.07	0.750	0.250	0.009	0.028
Ni	0.02	0.2	0.230	0.010	0.087	2
Cu	0.02	0.2	5.0	0.050	0.004	0.4
Sr	0.3	3	46.0	--	0.007	--
Cd	<0.001	<0.01	0.050	0.010	<0.02	<0.004
Sb	0.001	0.01	7.50	0.200	0.0001	0.005
Pb	0.006	0.06	0.250	0.050	0.024	0.005

*Flow rate of 10,000 liters per hour.

TABLE 6-27. SUMMARY OF C_7 - C_{16} ORGANIC IN THE WASTE WATER - OIL-FIRING

Carbon Number	mg/l	Carbon Number	mg/l
C_7	ND*	C_{13}	ND
C_8	ND	C_{14}	<0.1
C_9	ND	C_{15}	<0.1
C_{10}	<0.1	C_{16}	ND
C_{11}	ND		
C_{12}	ND	Total C_7 - C_{16}	<0.3

*ND means none detected.

SOLID WASTE

Three solid waste streams are produced by the system:

- Bottom ash;
- Fly ash;
- Scrubber cake.

Table 6-28 shows the approximate quantities of bottom ash and scrubber cake that were produced. Only small quantities of fly ash were collected during the test period due to the inefficiency of multiclones in capturing fine particulates generated during oil firing.

The scrubber cake produced after filtration has the appearance of a clayey silt. Its grain size is quite uniform and characteristic of silty soils, but its behavior closely resembles a clay in many respects. As obtained from the vacuum filter, the scrubber cake consists of small lumps and appears to be relatively dry; in actuality, however, the water content generally ranges from about 30 to 50%.

Assuming that calcium sulfite hemihydrate ($CaSO_3 \cdot 1/2\ H_2O$) is the principal product from SO_2 scrubbing and Na_2SO_3 regeneration, data presented in Table 6-29 represent the estimated composition of scrubber cake produced during oil-firing. Although the scrubber cake production rate was not measured for Test 202-4, it has been estimated as the average of production rates determined for other oil-fired tests performed. Data presented in Table 6-29 indicate that the cake is composed of 44 to 50% unbound water and at least 47% calcium sulfite hemihydrate. These data reflect the low particulate emissions which are characteristic of oil firing. Only 1% of the scrubber cake is estimated to be particulate.

Although the scrubber cake material is composed predominately of relatively insoluble solids (calcium sulfite, calcium sulfate, and some calcium carbonate), the intersititial water does contain soluble residues of lime, sulfate, sulfite and chloride salts. Trace elements in the fly ash may also contribute to the leachate from the disposed scrubber cake and are of special concern. Concentrations of 20 trace elements in the scrubber

TABLE 6-28. SOLID WASTE PRODUCTION RATES - OIL FIRING

Test	Bottom Ash		Scrubber Cake*	
	kg/hr	ng/J	kg/hr	μg/J
202-1	<1	< 7.4	400	2.9
202-2	<1	< 7.4	550	4.1
202-3	<1	< 7.6	380	2.9
202-4	<1	< 8.3	Not Measured	
203	<1	<11.1	Not Measured	

*Scaled up to represent 100% of the flue gas for boiler No. 4.

TABLE 6-29. ESTIMATED SCRUBBER CAKE MASS BALANCE FOR OIL FIRING - TEST 202-4

Component	Contribution to Scrubber Cake	
	kg/hr	Weight %
Fly Ash Removed by Scrubber	5	1
$CaSO_3 \cdot 1/2\ H_2O$ Formed from SO_2 Scrubbing and Na_2SO_3 Regeneration	210	47
$CaSO_4$, $CaCO_3$, Na_2SO_4, $Ca(OH)_2$ $NaHSO_3$ and Na_2SO_3 Losses (Estimated)	6 - 35	1 - 8
Water	193 - 222	44 - 50
Total	443*	100

*Total cake production rate was estimated from the average of tests 202-1, 202-2 and 202-3.

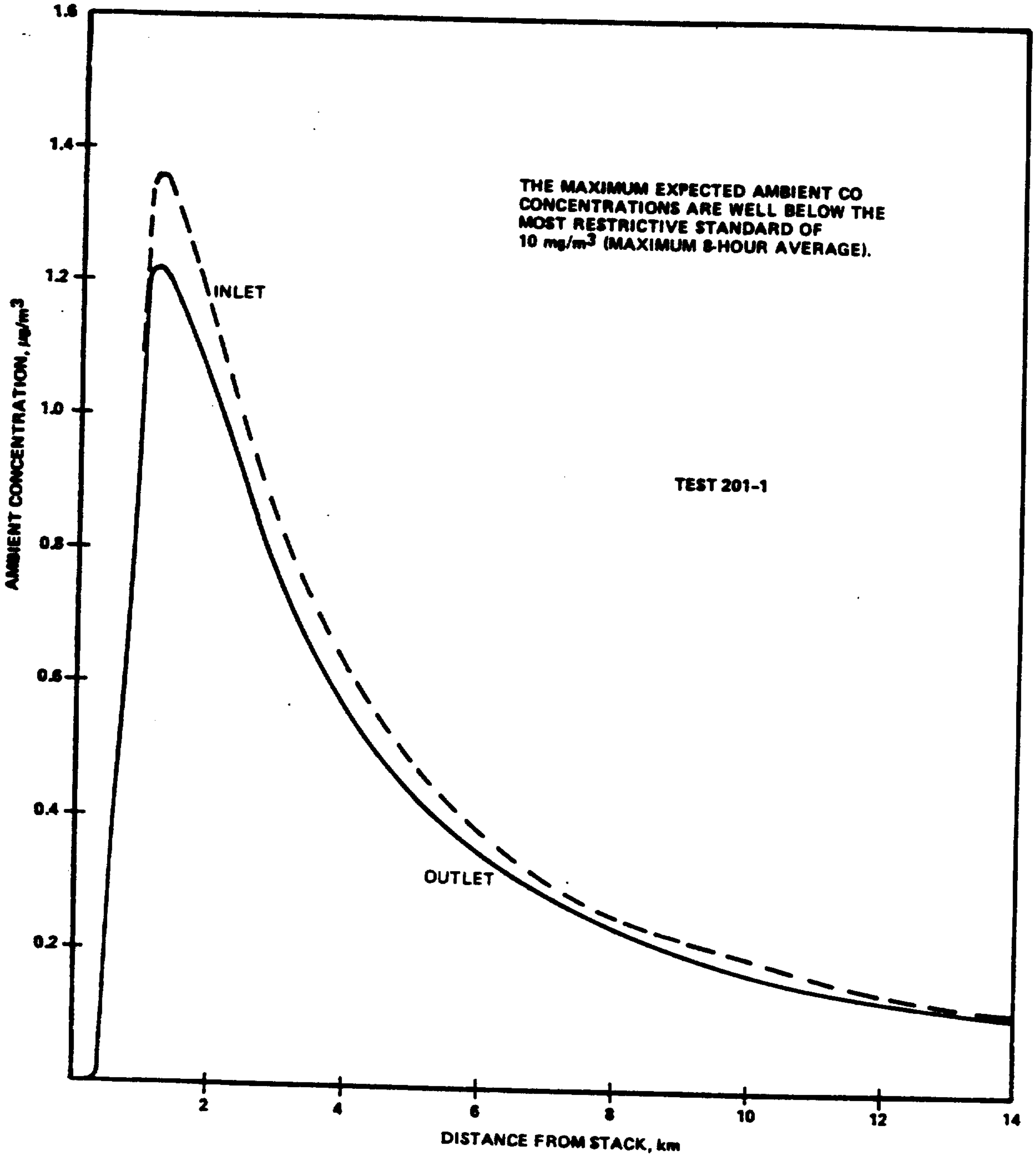

Figure 6-4. Relative CO air quality under typical weather conditions - oil firing

TABLE 6-30. INORGANIC CONTENT OF SCRUBBER CAKE FROM OIL FIRING (DRY BASIS) - TEST 202-4

Element	Concentration µg/g	MATE Value, µg/g		Degree of Hazard	
		Health	Ecology	Health	Ecology
Ca	200,000	480	32	417	6,250
Mg	3,799	180	174	21	22
Sb	3*	15	0.4	0.2	7.5
As	15*	0.5	0.1	30	150
B	40	93	50	0.4	0.8
Cd	1*	0.1	0.002	10	500
Cr	15	0.5	0.5	30	30
Co	19*	1.5	0.5	13	38
Cu	16	10	0.1	2	160
Fe	2,164	3.0	0.5	721	4,328
Pb	6*	0.5	0.1	12	60
Mn	6	0.5	0.2	32	80
Mo	14*	150	14	0.1	1
Ni	132	0.45	0.02	293	6,600
V	203	5.0	0.3	41	677
Zn	36	50	0.2	0.7	180
Se	9*	0.10	0.05	90	180
Sr	239	92	--	2.6	--
Al	1,684	160	2.0	11	842
Zr	37	15	--	2.5	--
Total	208,450				

*SSMS analyses were utilized where ICPOES analysis provided upper limit data only.

TABLE 6-31. MASS BALANCE OF TRACE ELEMENTS - TEST 202-4

Element	Oil Feed g/min	Scrubber Cake g/min	Scrubber Outlet g/min	Percent[‡] Recovery
Ca	16.4	50,000	2.8	**
Mg	(12.2)[†]	950	1.2	>1,000
Sb	(2.4)	0.8*	0.2	42
As	(5.9)	3.9*	1.2	68
B	(20.9)	10.0	1.5	55
Cd	(11.0)	0.2*	2.6	25
Cr	3.6	3.9	0.7	125
Co	(3.9)	4.7*	0.5	133
Cu	4.2	4.1	0.3	105
Fe	36.7	541	11.0	>1,000
Pb	(7.9)	1.5*	0.5	25
Mn	(1.2)	4.0	0.2	350
Mo	(8.7)	3.5*	1.0	52
Ni	47.7	33.0	7.9	91
V	108.8	50.7	32.3	76
Zn	8.9	9.1	2.7	133
Se	(2.0)	2.4*	0.2	136
Sr	0.7	59.8	0.04	>1,000
Al	10.4	421	18.9	>1,000
Zr	(0.6)	9.2	0.04	>1,000

* SSMS data were utilized where ICPOES analysis provided upper limit data only.

[†] ICPOES data from the analysis of scrubber inlet particulates were utilized when fuel analysis provided upper limit data only.

[‡] Percent recovery of a trace element is 100 times the ratio of its total emission rate (scrubber cake plus scrubber outlet) to its feed rate.

** Percent recovery for calcium is not calculated because most of the calcium in the scrubber cake is from the lime slurry.

ANNUAL EMISSIONS

Table 6-32 presents an estimate of the annual emissions of the major pollutants for the controlled and uncontrolled case. It was assumed that the boiler operates at 100% load, 87% of the year (7560 hours/year), and that oil is the only fuel burned.

AIR QUALITY ASSESSMENT - OIL FIRING

Simplified air quality models were used to determine relative air quality resulting from uncontrolled and controlled emissions. The ambient air quality values are approximate only. The emphasis should be placed on the relative values for each case as opposed to their absolute values.

Worst case weather conditions and typical weather conditions were considered. The worst case was assumed to be plume trapping. An equation proposed by Bierly and Henson [Ref. 7] was used with the following assumptions: inversion height 100 meters, wind speed 1.0 meter/second, D class stability (neutrally stable) in the mixing layer and an effective stack height of 50 m (164 ft). The typical case was assumed to correspond to the standard Gaussian convective diffusion equation, [Ref. 8]. The following conditions were used: wind speed 4.0 meters/second and D class stability. These represent conditions that could reasonably be expected to occur almost anywhere in the country. Typical does not mean average. It was assumed that all species were inert. No photochemical reactions were considered. (See Appendix A for details.)

Figures 6-1 through 6-8 present plots of approximate ground level ambient air quality as a function of distance directly downwind from a single 10 MW equivalent source. Data for NO_x, CO, SO_2 and particulates are presented. The purpose of these figures is not to attempt to accurately predict air quality but rather to compare the effects of controlled and uncontrolled emissions under an arbitrary but realistic set of meteorological conditions. It is implicit in this approach that each set of meteorological conditions remains constant for a sufficient length of time

TABLE 6-32. ANNUAL EMISSIONS - OIL FIRING[*]

	Pollutant	kg/year Scrubber Inlet	 Scrubber Outlet	% Difference
Gaseous	NO_x (as NO_2)	164,230	157,390	- 4
	SO_2	906,020	24,453	- 97
	SO_3	7,249	5,183	- 28
	$SO_4^{=}$	20,894	8,303	- 60
	CO	4,991	4,845	- 3
	Organics (as CH_4)	2,272	2,500	+ 16
	C_1 - C_6	<4,164[†]	<4,164[†]	--
	C_7 - C_{16}	155	18	- 88
	$>C_{16}$	2,381	392	- 83
	Total particulates[‡]	53,832	13,686	- 75
	<1μ	--	11,359	--
	1 - 3μ	--	1,642	--
	3 - 10μ	--	684	--
	>10μ	--	0	--
		m^3/year		
Liquid	Blowdown/waste water	~76,000	~76,000	0
	Cooling water	~86,000	~86,000	0
		kg/year		
Solid	Bottom ash	~ 7,600	~ 7,600	0
	Fly ash	~15,000	~15,000	0
	Scrubber cake	0	3,011,000	-

---

[*] Assuming 100% load, 45 weeks per year (7,560 hrs/year).

[†] These values represent the detection limit of the instrument used.

[‡] These values represent oil firing particulate with a minimum of coal ash contamination.

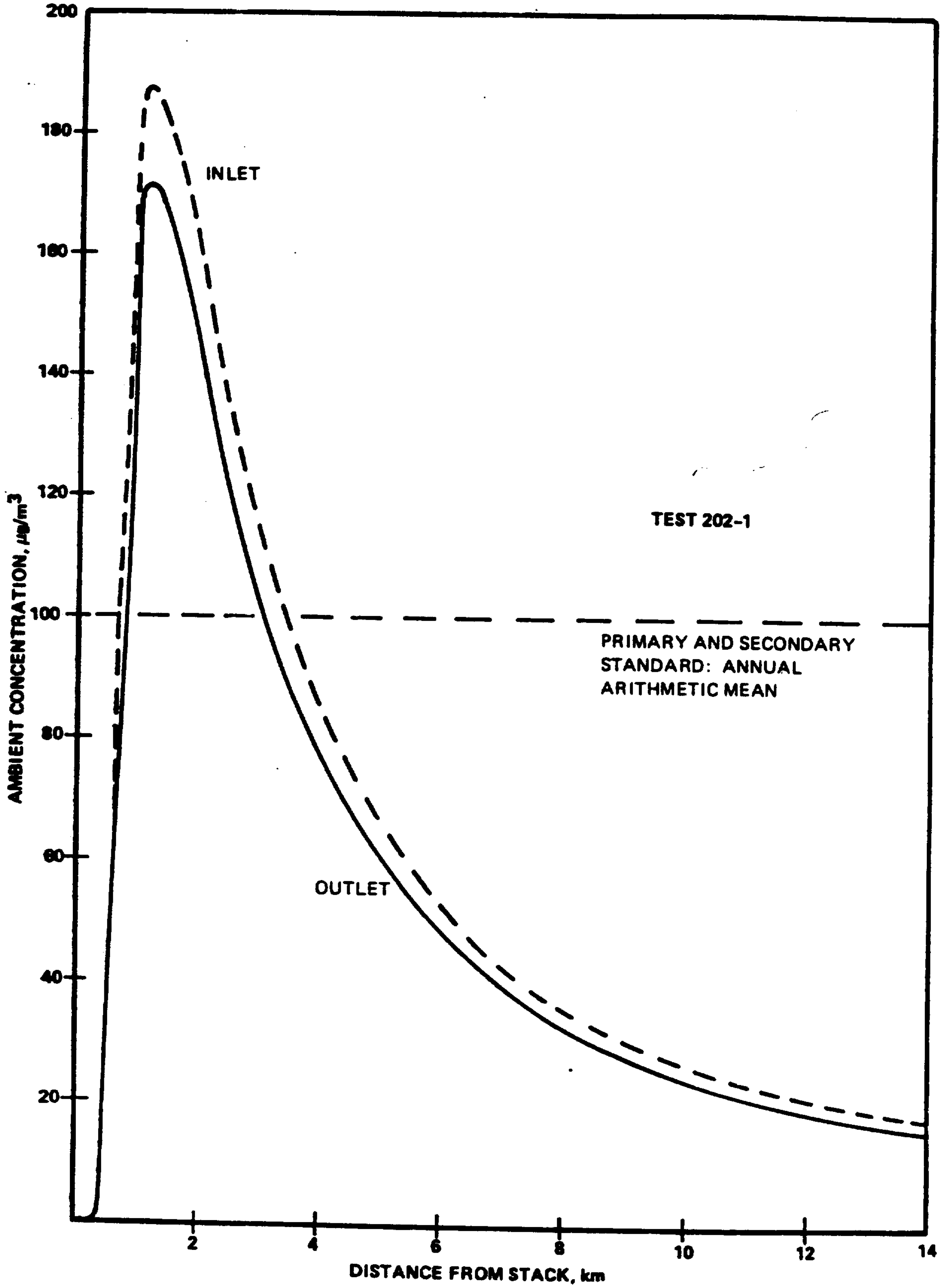

Figure 6-1. Relative NO_x air quality under worst case weather conditions - oil firing

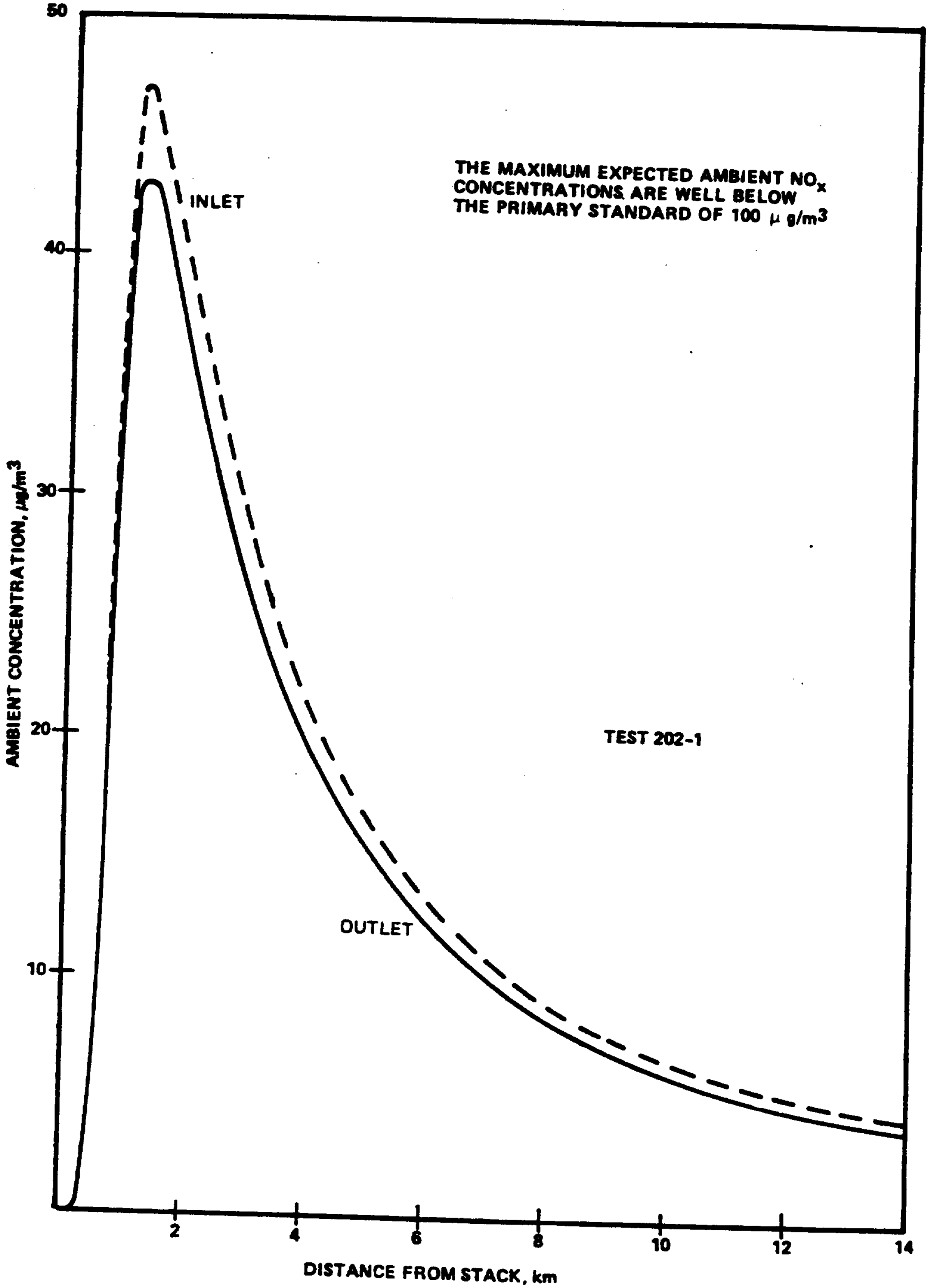

Figure 6-2. Relative NO_x air quality under typical weather conditions - oil firing

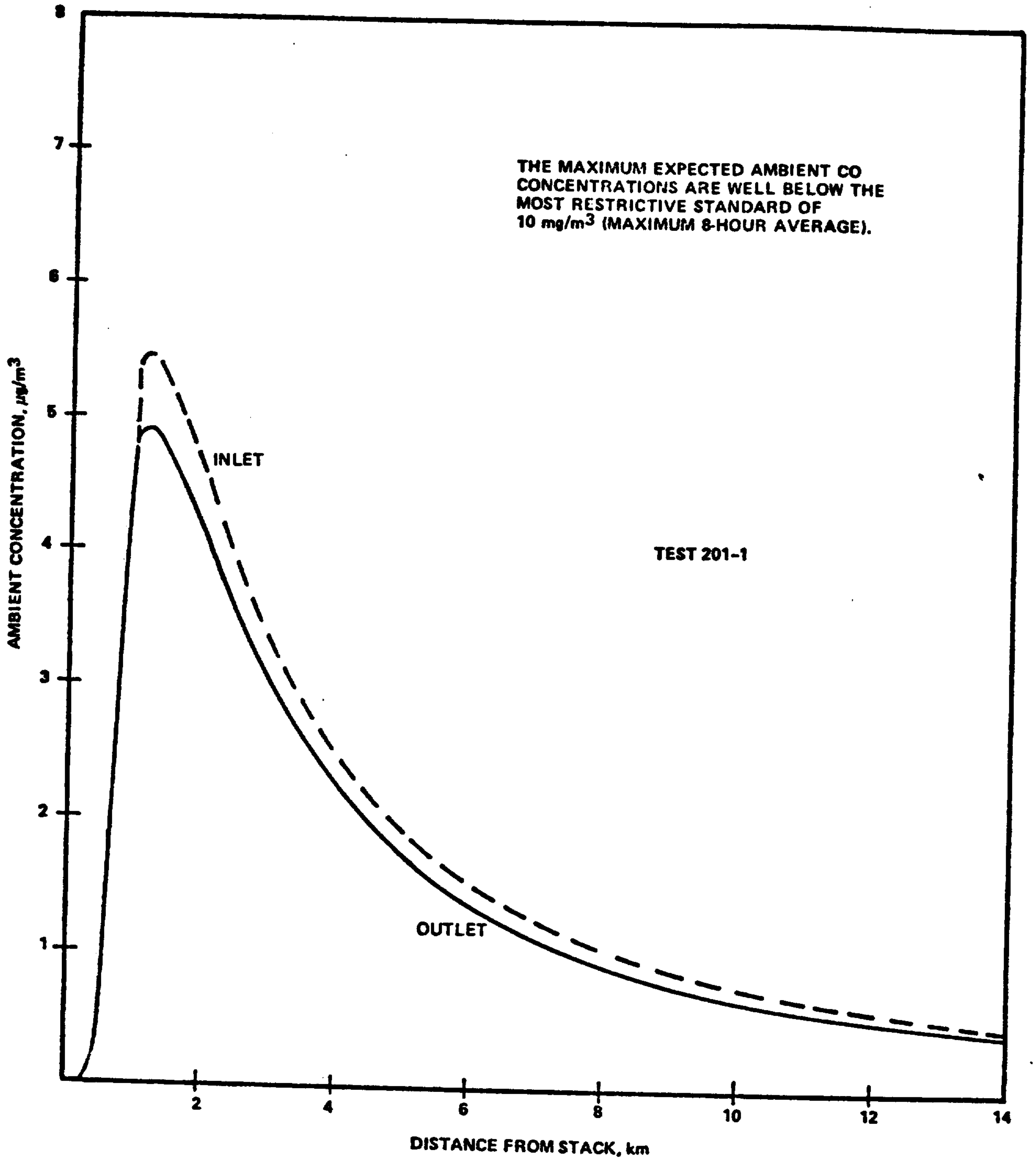

Figure 6-3. Relative CO air quality under worst case weather conditions - oil firing

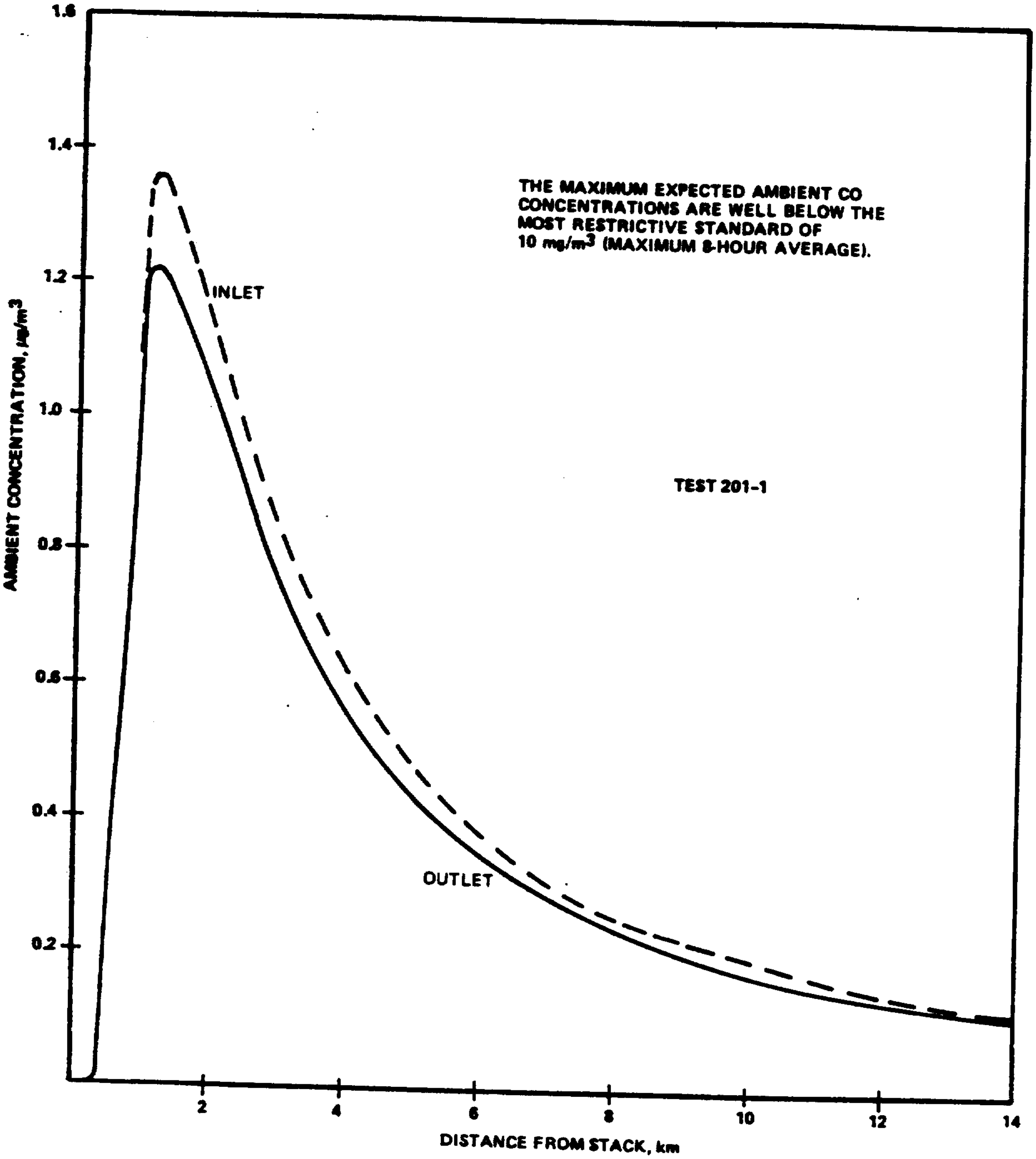

Figure 6-4. Relative CO air quality under typical weather conditions - oil firing

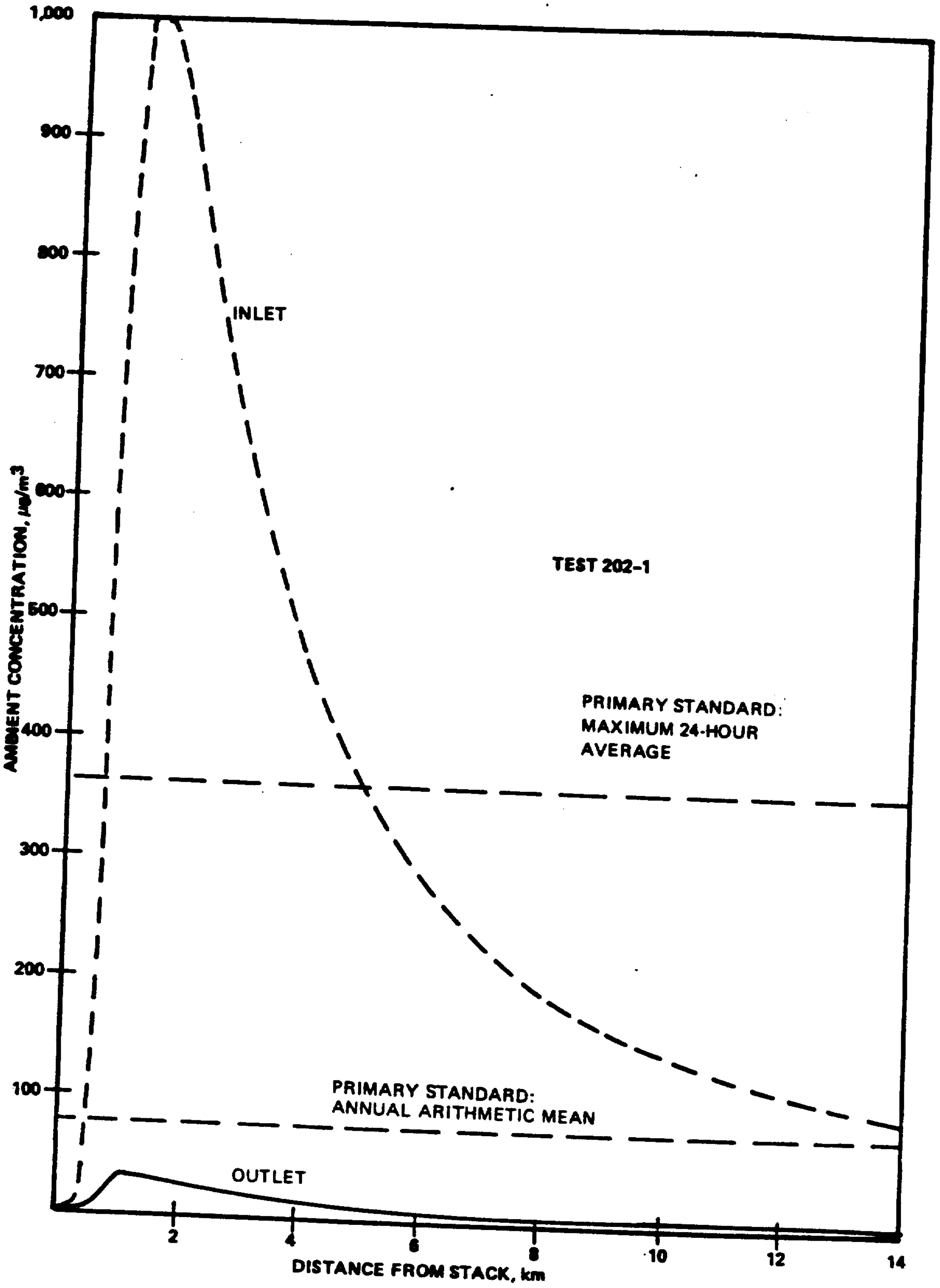

Figure 6-5. Relative SO_2 air quality under worst case conditions - oil firing

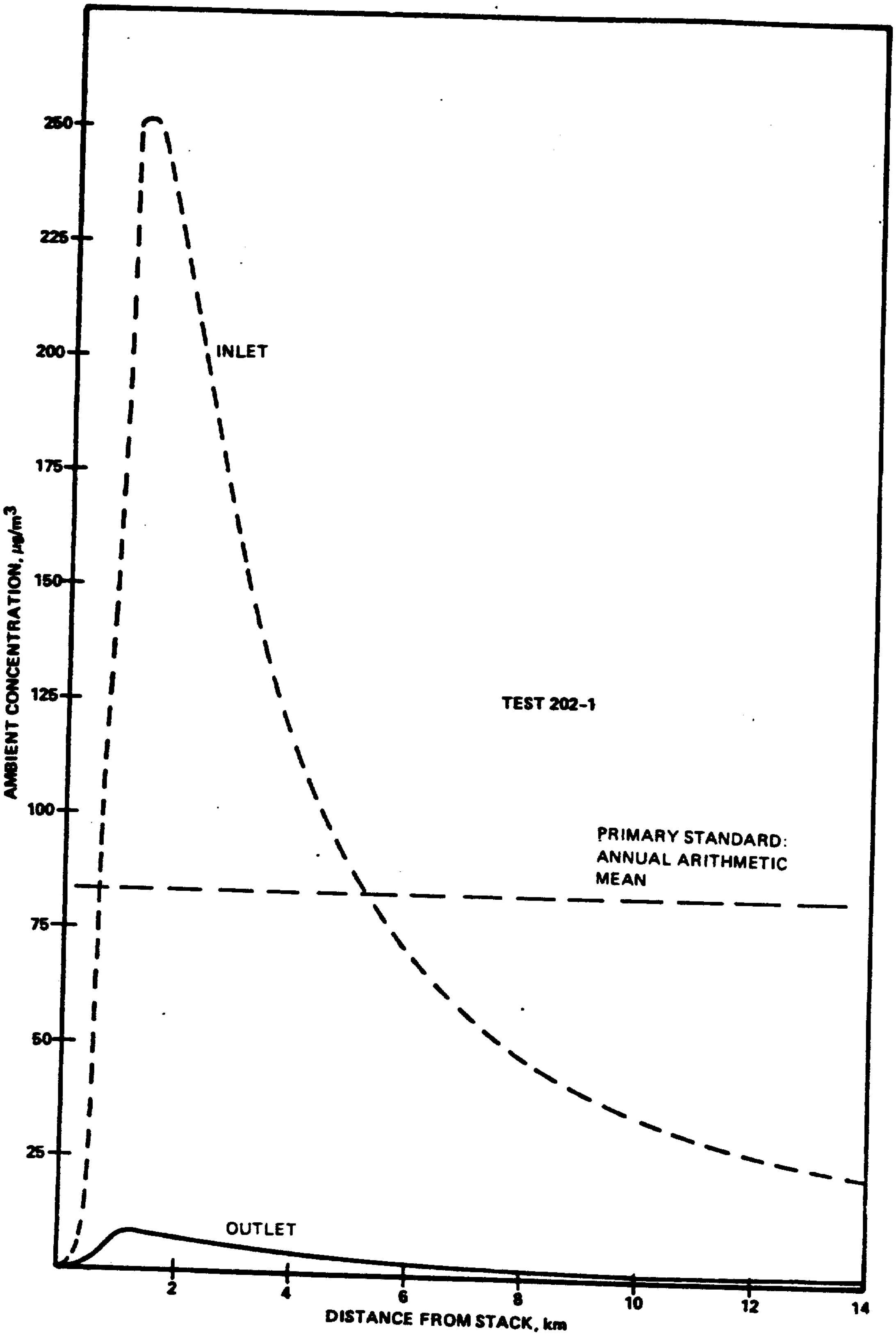

Figure 6-6. Relative SO_2 air quality under typical weather conditions - oil firing

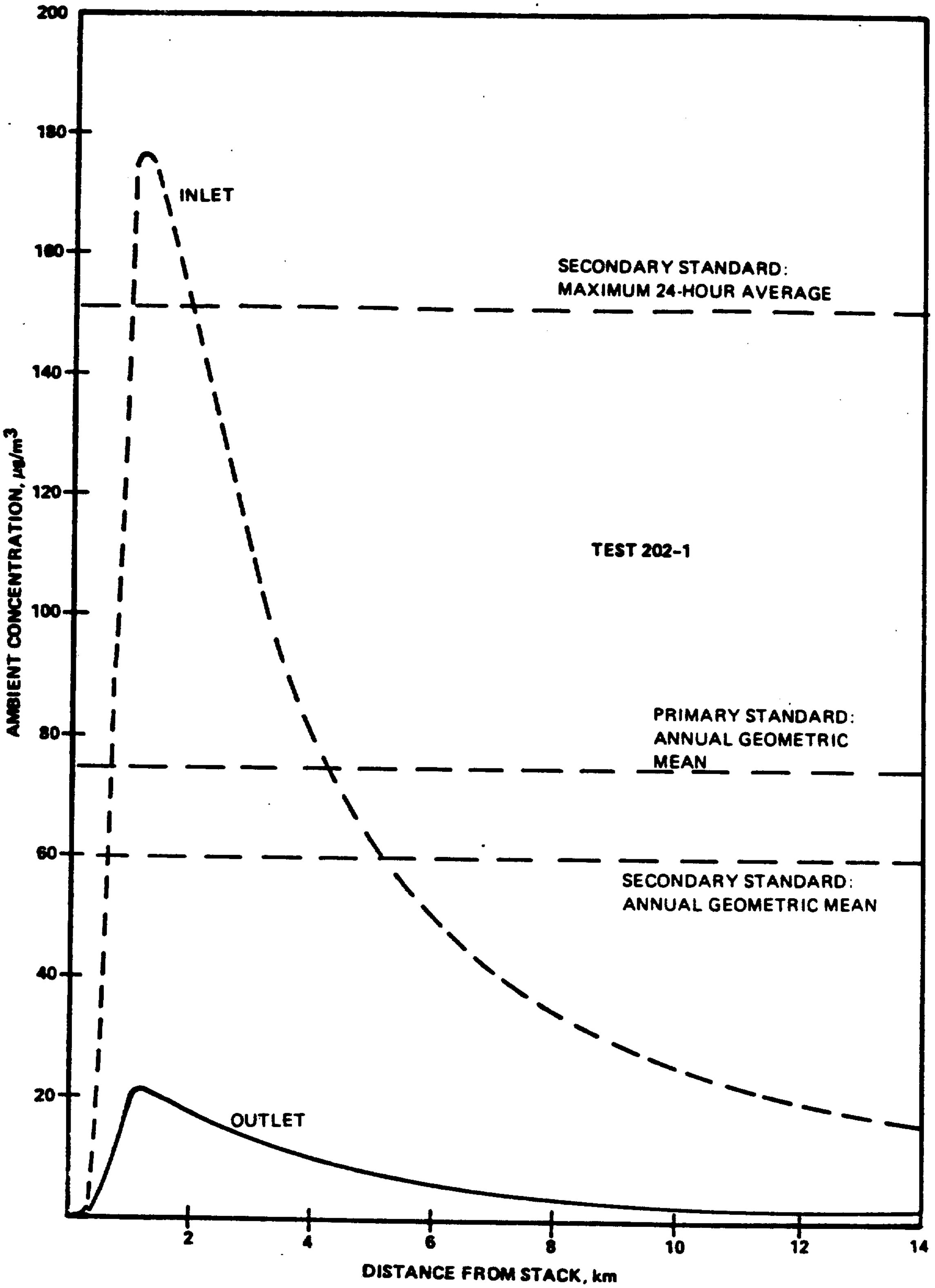

Figure 6-7. Relative particulate air quality under worst case weather conditions - oil firing

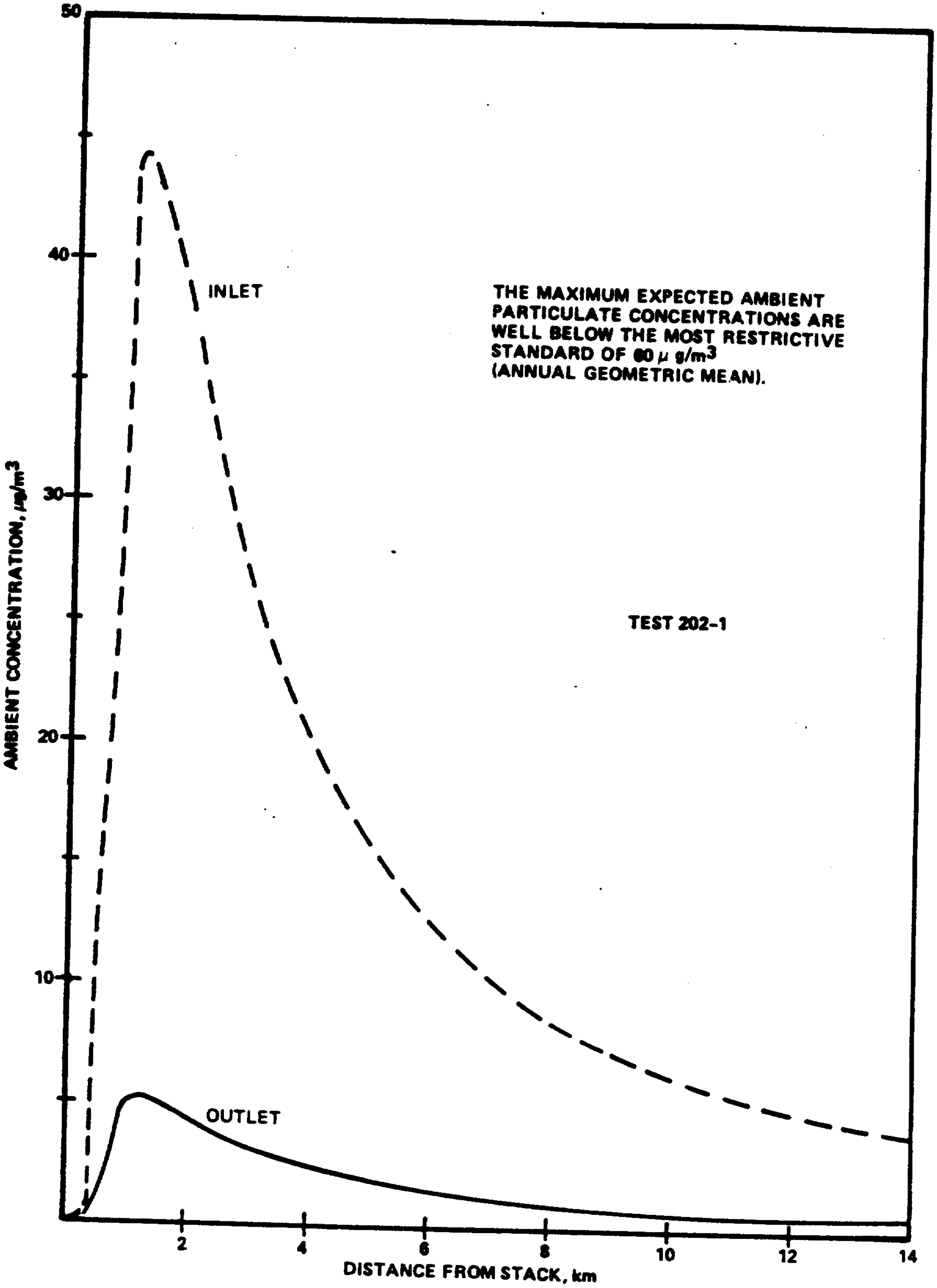

Figure 6-8. Relative particulate air quality under typical weather conditions - oil firing

for the ambient air quality to reach steady state conditions at each distance. Note also that the plots represent a single line extending directly downwind from the source.

Table 6-33 presents a summary of the ambient air quality standards for each pollutant. The standards are also shown on each plot.

Keeping in the caveats mentioned above, several observations can be made:

- The NO_x standard is exceeded under worst case weather conditions but not under typical conditions. Since the scrubber does not remove significant amounts of NO_x, there is no substantial difference between the controlled and uncontrolled cases. (The boiler has no NO_x controls.)
- CO standards are not exceeded under any conditions. The most restrictive standard is 10 mg/m^3 (10,000 μg/m^3) while the maximum predicted level is only about 0.06% of that value.
- Under worst case conditions uncontrolled SO_2 emissions result in both primary standards being exceeded. For controlled emissions no standards are exceeded. Under typical conditions the only annual primary standard is exceeded by uncontrolled emissions. For controlled emissions no standards are exceeded.
- One primary and both secondary standards are exceeded by uncontrolled particulate emissions under worst case weather conditions. Controlled emissions do not result in the violation of any standard. No standards are violated under typical weather conditions.

TABLE 6-33. NATIONAL AMBIENT AIR QUALITY STANDARDS FOR CRITERIA POLLUTANTS

Pollutant	Pollutant Standard	
	Primary[*]	Secondary[†]
Nitrogen dioxide	100 μg/m^3 (0.05 ppm) annual arithmetic mean.	Same as primary
Carbon monoxide	10 mg/m^3 (0 ppm) maximum 8-hour average; 40 mg/m (35 ppm) maximum 1-hour average.	Same as primary
Sulfur dioxide	80 μg/m^3 (0.03 ppm) annual arithmetic mean; 365 μg/m^3 (0.14 ppm) maximum 24-hour average.	1300 μg/m^3 (0.5 ppm) maximum 3-hour average.
Total suspended particulates	75 μg/m^3 annual geometric mean; 260 μg/m maximum 24-hour average	60 μg/m^3 annual geometric mean; 150 μg/m^3 maximum 24-hour average.

[*] Primary, necessary to protect the public health.

[†] Secondary, necessary to protect the public welfare.

CONCLUSIONS - OIL FIRING IN A 10 MW INDUSTRIAL BOILER WITH FGD

1) Uncontrolled emissions of criteria pollutants do not generally correspond with emission factors from AP-42. NO_x emissions were nearly 23% lower than the AP-42 emission factor, although they appear to be within the normal range for similar industrial units. CO emissions were nearly 63% lower than the AP-42 emission factor. SO_2 and total hydrocarbons corresponded well with their respective AP-42 emission factors. Particulate emissions, in the absence of coal ash contamination, are approximately twice the value tabulated in AP-42.

2) Sulfur dioxide removal data indicated an average scrubber efficiency of 97%. Controlled SO_2 emissions were 26.8 ng/J (0.06 lb/MM Btu) which is less than either existing or proposed NSPS limitations for utility boilers.

3) Particulate removal data indicate that, on the average, scrubber efficiency was 84% during the test period. However, based on particulate catches essentially free of coal ash contamination, the scrubber efficiency was approximately 75% for oil firing particulates.

4) Organic emissions determined by FID analysis were generally less than 5 ng/J (0.01 lb/MM Btu) and appear to be composed primarily of C_1 to C_6 hydrocarbons and organics heavier than C_{16}. However, gas chromatograph and gravimetric data indicate that FID values may be low by a factor of 2 to 3. Approximately 88 and 83% of the C_7 to C_{16} and higher than C_{16} organics, respectively, were removed by the scrubber.

5) The organic compounds identified in the gas samples were generally not representative of combustion-generated organic materials, but were compounds associated with materials used in the sampling equipment and in various analytical procedures. This again confirms the low level of organic emissions.

6) When emissions are uncontrolled, over 90% of the sulfur in the fuel feed is emitted as SO_2, less than 1% as SO_3, and 1.5% as $SO_4^=$.

7) SO_2 is efficiently removed by the scrubber (97 to 98% efficiency). The SO_3 removal efficiency (28 to 29%) suggests that SO_3 is present as fine liquid aerosols. $SO_4^=$ is about 60% removed by the scrubber, and so is probably associated with the larger particulates.

8) Of the 22 major trace elements analyzed in the flue gas stream, 11 exceeded their MATE values at the scrubber inlet while only 5 exceeded MATE values at the scrubber outlet. These 5 elements are arsenic, cadmium, chromium, nickel and vanadium. With the exception of chromium, elements exceeding their MATE values at the scrubber outlet were removed from the flue gas stream with efficiencies lower than the overall average removal efficiency of 87%.

9) Beryllium emissions were 0.001 mg/m^3 after scrubbing; this corresponds to half the MATE value for this element. At this emission concentration, the National Standard for Hazardous Air Pollutants limitation of 10 grams beryllium per day would only be exceeded by boilers of 100 MW capacity or greater.

10) The combined wastewater stream from the boiler operation may not pose an environmental hazard in terms of organic materials since the discharge concentrations of organics are all well below their MATE values. A similar conclusion may be drawn with respect to inorganic materials since inorganics, with the exception of nickel and copper, did not exceed their MATE values for liquid streams. Owing to uncertainty associated with SSMS analysis, nickel and copper may exceed their MATE values although this is not necessarily the case.

11) Polycyclic organic material (POM) was not found in the scrubber inlet or outlet streams at detection limits of 0.3 $\mu g/m^3$. MATE values for most POMs are greater than this detection limit. However, since the MATE values for at least two POM compounds - benzo(a)pyrene and dibenz(a,h)anthracene - are less than 0.3 $\mu g/m^3$, additional GC/MS analysis at higher sensitivity would be required to conclusively preclude the presence of all POMs at MATE levels.

12) Mass balance closure for 10 of the 20 trace elements analyzed is between 50 and 136 percent. Poorer mass balance closure was obtained for the remainder of trace elements due to the extremely low element concentrations and/or contamination of the scrubber recycle solution by coal firing components.

13) The scrubber cake produced contains about 1% oil fly ash. With the exception of antimony, boron, molybdenum and zinc, trace element concentrations in the scrubber cake exceeded their health based MATE values. All ecology based MATE values were exceeded by the trace element concentrations. Because the trace elements may leach from the disposed scrubber cake, these solid wastes must be disposed of in specially designed landfills.

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APPENDIX A

SIMPLIFIED AIR QUALITY MODEL

APPENDIX A

SIMPLIFIED AIR QUALITY MODEL

Simplified air quality models were used to determine relative air quality resulting from uncontrolled and controlled emissions. The ambient air quality values are approximate only. The emphasis should be placed on the relative values for each case as opposed to their absolute values.

Worst case weather conditions and typical weather conditions were considered. The worst case was assumed to be plume trapping. An equation proposed by Bierly and Henson was used with the following assumptions: inversion height 100 meters, wind speed 1.0 meter/second, D class stability (neutrally stable) in the mixing layer and one-hour averaging time. The typical case was assumed to correspond to the standard Gaussian convective diffusion equation. The following conditions were used: wind speed 4.0 meters/second, D class stability, and one-hour averaging time. These represent conditions that could reasonably be expected to occur almost anywhere in the country but are not specific to the area of the plant. Typical does not mean average. It was assumed that all species were inert. No photochemical reactions were considered.

There are several meteorological conditions which can produce high ground level pollutant concentrations. These conditions can result in plume coning, looping, fumigation, and trapping, all of which can cause high ambient concentrations. In the case of coning, high levels occur along the plume centerline. Looping causes high ground level concentrations at points where the plume impacts the ground. Fumigation causes high ground level concentrations which are generally lower than those from plume trapping.

For this study it was assumed that plume trapping constituted the worst case. That is, the case that would result in the highest ground level concentrations.

Plume trapping occurs when the plume is trapped between the ground surface and a stable layer aloft. Bierly and Hewson [1], have suggested the use of the following equation to account for the multiple eddy reflections from both the ground and the stable layer.

$$X\ (x,\ 0,\ z;\ H)\ =\ \frac{Q}{2\pi u\sigma_y\ \sigma_z}\left\{\exp\left[-1/2\ \left(\frac{z\ -\ H}{\sigma_z}\right)^2\right]\ +\ \exp\left[-1/2\left(\frac{z\ +\ H}{\sigma_z}\right)^2\right]\right.$$

$$+\ \sum_{N=1}^{J}\left[\exp\ -\ 1/2\left(\frac{z\cdot H-2NL}{\sigma_z}\right)^2\ +\ \exp\ -1/2\ \left(\frac{z+H-2NL}{\sigma_z}\right)\ ^2\right. \qquad (1)$$

$$\left.\left.+\ \exp\ -1/2\ \left(\frac{z-H+2NL}{\sigma_z}\right)^2\ +\ \exp\ -1/2\ \left(\frac{Z+H+2NL}{\sigma_z}\right)^2\right]\right\}$$

Where: X (x,y,z;H) = Concentration at point (x,y,z) assuming an effective stack height at H;
H = Effective stack height, meters;
Q = Pollutant emission rate, kg/hr;
μ = Mean wind speed, M/S
σ = Concentration distribution within the plume in the horizontal (σ y) and vertical (σ z) directions, unitless;
z = Height above the ground, meters;
J = Wind speed class index, unitless
N = Wind speed class index, unitless;
L = Height of the stable layer, meters.

At ground level (z = 0) and at the plume center line (y = 0) equation (1) reduces to:

$$X\ (x,0,0;\ H)\ =\ \frac{Q}{\pi u\sigma_y\sigma_z}\ \left\{\exp\left[-0.5\left(\frac{H}{\sigma_z}\right)^2\right]\ +\ \sum_{J=1}^{N=I}\left[\exp\ -0.5\ \left(\frac{H+2JL}{\sigma_z}\right)^2\right.\right.$$

$$\left.\left.+\ \exp\ -0.5\ \left(\frac{H\ -2JL}{\sigma_z}\right)^2\right]\right\} \qquad (2)$$

For the typical case, ground level concentrations were calculated using the standard Gaussian solution to the convective diffusion equation. This was obtained by neglecting the "inversion height" terms in equation (1), that is by setting z=0. The solution becomes:

$$X\ (x,\ 0,\ 0;\ H) = \frac{0}{\pi \mu \sigma_y \sigma_z}\ \exp\left[-1/2\left(\frac{H}{\sigma_z}\right)^2\right] \quad (3)$$

In equation 3, H is defined by:

$$H = H_s + \Delta H$$

Where H_s = physical height of the stack and ΔH = plume rise, both expressed in meters. There are more than 30 plume-rise formulas in the literature. All of which require empirical determination of one or more constants. For the purpose of this study, the Briggs plume rise formula was chosen to calculate the final plume rise in stable conditions.

$$\Delta H = 2.6\left(\frac{F}{\mu s}\right)^{1/3}$$

Where: μ = Wind speed, m/s;
s = Stability parameter, unitless;
F = Buoyancy flux.

The stability parameter, s, is defined as:

$$S = \frac{g}{T}\ \frac{\partial 0}{\partial Z}$$

Where: g = Gravitational constant, m/s^2 ;
T = Absolute ambient air temperature, °K.

Where: $\partial 0/\partial Z = (\partial T/\partial Z) + 9.8°C/km$, the potential temperature gradient.

The buoyancy flux, F, is defined as:

$$F = \frac{\Delta T}{T_s} gwr^2$$

Where: ΔT = Stack temperature minus the ambient air temperature, K° ;
T_s = Stack temperature, °K ;
g = Gravitational constant, m/s^2 ;
w = Stack exit velocity, m/s ;
r = Inside radius of the stack, m.

Table 1 shows the input data used in the plume rise calculations.

TABLE 1. INPUT DATA USED IN PLUME HEIGHT CALCULATIONS

	Coal	Oil
Stack Temperature (^oC)	51.7	55.6
Ambient Temperature (^oC)	20.0	20.0
Stack Velocity (m/s)	16.44	16.44
Stack Area (m^2)	0.245	0.245
Stack Height (m)	10.0	10.0
Wind Speed (m/s)	4.0	4.0

With the above input data effective stack heights of 56.0 m and 60.0 m were calculated for coal and oil firing, respectively. The difference was due entirely to variations in the flue gas temperature.

As shown in both equations (2) and (3) concentrations vary inversely with wind speed. As μ approaches zero, ground level concentrations become infinite. This means that at zero wind speed the Gaussian solution is no longer applicable. (The lower wind limit is about 1.0 m/s.) For plume trapping to occur and for the ground layer to become well mixed, the most stable ground layer must be chosen so that y and z in equation (2) remains as small as possible. D stability is such a case.

For the typical case, D stability occurs most often (see Table 2). The table shows D stability to be the most common of those listed.

TABLE 2. ANNUAL PERCENT FREQUENCY OF PASQUILL STABILITY CATEGORIES FOR ALL WIND DIRECTIONS AND SPEEDS, [4]

	Pasquill Stability Category					
	A	B	C	D	E	F
Birmingham, Alabama	1	7	12	44	36*	
Tucson, Arizona	2	10	14	33	41*	
Los Angeles, California	0	4	15	48	13	19
Miami, Florida	0	5	14	42	39*	
Chicago, Illinois	1	5	11	55	12	17
New York, New York	0	3	10	67	13	6
Philadelphia, Pennsylvania	0	5	11	51	14	18

*Indicates E and F categories combined.

Presented in Table 3 are the wind speed distribution and D stability for Baltimore, Maryland, for the period June - August, 1968. Winds in the range 3.6 to 5.2 m/s (7 to 10 knots) occur most often.

TABLE 3. FREQUENCY (PERCENT) OF PASQUILL STABILITY CATEGORY D; BALTIMORE, MARYLAND; BASED ON ALL REGULAR 3-HOURLY WEATHER OBSERVATIONS, JUNE - AUGUST, 1968; 1 KNOT = 0.515 M/S (HOLZWORTH, 1974)

Direction	Wind Speed (knots)						
	0-3	4-6	7-10	11-16	17-21	>21	Total
N	0.2	0.3	0.3	0.0	0.0	0.0	0.7
NNE	*	0.5	0.1	0.0	0.0	0.0	0.7
NE	*	0.3	0.1	0.0	0.0	0.0	0.4
ENE	*	0.4	0.1	0.0	0.0	0.0	0.6
E	*	0.8	1.5	0.1	0.0	0.0	2.5
ESE	*	0.4	0.4	0.0	0.0	0.0	0.8
SE	0.3	0.3	0.5	0.0	0.0	0.0	1.1
SSE	0.1	1.1	0.8	0.0	0.0	0.0	2.0
S	0.2	0.9	1.4	0.4	0.0	0.0	2.9
SSW	0.1	0.1	0.7	0.0	0.0	0.0	1.0
SW	*	0.4	0.4	0.1	0.0	0.0	1.0
WSW	0.2	0.8	0.4	0.4	0.0	0.0	1.8
W	0.1	1.1	1.6	0.9	0.0	0.0	3.7
WNW	*	0.3	0.5	0.8	0.0	0.0	1.6
NW	*	0.1	1.1	0.3	0.1	0.0	1.6
NNW	0.0	0.0	0.4	0.3	0.0	0.0	0.7

Total frequency of D stability = 23.1%
Frequency of calms distributed with D stability = 0.4%
*Indicates <0.05

REFERENCES FOR APPENDIX A

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APPENDIX B

ORGANIC ANALYSIS METHODS

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ORGANIC ANALYSIS METHODS

This section summarizes the philosophy and methods used for Level 2 organic analysis of the industrial samples. The purpose here is to present a summary of the results which have been previously reported and to present the methods and approaches used for the analysis. The methods are explained and the figures show how various samples from the Level 2 organic train as well as process and gas bag samples were analyzed using primarily GC/MS.

LEVEL 2 ORGANIC ANALYSIS PLAN

The Level 2 organic analyses have been designed to identify and quantify organic species. The analysis plan provides for the following type of information, listed according to the priority levels that have been assigned.

- Identification of compounds present at significant levels
- Identification of all compounds
- Quantification of all compounds

To achieve this prioritized listing, the steps outlined in the Level 2 priority flow diagram (Figure 1) have been followed. Primary analytical decisions are based on Level 1 analysis data and established minimum levels for compounds on the MEG and priority pollutant lists. Subsequent analytical decisions are based on cost effectiveness and a prescreening process. The prescreening is accomplished by analyzing all samples to the point of LC separation as shown in Figure 2. Once the preliminary analysis is complete, a determination is made as to whether it is cost effective to continue the analysis. At a minimum, volatile organic matter (C_2 - C_{16}) and polynuclear organic material (POM) were identified and quantified in all samples. The samples were paired for analysis as pre- and post-scrubber couples. Any determination made on one of the pair was automatically made on the other. The purpose of this effort was to maximize the amount of information related to scrubber efficiency and scrubber operation on various organic compounds. The central technique for Level 2 organic analysis was gas chromatography/mass spectrometry. The procedures outlined are the starting point for the overall analysis. Information gained in the initial phase was to be used to direct subsequent analysis if it was found necessary to continue beyond the prescreening phase.

Level 2 Analyses Performed

All samples including the process samples were analyzed through the prescreening phase using the procedures discussed. It was determined that further sample work up would not result in additional information based on the lack of organic compounds detected. The GC/MS was used on all samples for the prescreening process. The GC columns used together with sample preparation steps taken are presented in this report.

Conclusions

Table 1 summarizes the findings of the Level 2 organic analyses. Table 2 summarizes the samples analyzed by GC/MS. The lack of significant levels of organic materials suggests a very clean source as related to organic emissions. No polynuclear aromatic hydrocarbons were detected. In fact, no organic species which could be directly associated with combustion could be identified. Calculations of sample volume and sample concentration have been performed and confirm the limit of detectability of the GC/MS techniques as related to the effluent streams. There is no reason at this time to suspect anything but a very clean combustion source with extremely low level organic emissions.

LEVEL 2 ORGANIC ANALYSIS PHILOSOPHY

This Level 2 organic analysis plan is based on Level 1 analysis data and is intended for use on process, gas bag, and sampling train collected samples. The plan assumes that Level 1 analysis has been completed and the information from Level 1 analysis is available. The techniques discussed are implemented by a skilled mass spectrometrist, since at several points in the analysis, judgements and even modifications are necessary depending on sample source or what compounds are identified during the course of the analysis.

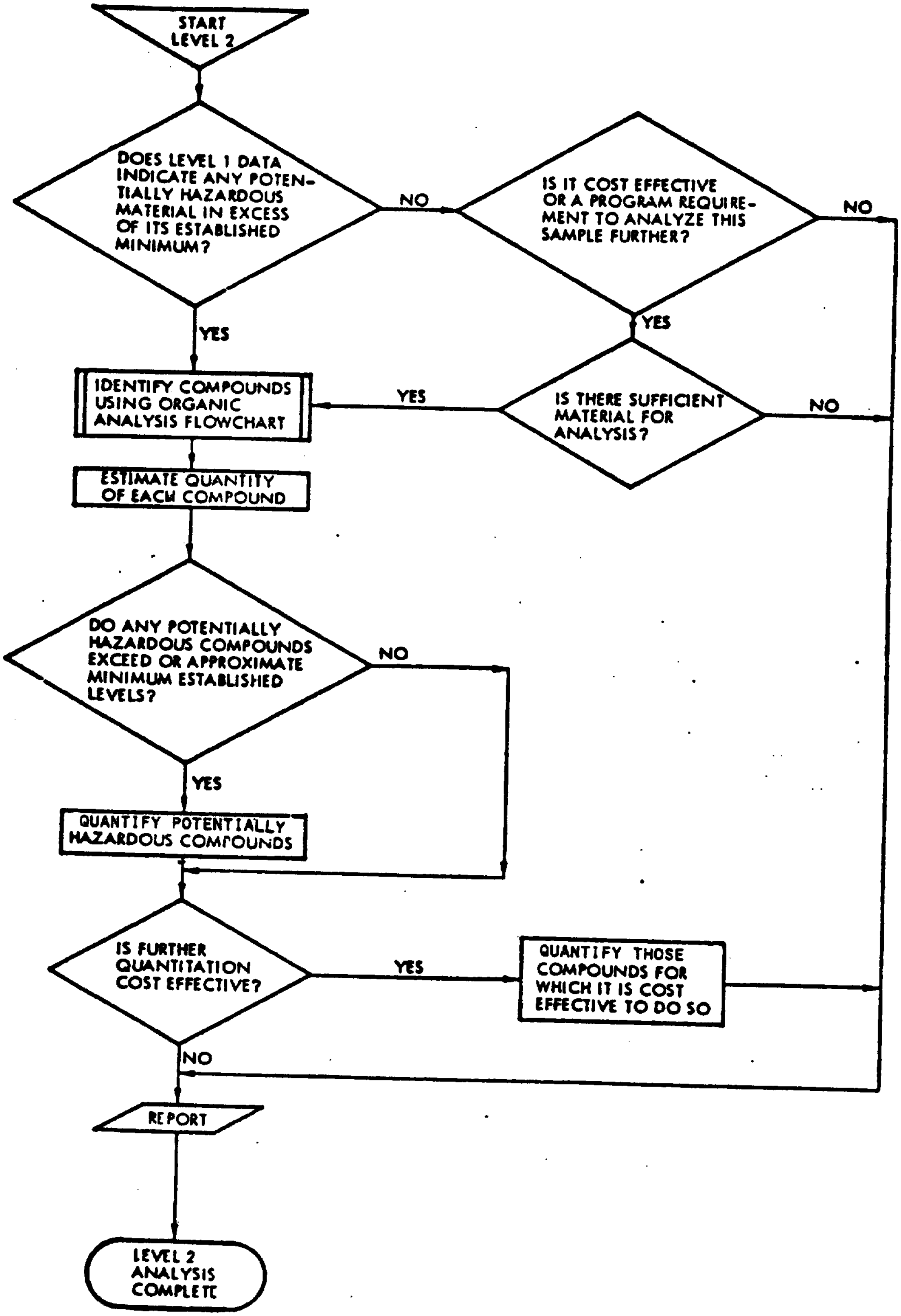
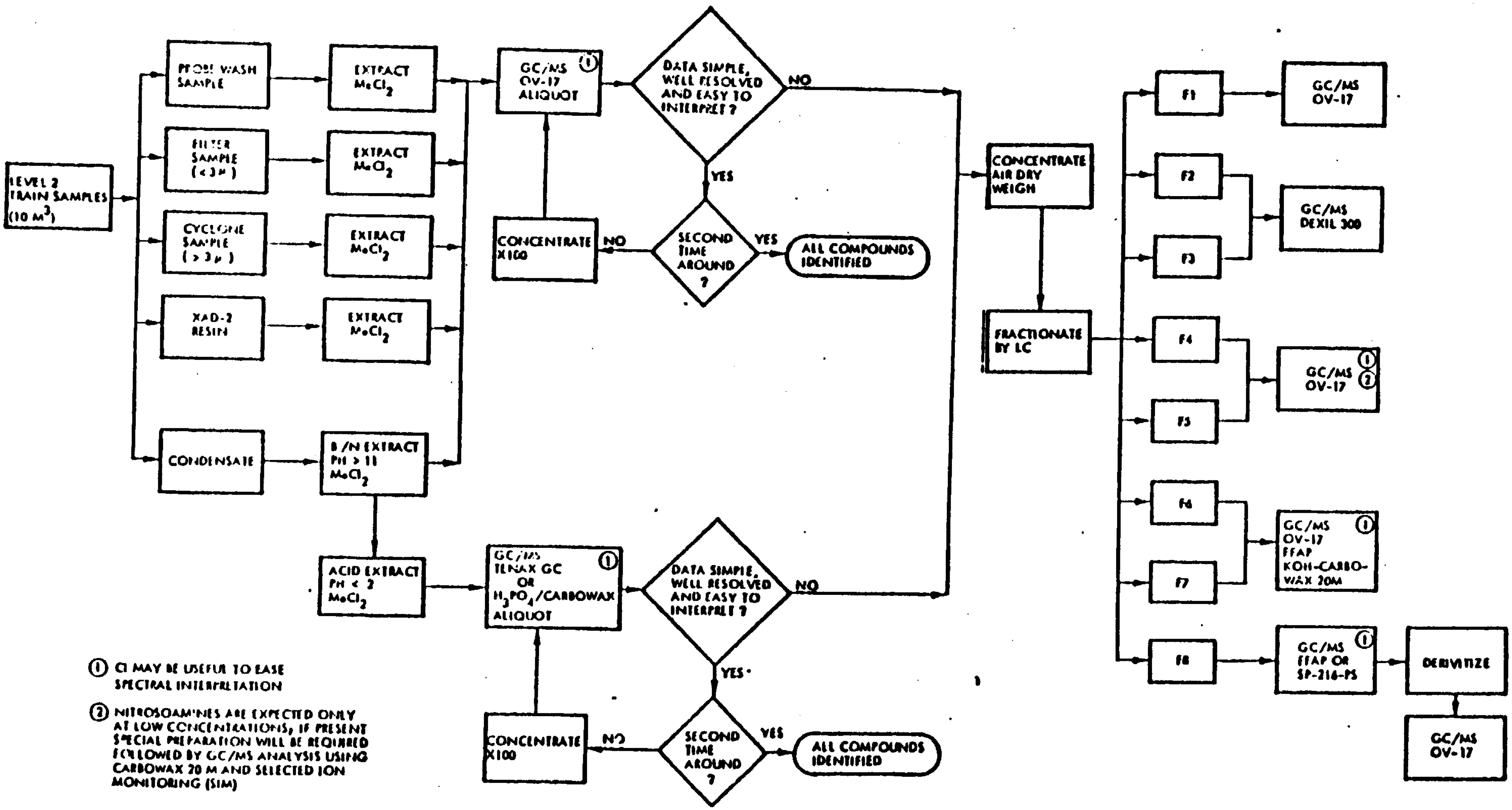


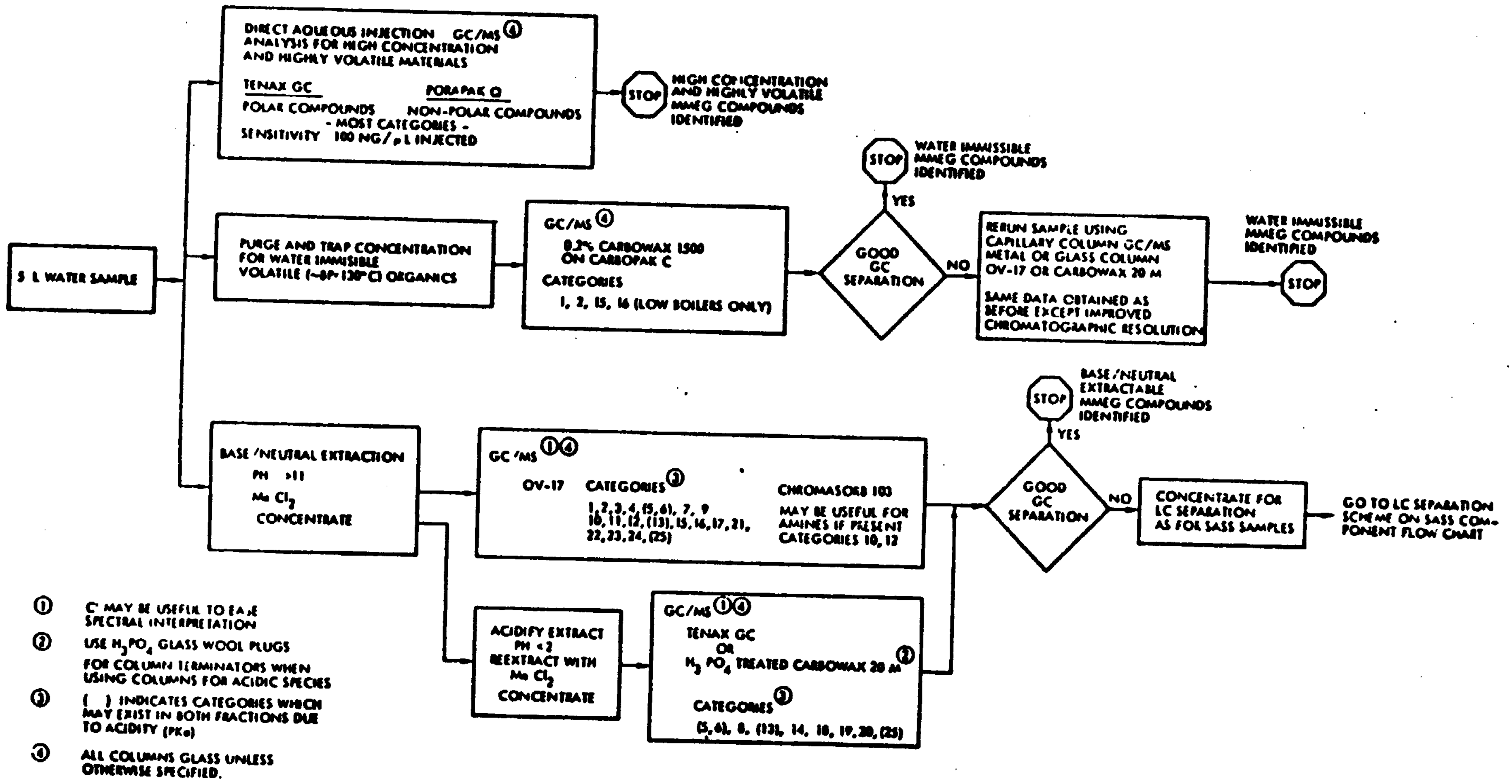
Figure 1. Logic flow chart for Level 2 organic analysis.



① CI MAY BE USEFUL TO EASE SPECTRAL INTERPRETATION

② NITROSOAMINES ARE EXPECTED ONLY AT LOW CONCENTRATIONS, IF PRESENT SPECIAL PREPARATION WILL BE REQUIRED FOLLOWED BY GC/MS ANALYSIS USING CARBOWAX 20 M AND SELECTED ION MONITORING (SIM)

Figure 2. Analysis of Level 2 samples from glass sampling train.



① C' MAY BE USEFUL TO EASE SPECTRAL INTERPRETATION

② USE H_3PO_4 GLASS WOOL PLUGS FOR COLUMN TERMINATORS WHEN USING COLUMNS FOR ACIDIC SPECIES

③ ( ) INDICATES CATEGORIES WHICH MAY EXIST IN BOTH FRACTIONS DUE TO ACIDITY (PKa)

④ ALL COLUMNS GLASS UNLESS OTHERWISE SPECIFIED.

Figure 3. General logic flow chart for Level 2 organic aqueous samples.

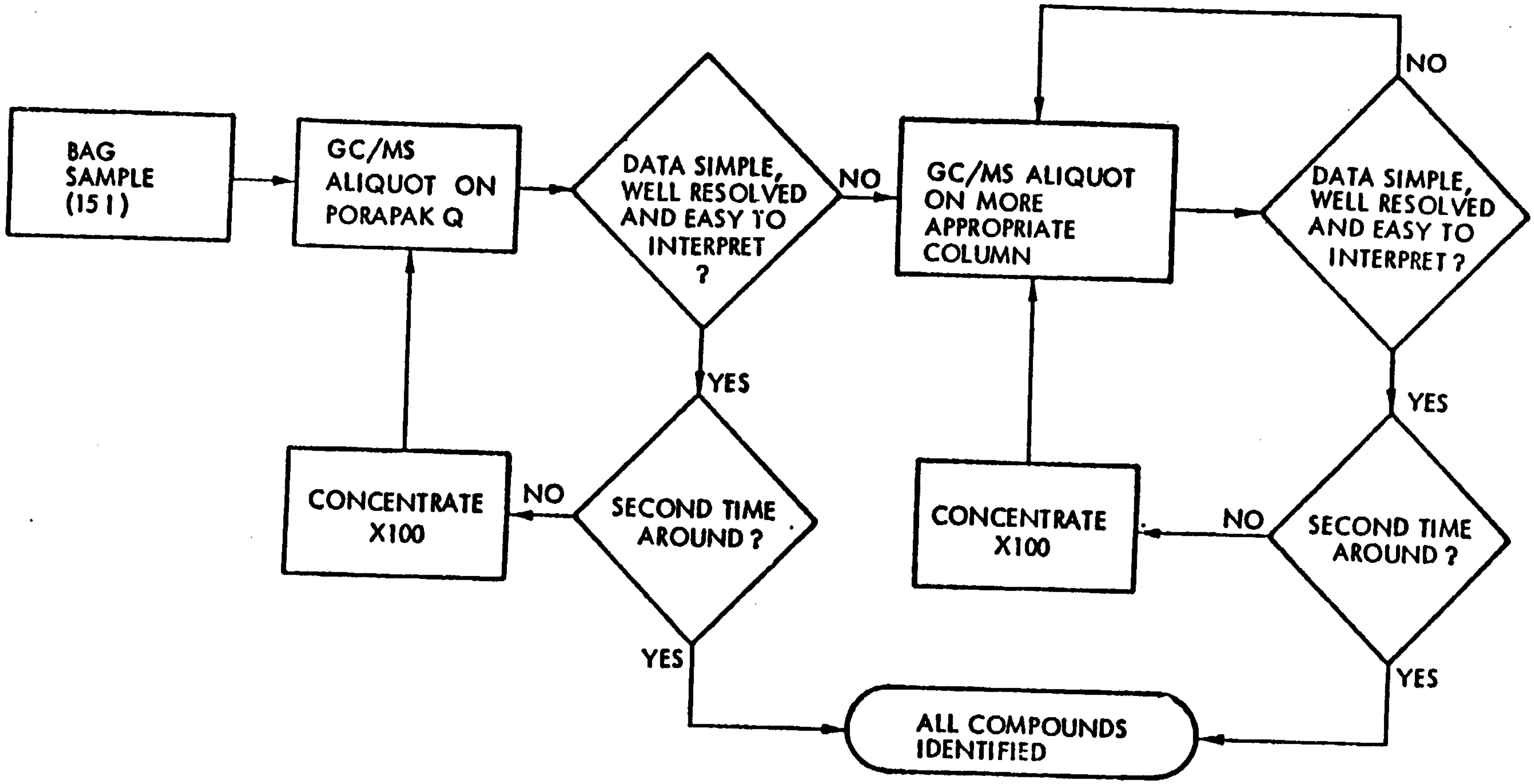


Figure 4. Lecel 2 analysis of gas bag samples.

TABLE 1. ORGANIC ANALYSIS RESULTS

COMPOUND NAME	FRACTION	ug/m³							
		Oil				Coal			
		201-2		201-3		202-2		202-3	
		IN	OUT	IN	OUT	IN	OUT	IN	OUT
Propionaldehyde	GB	170	380	54	-	200	-	142	-
Nitromethane	GB	-	-	-	-	-	-	63	-
Ethyl-n-butyl ether	GB	2000	1500	910	1500	1700	-	1000	-
Ethyl acetate	GB	-	-	-	-	-	-	-	2300
Hydrocarbon (C_6H_{14})	GB	-	-	380	-	-	-	-	-
Chloropropanol	PR	-	-	-	3.9	-	-	-	-
4-methyl-3-pentene-2-one*	PR	-	-	-	-	-	570	350	28
Unidentified alcohol	PR	-	4.0	-	-	-	-	-	-
Octanol	PR	-	-	-	-	-	-	45	-
Ketone (MW 138)*	PR	-	-	-	-	-	-	20	-
Ketone (MW 140)	PR	3.9	-	6.9	-	14	-	-	-
Phthalic anhydride	PR	-	-	-	-	-	-	29	-
Amyl benzoate	PR	—	-	-	-	-	1.6	-	-
Glycerol triacetate	PF	-	-	-	-	-	-	42	-
Methyl sub aromatic	XR	1.7	-	-	-	-	-	-	-

GB = Grab bag samples
PR = Probe rinse

TABLE 2. PROCESS SAMPLES ANALYZED BY GC/MS

SAMPLE NUMBER	SAMPLE DESCRIPTION
201-2-1-S-KD	Coal-fired, Test #2, concentrated field extraction of 4 liters of scrubber water.
201-3-1-S-KD	Coal-fired, Test #3, concentrated field extraction of 4 liters of scrubber water.
202-2-1-S-KD	Oil-fired, Test #2, concentrated field extraction of 4 liters of scrubber water.
202-3-1-S-KD	Oil-fired, Test #3, concentrated field extraction of 4 liters of scrubber water.
202-2-1-S	Oil-fired, Test #2, unconcentrated field extraction of 4 liters of scrubber water.
202-3-1-S	Oil-fired, Test #3, unconcentrated field extraction of 4 liters of scrubber water.
201-2-1-B-S-KD	Coal-fired, Test #2, concentrated lab base/neutral extraction of 2 liters of field extracted scrubber water.
201-3-1-B-S-KD	Coal-fired, Test #3, concentrated lab base/neutral extraction of 2 liters of field extracted scrubber water.
202-2-1-B-S-KD	Oil-fired, Test #2, concentrated lab base/neutral extraction of 2 liters of field extracted scrubber water.
202-3-1-B-S-KD	Oil-fired, Test #3, concentrated lab base/neutral extraction of 2 liters of field extracted scrubber water.
201-2-1B-B-S-KD	Coal-fired, Test #2, concentrated lab base/neutral extraction blank.
201-2-1-B-S	Coal-fired, Test #2, unconcentrated lab base/neutral extraction of 4 liters of field extracted scrubber water.
201-2-1-B-S	Coal-fired, Test #3, unconcentrated lab base/neutral extraction of 2 liters of field extracted scrubber water.

TABLE 2. (Continued)

202-2-1-B-S	Oil-fired, Test #2, unconcentrated lab base/neutral extraction of 2 liters of field extracted scrubber water.
202-3-1-B-S	Oil-fired, Test #3, unconcentrated lab base/neutral extraction of 2 liters of field extracted scrubber water.
201-2-1B-B-S	Coal-fired, Test #2, unconcentrated lab base/neutral extraction blank.
201-2-1-A-S-KD	Coal-fired, Test #2, concentrated lab acid extraction of 2 liters of field extracted scrubber water.
201-3-1-A-S-KD	Coal-fired, Test #3, concentrated lab acid extraction of 2 liters of field extracted scrubber water.
202-2-1-A-S-KD	Oil-fired, Test #2, concentrated lab acid extraction of 2 liters of field extracted scrubber water.
202-3-1-A-S-KD	Oil-fired, Test #3, concentrated lab acid extraction of 2 liters of field extracted scrubber water.
201-2-1-1B-A-S-KD	Coal-fired, Test #2, concentrated lab acid extraction blank.
201-2-1-A-S	Coal-fired, Test #2, unconcentrated lab acid extraction of 2 liters of field extracted scrubber water.
201-3-1-A-S	Coal-fired, Test #3, unconcentrated lab acid extraction of 2 liters of field extracted scrubber water.
202-2-1-A-S	Oil-fired, Test #2, unconcentrated lab acid extraction of 2 liters of field extracted scrubber water.
202-3-1-A-S	Coal-fired, Test #2, unconcentrated lab acid extraction of 2 liters of field extracted scrubber water.
201-2-1B-A-S	Coal-fired, Test #2, unconcentrated lab acid extraction blank.
201-2-SC-S-KD	Coal-fired, Test #2, concentrated lab extraction of scrubber cake.
201-3-SC-S-KD	Coal-fired, Test #3, concentrated lab extraction of scrubber cake.
202-2-SC-S-KD	Oil-fired, Test #2, concentrated lab extraction of scrubber cake.
202-3-SC-S-KD	Oil-fired, Test #3, concentrated lab extraction of scrubber cake.

TABLE 2. (Continued)

201-3-FA-S-XD	Coal-fired, Test #3, concentrated lab extraction of fly ash.
201-2-SCB-S-KD	Coal-fired, Test #2, concentrated lab extraction blank.
201-2-SC-S	Coal-fired, Test #2, unconcentrated lab extraction of scrubber cake.
201-3-SC-S	Coal-fired, Test #3, unconcentrated lab extraction of scrubber cake.
202-2-SC-S	Oil-fired, Test #2, unconcentrated lab extraction of scrubber cake.
202-3-SC-S	Oil-fired, Test #3, unconcentrated lab extraction of scrubber cake.
201-3-FA-S	Coal-fired, Test #3, unconcentrated lab extraction of fly ash.
201-2-SCB-S	Coal-fired, Test #2, unconcentrated lab extraction blank.

The combination of gas chromatography and mass spectrometry is the central technique to this analysis plan. GC/MS combines the separation power of the gas chromatograph with the unexcelled identification potential of the mass spectrometer. The incorporation of a computer based data handling system with the GC/MS provides the most powerful compound identification technique available to the analyst. The technique is highly cost effective but requires an experienced spectrometrist to apply the technique and analyze the data generated. Judgments as to sample size, depending on instrument sensitivity, and mass range to be scanned, depending on instrument resolution, as well as selection of an alternate GC column for a specific sample, are at the discretion of the analyst. General direction can be given, however, a total analysis requires some modification of the procedures.

The most cost effective Level 2 analysis scheme is specific analysis based on compound category data obtained from Level 1. This information would provide data for GC column selection and would generally simplify the overall analysis. The analysis scheme outlined here is for all categories of compounds with the exception of those compounds which are volatile and are analyzed by the field GC technique, and those compounds which are reactive and chemically modified by sampling or standing.

The Level 2 analysis plan incorporates wet chemical separations, including sample extractions and liquid chromatography, and instrumental analysis using primarily GC/MS. The other techniques discussed have been applied in special cases but require further research into their application. These include high resolution mass spectrometry (HRMS), Chemical ionization mass spectrometry (CIMS), gas chromatography with selective detectors, and capillary column GC/MS. The proposed analysis plan is patterned after Level 1 which will provide information to ease the total sample burden imposed by the identification of a large number of organic compounds. A variety of specific GC columns is described together with appropriate conditions for their use on specific categories of compounds. If a category is known to be absent in a specific sample, based on information from Level 1, it is expected that this knowledge will be used to modify the analysis. Typical sensitivities for various analysis steps are given as a part of the specific method discussions. It is important that the analyst implementing the Level 2 plan, have a working knowledge of Level 1 organic analysis.

HARDWARE REQUIREMENTS AND OPTIONS FOR LEVEL 2 ANALYSIS

The primary tool for Level 2 analysis is a high sensitivity GC/MS instrument. A discussion of corollary GC/MS techniques, useful during the course of analysis, are also given together with their appropriate application.

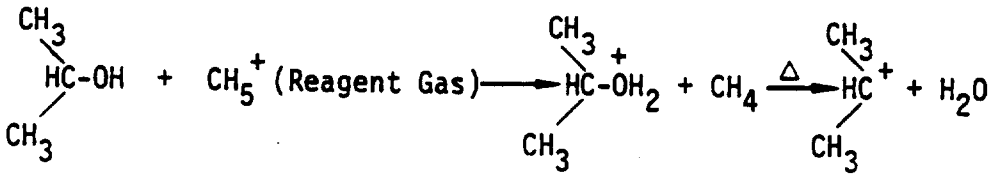
GC/MS

In order to apply GC/MS and obtain reliable data it is necessary to have a spectrometer which is capable of high speed scanning (i.e. recording a full mass spectrum in 3 seconds or less) with resolution that will allow separation nominal mass peaks to at least mass 600. The gas chromatograph should be capable of using glass columns since many materials to be analyzed are sensitive to metal surfaces. The mass spectrometer should be capable of chemical ionization with a variety of reagent gasses such as methane or isobutane. The ability to use capillary columns is useful in many of the GC/MS analysis. The incorporation of a computer based data handling system eases the labor involved in acquiring mass spectral data, and reduces the time for data reduction and interpretation. The computer does not eliminate the need for an experienced mass spectrometrist, it merely provides a more cost effective means of handling large volumes of mass spectral data.

Chemical Ionization (CI) Mass Spectrometry

Normal mass spectrometry is done by bombarding the sample with electrons at an energy level of 70 electron volts (eV). The ionization process produces a spectrum which contains characteristic fragment ions from the molecule under study. In many cases, a molecular ion is produced (i.e., the ion representative of molecular weight) and its identification is unambiguous, however, in some cases, no molecular ion is produced or it is present at such a low level that it cannot be identified. The most important peak in any mass spectrum is the molecular ion since a knowledge of molecular weight reduces the total number of organic compound possibilities substantially. Electron ionization does provide a great deal of compound structure information, but when the molecular ion is absent much information is lost, making spectral interpretation difficult or impossible.

Chemical ionization incorporates a reagent gas to perform the ionization process. The use of methane or isobutane for the chemical ionization process are most common. When these reagent gases are used, the energy of ionization is reduced from 70 eV to about 7 eV. The result is ionization of a sample without sufficient excess energy to cause significant fragmentation and in most cases the "pseudo" molecular ion dominates the spectrum yielding molecular weight information. The CI process involves a transfer of a proton from the reagent gas to the sample when ionization occurs. The resulting spectrum is a "pseudo" molecular ion at 1 mass unit higher than the molecular weight of the compound. Chemical ionization should always be used in conjunction with electron ionization for spectral interpretation. As is true with most analytical techniques, chemical ionization is not without its difficulties. The ionization of many materials such as alcohols, causes a protonation of the hydroxyl group followed by a loss of water from the "pseudo" molecular ion by a thermal process. An example of this type of ionization is given below.



The loss of water from the "pseudo" molecular ion is primarily dependent on source temperature, and is increased with higher temperatures. This fragmentation process may not take place when electron ionization is used and in many cases causes confusion in the determination of molecular weight. Similar occurrances take place when primary amines are being studied, showing a loss of ammonia from the "pseudo" molecular ion, and to a lesser extend acids, ethers, esters, and halogenated compounds. Hydrocarbon samples are typically not sensitive to chemical ionization. This is especially true of straight chain hydrocarbons. Under CI conditions, straight chain hydrocarbons often show a loss of 1 from the molecular ion rather than an addition, together with a significant reduction in overall sensitivity. Materials which contain heteroatoms such as nitrogen, oxygen, sulfur, etc. generally show an increase in sensitivity relative to their electron ionization spectra. This variation in sensitivity is useful in identifying heteroatom structures in complex hydrocarbon samples using chemical ionization. Other reagent gases are available, (e.g. ammonia, nitrous oxide, and hydrogen), however, less work has been done with these reagents gases.

High Resolution Mass Spectrometry (HRMS)

The techniques discussed to this point require that the compound of interest be amenable to gas chromatography. Many materials, of course, cannot be chromatographed and therefore do not lend themselves to GC/MS. High resolution mass spectrometry is a technique by which one can analyze low volatility residual materials. Total compound identification may not be possible in all cases depending on mixture complexity, however, functional groups and heteroatoms can generally be identified unambiguously. The technique as discussed employs the direct insertion probe which is used to introduce the sample into the ion source of the mass spectrometer. The use of a high resolution data system together with the high resolution mass spectrometer is important in obtaining useful data in a reasonable amount of time. Full spectra should be recorded and the computer used to reduce the data to element maps for selected mass peaks. The element maps will give the elemental composition for mass peaks and an experienced mass spectrometrist can use this information to determine the compound types in a sample. The sophistication of a high resolution mass spectrometer is much greater than GC/MS and the sophistication of the operator must also be greater. The technique should be limited and applied only when deemed necessary since the availability of such equipment is not wide spread.

Infrared Spectroscopy

Infrared spectroscopy is very useful in determining compound functionality. The technique is not applied directly in this Level 2 plan since it is assumed that IR spectra have previously been recorded for Level 1. It is also assumed that this information is available and is used by the analyst to select appropriate GC columns and to insure that he has analyzed all materials by this Level 2 plan which were present in Level 1.

Capillary GC/MS

In some cases, packed columns do not provide the chromatographic resolution necessary to obtain good mass spectral data. In these cases the use of high resolution capillary columns is recommended. This is especially true in the direct analysis of the extracts prior to concentration, or liquid chromatographic fractionation. There are a wide variety of capillary columns available to the analyst. These columns include standard open tublar wall coated columns, SCOT columns, and micro packed columns. For the beginner, the use of a SCOT column is recommended, since it is more tolerant of temperature and sample size, while providing increased resolution over its packed column counterpart. The liquid phase chosen for a capillary column is generally based on information obtained using packed columns. A wide variety of liquid phases are available, however, due to their expense, only a selected few columns are expected to be used routinely. For general application in Level 2 analysis, it is recommended that a OV-17 SCOT column and a Carbowax 20M SCOT column, which are between 50 and 100 ft. in length be used. These two columns will satisfy 90% of the requirements for capillary column GC.

SAMPLE PREPARATION AND EXTRATION PROCEDURES

The preparation and extraction procedures described in this section are similar to those used in Level 1 analysis. For those analysts familiar with Level 1 analysis, the only modification is in the extraction of the condensate of the XAD-2 sorbent trap.

Probe Wash, Cyclones, and Filter from Level 2 Train Samples

The probe wash, cyclones, and filter samples are prepared for analysis by extraction with methylene chloride. The extractions should be conducted using a Soxhlet apparatus for 24 hours. The Soxhlet cup should have been previously extracted to remove contamination which would lead to erroneous results following the established procedures outlined for Level 1 analysis.

XAD-2 Sorbent Trap

The XAD-2 resin from the sorbent trap should be extracted with methylene chloride using a large Soxhlet apparatus. The procedure for this extraction as well, as resin preparation are, identical to Level 1 procedures.

Extraction of the Condensate

The condensate from the sorbent trap should first be extracted with methylene chloride after the pH has been adjusted to 11 or greater with 6N sodium hydroxide. This base/neutral extract should be set aside for subsequent analysis. The solution pH is then adjusted to less than 2 using 6N hydrochloric acid and the extraction with methylene chloride repeated. This division of the condensate sample into two extracts may eliminate the need for an LC separation step, making the overall analysis less expensive and time consuming.

PRESCREENING ANALYSIS OF THE EXTRACTS FOR ORGANIC COMPOUNDS

Concentration of extracts prior to analysis causes the loss of most materials with boiling points below about C_8 (220°C). To obtain data on low boiling extracted compounds from the sampling train samples, GC/MS analysis is run on the sample prior to concentration. A 5 cc aliquot of the extract should be saved for this analysis. One GC/MS run on each sample is made using a general purpose column. If specific classes of compounds are found to be present from the Level 1 LC fraction data for a given extract, repeat analysis of the uncondensed extract may be necessary to determine if more volatile materials in the same compound class are present. Column selection and the rerun of a sample should be based on the categories identified from the Level 1 analysis of the LC fractions.

Prescreening GC/MS Analysis of the Probe Wash, Cyclones, and Filter Extracts

The GC/MS analysis of the probe wash, cyclones and filter extracts should be run using the chromatographic conditions given below.

Liquid phase-OV-17
Liquid loading-3%
Solid Support-Chromasorb W, AW, DMCS
Column type-glass
Column size - 2 mm ID x 2 meters long
Temperature program-50°C for 5 minutes, 50-280°C at 6°C per minute
Hold at maximum until all peaks elute.
Injector temperature-280°C
Detector and transfer line to separator temperature-280°C
Flow rate of helium-30cc per minute

Sample size - 5 μl
Sensitivity 3 $\mu g/m^3$

This set of chromatographic conditions is general and is designed to separate and quantify most organic compounds suspected to be present in a sample. Specific categories and concentrations determined from the LC fractionation step may dictate the use of an alternate column and/or modification of the conditions for this column. This judgement can be made only by the analyst based on his ability to interpret the GC/MS data. The complexity of this extract is expected to vary widely depending on the source. When a sample is highly complex, the use of chemical ionization mass spectrometry is recommended. Chemical ionization may aid in the interpretation of individual mass spectra, especially if no molecular ion is present in the EI spectrum.

When problems of chromatographic resolution are present due to sample complexity, the use of capillary GC/MS may aid compound identification. Liquid phase selection should be made based on data from the Level 1 data. A good starting column would be a 50 foot OV-17 SCOT column. The application of capillary GC/MS is discussed elsewhere in this section.

Prescreening GC/MS Analysis of the XAD-2 Resin Extract

The procedure outlined for the probe, cyclones, and filter extract, is adequate for the methylene chloride extract of the XAD-2 sorbent material. No special precautions other than those discussed above are necessary. The sensitivity of this analysis is also expected to be 3 ug/m^3.

Prescreening GC/MS Analysis of the Condensate Extract

The condensate extract consists of two parts, a base/neutral fraction and an acid fraction. The GC/MS analysis of these fractions is based on the polarity of compounds expected to be present. The separation of the condensate into two parts is to possibly eliminate the need for an LC fractionation step on this sample and to assure total organic removal from the condensate. The base/neutral fraction may be somewhat complex but the acid fraction should be relatively clean. If the chromatograms are not too complex, it is advisable to concentrate the samples 100 fold and repeat this analysis to increase the overall sensitivity without having to do LC fractionation. A probe HRMS run on the residue of the sample will provide information on the compounds which are not amenable to GC/MS. If both fractions are complex, the samples should be blended prior to LC fractionation, however, if only one fraction is complex, only that fraction need be submitted for further workup.

GC/MS Analysis of the Base/Neutral Fraction of the Condensate

The same procedure outlined for the probe, cyclones, and filter extracts is applied to the base/neutral fraction of the condensate. Sensitivity of this analysis is expected to be 3 μg/m^3.

GC/MS Analysis of the Acid Fraction of the Condensate

Due to the polarity and the acidic nature of the acid fraction, a polar column is used for this analysis. For prescreening of the acid fraction a phosphoric acid treated carbowax 20M column is recommended. Other columns such as tenax and FFAP will also work. When using the carbowax column, phosphoric acid treated glass wool should be used to plug the column ends. This will minimize adsorption of acidic species. The gas chromatographic procedure for the carbowax column is given below:

Liquid phase - 3% phosphoric acid and 10% carbowax 20M

Solid support - Chromasorb W-AW

Column type - glass

Column size - 2 MM ID x 2 meter long

Temperature program - 50°C for 5 minutes; 50-180° at 4°C per minute. Hold at maximum until all peaks elute.

Injector temperature - 190°C

Detector and transfer line to separator temperature - 190°C

Flow rate of helium - 30cc per minute

Sample size - 5 μl

Sensitivity - 5 μg/m^3

Ultimate Organic Compound Identification

Once the prescreening GC/MS work has been completed on the extracted samples, a general idea of compound type or class is available. If no significant organic compound presence is found the Level 2 analysis can be stopped at this point. If materials are detected and have not been satisfactorily identified, the analysis should continue on those samples using the following procedures.

The next step is to separate the various extracts, after they have been condensed, by liquid chromatography to permit compound identification. The purpose of this LC procedure is to separate the samples into approximate classes based on polarity using a gradient elution technique. The detailed procedure for the LC fractionation is given in the Level 1 manual. The LC separation is not a high resolution technique, therefore overlap in the compound classes in many of the fractions is common. The procedure for Level 1 is followed, even though several of the fractions are blended after separation prior to analysis. The blending of fractions is due to compound class similarity and allows a more cost effective GC/MS analysis. Table 3 gives the blending of the fractions following the LC separation using the solvent gradient outlined in Table 4 . (Unblended aliquots can be analyzed if the analyst decides complexity warrants).

Table 3. LC FRACTION BLENDING

LC Fraction	Blend
1	A
2	B
3	
4	C
5	
6	D
7	

Sample size - 5 μl

Sensitivity - 3 $\mu g/m^3$

The compounds generally found in LC fractions 2 and 3 also not amenable to chemical ionization. Electron ionization spectra of these materials should be sufficient for compound identification.

GC/MS Analysis Fraction C (4 & 5)

Fraction C represents classes of compounds with increased polarity over the previous fractions. Several intermediate polarity nitrogen, sulfur, and oxygen containing compounds elute in these fractions. Analysis of this material is best suited to an intermediate polarity silicon column of which there are several to choose from. The chromatographic conditions given below represent a compromise for this class of materials.

Liquid Phase - OV-17

Liquid loading - 3%

Solid support - chromasorb W

Column type - glass

Column size - 2 mm ID x 2M long

Temperature program - 50°C for 5 minutes; 50-290°C at 6°C per minute. Hold at maximum until all peaks elute.

Injector temperature - 290°C

Detector and transfer lines to separator temperature - 290°C

Flow rate of helium - 30 cc per minute

Sample size - 5 μl

Sensitivity - 3 $\mu g/m^3$

Due to the nature of these classes of compounds and the fact that they generally contain heteroatoms, chemical ionization is recommended as a supplemental technique to aid in the interpretation of the mass spectral data.

GC/MS Analysis of Fraction D (6 & 7)

LC fractions 6 and 7 represent a complex mixture of compounds which are rather polar and have widely varying acidities. In these two fractions both basic and acidic compounds elute together, and such mixtures are not amenable to a single gas chromatographic column. Without previous information as to the nature of compounds present, it is necessary to run this fraction on at least three different GC columns in order to insure that all materials in the sample have been identified.

The columns selected for these analyses (given below) include an intermediate polarity silicon column, a column designed to elute free fatty acids and glycols, and another to elute free amines. A class of compounds known as nitrosoamines elute in this fraction. These materials are very toxic even at low concentrations. An attempt to analyze for nitrosoamines in this mixture, without special care would be virtually impossible. If nitrosoamines are expected, special precautions should be taken. Specifically designed clean up steps should be used followed by chromatographic analysis with a column such as carbowax 20M, which is especially good for nitrosoamines at low concentration.

Liquid Phase OV-17
Liquid loading - 3%
Solid support - Chromasorb W
Column type - glass
Column size - 2 mm ID by 2 meters long
Temperature program - 50°C for 5 minutes; 50-300°C at 6° per minute. Hold at temperature maximum until all peaks elute.
Injector temperature - 290°C
Detector and transfer line to separator temperature - 290°C
Flow rate of helium - 30 cc per minute
Sample size - 5 microliters
Sensitivity - 3 $\mu g/m^3$

This column is designed to elute those compounds with intermediate polarity such as esters, ketones, and nitrogen heterocycles. The more polar materials are better suited to an FFAP column described below.

Liquid Phase - FFAP

Liquid loading - 10%

Solid Support - Chromasorb W-AW

Column type - glass

Column size - 2 mm ID by 2 meters long

Temperature programs - 50°C for 5 minutes; 50-230°C at 6° per minute. Hold at temperature maximum until all peaks elute.

Injector temperature - 240°C

Detector and transfer line to separator temperature - 250°C

Flow rate of helium - 30 cc per minute

Sample size - 5 μl

Sensitivity - 10 $\mu g/m^3$

The basic compounds such as amines are better suited to columns specific for basic materials. The following set of conditions will provide good chromatographic separation for basic compounds.

Liquid Phase - 10% carbowax 20M - 3% KOH

Solid Support - Chromasorb W

Column type - glass

Column size - 2 mm ID by 2 meters long

Temperature program - 50°C for 5 minutes 50-180 at 6° per minute. Hold at temperature maximum until all peaks elute.

Injector temperature - 180°C

Detector and transfer line to separator temperature - 190°C

Flow rate of helium - 30 cc per minute

Sample size - 5 μl

Sensitivity - 10 $\mu g/m^3$

The use of these three columns should provide compound identification on fractions 6 and 7. Alternate columns may be used if information from the GC/MS analysis of the original extracted material shows specific categories present.

LEVEL II ANALYSIS OF PROCESS WATER SAMPLES

This Level 2 plan for analysis of water samples is taken from the Sampling and Analysis Procedures for the Survey of Industrial Effluents for Priority Pollutants, published by the Environmental Protection Agency, Cincinnati, Ohio. The schematic plan is outlined in Figure 3-3. The analysis is divided into three parts. The first is a direct injection of the aqueous sample for the determination of very high concentrations of organic materials and those compounds which are not amenable to the Bellar purge and trap technique. The second step is the purge and trap technique where an aqueous sample is purged with an inert gas, and the water immiscible volatile organic compounds are trapped on a Tenax solid sorbent prior to GC/MS analysis. Finally, the sample is extracted, first at an alkaline pH followed by an acidic pH extraction to separate the higher boiling and water miscible organics which may be either neutral, basic, or acidic.

Direct Aqueous Injection GC/MS

When impurities in the water exits at very high concentration, they can be most easily determined, both qualitatively and quantitatively by direct aqueous injection of the water sample. Typically, a 5 microliter sample of the water is injected onto an appropriate GC column such as Tenax for polar compounds and Porapak Q for non-polar compounds using the conditions given below. The direct injection technique is also useful for the analysis of extremely volatile impurities which cannot be determined by the purge and trap technique.

Tenax GC

Column type - Tenax GC

Column material - glass

Column size - 2 mm ID x 2 meter long

Temperature program - $50^{\circ}C$ for 5 minutes; $50-300^{\circ}C$ at 6° min; Hold at maximum until all peaks elute.

Injector temperature - $280^{\circ}C$

Detector and transfer line to separator temperature - $280^{\circ}C$

Flow rate of helium - 30 cc per minute

Sample size - 5 μl

Sensitivity - 100 μg/l

Tenax GC is a gas-solid chromatographic material. It does not contain a liquid phase and has very good temperature stability. It tends to elute polar materials with ease, however, non polar compounds are highly retained on the column. The ultimate sensitivity achieved with this column is somewhat lower than many others due to its adsorbtive character.

Porapak Q

Porapak Q is a porous polymer which is also a gas solid absorbent, and will elute most nonpolar compounds with good resolution.

Column type - Porapak Q

Column length - 4 mm ID by 2M long

Temperature program - Room temperature to 240°C at 6°C per minute. Hold at maximum until all peaks elute.

Sample size - 5 µl

Sensitivity - 100 µg/l

Purge and Trap Concentration Technique

The purge and trap technique is designed to concentrate those organic compounds from water which are immiscible and have a boiling range up to about 130°C, very low boiling immiscible materials are not trapped by this technique. The apparatus used for this analysis consists of a purging chamber in which the sample is placed. The chamber is purged with an inert gas such as helium at a flow rate of 40 cc per minute. The purge time is approximately 12 minutes. The organic vapors are trapped on a a Tenax and silica gel column which is subsequently heated. The desorbed gases are injected into a gas chromatograph, followed by separation on a carbowax 1500 column.

Liquid phase - 0.2% Carbowax 1500

Solid support - Carbopak C

Column type - glass

Column size - 2 mm ID by 3 meters long proceeded by a short column of 3% Carbowax 1500 on Chromasorb W

Helium flowrate - 30 cc per minute

Temperature program - room temperature during trap desorption followed by rapid heating to 60°C hold for 4 minutes then program at 8°C per minute to 170°C and hold for 12 minutes or until all compounds have eluted.

Sensitivity - variable depending on trapping efficiency, must be determined daily when analysis technique is used. Internal standard must be used for quantitation.

The column used in this analysis has very high resolution for nonpolar materials which are low boiling. These include categories 1, 2, 15, and 16 of the MEG list. If the sample is highly contaminated and chromatographic resolution is insufficient for compound identification, the use of a capillary column, either OV-17 or Carbowax 20M, may be used as a substitute in this analysis.

When using the purge and trap technique it is necessary to run blank water samples between each analysis sample. It is also necessary to bake the trap during the course of the GC run to remove all possible interferring organic substituents which may cross over from one sample to the next due to insufficient trap heating.

Extraction of Water Samples for GC/MS Analysis

The extraction of water samples for analysis by GC/MS is identical to the procedure outlined for the condensate sample of the sampling train. If the chromatographic analysis of the extracts are complex and incomplete compound identification results, the LC fractionation step should be implemented as outlined in Figure 2-2. The sensitivity of this technique is 7 g/l.

ANALYSIS OG GAS BAG SAMPLES BY GC/MS

The gas bag samples are analyzed by expulsing a known volume of the gas and trapping on a tenax support. The tenax trap is then heated and the desorbed compounds are condensed in a LN_2 trap before injection onto a Porapak Q GC column. The sample is chromatographed and spectra recorded for each peak which elutes. Blank bag samples must run to correct for normal bag background.

ANALYSIS OF BULK SOLID SAMPLES

Bulk solid samples such as scrubber cake and fly ash are extracted with methylene chloride using a Soxhlet apparatus. The sample is then analyzed by GC/MS using the same procedures as discussed earlier. The sensitivity for this technique, based on a 5 g sample, is 4 g/kg. If more sensitivity is required a larger sample must be used.

APPENDIX C

INORGANIC ANALYSIS METHODS

APPENDIX C
INORGANIC ANALYSIS METHODS

The comparative assessment tests conducted at the Firestone boiler were designed to study the effect of emission control devices on the flue gas composition. As part of this program, Level 1 and comprehensive Level 2 sampling and analysis procedures were used to study the inorganic compounds in the flue gas streams. The Level 2 sampling consisted of using modified method 5 train for particulate matter in the flue gas and the controlled condensation system for the H_2SO_4 content of the flue gas. These trains are shown in Figures 1 and 2. In this approach, the Level 1 SSMS elemental data was to be the focus of identification efforts on specific elements. The criteria used for the evaluation was MEG compounds and MATE values[1] developed from the Industrial Environmental Research Laboratory of the EPA at Research Triangle Park.

After the Level 1 data was reviewed, specific analytical techniques were used to look for compounds in the sample. These methods included:

- Thermogravimetric Analysis (TGA) — Used to determine drying temperatures or stability data.
- Polarized Light Microscopy (PLM) — Used visually to identify materials present in the sample.
- Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) — Used to determine accurate inlet/outlet concentration of elements.
- Fourier Transform IR (FTIR) — Used to identify inorganic compounds from specific IR band correlations.
- X-Ray Diffraction (XRD) — Used to directly identify crystalline material in the solid samples.
- Electron Spectroscopy for Chemical Analysis (ESCA) — Used to study the surface and sub-surface sulfur concentrations and oxidation state of bulk samples.
- Secondary Ion Mass Spectrometry (SIMS) — Used to study the surface and sub-surface composition of bulk samples.
- Scanning Electron Microscope with Energy Dispersive X-Ray Fluorescence (SEM-EDX) — Used to obtain high resolution photographs and elemental composition of single particles.
- Transmission Electron Microscope with Selective Area Electron Diffraction (TEM-SAED) — Used to identify individual particles by their electron diffraction pattern.

In addition to these instrument methods, specific anion analyses for Cl^-, F^-, NO_3^-, and $SO_4^=$ were run on all the samples.

The following sections will discuss the results from each of the techniques. Specific correlation found in the data will be presented in the discussion section.

RESULTS OF ANALYSES

Complete sets of samples were available for Test 201-1 (coal) and 202-4 (oil). Only these sample sets were analyzed, since the boiler operated at 85 percent or better load through all of the tests.

The following sections contain the data from each of the methods employed for each sample analyzed. In some cases, two or more methods will be discussed together for comparison purposes.

Evaluation of Level 1 SSMS Data

The SSMS data was reviewed and compared to the air MATE values for the most toxic MEG compound of each element. The comparison consists of determining the ratio of the value found in each sample to the appropriate MATE value. It has been decided, in view of the relative inaccuracy (factor of 2-3) of SSMS, that any ratio of sample to MATE air value exceeding 0.5 would require further research be focused on those elements. Table 1 shows an example of how the Level 1 data was reduced for the Site 203 outlet sample. Both the coal (200) and the oil (203) sites outlet SSMS data were evaluated in this fashion, and the results exceeding 0.5 percent of their MATE values are tabulated in Table 2. Though the oil samples had a lower inlet particulate loading, the number of elements exceeding their MATE values was high for the oil outlet emission values. The following analyses seek to find more quantitative information about these elements, and determine the exact species present.

TGA Test Results

TGAs were run on all available loose particle samples. These included: 201-1-I cyclone and filter, 201-1-scrubber cake, 202-4-cyclone and 202-4 scrubber cake. The analyses were performed using a duPont 950 instrument in a N_2 atmosphere at up to 600°C; the spectra may be found in Appendix A. Both 201-1-I cyclone and filter material showed little weight loss up to 500°C. After that point, a steady weight loss was noted. The

TABLE 1. EXAMPLE OF LEVEL 1 SSMS DATA REDUCTION FOR 203 OUTLET

CATEGORY	COMPOUND	MATE AIR µg/m³ (ppm)	MATE WATER µg/l HEALTH	MATE WATER µg/l ECOLOGY	MATE LAND µg/l HEALTH	MATE LAND µg/l ECOLOGY	SAMPLE µg/m³ (ppm) µg/l	RATIO SAMPLE/MATE	LEVEL 2 REQUIRED Y=YES N=NO
27. LITHIUM	Li	2.2×10	3.3×10^2	3.8×10^2	7.0×10^{-1}	7.5×10^{-1}	<1	0.04	N
	Li^+	2.2×10	3.3×10^2	3.8×10^2					
	LiF (as Li)	2.2×10	3.3×10^2	3.8×10^2					
	Li_2CO_3 (as Li)	2.2×10	3.3×10^2	3.8×10^2					
	LiH	2.5×10	3.8×10^2	N					
28. SODIUM	Na^+	5.3×10^4	8.0×10^5	N	1.6×10^3	N			
	NaOH	2.0×10^3	3.0×10^4	N	6.0×10	N			
29. POTASSIUM	KOH	2.0×10^3	3.0×10^4	N	6.0×10	N	24500	12.3	Y
	K	N	N	N	N	N	325	0.16	N
	K^+ (as K)	N	N	2.3×10^4	N	4.6×10			
30. RUBIDIUM	Rb^{+1}	1.21×10^5	1.82×10^6	N	3.64×10^3	N			
31. CESIUM	CS^{+1}	8.19×10^4	1.23×10^6	N	2.46×10^3	N			
32. BERYLLIUM	Be	2.0	3.0×10	5.5×10	6.0×10^{-2}	1.1×10^{-1}	1	0.5	Y
	Be^{++}	2.0	3.0×10	5.5×10	6.0×10^{-2}	1.1×10^{-1}			
	BeO (as Be)								
	$BeO \cdot Al_2O_3 \cdot SiO_2$ (as Be)	2.0	3.0×10	5.5×10	6.0×10^{-2}	1.1×10^{-1}			
33. MAGNESIUM	Magnesium, Mg	6.0×10^3	9.0×10^4	8.7×10^4	1.8×10^2	1.7×10^2	4640	0.78	Y
	Mignesium Ion, Mg^{++}	6.01×10^3	9.0×10^4	8.7×10^4	1.8×10^2	1.7×10^2			
	Magnesium Oxide, MgO	1.01×10^4	1.5×10^5	1.0×10^5	3.0×10^2	2.0×10^2			
	Magnesium Fluoride, MgF_2 (as Mg)	6.0×10^3	9.0×10^4	8.7×10^4	1.8×10^2	1.7×10^2			
	Magnesium Sulfate, $MgSO_4$ (as Mg)	6.0×10^3	9.0×10^4	8.7×10^4	1.8×10^2	1.7×10^2			
	Magnesite, $MgCO_3$ (as Mg)	6.0×10^3	9.0×10^4	8.7×10^4	1.8×10^2	1.7×10^2			
	Dolomite, $MgCO_3 \cdot CaCO_3$ (as Mg)	6.0×10^3	9.0×10^4	8.7×10^4	1.8×10^2	1.7×10^2			
	Asbestos (as Mg)	6.0×10^3	9.0×10^4	8.7×10^4	1.8×10^2	1.7×10^2			
34. CALCIUM	Calcium Ion, Ca^{++}	1.6×10^4	2.4×10^5	1.6×10^4	4.8×10^2	3.2×10	297	0.02	N
	Calcium Fluoride, CaF_2	N	N	N	N	N			
	Calcium Carbonate, $CaDO_3$	N	N	N	N	N			
	Calcium Sulfate, $CaSO_4$	N	N	N	N	N			
	Dolomite, $MgCO_3 \cdot CaCO_3$	N	N	N	N	N			

TABLE 2. SAMPLE TO MATE RATIOS ≥ 0.5

200-Outlet	203-Outlet	
Li	Na	Sb
Be	Be	S
Si	Mg	V
As	Ba	Cr
S	Si	Fe
Cr	Pb	Co
Fe	P	Ni
Ni	As	Cd

202-4-I-cyclone sample showed a completely different thermal weight loss profile. That sample showed an immediate loss of 1 percent up to 50°C, 1 percent between 50 and 100°C, 2 percent from 100 to 425°C and 26 percent from 425 to 600°C. The first two weight losses probably represent water of hydration and the final weight loss was probably due to a decomposition or volatilization.

If the composition of a sample is known, TGA can be used to quantitate a compound based on a specific weight loss due to waters of hydration or decomposition patterns. In this case, $CaSO_3 \cdot 1/2H_2O$ should be present in the scrubber cake, and at ~100°C all of the H_2O molecules are lost. Based on the weight fraction of H_2O in $CaSO_3 \cdot 1/2H_2O$ and the percentage weight loss between 25 to 125°C, an upper limit to the amount of $CaSO_3$ present in the scrubber cake can be set. The 201-1-scrubber cake (Attachment A) shows an initial weight loss probably due to moisture in the sample. The second plateau between 50 and 125°C could be due to the loss of the water hydration. This weight change indicates that as much as 27 percent $CaSO_3 \cdot 1/2$ was present in the 201-1-scrubber cake. No similar plateau was found in the 202-4-scrubber cake.

PLM and SEM-EDX

PLM analysis of samples from the coal (201) and oil (202) tests was completed on the following samples:

- 201-1-flyash
- 201-1-I-cyclone

- 201-1-I-filter
- 201-1-scrubber cake
- 201-1-0-filter
- 202-4-I-cyclone
- 202-4-I-filter
- 202-4-scrubber cake
- 202-4-0-filter

PLM analysis consists of viewing the samples under a microscope to study: size, shape, color, and color fracture index of the particles. Using these and other physical properties, an analyst can identify individual particles with diameters as small as ∿0.5μ. Below that level SEM must be used to provide an image of the particles for morphological study.

The EDX attachment provides elemental composition information for selected areas of a particle. Thus, SEM-EDX can be used to identify an unknown particle from its elemental composition as well as its general morphology. In this section selected SEM-EDX photographs will be used to illustrate and support the discussion of the PLM results. The entire set of PLM photographs may be found in Attachment B.

A particle size distribution of each powder sample was determined using optical microscopy with manual sizing. The results of this analysis along with the calculated arithmetic mean diameter of the particles in each sample are presented in Table 3.

Table 4 displays the results of the polarized light microscope analysis. Estimated weight percentages, estimated modal size, and size range for each component in each sample are summarized in this table.

Three of the nine samples (201-1-0-Filter, 202-4-I-Filter and 202-4-0-Filter) were impacted on glass fiber filters. These were so heavily loaded that particles could not be distinguished from one another. An attempt was made to remove particles by "teasing" them off with a needle. This was unsuccessful because the particles firmly adhere to one another and the filter. For this reason, no overall particle size distribution was performed on these samples, nor was SEM-EDX analysis possible.

TABLE 3. OVERALL SIZE DISTRIBUTION

Size Ranges	201-1-Flyash	201-1-I-Cyclone	202-4-I-Cyclone
<3.2μm	20.8%	39.6%	21.2%
3.2-6.4	21.3%	26.9%	28.1%
6.4-12.8	19.9%	17.0%	26.6%
12.8-19.2	17.6%	9.9%	11.3%
19.2-32.0	12.0%	5.2%	8.9%
32.0-48.0	5.1%	0.9%	2.5%
48.0-64.0	2.3%	0.5%	0.5%
64.0-96.0	0.5%	0.0	1.0%
96.0-128	0.5%	0.0	0.0
>128μm	0.0	0.0	0.0
Arithmetic Mean Diameter	13.4μm	6.63μm	10.4μm

Size Ranges	201-1-I-Filter	201-1-Scrubber Cake	202-4-Scrubber Cake
<1.0μm	19.6%	33.0%	37.7%
1.0-2.0	22.5%	20.9%	29.1%
2.0-3.0	16.7%	13.1%	11.2%
3.0-4.0	10.5%	10.2%	9.9%
4.0-6.0	12.0%	10.7%	7.2%
6.0-8.0	8.6%	5.3%	2.2%
8.0-10.0	4.3%	2.4%	0.4%
10.0-14.0	2.9%	2.4%	1.3%
14.0-20.0	1.0%	1.5%	2.2%
>20.0μm	0.0	0.5%	0.9%
Arithmetic Mean Diameter	3.32μm	2.99μm	2.78μm

TABLE 4. PLM ANALYSES RESULTS

COAL FIRED BOILER SAMPLES

Components	201-1-Flyash			201-1-I-Cyclone			201-1-I-Filter			201-1-Scrubber Cake			201-1-0-Filter
	A	B	C	A	B	C	A	B	C	A	B	C	A
Partially fused flyash	65-80%	30	5-140	55-7%	25	5-65	40-55%	12	5-40	55-70%	20	4-60	
Flyash	1-5%	4	1-20	10-20%	4	1-16	35-50%	2	<1-13	10-20%	5	1-15	
Oil soot	5-15%	25	2-100	10-20%	15	2-80	10-25%	8	1-40	10-20%	15	1-60	25-40%
Magnetite	10-20%	12	3-45	10-20%	12	3-25	<2%	5	2-14	1-5%	10	5-45	
Iron oxide	2-5%	15	1-40	1-5%	7	<1-50	<2%	5	1-18	<2%	3	1-21	15-25%
Coke	1-5%	40	5-160	<2%	60	6-100							
Quartz	<2%	12	5-60	<2%	20	5-40							
Calcite										<1%	6	1-10	1-5%
$CaSO_3 \cdot 1/2H_2O$										10-20%	6 (length)	3-21 (length)	50-65%
Unknown sulfate													

OIL FIRED BOILER SAMPLES

Components			201-4-I-Cyclone			202-4-I-Filter	202-4-Scrubber Cake			202-4-0-Filter
			A	B	C	A	A	B	C	A
Partially fused flyash			20-35%	20	6-40					
Flyash			1-5%	3	<1-15					
Oil soot			60-75%	20	<1-140	10-20%	1-5%	30	1-80	
Magnetite			<2%	12	3-50					
Iron oxides			<1%	8	3-35	15-30%				5-10%
Unknown sulfate			1-5%			45-60%				50-65%
$CaSO_3 \cdot 1/2H_2O$							95%+	30	2-80	
Calcite						1-5%				
Water droplets						15-30%				30-45%

Key: A - Estimated weight percent
B - Estimated modal diameter (μm)
C - Size range (μm)

Particles found in most samples were flyash, partially fused flyash, oil soot, and iron oxide (hematite and magnetite). Traces of quartz shards, coke, and calcite were found in many samples. Both scrubber cake samples contained calcium sulfite hemi-hydrate ($CaSO_3 \cdot 1/2H_2O$). That hydrate was the principal component of sample 202-4-scrubber cake.

Regardless of whether coal (series 201) or oil (series 202) was used to fire the boiler, oil soot was found in the samples collected. There was, however, a difference in the appearance of the oil soot from the two series. Figure 1 shows oil soot in sample 202-4-I-cyclone collected during oil combustion. The oil soot is largely in the form of complete cenospheres with smooth, unbroken walls. Oil soot from sample 201-1-flyash which is representative of the oil soot in all the 201 series samples is shown in Figure 2. It appears to be broken, abraded, and has a grainy surface texture. The more worn appearance of the 201 series oil soot indicates that it was probably oil soot retained in the ducts from some earlier oil combustion. It was probably not freshly produced oil soot from oil combustion which occured during the sampling period.

Descriptions of the individual samples follow.

Coal Fired Samples --

Sample 201-1-Flyash --

Between 65-80 percent of the sample mass is partially fused flyash. These are the large white particles seen in Figure B-3. The opaque white appearance is due to reflection off air bubbles entrapped in the transparent, glassy, colorless material which comprises the partially fused flyash. In this sample these particles are very large, roughly spherical, up to 14μ in diameter. Figure 3 shows a SEM photograph of a partially fused flyash particle with its elemented analysis.

Magnetite comprises 10-20 percent of the sample mass. These shiny black spheres range in diameter from 3 to 40μ, with an average size of about 12μ. They are easily detectable by moving a magnet near the sample and watching for a corresponding motion in the sample. Figure 4 shows a SEM photo of an iron oxide particle.

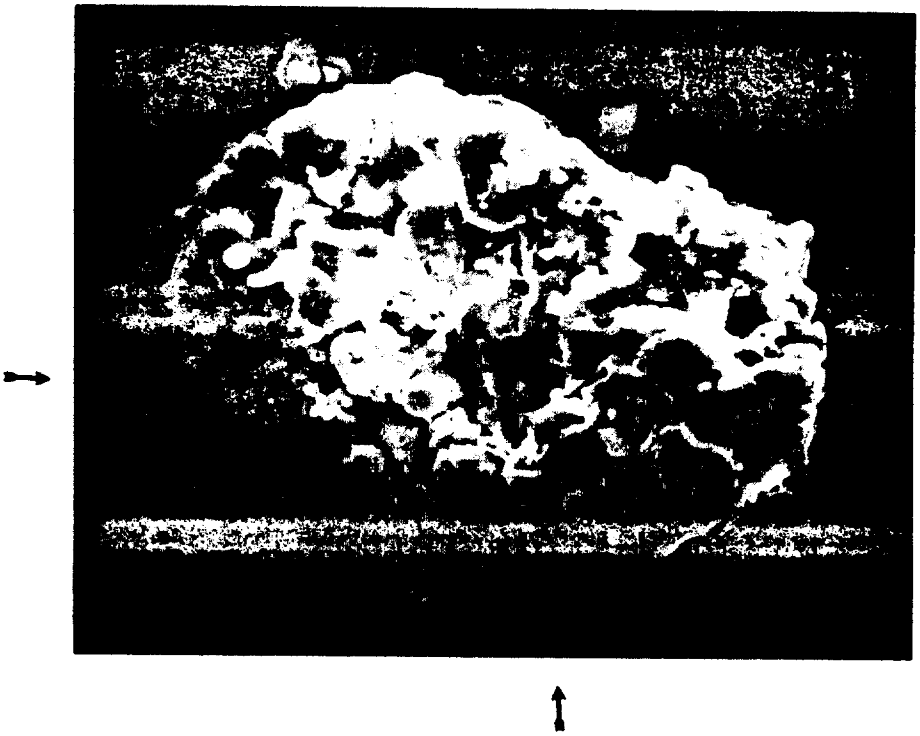


Figure 3. SEM-EDX of partially fused flyash from 201-1-Flyash. Elements present at position marked: Si, Fe (strong); K, Ti (medium) and Cu (trace).

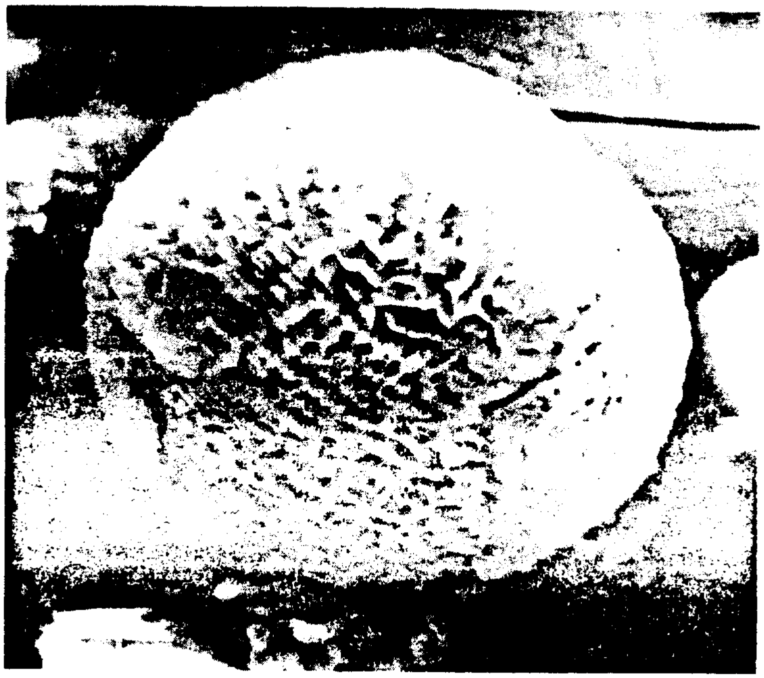


Figure 4. SEM-EDX of iron oxide particle from 201-1-Flyash. Approximately 36μ diameter. Elements present: Fe (strong); Si (weak).

Oil soot was also present, primarily as fragments of cenospheres. There are many intact cenospheres in this sample, however, they looked worn and abrated as previously described. Oil soot represented 5-15 percent of the sample mass.

The flyash ranged in color from clear, colorless spheres to golden, brown, or red spheres. All are transparent and around 10 percent contain air bubbles. The average diameter was estimated to be 4μ and the largest flyash sphere seen was 20μm in diameter. Flyash was a minor sample component, contributing less than 5 percent of the total mass.

Up to 5 percent of this sample was iron oxides. Most of these were hematite: nonmagnetic, red or orange red, roughly spherical, birifringent particles. Trace components were quartz shards and a few large (>100μ in diameter) pieces of coke.

Sample 201-1-Cyclone --

As in the 201-1-flyash sample, the glassy masses of partially fused flyash were the largest sample components (55-70 percent of the sample mass). In general, this component was morpholically similar to that in the 201-1-flyash sample but smaller in size (see Figure B-4). The largest particle of partially fused flyash found in this sample had a diameter of only 65μ as compared with 140μ in the 201-1-flyash sample. Most of the partially fused flyash particles in this sample were between 20 and 30μ m in diameter.

Oil soot was a major component at 10-20 percent of the sample mass. Few intact spheres were present, most were large portions of the spheres and fragments. As in the other 201 series samples, the oil soot appeared more abraded than in the 202 series samples. The average diameter of an oil soot particle was about 15μ, but they range from 2μ up to 80μ.

Magnetic particles also constituted about 10-20 percent of the sample mass. These black, opaque spheres average about 12μ in diameter and spheres up to 25μ in diameter were seen in this sample.

About 10-20 percent of this sample was flyash (Figure 5). These transparent spheres ranged from colorless to dark brown but most were yellow-tan in color. A small portion of these spheres contain air bubbles

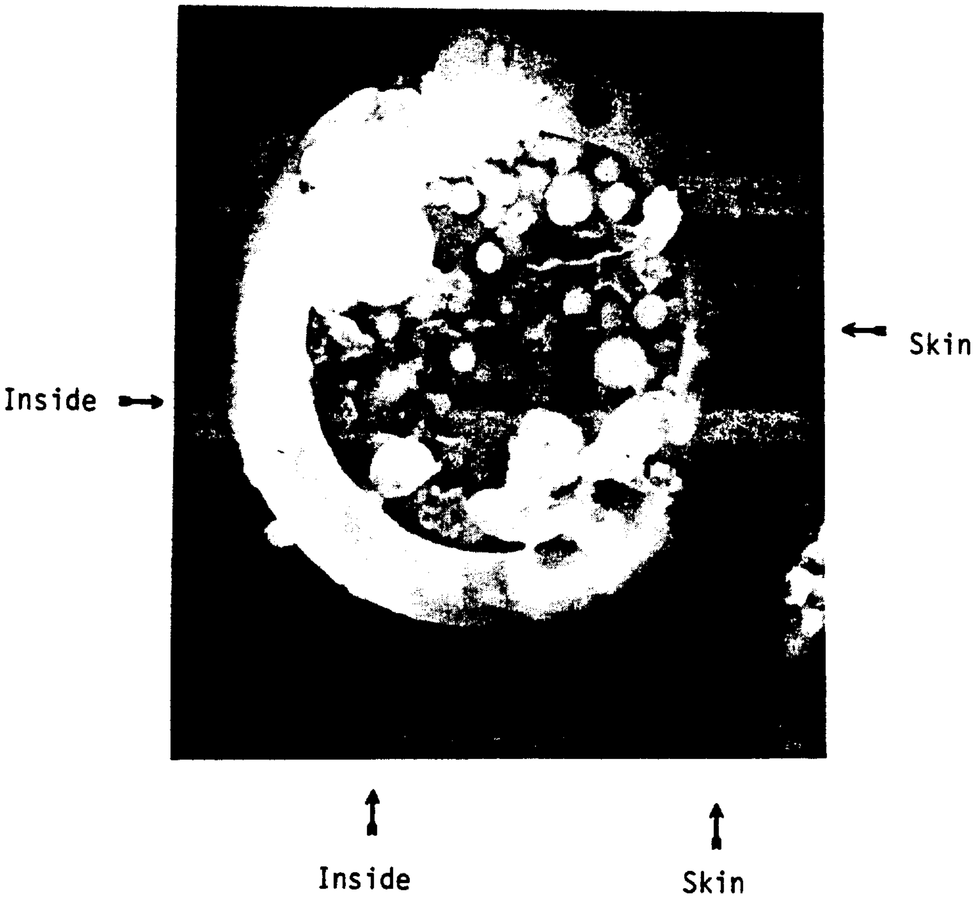


Figure 5. SEM photo of a cenosphere from 201-1-I-Cyclone. Elemental composition by area:

1. Inside: Si, Fe (strong), Ti, Ca, K (medium)
2. Skin: Si (strong), Ca (medium), Ti, Fe (weak).

and some had an orange peel surface texture. Their average diameter is 4μm and almost all were between 1μm and 12μm. The largest sphere seen had a diameter of 16μm. Figure B-5 is an example of the type of cenospheres found in this sample.

Quartz shards, coke, and iron oxides are trace sample components. The quartz shards are sharp and look freshly broken. Most of the iron oxide is in the form of hematite.

<u>Sample 201-1-I-Filter</u> --

It should be noted in the particle size distribution tabulation (Table 3) there were not as many large particles (>20μm) in this sample

(Figure 6) as in the other powder samples analyzed (Figure 3 or 4, for example). This sample appeared to be composed primarily of partially fused flyash and flyash.

The partially fused flyash was similar to that in the samples already discussed except that it was considerably smaller. The average diameter is only 12μm (maximum diameter: 40μm) as compared with a 30μm average diameter in sample 201-1-flyash and a 25μm average diameter in sample 201-1-I-cyclone. Partially fused flyash is 40-55 percent of the sample mass.

Glassy flyash spheres contribute 35-50 percent of the sample mass. As with the partially fused flyash, the glassy flyash was morphologically similar to that in the other samples (Figure 7) but generally smaller. The flyash had an average diameter of 2μm. Both the 201-1-flyash and 201-1-I-cyclone contained flyash with an average diameter of about 4μm.

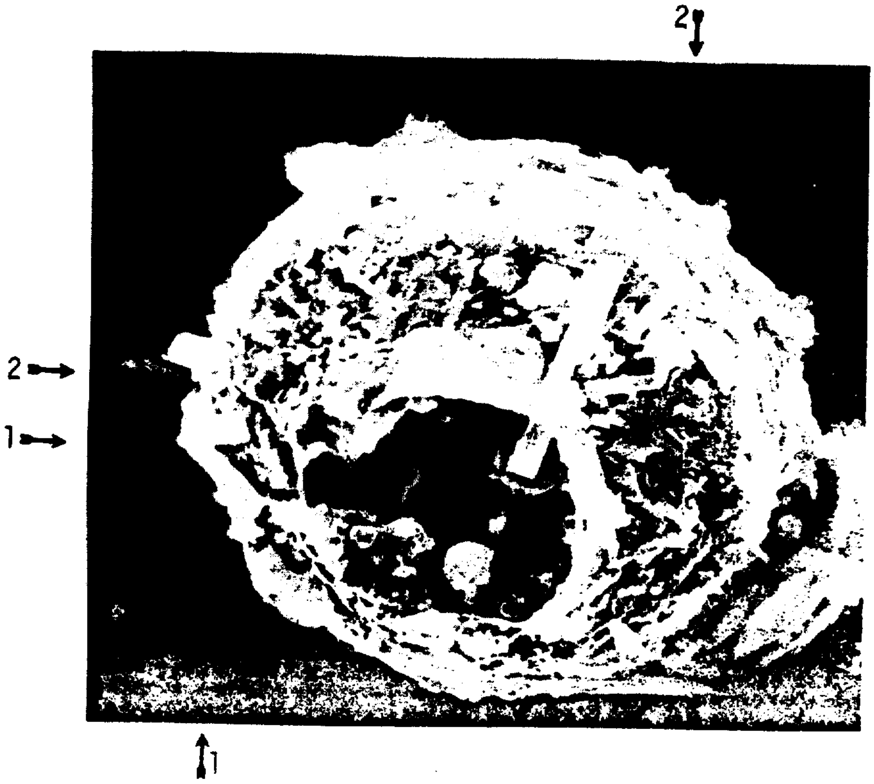


Figure 6. SEM photo of $CaSO_3.1/2H_2O$ laths impacted on flyash cenosphere. Elements present are:

1. Fe, S (strong); Si, Ca (medium)
2. Fe (strong); Si, Ca, S (weak).

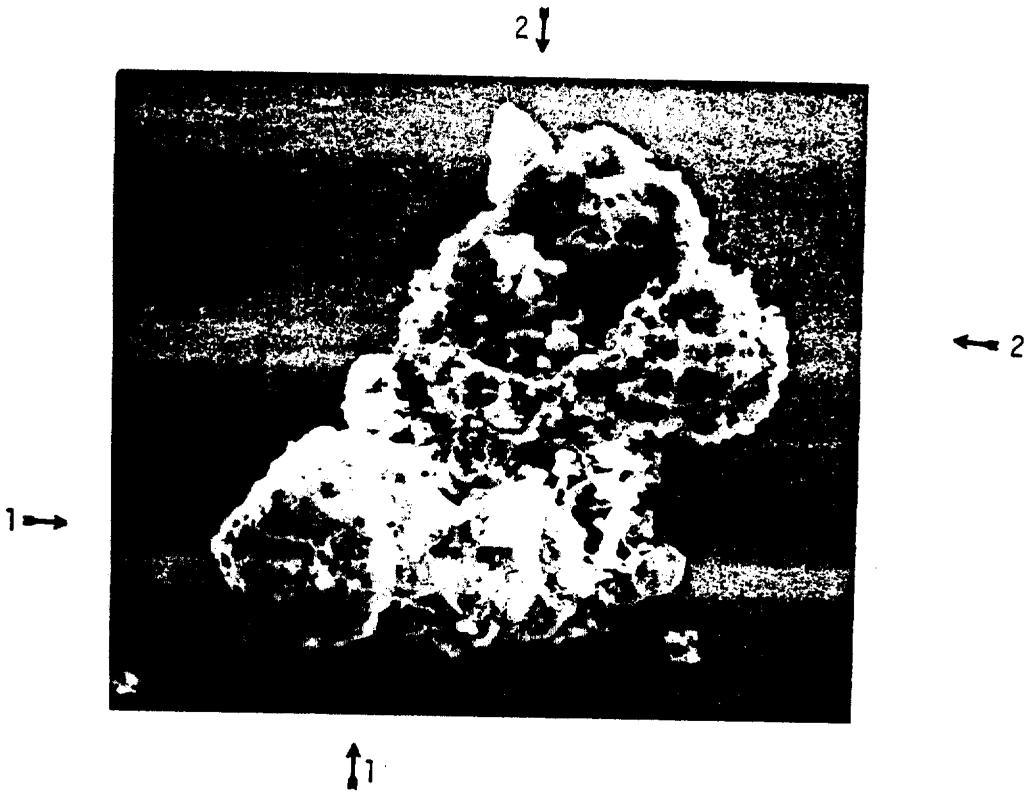


Figure 7. SEM photo of typical aggregates found in 201-scrubber cake. Elements present:

1. Si, Fe (strong); K (weak)
2. Ca, S, Si (strong); Fe (weak).

Fragments of oil soot cenospheres composed 10-25 percent of the sample mass. The oil soot appeared crushed and eaten away and no intact spheres were seen. Magnetite and iron oxides were trace sample components. Iron oxides were present primarily as hematite.

Sample 201-1-Scrubber Cake --

Partially fused flyash was again the largest sample component, 55-70 percent of the sample mass. It was similar in morphology (Figure 8) to that seen in previously discussed 201 series samples. The average diameter was 20μ and the range was from 4 to 60μ.

Several flat, thin particles (Figure 9) (laths) were identified as $CaSO_3 \cdot 1/2H_2O$. This form of $CaSO_3 \cdot 1/2H_2O$ comprised the largest portion of the $CaSO_3 \cdot 1/2H_2O$ present. Spherulites of $CaSO_3 \cdot 1/2H_2O$ were also present. The spherulites in this sample were covered with other particles such as

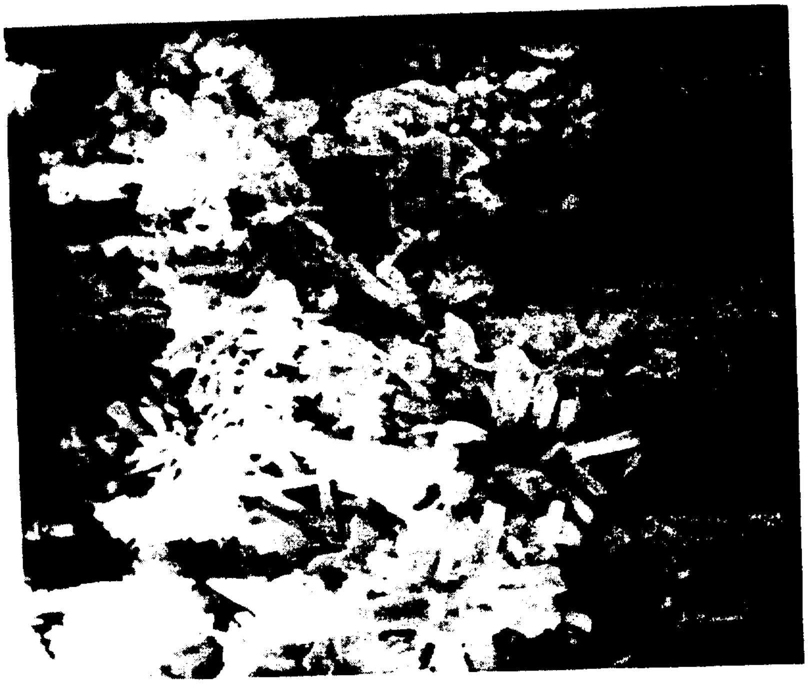


Figure 8. 1000X SEM photo of spherelites found in 204-4-scrubber cake. Elemental analysis: Ca, S (strong).

Figure 9. 600X SEM photo of "ball of twine" in 202-4-scrubber cake. Elemental analysis: Ca, S (strong).

oil soot fragments and flyash (Figure B-10) in them. Figures 6 and 7 show examples of the large amounts of flyash present in the 201 series scrubber cake. In Figure 6 a crystal (area 1) impacted on the cenosphere was analyzed by EDX. The elemental composition identifies it as $CaSO_3$, but the strong Fe signal from the cenosphere surface indicates the thinness of the crystals. Analysis of an aggregate shown in Figure 7 by area showed the presence of $CaSO_3$ in area 2 and flyash in area 1. The $CaSO_3 \cdot 1/2H_2O$ is 10-20 percent of this sample as compared with 80-95 percent of the 202-4- scrubber cake sample.

Ten-twenty percent of this sample was oil soot, almost all of which was in the form of broken fragments with an average diameter of 15μm and a size range of 1 to 60μm in diameter.

The flyash particles in this sample were similar to that in other samples. Their color was primarily tan although they ranged from colorless to brown with an occasional red sphere. All were transparent, a few contained air bubbles and some had an orange peal surface texture. All forms of flyash were responsible for 10-20 percent of the sample mass. The average flyash diameter was about 5μ.

<u>Sample 201-1-0-Filter</u> --

This sample appeared to be composed primarily of fine carbonaceous particles on a filter saturated with unknown sulfate crystals (Figure B-11). The bright birifringence (speckled color) of the filter examined under polarized light may be due to the unknown within the filter.

The fine carbonaceous particles were probably oil soot. This hypothesis is based on the appearance of these particles with oil soot being the major carbonaceous component in all of the other 201 series samples. An analysis for vanadium (associated with oil soot) would confirm or refute this supposition.

Low temperature ashing of a small portion of this sample removed the carbonaceous material, revealing iron oxides (Figure B-12). Both hydrated (yellow) and unhydrated (red) iron oxides were present. Overall, iron oxides probably accounted for 15-25 percent of the sample mass. Calcium carbonate (calcite) particles were also seen after ashing, however, they did not contribute more than 5 percent of the total mass.

Oil Fired Boiler Samples

Sample 202-4-I-Cyclone --

Oil soot, both complete cenospheres and fragments, was the largest sample component, comprising 60-75 percent of the sample mass (Figure B-13). They ranged in diameter from <1μm for fragments up to 140μm for an intact cenosphere. The average diameter for the latter was about 50μm.

A highly birifringent mineral has crystallized on some of the oil soot (Figure B-14). Its identity is unknown but its crystal form and birifringence was similar to some of the crystallized minerals on the 202-4-0 sample (Figure B-22). It did not account for more than 5 percent of the sample mass.

Unfused ash similar to that in the 201 series samples was present in this sample, about 20-35 percent of the sample mass. The ash average 20μ in diameter and ranged for 6 to 40μ.

The largest flyash sphere seen in this sample was 15μ in diameter. The flyash in this sample was generally quite small, averaging 3μ in diameter. Some of the larger spheres contained air bubbles. Less than 5 percent of the sample was flyash.

Magnetite and hematite were trace components. They were similar in morphology to those seen in the 201 series samples.

Sample 202-4-I-Filter --

This sample appeared to be very similar to the 201-1-0 sample (Figure B-15). It contained <1μ reflective carbonaceous particles (10-20 percent of the sample mass) deposited on a filter saturated with crystallized, unknown sulfates (45-60 percent of the sample mass). There were water droplets on this filter which contributed 15-30 percent of the sample mass.

After low temperature ashing this sample, iron oxides could be seen (Figure B-16). They were similar to those of the ashed carbonaceous particles and are also <1μm in diameter. The hydrated (yellow) and unhydrated (red) iron oxides were present in approximately equal amounts and appeared segregated on the filter. These contributed 15-30 percent of the sample mass.

Traces of birifringent calcium carbonate particles can be seen after ashing. These, however, did not compose more than 5 percent of the sample mass.

Sample 202-4-Scrubber Cake --

This sample was almost entirely composed of $CaSO_3 \cdot 1/2H_2O$ spherulites (see Figure B-17). Figure B-18 shows the spherulites with the compensator in place. The SEM photo in (Figure 8) clearly shows the spherulites in the 202-4-scrubber cake. Note also the lack of flyash in the sample. The SEM photo (Figure 9) shows a "ball of twine" which turns out to be composed of Ca and S indicating $CaSO_3$. The spherulites ranged for 15 to 80μm in diameter with an average diameter of about 30μm. Thin, plate-like sheets (seen in Figure B-19) were also present, probably being $CaSO_3 \cdot 1/2H_2O$. This form accounted for only a small part of the sample mass.

Oil soot fragments and calcium carbonate particles were minor sample components. Neither contributed more than 5 percent of the sample mass.

Sample 202-4-0 --

This filter has an overall blue-green color (Figure B-20). The color was probably due to some cation dissolved in water droplets which covered and were absorbed into the glass fiber filter. About 30-45 percent of the sample appeared to be water. Because of this, there was a continuous change in the crystal forms found on that filter resulting from dissolution of chemicals and recrystallization. Two of the crystal forms found initially on this filter are shown in Figures B-20 and B-21. Figures B-22 and B-23 show recrystallized forms after the filter remained in the immersion oil for several weeks. Manipulation of the filter caused redissolution of those crystals as shown in Figure B-23. Crystals similar in morphology to those in Figure B-23 were seen forming in water droplets which had been moved off of the filter. The identity of the crystals is not known at this time, however, it was at least partially calcium sulfite hemi-hydrate and the rest was an unknown sulfate. Later analyses will seek to determine their identity more precisely.

Low temperature ashing of this sample revealed that hydrated iron oxides constitute 5 to 10 percent of the sample mass. The oxides were fine, grainy yellow particulates. Figure B-24 shows the filter after ashing.

Anion and Elemental Data

The modified Method 5 train was operated at the inlet and outlet of the FGD. The particulate matter collected in the probe, cyclone, filter and impinger system was dissolved and then analyzed for 20 elements by the EPA Corvallis Laboratory using ICPOES. Particulate aliquots from these samples were extracted with hot water and then HNO_3. The extraction solutions were analyzed for Cl^-, F^-, NO_3^- (except HNO_3 extract) and $SO_4^=$ by specific ion electrodes or standard wet chemical procedures. The results of these analyses are detailed in Tables 5, 6, and 7.

The anion analysis (Table 5) showed that $SO_4^=$ was the predominant anion in all the samples. Chloride was the ion found in the second greatest concentration (< 1 percent of the sulfate value).

Performing both water and acid extractions of the sample, provides additional information with respect to the type of species present. For example, 201-1-I $SO_4^=$ was primarily HNO_3 soluble, whereas at the outlet only 3 percent of the sulfate was found in the NHO_3 extract. Clearly the nature of the sulfur species was altered by the sulfur species scrubber process (see Section 3).

The elemental data shown in Tables 6 and 7 show trace element concentrations in gm/m^3. The 20 elements listed represent those elements which could be analyzed by the specific ICPOES instrument. Earlier SSMS analysis of sample 200-0 showed 8 elements exceeding their MATE values by a factor >0.5. Of those eight elements, three (Ni, Fe,and Cr) were analyzed by ICPOES in 201-1-0 and they were found to exceed their MATE values. The fact that all three elements again exceeded their MATE values by a factor >0.5 indicates that the SASS train did not cause artificially high Ni, Cr or Fe values through contamination, since all Level 2 samples were obtained using a glass train. In the oil fired case Ni and Cr concentration ratios to MATE values were >0.5, and Fe was not. From the SSMS data, sixteen elements exceeded their MATE ratios. Ten of these elements were analyzed by ICPOES. Only 5 elements (Ar, V, Cr, Ni, Cd) of this set exceeded the MATE ratio.

TABLE 5. ANION CONCENTRATION INLET & OUTLET OF FGD, mg/m^3

	Cl^-		F^-		NO_3^-	$SO_4^=$	
Site	Hot Water Extract	HNO_3 Extract	Hot Water Extract	HNO_3 Extract	Hot Water Extract	Hot Water Extract	HNO_3 Extract
201-1-Inlet	1.605	9.262	0.503	0.012	<1.14	36.7	117.4
201-1-0 Inlet	<0.005	<0.004	<0.070	<0.006	<0.585	18.6	0.5
202-4-Inlet	0.463	<0.006	0.045	0.009	0.235	39.7	30.7
202-4-Outlet	0.223	<0.006	0.006	<0.002	0.102	24.5	3.5

Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C9

SF= 1.466
DAT= 5.00
201 1 I FIL

12/13/77

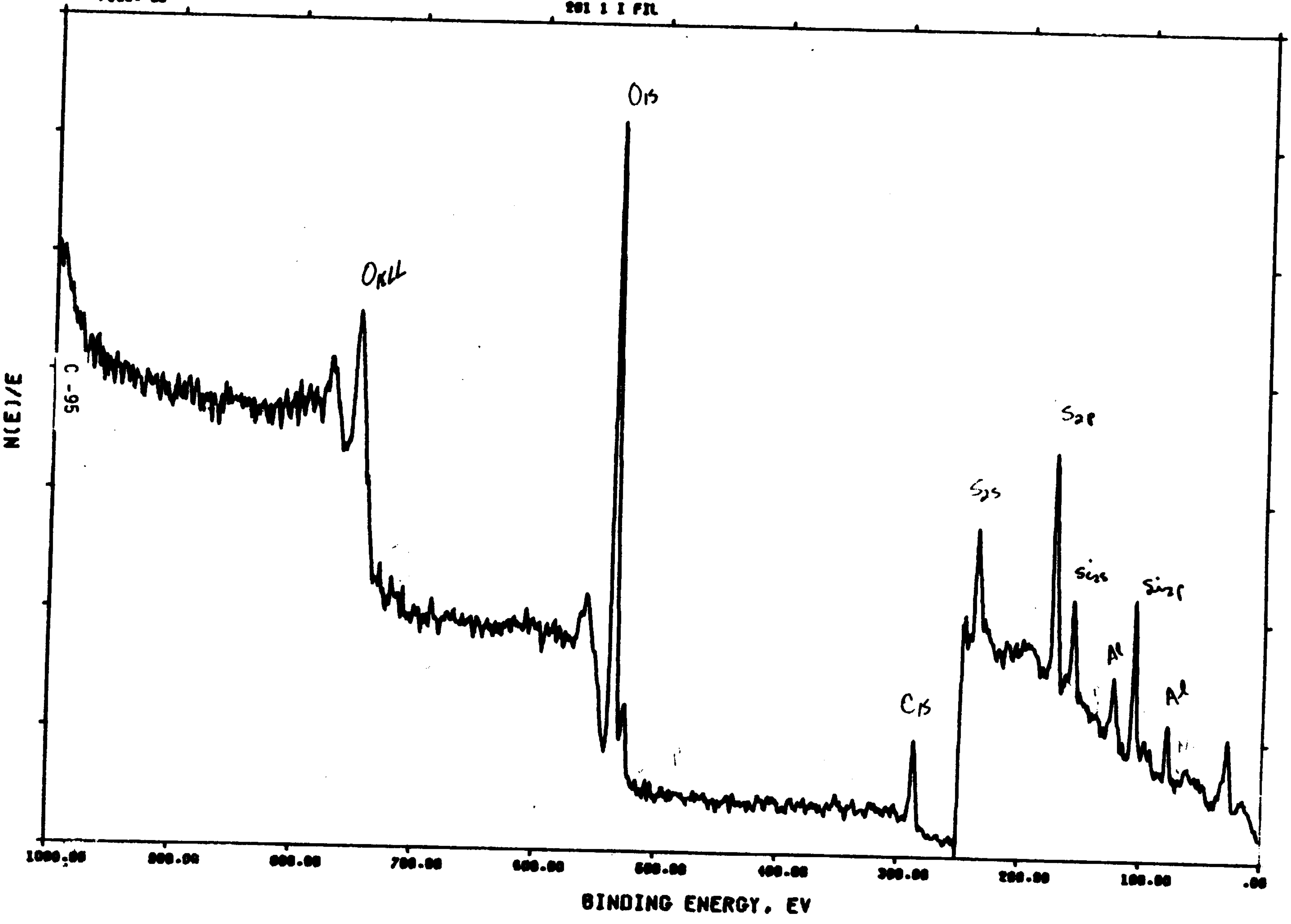


TABLE 7. TEST 201-1 (COAL) TRACE ELEMENT SAMPLING RESULTS

Element	Trace Element Composition, mg/m^3	
	Inlet	Outlet
Ca	73.80	0.036
Mg	19.00	0.011
Sb	3.74	0.025
As	7.83	0.224
B	5.81	0.334
Cd	0.47	0.001
Ca	2.60	0.132
Co	3.55	0.012
Cu	9.56	0.020
Fe	454.00	2.400
Pb	8.48	0.021
Mn	0.78	0.015
Mo	9.97	0.027
Ni	1.37	0.063
V	3.05	0.058
Zn	2.28	0.048
Se	3.19	0.099
Sr	10.50	0.058
Al	480.00	2.570
Zr	1.62	0.018

XRD and TEM-SAED Results

Both XRD and TEM-SAED have the capability to identify compounds present in a sample. XRD is normally used on bulk samples and has a sensitivity of ~0.5 percent in most cases, but under the best conditions can see 0.05 percent. TEM-SAED on the other hand is used for single particle identification. Consequently thick particles or large aggregates produce indistinct diffraction patterns.

Only the loose particulate matter could be analyzed by TEM-SAED, and few of the TEM-SAED photographs provided much more detail than the SEM photos. Difficulty in breaking up aggregates and the size of most of the particles reduced the number of diffraction lines obtained. The information that was derived from TEM-SAED tended to confirm the XRD results, so only two examples of TEM-SAED results will be shown.

All of the particulate samples were analyzed by XRD. The three glass fiber filter samples were run directly and were subsequently subjected to an ultrasonic Freon bath for fifteen minutes to extract the particles from the filter. This process did not yield significant amounts of particles. Therefore, the filters were subjected to an ethyl alcohol, ultrasonic bath. The alcohol, the suspended particles and some glass fibers were then filtered through 200 mesh glass fiber and the resultant liquid evaporated. The particulate left in the evaporation dish were then placed in a diffractometer and compounds were identified by comparing the diffraction patterns to standard listings from the International Centre for Diffraction Data (JCPDS). The following sections discuss the individual results from the samples.

Coal Fired Samples --

These samples were: 201-1 Fly Ash, 201-1-I Cyclone, 201-1-I Filter (free powder), 201-1-Scrubber Cake and 201-1-0(1) Filter. An alcohol extraction of the last sample was also performed and the results included.

Four crystalline compounds were definitely identified in at least one of each of these samples. These were as follows.

Symbol	Name	Formula	JCPDS No.
Q	Alpha Quartz	SiO_2	5-490
M	Mullite	$Al_5Si_2O_{13}$	15-776
H	Hematite	Fe_2O_3	13-534
S	Calcium Sulfite Hemi-Hydrate	$CaSO_3 \cdot 1/2\ H_2O$	4-0588

Three crystalline compounds were determined as possibly present in at least one of each of the samples. These were:

Symbol	Name	Formula	JCPDS No.
C	Calcium Aluminum Ortho Silicate	$CaO \cdot Al_2O_3 \cdot 2SiO_2$	5-528
Cr	Cristobalite	SiO_2	4-359
Tr	Tridymite	SiO_2	18-1170

On a comparative basis these crystalline species varied as follows in the five as-received samples:

Q - Fly ash > Cyclone ≈ Filter (Inlet)

> Scrubber Cake > Filter (Outlet)

M - Fly ash - Cyclone < Filter (Inlet)

> Scrubber Cake > Filter

H - Fly ash - Cyclone ≈ Filter (Inlet)

> Scrubber Cake > Filter (Outlet)

S - Positively identified in Scrubber Cake and possibly in Filter.

Large amount in former, trace in the latter.

C - (Not confirmed positively in any sample)

Fly ash ≈ Cyclone ≈ Filter (Inlet)

> Scrubber Cake > Filter (Outlet).

Figures A and B show examples of TEM studies of the 201-1-Fly Ash and 201-I-Inlet Filter. Details are obscured by the thickness of the samples and size of the aggregates formed during the sampling. Figure A does show a "haystack" quartz fiber and Figure B indicates that Fe_3O_4 might also be present.

Oil Fired XRD Results --

Four samples (202-4-I-Cyclone, 202-4-I-Filter, 202-4-Scrubber Cake and 202-4-O-Filter) were run direct and alcohol extractions of the filter samples were obtained and run.

Symbol	Name	Formula	JCPDS No.
Q	Alpha Quartz	SiO_2	5-490
M	Mullite	$Al_5Si_2O_{13}$	15-776
S	Calcium Sulfite Hemi-Hydrate	$CaSO_3 \cdot 1/2\ H_2O$	4-0588

No comparative determination of amount of species present in each sample could be made for the oil fired burner samples; however, the following comments should be noted about each sample.

Test Sample 202-4-I-Cyclone --

Cristobalite and tridymite (forms of quartz) possibly present and may contribute to the very strong 4.11 peak; however, their presence cannot fully account for its very high intensity. This same peak also appears in the scrubber cake, but not on the filter samples.

Test Sample 202-4-I-Filter --

The many unidentified peaks at large d spacings from this sample seem to be indicative of vanadyl sulfate in various degrees of hydration; however, no listed compound could be positively identified. Vanadyl sulfate is very

Figure A. TEM photo of 201-1 Fly ash showing quartz studies.
Materials present: αQuartz Kaolinite.

Figure B. TEM photo of 201-1-I-Filter.
Material present: αQuartz, Fe_3O_4.

soluble in water and the peaks shown on this chart may indicate a spectrum of hydrated states, many of which are not yet listed in the JCPDS cards.

The alcohol extraction specimen seems to confirm this since $V_2(SO_4)_3$, 23-723, was positively identified. However, this identification must be considered in the light of chemical reactions occurring during the extraction. In particular V_2O_3 could have reacted with an acidic sulfate and formed $V_2\ (SO_4)_3$.

Test Sample 202-4-Scrubber Cake --

Calcium sulfite hemi hydrate, $CaSO_3 \cdot 1/2\ H_2O$ (4-588) was identified as present. There were a number of peaks which could not be identified, most notable was that at 4.11 d spacing.

Test Sample 202-4-0-Filter --

The same comments are applicable for this sample and its extract as for 202-4-I-Filter, except that there were fewer peaks, **indicating fewer varieties of crystalline specimens.**

There was not sufficient similarity between these four samples from the oil burner to compare the relative amount of crystalline species between them.

Summary --

Table 8 summarizes the results from the XRD and TEM studies.

FTIR Analysis Results

Infrared analysis of samples was performed using a Nicolete Fourier Transform IR Spectrometer. The loose particle samples were run in the region of 1900 cm^{-1} to 400 cm^{-1} as a mull of mineral oil between AgCl windows to prevent ionic exchange variations that could occur with KB pelleting procedures. The data obtained is in a digital form and thus can be manipulated by the instrument in a variety of ways. In particular spectra can be subtracted from each other to remove impurities or as a means of identifying unknown materials. Samples of the 201-1 fly ash was extracted in HNO_3 and H_2O and used as a reference spectra for removal of the mineral background. When the subtraction was performed, the resulting spectra proved to be too difficult to interpret. In general the use of

TABLE 8. XRD and TEM-SAED SAMPLE COMPOSITION ANALYSES

	Samples	Definite	Possible
Coal-fired (201-1-)	Flyash	Q; M; H; S α-quartz, mullite, Fe_2O_3, $CaSO_3 \cdot 1/2H_2O$	$CaO \cdot Al_2O_3 \cdot 2SiO_2$
	Cyclone	α-quartz, mullite, Fe_2O_3	$CaO \cdot Al_2O_3 \cdot 2SiO_2$
	Filter (inlet)	$Na_2Al_2Si_2O_8 \cdot H_2O$ α-quartz, mullite	$CaO \cdot Al_2O_3 \cdot 2SiO_2$
	Filter (outlet)	$NaHSO_4$ α-quartz, mullite	Fe_2O_3, $CaSO_3 \cdot 1/2H_2O$
	Scrubber Cake	$CaSO_3 \cdot 1/2H_2O$ α-quartz, mullite, Fe_2O_3	Na_2SO_4, $CaO \cdot Al_2O_3 \cdot 2SiO_2$
Oil-fired (202-4-)	Cyclone	α-quartz	
	Filter (inlet)	---	$FeSi_2O_5$; $NaAl(SO_3)$; Fe_3S_4 $VO(SO_4)$
	Filter (inlet) extracted	1/2 $(SO_4)_3$	
	Scrubber Cake	$CaSO_3 \cdot 1/2H_2O$	$CaSO_4$; Zn_2SO_4
	Filter (outlet)	---	$Na_2Si_2O_5$; $KFeSi_3O_8$
	Filter (outlet) extracted	i/2 $(SO_4)_3$	

FTIR's subtraction capability was not possible due to the complexity of the spectra obtained, difficulty in preventing band shifts due to hydration, particle size effects and the lack of having the correct compounds in the computer library. As it will be shown in the discussion section, FTIR, even with these limitations, provided significant information in the identification of $NaHSO_4$ in the outlet samples. For the next test site samples an effort will be made to:

- Dry and store all samples to the same degree of moisture content
- Establish grinding procedures for the samples
- Add key compounds to the computer library for subtraction work.

The following sections briefly describe the FTIR results. All the spectra obtained are found in Attachment C.

Test Sample 201-1-Cyclone --

No correlation of the spectrum with any specific materials was possible. It is believed that most of the spectrum was due to either silicates in the fly ash or a cell interference caused by placing insufficient sample between the windows.

Test Sample 201-1-Filter --

The main spectral bands for this sample are shown below with SiO_2 for comparison:

Sample (cm^{-1})	SiO_2 (cm^{-1})
1460 (sp)	
1375 (sp)	
1075 (vb)	1075 B
797 w	800 m
780 w	
555 w	570 w

The 1375 and 1460 bands could be due to the mineral oil mull, which could not be totally subtracted. The band at 1075 is very broad and is not of great utility in identification. The 800 and 570 bands for SiO_2 match up reasonably well, but the 797 band disappeared after HNO_3/H_2O extraction, which should not happen if SiO_2 was present.

Test Sample 201-1-Scrubber Cake --

This spectrum had little detail, as though several weak lines could have been assigned to the $CaSO_3$, $CaSO_4$ and Na_2SO_4 known to be present in the sample. The low level of detail probably was due to the high moisture content of the samples.

Test Sample 201-1-0-Filter --

The spectrum from this sample was attained directly from the filter using Attenuated Total Reflectance (ATR) techniques. ATR was used because the particles were embedded in the filter. The spectrum was reasonably rich in bands and a possible assignment ($NaHSO_4 \cdot H_2O$) was made based on the following comparison:

	Sample (cm^{-1})	$NaHSO_4 \cdot H_2O$	
	1660 (m)	(H_2O)	
	1235 (m)	1350	Broad
Broad	1160 (m)	1150	
	1120 (w)		
	1095 (w)		
	1080 (m)	1080	Broad
	1038 (s)	1040	
	857 (s)	865 (s)	
	773 (w)	775 (m)	
	653 (w, sh)	650 (w, sh)	
	620 (m)	605 (m)	

As a test to see whether the inlet filter contained any materials similar to those on the outlet filter, an electronic subtraction of the spectrum of the 201-1-I-Filter from the 201-1-O-Filter was performed (see Appendix C). No change was seen in the 201-1-O-Filter spectrum, indicating the $NaHSO_4$ was unique to the outlet.

Sample 202-4-I-Cyclone and 202-4-I-Filter --

The cyclone spectrum exhibited many medium to weak peaks in the 1200-800 cm^{-1} region. None of these bands could be attributed to sulfate or any other material. The inlet filter was scanned using ATR and the background filter spectrum was electronically subtracted. In general it had many characteristics of 201-1-O-Filter, with additional fine structure superimposed on the strong bands. A comparison between the filter and $NaHSO_4 \cdot H_2O$ is shown below:

Sample, cm^{-1}	$NaHSO_4 \cdot H_2O$, cm^{-1}
1645 (s)	1660 (s)
1155 (s)	1175 (s)
1047 (s)	1045 - 1075 (b, s)
863 (s)	865 (s)
745 (s)	
775 (db, w)	

The bands are shifted slightly, but that could be due to the degree of hydration. No oxides such as SiO_2 or Fe_3O_4 can be seen.

Test Sample 202-4 Scrubber Cake --

The scrubber cake spectrum showed many of the bands seen in the cyclone material except bands in the 621-645 cm^{-1} region. The spectrum details and possible compounds are shown below:

Sample, cm^{-1}	$CaSO_3 \cdot 2H_2O$, cm^{-1}	Fe_3O_4, cm^{-1}
1625 (b)	1625	
1305		1325
1150		

Sample, cm^{-1}	$CaSO_3 \cdot 2H_2O$, cm^{-1}	Fe_3O_4, cm^{-1}
1112	1100	
955 (b)	955 (b)	
721		721
621	653	
585		570
542		
500		
460		
455	452	

The shifts in the $CaSO_3$ spectrum are probably due to the moisture content of the samples.

Test Sample 202-4-0-Filter --

The outlet filter, while similar to 201-1-0 has fewer details and seems to consist of bands entirely assignable to $NaHSO_4$:

Sample, cm^{-1}	$NaHSO_4 \cdot H_2O$, cm^{-1}
1645 (s)	1660 (s)
1155 (s)	1175 (w)
1047 (s)	1060 (b, s)
863 (s)	865 (s)
745 (w)	775 (m)
725 (w, db)	

ESCA AND SIMS ANALYSIS RESULTS

Both ESCA and SIMS are surface analysis techniques. In ESCA, X-rays bombard the sample and knock out inner electrons. Depending on the sample material and parent element, the electron escape depth can be as much as 50 Å, but is normally closer to 25 Å. The electrons which do escape the sample, are energy classified in a electron spectrometer. Knowing the X-ray energy, the binding energy of the electrons can be calculated. Since the binding energy can be influenced by the electron density at the element, changes in an elemental binding energy for a given electron can be correlated with the oxidation state of the parent element. This approach has been used with great success in determining sulfur oxidation states. Depth profile information is obtained by etching the sample with an Ar^+ beam and repeating the ESCA scan.

SIMS uses a beam of Ar^+ (or O) to remove and ionize layers of elements from a sample. The ions are then identified by a mass spectrometer and the ion output can be plotted. The following sections will discuss the results of these tests.

ESCA Results

The original ESCA survey scans are found in Attachment D. All nine of the solid samples were analyzed and most were re-analyzed after a 75 Å Ar^+ etching. The results of these tests are summarized in Table 9 as surface atom percent concentrations. While ESCA's sensitivity for elements on the surface is excellent, bulk sensitivity is ∿0.1 percent. With this in mind, the atom percent data shows no undue surface concentrations of heavy or volatile trace elements. Overall the coal samples contained more surface K, Ca, Fe, and Al than the oil samples, while significant differences between samples were seen for C. The inlet 202-4 cyclone contained a large amount of C and probably was due to the large soot particles seen earlier in the PLM studies.

The main use of ESCA was in the study of the sulfur depth profile in the samples. Comparing 201-1-cyclone to 201-1-Filter, the sulfur surface content appeared similar. The sharp drop in S atom percent after etching of the inlet filter sample indicates some surface coating of the particles occurred. One technique to study surface concentrations versus bulk composition is to normalize the data to a bulk concentration element. In this study Al rather than Si was chosen since 201-1-O-F, 202-4-I-F, and 202-4-O-F were run directly on the filter and the Si content of the filter would mask the true changes. Figure C is a plot of the S/Al ratio for 201-1-O-F Ar^+ etched to a depth of 750 Å. Note that there is some surface dependence of S, but that the curve levels off after ∿275 Å. These data indicate that while there may be some surface concentration of S in the 201-1-O-Filter, it probably is on a particle composed of solid sulfate. This would be the case if H_2SO_4 condensed on the $NaHSO_4$ particles that appear to be present.

TABLE 9. SURFACE ATOM PERCENT FROM ESCA DATA

Sample*	O	Na	S	Si	Al	Fe	Cl	P	V	Ca	C	K
201-1-I Cyclone	57	4	11	6	7	2	2	1				
201-1-I Filter	56	2.4	11.5	14.1	8	1.4	1.5	1.2		2		
201-1-I Filter 76 Å SP	54.2	2.1	4.0	17.9	12.6	2.1	1.3	2.2	1.0	2.7		
201-1-0 Filter	45.7	5.5	13.2	7.1	2.2		1.2	1.1	0.7	1.3	14.9	7.1
201-1-0 75 Å SP	48	7.4	11.5	9.0	5.2	1.2	1.1	1.1		1.1	12.1	1.8
201-1-0 150 Å SP	48.3	9.1	10.0	10.1	7.7	1.2	1.2	1.2			10.0	1.2
201-1-0 300 Å SP	48.3	8.8	8.0	10.6	9.6	2.1	1.0	1.2	0.5		8.0	1.8
201-1-0 500 Å SP	47.9	7.3	6.7	10.8	13	1.7	1.2	1.1		1.2	8.1	1.1
201-1-0 750 Å SP	47	7.3	6.1	11.6	11.0	2.3	0.9	1.5	0.5	1.0	8.8	1.6
201-1 Flyash	44.6	2.6	7.6	13.9	7.5	1.2	1.2	1.2	0.4		18.1	1.6
201-1 Scrubber Cake	47	10.0	14.8	3.2	3.7	0.6	1.5	0.9		5.8	9.9	2.6
202-4-I Cyclone	38.5	3.2	12.9	2.6	2.3		1.4	0.6	1.2		37.4	
202-4-I Filter	48.6	4.2	10.7	11.8	3.1		1.3	1.5	1.7		17.2	
202-4-I Filter 76 Å SP	46.3	4.7	6.5	17.1	3.3	0.8	1.4	1.1	3.3	0.9	12.9	1.7
202-4-0 Filter	46.6	5.8	9.9	14.9	3.5	1.3	2.4	1.7	1.8		14.5	
202-4-0 Filter 76 Å SP	53.5	3.2	6.8	22.0	4.0		1.3	1.0	2.0		6.2	
202-4-SC	41	9.8	15.3	2.1	2.3	1.7	2.1	1.1	1.4	6.5	12.7	3.6
Filter Blank	38.4	5.8	7.5	24.7	1.8	1.1	1.6	1.1	0.9		17.2	
Filter Blank 75 Å SP	47.3	8	2	28.5	3.2		0.9	2.6	0.6	1.2	4.4	1.3

*Å SP refers to Depth of Ar^+ sputtering in Å.

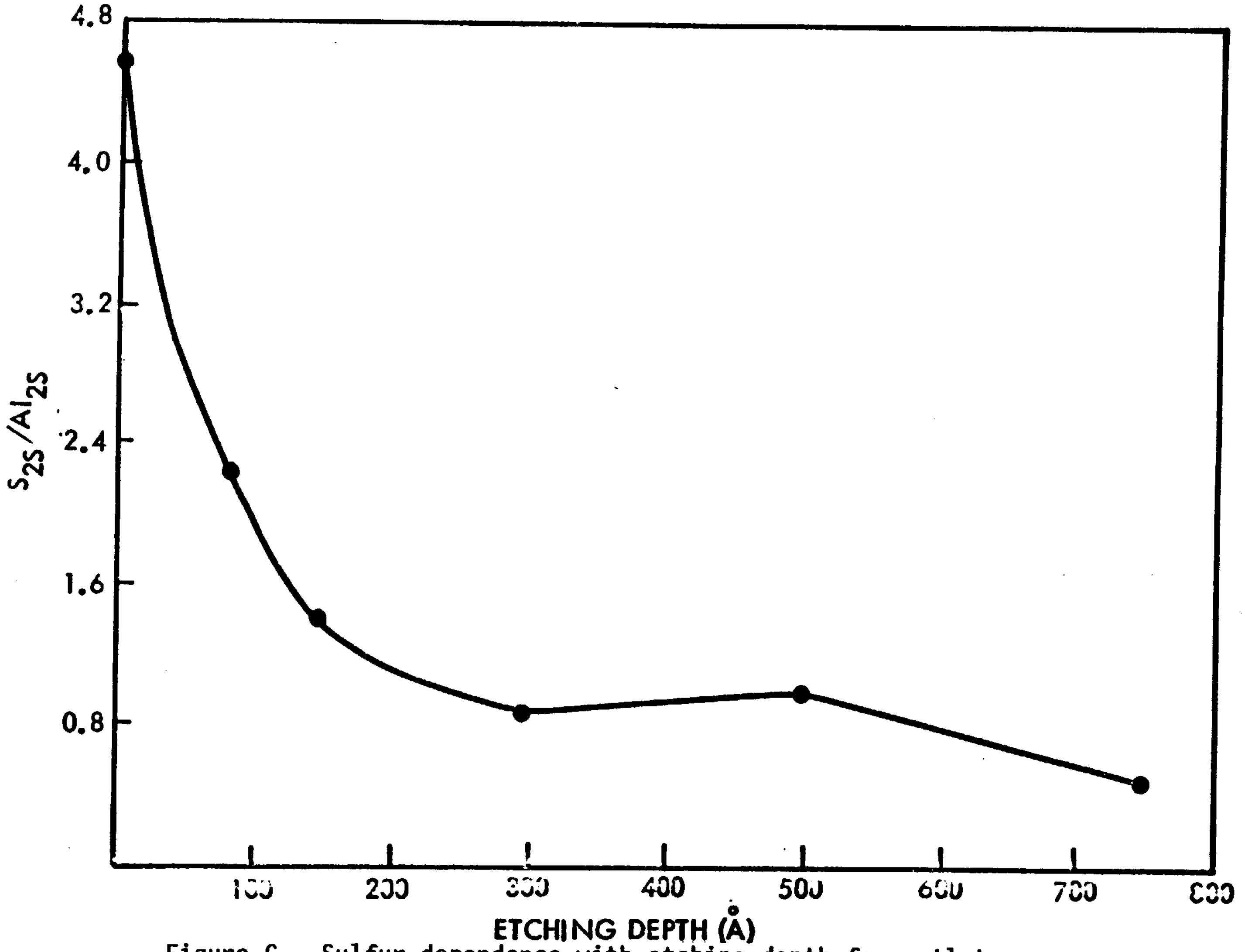


Figure C. Sulfur dependence with etching depth for outlet coal fired filter sample.

The 201-1-I-Cyclone and filter samples show a sharp decline to S/Al values for below the 201-1-0-Filter even at 750 Å, indicating a high surface concentration, perhaps from SO_2 absorption.

SIMS Results

SIMS analysis up to mass 150 was performed on all solid samples. The profiling rate was determined by etching a known thickness substrate of SiO_2 over Ga. It was determined that the Ar^+ beam removed approximately 0.78 Å/sec. The output from each etching was stored as uncorrected (for abundance and ionization probability) ion counts. This raw data was reduced and drawn as a plot of intensity of the element ratioed to Si versus time in seconds (depth). The entire set of those plots are found in Appendix E. Elements that have a surface dependence would show a decay curve with increasing depth. Only 14 elements were plotted because of space limitation, but they are representative of the elements found in the sample. In the 201-1 series no clear-cut surface dependence is seen. The cyclone and inlet filter plots look very similar, with the exception of some anomolies for the Li → Ca plot. The outlet filter samples show a large difference in shape and element distribution compared to the inlet filter. One significance of this differenece is not clear since results from a free particle are being compared to an impacted particle on a filter.

The 202-4 gas particulate samples show several interesting characteristics:

- Li, Na, Mg and to some extent Al and Fe show a maxima near 400 seconds (280 Å)
- The inlet filter shows little surface dependence for Ti → Ba, but the outlet curves show a much slower decay curve and an apparent enrichment.

More precise information about compositional changes in the sample are shown in Table 10. There the atom concentration shown represents isotope abundance and ionization probability corrected data. Comparisons can be made across the FGD by looking at inlets versus the outlets. Care should be exercised, however, since the 201-1-0-Filter has impacted particles in a filter compared to the loose particle samples for the 201-1-I-Filter/Cyclone. This same problem exists for the 202-4-I-Cyclone versus the 202-4-0-Filter.

TABLE 10. ATOM CONCENTRATION AT A DEPTH OF 1400 A FOR GAS PARTICULATE SAMPLES

Element	201-1-I-Cyclone	201-1-I-Filter	201-1-0-Filter	202-4-I-Cyclone	202-4-I-Filter	202-4-0-Filter*
Li	922 ppm	0.10%	770 ppm	0.11%	291 ppm	37 ppm
Na	1.05%	1.33%	22.84%	2.27%	9.57%	10.36%
Mg	0.92%	0.77%	1.34%	1.06%	4.51%	2.44%
Al	18.48%	19.28%	9.17%	11.7%	8.1%	5.04%
Si	18.74%	17.88%	10.42%	22.44%	12.3%	23.13%
K	3.23%	3.62%	2.55%	2.75%	3.32%	2.68%
Ca	1.59%	1.91%	2.17%	2.62%	3.75%	3.55%
Ti	0.88%	0.89%	0.15%	0.42%	0.26%	890 ppm
V	294 ppm	310 ppm	187 ppm	0.97%	3.06%	1.22%
Cr	322 ppm	279 ppm	141 ppm	760 ppm	670 ppm	203 ppm
Mn	304 ppm	314 ppm	140 ppm	251 ppm	759 ppm	298 ppm
Fe	4.82%	4.02%	1.21%	5.44%	4.87%	1.42%
Sr	752 ppm	784 ppm	119 ppm	758 ppm	445 ppm	99 ppm
Ba	232 ppm	268 ppm	42 ppm	449 ppm	516 ppm	42 ppm

*Concentrations at 1200 Å depth.

Changes can be seen in some of the elements with particle size (cyclone to filter) and across the FGD (inlets versus outlets). In particular a large enrichment is seen in the Na content of the outlet 201-1 filter sample.

DISCUSSION

The results of the test program were described in the preceding sections and to some extent discussed. The following sections will present two major conclusions from the test program.

Trace Element Enrichment Across the FGD

As it has been shown in Section 2.4.3 the overall emission rate of trace elements was reduced by the FGD. However this data only tells part of the story. Tables 11 and 12 show the mass loading, percentage removal and enrichment trend. The enrichment trend was calculated by determining the ratio of the mass loading of an element to the mass loading of Al. The ratio normalizes the data and allows comparison of the results.

The average percentage removal varied between the coal and oil tests. It is believed this is more a mathematical result of low input values for oil compared to a baseline scrubber output. In the coal case a much greater input is compared to the same baseline output, which would result in an artificially greater removal efficiency.

On the other hand, the enrichment trend data shows that while lower mass outputs are attained, the composition of output is drastically different from the input. Summarized below in Table 13 are the elements which show a position enrichment.

The data can be differentiated into those elements showing between 0-30 percent, 31-60 percent and >61 percent either positive or negative enrichment trends. In the coal case for positive trends 31 percent showed a 0-30 percent, 31 percent between 31-60 percent increase and 38 percent showed >61 percent increase. The same comparison for oil was: 22 percent, 0 percent, and 82 percent, respectively.

Several researchers 2, 3, 4, 5 have found elements such as Sb, As, Cd, Cr, V, Zn, and Se inhibit concentration increases with decreasing particle size.

TABLE 11. TEST 201-1 (COAL) TRACE ELEMENT SAMPLING RESULTS

Element	Trace Element Composition, mg/m^3		Percentage Removal	Enrichment Trend		
	Inlet	Outlet		> 30%	30 - 60%	< 60%
Ca	73.8	0.036	>99.9			-
Mg	19.0	0.011	99.9			-
Sb	3.74	0.025	99.3	+		
As	7.83	0.224	97.1			+
B	5.81	0.334	94.3			+
Cd	0.47	0.001	99.8			-
Cr	2.60	0.132	94.9			+
Co	3.55	0.012	99.7		-	
Cu	9.56	0.020	99.8			-
Fe	454	2.40	99.5	-		
Pb	8.48	0.021	99.8		-	
Mn	0.78	0.015	98.1			+
Mo	9.97	0.027	99.7		-	
Ni	1.37	0.063	95.4			+
V	3.05	0.058	99.6			+
Zn	2.28	0.048	97.9			+
Se	3.19	0.099	96.9			+
Sr	10.5	0.048	99.4	+		
Al	480	2.57	99.5			
Zr	1.62	0.018	98.9			+
			Average 98.5 ± 1.8			

TABLE 12. TEST 202-4 (OIL) TRACE ELEMENT SAMPLING RESULTS

Element	Trace Element Composition, mg/m^3		Percentage Removal	Enrichment Trend		
	Inlet	Outlet		> 30%	30 - 60%	< 60%
Ca	0.411	0.070	83.0			+
Mg	0.309	0.030	90.3	+		
Sb	0.062	0.006	90.3	+		
As	0.146	0.030	79.5			+
B	0.531	0.039	92.7	-		
Cd	0.280	0.066	76.4			+
Cr	0.166	0.018	89.2	+		
Co	0.104	0.012	88.5		+	
Cu	0.539	0.007	98.1			-
Fe	4.847	0.277	94.3		-	
Pb	0.197	0.013	93.4	-		
Mn	0.031	0.004	87.1		+	
Mo	0.217	0.025	88.5		+	
Ni	1.076	0.204	81.0			+
V	2.690	0.822	69.4			+
Zn	0.609	0.065	89.3	+		
Se	0.050	0.006	88.0		+	
Sr	0.043	0.001	97.7			-
Al	5.678	0.484	91.5			
Zr	0.015	0.001	93.3	-		
			Average 88.1 ± 7.1			

TABLE 13. ELEMENTS SHOWING POSITIVE ENRICHMENT TRENDS

Coal	Oil
Sb, As, B, Cr, Mn, Ni, V, Zn, Se, Zr,	Ca, Mg, Sb, As, Cd, Cr, Co, Mn, Mo, Ni, V, Zn, Se

The importance in this bulk data is that it indicates either:

1. The FGD selectively removes certain elements, concentrating the rest, or, more likely,
2. The mist eleminator system on the FGD has low removal efficiency for small particles which contain the trace elements.

Further tests are needed in which bulk and size dependent data is taken at the inlet and outlet of the FGD. However, the data shown should signal a concern on the part of FGD designers that fine particle removal is as important as SO_2 removal to the environment.

Scrubber Generated Particulate Matter

During this test, a CCS and a modified Method 5 train were operated at both the inlet and outlet of the FGD. The modified Method 5 train used a cyclone and filter at the inlet but only a filter at the outlet of the FGD. Cyclone/Filter oven temperatures were maintained near 175°C. Because both oil and coal were burned during the tests at this industrial boiler, a direct comparison of scrubber outputs was possible. Table 14 shows the SO_2 concentration, mass loading, and average gas flow across the scrubber during the test program. Even though the inlet (I) mass loading for coal versus oil differed by a factor of 25, the outlet (O) mass loadings were within 10 percent of each other. These data were the first indication that the scrubber output might be independent of input conditions, and that a baseline emission rate for the FGD existed. In order to determine the validity of this statement an analysis effort following the IERL-RTP Level 2 inorganic analysis procedures developed by TRW was initiated.

TABLE 14. FLUE GAS CONDITIONS ACROSS THE SCRUBBER

	SO_2 Concentration, ppm	Mass Loading, mg/m^3	Average Gas Flow Across the Scrubber, dscm/min
Coal			
201-1-I	1114	7180	89.3
201-1-0	33.8	48	
201-4-I	913	8660	
201-4-0	48.2	53	
Oil			
202-1-I	2969	452	
202-1-0	33.2	55	
202-4-T	1009	182	152.7
202-4-0	22.2	46	

In Table 15 the sulfate extraction values for the 201-1 (coal) and the 202-4 (oil) samples are tabulated. The sulfate values for water and acid soluble sulfates are shown as well as the total inlet (I) and outlet (0) concentration. While the coal showed a greater inlet concentration for sulfate than the oil, both the coal and oil outlet concentrations are relatively close. Surprisingly, the oil has a higher outlet concentration. The higher flue gas velocity in the scrubber during the oil tests could have reduced the efficiency of the mist eliminator system, reducing the particle removing capability of the scrubber.

Studying Table 15 further, there is an apparent change in the chemical form of the outlet sulfate versus the inlet sulfate. This change is clearly shown from the difference in the solubility between the water extractable and the acid extractable portions of the inlet and outlet 201-1 filters. Because the sulfate found represented 57 percent and 40 percent of the total outlet particle catch for oil and coal respectively, an effort was made to identify the chemical species inlet and outlet to the FGD. In this way any modification of the particle matter by the FGD could be traced.

TABLE 15. TOTAL SULFATE VALUES FROM THE MODIFIED METHOD 5 TRAIN

Sample	Sulfate Extraction Values (mg/m^3)		
	Hot H_2O Extraction	HNO_3 Extraction	Total
201-1 Coal Inlet			
Probe		0.2	--
Cyclone (>3μ)	<100	107.0	107.0
Filter	36.7	10.2	46.9
Inlet Total	36.7	117.4	154.1
201-1 Coal Outlet			
Probe	--	--	--
Filter	18.6	0.5	19.1
Outlet Total	18.6	0.5	19.1
202-4 Oil Inlet			
Probe	--	29.0	29.0
Cyclone (>3μ)	10.4	0.7	11.1
Filter	29.3	1.0	30.3
Inlet Total	39.7	30.7	70.4
202-4 Oil Outlet			
Probe	--	3.5	3.5
Filter	24.5	<0.33	24.5
Outlet Total	24.5	3.5	28.0

ESCA analysis of the inlet and outlet filter material showed only S(VI) present even after Ar^+ etching was employed to remove 150 Å of material. A series of Fourier Transform IR (FTIR) scans were made directly from the inlet and outlet filters using attenuated total reflectance techniques. In the coal case, the inlet filter showed only a few weak lines providing little anion information. The IR bands for the coal outlet filter are shown in Table 16. A search of typical sulfate compounds showed little correlation with these bands. However, $NaHSO_4$-H_2O had several bands (Table 17) that matched the spectra. The size of the water band at 1660 cm^{-1} indicated a high degree of hydration, and could explain the differences in the sample spectra and the reference $NaHSO_4$. The fact that the filter material was deliquescent is in line with the nature of a bisulfate.

TABLE 16. FTIR BANDS, cm

Coal Filter		Oil Filters	
Outlet	$NaHSO_4 \cdot H_2O$	Inlet	Outlet
653 (w, sh)	650 (sh)		
773 (w)	775 (m)		
857 (s)	865 (s)	863 (s)	872 (s)
1038-1160 (s, b)	1040-1080 (b)	1047 (s)	1040 (s)
1235 (m)	1150-1350 (vb)	1155 (s)	1160 (s)
1660 (b)		1645 (b)	1645 (b)

XRD analysis was able to confirm the presence of $NaHSO_4$ on the outlet, but not the inlet filter. The implication from these results was that the $NaHSO_4$ could have resulted from a scrubber generated emission of $NaHSO_3$, which was oxidized during collection and storage.

The FTIR and XRD analyses of the oil filters were not as conclusive. The FTIR spectra of the inlet and outlet filters was similar and thus in both samples $NaHSO_4$ was indicated. X-Ray Diffraction could not confirm the presence of $NaHSO_4$ in either sample, because of its low concentration (<1 percent) or the high degree of moisture in the samples.

TABLE 17. H_2SO_4 CONCENTRATION, mg/dscm (ppm)

Run	Inlet	Outlet	Scrubber Efficiency (%)
201-1	20.7* (5.09)*	14.3 (3.51)	31
201-4	15.5* (3.80)*	11.0 (2.69)	29
Average 201	18.1	12.7	30
202-1	25.2 (6.19)	17.9 (4.39)	29
202-4	31.6 (7.74)	22.7 (5.58)	28
Average 202	28.4	20.3	29

*Values corrected (+12%) for loss of H_2SO_4 to fly ash on filter.

Because the HSO_4^- was found on the inlet and outlet oil sample filters, it could have been an artifact from H_2SO_4 collecting on the filters. Table 16 shows the results of the H_2SO_4 sampling tests. Interestingly, the oil fired case had much higher H_2SO_4 values. This is possibly due to the high V content found in the flue gas. However, even these H_2SO_4 levels were not high enough to account for all of the $SO_4^=$ seen on the outlet filters. In the coal and oil samples an excess of 6.4 and 7.7 mg/m^3 of $SO_4^=$ respectively was unaccounted for. Once again outlet values for sulfate are quite close, even though the inlets differed greatly.

One final test was run on the outlet filters using Secondary Ion Mass Spectrometry. In this method, layers of a particle are removed, ionized, and analyzed by the mass spectrometer to produce an elemental depth profile of the sample. At a depth of 1400 Å the mole percent of Na suddenly increased from 1.33 to 22.84% for the inlet to outlet coal filters. Even correcting for a 7% contribution from the filter background for the outlet sample, there was a distinct change in the bulk particle composition between the inlet and outlet. The mole percent from Na for the oil filter data (7.2 vs 10.4%) showed an increase of roughly 50%, but since both inlet and outlet oil filter samples were analyzed directly on the filter, the large background Na of the filter probably masked any change in the sodium concentration.

In summary the following statements can be made:

- Outlet mass loadings for coal and oil combustion in the industrial boiler were within 10 percent of each other.
- Sulfate outlet values for oil and coal combustion are relatively similar considering the difference between inlet conditions.
- Outlet sulfate species are more water soluble than the inlet species.
- FTIR analysis confirmed the presence of $NaHSO_4$ in the coal combustion outlet samples.
- XRD analysis confirmed the presence of $NaHSO_4$ in the coal combustion outlet samples.
- Outlet H_2SO_4 concentrations were not adequate to account for all of the sulfate collected.

Based on these findings, it is believed that the baseline scrubber emission of $NaHSO_4$ is on the order of 6 to 7.7 mg/m^3 (the difference of total sulfate minus H_2SO_4 concentration). If one assumes that only 50 percent of the H_2SO_4 was collected because of the high filter temperature (175°C), then the scrubber contribution could be as high as 12 to 18 mg/m^3.

It should also be considered that the reason for the clear-cut enrichment of Na in the outlet 201-1 case was a result of operating conditions. Either an operational problem or error could have caused Na loss during the coal run. Further investigation of FGD operation during 201-1 tests should be made to isolate any engineering problems.

REFERENCES FOR APPENDIX B

1. Cleland, J.G.; G.L. Kingsbury. Multimedia Environmental Goals for Environmental Assessment, Volume I and II. EPA-600/7-77-136a, (1977).
2. Lee, R.E. et al. Environ. Science and Technical, 9 (7), 643, (1975).
3. Davison, R.L. et al. Environ. Science and Technical, 8 (13), 1107 (1974).
4. Lee, R.E. and von Lehmden, D.J. JAPCA, 23 (10), 853, (1973).
5. Toca, F.M. Diss. Abstr. Int., 33, 3156B (1973).
6. Maddalone, R.F., S.F. Newton, R.G. Rhudy, R.M. Statnick. "Laboratory ad Field Evaluation of the Controlled Condensation System (Goksoyr/Ross) for SO_3 Measurements in Flue Gas Streams." National APCA Meeting, (1977).

APPENDIX C

ATTACHMENT A

TGA SCANS

PART NO. 990008

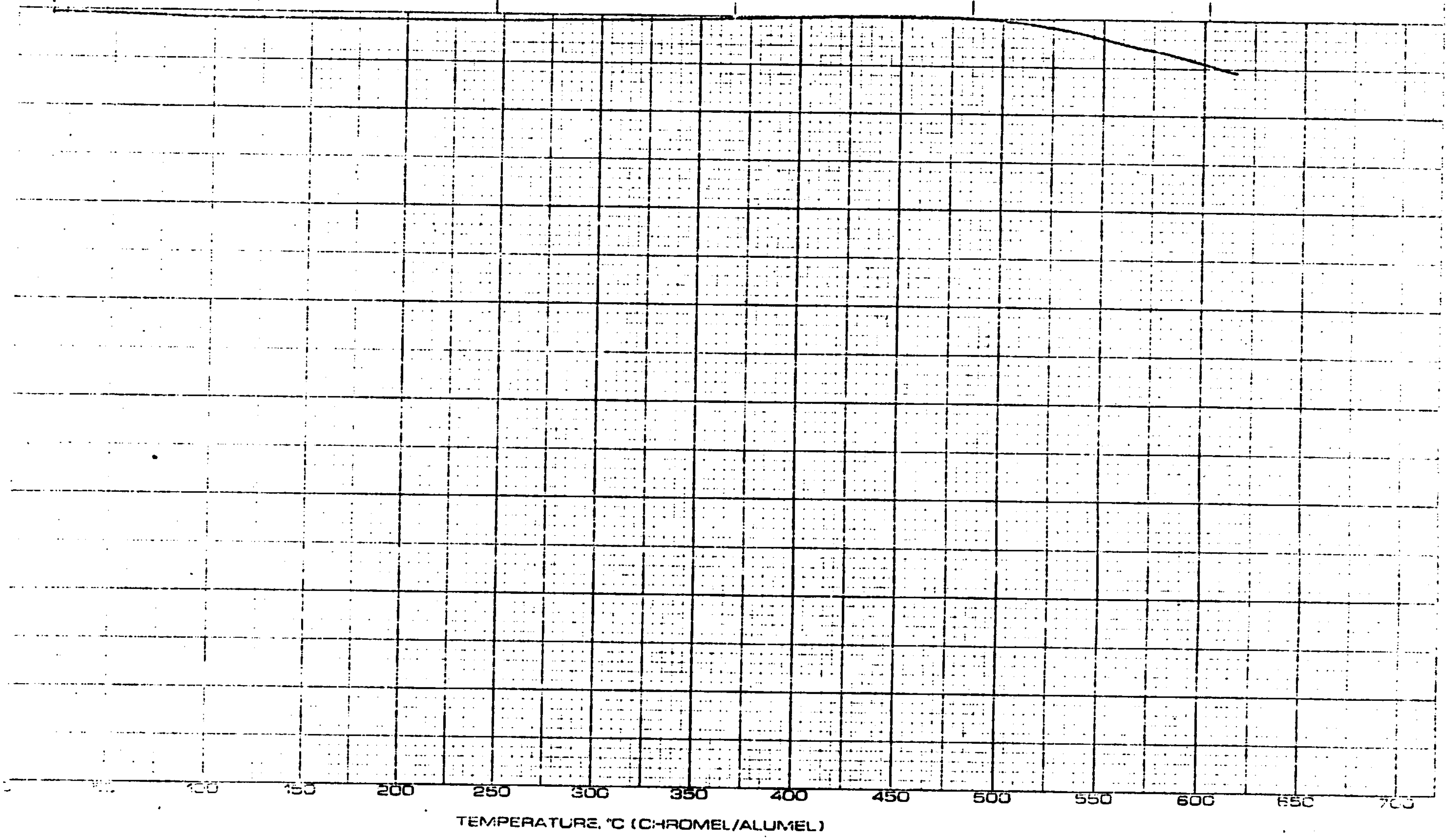
RUN NO. ___ DATE 8/11/77
OPERATOR KENNEDY
SAMPLE
261-1-II-F. H[illegible]
ATM. ___
FLOW RATE N2

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT ___ COOL ___ ISO ___
SHIFT, in 0

DTA-DSC
SCALE, °C/in ___
(mcal/sec)/in ___
WEIGHT, mg ___
REFERENCE ___

TGA
SCALE, mg/in .2
SUPPRESSION, mg ___
WEIGHT, mg 9.350
TIME CONST., sec 1
dY, (mg/min)/in ___

TMA
SCALE, mils/in ___
MODE ___
SAMPLE SIZE ___
LOAD, g ___
dY, (10X), (mils/min)/in ___



TEMPERATURE, °C (CHROMEL/ALUMEL)

DATE 3/22/77

OPERATOR Kennedy

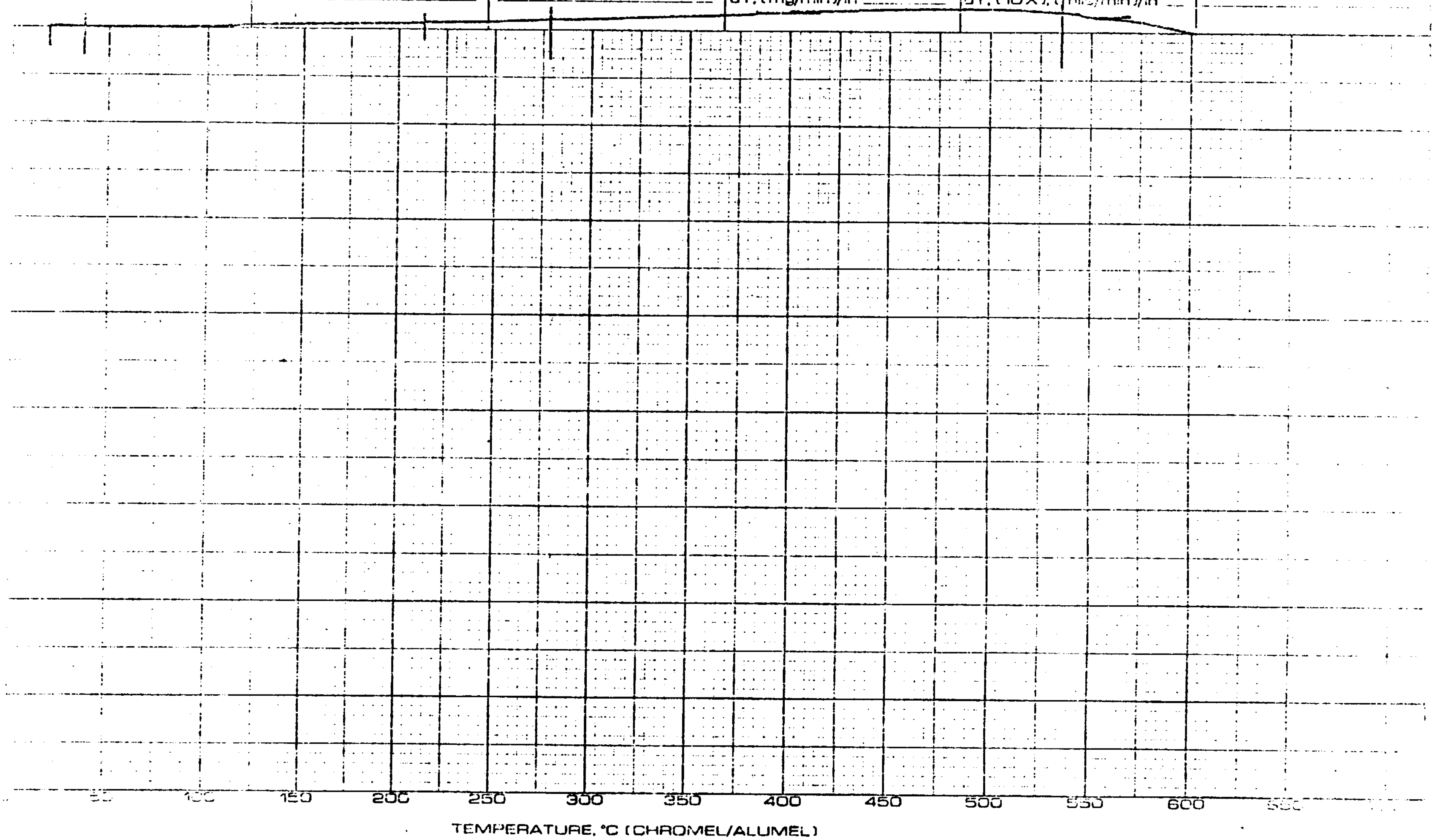
SAMPLE:

201-1-I-Cyclone

ATM.

FLOW RATE N_2

T-AXIS	DTA-DSC	TGA	TMA
SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in .2	SCALE, mils/in
PROG. RATE, °C/min 10	(mcal/sec)/in	SUPPRESSION, mg	MODE
HEAT COOL ISO	WEIGHT, mg	WEIGHT, mg 2.15	SAMPLE SIZE
SHIFT, in 0	REFERENCE	TIME CONST., sec 1	LOAD, g
		dY, (mg/min)/in	dY, (10X), (mils/min)/in



PART NO. 990089

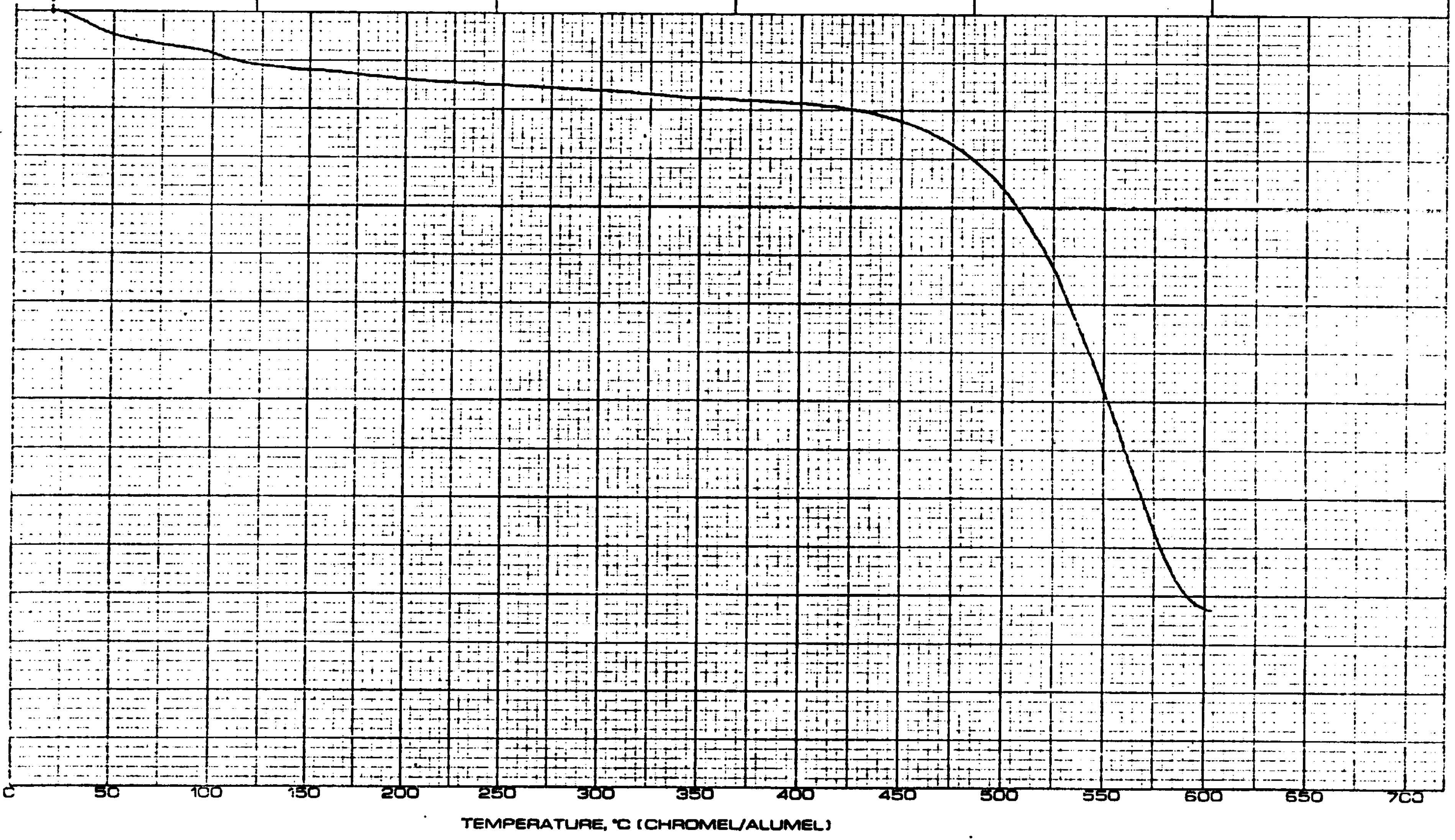
RUN NO. ___ DATE 12/19/77
OPERATOR KENNEDY
SAMPLE:
202-4-I-cyclone
ATM ______ @ ______
FLOW RATE N2

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT. .. COOL... ISO...
SHIFT, in 0

DTA-DSC
SCALE, °C/in ______
(mcal/sec)/in ______
WEIGHT, mg ______
REFERENCE ______

[✓ TGA]
SCALE, mg/in .2
SUPPRESSION, mg ______
WEIGHT, mg ~3.10
TIME CONST., sec 1
dY, (mg/min)/in ______

TMA
SCALE, mils/in ______
MODE ______
SAMPLE SIZE ______
LOAD, g ______
dY, (10X), (mils/min)/in ______



[illegible] NO. 990038

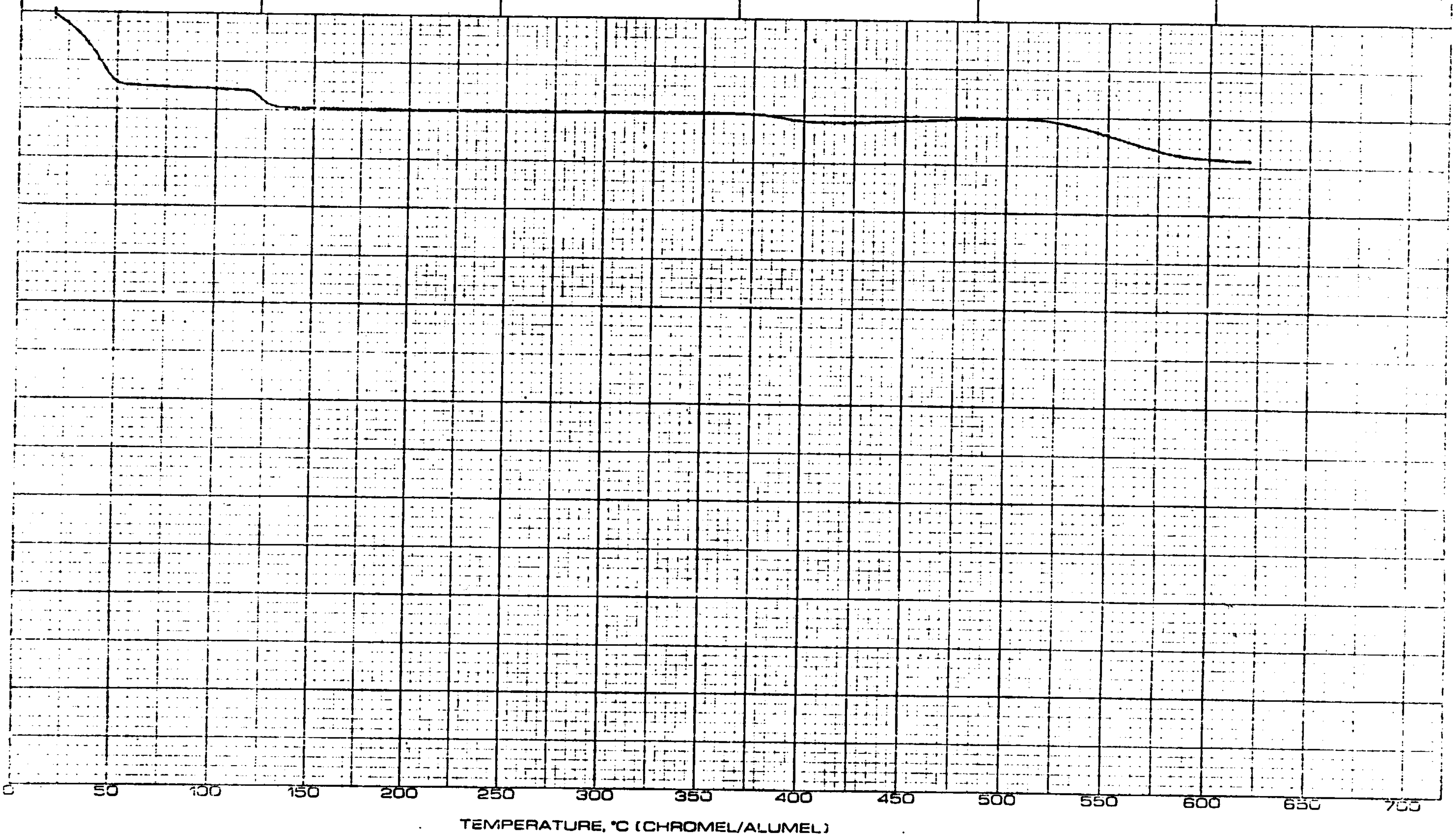
RUN NO.___ DATE 12/20/77
OPERATOR KENNEDY
SAMPLE:
201-1. Scrubber
Cake
ATM______ @______
FLOW RATE N₂

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min 10
HEAT___ COOL___ ISO___
SHIFT, in 0

DTA-DSC
SCALE, °C/in ______
(mcal/sec)/in ______
WEIGHT, mg ______
REFERENCE ______

TGA
SCALE, mg/in .5
SUPPRESSION, mg ______
WEIGHT, mg 7.50
TIME CONST., sec 1
dY, (mg/min)/in ______

TMA
SCALE, mils/in ______
MODE ______
SAMPLE SIZE ______
LOAD, g ______
dY, (10X), (mils/min)/in ______



PART NO. 990088

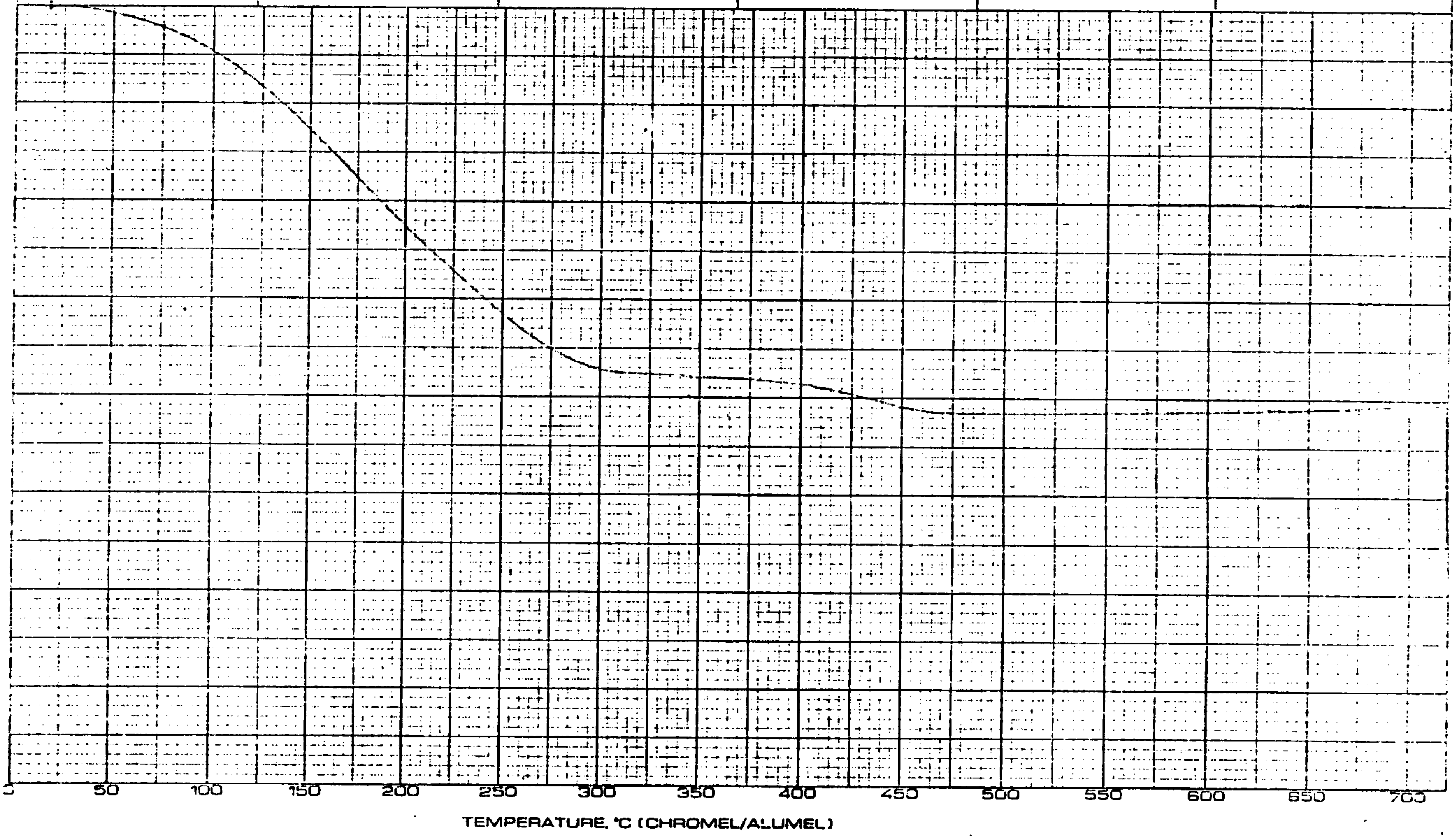
RUN NO.___ DATE 11/16/77
OPERATOR KENNEDY
SAMPLE:
202.4
FILTER CAKE
ATM___
FLOW RATE N₂

T-AXIS
SCALE, °C/in 50
PROG. RATE, °C/min___
HEAT___COOL___ISO___
SHIFT, in 0

DTA-DSC
SCALE, °C/in___
(mcal/sec)/in___
WEIGHT, mg___
REFERENCE___

[✓ TGA]
SCALE, mg/in___
SUPPRESSION, mg___
WEIGHT, mg 12.75
TIME CONST., sec. 1
dY, (mg/min)/in___

TMA
SCALE, mils/in___
MODE___
SAMPLE SIZE___
LOAD, g___
dY, (10X), (mils/min)/in___



APPENDIX C

ATTACHMENT B

PLM PHOTOGRAPHS

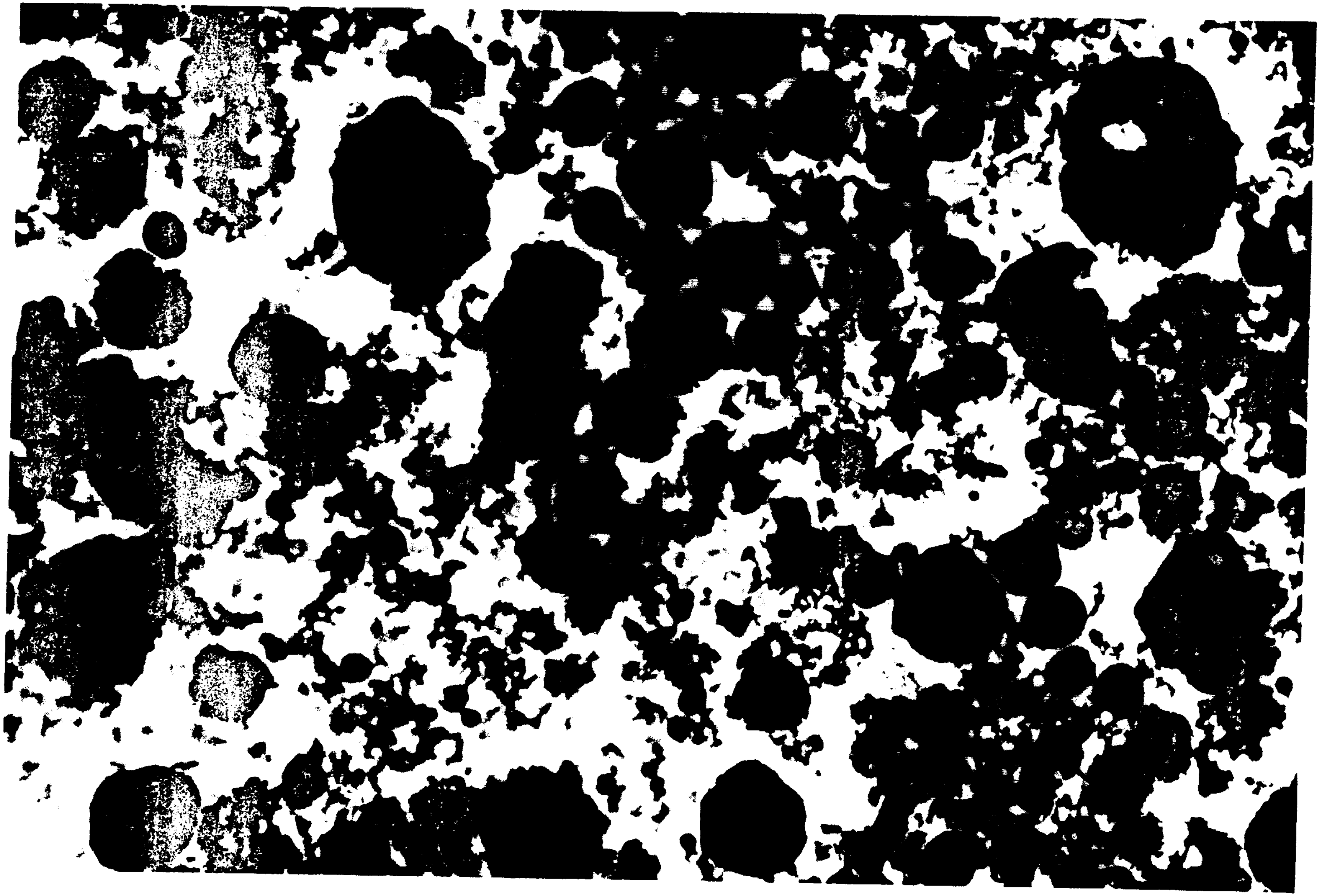


FIGURE B-1. 202-4-I-Cyclone, showing oil soot collected during oil combustion partially uncrossed polars (pup) 51X

FIGURE B-2. 201-1-Flyash, showing oil soot typical of that collected during coal combustion; PUP, 131X

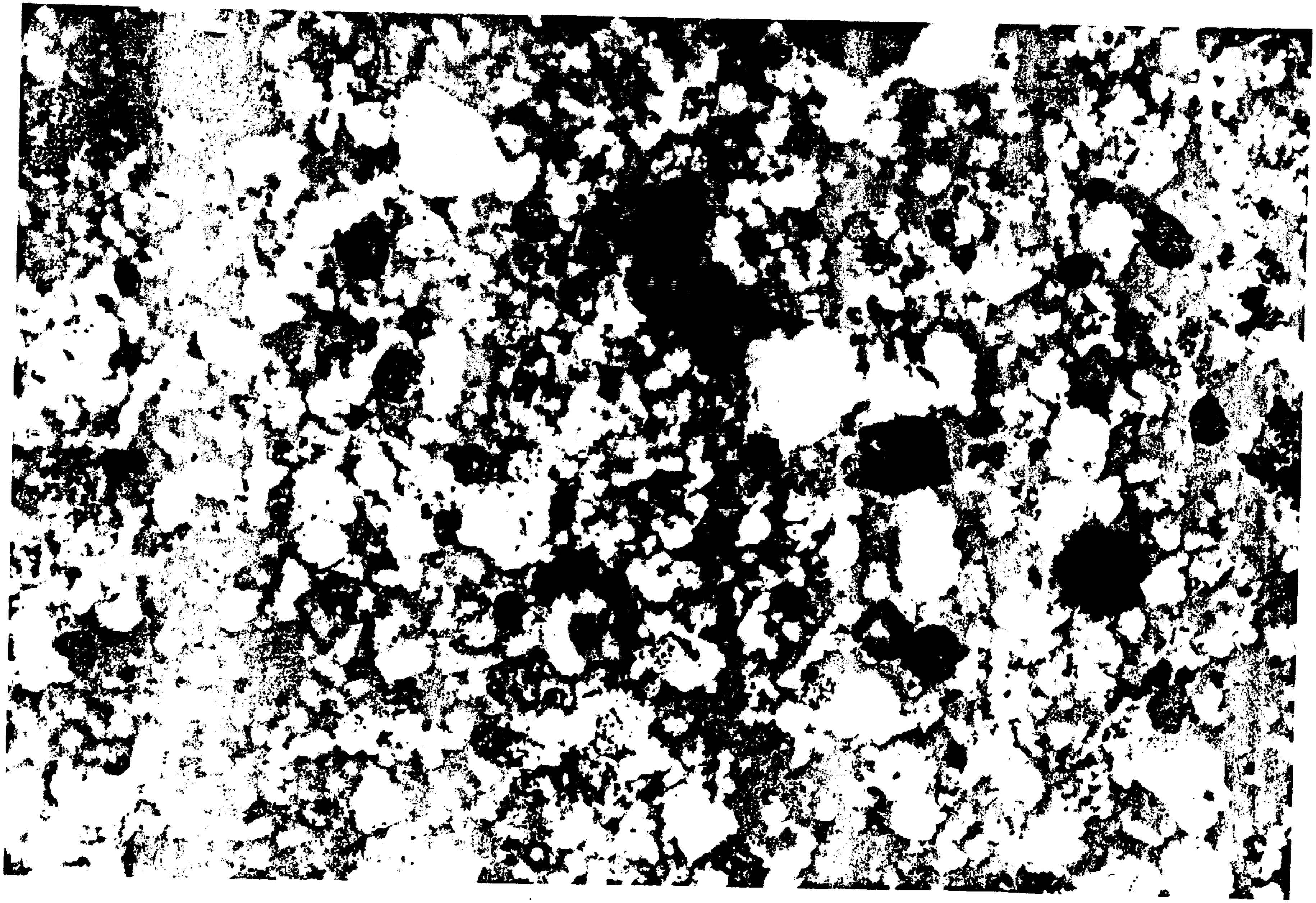


FIGURE B-3. 201-Flyash, showing partially fused flyash, oil soot, and ion oxide; transmitted and reflected light (R&L), PUP, 51X

FIGURE B-4. 201-1-I-Cyclone, showing partially fused flyash and oil soot; R&L, PUP, 51X

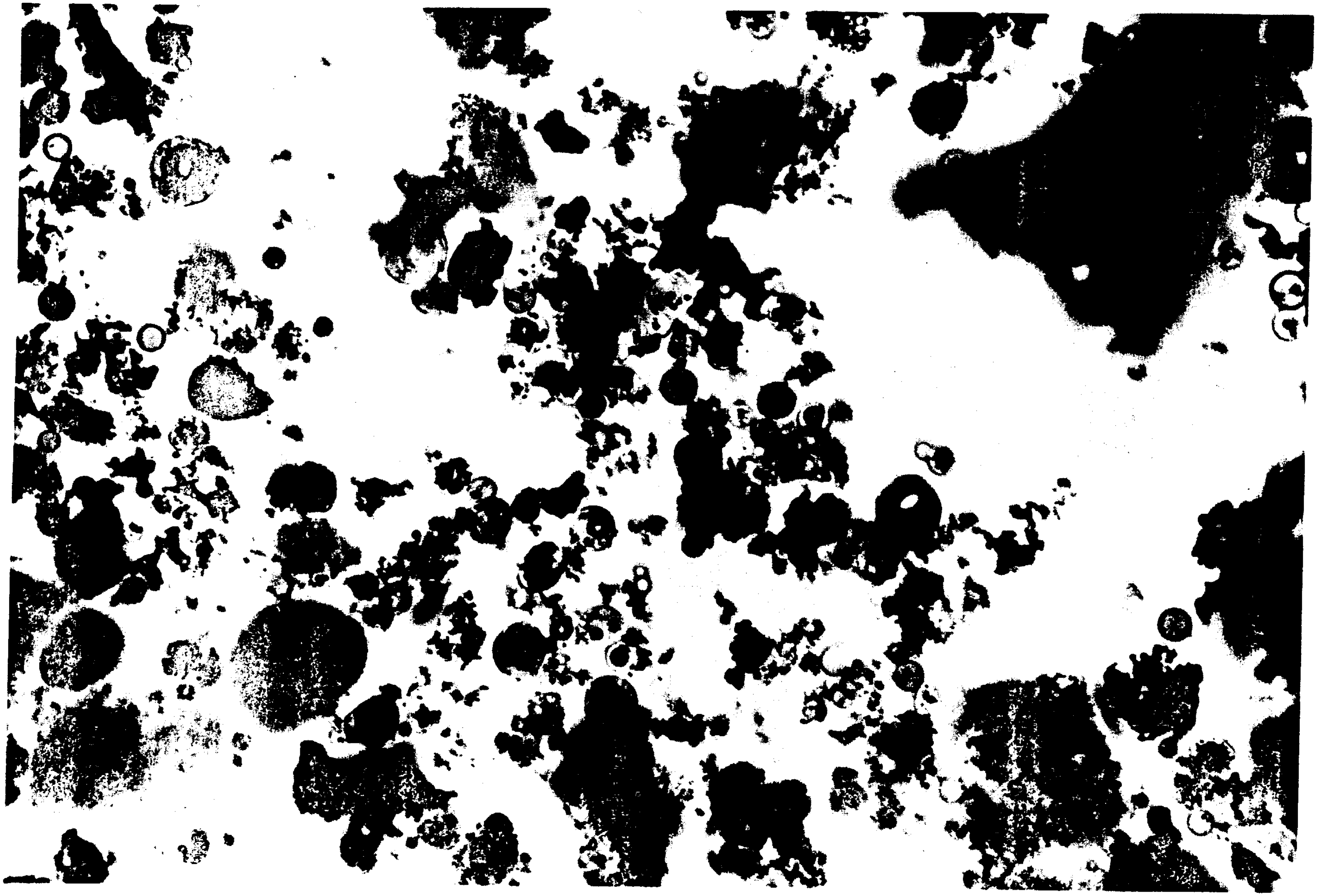


FIGURE B-5. 201-1-I-Cyclone, showing the flyash (some with air bubbles); PUP, 131X

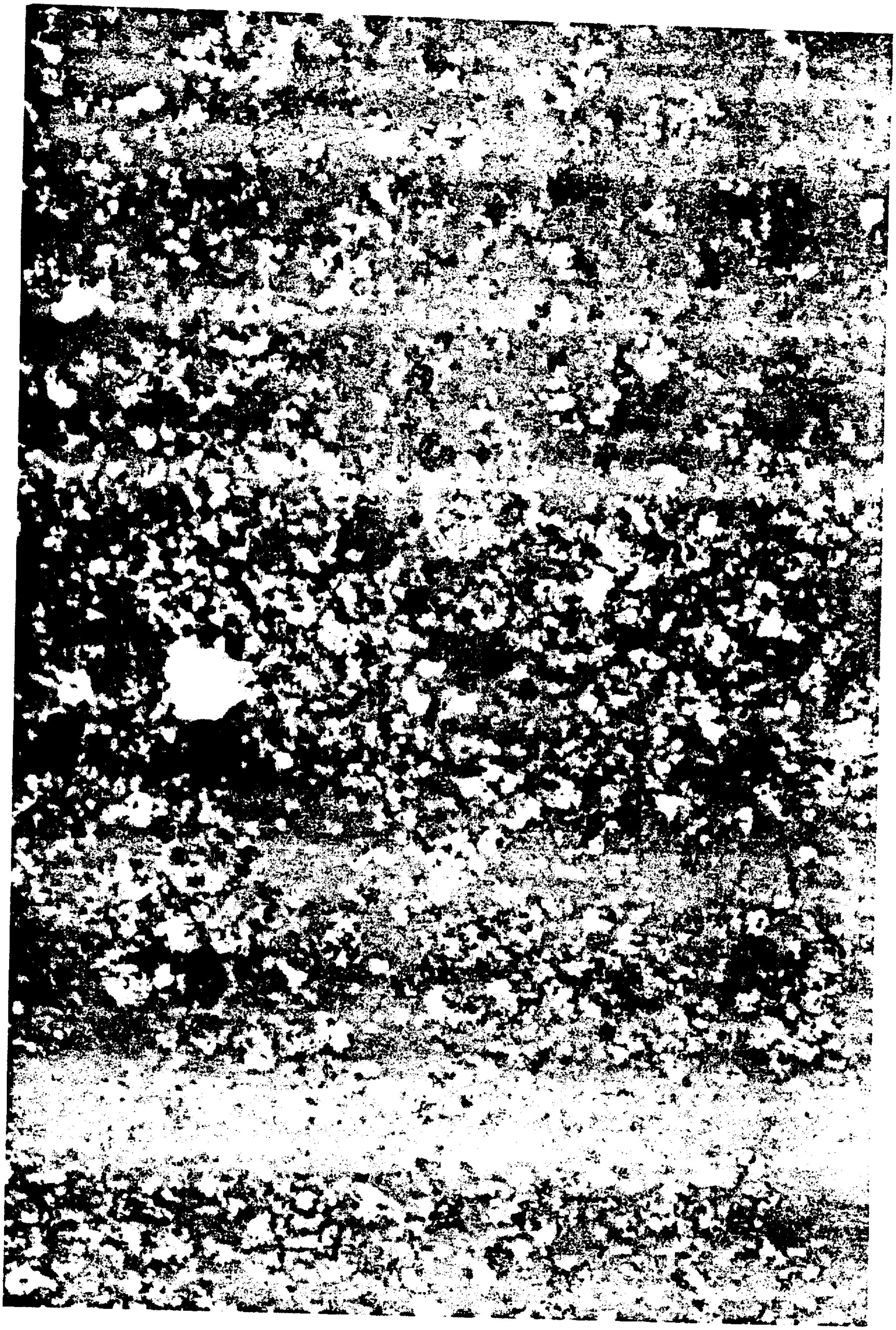


FIGURE B-6. 201-1-I-Filter, showing partially fused flyash and oil soot, also, overall smallness of particle size; R&L, PUP, 51X

FIGURE B-7. 201-1-I-Filter, showing flyash; PUP, 131X

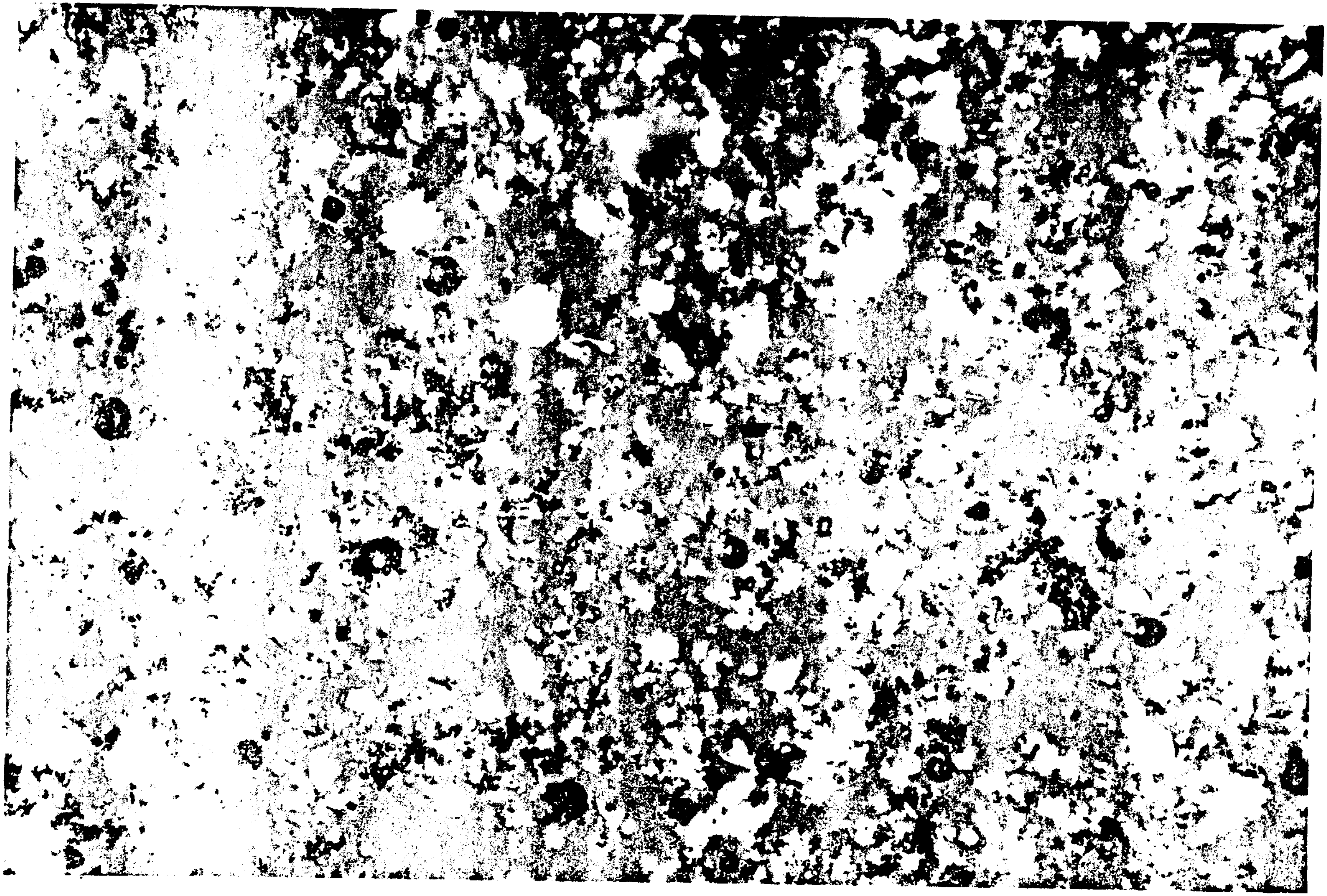


FIGURE B-8. 201-1-Scrubber cake, showing partially fused flyash and oil soot; R&L, PUP, 51X

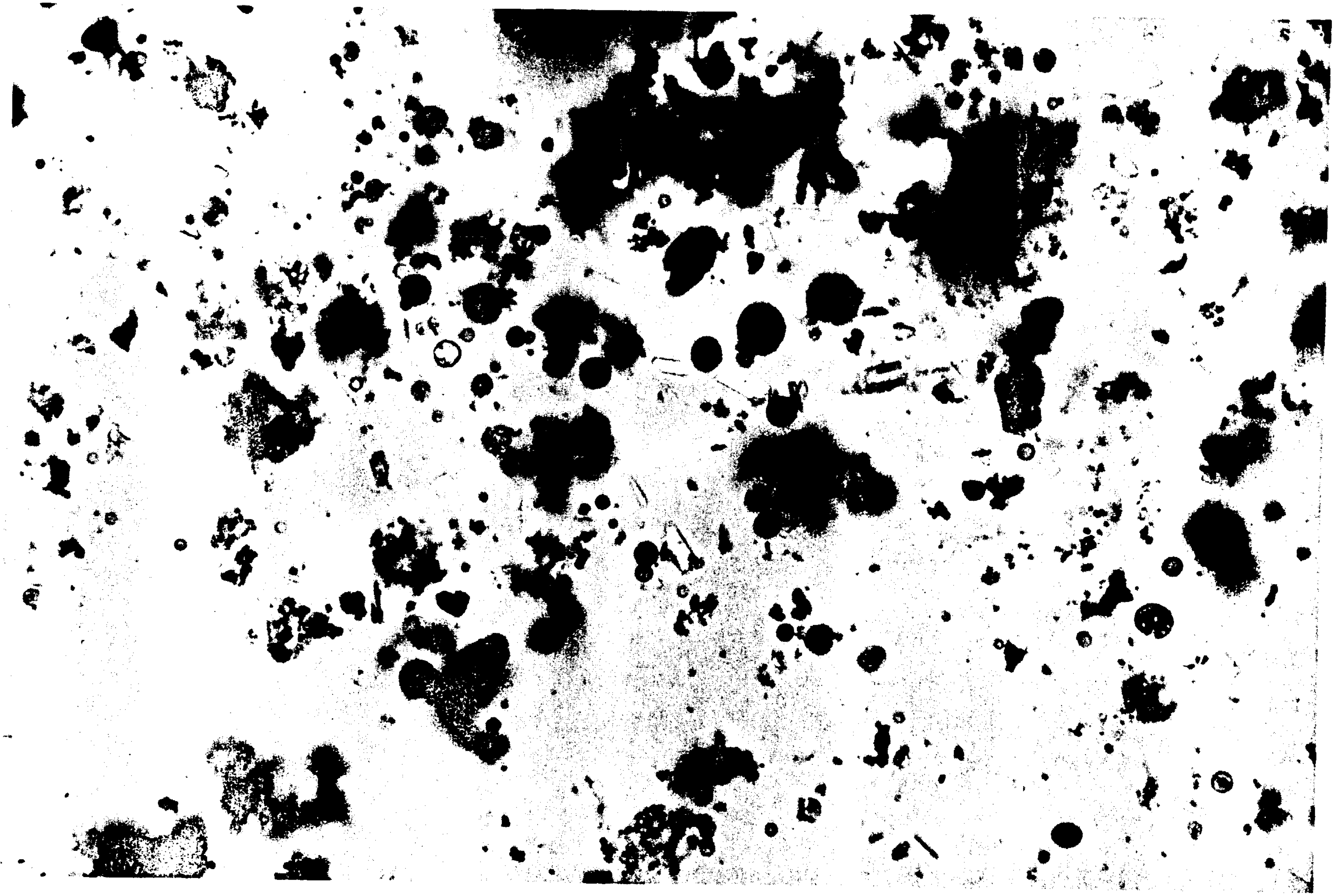


FIGURE B-9. 201-1-Scrubber cake, showing $CaSo_3$. 1/2 H_2O laths; PUP, 131X

FIGURE B-10. 201-1-Scrubber cake, showing foreign particulates incorporated in spherilites; PUP 131X

FIGURE B-11. 201-1-0, showing carbonaceous coating on material embedded in the filter.

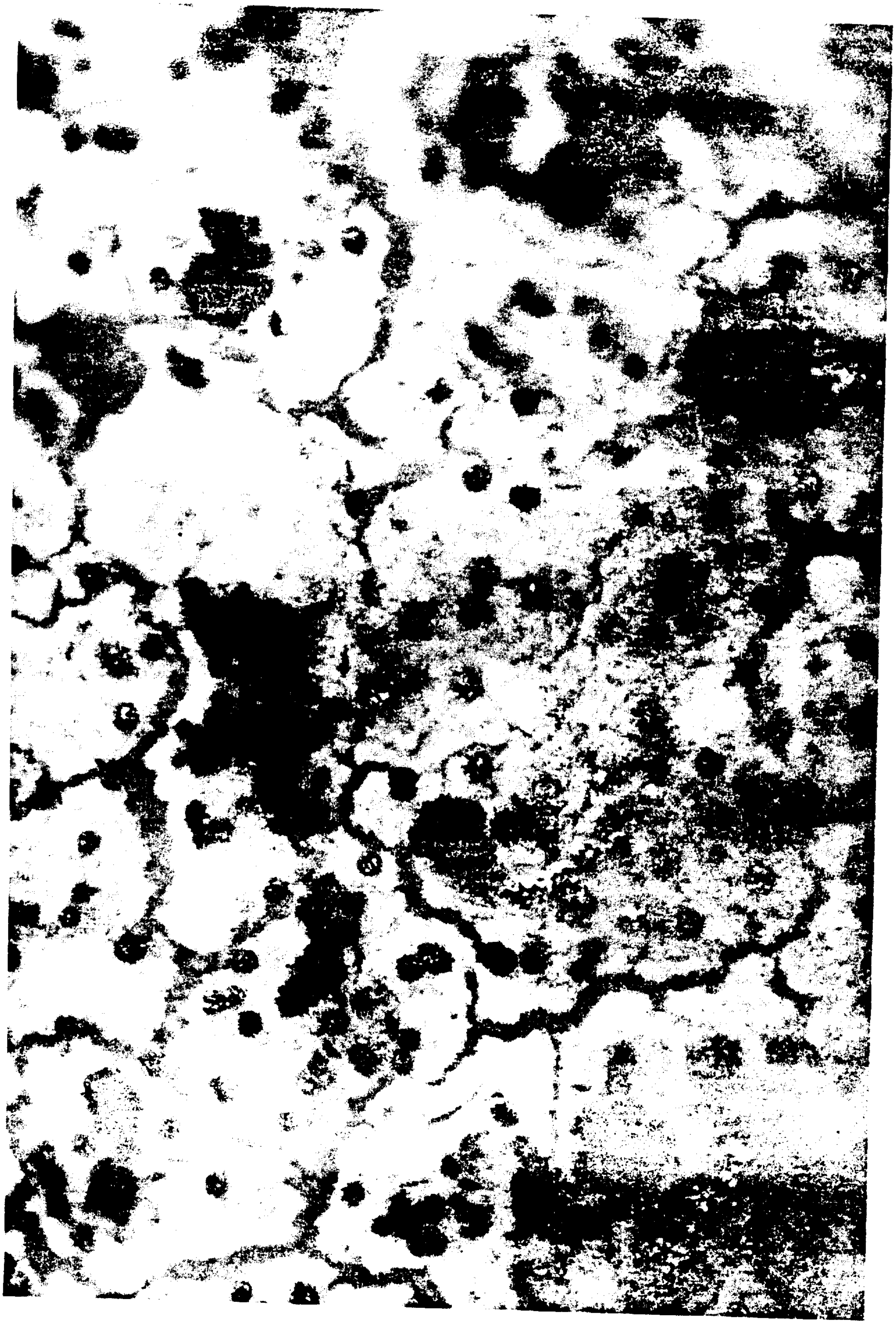


FIGURE B-12. 201-1-0, after LTA revealing minerals; R&L, PUP, 51X

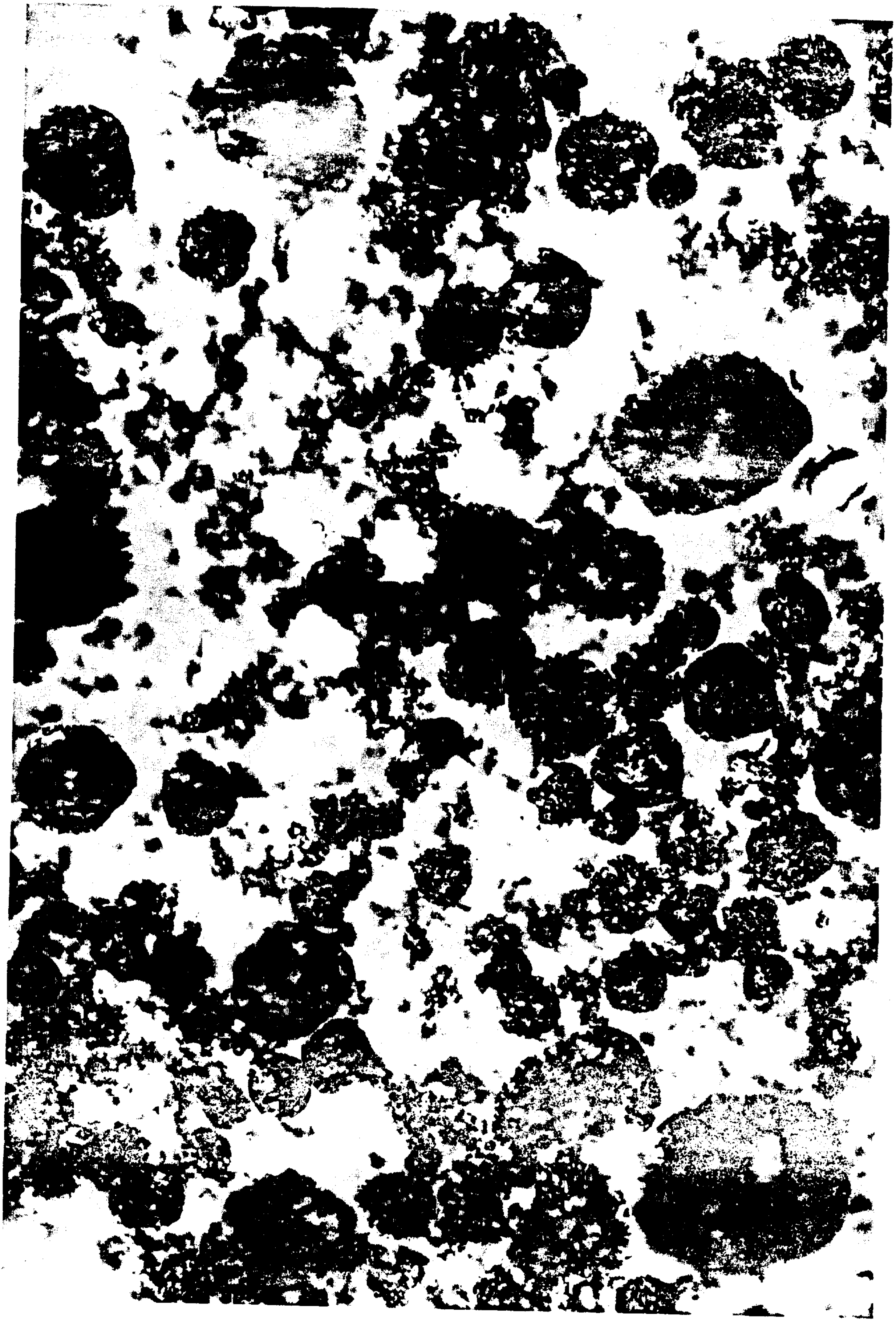


FIGURE B-13. 202-4-I-Cyclone, showing oil soot; R&L, PUP, 51X

FIGURE B-14. 202-4-I-Cyclone, showing crystals of an unknown sulfate oil soot; PUP, 131X

FIGURE B-15. 202-4-I, showing carbonaceous particles on briefing on the background; R&L, PUP, 51X

FIGURE B-16. 202-4-I, after LTA, revealing mineral background; R&L, PUP, 51X

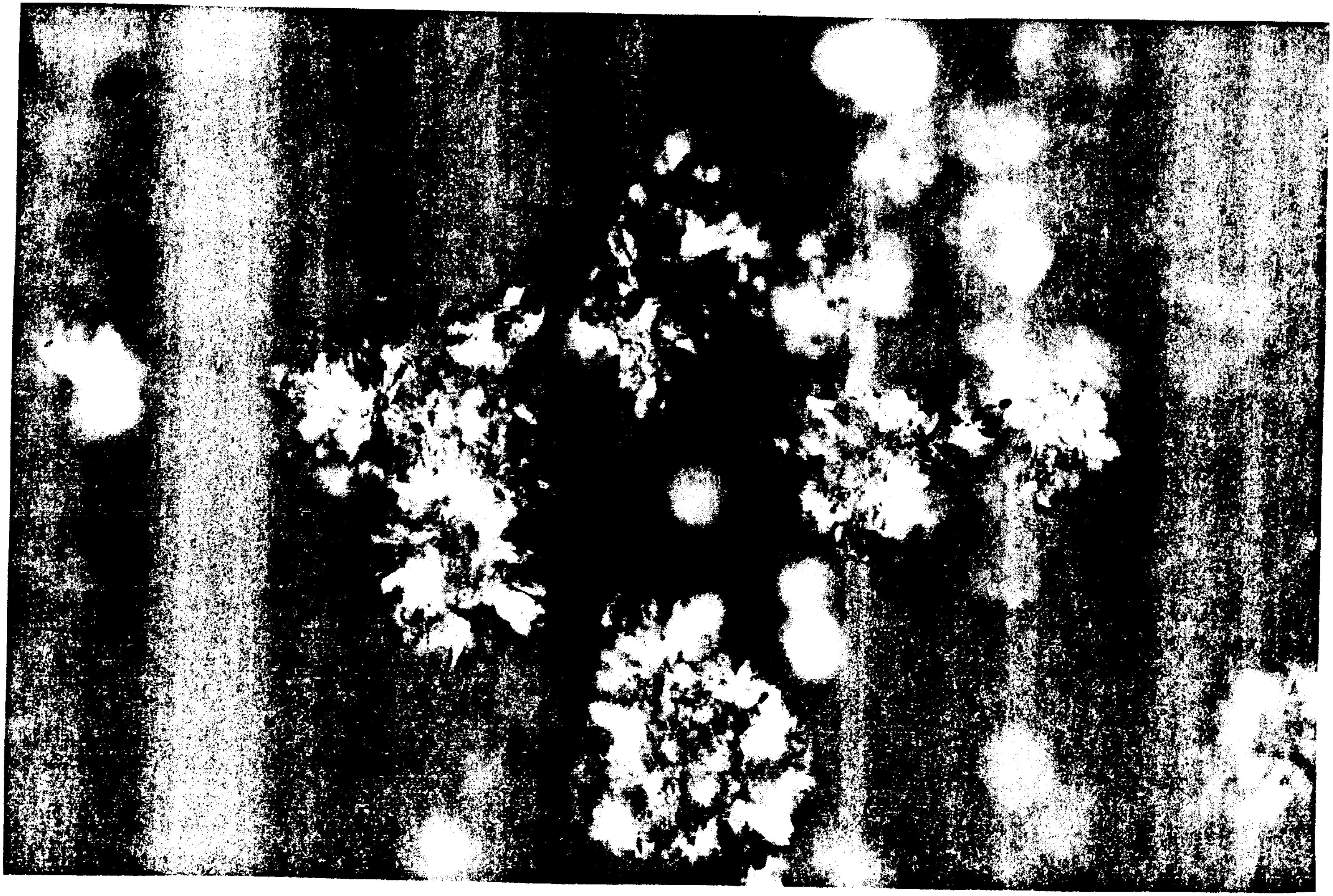


FIGURE B-17. 202-4-scrubber cake, showing spherilities; PUP, 131X

FIGURE B-18. 202-4-scrubber cake, spherilite with first order red plate compensator; completely crossed polars, 131X

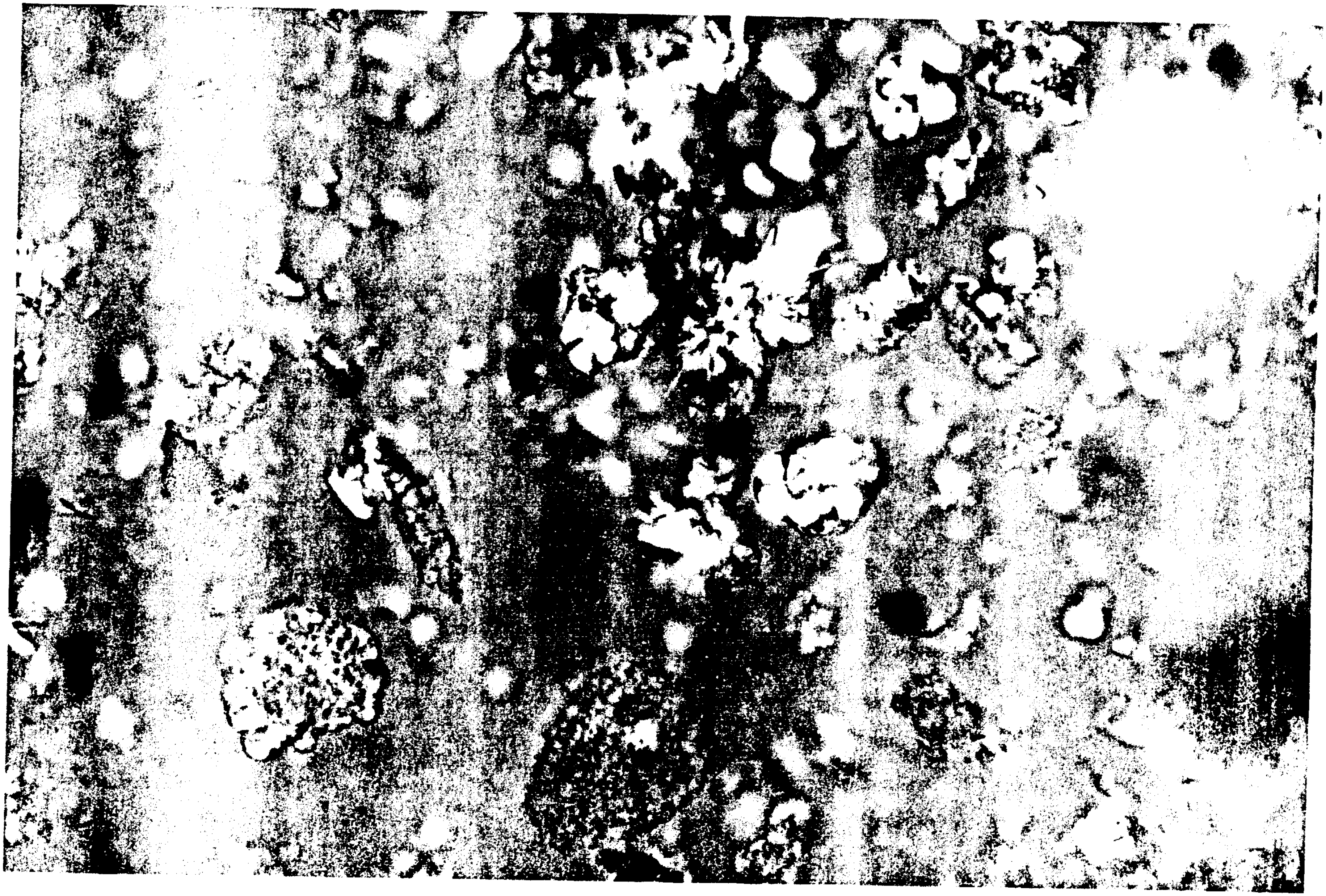


FIGURE B-19. 202-4-scrubber cake showing spherilities, laths and plates of $CaSO_3$. 1/2 H_2O; PUP, 131X

FIGURE B-20. 202-4-0, showing sulfate crystals on filter, as well as the blue droplets; PUP, 51X

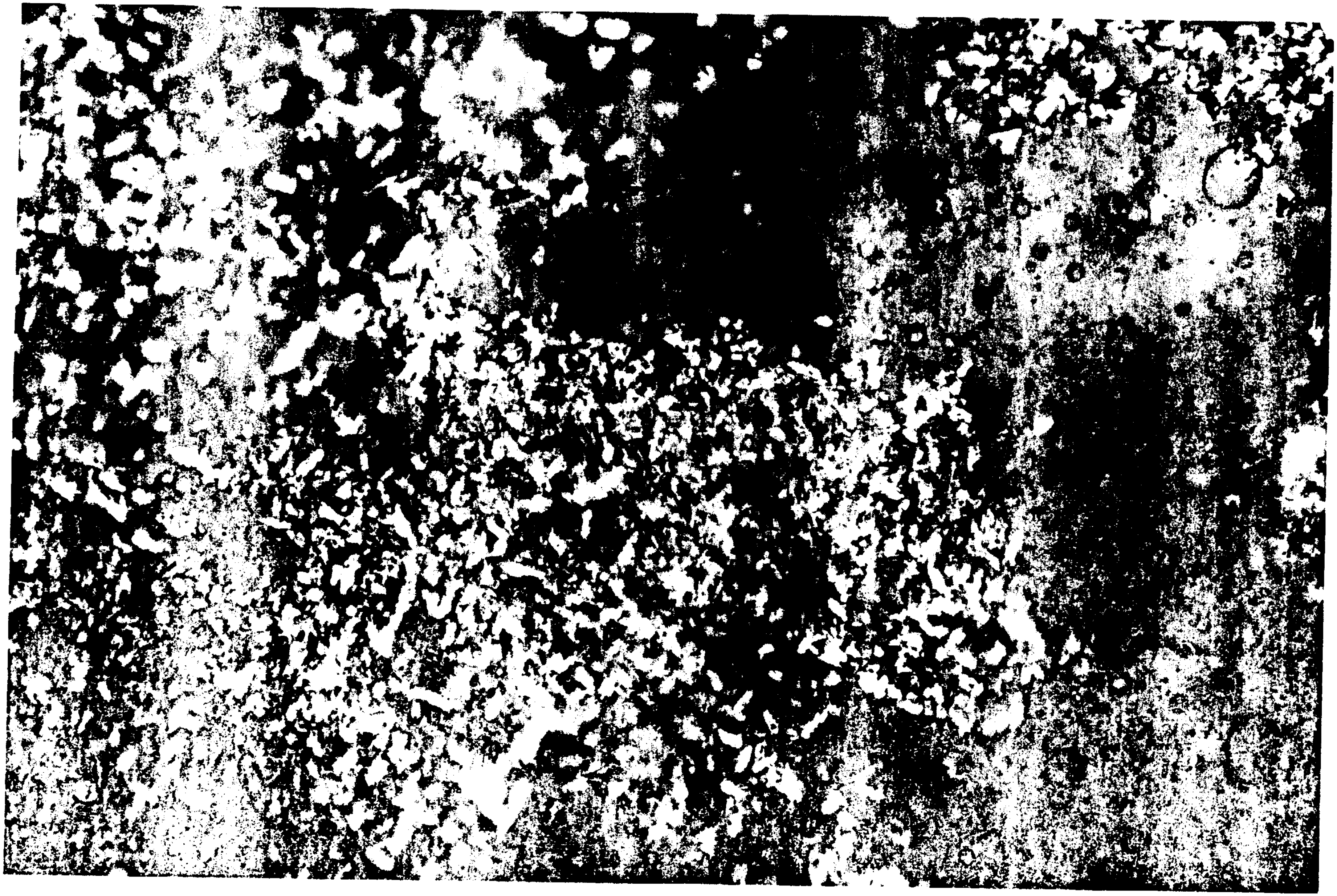


FIGURE B-21. 202-4-0, showing another crystal form on filters PUP, 51X

FIGURE B-22. 202-4-0, showing recrystallization on filter, after sitting; PUP, 51X

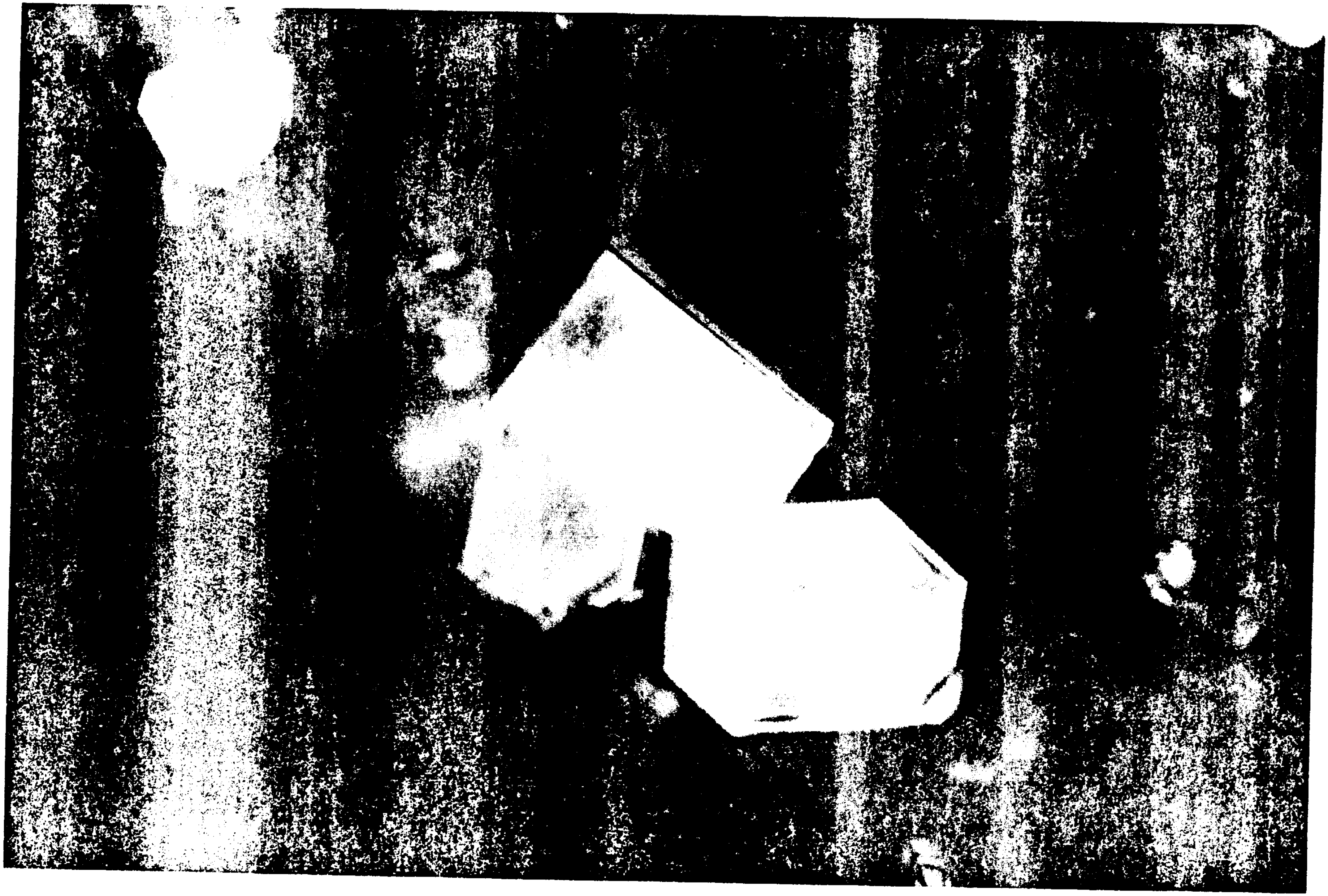


FIGURE B-23. 202-4-0, showing another type of recrystallization on filter; PUP, 51X

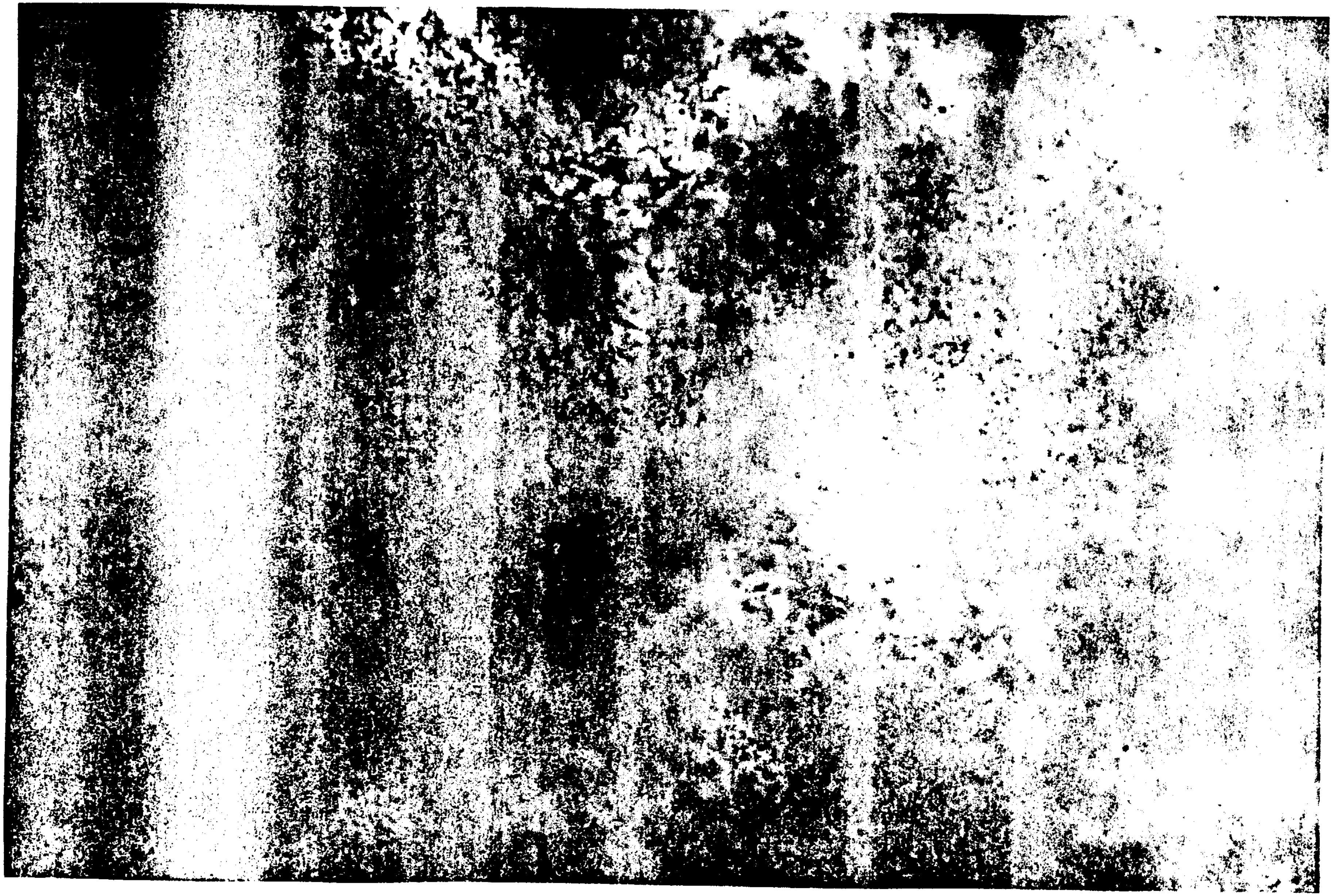
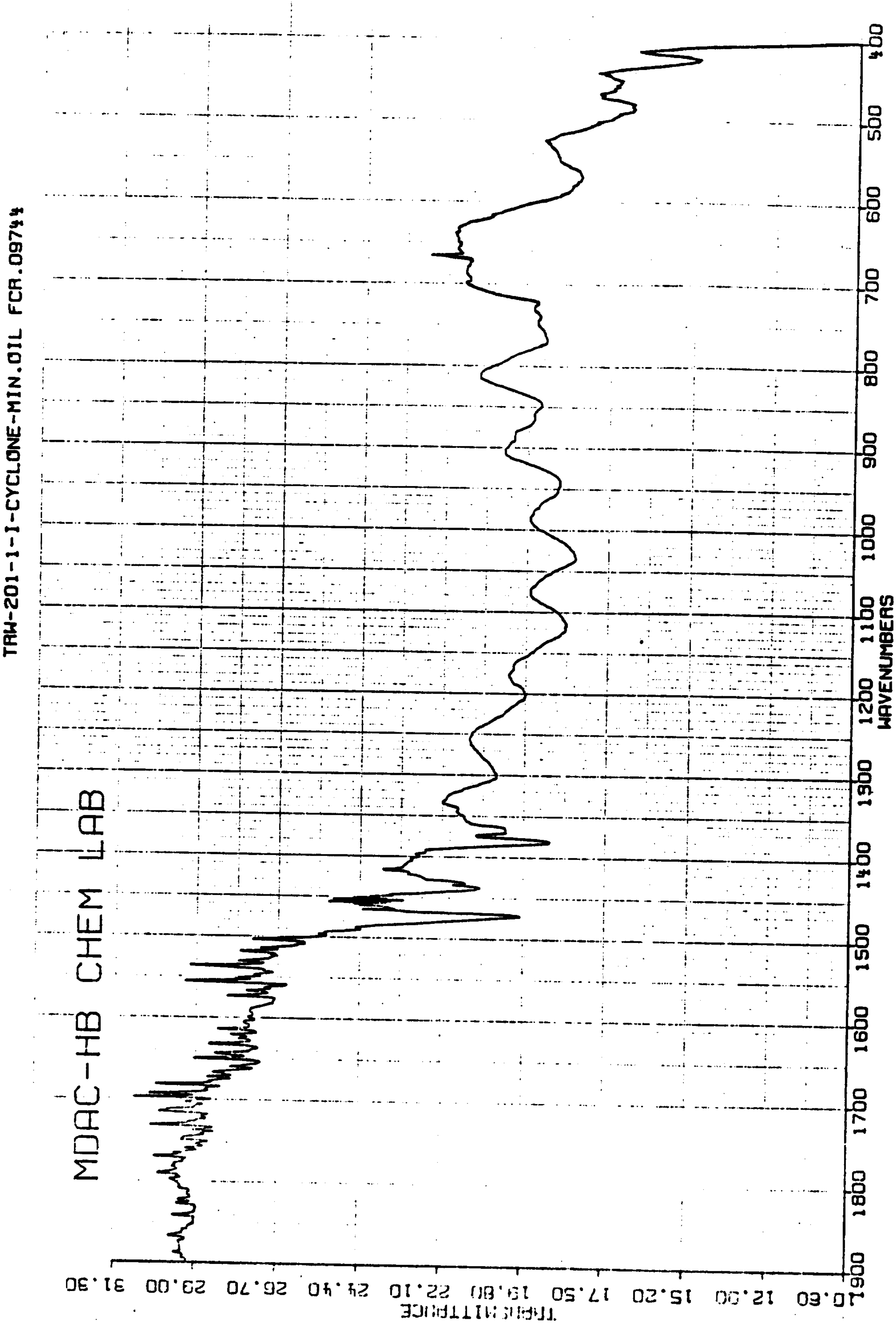


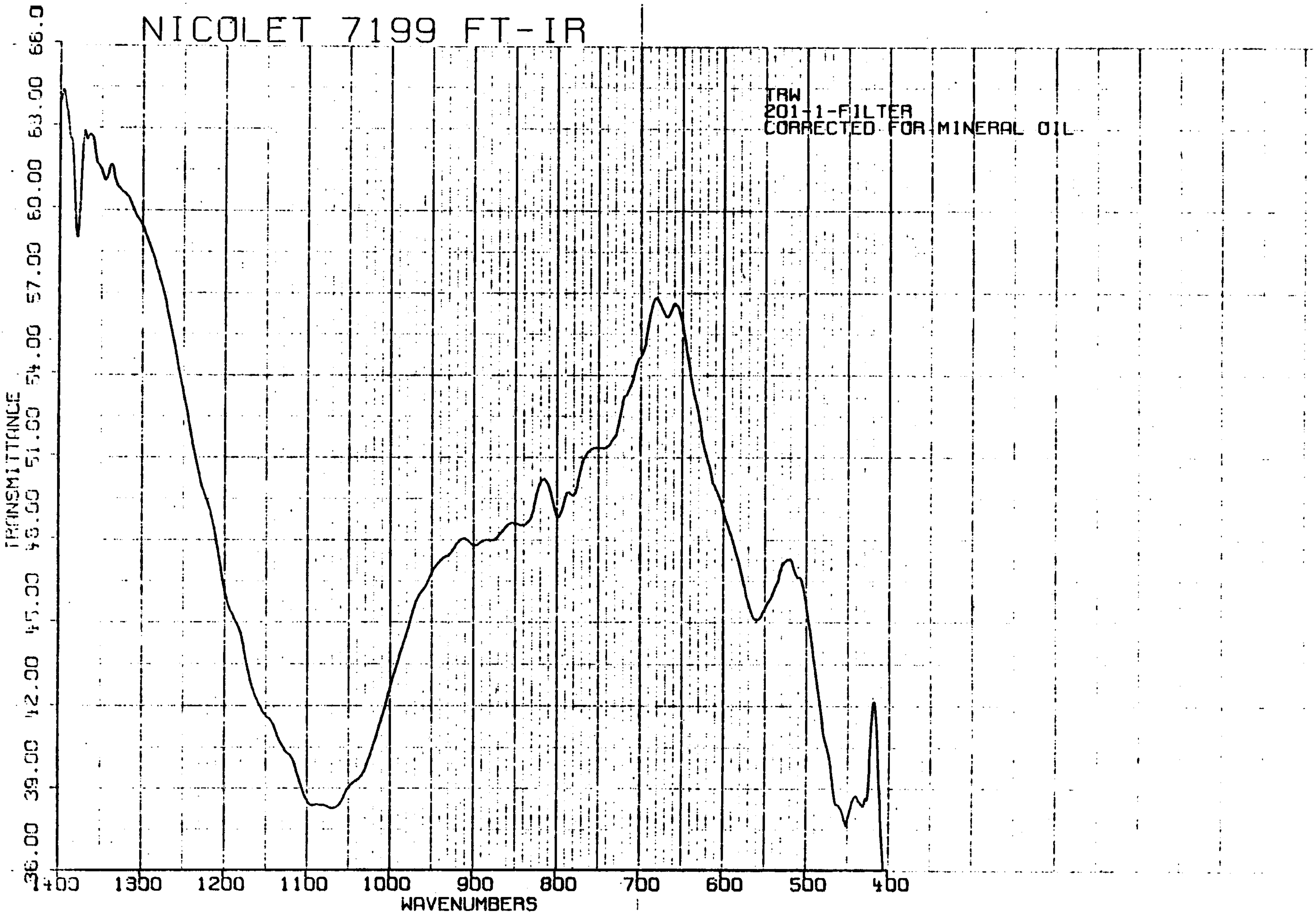
FIGURE B-24. 202-4-0, after LTA, revealing minerals; R&T, PUP, 51X

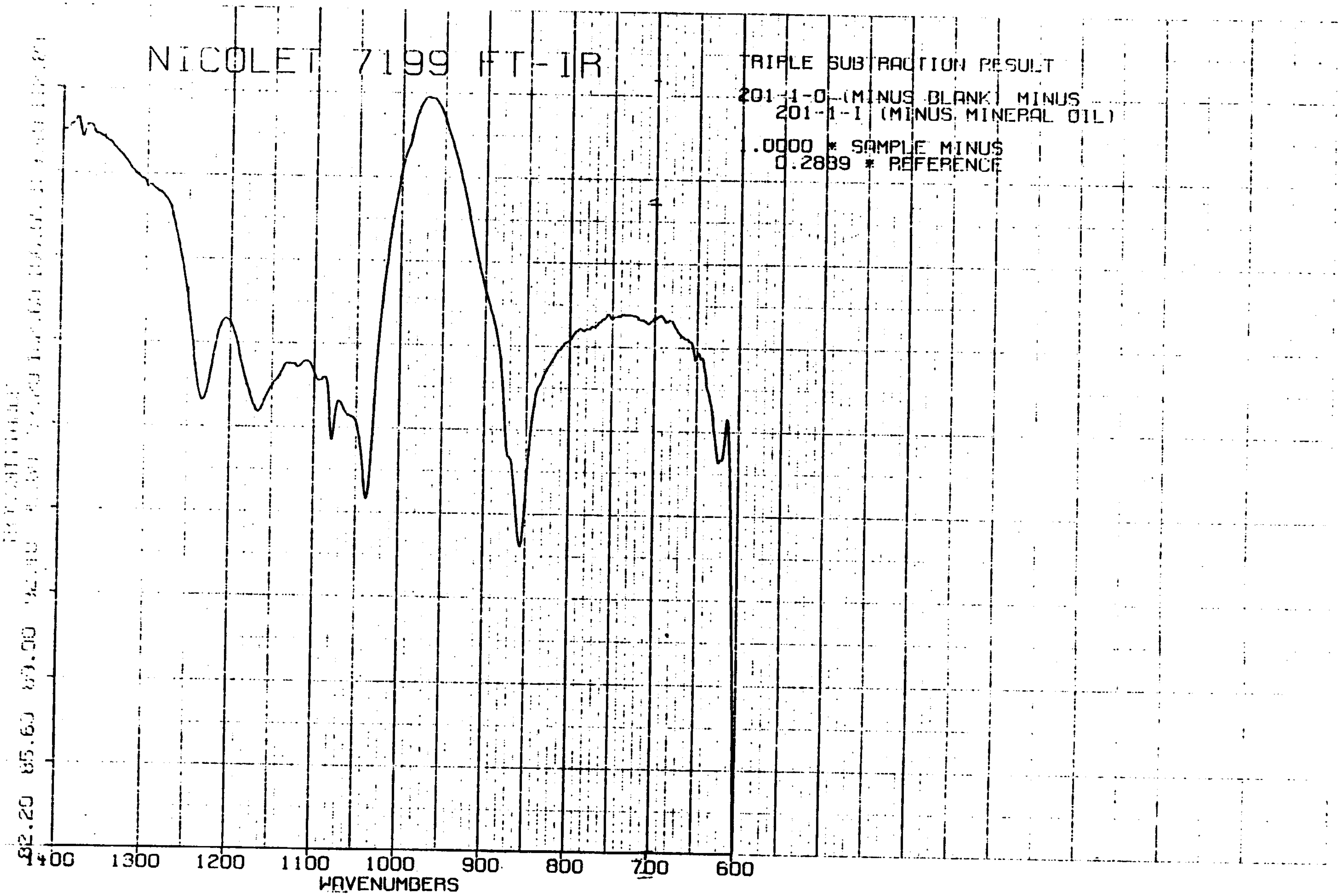
APPENDIX C

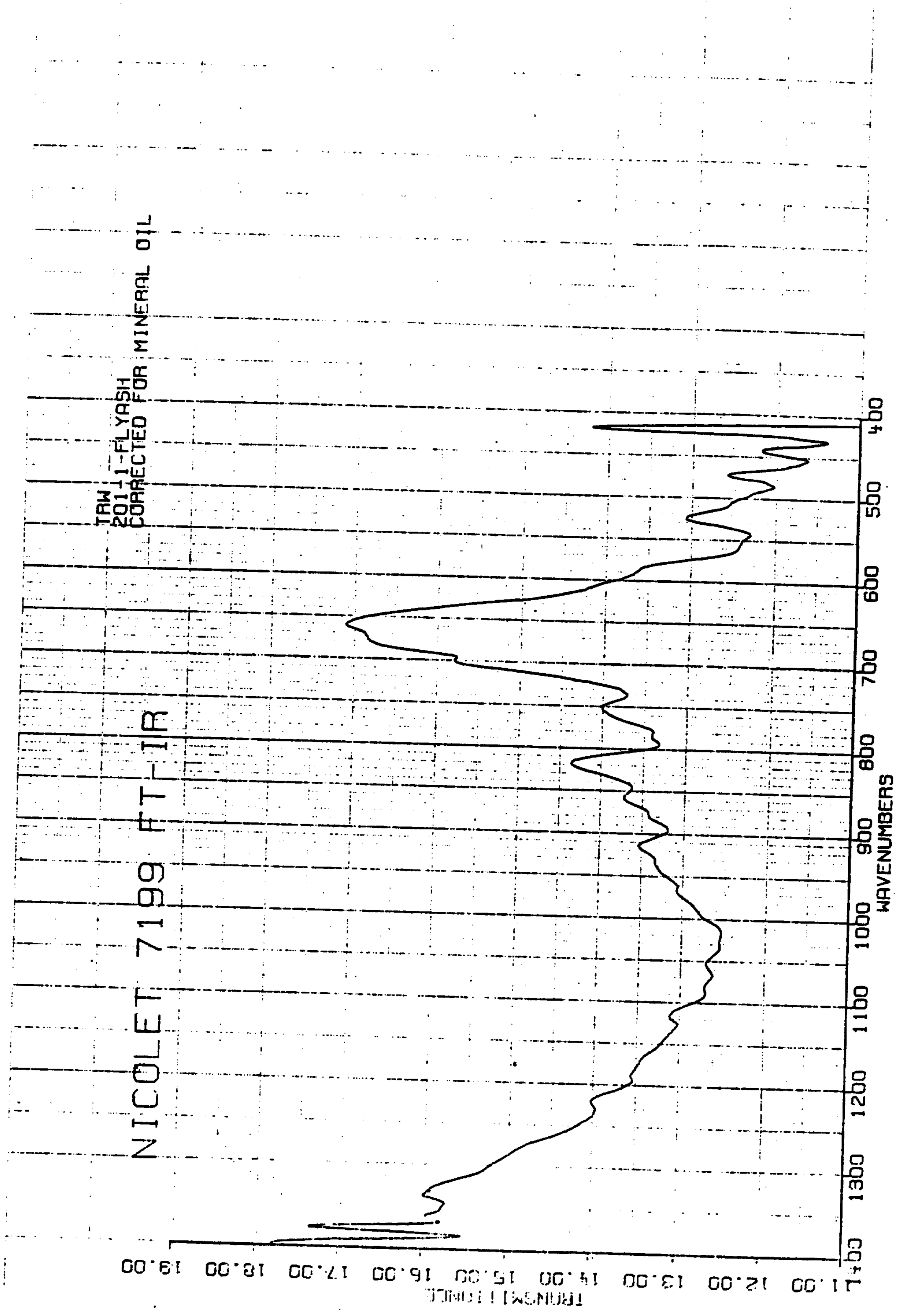
ATTACHMENT C

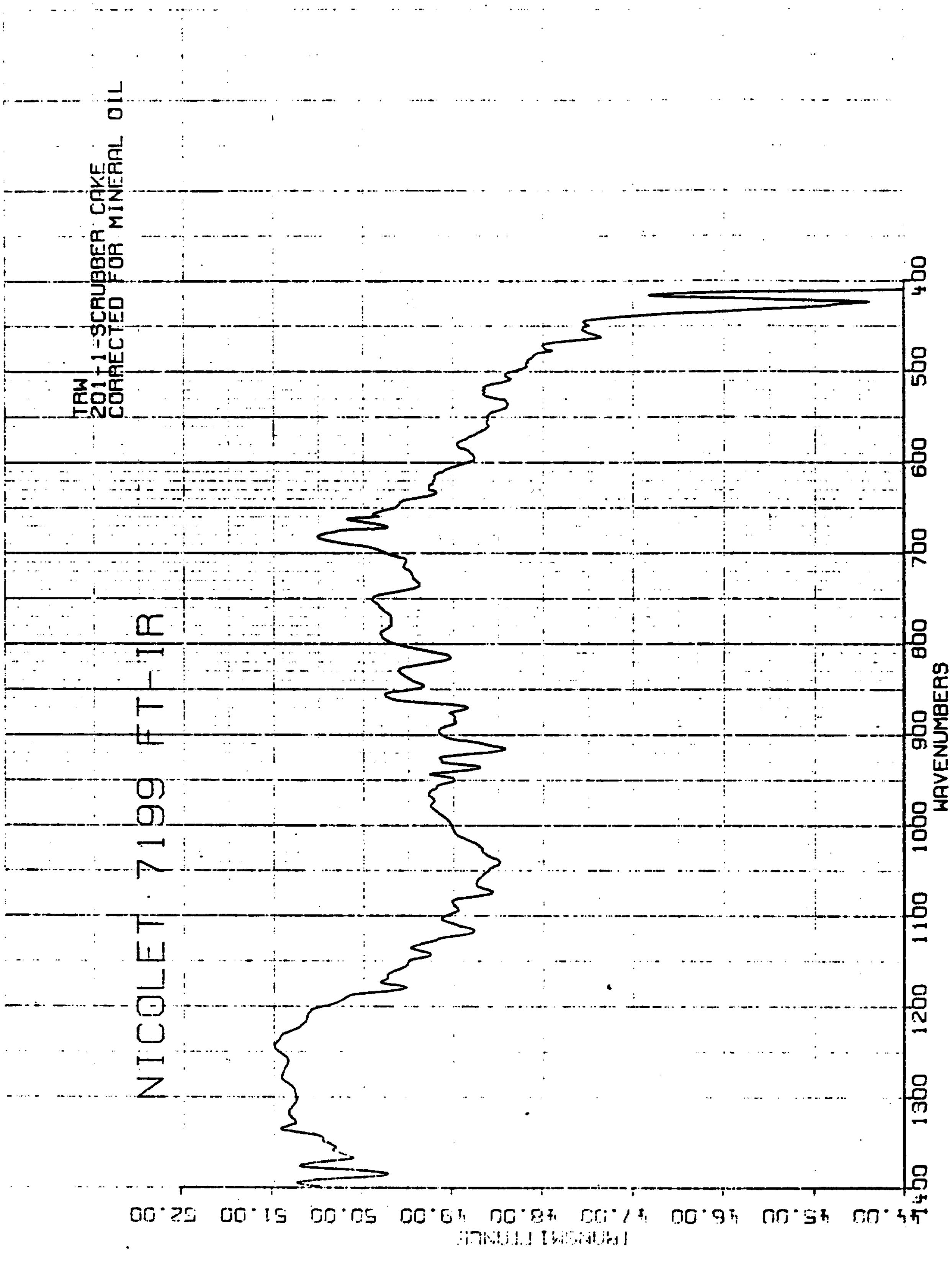
FTIR SPECTRA


TRW-201-1-I-CYCLONE-MIN.OIL FCR.0974%
MDAC-HB CHEM LAB
WAVENUMBERS
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600
1700
1800
1900
TRANSMITTANCE
10.60
12.90
15.20
17.50
19.80
22.10
24.40
26.70
29.00
31.30

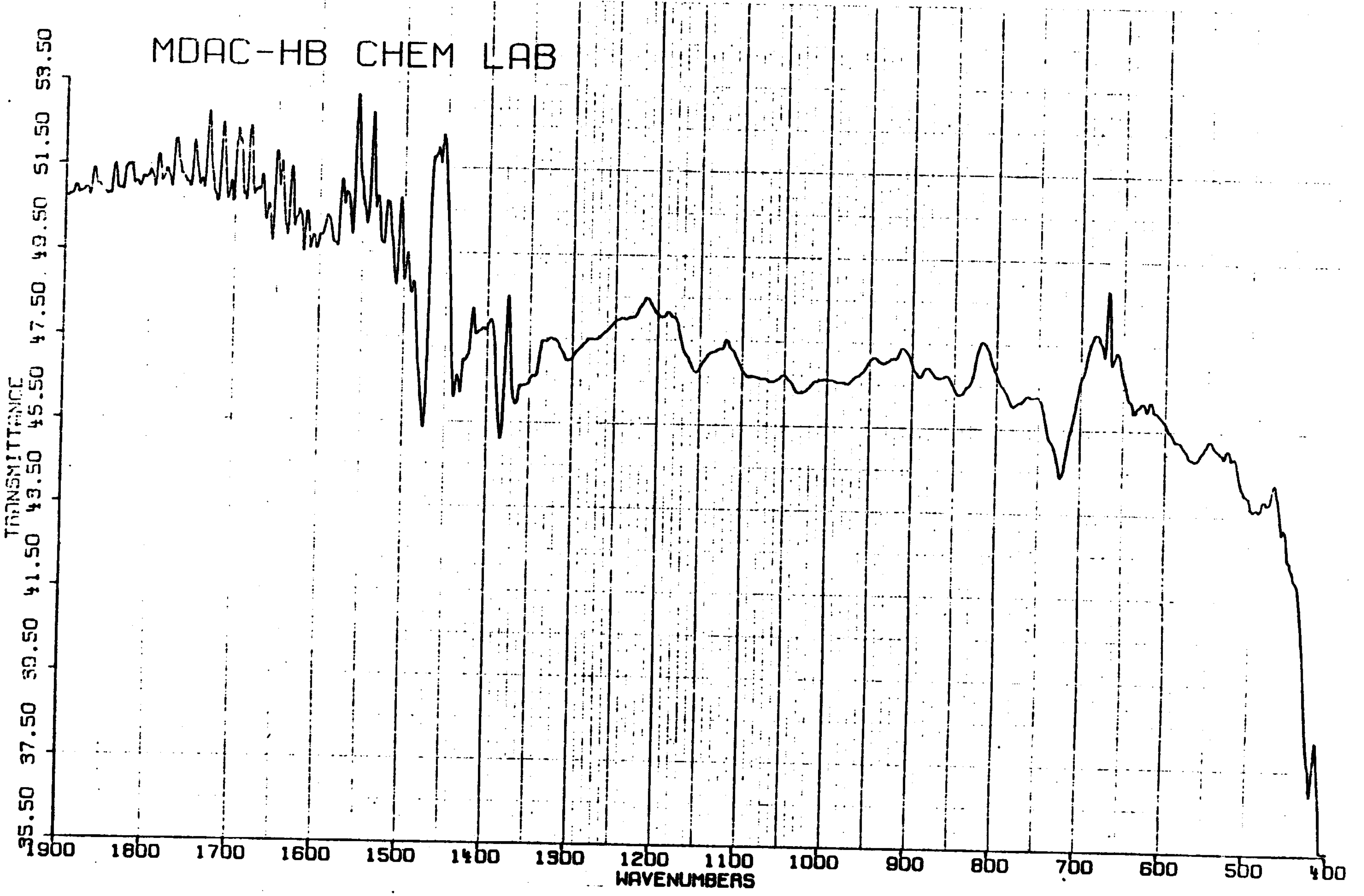

NICOLET 7199 FT-IR
TRW
201-1-FILTER
CORRECTED FOR MINERAL OIL
TRANSMITTANCE
66.0
63.00
60.00
57.00
54.00
51.00
48.00
45.00
42.00
39.00
36.00
1400
1300
1200
1100
1000
900
800
700
600
500
400
WAVENUMBERS

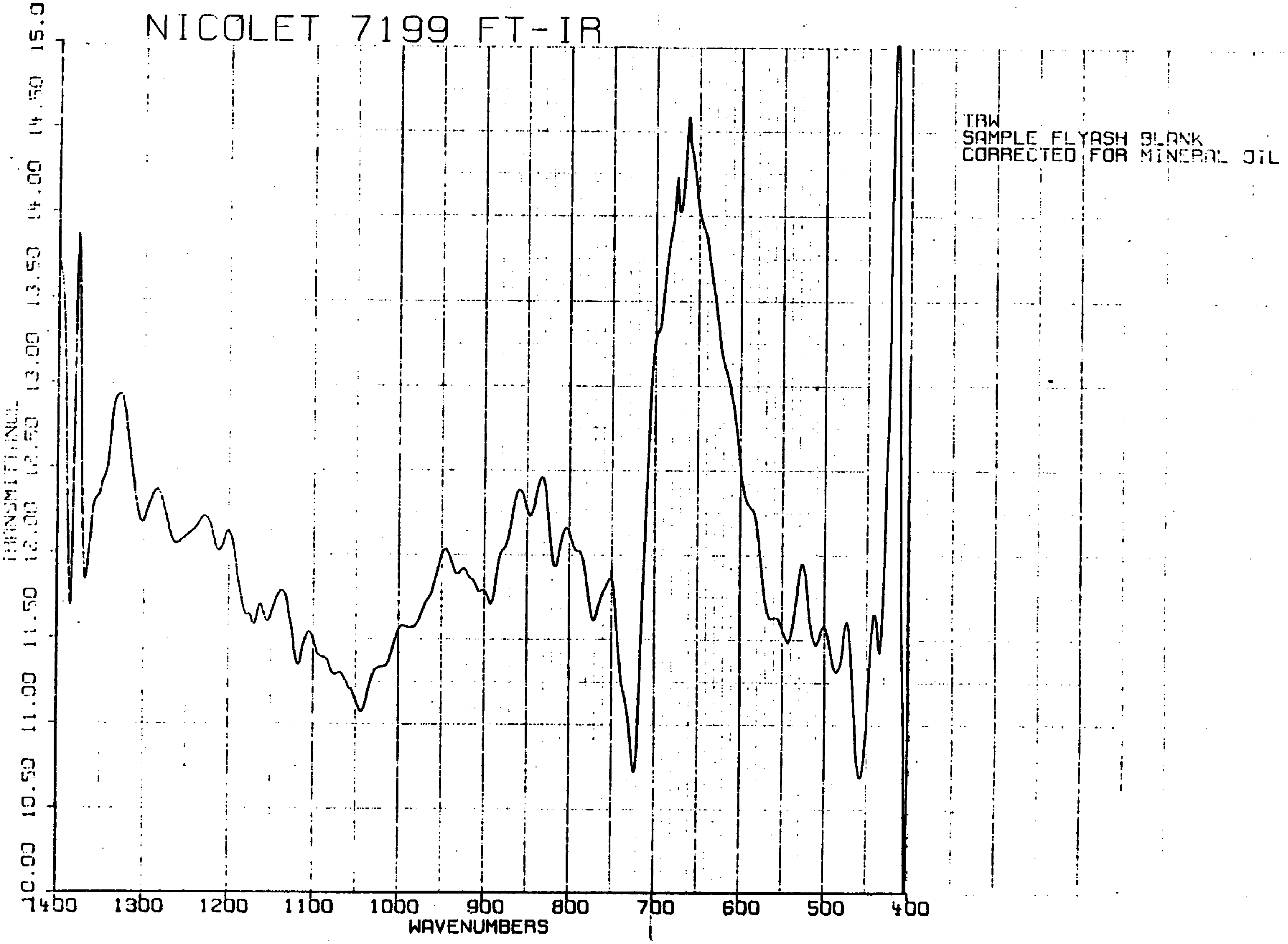

NICOLET 7199 FT-IR
TRIPLE SUBTRACTION RESULT
201-1-0 (MINUS BLANK) MINUS
201-1-I (MINUS MINERAL OIL)
1.0000 * SAMPLE MINUS
0.2889 * REFERENCE
82.20
85.60
89.00
92.40
1400
1300
1200
1100
1000
900
800
700
600
WAVENUMBERS


NICOLET 7199 FT-IR
TRW
201-1-FLYASH
CORRECTED FOR MINERAL OIL
400
500
600
700
800
900
1000
1100
1200
1300
1400
WAVENUMBERS
11.00
12.00
13.00
14.00
15.00
16.00
17.00
18.00
19.00
TRANSMITTANCE

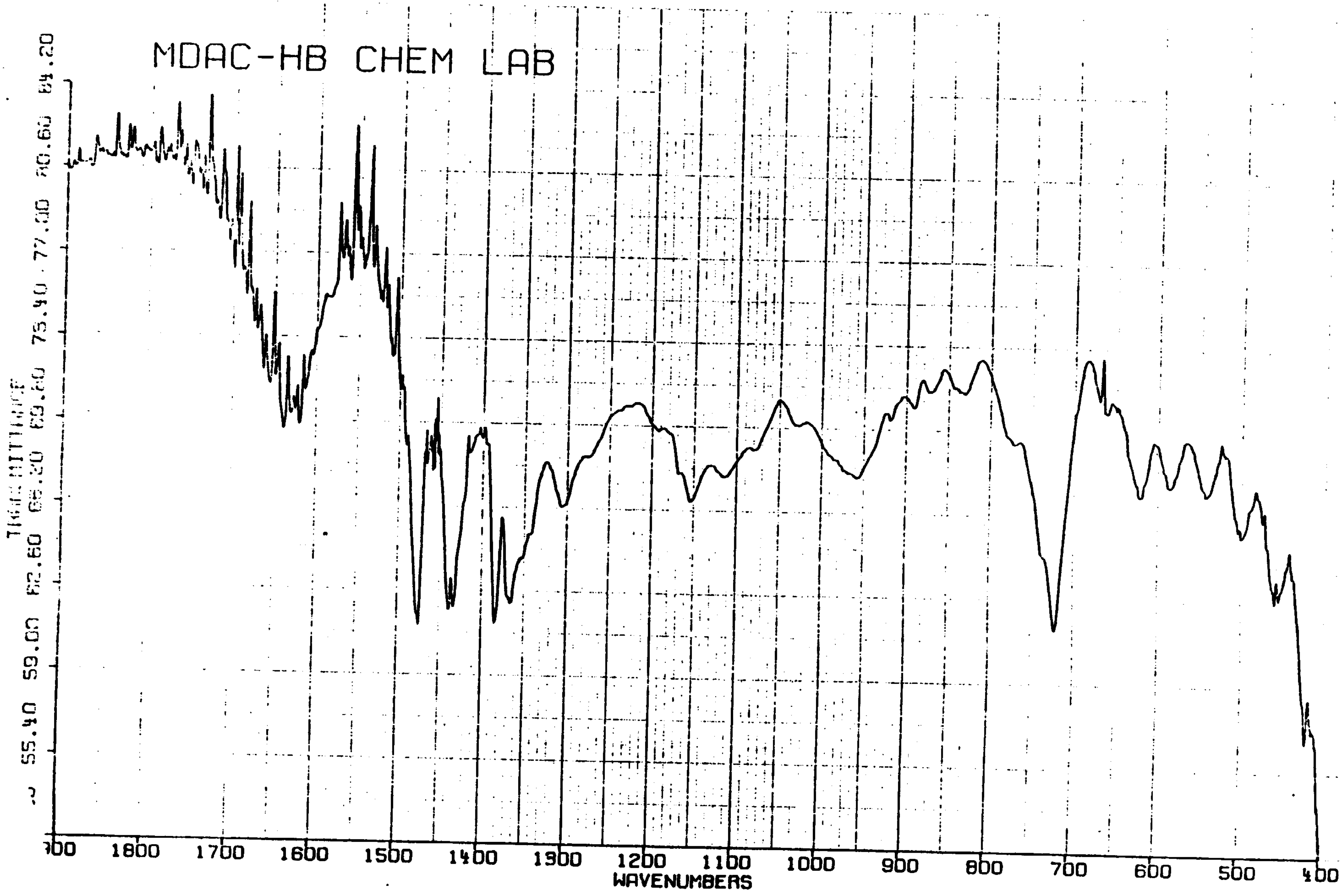

TRW
201-1-SCRUBBER CAKE
CORRECTED FOR MINERAL OIL
NICOLET 7199 FT-IR
WAVENUMBERS
400
500
600
700
800
900
1000
1100
1200
1300
1400
TRANSMITTANCE
44.00
45.00
46.00
47.00
48.00
49.00
50.00
51.00
52.00

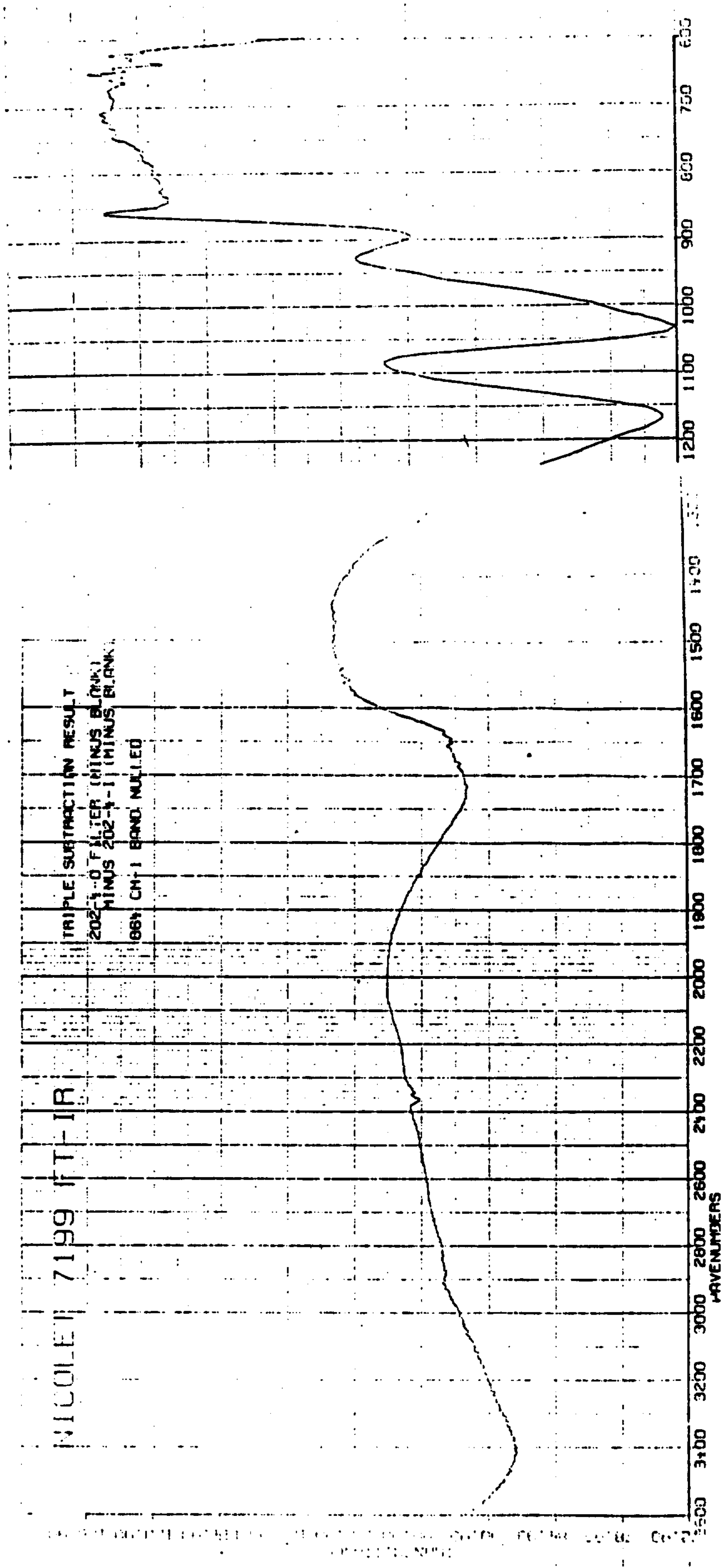
TAW-202-4-I-CYCLONE - MIN.OIL FCR.05225 SMOOTHED 9 PTS

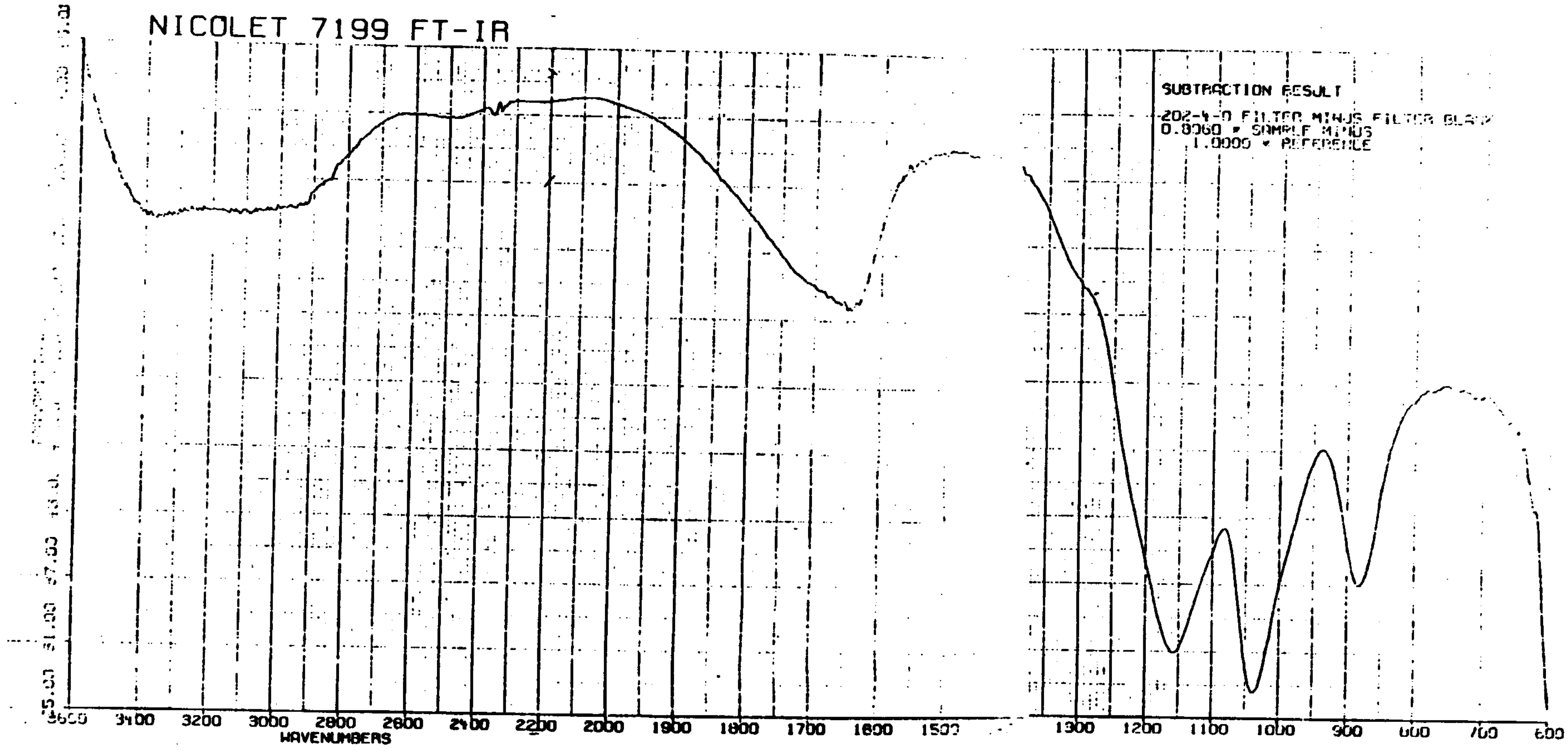


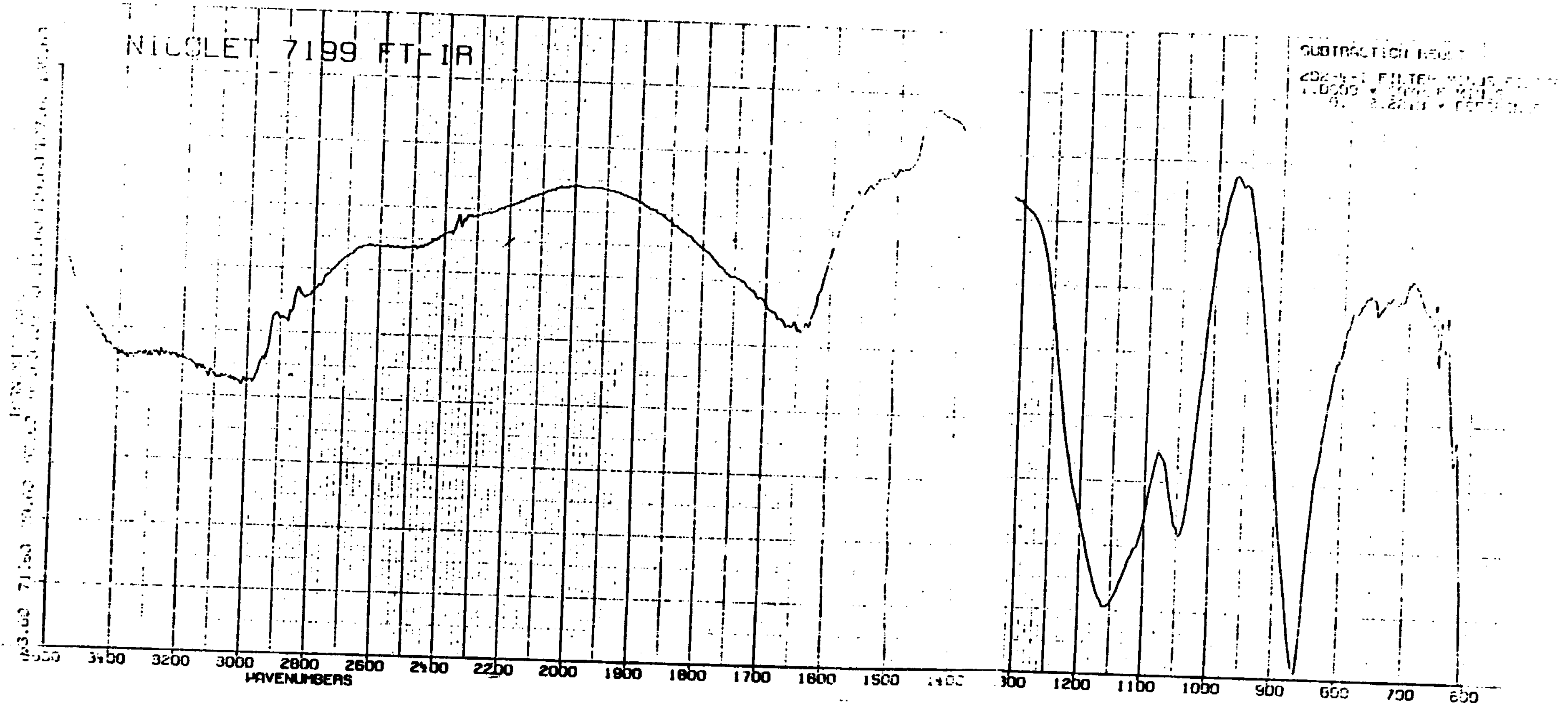

NICOLET 7199 FT-IR
TRW
SAMPLE FLYASH BLANK
CORRECTED FOR MINERAL OIL
TRANSMITTANCE
15.0
14.50
14.00
13.50
13.00
12.50
12.00
11.50
11.00
10.50
10.00
1400
1300
1200
1100
1000
900
800
700
600
500
400
WAVENUMBERS

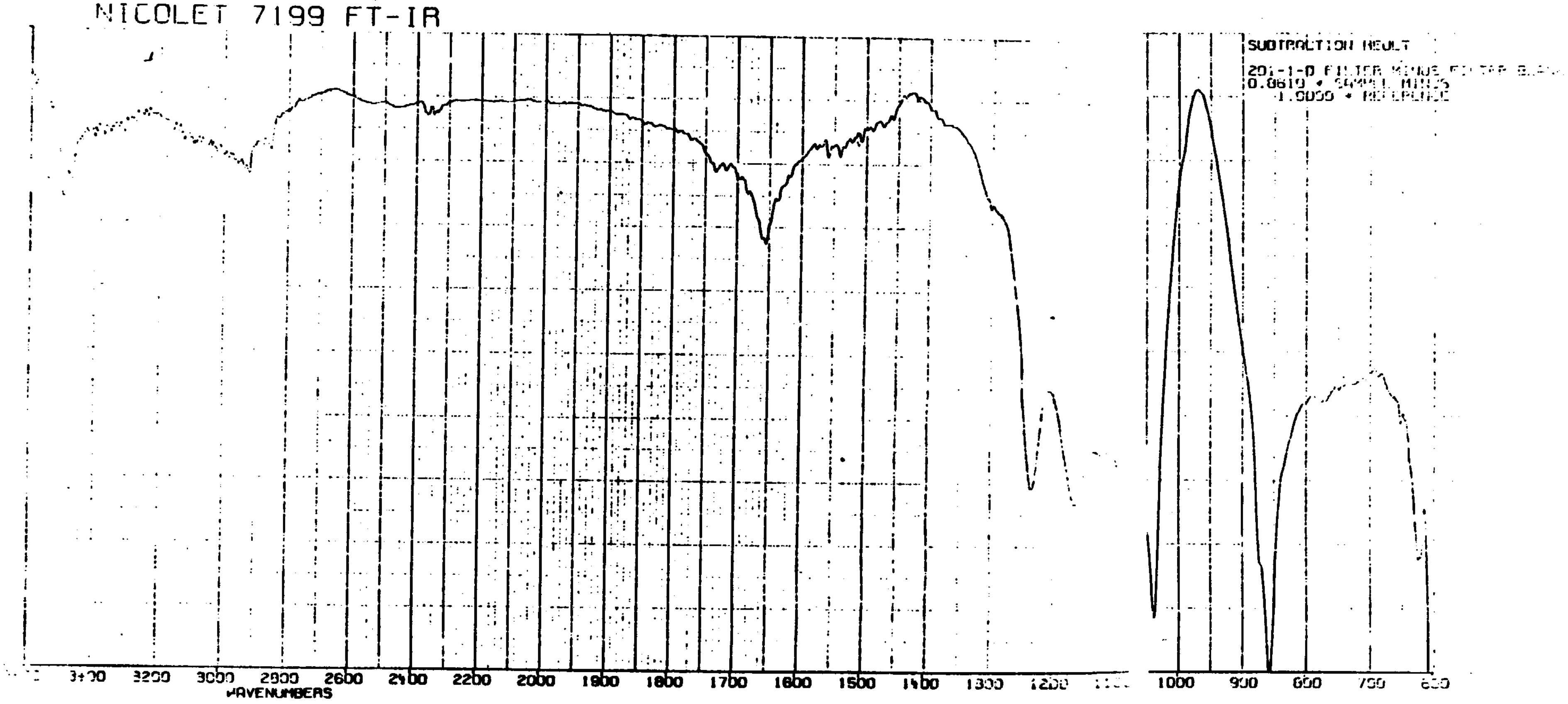
TAW-202-4-SCAB.CAKE - MIN.OIL FCA.04177




NICOLET 7199 FT-IR
TRIPLE SUBTRACTION RESULT
202-4-0 FILTER (MINUS BLANK)
MINUS 202-4-1 (MINUS BLANK)
86% CM-1 BAND NULLED
WAVENUMBERS
3400
3200
3000
2800
2600
2400
2200
2000
1800
1900
1700
1600
1500
1400
1200
1100
1000
900
800
700
600


NICOLET 7199 FT-IR
SUBTRACTION RESULT
202-4-D FILTER MINUS FILTER BLANK
0.8060 * SAMPLE MINUS
1.0000 * REFERENCE
35.00
41.00
47.00
3600
3400
3200
3000
2800
2600
2400
2200
2000
1900
1800
1700
1600
1500
1300
1200
1100
1000
900
800
700
600
WAVENUMBERS

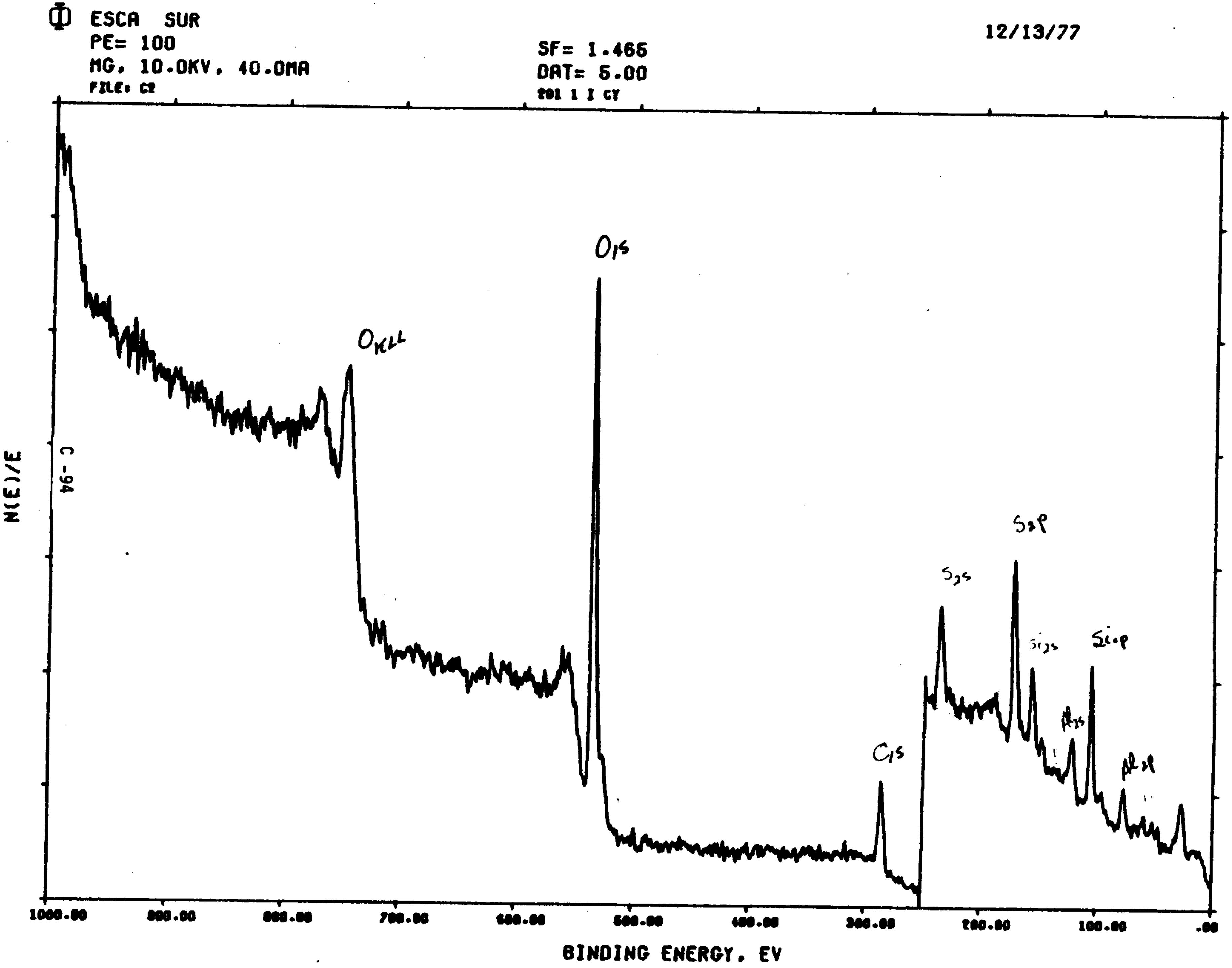

NICOLET 7199 FT-IR
SUBTRACTION RESULT
FILTER
1.0000
63.60
71.60
3500
3400
3200
3000
2800
2600
2400
2200
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
WAVENUMBERS

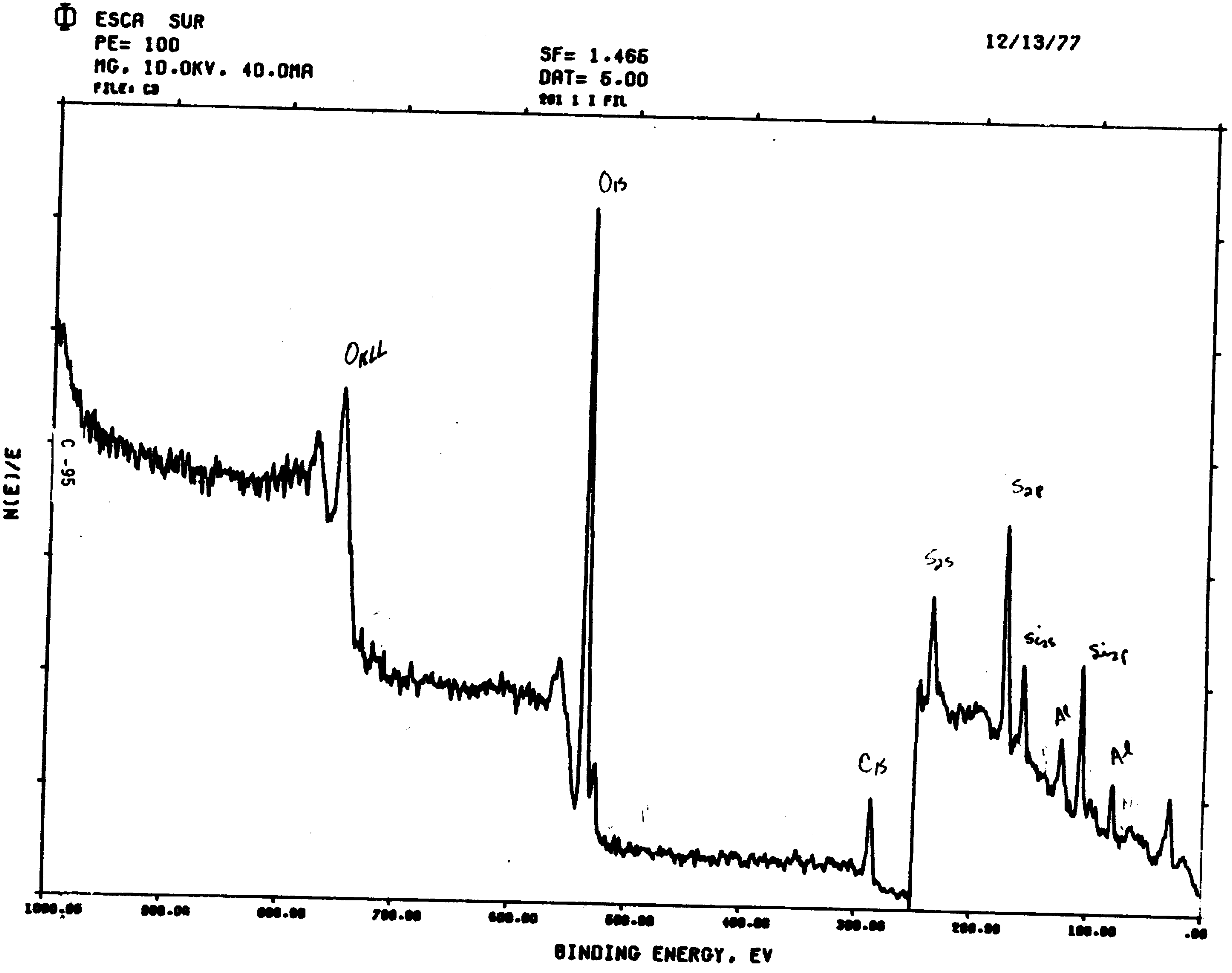

NICOLET 7199 FT-IR
SUBTRACTION RESULT
201-1-D FILTER MINUS FILTER BLANK
0.0619 * SAMPLE MINUS
1.0055 * REFERENCE
3400
3200
3000
2800
2600
2400
2200
2000
1800
1800
1700
1600
1500
1400
1300
1200
1000
900
800
750
650
WAVENUMBERS

APPENDIX C

ATTACHMENT D

ESCA SPECTRA

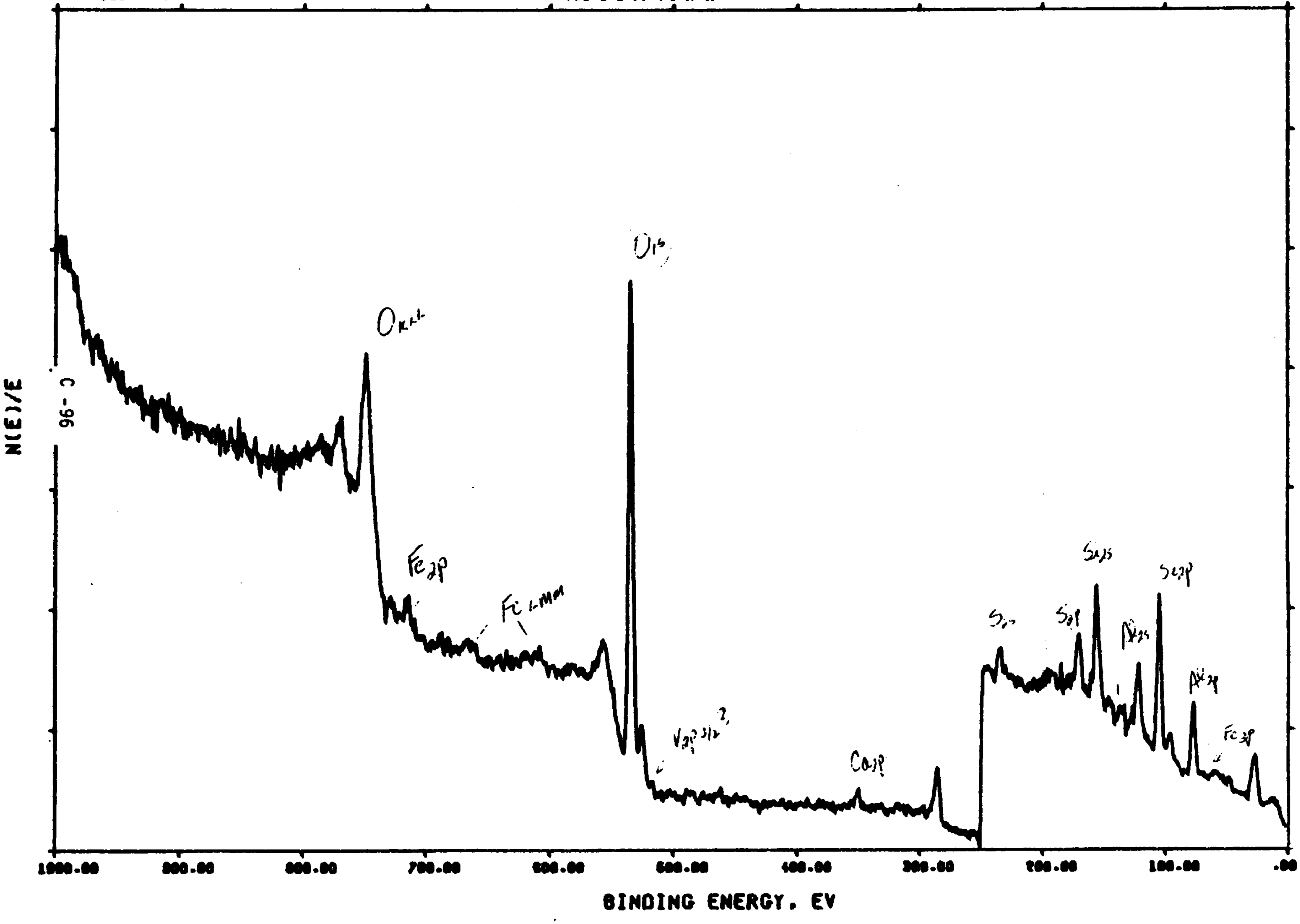

Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C2
SF= 1.465
DAT= 5.00
201 1 I CY
12/13/77
N(E)/E
C -94
O_{KLL}
O_{1s}
C_{1s}
S_{2s}
S_{2p}
Si_{2s}
Si_{2p}
Al_{2s}
Al_{2p}
1000.00
900.00
800.00
700.00
600.00
500.00
400.00
300.00
200.00
100.00
.00
BINDING ENERGY, EV

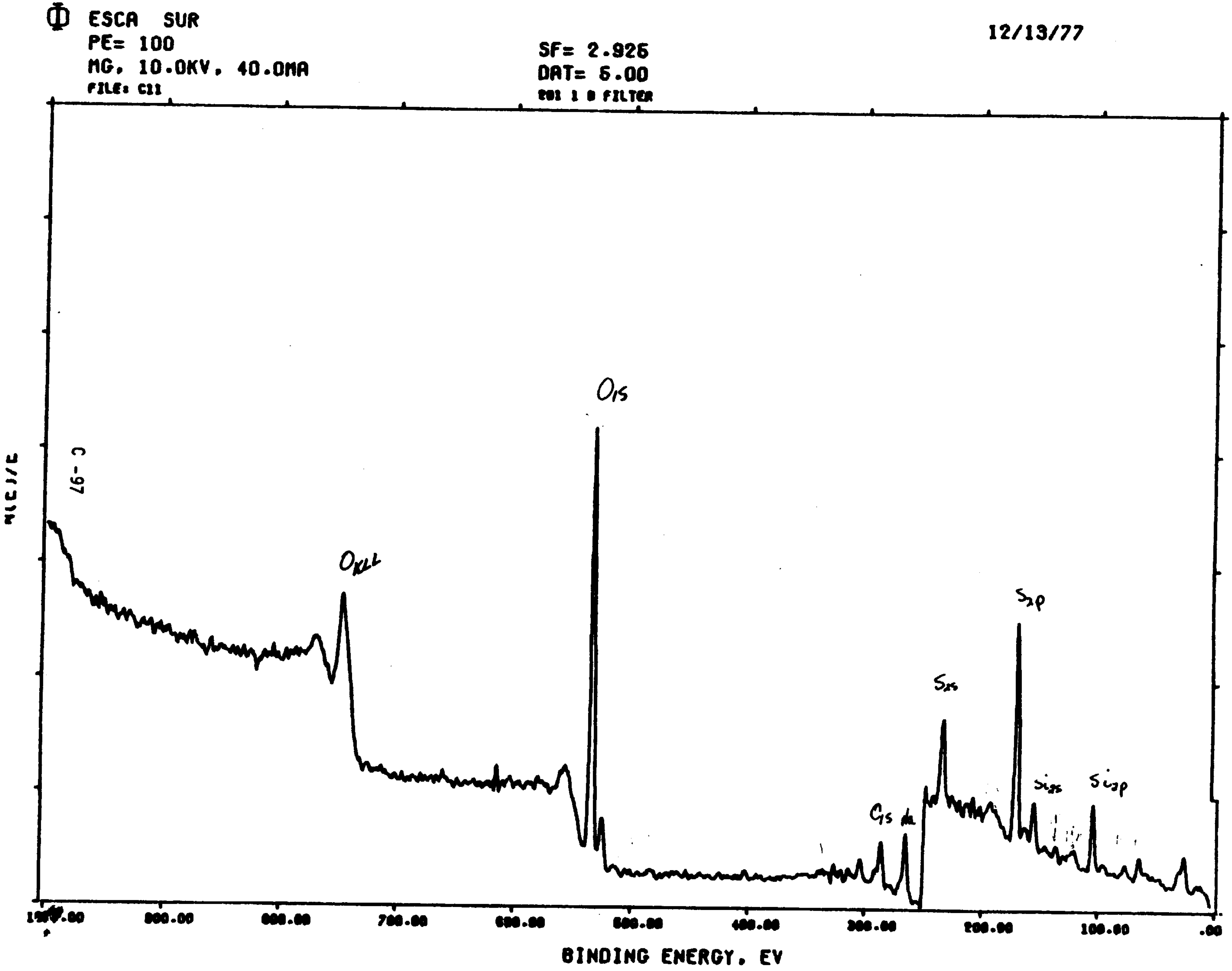

Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C9
SF= 1.466
DAT= 5.00
201 1 I FIL
12/13/77
C -95
N(E)/E
O1s
OKLL
C1s
S2s
S2p
Si2s
Si2p
Al
Al
1000.00
900.00
800.00
700.00
600.00
500.00
400.00
300.00
200.00
100.00
.00
BINDING ENERGY, EV

Φ ESCA SUR
PE= 100
MG. 10.0KV, 40.0MA
FILE: C34

SF= 1.960
DAT= 7.60
201 1 I FP 75 A 8P

12/14/77

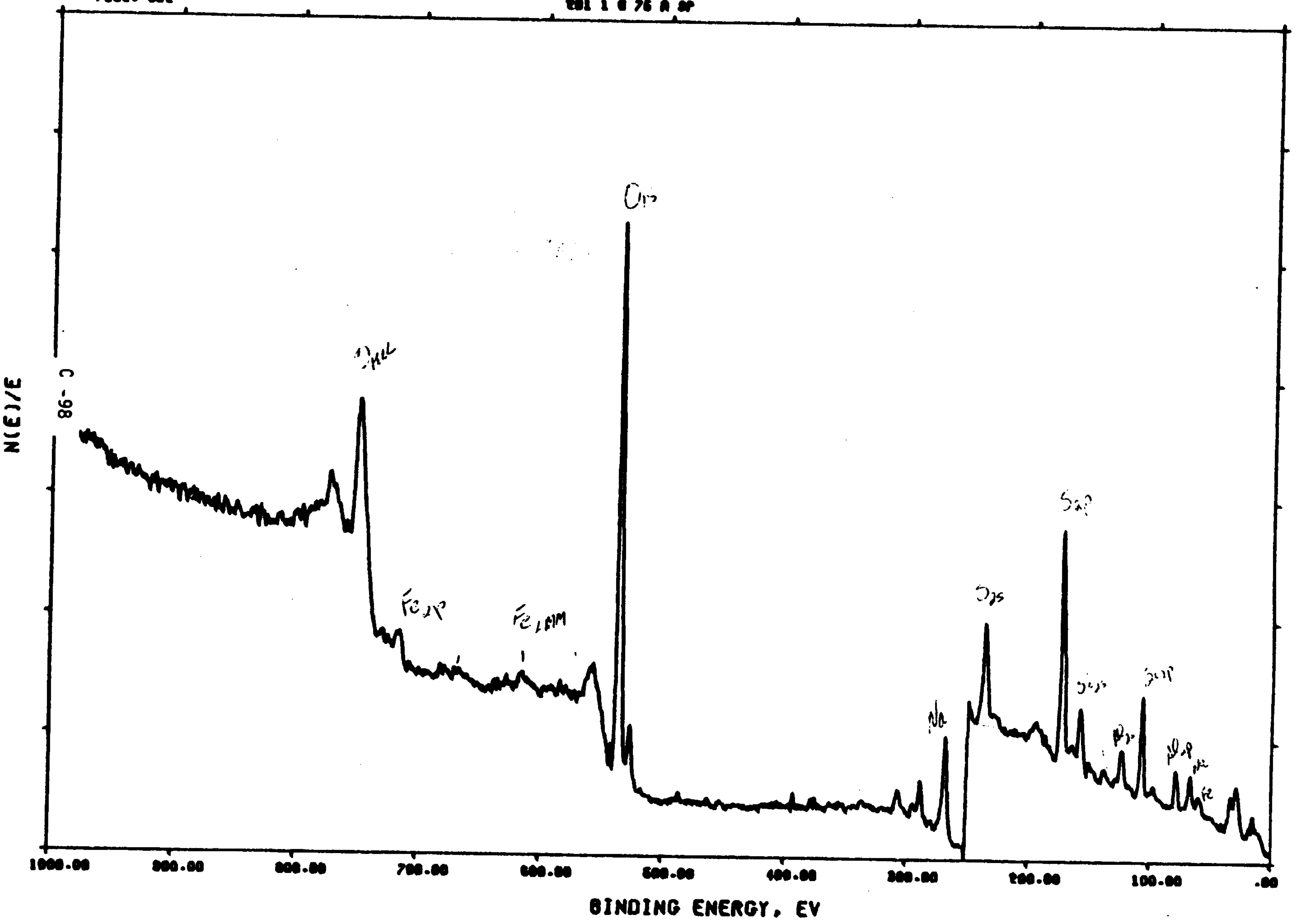


ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C11
SF= 2.926
DAT= 6.00
201 1 0 FILTER
12/13/77
C -97
N(E)/E
O_{KLL}
O_{1s}
C_{1s}
S_{2s}
S_{2p}
Si_{2s}
Si_{2p}
1000.00
900.00
800.00
700.00
600.00
500.00
400.00
300.00
200.00
100.00
.00
BINDING ENERGY, EV

Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C2R

SF= 2.925
DAT= 5.00
201 1 @ 76 A SP

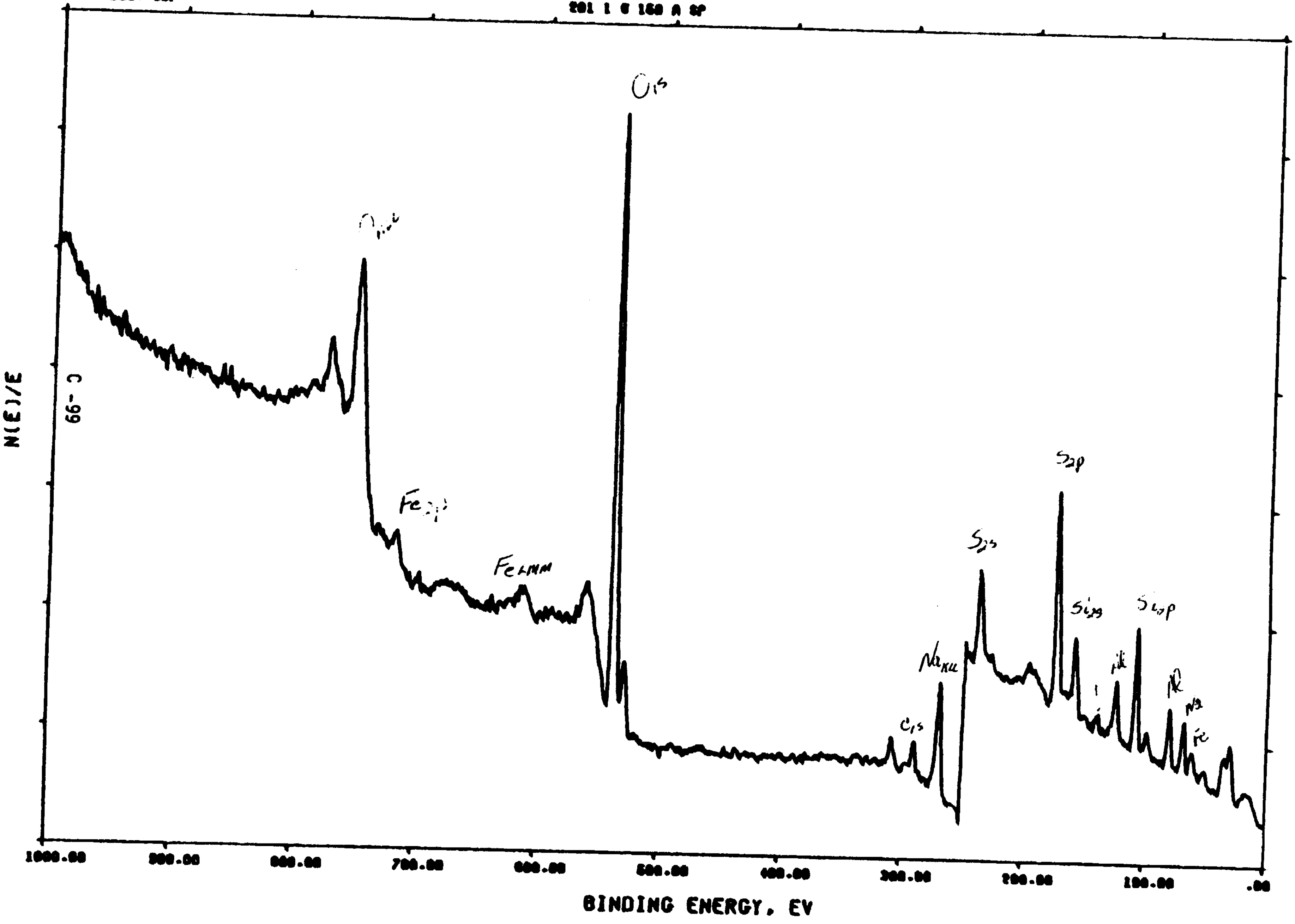
12/14/77



Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C37

SF= 2.926
DAT= 5.00
201 1 @ 160 A SP

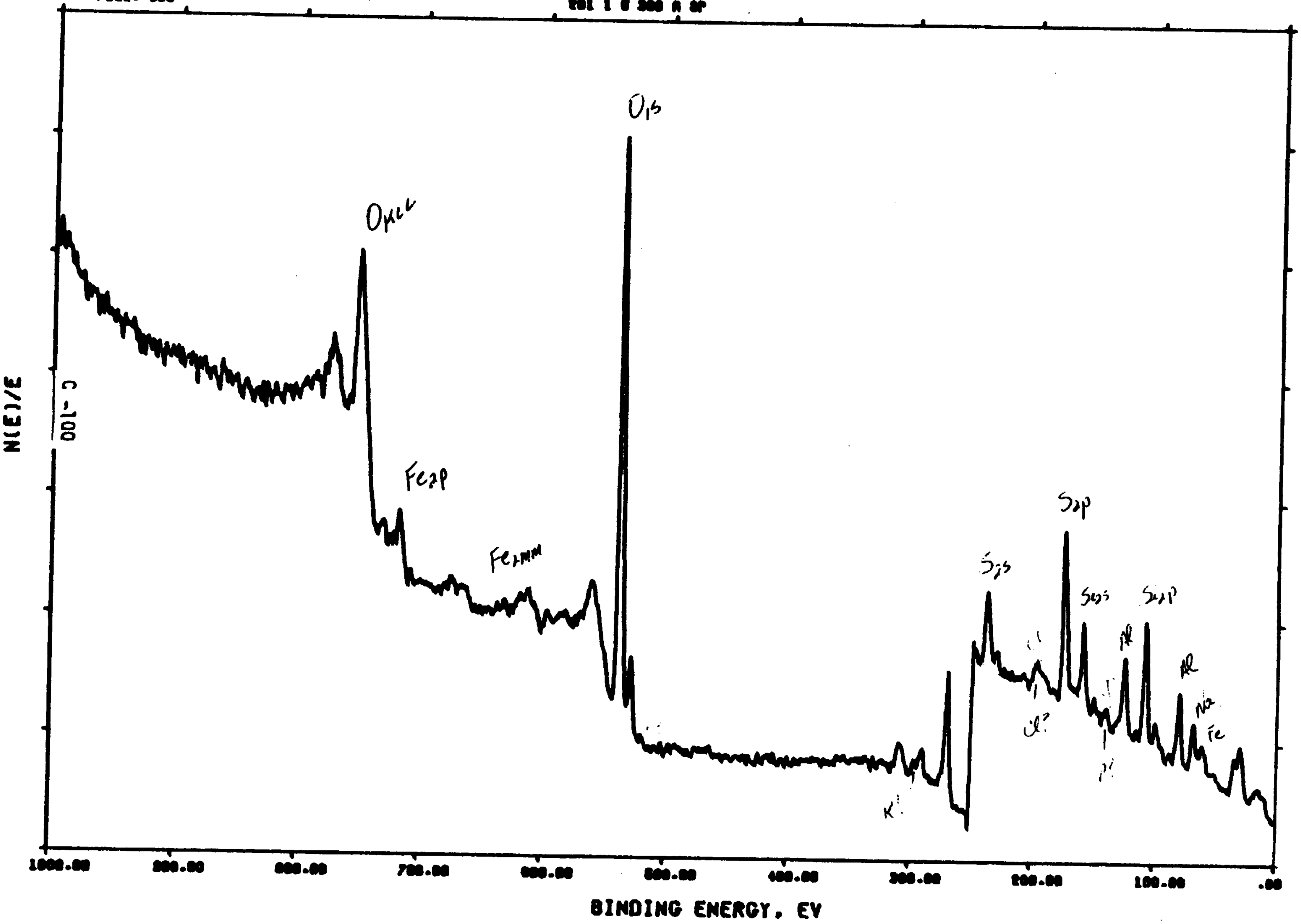
12/14/77



Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C00

SF= 2.926
DAT= 5.00
201 1 0 300 A SP

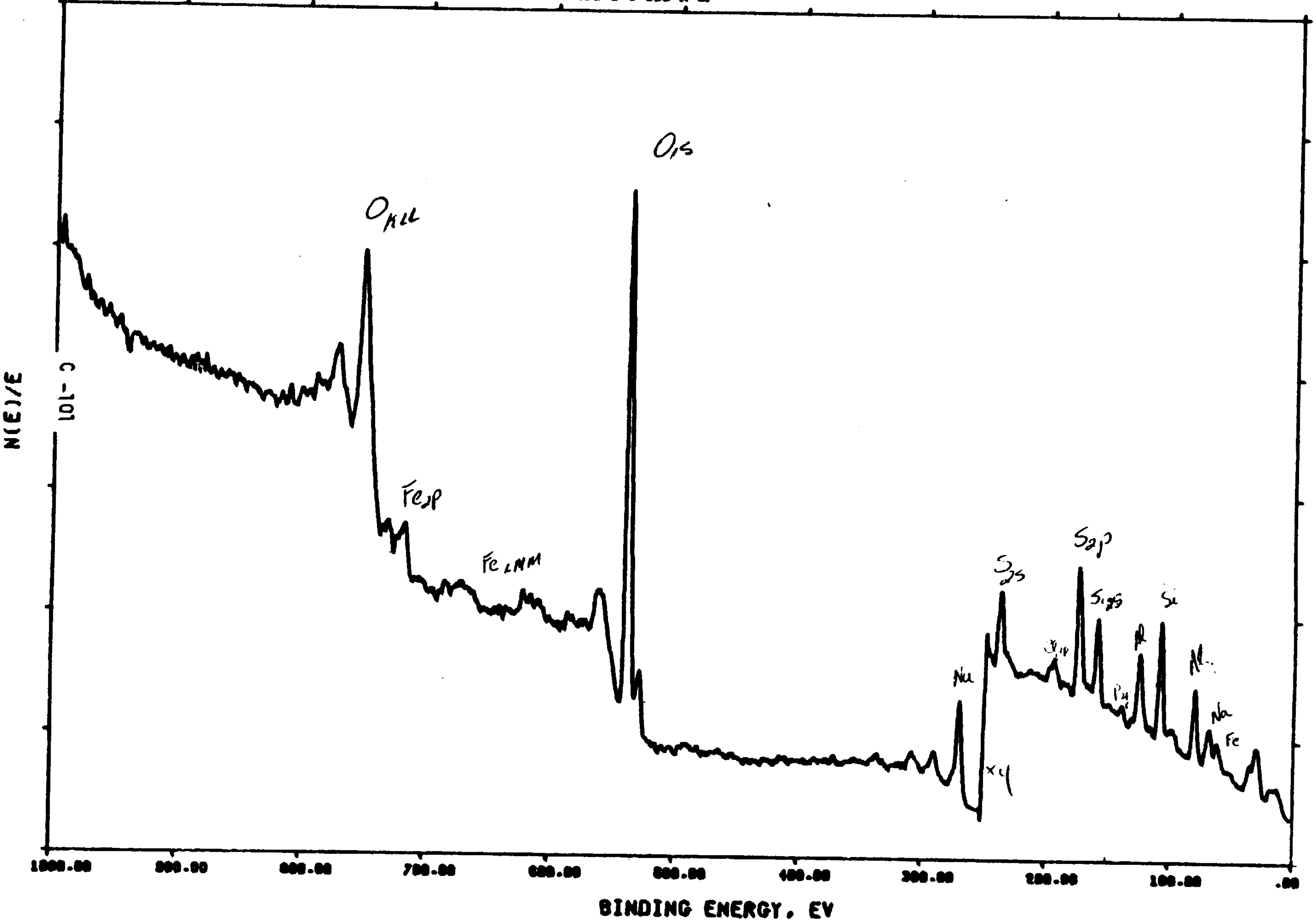
12/14/77



Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C30

SF= 2.925
DAT= 5.00
201 1 0 000 A 2P

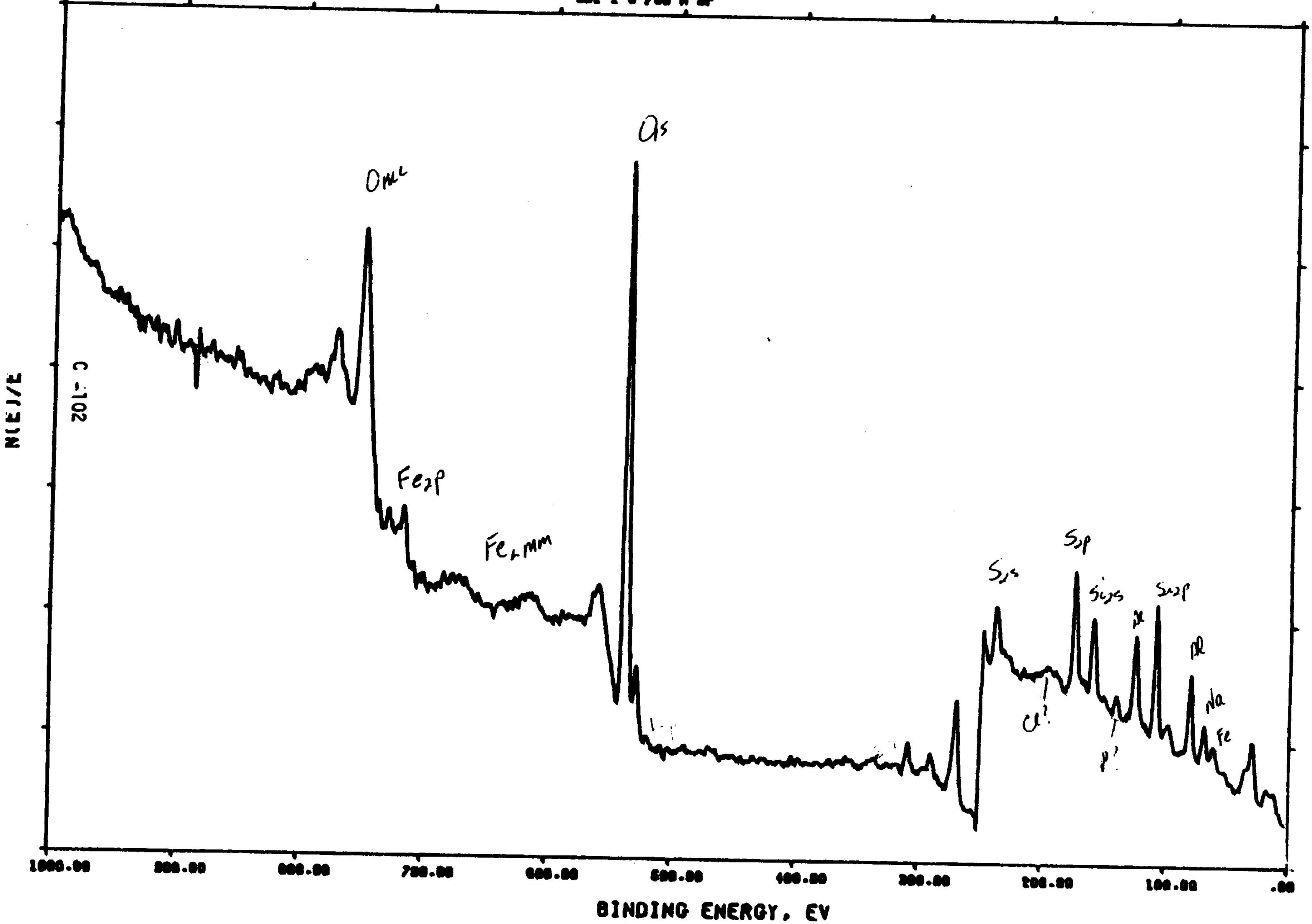
12/14/77



Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C40

SF= 2.925
DAT= 6.00
201 1 6 700 A SP

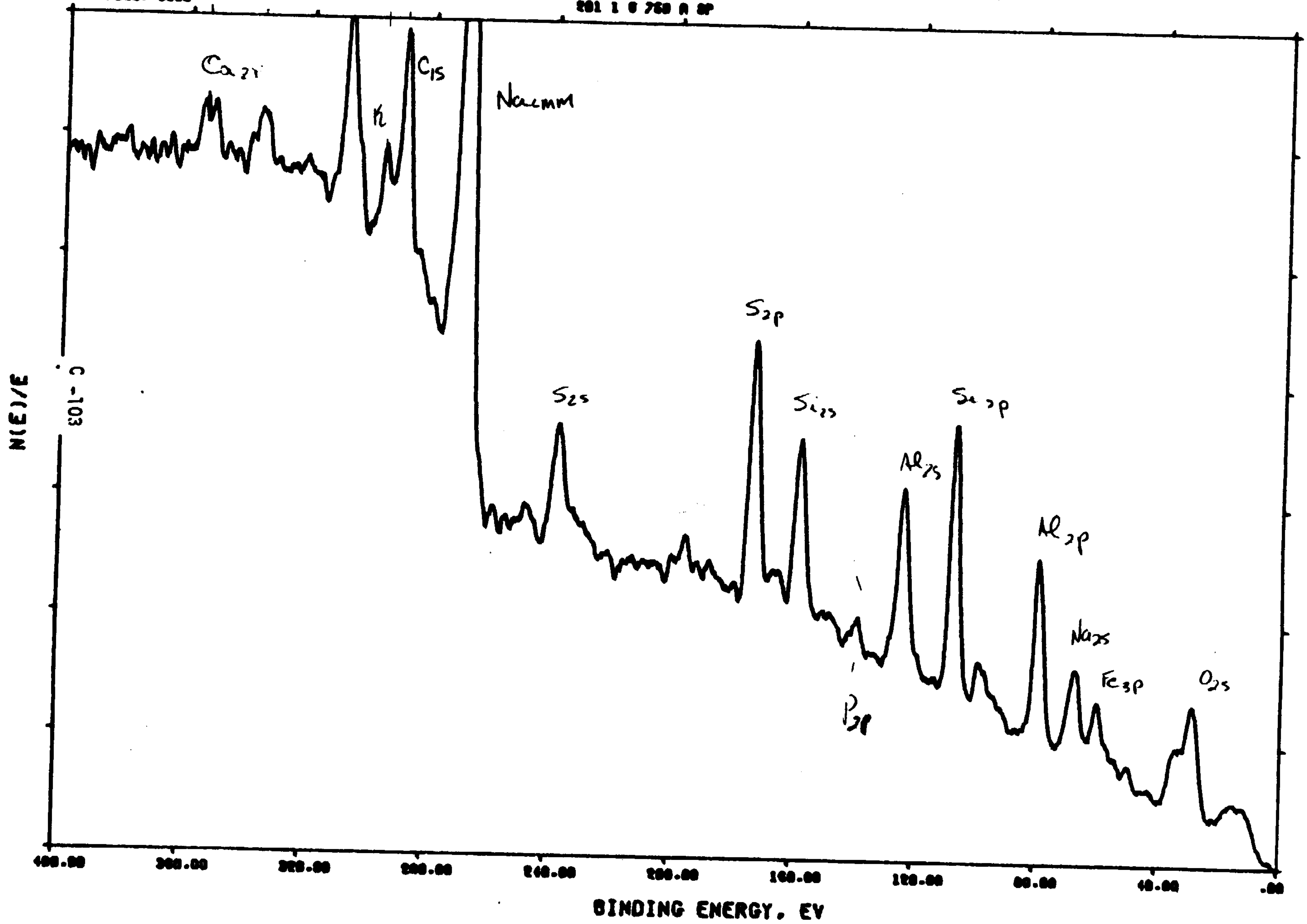
12/14/77



Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: [illegible]

SF= .365
DAT= 13.34
201 1 0 750 A SP

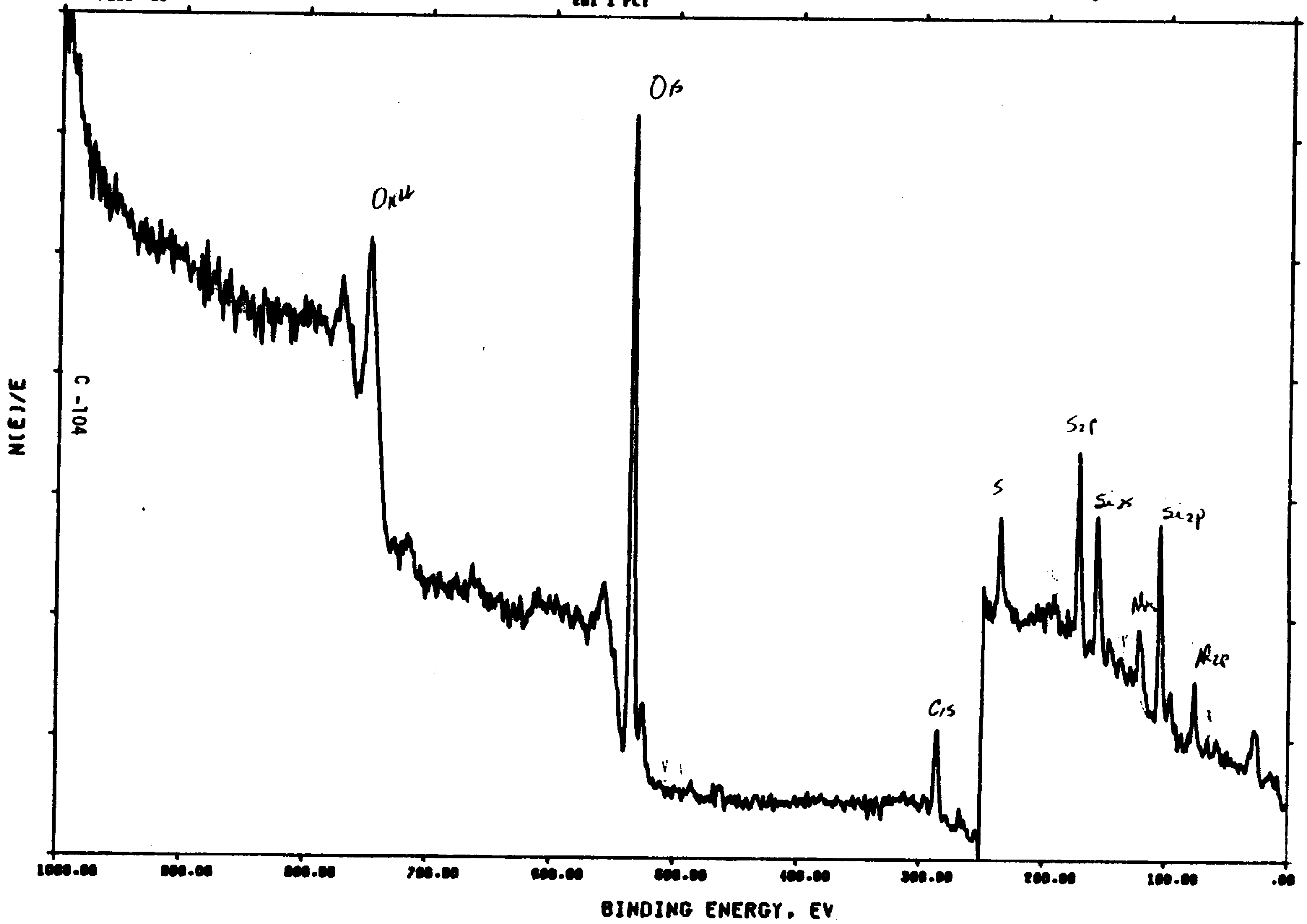
12/14/77



Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C6

SF= .976
DAT= 5.00
201 1 PLY

12/13/77

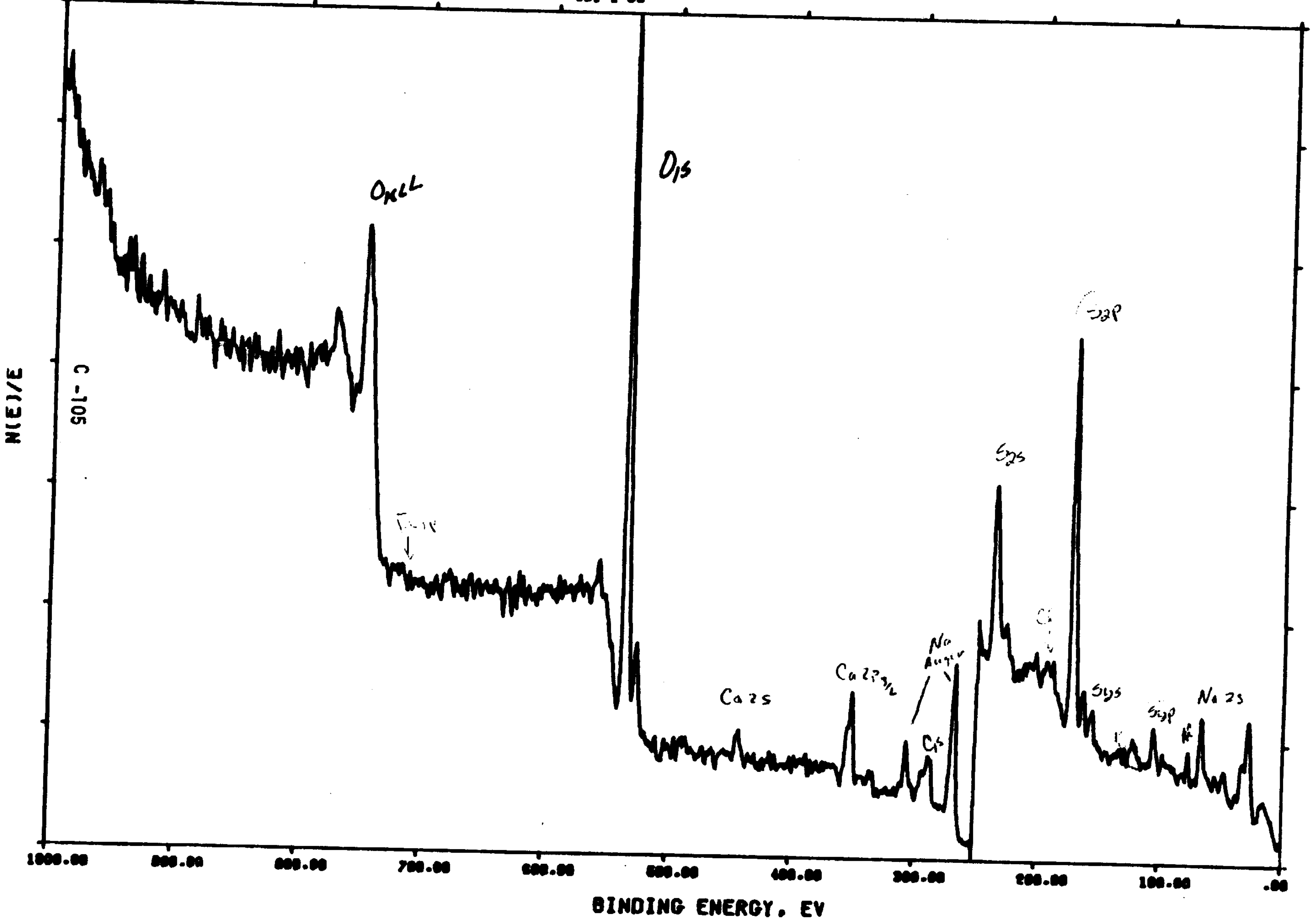


C -104

Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C4

SF= 1.466
DAT= 5.00
281 1 SC

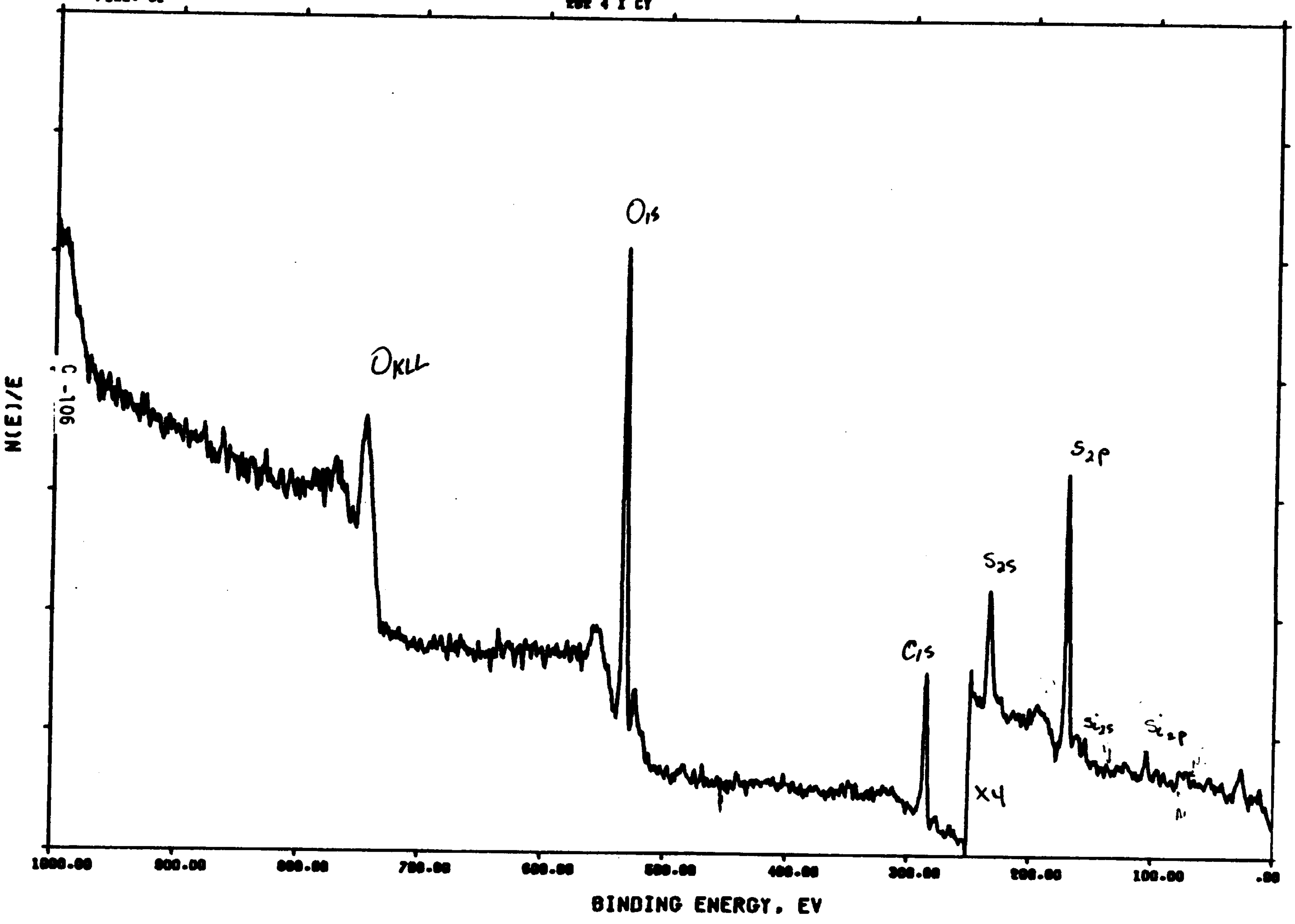
12/13/77

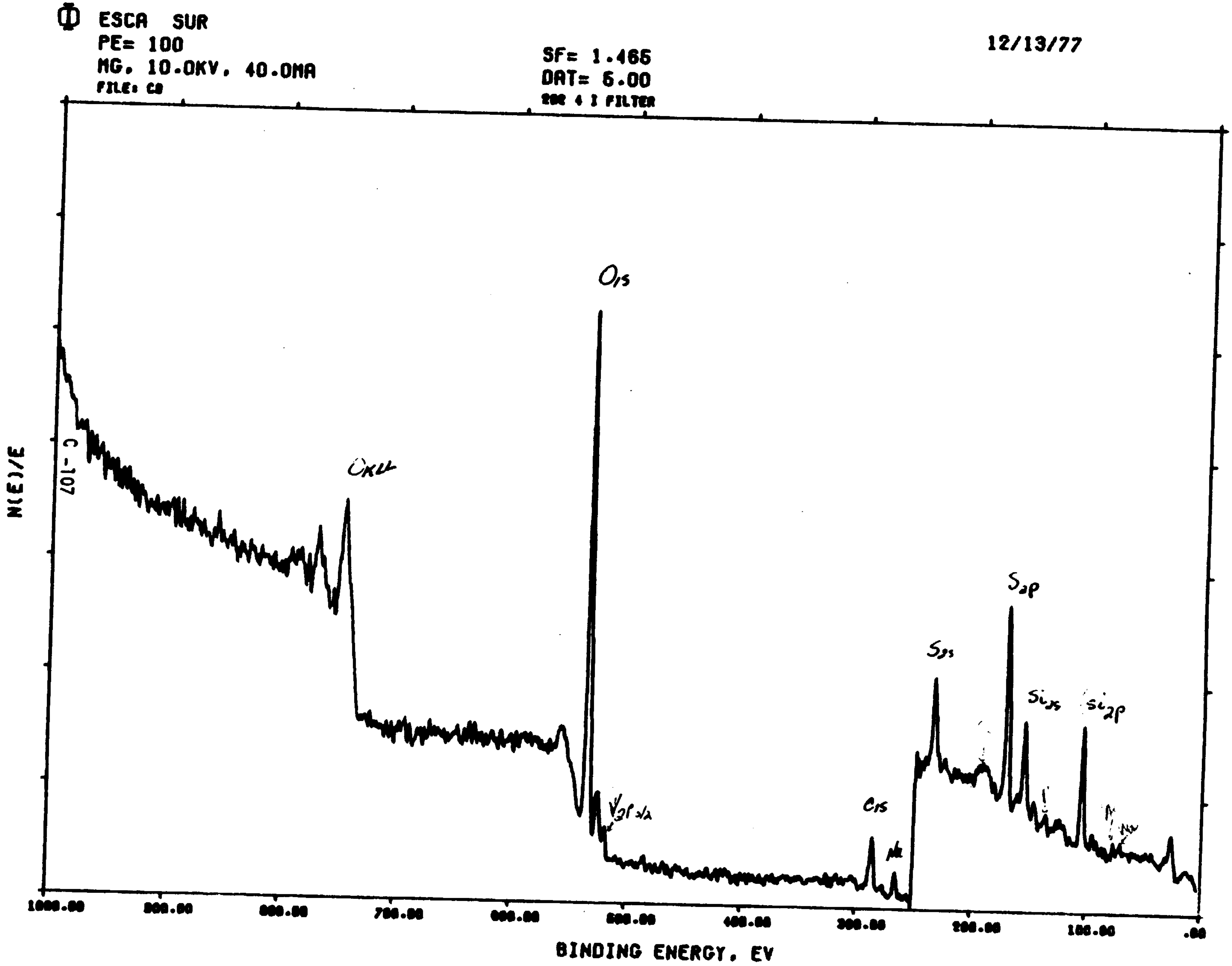


Φ ESCA SUR
PE= 100
MG. 10.0KV, 40.0MA
FILE: C1

SF= 1.466
DAT= 5.00
202 4 I CY

12/13/77





Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C0

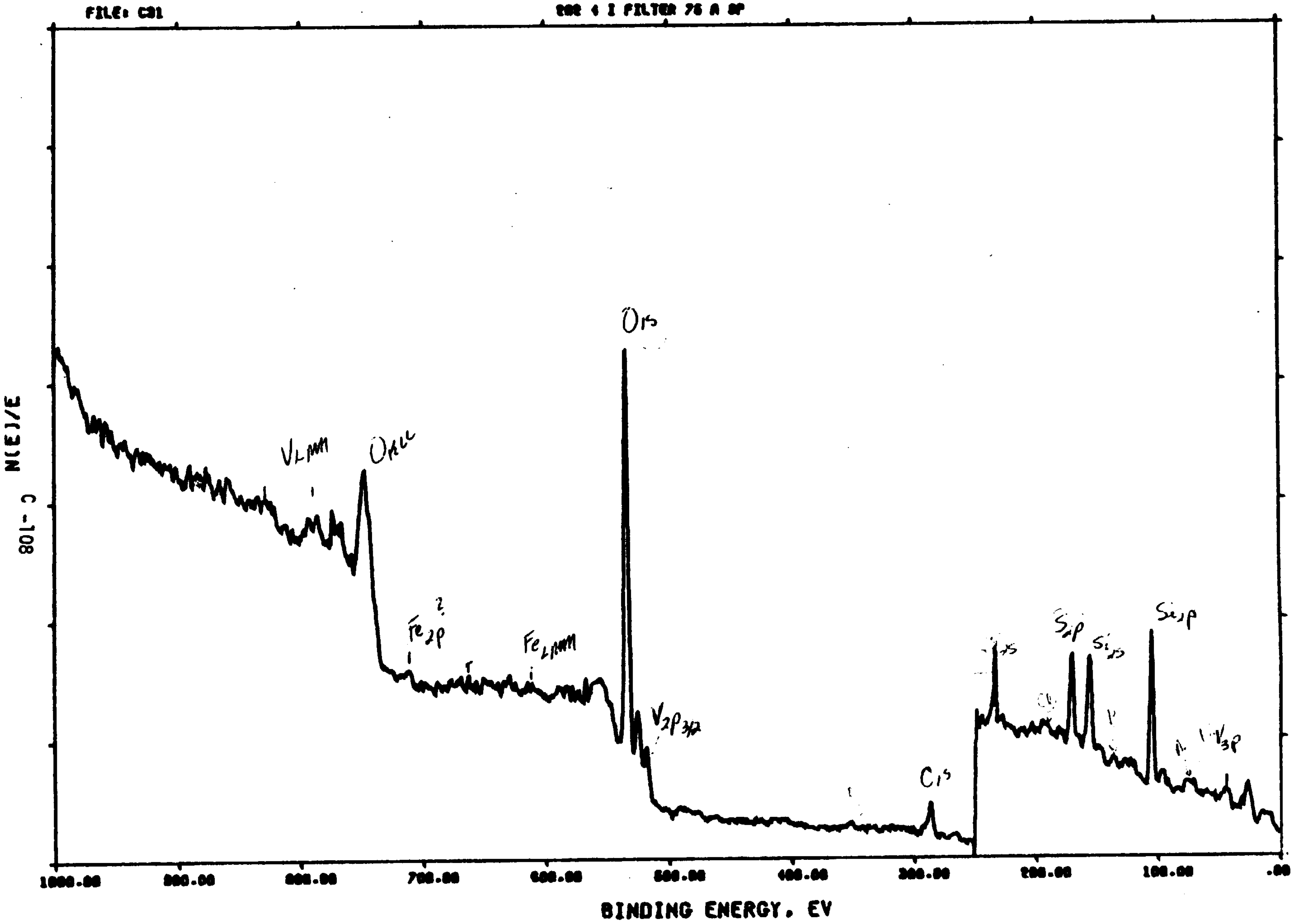
SF= 1.465
DAT= 6.00
200 4 I FILTER

12/13/77

Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C31

SF= 2.340
DAT= 6.25
[illegible] 4 I FILTER 75 A SP

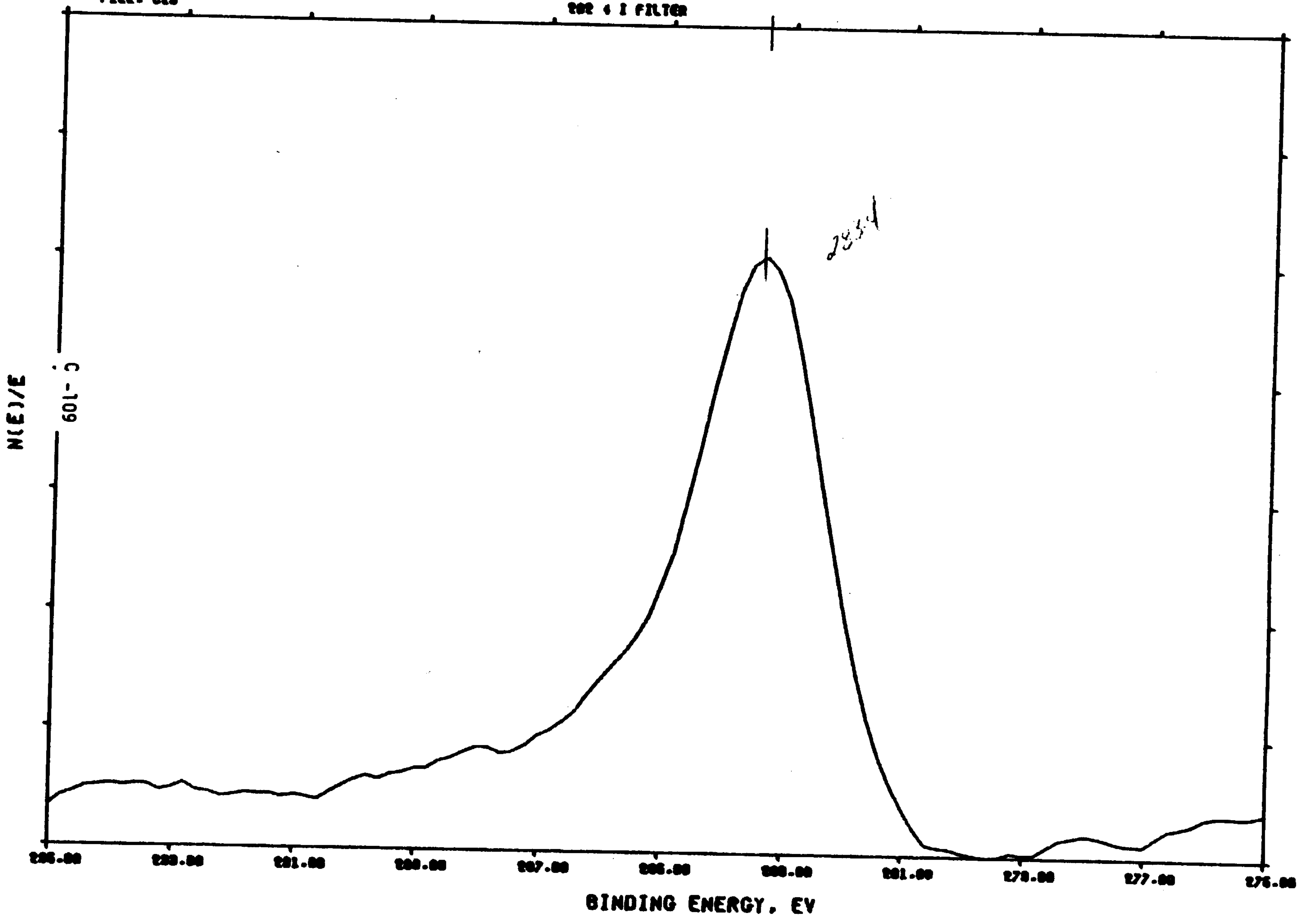
12/14/77

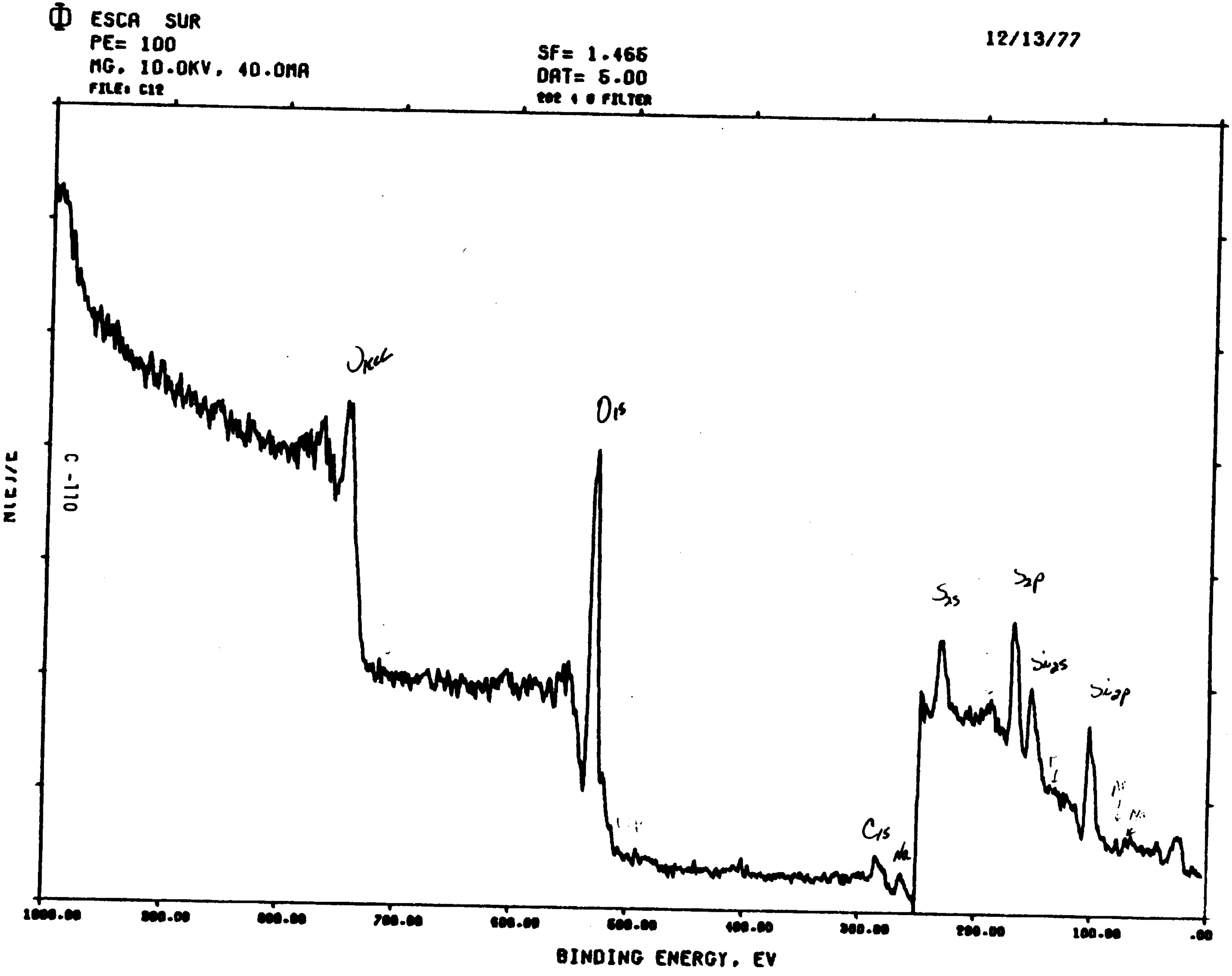


Φ ESCA MUL
PE= 50
MG, 10.0KV, 40.0MA
FILE: C20

EL= C 1
SF= .048
DAT= 10.10
200 4 I FILTER

12/13/77

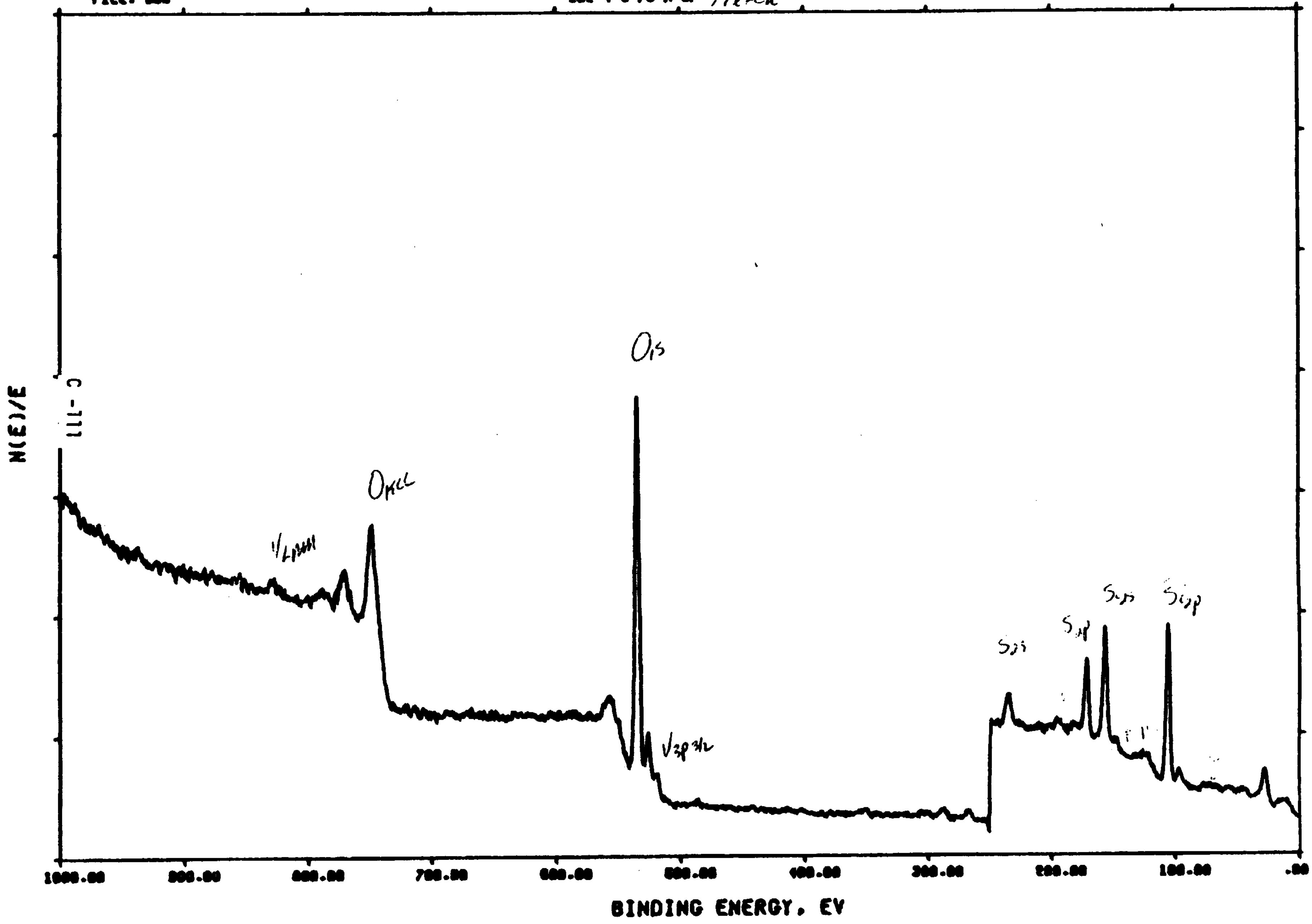



ESCA SUR
PE= 100
MG. 10.0KV, 40.0MA
FILE: C12
SF= 1.466
DAT= 5.00
202 4 0 FILTER
12/13/77
N(E)/E
C -110
O_{KLL}
O_{1s}
C_{1s}
Na
S_{2s}
S_{2p}
Si_{2s}
Si_{2p}
Na
1000.00
900.00
800.00
700.00
600.00
500.00
400.00
300.00
200.00
100.00
.00
BINDING ENERGY, EV

Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: [illegible]

SF= 2.926
DAT= 10.00
[illegible] 4 6 76 A [illegible] Filtch

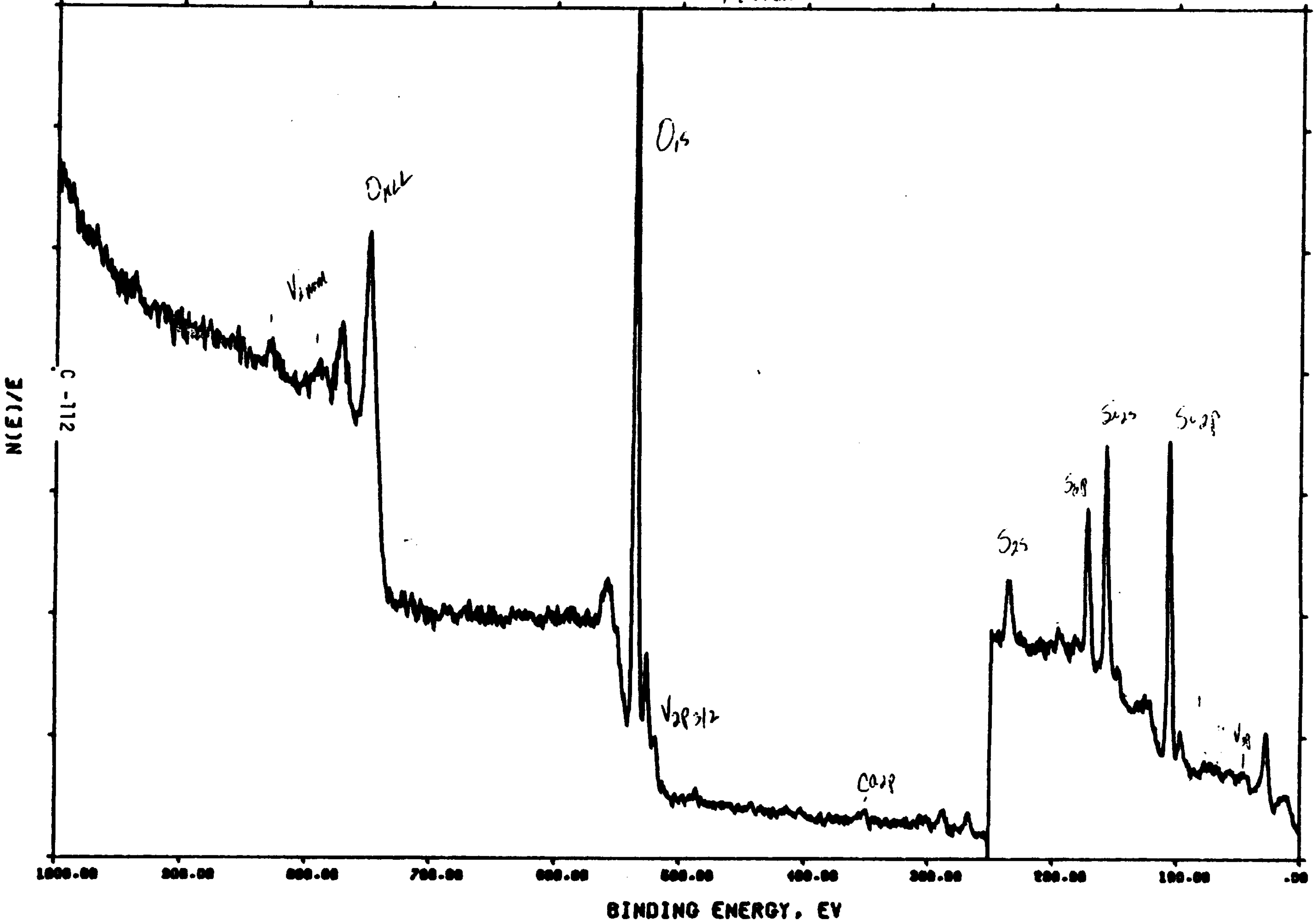
12/14/77



Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C33

SF= 1.462
DAT= 10.00
[illegible] 1 0 76 A SP Fi l/eh

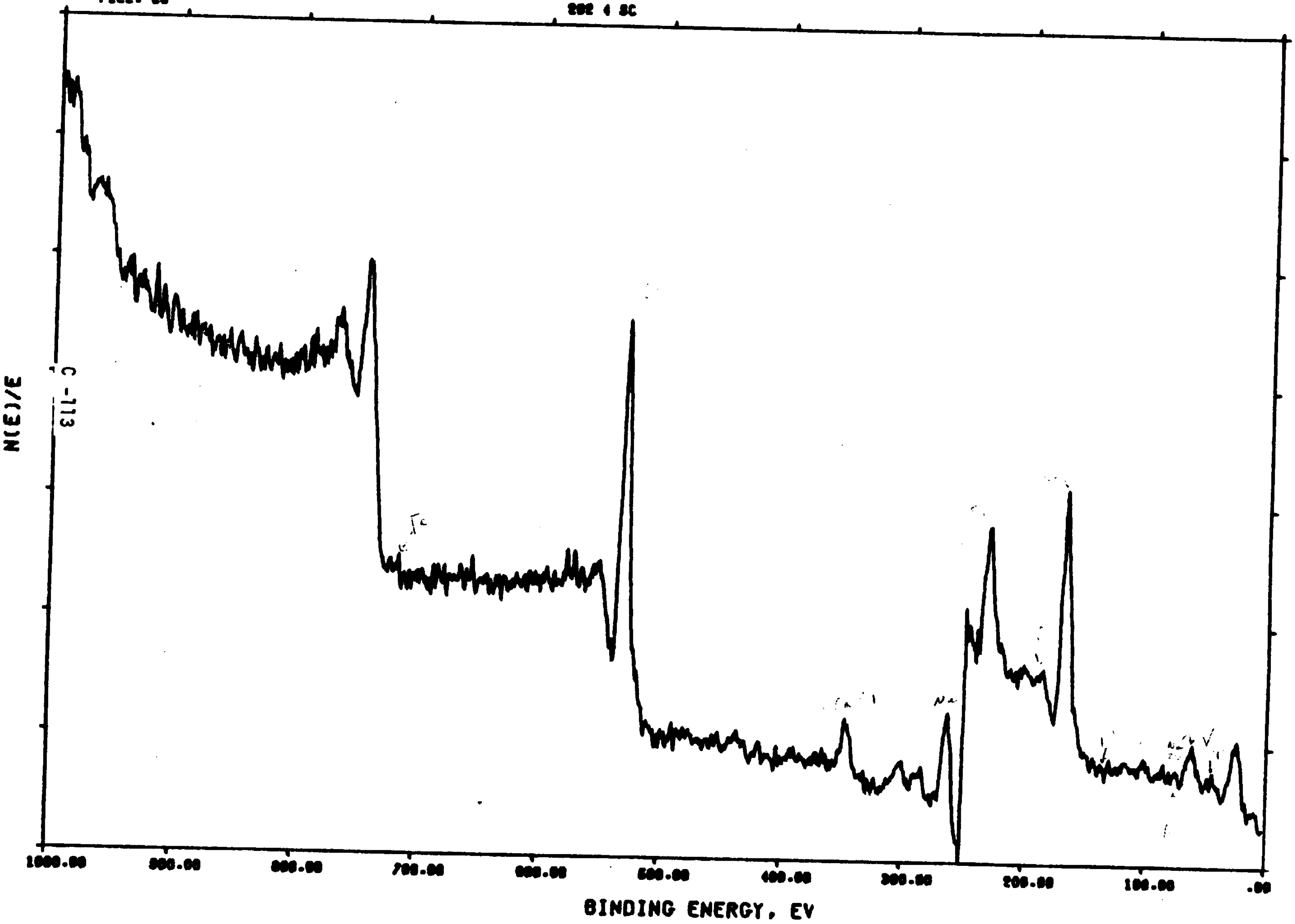
12/14/77



Φ ESCA SUR
PE= 100
MG. 10.0KV, 40.0MA
FILE: C6

SF= 1.465
DAT= 6.00
202 4 SC

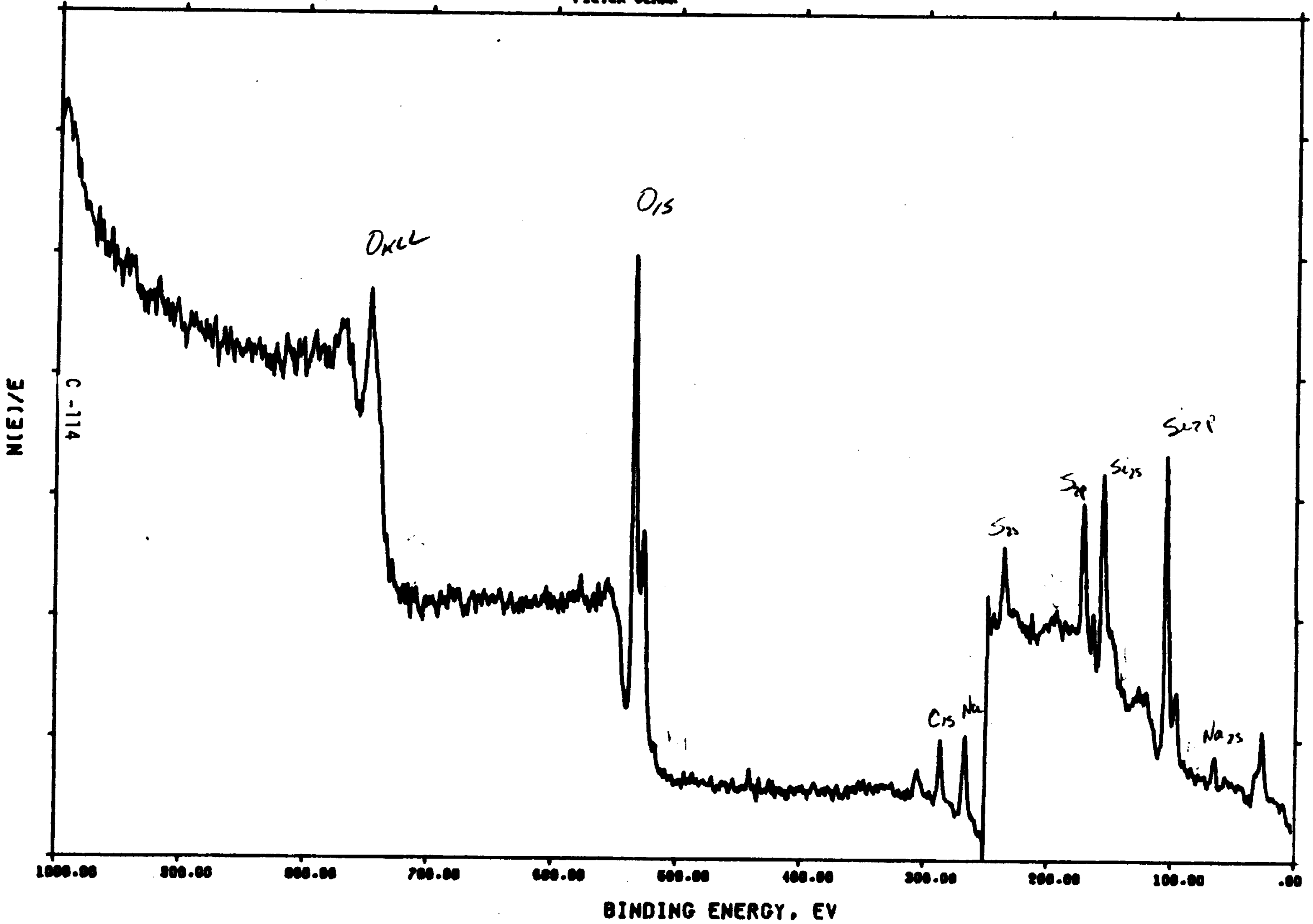
12/13/77



Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C9

SF= 1.465
DAT= 5.00
FILTER BLANK

12/13/77

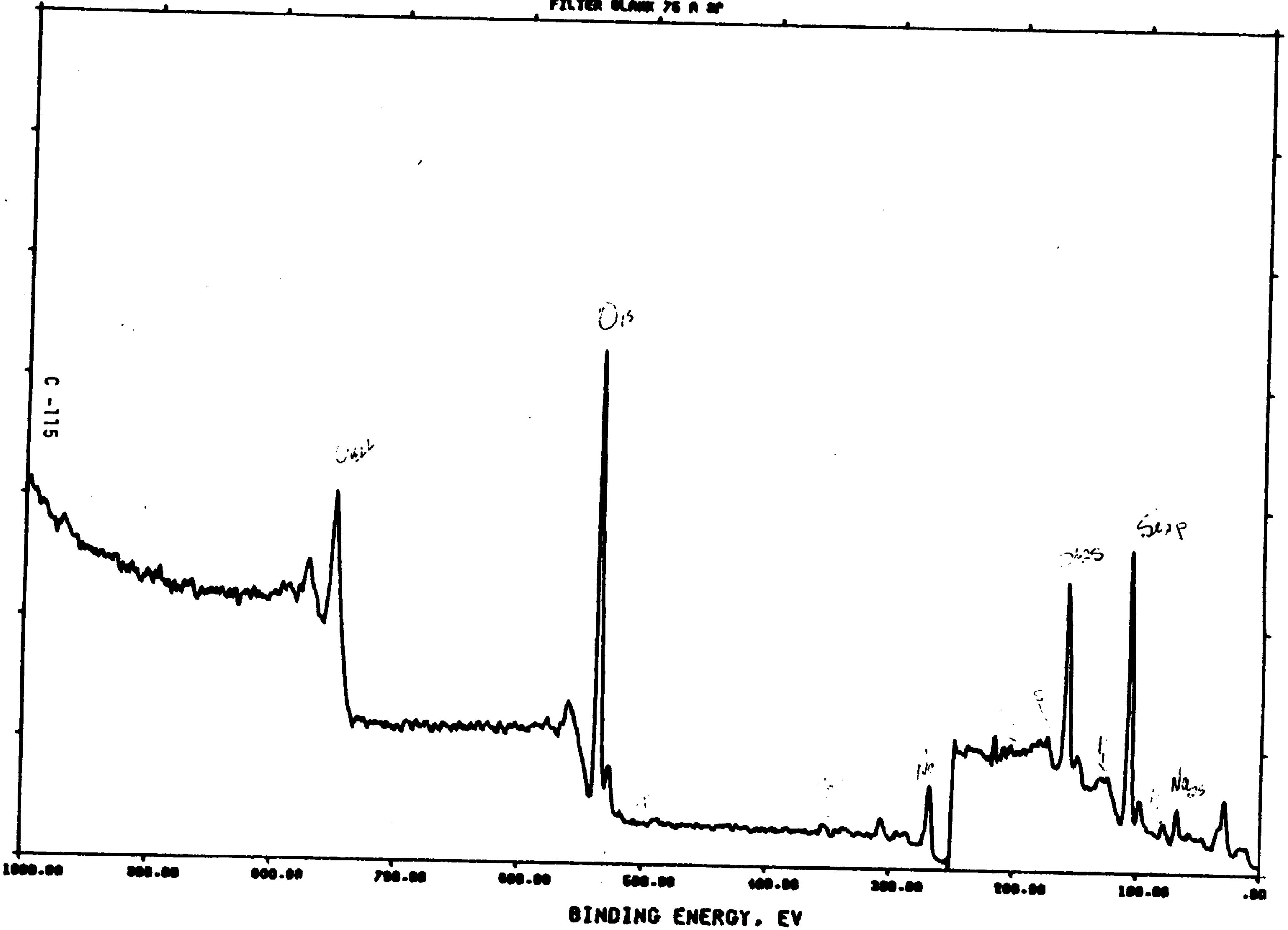


C -114

Φ ESCA SUR
PE= 100
MG, 10.0KV, 40.0MA
FILE: C90

SF= 3.900
DAT= 3.76
FILTER BLANK 76 A SP

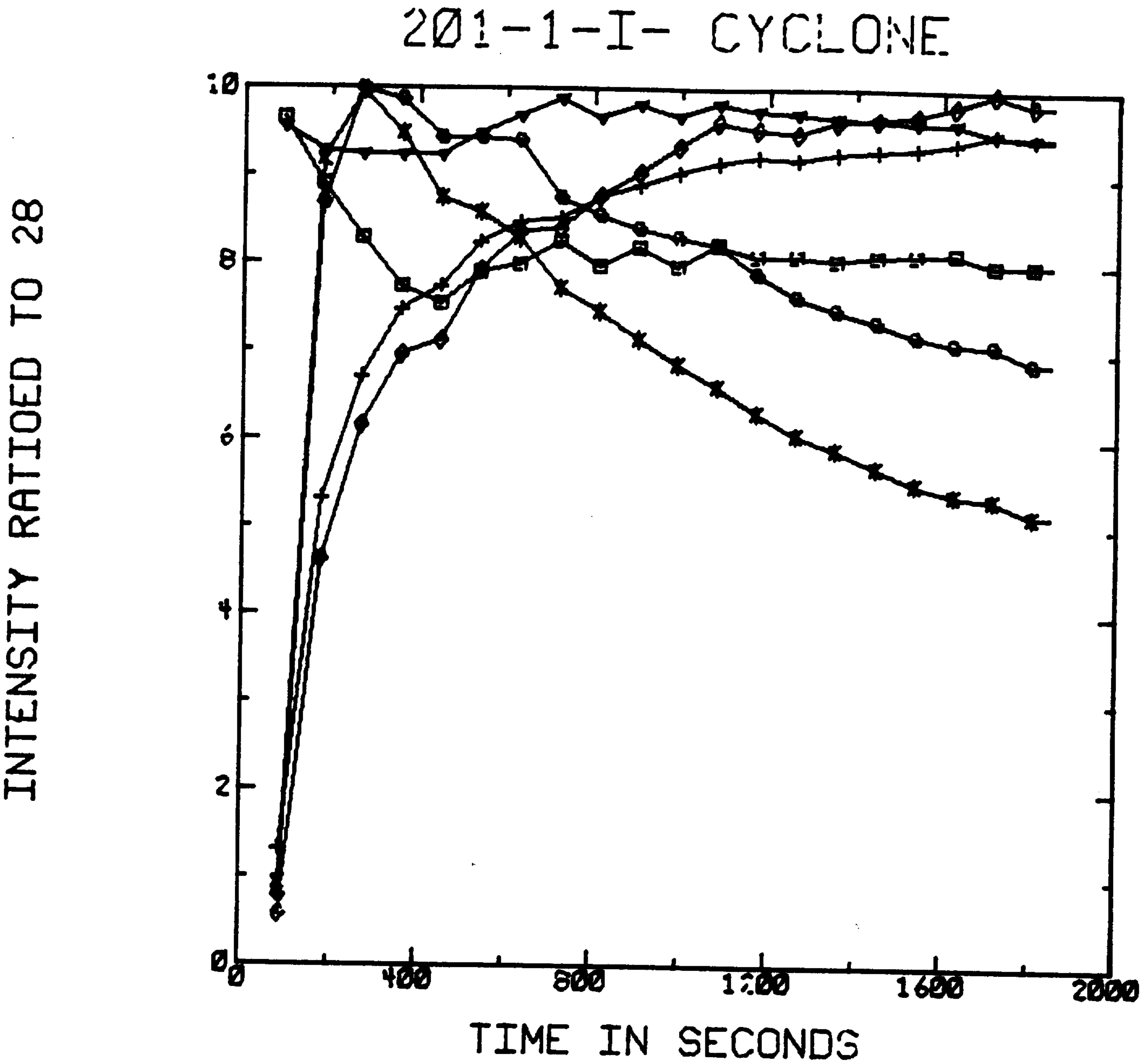
12/14/77



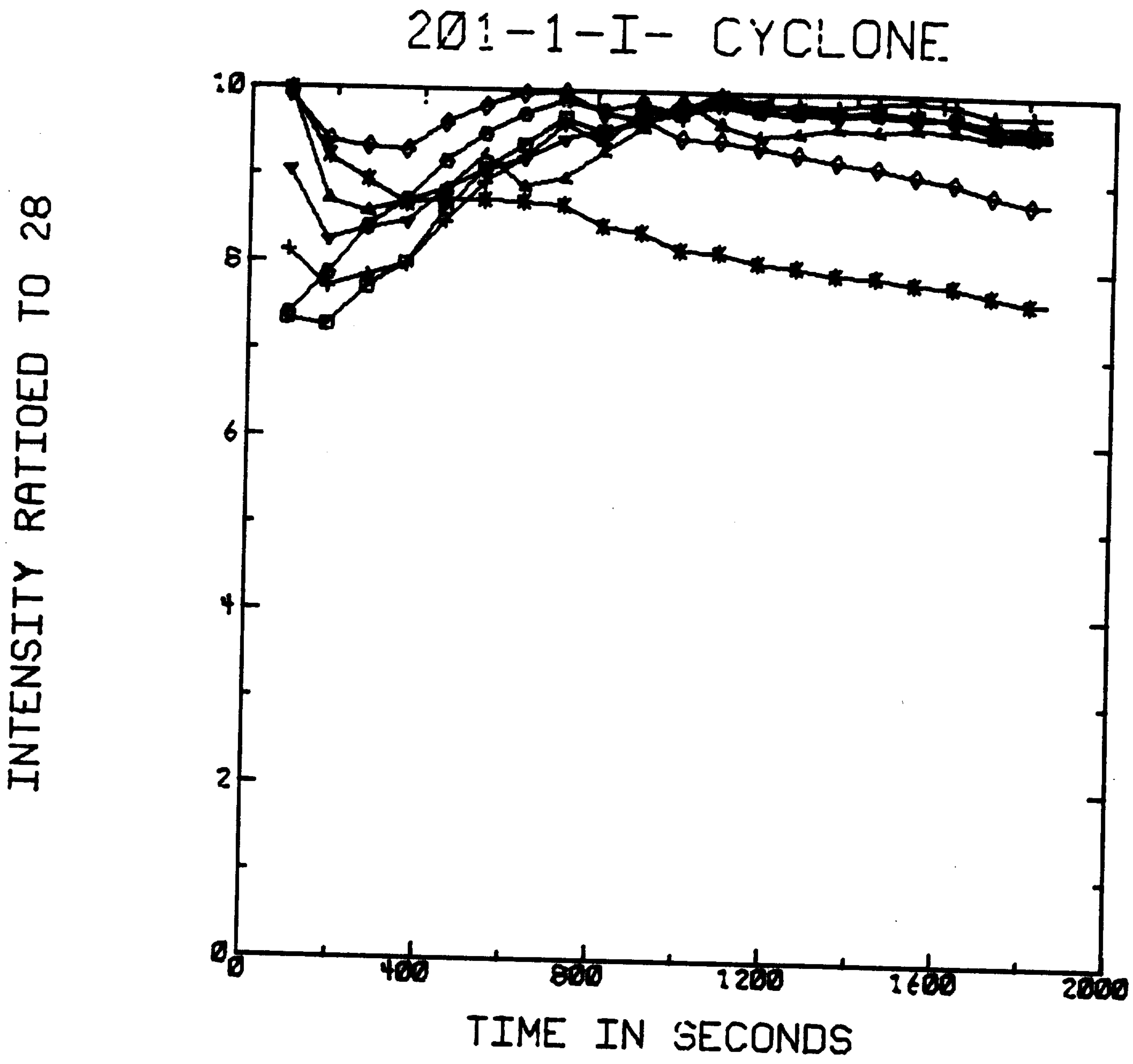
APPENDIX C

ATTACHMENT E

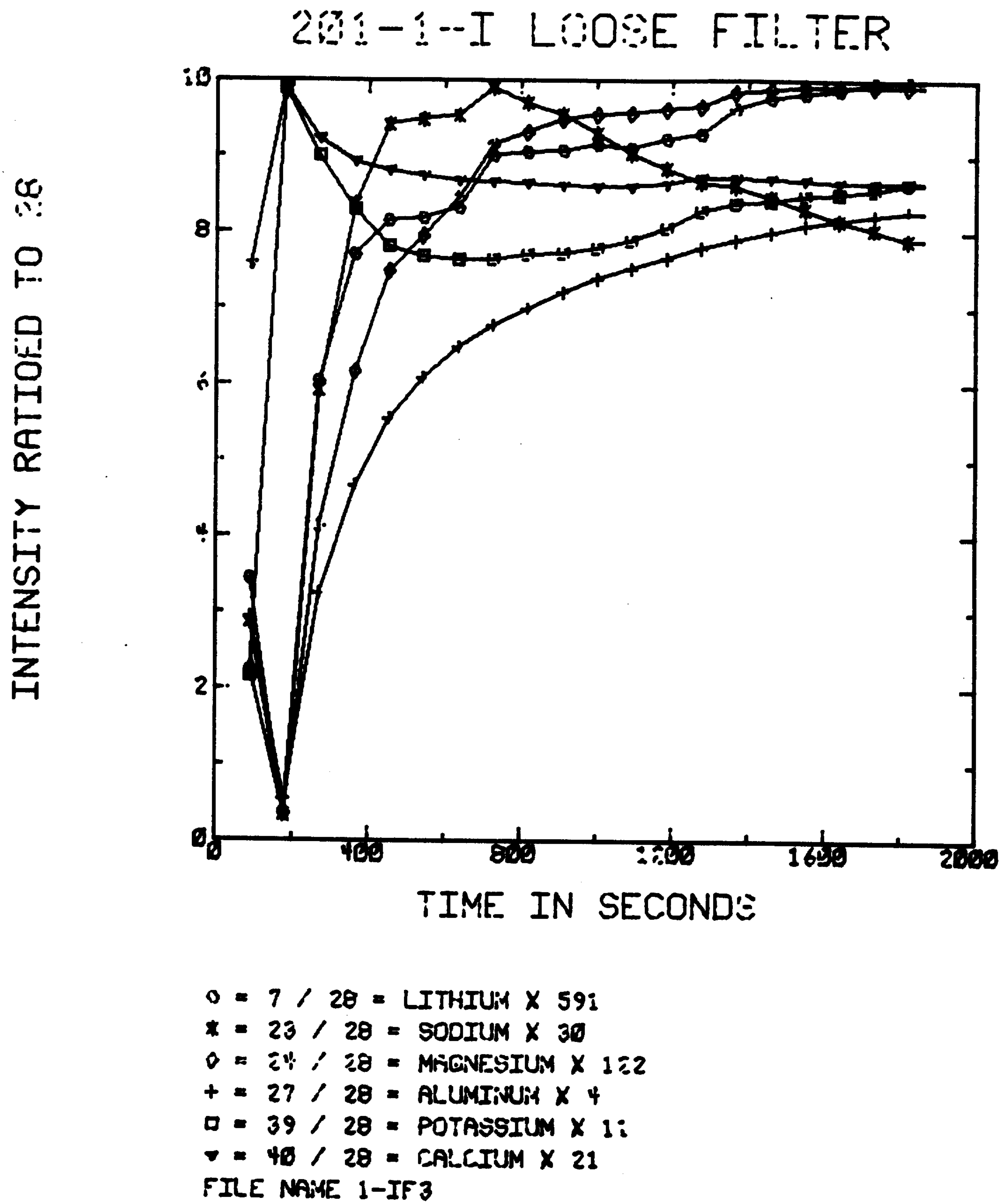
SIMS DATA DEPTH PROFILE PLOTS



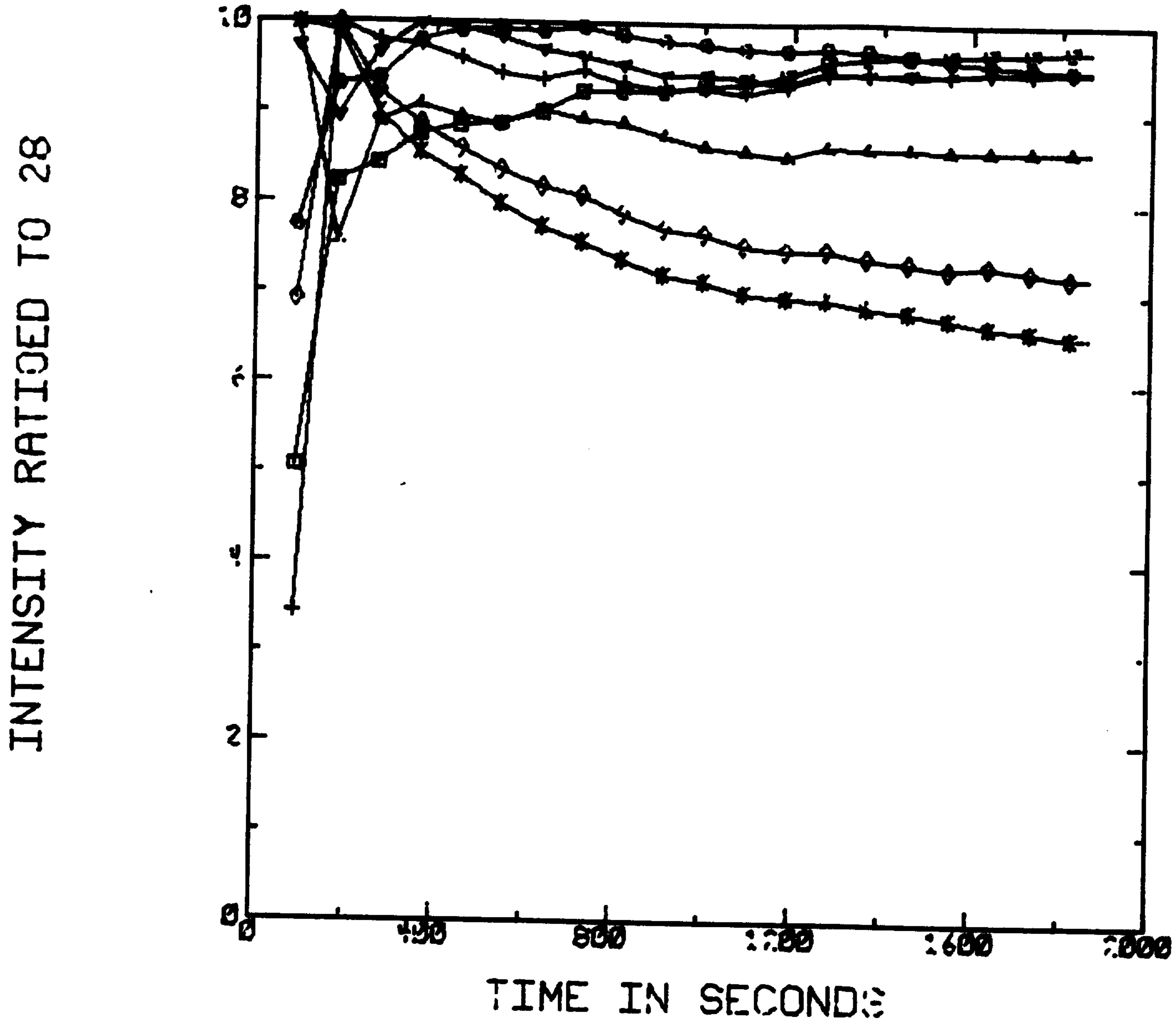
○ = 7 / 28 = LITHIUM X 468
✱ = 23 / 28 = SODIUM X 26
◇ = 24 / 28 = MAGNESIUM X 106
+ = 27 / 28 = ALUMINUM X 5
□ = 39 / 28 = POTASSIUM X 12
▽ = 40 / 28 = CALCIUM X 29
FILE NAME 1-IC2



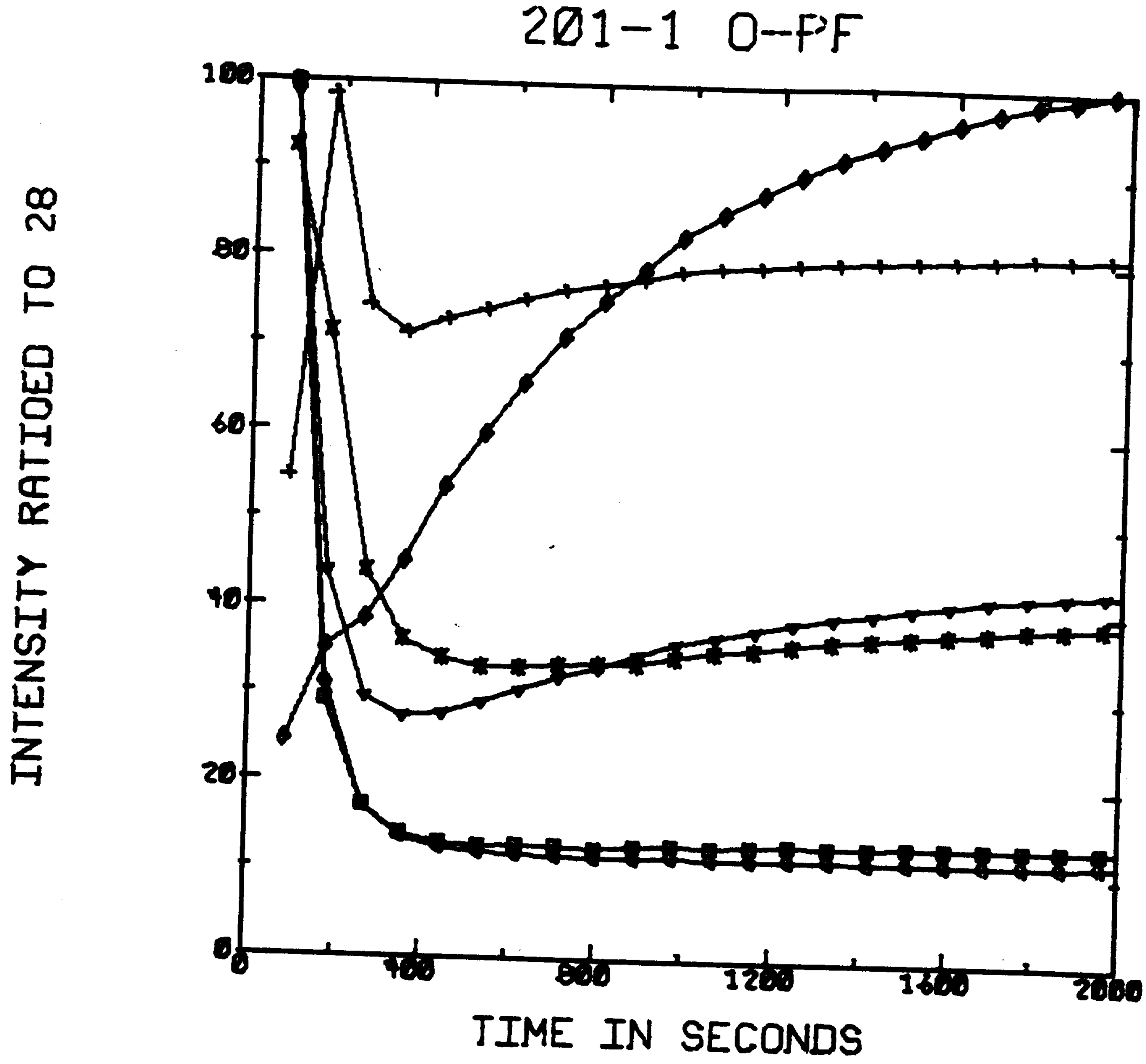
○ = 48 / 28 = TITANIUM X 95
✱ = 51 / 28 = VANADIUM X 1444
◇ = 52 / 28 = CHROMIUM X 2295
\+ = 55 / 28 = MANGANESE X 2678
□ = 56 / 28 = IRON X 25
▽ = 88 / 28 = STRONTIUM X 675
△ = 138 / 28 = BARIUM X 2936
FILE NAME 1-IC2


201-1-I LOOSE FILTER
INTENSITY RATIOED TO 28
10
8
6
4
2
0
0
400
800
1200
1600
2000
TIME IN SECONDS
○ = 7 / 28 = LITHIUM X 591
* = 23 / 28 = SODIUM X 30
◇ = 24 / 28 = MAGNESIUM X 122
+ = 27 / 28 = ALUMINUM X 4
□ = 39 / 28 = POTASSIUM X 11
▼ = 40 / 28 = CALCIUM X 21
FILE NAME 1-IF3

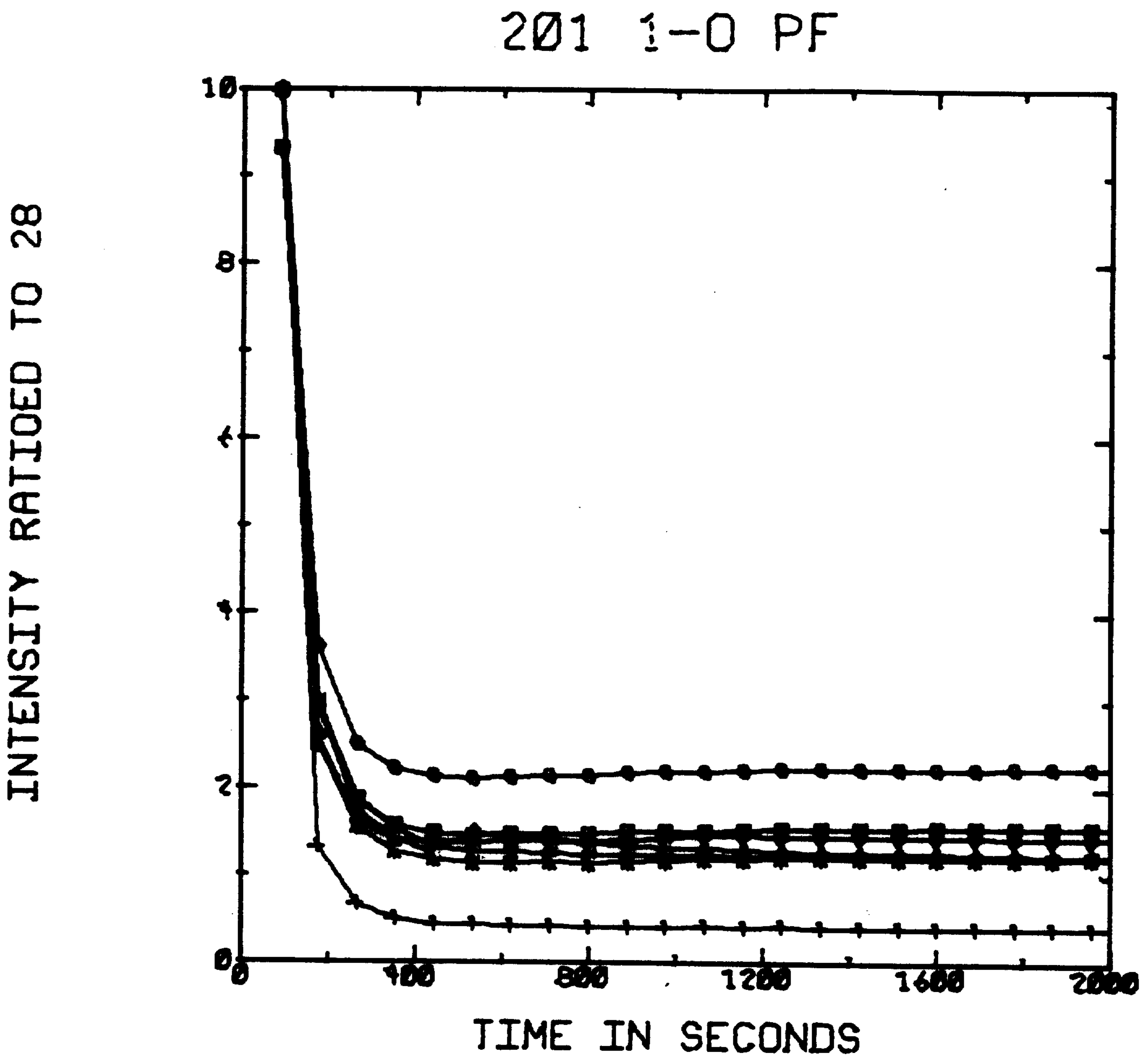
201-1-I LOOSE FILTER



○ = 48 / 28 = TITANIUM X 88
✱ = 51 / 28 = VANADIUM X 1116
◇ = 52 / 28 = CHROMIUM X 1834
+ = 55 / 28 = MANGAGESE X 2395
□ = 56 / 28 = IRON X 29
▼ = 88 / 28 = STRONTIUM X 614
▲ = 138 / 28 = BARIUM X 2190
FILE NAME 1-IF3

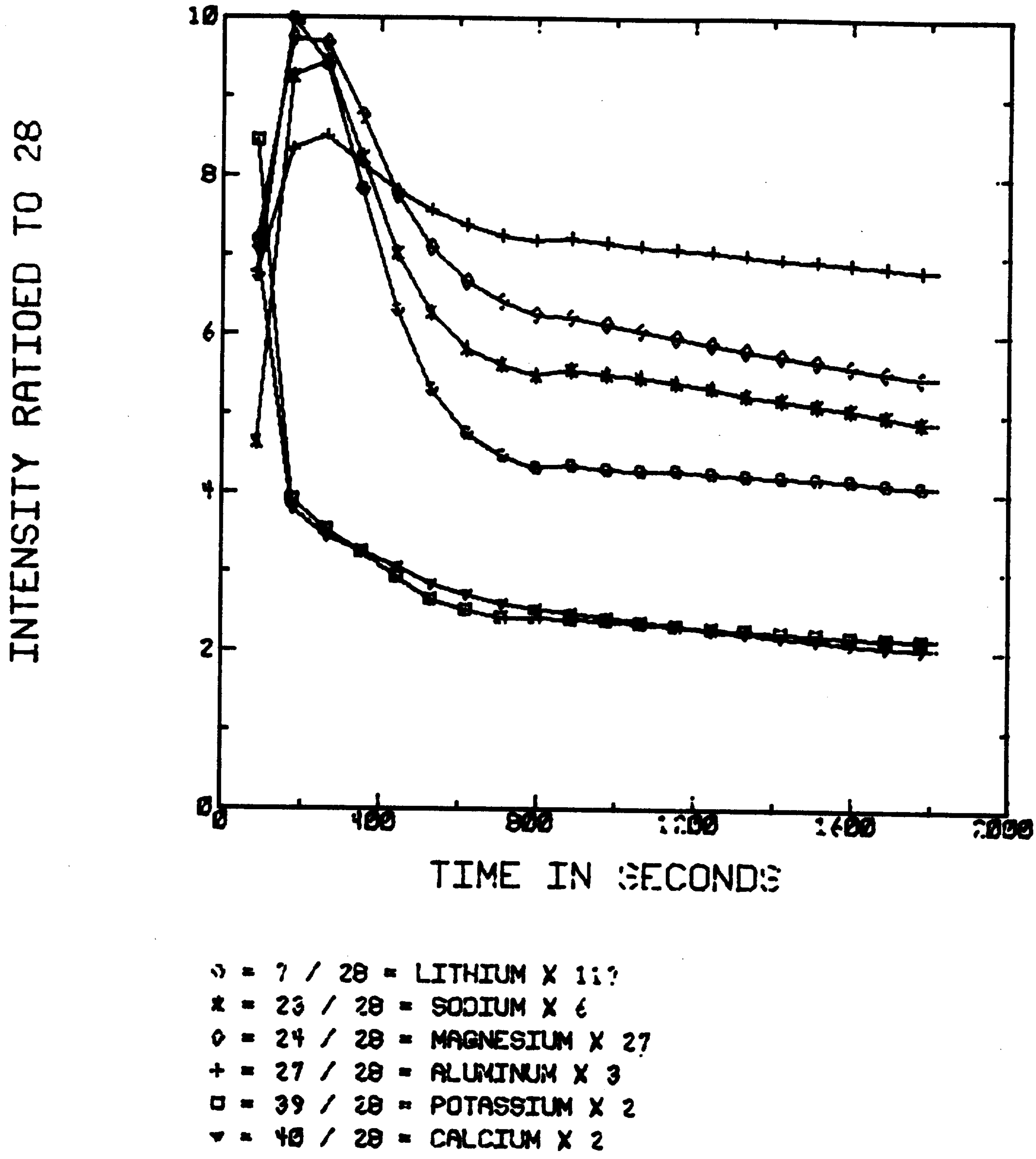


o = 7 / 28 = LITHIUM X 520
* = 23 / 28 = SODIUM X 5
◊ = 24 / 28 = MAGNESIUM X 411
+ = 27 / 28 = ALUMINUM X 48
□ = 39 / 28 = POTASSIUM X 14
▼ = 40 / 28 = CALCIUM X 53
FILE NAME IRV13



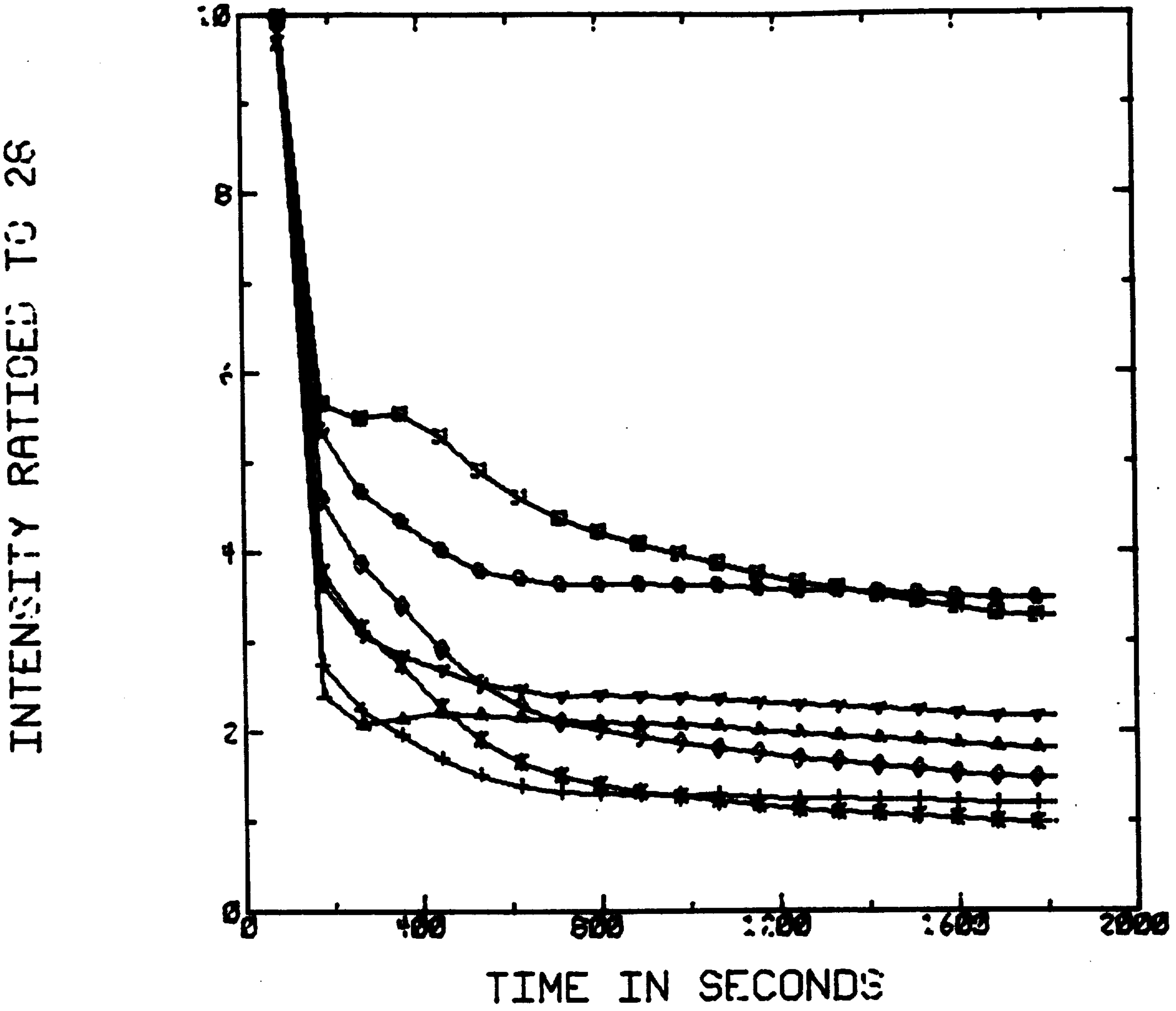
o = 48 / 28 = TITANIUM X 74
x = 51 / 28 = VANADIUM X 201
◇ = 52 / 28 = CHROMIUM X 425
\+ = 55 / 28 = MANGANESE X 133
□ = 56 / 28 = IRON X 9
▼ = 88 / 28 = STRONTIUM X 300
▲ = 138 / 28 = BARIUM X 1160
FILE NAME TRW13

202-4-I-CYCLONE

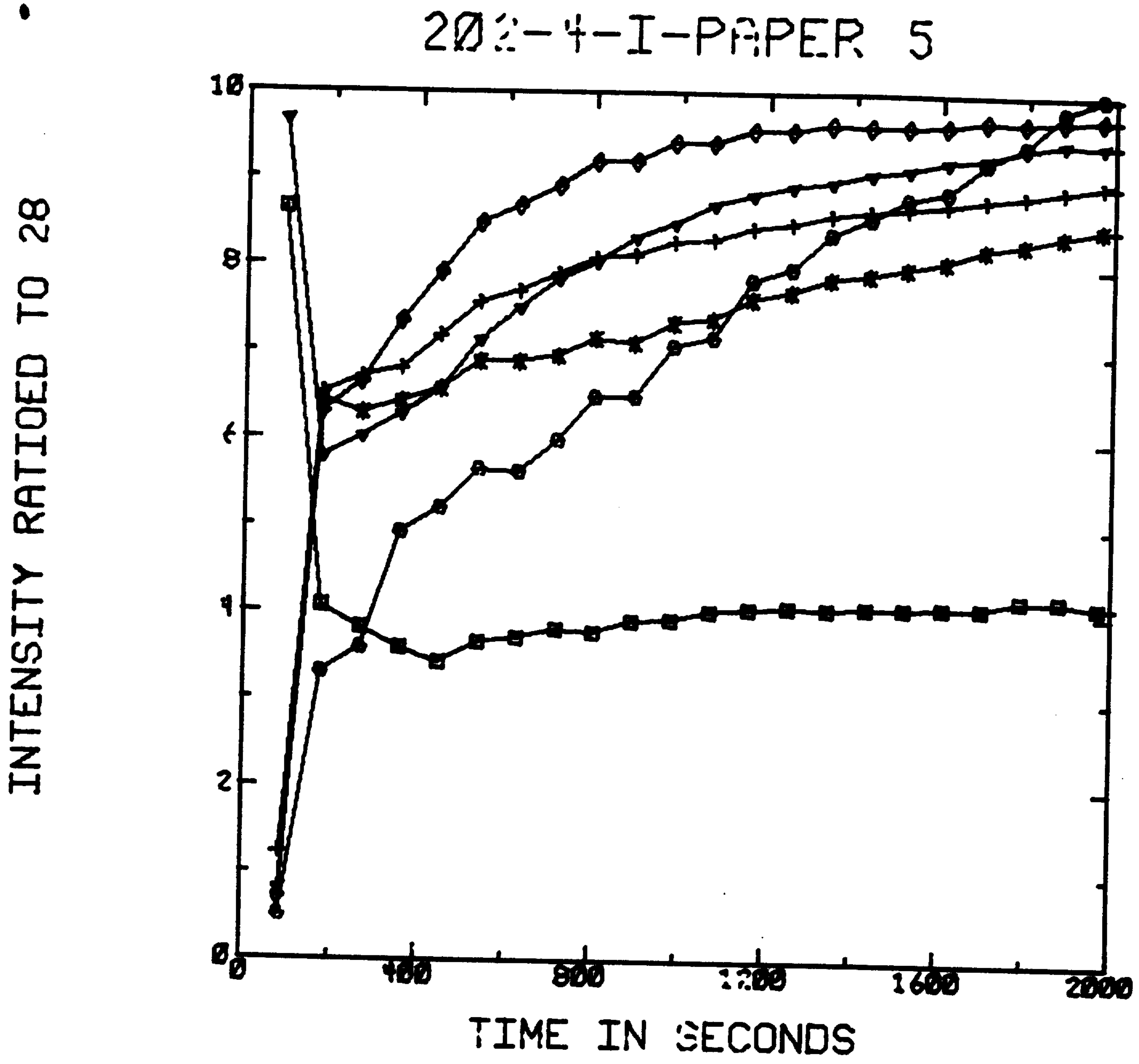


FILE NAME 202CY

202-4--I-CYCLONE

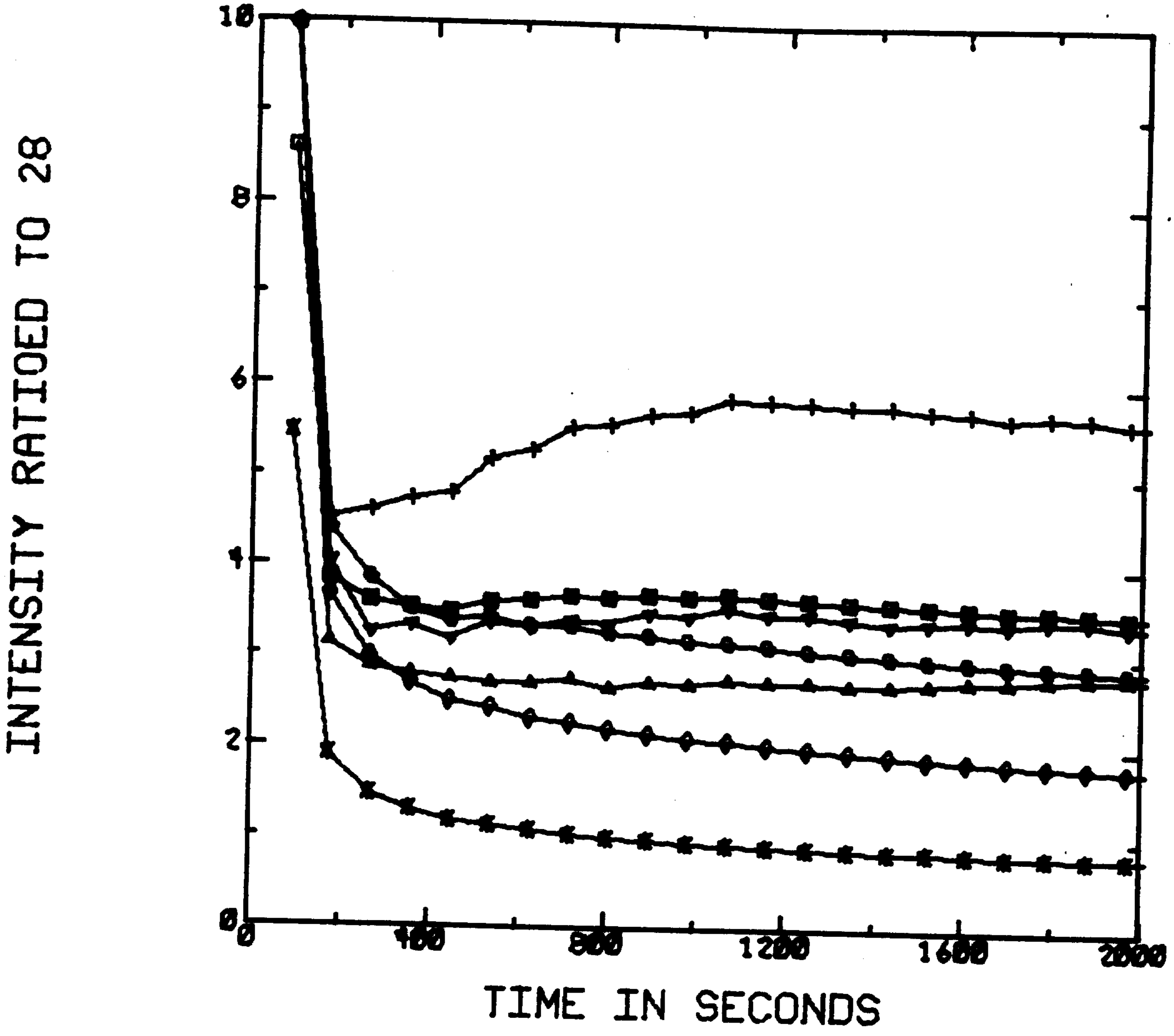


○ = 48 / 28 = TITANIUM X 38
✱ = 51 / 28 = VANADIUM X 3
◇ = 52 / 28 = CHROMIUM X 77
+ = 55 / 28 = MANGANESE X 210
□ = 56 / 28 = IRON X 4
▼ = 88 / 28 = STRONTIUM X 80
▲ = 138 / 28 = BARIUM X 153
FILE NAME 202CY



o = 7 / 28 = LITHIUM X 1330
* = 23 / 28 = SODIUM X 3
◇ = 24 / 28 = MAGNESIUM X 14
\+ = 27 / 28 = ALUMINUM X 7
□ = 39 / 28 = POTASSIUM X 4
▼ = 40 / 28 = CALCIUM X 8
FILE NAME 24FP

202-4-I-PAPER 5



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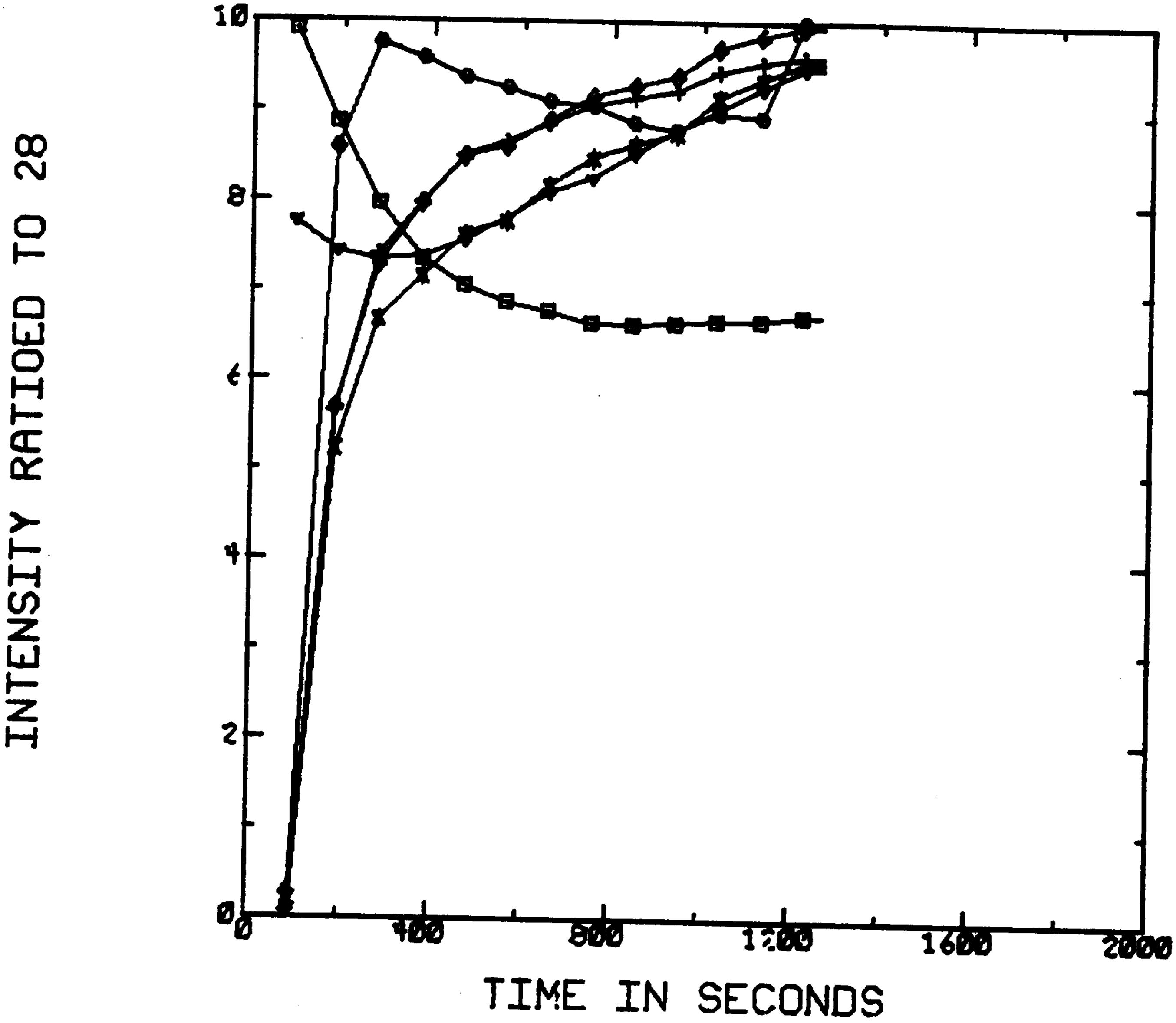
202-4-0 FILTER



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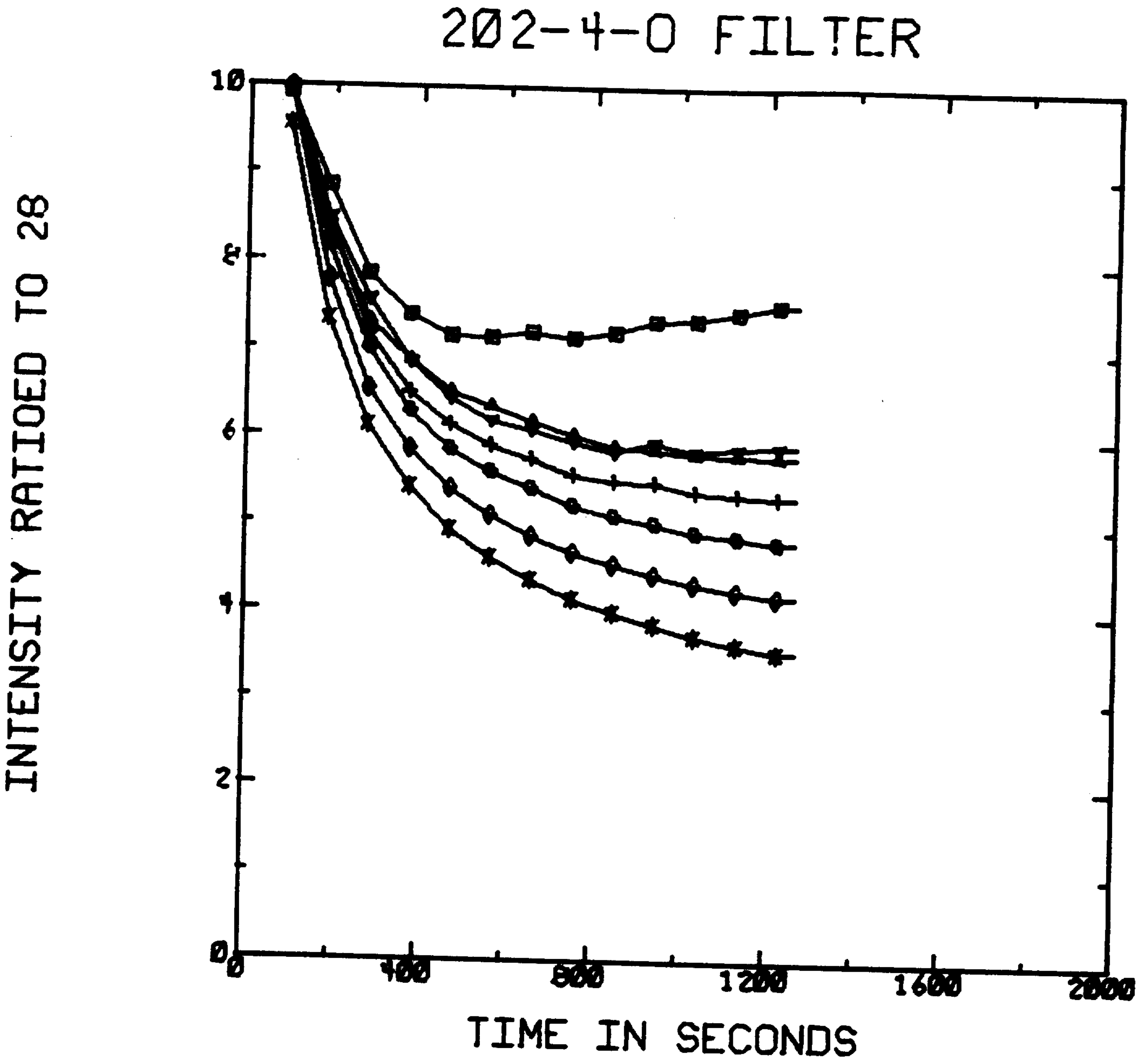

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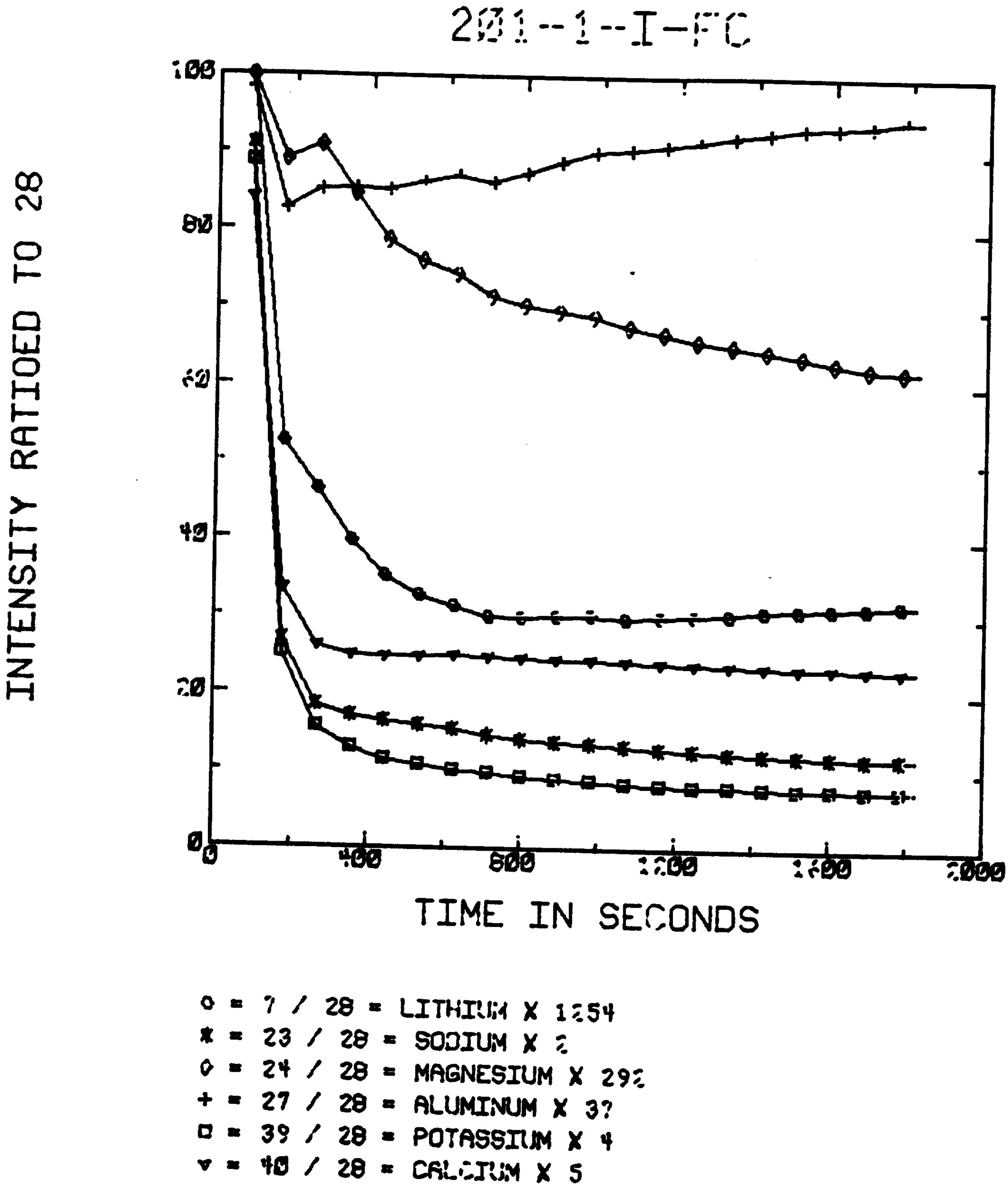

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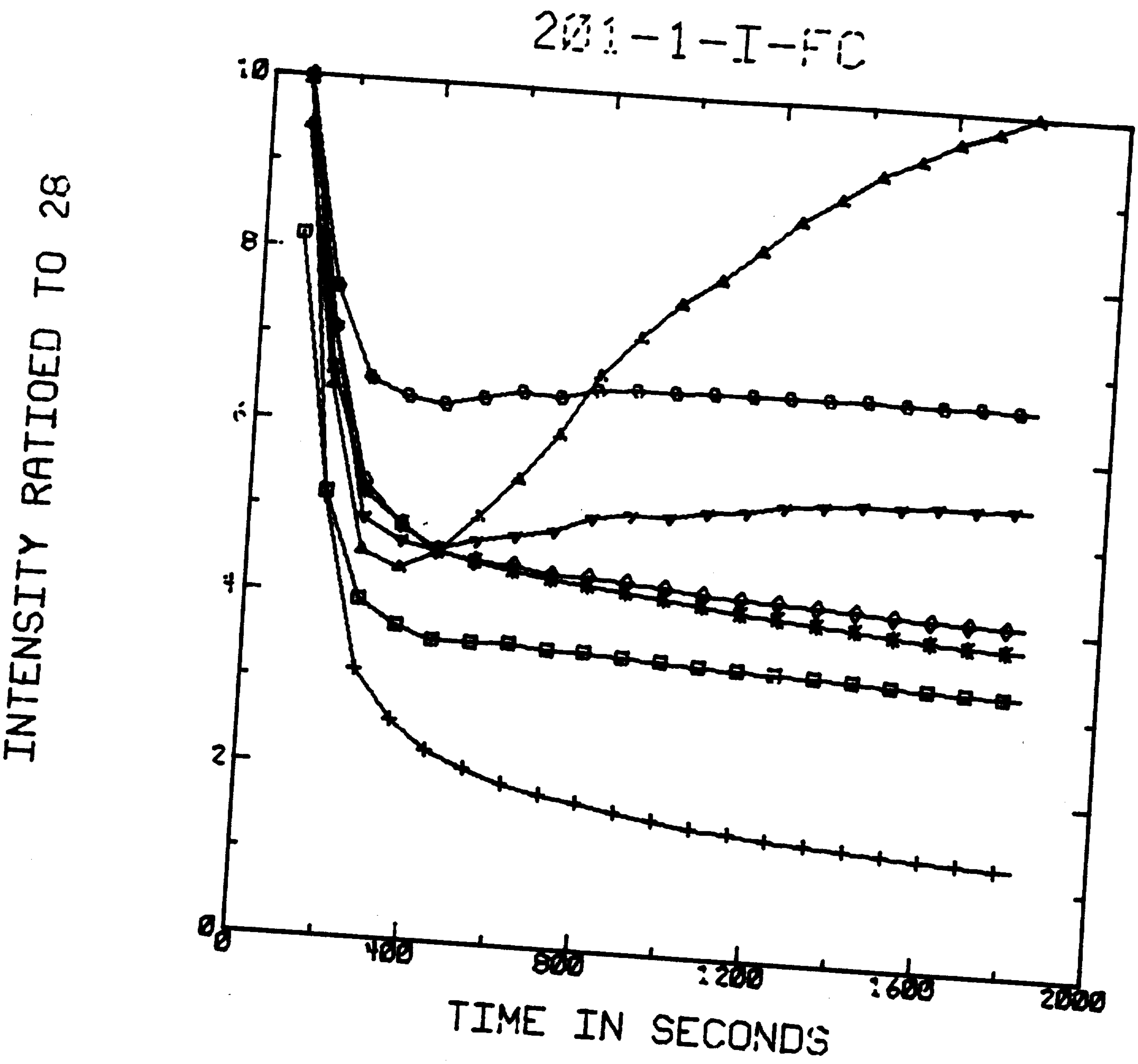

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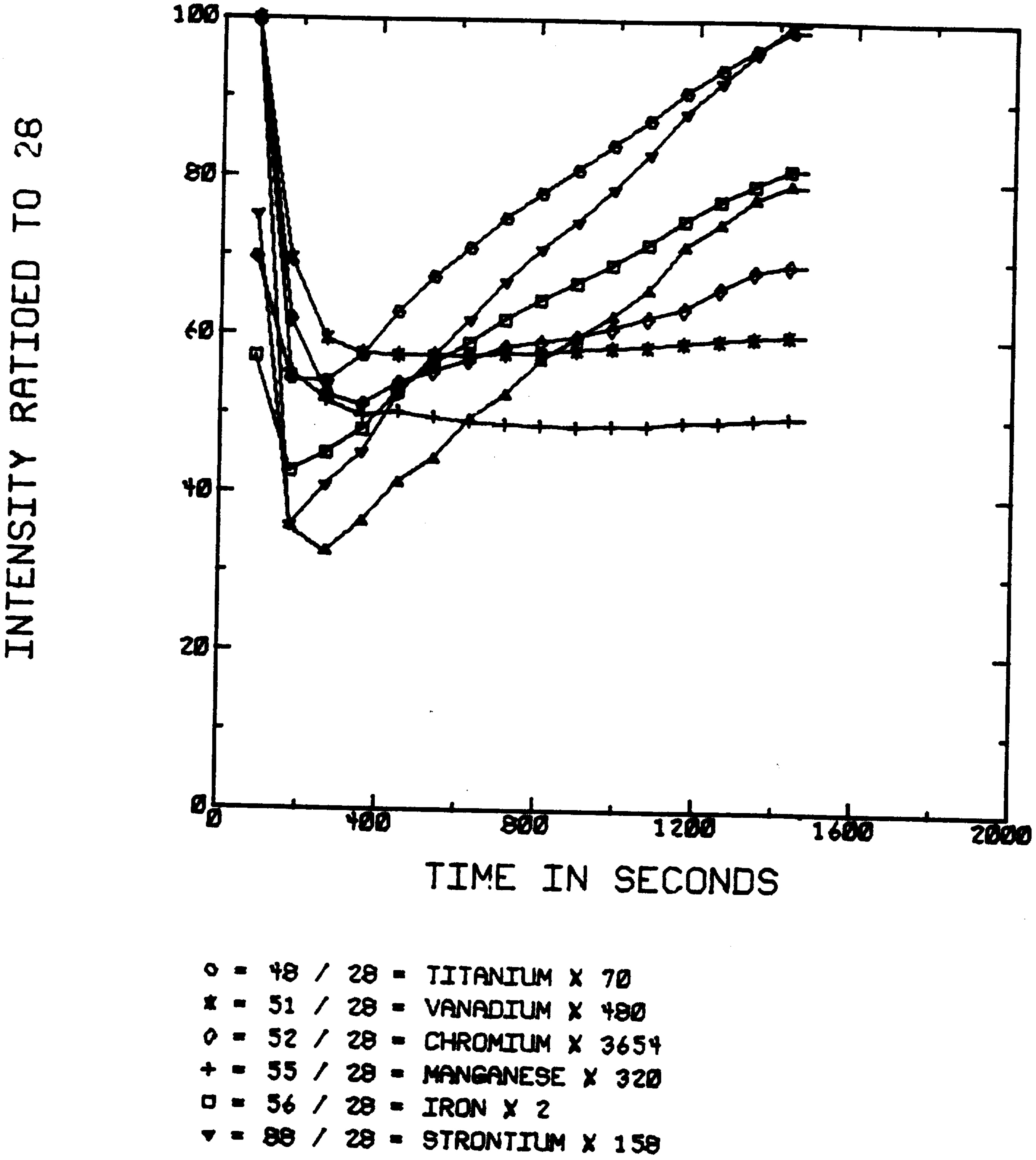
202-4 SCRUBBER CAKE

FILE NAME TRW10

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(Please read Instructions on the reverse before completing)

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2.

3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE Environmental Assessment of Coal- and Oil-firing in a Controlled Industrial Boiler; Volume III. Comprehensive Assessment and Appendices

5. REPORT DATE August 1978

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S) C. Leavitt, K. Arledge, C. Shih, R. Orsini, W. Hamersma, R. Maddalone, R. Beimer, G. Richard, and M. Yamada.

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9. PERFORMING ORGANIZATION NAME AND ADDRESS
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15. SUPPLEMENTARY NOTES IERL-RTP project officer is Wade H. Ponder, Mail Drop 61, 919/541-2915.

16. ABSTRACT The report gives results of a comparative multimedia assessment of coal- versus oil-firing in a controlled industrial boiler, to determine relative environmental, energy, economic, and societal impacts. Comprehensive sampling and analyses of gaseous, liquid, and solid emissions from the boiler and its control equipment were conducted to identify criteria pollutants and other species. Major conclusions include: (1) While the quantity of particulates from oil-firing is considerably less than from coal-firing, the particles are generally smaller and more difficult to remove, and the concentration of particulates in the treated flue gas from oil-firing exceeded that from coal-firing. (2) NOx and CO emissions during coal-firing were about triple those during oil-firing. (3) Sulfate emissions from the boiler during coal-firing were about triple those during oil-firing; however, at the outlet of the control equipment, sulfate concentrations were essentially identical. (4) Most trace element emissions (except vanadium, cadmium, lead, cobalt, nickel, and copper) are higher during coal-firing. (5) Oil-firing produces cadmium burdens in vegetation approaching levels which are injurious to man; coal-firing may produce molybdenum levels which are injurious to cattle. (6) The assessment generally supports the national energy plan for increased use of coal by projecting that the environmental insult from coal-firing is not significantly different from that from oil-firing.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Nitrogen Oxides	Pollution Control	13B	07B
Assessments	Carbon Monoxide	Stationary Sources	14B	
Boilers	Sulfates	Environmental Assessment	13A	
Combustion	Sulfur Oxides		21B	
Fuel Oil	Trace Elements	Industrial Boilers	21D	06A
Coal	Chemical Analysis	Particulate		07D
Dust			11G	

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