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PROPULSION AND FIRE PROTECTION BRANCH

INTERIM REPORT

PROGRESS AS OF JULY 25, 1974: ACTIVITY 181-521-010, "DEVELOP A TOXIC GAS EMISSION CRITERIA FOR INTERIOR MATERIALS"

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INTRODUCTION

Purpose

The purpose of this report is to document visual aids (vugraphs) presented at a progress review meeting convened at the National Aviation Facilities Experimental Center (NAFEC) on July 25, 1974, for Activity 181-521-010, "Develop a Toxic Gas Emission Criteria for Interior Materials."

Background

NAFEC was assigned the task of measuring the concentration of a selected number of toxic gases present in the combustion products of wide-bodied aircraft cabin materials. Conceptually, this data in conjunction with appropriate toxicity information will be used to compute some toxicity index which presumably will permit the elimination of the poorest ranked materials. This approach is similar to the current Federal Aviation Administration (FAA) flammability and proposed smoke regulations. It was decided that this assignment could be most expeditiously accomplished by using colorimetric detector tubes to measure the toxic gas concentrations in the National Bureau of Standards (NBS) chamber, an approach taken by the NBS in 1968 in testing materials for NAFEC. With regard to their possible application in a regulation, the colorimetric tubes offer the advantages of low cost, simplicity and speed of measurement in contrast to their somewhat uncertain applicability for combustion gas analysis. Because of the latter, substantial measurements will be made using ion selective electrodes, an IR spectrophotometer and a CO gas analyzer (NDIR). In addition, the concentration of the selected toxic gases will be measured as a function of time, instead of at the time of peak smoke accumulation only as done in the earlier NBS work. Seventy-five representative wide-bodied cabin materials donated by the airframe and seat manufacturers have been selected for analysis.

From last summer until the first of the year, NAFEC efforts under this activity were almost entirely devoted toward developing a capability and facility for combustion gas analysis. The program review presentation described work conducted since January to examine the characteristics of measurements made of toxic gas concentration levels inside the NBS chamber.

The first part of the essentially two-part presentation was devoted to some of the earlier work performed, for example, to examine the reproducibility and homogeneity of CO in a combustion gas mixture inside the NBS chamber. More recent work conducted during the 2-1/2 months preceding the progress review after the completion of the chemistry laboratory was described in the second part of the presentation. The goal here was to develop a reliable method for measuring the HCl concentration as a function of time from burning vinyls in the NBS chamber.

DISCUSSION

The colorimetric tube calibration scale is valid when a gas sample is taken with the manufacturer's hand pump. Each tube in turn has unique flow characteristics, or sampling time, which can vary from 3-4 seconds to several minutes, depending on the tube and the concentration measurement range (number of pump strokes). Consideration of these operational characteristics and the possibility of rapid changes in gas concentration dictated an approach whereby samples would be taken periodically from the NBS chamber and subsequent colorimetric tube measurements would permit construction of a concentration versus time curve for each of the toxic gases of interest. Combustion gas samples are drawn into 10-liter Saran bags which have the advantages of good chemical resistance, low permeability and low cost. The bags are placed in a wooden vacuum box (Figure 1) maintained at a pressure of -8 inches of Hg. At these conditions, a 10-liter sample can be taken in about 10 seconds. In order to evaluate the magnitude of wall losses, a test was conducted for each of the selected toxic gases utilizing typical cabin materials. Colorimetric tube measurements directly from the NBS chamber were compared with similar measurements of Saran bag samples taken at the same (mean) time during the test. The results demonstrated that substantial wall losses could be expected for HF and HCl, and that these gases must be measured directly from the chamber. Additional tests demonstrated that the measured reduction in smoke and CO from bag sampling corresponded reasonably well with the theoretical reduction (2 percent/bag). The wooden vacuum box eliminates the contamination problems associated with a pump.

There was some concern that the concentration of CO from the NBS chamber propane/air burner might be significant. The contribution of CO from the burner was measured at the geometric center of the chamber with the LIRA gas analyzer (Figure 2). The level of CO from the burner, increasing at a rate of approximately 3 ppm per minute, is negligible compared to the concentration in combustion gas mixtures from cabin materials tested thus far.

The distribution of the gas mixture species of interest inside the NBS chamber will dictate the selection of the optimum sampling location. A sample should be taken that contains a representative or average level of each of the gases. Carbon monoxide was the first and most extensively measured gas with regard to distribution within the chamber. Numerous measurements were made with the LIRA gas analyzer along the vertical center symmetry line and at the corners of three horizontal planes during flaming combustion tests of filter paper. Figure 3 shows data from the former series of tests. The vertical CO profiles at selected test times are plotted. The concentration of CO measured one inch below the ceiling is above the average value (black dot) during the first 2 minutes of the test, but drops below the average beyond 3.5 minutes. Conversely, the CO concentration near the chamber floor is low at the beginning of the test. Measurements at 12, 18, 24 and 30 inches above the floor are in fairly good agreement with one another for the entire test. One can conclude from this data that a gas sample taken from the geometric center contains a representative level of CO. The more reactive gases like HCl and HF do not necessarily exhibit the same relatively homogeneous distribution as CO (HCl stratification measurements are discussed later). This data demonstrates that sampling from the chamber ceiling can give misleading results. Similar measurements in the four corners and center of three horizontal planes also demonstrated relatively good agreement; e.g., a coefficient of variation less than 5 percent after 3-4 minutes for planes 6 and 18 inches below the ceiling.

One criterion for judging the merit of a test method is its repeatability. Nine replicate flaming exposure tests of filter paper were conducted with the NBS chamber. Measurements were made of the smoke level in the standard manner (Figure 4) and the concentration of CO at the geometric center with a LIRA gas analyzer (Figure 5). The smoke data exhibited good repeatability and a fairly constant scatter throughout the entire 10-minute test. A similar behavior was evidenced by the CO data which also had a better (lower) coefficient of variation; i.e., measurements of CO were more repeatable than smoke.

Four replicate tests were conducted using a procedure for making colorimetric tube measurements which is typical of that to be followed during evaluation of the 75 cabin materials. Urethane seat foam was tested in the NBS chamber under flaming exposure conditions. Eight gas samples from the geometric center of the chamber were collected in Saran bags at one-minute intervals using the vacuum box described earlier. After the test, the box (and bags) was returned to atmospheric pressure and colorimetric tube measurements were made of the sampled gas mixtures. There were no detectable levels of HF, NH_3, H_2S, SO_2 or $COCl_2$. The concentration of CO, HCN, NO_x and HCl at the eight sampling times is shown in Figure 6 for one of the tests. The most rapid change in species concentration occurred over the first minute of the test, when a substantial portion of the test specimen was observed to be consumed by flames. Hydrogen chloride apparently formed from the decomposed foam blowing agent (the level is low because of bag wall adsorption). Two procedural changes will be included in future tests utilizing colorimetric tubes: (1) HCl and HF measurements will be made directly from the chamber; and (2) aldehydes and TDI will also be measured.

Smoke data from the four replicate tests are shown in Figure 7. The first three tests agree quite well with one another, while the fourth test (June 25, 1974) is noticeably below although still reasonably close to the other data. The urethane sample for the fourth test appeared to burn with higher and more persistent flames than the earlier three test samples, which explains the lower smoke level (less smoke from more complete combustion). The concentrations of carbon monoxide measured with a LIRA gas analyzer and HCN measured with colorimetric tubes for the four replicate tests are shown in Figures 8 and 9, respectively. The repeatability of the CO measurements for urethane foam are poorer than those of smoke for the same material (Figure 7) or CO for filter paper (Figure 5). The poor CO repeatability of urethane can be attributed to the physical aspects and variability of its combustion in the NBS chamber. Most of the urethane is consumed during the first minute of the test; thereafter, combustion is primarily confined to the sample holder trough where the melted drippings are accumulated (until overflow) and ignited by two propane/air flamelets. Apparently, this arrangement allows for a variation in the intensity and persistence of flaming, which will affect the level of combustion gases. The smoke level does not exhibit the data scatter only because it levels off early in the test and is more dependent upon the physical mechanisms of agglomeration, condensation, etc. rather than combustion. In contrast to urethane, the filter paper burns slowly and continuously without melting or dripping and both the smoke and CO increase throughout the test. The HCN levels shown in Figure 9 have the same overall relative position for the four tests as the CO data, although the difference between tests of some of the measured concentrations was obscured by the inaccuracies of the colorimetric tubes.

Ancillary tests to determine the usefulness and limitations of the colorimetric tubes were performed using the aforementioned urethane combustion gas mixtures. The results are summarized below:

1. The concentration of CO measured with colorimetric tubes is 40 to 50 percent greater than corresponding LIRA IR gas analyzer measurements.

2. Species concentration measurements utilizing colorimetric tubes from different batches are in good agreement (coefficient of variation less than 10 percent).

3. The subjective reading of the stain length (concentration) indication on a used colorimetric tube by two people, independently, was found to be in good agreement (coefficient of variation between 5 and 10 percent).

4. The distinctiveness of the stain length worsens if the sample volume (number of pump strokes) is decreased, as is the case when the tube is operated at the high measurement range. These findings are also listed in Figure 10, which has been slightly modified to include results attained since the progress review meeting.

As originally planned, the toxicity of burning materials would be determined by testing the materials in the NBS chamber under both flaming and smouldering fire exposure conditions, and analyzing the gaseous products using IR spectroscopy, ion selective potentiometry and colorimetric tubes (Figure 11). Presently, utilization of the IR spectrophotometer on this activity will be limited to qualitative analysis of combustion gas mixtures collected in Saran bags. This instrument could be used for quantitative measurements of selected gases (e.g., CO, SO_2, HCN) provided that a time-consuming calibration is frequently conducted. NAFEC has established a blanket purchase agreement (BPA) with Scientific Gas Products, Inc., to procure calibration gases expeditiously to be used for the above-mentioned purpose, or to examine sampling bag or NBS chamber gas decay curves, calibrate the colorimetric tubes, determine impinger efficiency, etc. When using reactive calibration gases, it is necessary to allow the wall adsorption-desorption to equilibrate before measuring the steady-state gas concentration. Figure 12 shows the concentration of HCl in a Teflon bag measured by periodically taking syringe samples and analyzing with the chloride ion selective electrode. Approximately 50 minutes were required before the HCl concentration leveled off. At this time in the activity, ion selective potentiometry using impinger or syringe sampling will be heavily relied upon for quantitative gas analysis. NAFEC recently acquired an attenuated total reflectance (ATR) attachment to the IR spectrophotomer for identification of unknown materials.

The ion selective electrodes apart from the gas mixture sampling system have certain recognizable limitations when applied to quantitative gas analysis in a multicomponent gas mixture (Figure 13). Because of observed shifts in the calibration curve, possibly from leakage of outer reference electrode solution into the sample solution or adsorption of polar organic species on both the working and reference electrode, standard NAFEC practice is to calibrate each electrode immediately prior to utilization for gas measurements. As the name implies, the ion selective electrodes are not necessarily only responsive to the specific gas of interest. For example, the chloride electrode will also detect with reduced sensitivity the presence of bromide, sulfide and cyanide ions. This effect was encountered in HCl measurements of the effluent from combustion tube pyrolysis of a PVC/wool blend. The HCl concentration exceeded the theoretical value based on an assumed complete conversion of all chlorine in the PVC to HCl, apparently because of the additional detection of large quantities of HCN from the wool. It was also determined that the solute will influence the detection threshold of the chloride electrode. Distilled water has a factor of 100 lower detection limit than NaOH (0.1 ppm versus 10 ppm of chloride ion concentration in solution, respectively). When first used, the cyanide electrode displayed a seemingly endless variation in output potential that appeared to preclude its usefulness for quantitative analysis. However, over a sufficiently long time interval, the output potential eventually reached a steady-state value. The variation of potential as a function of time is shown in Figure 14 for a 1.26×10^{-5} M CN^- in 0.10 M KOH solution (top) and the 0.10 M KOH solution alone (bottom). At 15 minutes, the potential is clearly approaching a steady-state condition. By selecting a fixed stirring rate for the solution and geometrical location of the electrodes in solution, and by awaiting sufficient time for equilibration of the potential, a repeatable, usable calibration can be made of the cyanide electrode of the form shown in Figure 15. This calibration procedure has been successfully applied thus far to the measurement of the HCN concentration in the combustion products from urethane and wool.

Considerable time and effort was devoted toward developing a reliable method for continuously measuring the HCl concentration in the NBS chamber. Periodic impinger sampling with subsequent chloride electrode analysis was initially felt to be the best approach for constructing the HCl concentration versus time curve. A schematic diagram of such a typical sampling system (also used for HCN analysis) is shown in Figure 16. The system is composed of a glass probe, polypropylene tubing, a filter to trap smoke particulates and safeguard the frits from clogging, a manifold of fritted impingers (as many as 10 impingers connected in parallel), flow measurement devices and a vacuum pump. This system has several areas of difficulty. Numerous plumbing connectors and stop cocks are potential leakage sources that require frequent inspection and attention. A lengthy calibration is required before each test of the flow rate upstream of the impingers in terms of the downstream indication. However, these difficulties are manageable and the system has been used to collect accurate sample volumes by collecting consecutive one-minute samples for all 10 impingers.

An important part of the impinger sampling system is the filter required to protect the frits. Three filter materials (Teflon, polypropylene and glass fiber) were individually evaluated in three different filter holders (Teflon, steel and poly ethylene) by measuring the chloride collected in the filter assembly after combustion gas sampling that could be recovered by rinsing with distilled water. The best results (lowest adsorbed HCl) were obtained with a polypropylene filter in a Teflon or polyethylene filter holder (Figure 17). The percentage of measurable HCl from the combustion of PVC foam in a tube furnace (see Figure 23 described later) recovered in the filter assembly for the polyethylene holder and three filter materials evaluated is shown in Figure 18. For the polypropylene and Teflon filter materials, the chloride losses in the filter assembly are relatively low, 13.3 and 15.5 percent, respectively, compared to the glass fiber material. Note that the remaining chloride was measured from the residue on the walls of the combustion tube.

As mentioned previously, it is important to take a sample from the NBS chamber that contains a representative or average concentration of each gas being measured. Three tests were conducted to examine the stratification of HCl on the center vertical line during smouldering combustion of PVC. Simultaneous impinger samples were continuously taken over a 10-minute interval at three locations: 6, 18 and 30 inches below the ceiling (Figure 19). On a time-averaged basis, the HCl concentration decreased from the ceiling to the floor during two of the three tests; a fairly uniform concentration was evidenced for the remaining test. For all three tests, the concentration at the geometric center was slightly less than, but within 10 percent of, the average concentration.

The repeatability of HCl measured at the geometric center of the NBS chamber was determined for six equivalent samples of PVC under smouldering exposure conditions. The manifolded impinger sampling system (Figure 16) was used to obtain 10 consecutive one-minute samples. Figure 20 contains the HCl concentration-time "curves" from three tests constructed by connecting the average calculated concentration plotted at the mean sampling time. The data exhibits large fluctuations and variations between tests. The difference in concentration between tests can somewhat be explained by the significant and highly variable HCl losses in the filter assembly. However, one can only surmise that the large fluctuations are possibly an indication of HCl clouds passing in and out of the sampling location. In spite of these differences, the relative standard deviation (RSD) of the maximum HCl concentrations for the three tests is only 19 percent. A summary tabulation of the six replicate tests is shown in Figure 21. The total quantity of HCl collected within the 10 impingers and filter assembly is recorded in the third column; a maximum difference of over a factor of 2 was measured. The maximum HCl concentration and from this the theoretical yield, calculated from the measured chloride ion concentration in the impinger solution and the measured sample volume, was fairly close for all tests except test No. 5. Because of the large HCl losses in the filter assembly and the averaging-out of the true concentration-time curve by taking one-minute samples, the replacement of the manifolded impinger system by rapid, small-sample-volume syringe sampling is being investigated.

A mass balance was conducted on the HCl measured in the NBS chamber and manifolded impinger sampling system for smouldering combustion of PVC (98 percent pure). Surprisingly, the glass probe and polypropylene sample line together and the NBS chamber wall losses each only added up to about 1 percent of the total chloride collected (Figure 22). The chamber wall loss was determined by measuring the quantity of adsorbed HCl on a one-square-foot piece of Teflon film adhered to the wall during the test and multiplying by the surface area of the chamber walls, floor and ceiling (42 ft^2). Almost all the measurable chloride is found in the impingers (78 percent) and filter assembly (21 percent).

Because of the variation between tests and high fluctuations of HCl measurements in the NBS chamber (Figure 20), a series of tests were conducted with the more efficient and accountable combustion tube assembly. This apparatus consists of a flow meter, glass tube which incases the test specimen, cylindrical tube furnace which surrounds the glass tube, filter, impinger and vacuum pump (Figure 23). A large number of tests were conducted in a period of one week just prior to the progress review meeting. The immediate objective was to attempt to impart to the analytical procedures developed for HCl measurement some degree of credence by determining if the theoretical yield of HCl from pure PVC (58.3 percent) could be recovered. For a typical run, the furnace is set at the desired temperature (usually 600°C), an airflow rate of 200 cc/min is established, and the test is initiated when the combustion tube holding the specimen is placed in the furnace. The entire effluent is passed through the impinger for a sufficiently long period of time to assure complete material degradation (usually 10 minutes). Also, since the combustion tube and filter residues can be readily removed for analysis, a complete accounting can be made of the weight of HCl produced during combustion of the PVC. The majority of the PVC materials tested in the tube furnace produced an HCl level that was within ±10 percent of the theoretical yield.

A number of tests were conducted to determine the effect of several test parameters; viz, sample weight, test time and ventilation rate. Figure 24 is a plot of hydrogen chloride recovery (miligrams of HCl per gram of sample) versus PVC foam sample weight. The HCl recovery levels off at a specimen weight of about 25 to 30 miligrams. Apparently, efficient combustion of the smaller samples was responsible for the greater HCl recovery from these materials, since a tar-like residue observed on the tube wall after tests of the heavier samples was not evidenced for the lighter samples. A similar behavior resulted when HCN was measured in the combustion effluent of Nomex fabric at 600°C (Figure 25). On the basis of these trends, a sample weight of 100 mg has been standardized upon for future combustion tube studies.

Adequate time must be allowed for the completion of sample combustion in the tube furnace. Hydrogen cyanide was again measured during the combustion of Nomex fabric over test times extending from 1 to 10 minutes (Figure 26). After about 3-5 minutes, the increase of HCN with time is gradual, indicating that the combustion is nearly complete in this regime. As mentioned previously, a 10-minute test time is normally used. Examination of the effect of ventilation rate (Figure 27) demonstrated that airflows of 400 cc/min would delete the HCN yield by a factor of about one-third compared with airflows of 200 cc/min or less. Since the production of HCN is a strong function of temperature, evidently the high ventilation rate cooled down the combustion temperature. A ventilation rate of 200 cc/min is normally used. Figures 25 through 27 include test results obtained since the review meeting and were added to this report because of their relevency to the analysis of test parameters affecting the performance of the combustion tube assembly.

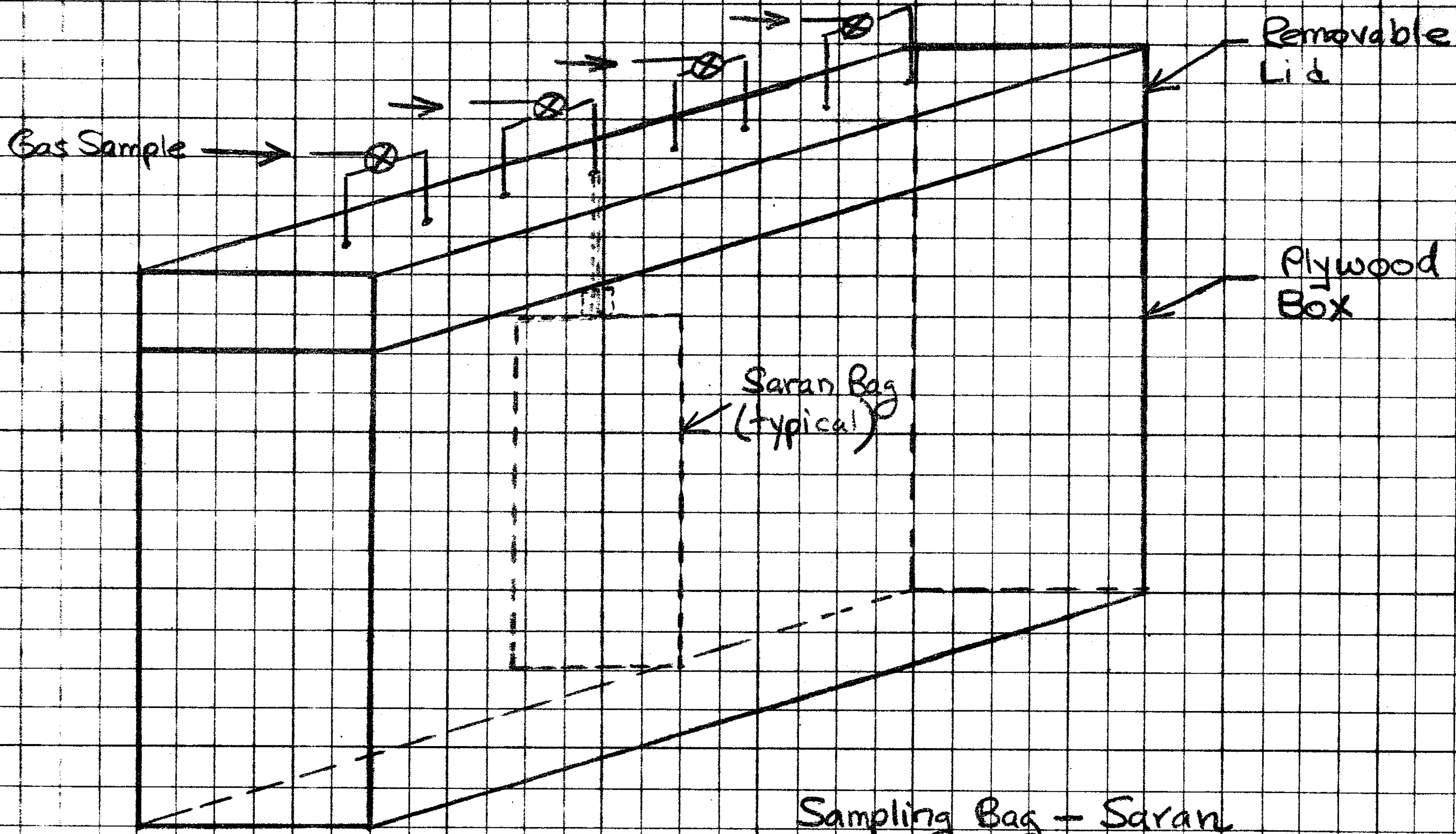
At lower sample weights, the increase in HCl or HCN recovery observed for PVC foam (Figure 24) and Nomex (Figure 25), respectively, is not necessarily a characteristic trend for all materials. Combustion tube analysis of PVC (98 percent pure) showed a completely opposite behavior, with less functional dependence on sample weight, than either the PVC foam or Nomex (Figure 28).

The distribution of measurable HCl in the combustion tube assembly for four PVC material compositions is shown in Figure 29. Almost the entire quantity of HCl is collected in the impinger for the PVC fabric and plastic. However, for the PVC/wool-blended fabrics, the relative quantity of HCl on the glass tube and filter assembly increases drastically as the PVC content is reduced. Within experimental accuracy, the entire theoretical yield was recovered from the first three materials; however, as reported earlier, the unreasonably large amount of apparent HCl from the 24 percent PVC/76 percent wool fabric is probably an additive interference of HCN from the wool.

A summary of findings with regard to HCl measurement in a combustion gas mixture is shown in Figure 30. For the impinger sampling system, changes in temperature and pressure within the NBS chamber and the opening and closing of stop cocks when the sampling impinger is changed produce flow fluctuations that are a source of possible error. Because of negligible measurable adsorption, the glass probe and polypropylene sampling line do not require modification; however, significant HCl losses in the filter assembly for some tested materials attest to the necessity for further filter material/design investigations. Stratification measurements of HCl and CO in the NBS chamber thus far indicate that a representative sample is obtained at the geometric center and that a fan or multiple probing may not be necessary. Reproducibility and recovery of HCl in the NBS chamber was generally poor for the first PVC material evaluated. This behavior will be dependent upon the material composition and HCl concentration level. No clear relationship has been found for HCl recovery in terms of chamber conditioning. Finally, quantitative HCl recovery is obtainable with the combustion tube furnace, but the results are influenced by test parameters such as sample weight and composition.

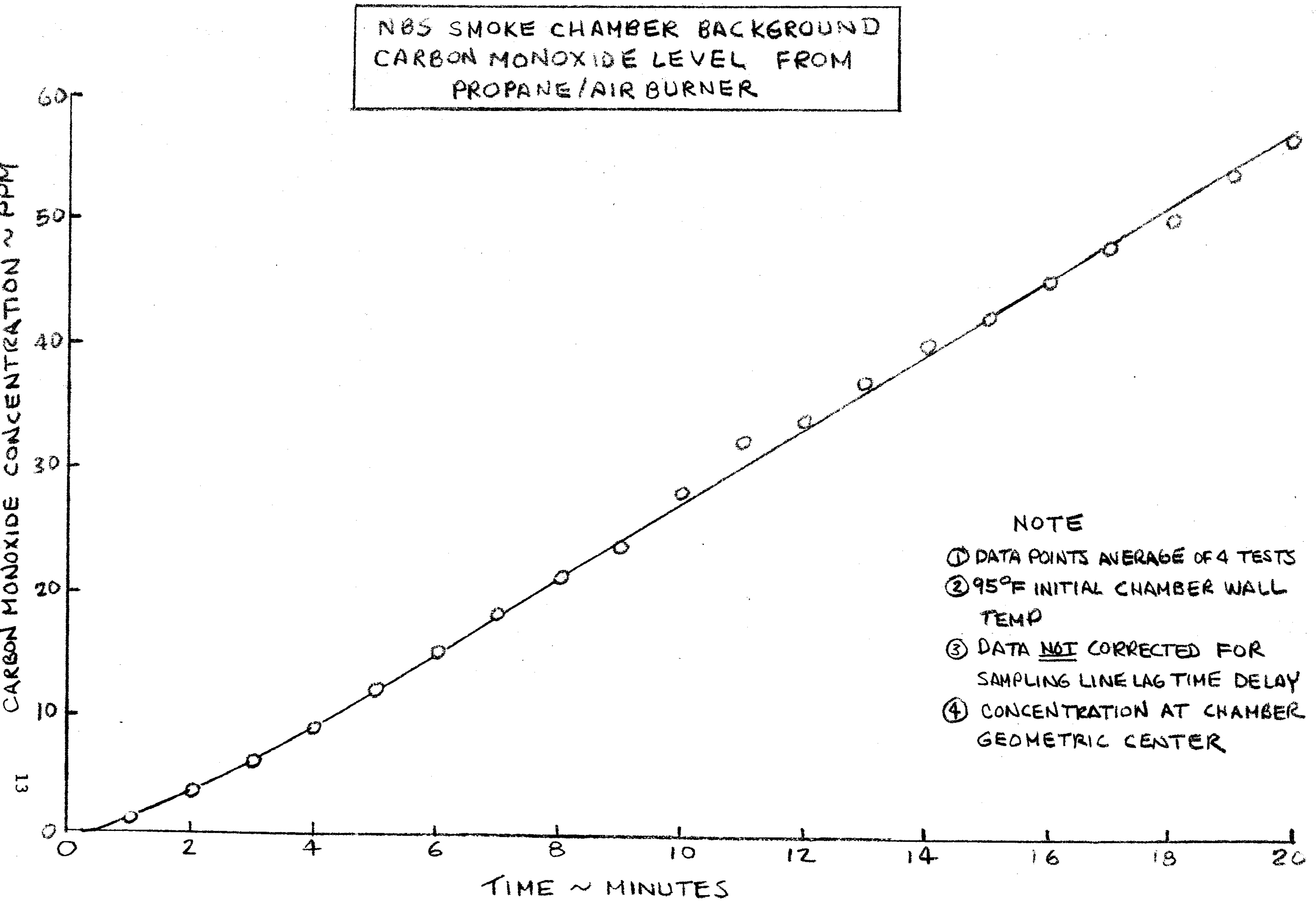
In view of some of the difficulties associated with using colorimetric tubes for combustion gas analysis and measuring the concentration of toxic combustion gases in the NBS chamber as a function of time, it is recommended that efforts in the immediate future at least should consist of a coordinated approach using a combustion tube and thermogravimetric analysis in addition to the NBS chamber (Figure 31). Preliminary experiments have demonstrated that quantitative data can be attained with a combustion tube. Thermogravimetric analysis provides a measurement of mass loss as a function of temperature with heating rate a selected parameter. Inclusion of the combustion tube and thermogravimetric analyses into the test program requires very little additional manpower and the additional data to better characterize a material is worth the increased effort.

VACUUM SAMPLING BOX



Sampling Bag – Saran
Sample Volume – 10 liters
Vacuum – 8 in Hg
Sampling Time – 10 seconds

FIGURE 1

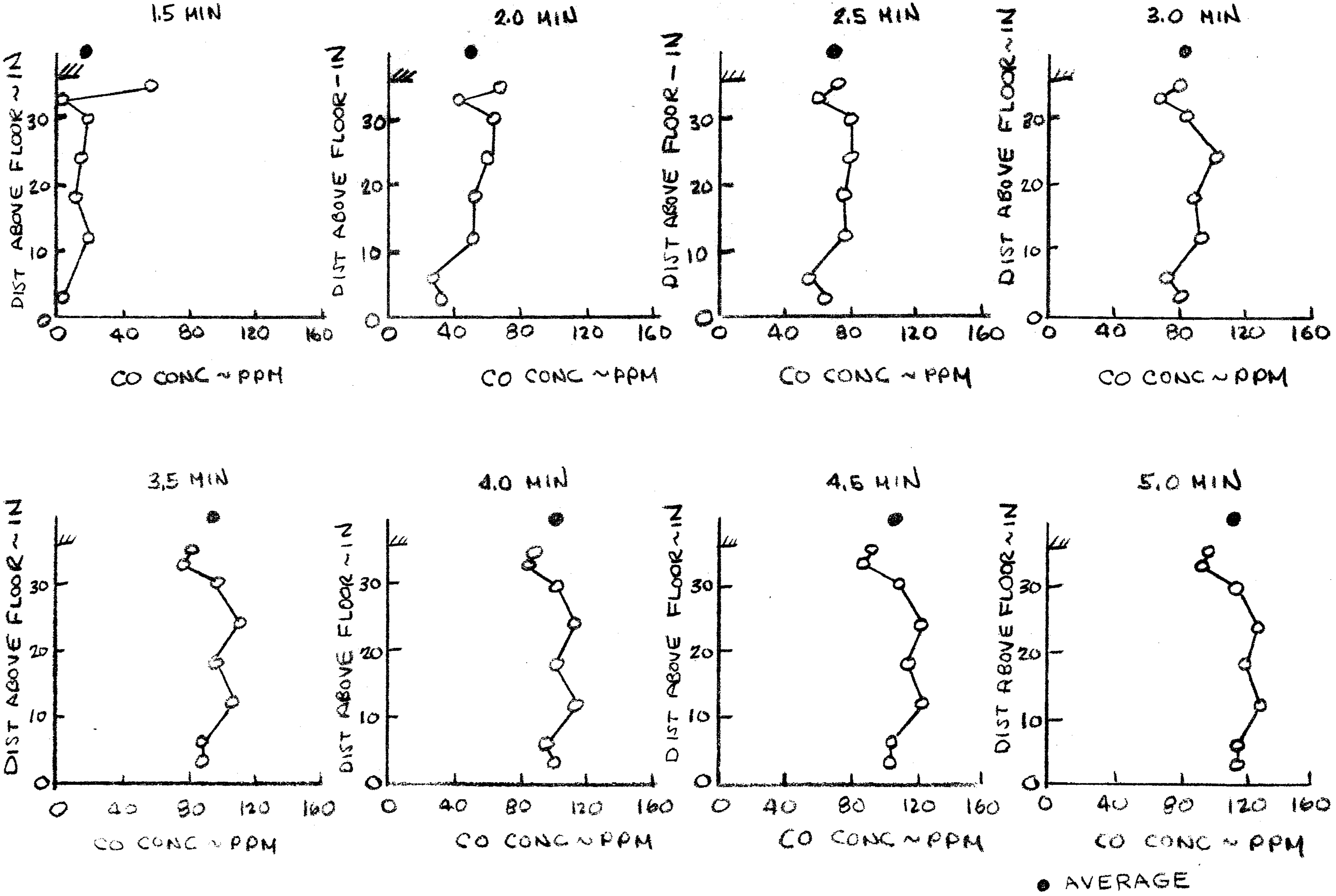


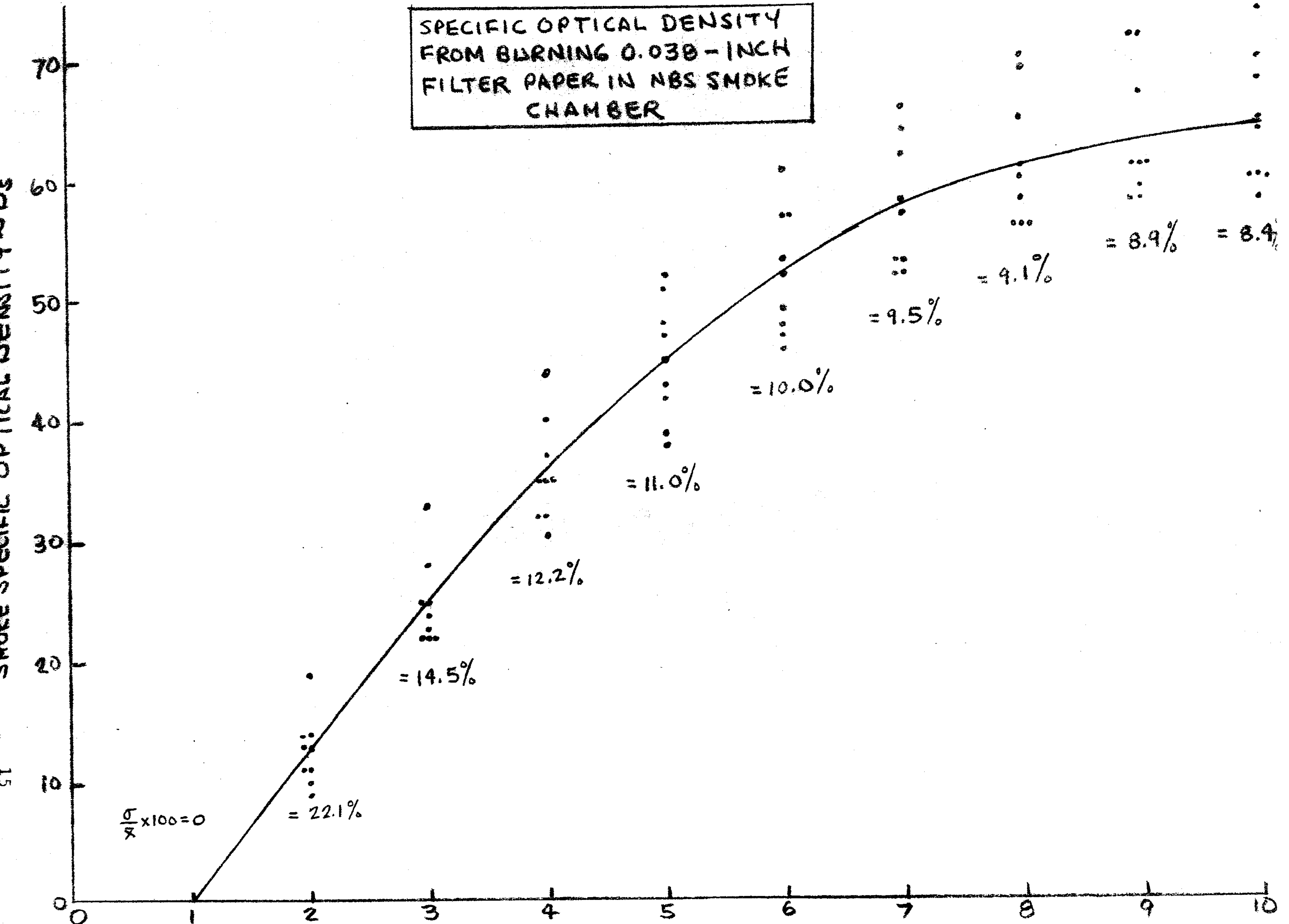
NBS SMOKE CHAMBER BACKGROUND
CARBON MONOXIDE LEVEL FROM
PROPANE/AIR BURNER

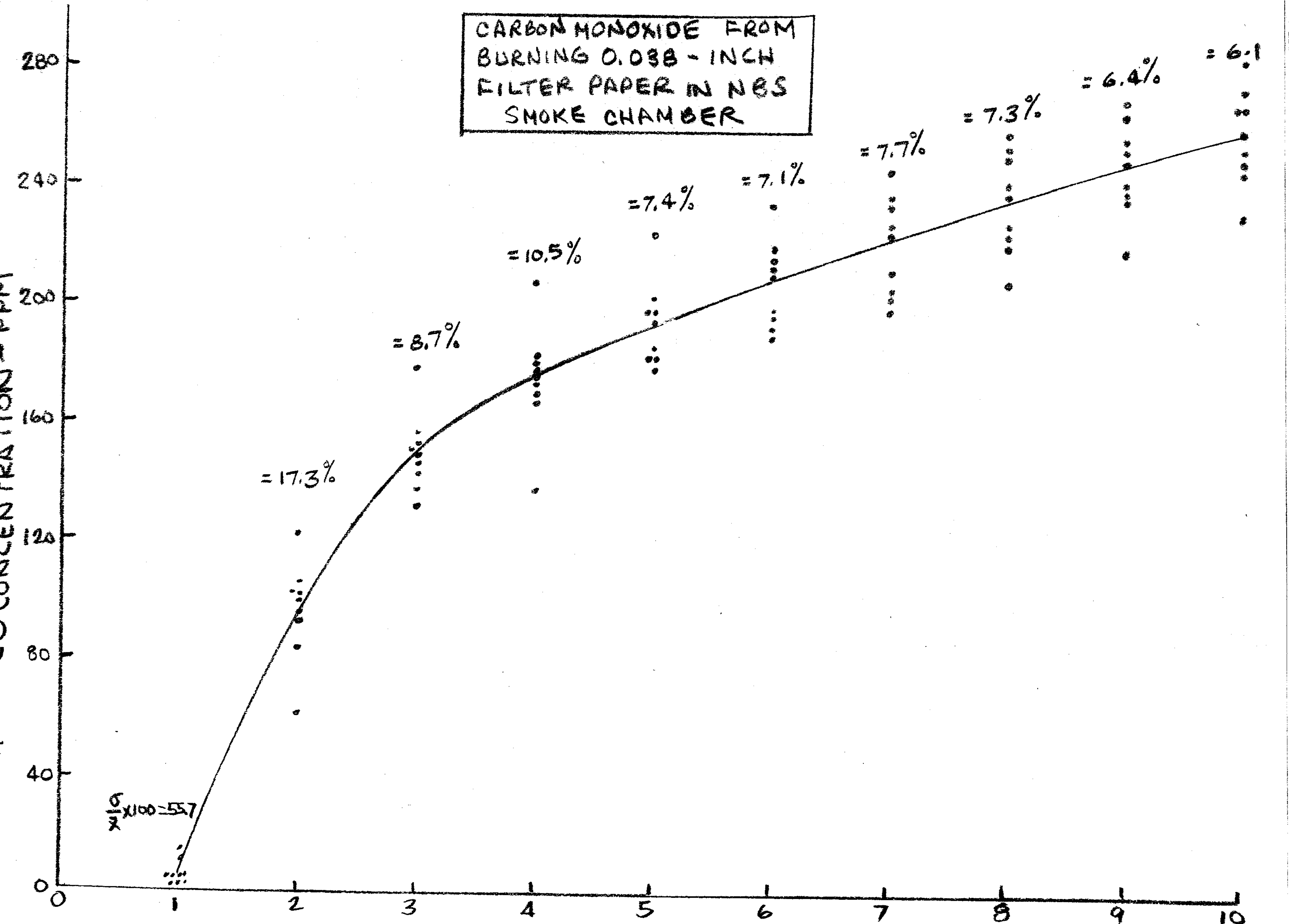
NOTE

① DATA POINTS AVERAGE OF 4 TESTS
② 95°F INITIAL CHAMBER WALL TEMP
③ DATA <u>NOT</u> CORRECTED FOR SAMPLING LINE LAG TIME DELAY
④ CONCENTRATION AT CHAMBER GEOMETRIC CENTER

STRATIFICATION OF CARBON MONOXIDE IN THE NBS SMOKE CHAMBER DURING FLAMING EXPOSURE OF FILTER PAPER




SPECIFIC OPTICAL DENSITY FROM BURNING 0.038-INCH FILTER PAPER IN NBS SMOKE CHAMBER
SMOKE SPECIFIC OPTICAL DENSITY Ds
0
10
20
30
40
50
60
70
0
1
2
3
4
5
6
7
8
9
10
σ/x ×100=0
= 22.1%
= 14.5%
= 12.2%
= 11.0%
= 10.0%
= 9.5%
= 9.1%
= 8.9%
= 8.4

CARBON MONOXIDE FROM BURNING 0.038 - INCH FILTER PAPER IN NBS SMOKE CHAMBER
O CONCENTRATION - PPM
0
40
80
120
160
200
240
280
0
1
2
3
4
5
6
7
8
9
10
$\frac{\sigma}{\bar{x}} \times 100 = 55.7$
= 17.3%
= 8.7%
= 10.5%
= 7.4%
= 7.1%
= 7.7%
= 7.3%
= 6.4%
= 6.1

STRACTIFICATION OF HYDROGEN CHLORIDE IN THE NBS SMOKE CHAMBER & SMOLDERING COMBUSTION OF PVC.

TEST NO	SAMPLE WEIGHT (g.)	CHLORIDE COLLECTED (µg/l) AT VARIOUS SAMPLE PROBE DEPTHS		
		6"	18"	30"
1	12.58	3,160	2,750	3,360
2	12.71	4,150	3,360	2,710
3	12.77	1,330	1,095	935

FIGURE 19

Reproducibility of the Hydrogen Chloride Concentration ~ Time Curve : Smoldering Combustion of PVC at 18 inches

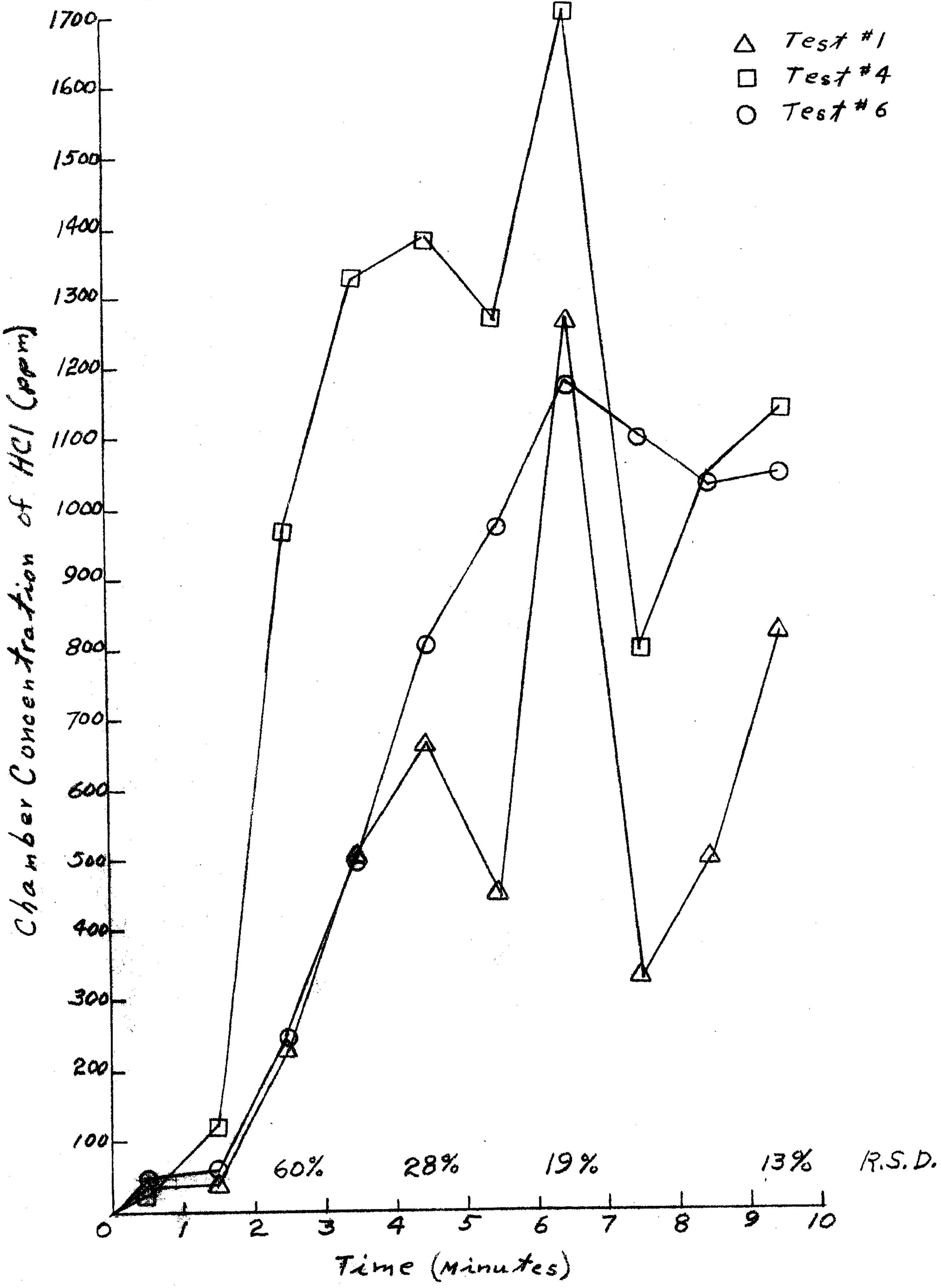


FIGURE 20

THE EFFECT OF CHAMBER CONDITIONING ON HYDROGEN CHLORIDE RECOVERY

TEST NUMBER	SAMPLE WEIGHT (g)	CHLORIDE COLLECTED (μg)	MAXIMUM CONCENTRATION (PPM)	FILTER (μg)	FILTER HOLDER (μg)	THEORETICAL YIELD (%)
1	13.07	7,920	1,270	100	4,900	14
2	12.44	11,845	1,160	182	7,750	13
3	12.36	6,790	1,290	68	51	15
4	12.24	6,960	1,710	128	310	20
5	12.84	15,540	4,690	410	74	52
6	12.38	6,980	1,180	95	2200	14

FIGURE 21

MASS BALANCE FOR HYDROGEN CHLORIDE IN THE NBS SMOKE CHAMBER: SMOLDERING COMBUSTION OF 98% PURE PVC.

SAMPLE WEIGHT	4.9	g
CHLORIDE COLLECTED	9,630	μg
GLASS PROBE	0.7	%
SAMPLE LINE	0.3	%
FILTER ASSEMBLY	21	%
IMPINGERS	78	%
CHAMBER WALL	0.9	%
THEORETICAL YIELD	38	%

FIGURE 22

COMBUSTION TUBE ASSEMBLY

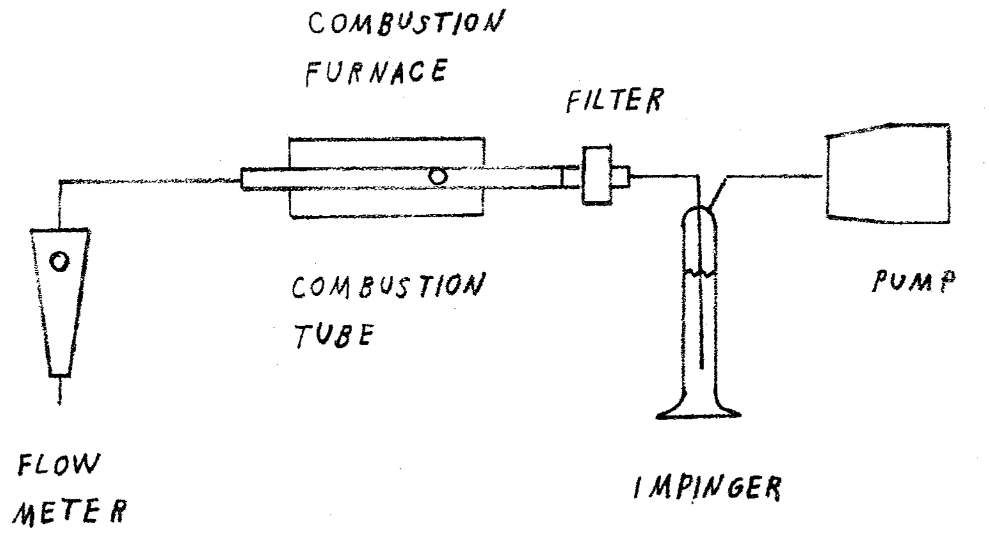


FIGURE 23

HYDROGEN CHLORIDE RECOVERY FROM PVC FOAM AS A FUNCTION OF SAMPLE WEIGHT

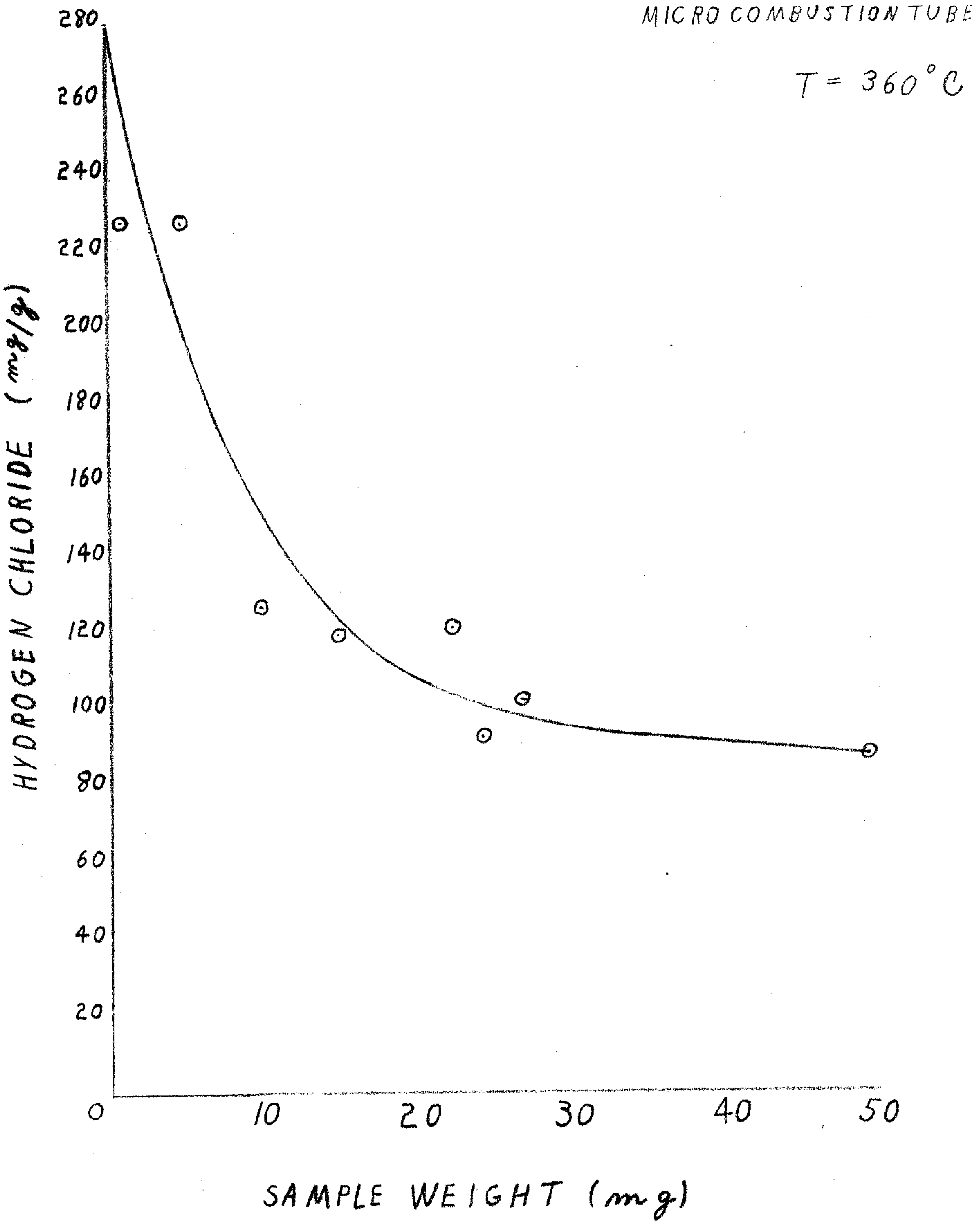


FIGURE 24

RECOVERY OF HYDROGEN CYANIDE
FROM THE COMBUSTION TUBE FURNACE
FOR A NOMEX FABRIC AS A FUNCTION
OF SAMPLE WEIGHT

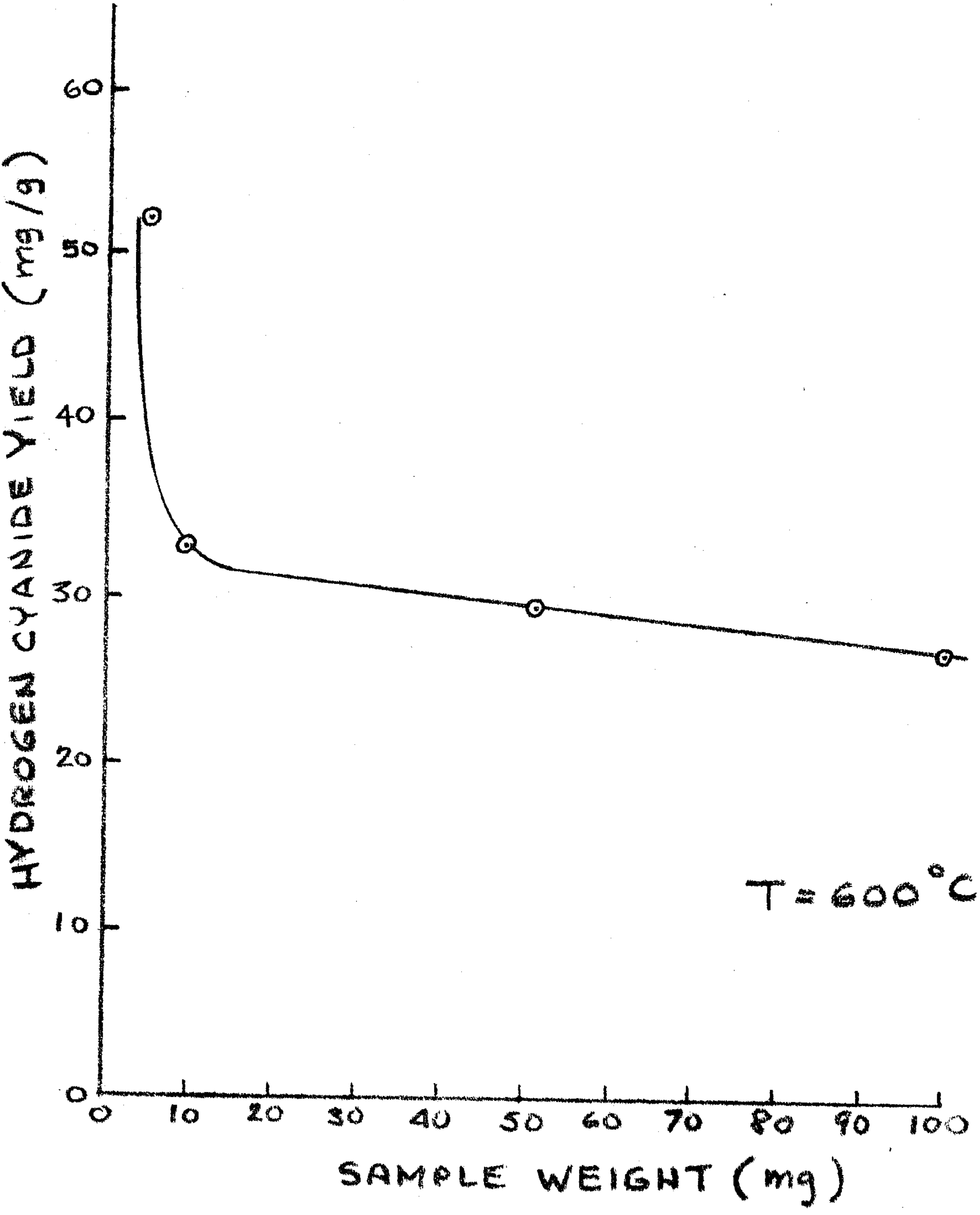


FIGURE 25

THE EFFECT OF TEST TIME ON HYDROGEN CYANIDE RECOVERY FROM A NOMEX FABRIC TESTED IN THE MICRO COMBUSTION FURNACE

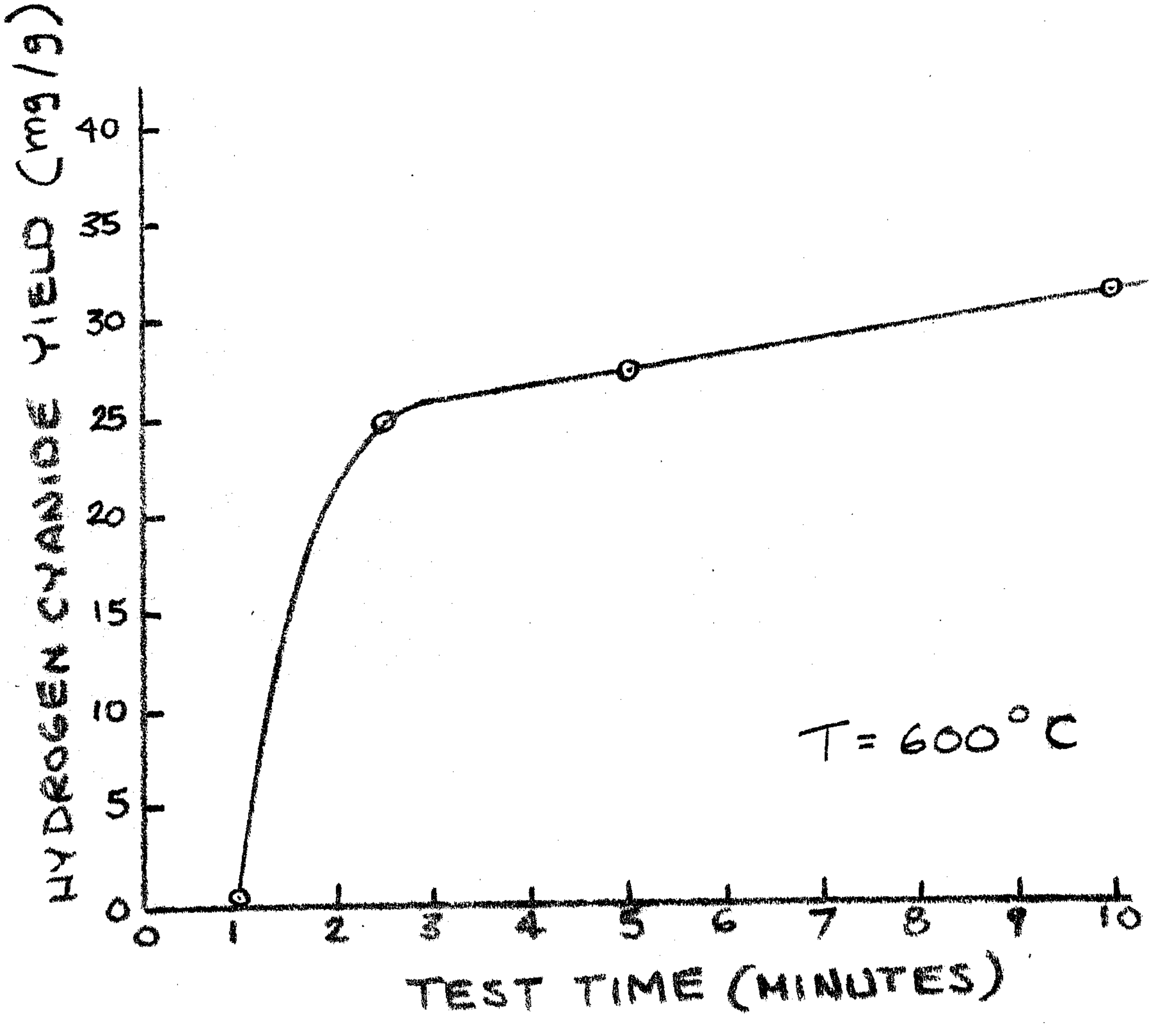


FIGURE 26

THE EFFECT OF VENTILATION RATE ON THE RECOVERY OF HYDROGEN CYANIDE FROM THE MICRO COMBUSTION FURNACE

VENTILATION RATE (cc/min)	SAMPLE WEIGHT (mg)	HCN YIELD (mg/g)
50	10.4	35.8
100	10.3	31.0
200	9.8	33.5
400	9.8	23.3

SAMPLE : NOMEX

TEST TIME : 10 MINUTES

FIGURE 27

HYDROGEN CHLORIDE RECOVERY AS A FUNCTION OF SAMPLE WEIGHT: COMBUSTION TUBE ANALYSIS OF 98% PURE PVC

SAMPLE WEIGHT (g)	THEORETICAL YIELD (%)	IMPINGERS (%)
0.0301	114.5	99.5
0.0300	109.8	99.7
0.0217	105.1	99.1
0.0158	95.5	98.7
0.0033	91.9	93.8

FIGURE 28

HYDROGEN CHLORIDE DISTRIBUTION IN THE COMBUSTION TUBE SYSTEM AS A FUNCTION OF SAMPLE MATERIAL COMPOSITION

SAMPLE MATERIAL COMPOSITION	GLASS TUBE (%)	FILTER (%)	FILTER HOLDER (%)	IMPINGER (%)	THEORETICAL YIELD (%)
PVC PLASTIC (98 %)	0.15	0.2	0.3	99.4	103.4
PVC FABRIC (100 %)	0.14	0.15	0.2	99.4	105.2
PVC FABRIC (51 %)	15.9	3.7	1.2	78.6	106.5
PVC FABRIC (24 %)	28.5	18.8	3.1	49.7	165.6

FIGURE 29

SUMMARY OF FINDINGS FOR THE MEASUREMENT OF HCl IN A COMBUSTION GAS MIXTURE

① IMPINGER FLOW SYSTEM

Ⓐ TEMPERATURE, PRESSURE, AND FLOW FLUCTUATI
ARE A SOURCE OF POSSIBLE ERROR

Ⓑ PROBE AND SAMPLE TRANSFER LINES DO NOT
REQUIRE ANY ADDITIONAL MODIFICATIONS

Ⓒ FILTER ASSEMBLY DOES REQUIRE ADDITIONAL
INVESTIGATION

② NBS SMOKE CHAMBER

Ⓐ SOME INDICATION THAT SEVERAL GASES MAY
BE STRATIFIED WITHIN THE CHAMBER

① FAN
② MULTIPLE SAMPLING PROBES

Ⓑ REPRODUCIBILITY OF PEAK CONCENTRATIONS AND
SAMPLE RECOVERY IS GENERALLY POOR

① % THEORETICAL YIELD

Ⓒ CONDITIONING THE CHAMBER MAY HAVE SOME
EFFECT ON SAMPLE RECOVERY, BUT NOT A
SIGNIFICANT AMOUNT

③ MICRO COMBUSTION TUBE

Ⓐ GENERALLY QUANTITATIVE SAMPLE RECOVERY

Ⓑ SAMPLE PARAMETERS (WEIGHT, COMPOSITION)
GREATLY INFLUENCE THE RESULTS

FIGURE 30

RECOMMENDATIONS

APPLY A COÖRDINATED APPROACH TO THE ANALYSIS OF TOXIC COMBUSTION GASES. THIS APPROACH WOULD EMPLOY THREE PRIMARY TEST METHODS TO CHARACTERIZE MATERIALS.

1. NBS SMOKE CHAMBER
    - A) MAXIMUM SMOKE CONCENTRATION
    - B) CONCENTRATION-TIME PROFILE FOR SELECT TOXIC GASES
2. COMBUSTION TUBE
    - A) QUANTITATIVE GAS ANALYSIS
    - B) RELATIVE RANKING OF MATERIALS
        - 1.) CLASS RANKING
        - 2.) GENERAL RANKING
3. THERMAL GRAVIMETRIC ANALYSIS
    - A) WEIGHT LOSS VS. SAMPLE TEMPERATURE
    - B) CLOSELY CONTROLLED EXPERIMENTAL PARAMETERS

FIGURE 31

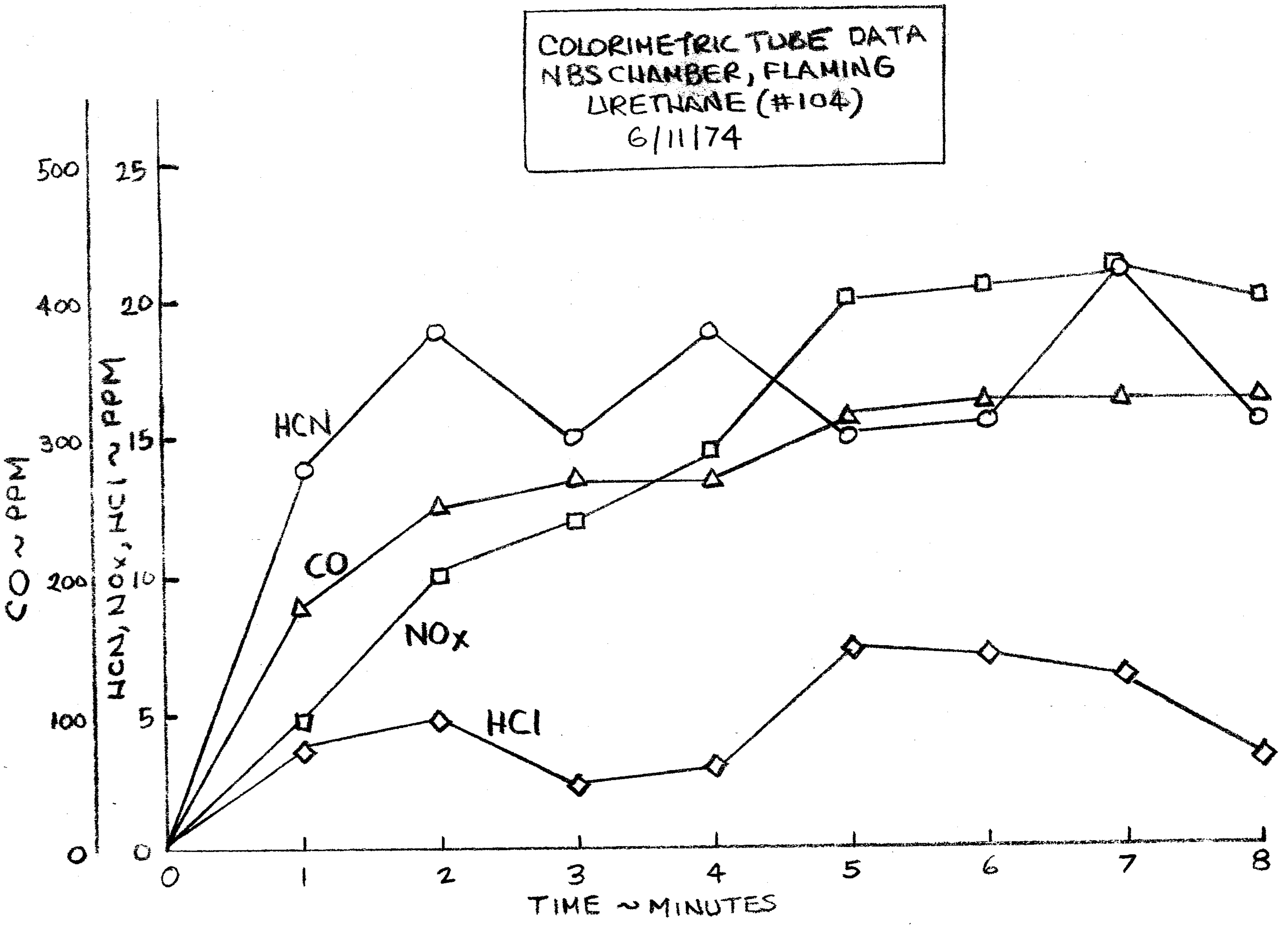
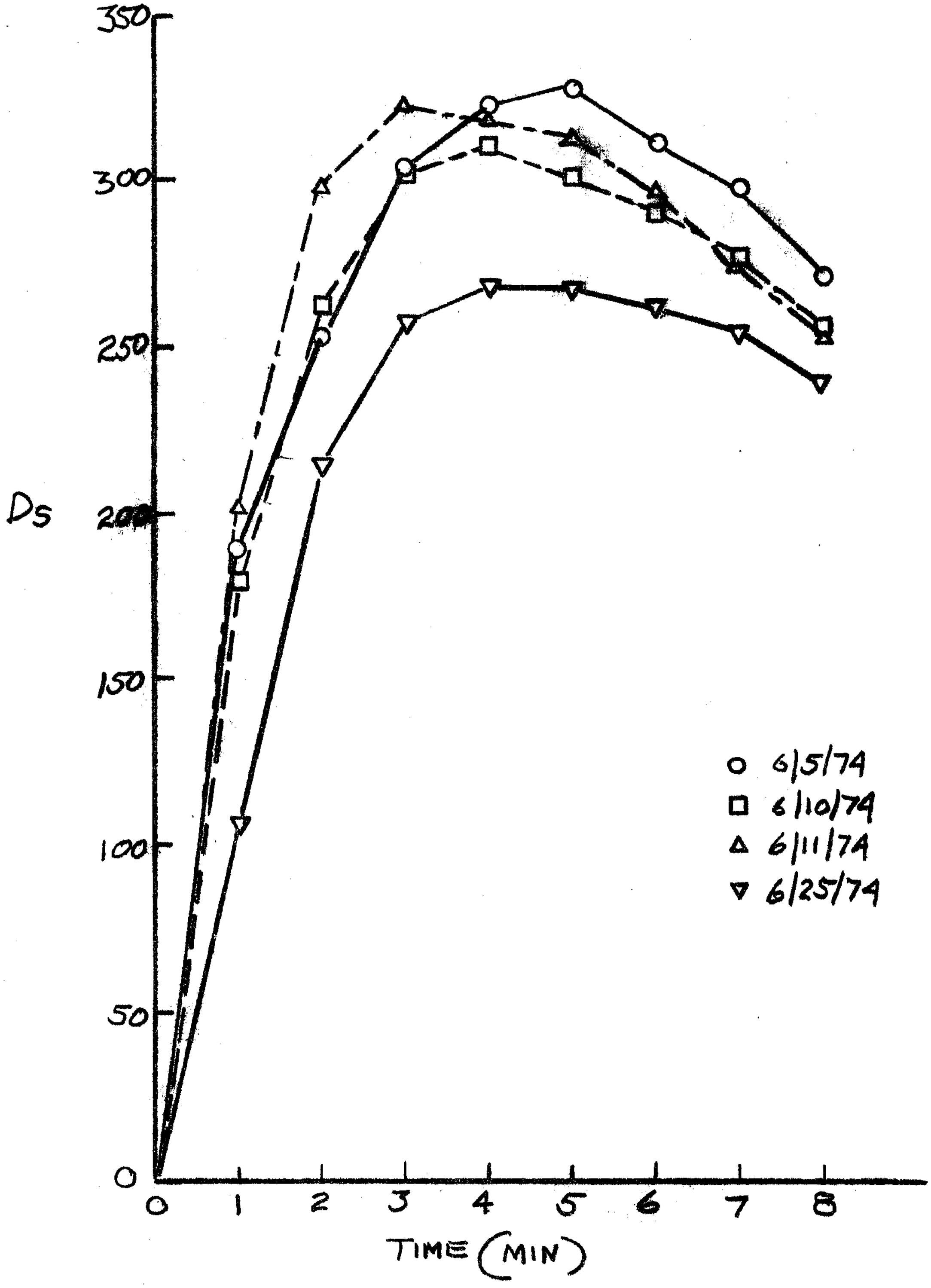

COLORIMETRIC TUBE DATA
NBS CHAMBER, FLAMING
URETHANE (#104)
6/11/74
CO ~ PPM
HCN, NOx, HCl ~ PPM
500
400
300
200
100
0
25
20
15
10
5
0
HCN
CO
NOx
HCl
0
1
2
3
4
5
6
7
8
TIME ~ MINUTES

FIGURE 6



SPECIFIC OPTICAL DENSITY
URETHANE FOAM (#104)
FLAMING EXPOSURE

FIGURE 7

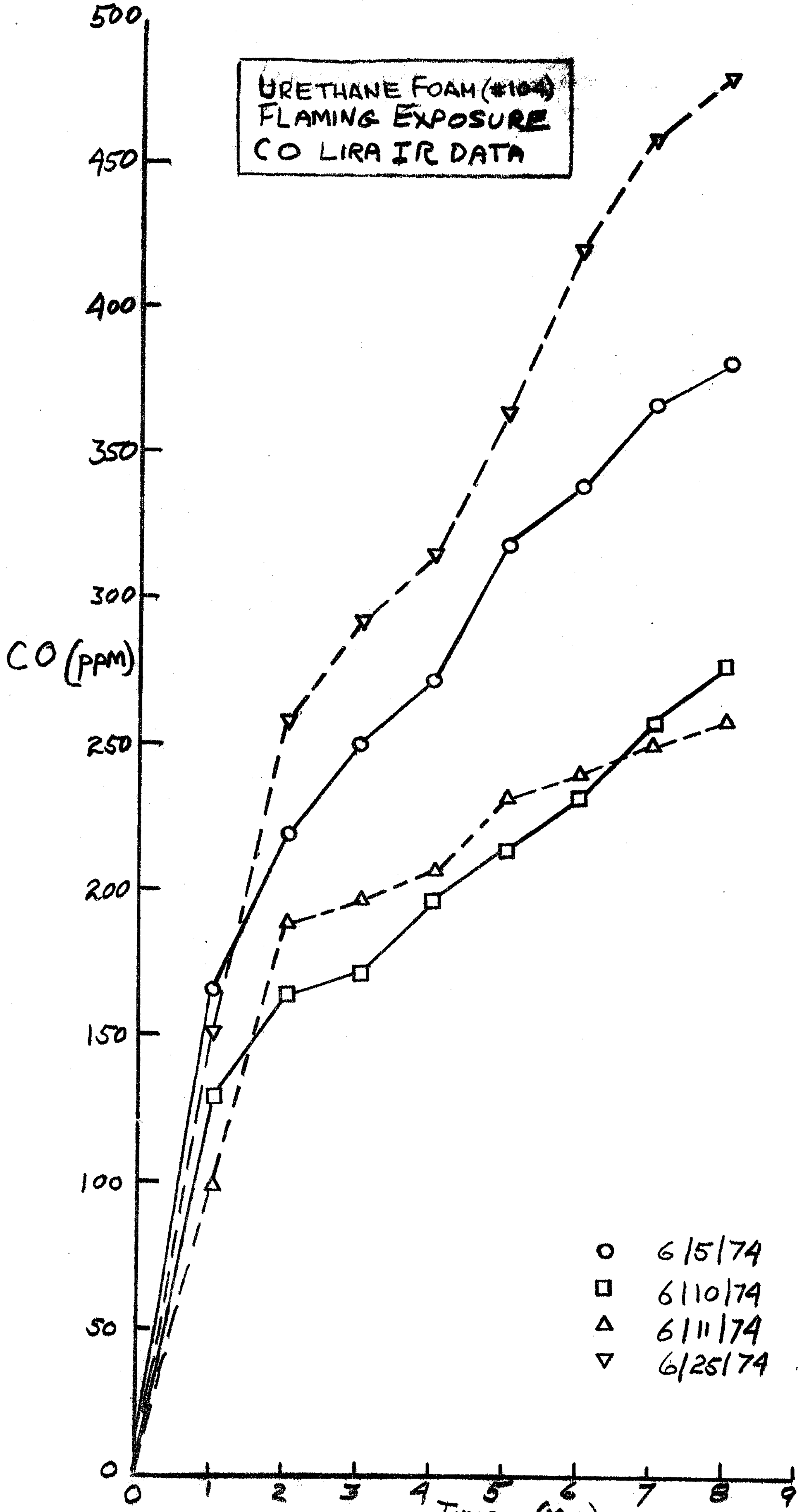
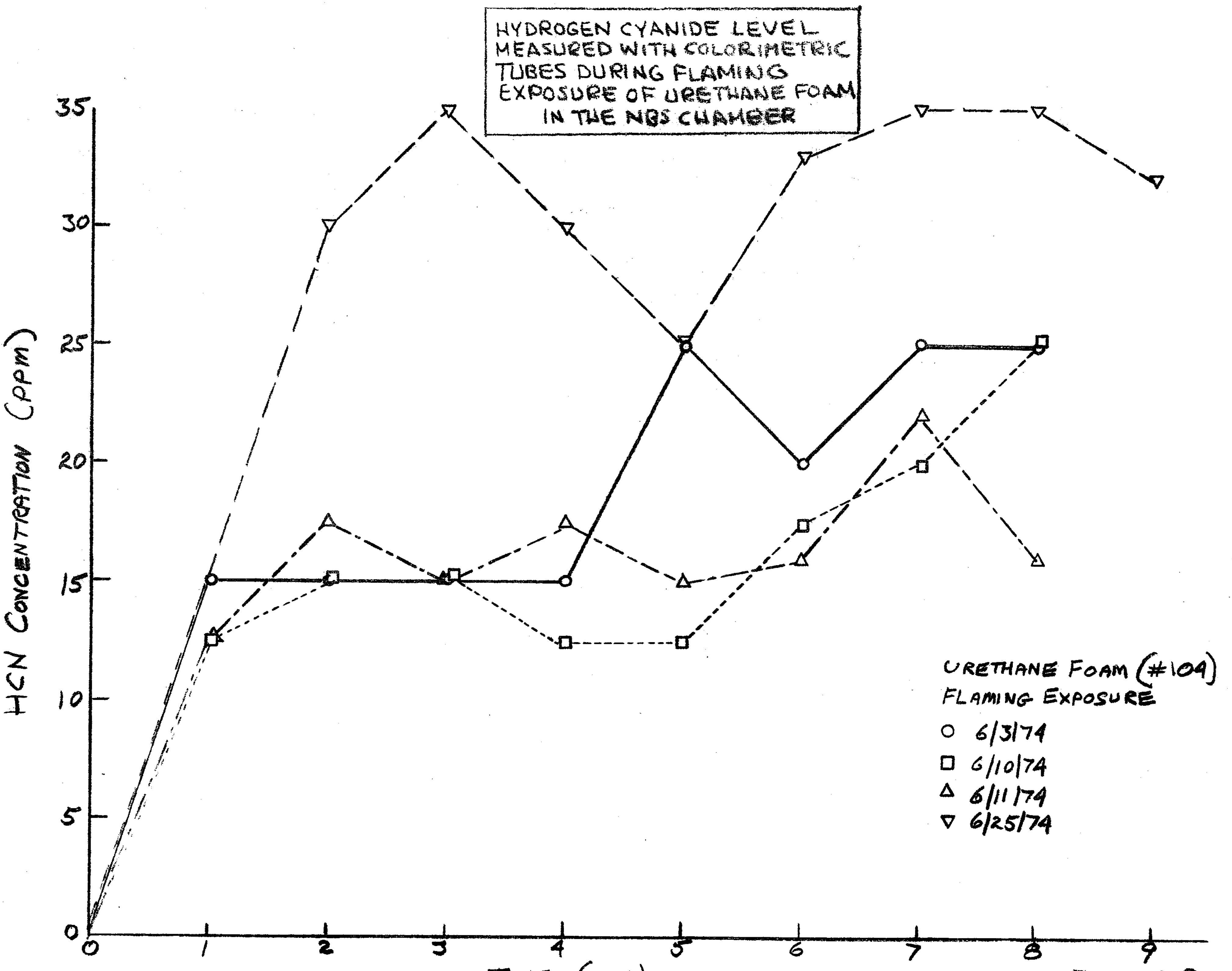

URETHANE FOAM (#104)
FLAMING EXPOSURE
CO LIRA IR DATA
CO (PPM)
500
450
400
350
300
250
200
150
100
50
0
0
1
2
3
4
5
6
7
8
9
○ 6/5/74
□ 6/10/74
△ 6/11/74
▽ 6/25/74

FIGURE 8


HYDROGEN CYANIDE LEVEL MEASURED WITH COLORIMETRIC TUBES DURING FLAMING EXPOSURE OF URETHANE FOAM IN THE NBS CHAMBER
HCN CONCENTRATION (PPM)
0
5
10
15
20
25
30
35
0
1
2
3
4
5
6
7
8
9
URETHANE FOAM (#104)
FLAMING EXPOSURE
○ 6/3/74
□ 6/10/74
△ 6/11/74
▽ 6/25/74

UTILIZATION OF COLORIMETRIC TUBES AND SAMPLING BAGS

1. SUBJECTIVE READING OF STAIN LENGTH (CONCENTRATION) IN GOOD AGREEMENT
2. COLORIMETRIC TUBE MEASUREMENTS ARE REPRODUCIBLE (GOOD QUALITY CONTROL)
3. CO COLORIMETRIC TUBE INDICATES 40-50% HIGH IN URETHANE COMBUSTION GAS MIXTURES
4. HCl COLORIMETRIC TUBE RANGE (500 PPM) IS SIGNIFICANTLY BELOW THE LEVEL OF HCl PRODUCED BY SOME MATERIALS TESTED IN THE NBS CHAMBER
5. CO, HCN, NO_x, SO_2 AND ALDEHYDES CAN BE MEASURED IN SARAN BAG COMBUSTION GAS SAMPLES (NO APPARENT BAG LOSSES)
6. HCl AND HF MUST BE MEASURED DIRECTLY FROM THE NBS CHAMBER (OVER 90% BAG LOSSES)
7. COLORIMETRIC TUBE ACCURACY DECREASES SIGNIFICANTLY ON THE HIGH SCALE (LEAST # OF PUMP STROKES)
8. $COCl_2$, NH_3 AND H_2S HAVE NOT BEEN DETECTED IN THE COMBUSTION GASES OF MATERIALS TESTED THUS FAR

FIGURE 10

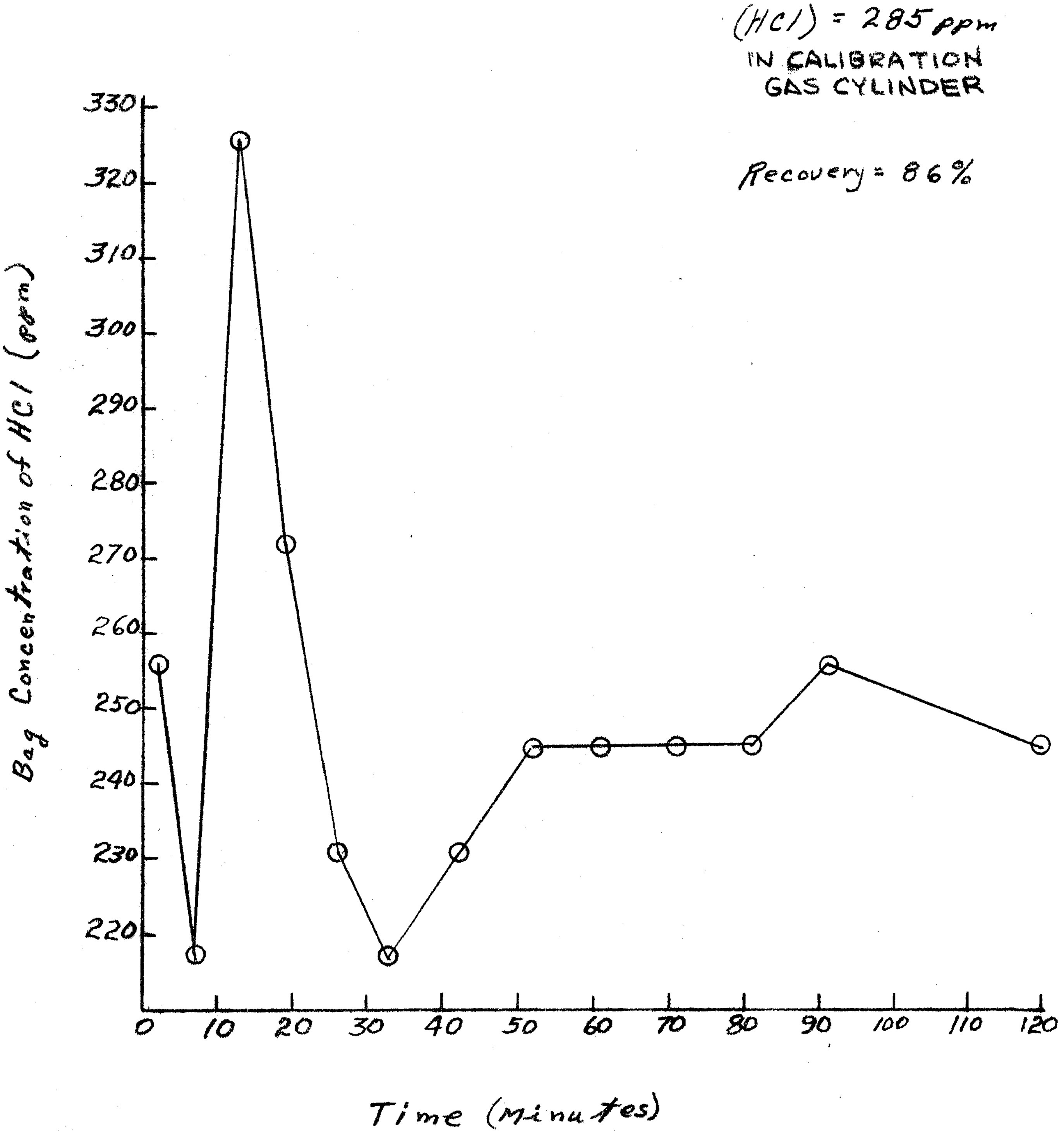
TOXICITY OF BURNING MATERIALS
METHOD OF ANALYSIS

1. COMBUSTION OF MATERIALS:
    - a. NBS SMOKE CHAMBER
        - 1. SMOLDERING - ONE TEST
        - 2. FLAMING - ONE TEST
2. QUALITATIVE ANALYSIS:
    - a. INFRARED SPECTROSCOPY
        - 1. GASES
            - a. BAG SAMPLING
            - b. CALIBRATION GASES
                - 1 INFRARED CALIBRATION
                - 2. DECAY CURVES
                - 3. DETECTOR TUBES
                - 4. IMPINGER EFFICIENCY
        - 2. MATERIALS
            - a. ATR
3. QUANTITATIVE ANALYSIS:
    - a. ION SELECTIVE POTENTIOMETRY
        - 1. IMPINGER SAMPLING

FIGURE 11

Concentration - Time Curve for Hydrogen Chloride in a Conditioned Teflon Bag

Syringe Sampling


(HCl) = 285 ppm
IN CALIBRATION
GAS CYLINDER

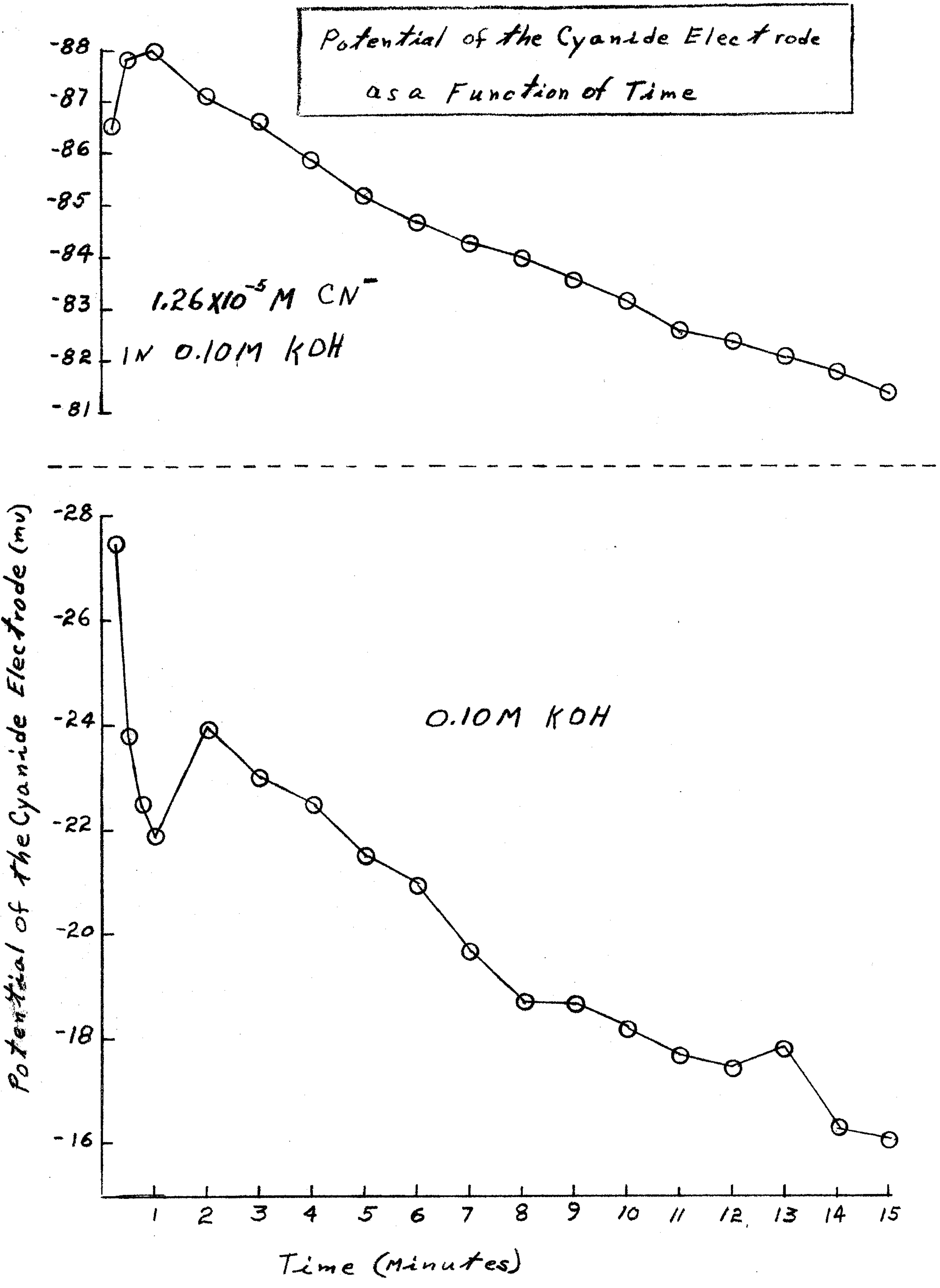
Recovery = 86%

FIGURE 12

ION SELECTIVE ELECTRODES

1. SHIFTS IN THE CALIBRATION CURVE
    a. REFERENCE ELECTRODE
    b. ADSORBED SPECIES
2. SELECTIVE RESPONSE TO SEVERAL IONS
    a. CHLORIDE ELECTRODE
        1. SULFIDE, BROMIDE, CYANIDE
        2. HIGH RECOVERY OF CHLORIDE FROM WOOL/PVC BLENDS
3. LIMIT OF DETECTION
    a. CHLORIDE ELECTRODE
        1. 0.1 PPM IN WATER
        2. 10 PPM IN NAOH
4. STABILITY OF ELECTRODE RESPONSE
    a. CYANIDE ELECTRODE
        1. DRIFTING POTENTIALS
        2. TIME OF ANALYSIS

FIGURE 13



Potential of the Cyanide Electrode as a Function of Time

FIGURE 1A

CALBRATION CURVE FOR CYANIDE IN 0.1M KOH

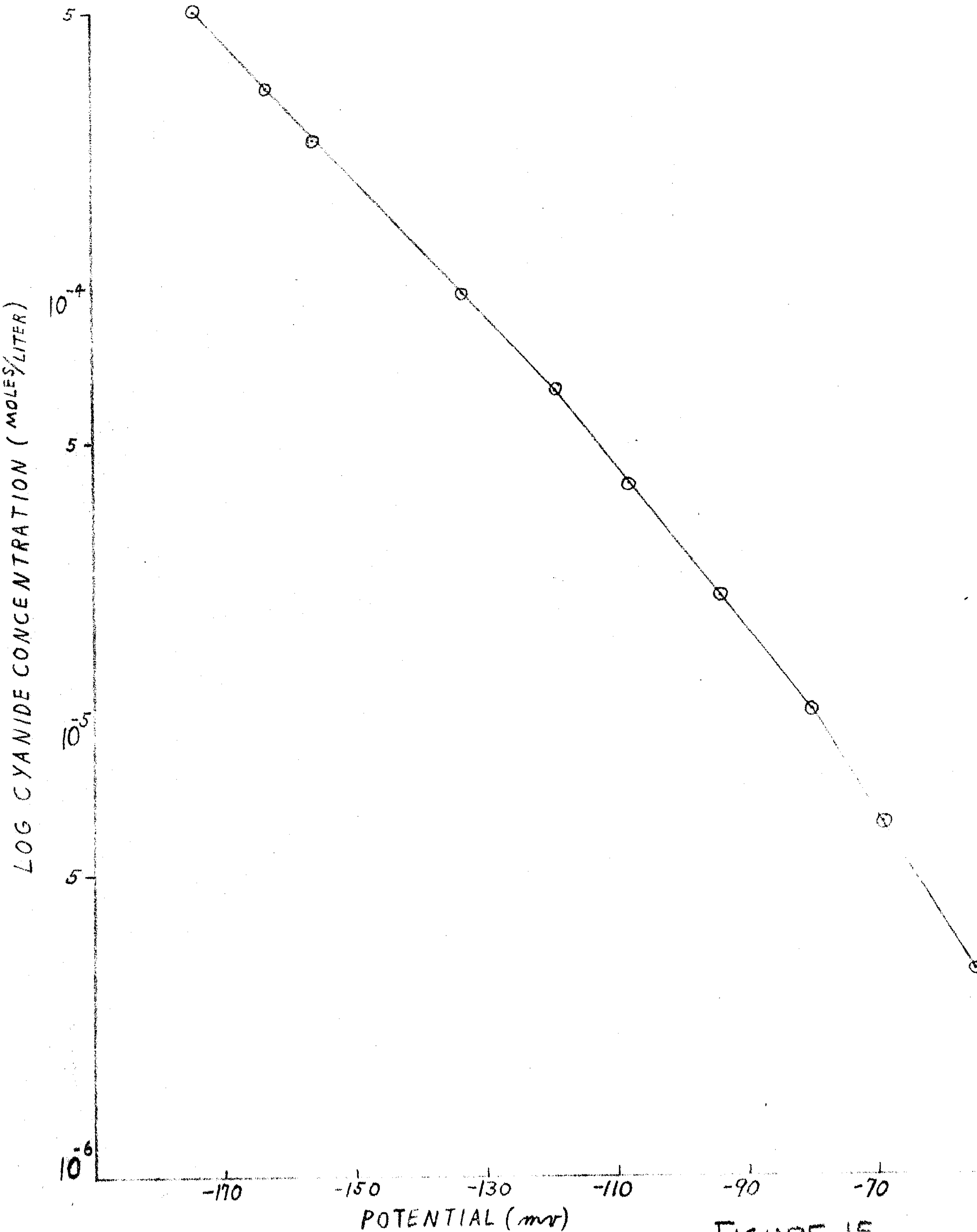


FIGURE 15

SCHEMATIC DIAGRAM OF THE IMPINGER SAMPLING SYSTEM

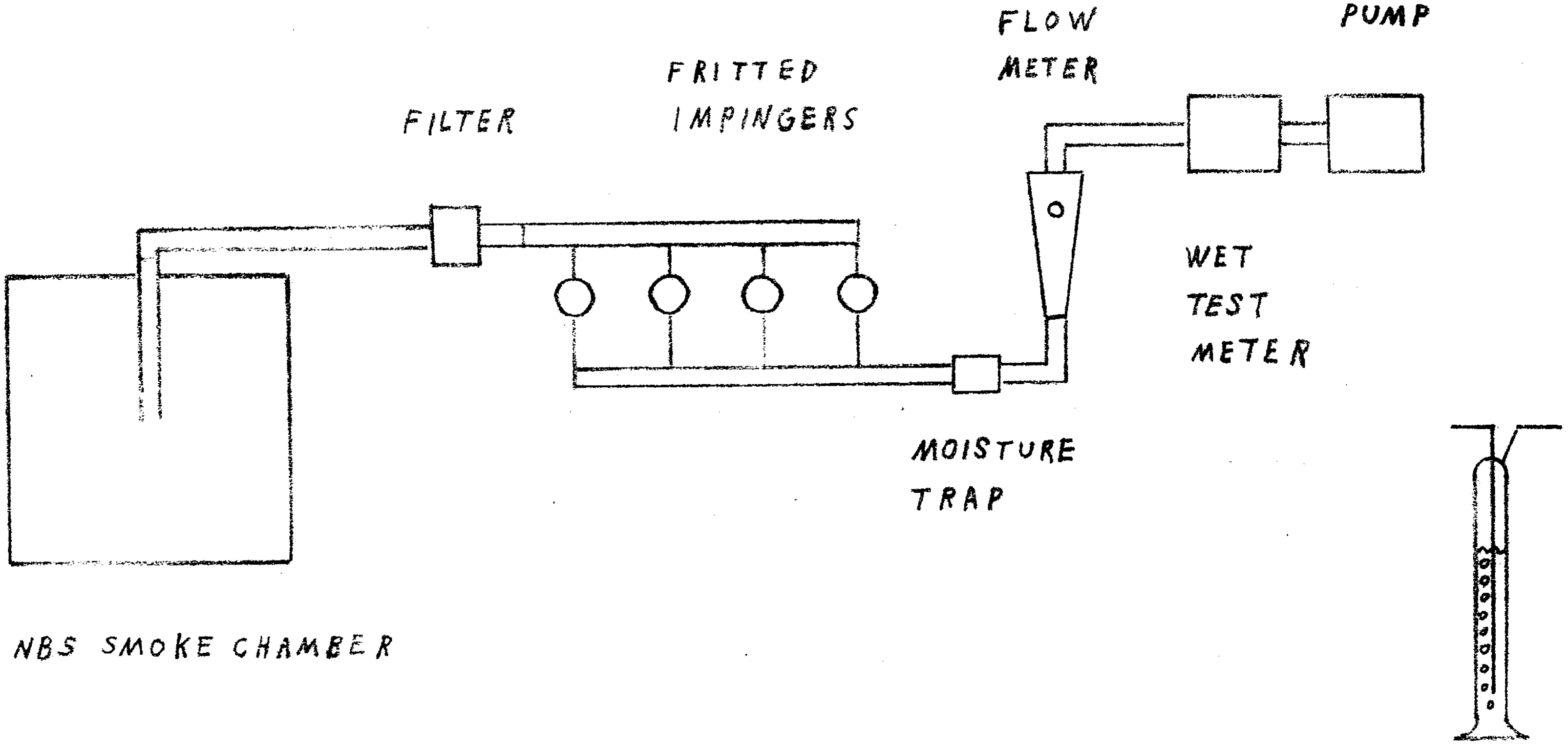


FIGURE 16

APPLICABILITY OF FILTER MATERIALS AND FILTER HOLDERS TO THE ANALYSIS OF HYDROGEN CHLORIDE

	FILTER HOLDER		
FILTER	STEEL	POLYETHLENE	TEFLON
GLASS FIBER	POOR	POOR	POOR
POLYPROPYLENE	POOR	GOOD	GOOD
TEFLON	POOR	POOR	POOR

FIGURE 17

HYDOGEN CHLORIDE RECOVERY AS A FUNCTION OF FILTER MATERIAL: COMBUSTION TUBE ANALYSIS OF A PVC FOAM

FILTER MATERIAL	FILTER (%)	IMPINGER (%)
POLYPROPYLENE	13.3	66.7
TEFLON	15.5	61.8
GLASS FIBER	42.4	48.0

POLYETHYLENE FILTER HOLDER

FIGURE 18