EPA-650/2-74-006

December 1973

Environmental Protection Technology Series

DEVICE FOR COLLECTION AND ASSAY OF AMBIENT GASES

Office of Research and Development
U.S. Environmental Protection Agency
Washington, DC 20460

EPA-650/2-74-006

DEVICE FOR COLLECTION AND ASSAY OF AMBIENT GASES

by

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Contract No. 68-02-0657

Project Element No. 1AA010

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Prepared for

OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

December 1973

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SECTION 1

INTRODUCTION

Most current methods for collection and assay of ambient pollutant gases involve liquid media in bubblers or impingers. These techniques suffer from generally poor collection efficiency, limited sampling capacity, tedious or cumbersome operation, and special handling requirements. They are also troublesome for storage and transportation of reagents, equipment, and collected samples. These drawbacks have provided the impetus for developing better, simpler collection devices. Ambient gas collectors based on solid absorbents offer the most attraction for development, since they would possess the essential physical characteristics to provide simplicity, ruggedness, large capacity for air sampling, stability, and wide selection of analytical methods.

Under EPA Contract No. 68-02-0657, Bendix Research Laboratories developed such a solid-state collection device and transfer interface device for nitrogen oxides. These devices have been evaluated under laboratory conditions and are believed to be highly promising. However, more rigorous field testing is necessary to validate their merits in actual conditions. Presently only very limited field evaluation has been conducted. The scope and main objectives of this development program were as follows:

(1) Design, fabricate, and evaluate small, simple inexpensive collection devices with solid chemical absorbents that

quantitatively collect atmospheric gases under realistic field conditions. The device should require a minimum of non-technical training for proper use and should survive mail shipment without damage or loss of sample. Devices for collection and transportation of nitrogen dioxide (NO_2) and nitric oxide (NO) have first priority, with development of a prototype device for these gases the primary goal. The physical design of the collection device should be such that it can adapt readily to collection of lower priority gases such as sulfur dioxide (SO_2), carbon monoxide (CO), formaldehyde (HCHO), and more complex organic compounds.

(2) Develop an interface device that quantitatively transfers the gas sample, or its derivative, from the collector to an appropriate analytical instrument. The interface device should operate as simply as possible consistent with quantitative sample transfer to specific or multi-pollutant analyzers. The analyzers could range from inexpensive manual intruments to automated, multicomponent analyzers.

The extensive program effort resulted in the following:

- A long list of candidate solid chemical absorbents for NO, NO_2, or both NO and NO_2 (NO_x) collection and their evaluation.
- Selection of triethanolamine hydrochloride (TEA•HCl), m.p. 177-179, for selective NO_2 collection and cobalt oxide for NO and NO_2 collection.

- A collector unit which is
    - Capable of selective and quantitative collection of NO_2 and NO
    - Easy to assemble and disassemble
    - Lightweight (<350g) and rugged
    - Suitable for mailing
    - Adaptable through an interface to a chemiluminescence NO_x analyzer, a gas chromatograph, or a wet chemical analyzer.
    - Easily installed in an air sampler, requiring no special tools or skills.
    - Reusable.
- An air sampling system capable of continuous, unattended operation using 12V DC or 110V AC power.
- A weatherproof shelter to house collector unit, sampling system, timer, and batteries.
- An interface device for recovering pollutant samples from collection cartridges for subsequent analysis.

The details of the different phases of the program are discussed in the following sections. Section 2 contains the instrument description, while Section 3 presents experimental techniques and data analysis. Summary and recommendations are given in Section 4.

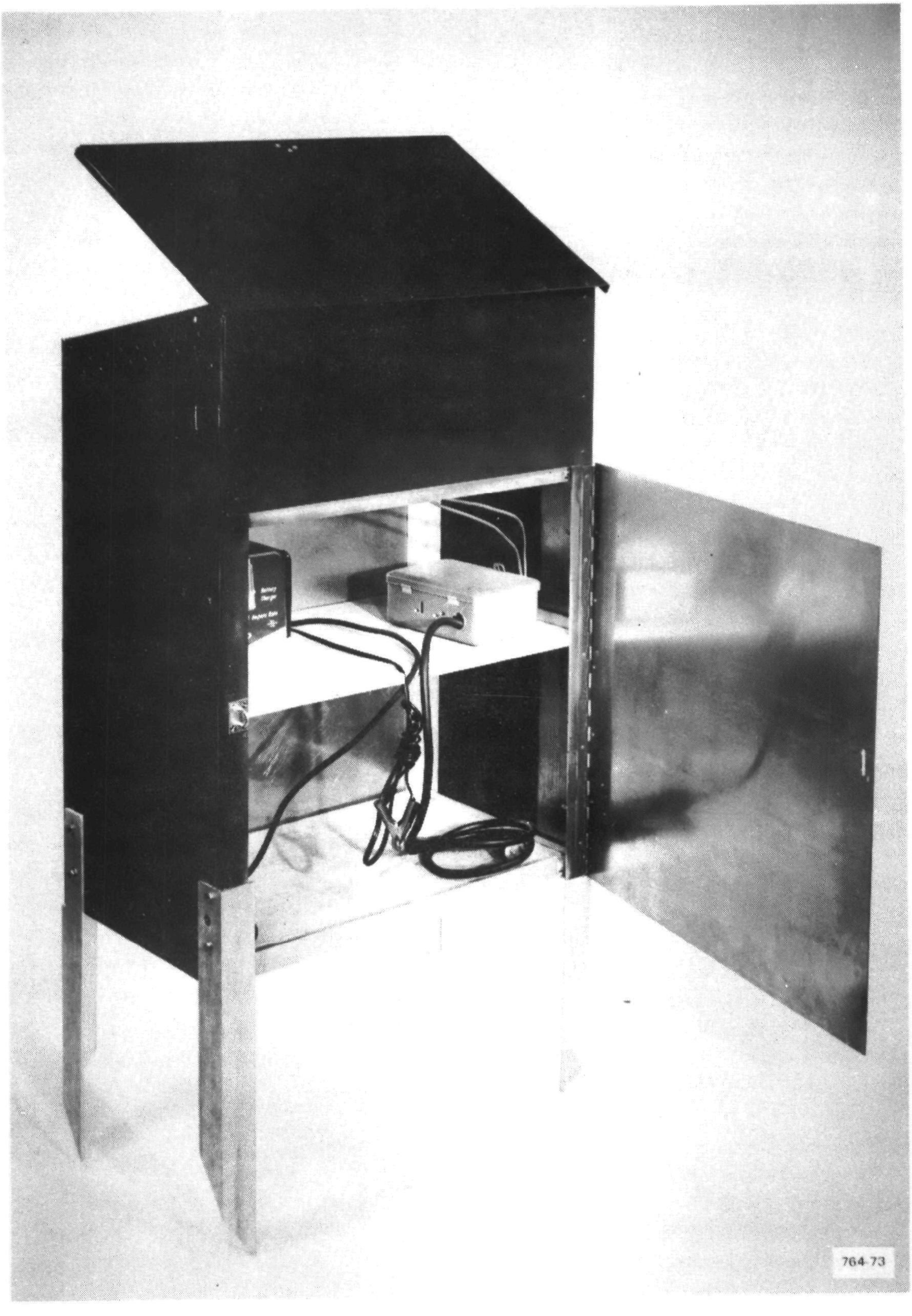


Figure 1 - Collector System

SECTION 2

COLLECTOR SYSTEM DESIGN

2.1 COLLECTOR SYSTEM

The collector system consists of the following major components:

- Collector units
- Vacuum sample pump
- Power supply
- Timer
- System housing

The overall configuration of the system is shown in Figures 1 and 2. The collector pump and collector unit are housed on the top shelf; the second shelf contains the timer and power supply and thus is the control shelf; the bottom shelf holds the battery. A locked door is provided in the front for access to the control switches and battery. The housing is made from 16-gage aluminum with wooden shelves; it has a slanted roof to drain rain or snow. Side holes provide ventilation and ports for a sampling line. The entire housing is hinged so that the housing will fold together into a flat package for easy transporting when the collector system components are removed. Instructions for assembly of the housing are given in Appendix B.

2.2 COLLECTOR UNIT

The collector unit consists of a cylindrical aluminum outer case which houses two Pyrex glass cartridges. These cartridges, individually protected by thin foam plastic covers, are joined tight with a Beckman

Teflon connector (#406). The assembled cartridges are secured into the aluminum case by inserting the inlet and outlet cartridge ends into Beckman bulkhead Teflon fittings (#427) attached to each threaded end-plate of the case. The details of construction are illustrated in Figures 3 and 4.

For actual assembly, one of the collector cartridges is first inserted into the Teflon bulkhead fitting (#427) on the left end-plate (Figure 3) and is secured by finger-tightening the nut on the fitting. The second cartridge is joined to the first via the Beckman Teflon connector (#406) with finger-tight sealing. Next, the bulkhead fitting (#427) is removed from the right end-plate. The free end of the second cartridge is inserted into the removed fitting and secured by tightening the nut. This subassembly (cartridges and fittings) with foam plastic covers is placed into the case, after which the right end-plate and its washer are tightened to the case. Finally, the bulkhead nut and the screw nut are tightened onto the end of the fitting protruding from the right end of the case. This completes the assembly of the collector unit. As assembled, the unit weighs less than 350 g.

A Millipore Swinex 13 #1 filter assembly made of plastic (catalog no. SXG S0130S) is attached to each end of the collector unit. This filter employs Gelman type-A glass fiber filters cut to size. The filter assembly has Luer-lock terminals and is attached to the bulkhead Teflon connector with a nylon female Luer-lock adapter. This adapter is made by cutting in half the Hamilton female/female Luer-lock connector

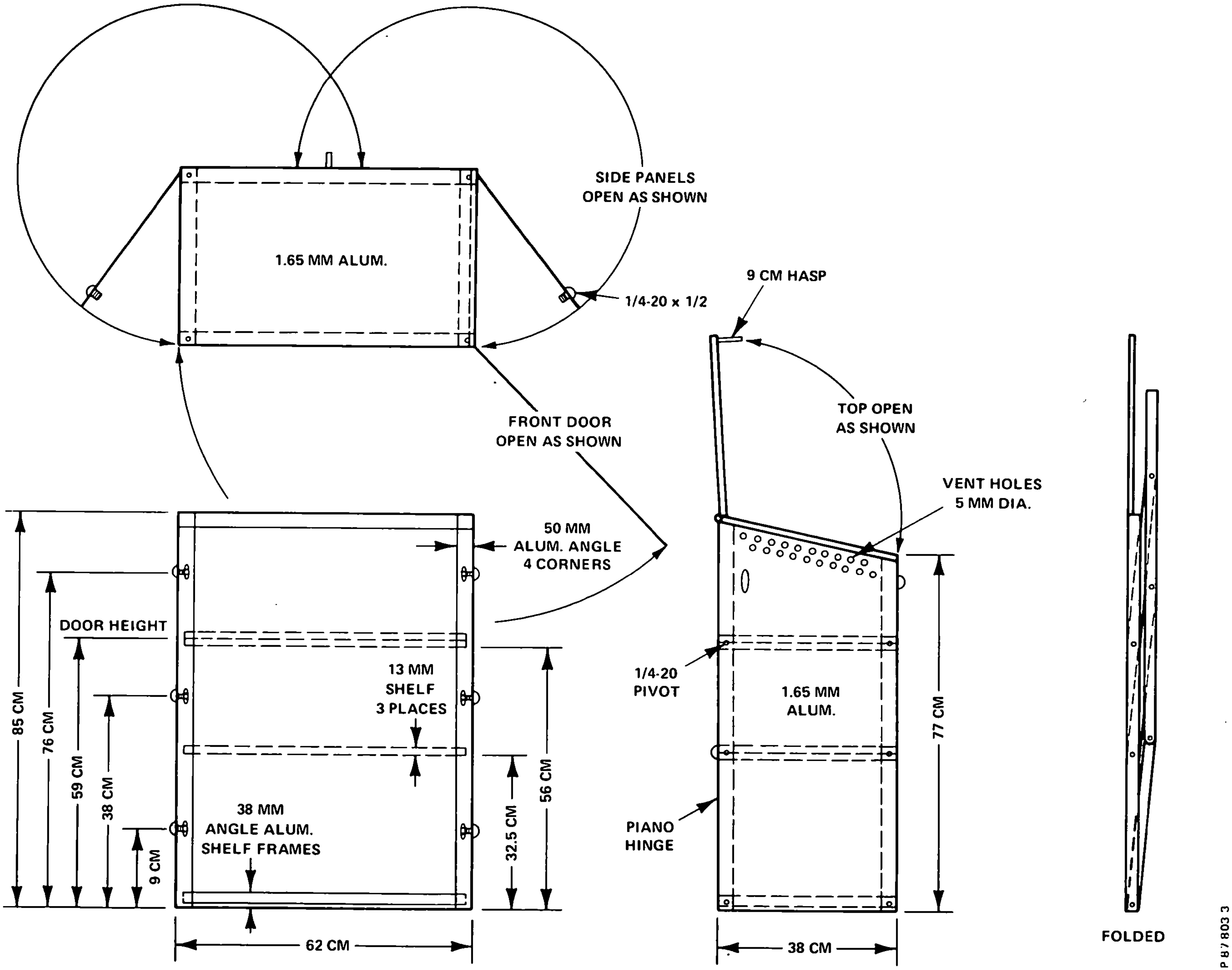

SIDE PANELS
OPEN AS SHOWN
1.65 MM ALUM.
1/4-20 x 1/2
FRONT DOOR
OPEN AS SHOWN
9 CM HASP
TOP OPEN
AS SHOWN
VENT HOLES
5 MM DIA.
50 MM
ALUM. ANGLE
4 CORNERS
DOOR HEIGHT
13 MM
SHELF
3 PLACES
85 CM
76 CM
59 CM
38 CM
9 CM
56 CM
32.5 CM
38 MM
ANGLE ALUM.
SHELF FRAMES
62 CM
1/4-20
PIVOT
1.65 MM
ALUM.
77 CM
PIANO
HINGE
38 CM
FOLDED
P87803 3

Figure 2 - Collector System Housing

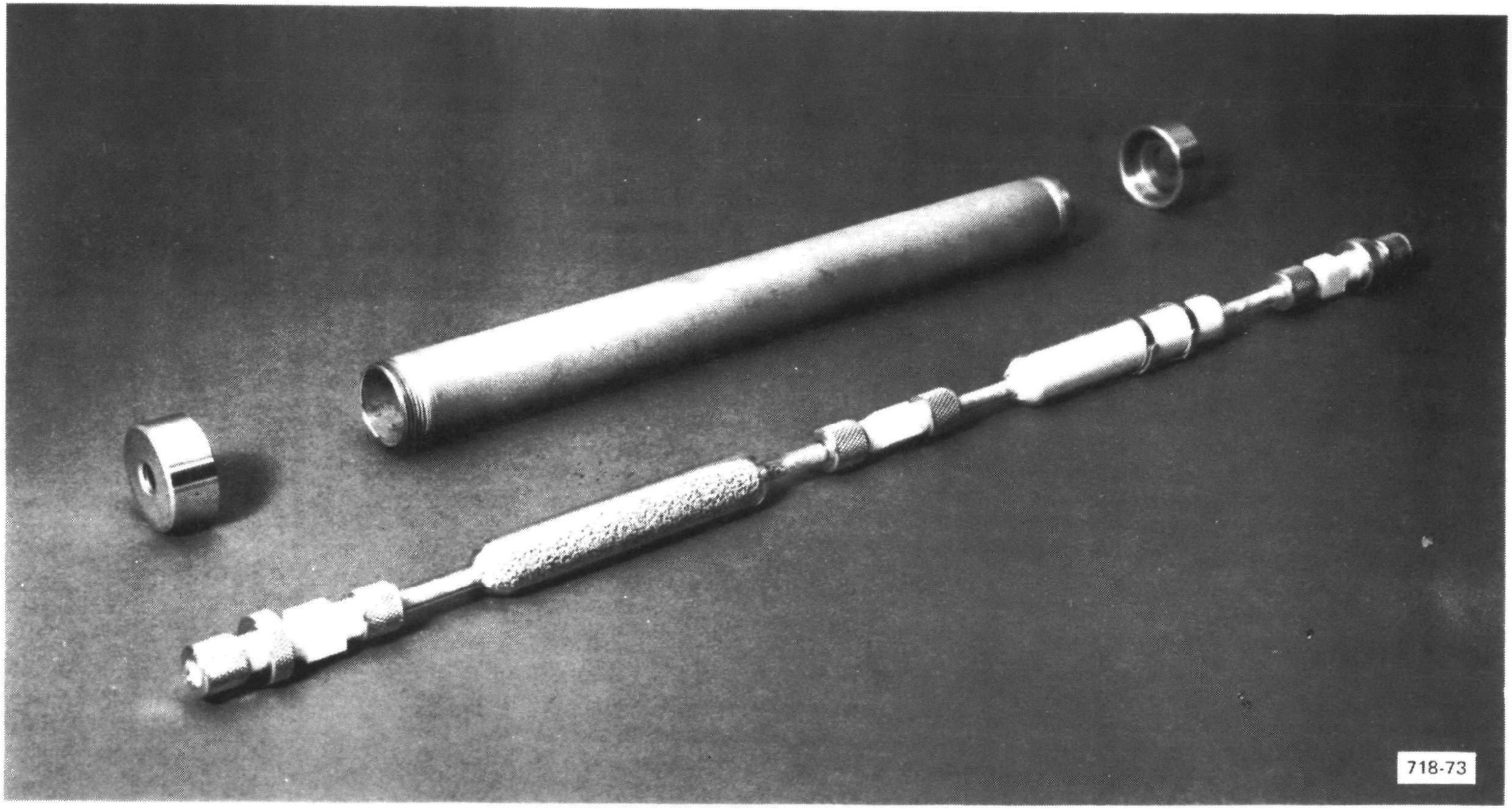


Figure 3 - Collector Unit Parts

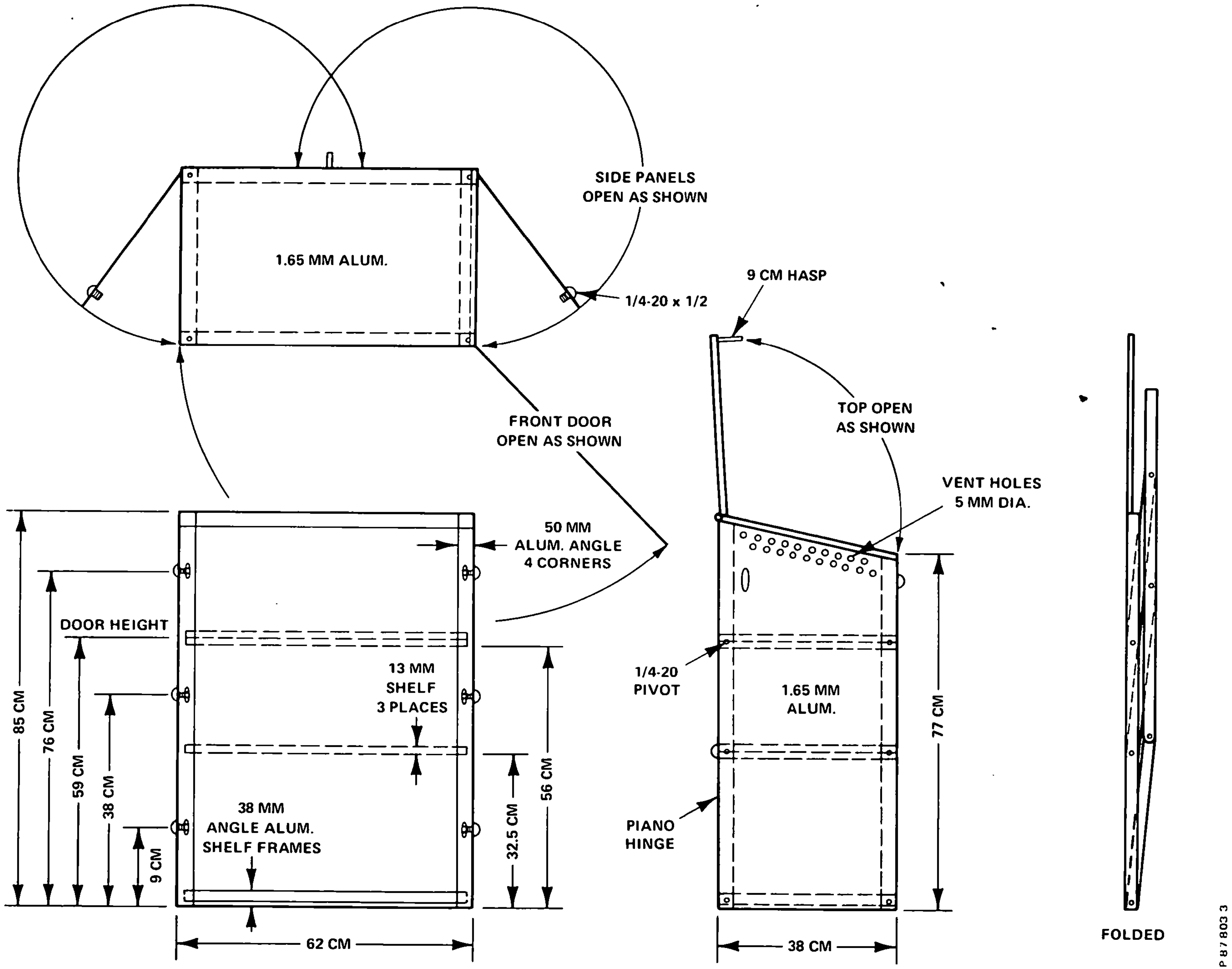

SIDE PANELS
OPEN AS SHOWN
1.65 MM ALUM.
1/4-20 x 1/2
FRONT DOOR
OPEN AS SHOWN
50 MM
ALUM. ANGLE
4 CORNERS
DOOR HEIGHT
13 MM
SHELF
3 PLACES
38 MM
ANGLE ALUM.
SHELF FRAMES
85 CM
76 CM
59 CM
38 CM
9 CM
32.5 CM
56 CM
62 CM
9 CM HASP
TOP OPEN
AS SHOWN
VENT HOLES
5 MM DIA.
1/4-20
PIVOT
1.65 MM
ALUM.
PIANO
HINGE
77 CM
38 CM
FOLDED
P87803 3

Figure 2 - Collector System Housing

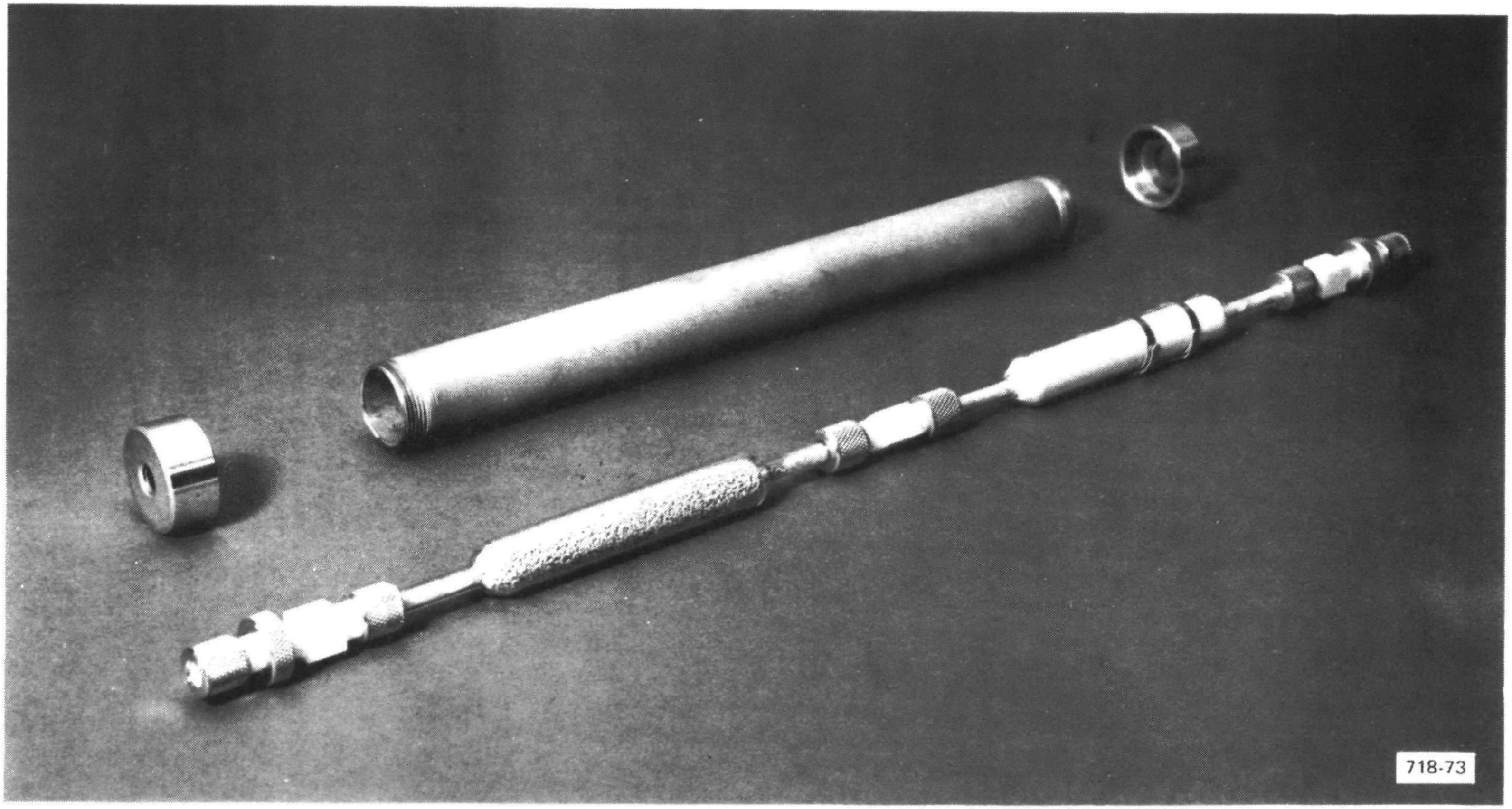
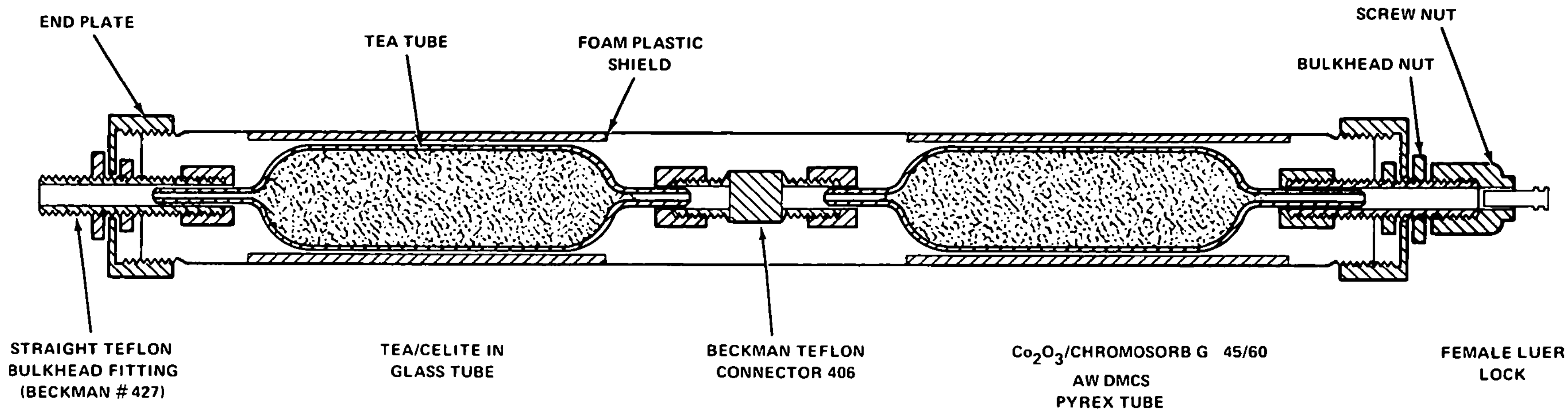
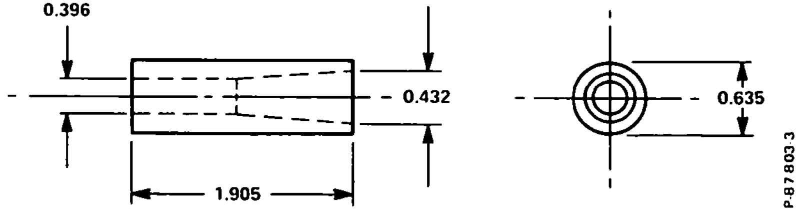


Figure 3 - Collector Unit Parts


END PLATE
TEA TUBE
FOAM PLASTIC SHIELD
SCREW NUT
BULKHEAD NUT
STRAIGHT TEFLON BULKHEAD FITTING (BECKMAN # 427)
TEA/CELITE IN GLASS TUBE
BECKMAN TEFLON CONNECTOR 406
Co_2O_3/CHROMOSORB G 45/60 AW DMCS PYREX TUBE
FEMALE LUER LOCK

(a) Collector Unit


0.396
0.432
1.905
0.635
P-87803-3

(b) Optional Filter Adapter

Figure 4 - Specifics of Collector Unit

(Hamilton catalog no. 86505); it is inserted into the Teflon connector and tightened with the screw nut. (The adapter can also be made by tapering the inside of 1.9-cm long Teflon tubing from 0.396 cm ID to 0.432 cm as shown in Figure 4.) The other end of the collector unit is also attached to a Millipore filter through a similar adapter and a Hamilton nylon male/male Luer-lock connector (Hamilton catalog no. 86506) which inserts into the female terminal of the filter. This filter is connected to the limiting critical orifice installed to the vacuum pump. This filter assembly, however, needs to be evaluated for its inertness to NO_x interconversion.

2.3 COLLECTOR CARTRIDGE

2.3.1 Cartridge Geometry

The collector cartridges for the two absorbents are identically constructed from Pyrex glass. Their dimensions are given in Figure 5. The inlets and outlets are 0.635 cm OD Pyrex tubing which readily inserts into the finger-tight Beckman Teflon connectors. In analysis, Beckman Teflon connectors are also used to connect the cartridge to the analytical instrument.

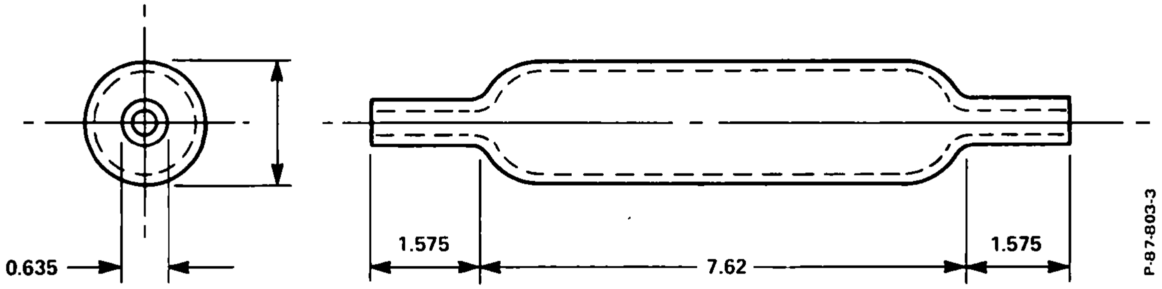


Figure 5 - Pyrex Glass Connector Cartridge

2.3.2 Cartridge Charging

In charging the cartridge, the packing is first prepared as directed. One end of the tube is packed with a silanized glass wool plug (Applied Science #14502). The prepared packing is then transferred into the cartridge with a clean spatula. The tube is constantly vibrated by hand while it is being packed. When the tube is filled, the open end is plugged with silanized glass wool. The difference in weights of cartridge before and after charging is the weight of packing material. It is important that the cartridge be carefully packed to ensure consistency in performance. A small difference in packing weight and pressure drop of charged cartridge is an indication of consistent packing.

2.4 PREPARATION OF ABSORBENT PACKINGS

2.4.1 Treatment of Celite

The Celite 15/30 mesh was obtained from Johns-Manville as a free sample. It is soaked in concentrated HCl for over 72 hr, drained, and washed to litmus paper neutral with distilled water. The washed Celite is then dried at 50-80°C, and brought to 250°C for 2 hr prior to firing at 1200°C for 12-48 hr. The Celite treated in this fashion is inert to NO. It absorbs NO_2 at room temperature, but releases it at 170-200°C. The cooled Celite is stored in a clean, capped jar placed in a dessicator.

2.4.2 Coating of TEA•HCl

About 20 g TEA•HCl (Eastman 1916) is dissolved in 80 cc distilled water. Then 40 g of treated Celite is added to the solution, which is stirred and allowed to stand for 30 min. The solution is evaporated to dryness at 80°C in a hood; during drying, the solution is occasionally shaken. The dried TEA•HCl/Celite is then stored in an oven set at 110-120°C. Packing prepared in this manner is ready for charging into the collector when cool. Each charged collector contains approximately 6g of packing. Before use, the charged collector needs to be conditioned at 160-170°C with either N_2 or air flow at 100-120 cc/min until no NO_X evolution is observed from the collector. The collector can then be cooled in a clean atmosphere, capped, and stored for future use. CAUTION: the conditioning temperature should not at any time exceed 170°C; beyond this temperature, decomposition may occur, thereby impairing the performance of the collector.

2.4.3 Cobalt Oxide (Co_2O_3)

The cobaltic oxide (J. T. Baker 1688) is a fine grayish-black powder (∿200 mesh). It is first packed into a large Pyrex tube, and heated at 500-550°C for 48 hr under nitrogen flow at 20-100 cc/min. When cooled, the powder is physically mixed well with Chromosorb G AW DMCS 45/60 mesh (Applied Science Lab) in approximately 1:2 by volume. This mixture is then used to charge the NO_X absorbent cartridge. The charging procedure is the same as that for the NO_2 absorbent cartridge. Prior to collection, the prepared cartridge must be conditioned at 420-450°C under air flow at 20-120 cc/min either overnight or until it no longer releases NO_X (as indicated by an NO_X analyzer). After cooling in a clean environment, the collector cartridge is ready for use, or should be capped for storage.

2.5 VACUUM PUMP (Gast Model 1531)

This pump (obtained from Gast Manufacturing Corp., Benton Harbor, MI 49022) is a 12V DC-operated Rotary Vane Vacuum/Compressor pump. It

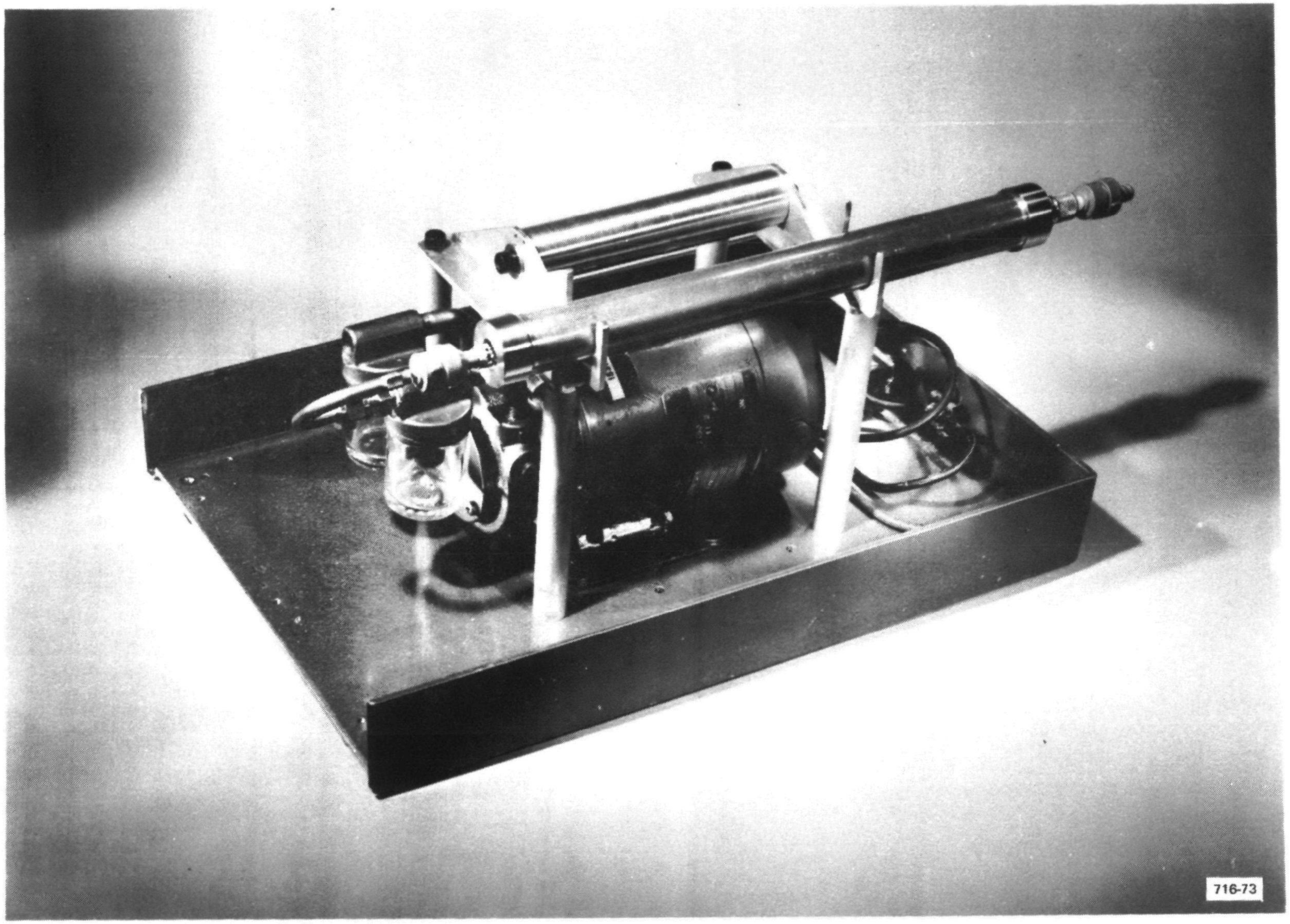


Figure 6 - Gas Pump and Collector Unit

has a free air flow of 42 ℓ/min. The pump draws 11.3 A current and can be powered by a 12 V auto battery or by a 12 amp-rate battery charger (110V AC). Figure 6 shows the pump and collector unit assembly.

The collector system flow rate is determined by the pressure drop exerted by the collector unit and filters. In order to eliminate the flow rate variations caused by uncertainty in the uniformity of each packing, a critical limiting orifice is placed between the pump and the collector outlet filter. The orifice provided with the unit gives a flow rate of 4.86 ℓ/min. Figure 7 shows the quick-connection of the collector, pump, and orifice.

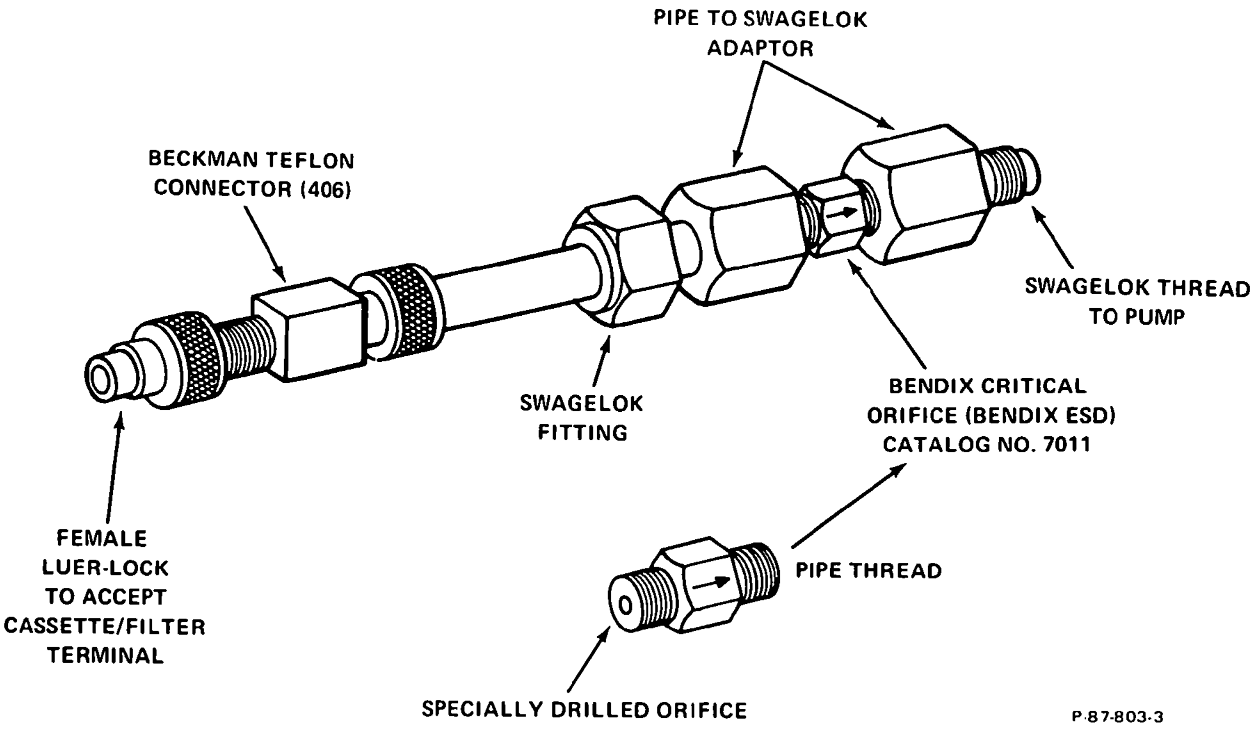

PIPE TO SWAGELOK ADAPTOR
BECKMAN TEFLON CONNECTOR (406)
SWAGELOK THREAD TO PUMP
BENDIX CRITICAL ORIFICE (BENDIX ESD) CATALOG NO. 7011
SWAGELOK FITTING
FEMALE LUER-LOCK TO ACCEPT CASSETTE/FILTER TERMINAL
PIPE THREAD
SPECIALLY DRILLED ORIFICE
P-87-803-3

Figure 7 - Connection for Collector Unit/Filter to Pump/Orifice

2.6 POWER SUPPLY

Either 110V AC or a 12V DC battery can be used as the power source. With 110V AC the collector unit is powered by the output of a 12V, 12A, battery charger (Model 126, R. N. Industries, Dearborn, MI 48126), which is in turn supplied by the 110V AC power line. A conventional 12V car battery provides a maximum of 12 hr continuous operation; a heavy duty 280 A truck battery can extend the operation time over 24 hr.

2.7 TIMER

The timer supplied with the collection system is a 110V AC-operated Intermatic Model T103 (International Register Company, 2624 W. Washington Blvd., Chicago 12, Illinois). This timer enables the collection unit to sample the air for a preset collection time interval of 1-24 hr when operated in the AC-mode.

2.8 OPERATION/MAINTENANCE

In actual operation, the operator carries the collector system to the chosen site and connects the collection unit to the pump orifice by finger-tightening the Beckman Teflon connector. (No special skills or tools are necessary.) Then the operator merely turns on the switch (either the battery or the timer). At the end of collection, the operator comes back to the sampler, turns off the switch, removes the collector unit, and caps the ends. (Either the Hamilton male Luer plug or a piece of 0.63 OD solid Teflon rod can serve as a cap for the collector unit. The plug goes readily to the filter adapter, while the Teflon rod can cap the unit terminals by replacing the filter adapter.) He can then carry the unit to the laboratory or send it out by mail for analysis of the collected oxides of nitrogen at a central laboratory.

Practically no maintenance of the collector system is required, other than changing the filter paper periodically. The critical orifice may be air-jet cleaned to remove any trapped particulates if it is accidentally contaminated. The pump requires no lubrication.

2.9 INTERFACE DEVICE

The interface device accepts one collection cartridge and is capable of providing sufficient heat to bring the collector to the temperature necessary to release absorbed nitrogen oxides for analysis. The device itself is a Kaowool-insulated aluminum block with holes drilled for the collector cartridge, a 250 W Hotwatt cartridge heater, a 0-500°C platinum temperature sensor (RFL 24928, 100 Ω), and a thermocouple. The specifications of the interface are given in Figure 8. The sensor and heater are operated by an RFL Model 71 Proportional Temperature Controller (RFL Industries, Inc., Boonton, N. J. 07005), which is powered by a 110V AC line. Figure 9 is a photograph of the interface device and the temperature controller. A 16-cm long rod is provided on the device for convenience in setting it up on an iron stand.

In operation, the interface device is set at the desired temperature (160-170°C for the NO_2 collector; 402°C for the NO collector); then the proper collector cartridge is inserted for analysis. The collector cartridge, of course, should be connected to an appropriate analyzer prior to its insertion into the interface device.

2.10 PARTS LIST

A parts list for the collection system is given in Table 1.

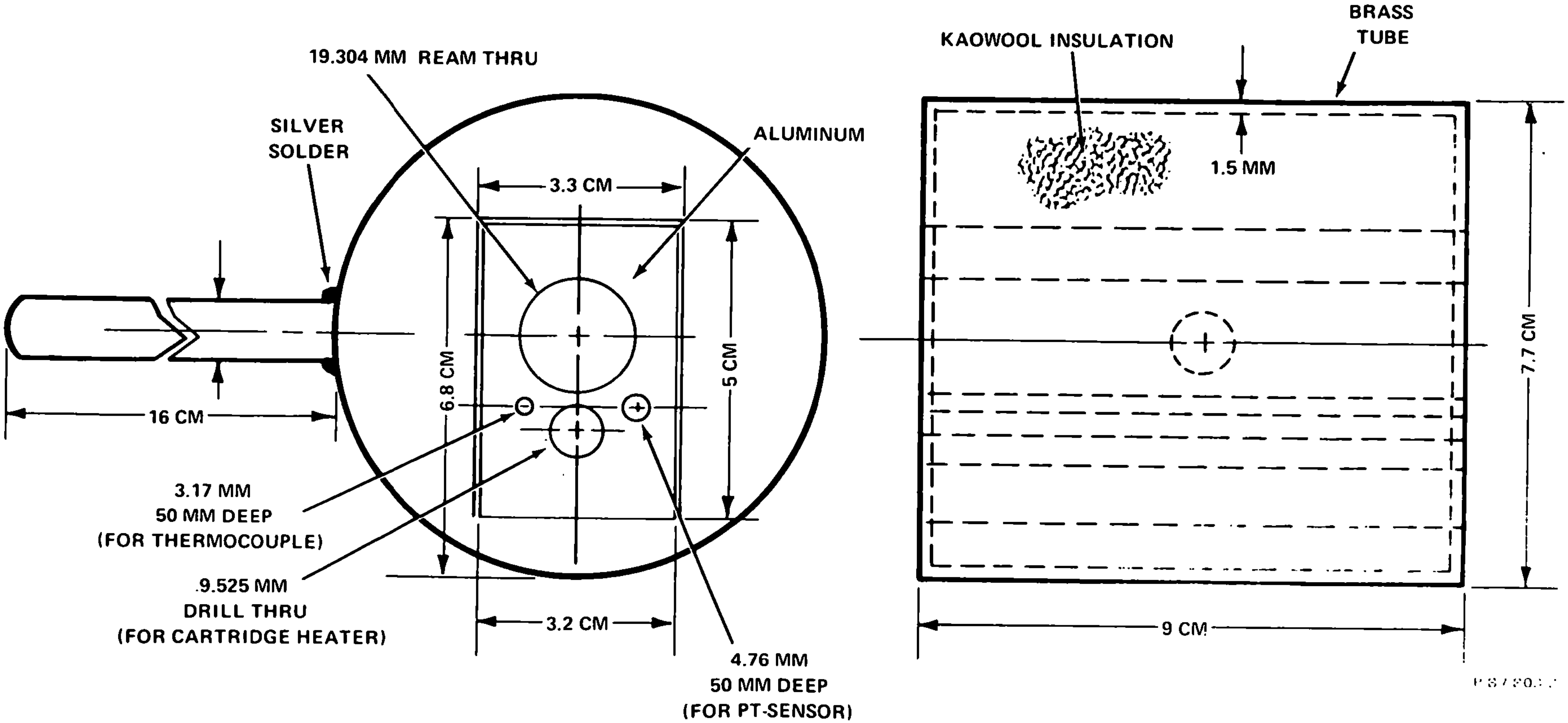

19.304 MM REAM THRU
SILVER SOLDER
ALUMINUM
3.3 CM
6.8 CM
5 CM
16 CM
3.17 MM
50 MM DEEP
(FOR THERMOCOUPLE)
.9.525 MM
DRILL THRU
(FOR CARTRIDGE HEATER)
3.2 CM
4.76 MM
50 MM DEEP
(FOR PT-SENSOR)
KAOWOOL INSULATION
BRASS TUBE
1.5 MM
7.7 CM
9 CM

Figure 8 - Details of Interface Device

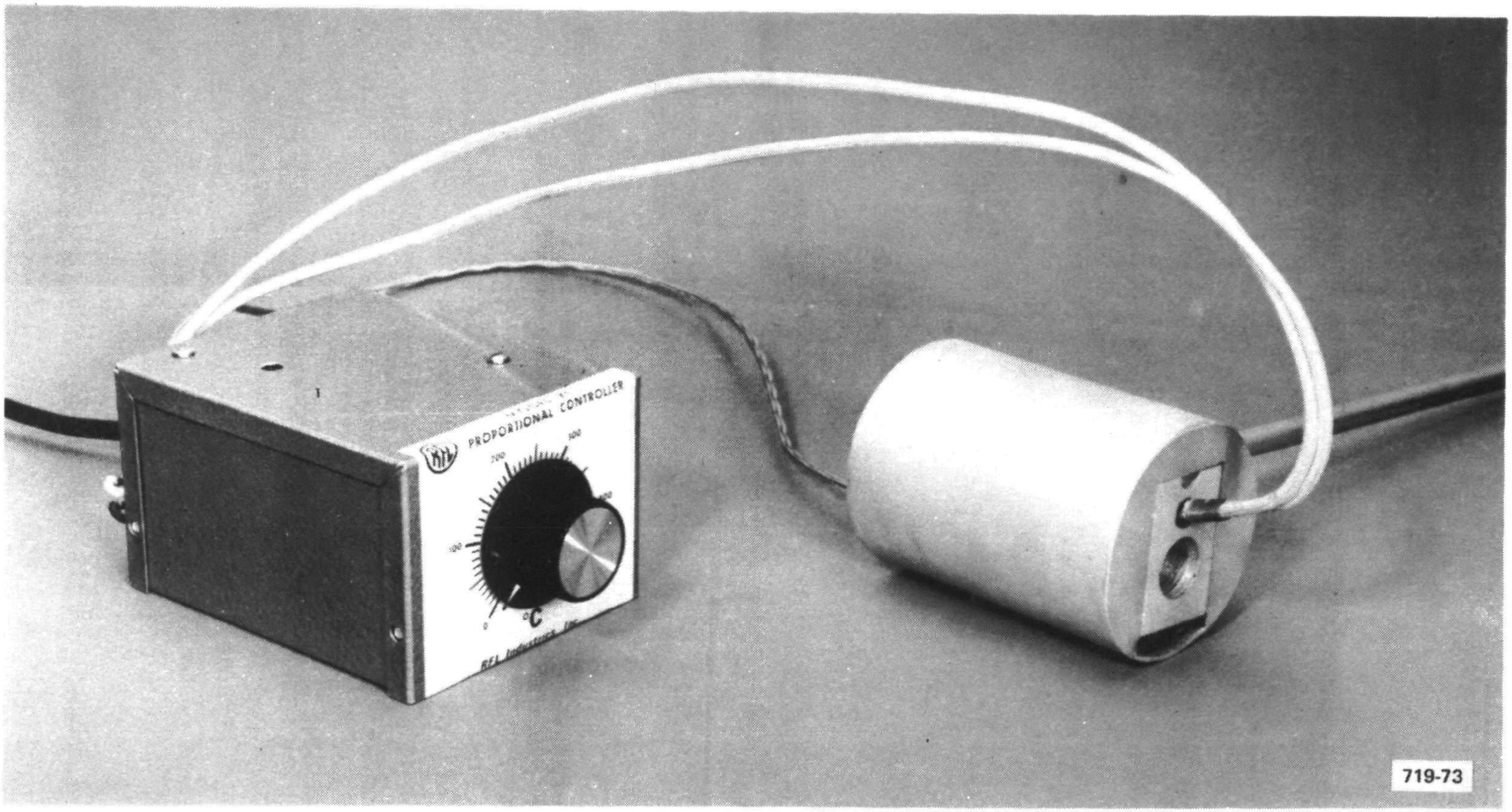

PROPORTIONAL CONTROLLER
°C
RFL Industries, Inc.
719-73

Figure 9 - Interface Device and Proportional Temperature Controller

Table 1 - Parts List for the Collection System

Item	Description, Model No.	Manufacturer
1	Collection System Housing Prototype	Bendix Research Laboratories Southfield, MI 48076
2	Collector Unit (Aluminum case)	Bendix Research Laboratories
3	Collector Cartridges (Pyrex tubing)	Bendix Research Laboratories
4	Plastic Filter, Millipore Cat. No. SXG S0130S, Swinex 13, No. 1 size	Millipore Filter Corp. Bedford, MA
5	Beckman Bulkhead Teflon-Connectors Cat. No. 427	Beckman, Inc. Southfield, MI 48075
6	Beckman Teflon Connectors Cat. No. 406	Beckman, Inc.
7	Hamilton female/female Luer-lock connector No. 86505	Hamilton, Box 7500 Reno, Nevada
8	Hamilton male/male Luer-lock connector No. 86511	Hamilton
9	Teflon adaptor for filter with Luer-lock terminals	Bendix Research Laboratories
10	Bendix Critical Limiting Orifice (for flow) Cat. No. 7011	Bendix Environmental Science Division, Baltimore, MD 21204
11	Gast Vacuum Pump, Model 1531, 12V DC Motor	Gast Manufacturing Corp. Benton Harbor, MI 49022
12	Timer, Intermatic, Model T 103	International Register Co. Chicago 12, Illinois
13	R. N. Battery Charger Model 126	R. N. Industries Dearborn, MI
14	Proportional Temperature Controller and Platinum Sensor, RFL Model 71	RFL Industries, Inc. Boonton, NJ 07005
15	Cartridge Heater, Hotwatt, 250W	Bendix Process Instruments Div. Ronceverte, W. Va.
16	Interface Device	Bendix Research Laboratories

Table 2 - Candidate Absorbents for NO_X Collection

GC phases/sorbent	Inorganic Bases	Alcohols, amines, amino-alcohols	Inorganic Salts
DuPont FCX-330	NaO·CaO	Triethanolamine	$NaClO_2$/Alumina
Halocarbon 11-14	NaOH	Triethanolamine hydrochloride	$(CrO_3+H_3PO_4)$/Quartz
Halocarbon 13-21	$LiOH \cdot H_2O$	2-(2-butoxyethoxy)ethanol	$(Na_2Cr_2O_7 + H_2SO_4)$/Glass Fiber
Fluorolube MD-10	$Na_2CO_3 \times H_2O$	1,1',1"-nitrilo-tri-2-propanol	$NiSO_4 \cdot 6H_2O$
Aroclor 1232		Triethyl N-tricarboxylate	CuO
Chlorinated Biphenyl-32		Triethanolamine Borate	Cu_2O
Silicone Oil GE, SF96		N,N'-(2-hydroxyethyl)-Piperazine	CoO
Armeen SD		N,N-Bis(2-hydroxyethyl)-o-toluene-sulfonamide	Co_2O_3
Hi-EFF-10B		2,2-Bis(hydroxymethyl)-2,2',2"-nitrilotriethanol(Bis-tris)	Fe_2O_3
Molecular Sieve 5A, 13A, 13X		2,2',2", 2"'-(ethylenedinitrilotetraethanol) (THEED)	$FeSO_4$
Activated Carbon		2,2',2", 2"'-(ethylenedinitrilotetra-2-propanol) (Quadrol)	$CoSO_4$
Alumina		Polyoxyethylene(8) Ethylenediamine	PbO
		Tris-(hydroxymethyl)aminomethane	PbO_2
		Tris-(hydroxyethyl)aminomethane	$CuSO_4$
		1,1,1-Tris-(hydroxymethyl)ethane	
		6-amino-1-hexanol	
		1.5-pentanediol	

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SECTION 3

DEVELOPMENT OF COLLECTION SYSTEM

3.1 INTRODUCTION

The total development program included five major efforts: (1) identification and characterization of solid chemical absorbents and supports, (2) development of collector cartridge and collector unit, (3) fabrication of interface device, (4) survey and selection of air sampling pump, and (5) assembly of collection system. Each of these efforts is discussed in the following subsections.

3.2 IDENTIFICATION AND CHARACTERIZATION OF SOLID CHEMICAL ABSORBENTS

3.2.1 Technical Approach

The effort of this phase centered around the rapid screening of candidate materials to be used as absorbents for the oxides of nitrogen. Those absorbents could be either of two forms: liquids that could be conveniently coated onto an inert solid support, or solids that could be either used by themselves or physically mixed with some suitable inert support. Candidates were chosen from literature references or from examination of chemical structures. They included: (a) inorganic bases, (b) gas chromatography stationary phases or solid sorbents, (c) organic bases, and (d) inorganic salts. Table 2 summarizes the candidates chosen for evaluation.

3.2.2 Evaluation Parameters

Candidate absorbents were screened on the basis of

- Ability to completely absorb either NO, NO_2, or both (NO_x)

- Inertness to NO_x, so that the absorbent surface does not catalyze $NO_2 \rightarrow NO$ interconversion.

If an absorbent met these requirements, it was evaluated for its ability to quantitatively release collected NO_x upon heating.

3.2.3 Test Setup

The absorbents were evaluated using the simple test fixture shown in Figure 10. This fixture has a one-liter mixing bulb for sample preparation which accepts the gas flows from the NO_X tank and from the diluent nitrogen tank. Appropriate flow controllers and needle valves are provided. The pressure of the bulb can be read from the pressure gage connected to it. The outlet of the bulb goes to a 50 cc buffering volume through a valve. This volume is open to a vacuum vent line or to the sample inlet of the absorbent to be evaluated.

The sample inlet branches, going to the NO_X analyzer (Bendix Chemiluminescence NO_X Analyzer) directly, or through the collector first and then to the analyzer and pump. A Pyrex cold-trap (ice water) is placed between the analyzer and the collector.

A septum port is installed in the line between the mixing bulb and the buffering volume for withdrawing prepared sample. Another septum port placed at the ambient inlet line is for sample injection. Of course, when the valves before and after the buffering volume are both open, the prepared sample is continuously drawn, either directly or via the collector path, into the NO_X analyzer. The nitrogen line and the vacuum vent allow the gas preparation system to be purged. All the gas

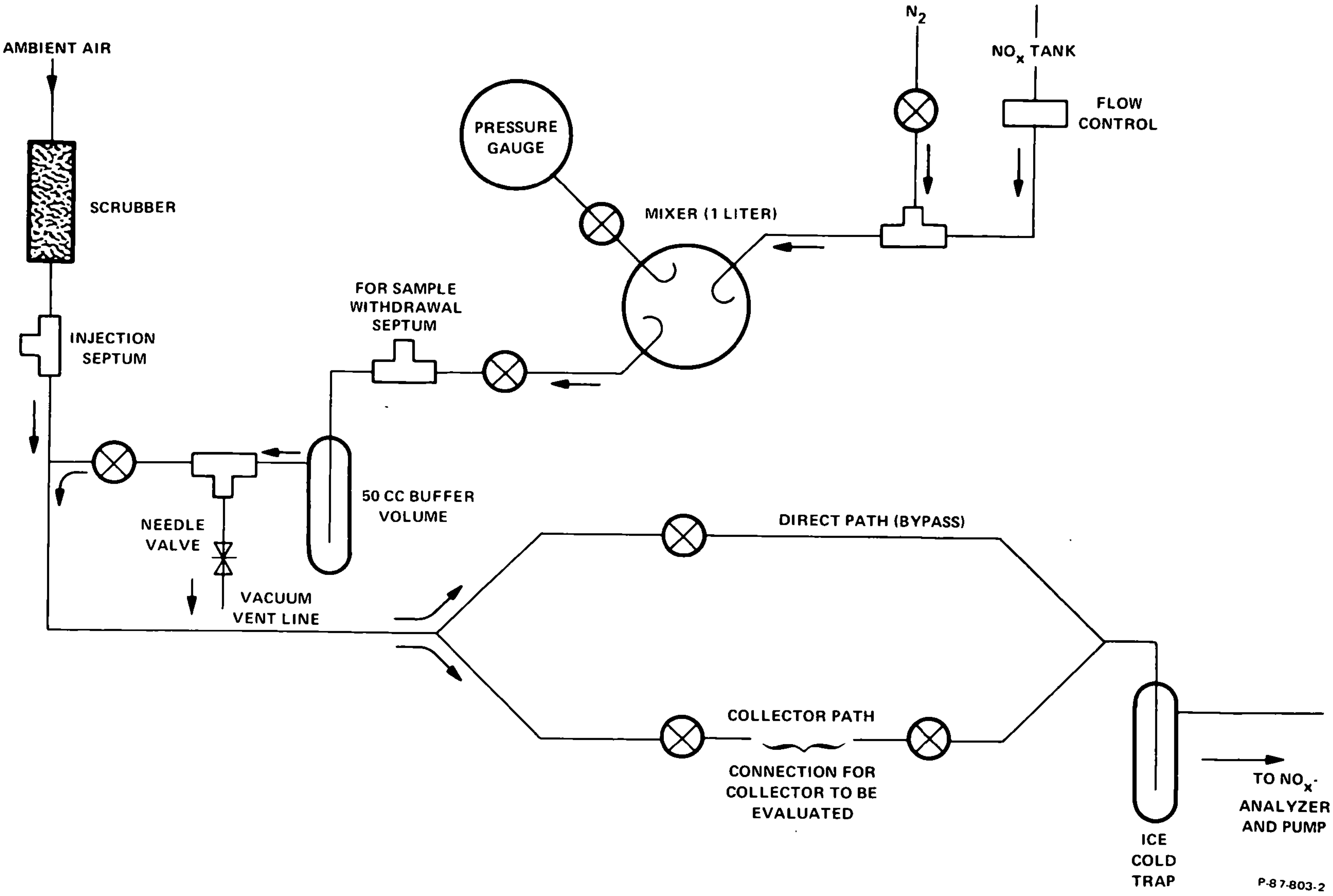
AMBIENT AIR
SCRUBBER
INJECTION SEPTUM
NEEDLE VALVE
VACUUM VENT LINE
50 CC BUFFER VOLUME
FOR SAMPLE WITHDRAWAL SEPTUM
PRESSURE GAUGE
MIXER (1 LITER)
N2
NOx TANK
FLOW CONTROL
DIRECT PATH (BYPASS)
COLLECTOR PATH
CONNECTION FOR COLLECTOR TO BE EVALUATED
ICE COLD TRAP
TO NOx-ANALYZER AND PUMP
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Figure 10 - Schematic of Test Setup for the Evaluation of Absorbents

lines are Teflon, and connectors are either Beckman Teflon-type or stainless steel. NO_X is supplied from a tank of calibrated mixture prepared by Cryogenic Sales, Inc. The sample prepared by this system has a concentration range of 1 ppm in NO_2 and 0.1 ppm in NO.

For evaluation, absorbent material was packed into a 2.5-cm OD Pyrex tube with 0.64-cm OD inlet and outlet. Silanized glass wool was used for end plugs. The tube had a ground-glass joint to allow easy packing.

3.2.4 Evaluation Method

The Bendix Chemiluminescence NO_X Analyzer gives readouts of $[NO_X]$ and [NO] in ppm. When a steady concentration of the oxide is present in the sample gas, the analyzer readout is a straight line (continuous mode). If the sample concentration has a short lifetime or is pulsed, a peak readout appears. The latter occurs when a sample is injected into the ambient air stream.

In evaluating a candidate as a potential absorbent, a steady concentration was first established in the gas system through the "direct path". The readouts were recorded as $[NO_X]_D$ and $[NO]_D$. Then the sample stream was routed to the "collector path" with a candidate absorbent in an inert cartridge. The readouts were recorded as $[NO_X]_C$ and $[NO]_C$. The difference between $[NO_X]$ and [NO] represents the concentration of $[NO_2]$. That is,

$$[NO_2]_D = [NO_X]_D - [NO]_D$$

$$[NO_2]_C = [NO_X]_C - [NO]_C$$

When $[NO_X]_C = 0$, the candidate material totally absorbs or removes the nitrogen oxides. If $[NO_X]_C = [NO]_C$, the material absorbs or removes NO_2. $[NO]_C = [NO]_D$ means that the candidate absorbent causes no change in the concentration of NO, thus implying the absence of $NO_2 \rightarrow NO$ conversion. More concisely,

$[NO_X]_C = 0$	Total removal of NO_X
$[NO_X]_C = [NO]_C$	Total removal of NO_2
$[NO]_C = [NO]_D$	No conversion of NO_2 to NO.

When these are not the case, the absorbent either removes NO_2 incompletely and/or catalyzes its conversion to NO. The percentages of NO_2 removal and conversion can be calculated as follows:

$$[NO_2]_D = [NO_X]_D - [NO]_D$$

$$[NO_2]_C = [NO_X]_C - [NO]_C$$

$$\Delta\ [NO_2]_{removal} = [NO_2]_D - [NO_2]_C$$

$$\%\ NO_2 \text{ removal} = \frac{\Delta\ [NO_2]_{removal}}{[NO_2]_D} \times 100$$

$$\%\ NO_2 \text{ absorption} = (\%\ NO_2 \text{ removal}) - (\%\ NO_2 \text{ conversion})$$

The evaluation of triethanolamine (TEA) coated onto Chromosorb W DMCS, as shown in Figure 11, serves as a sample calculation.

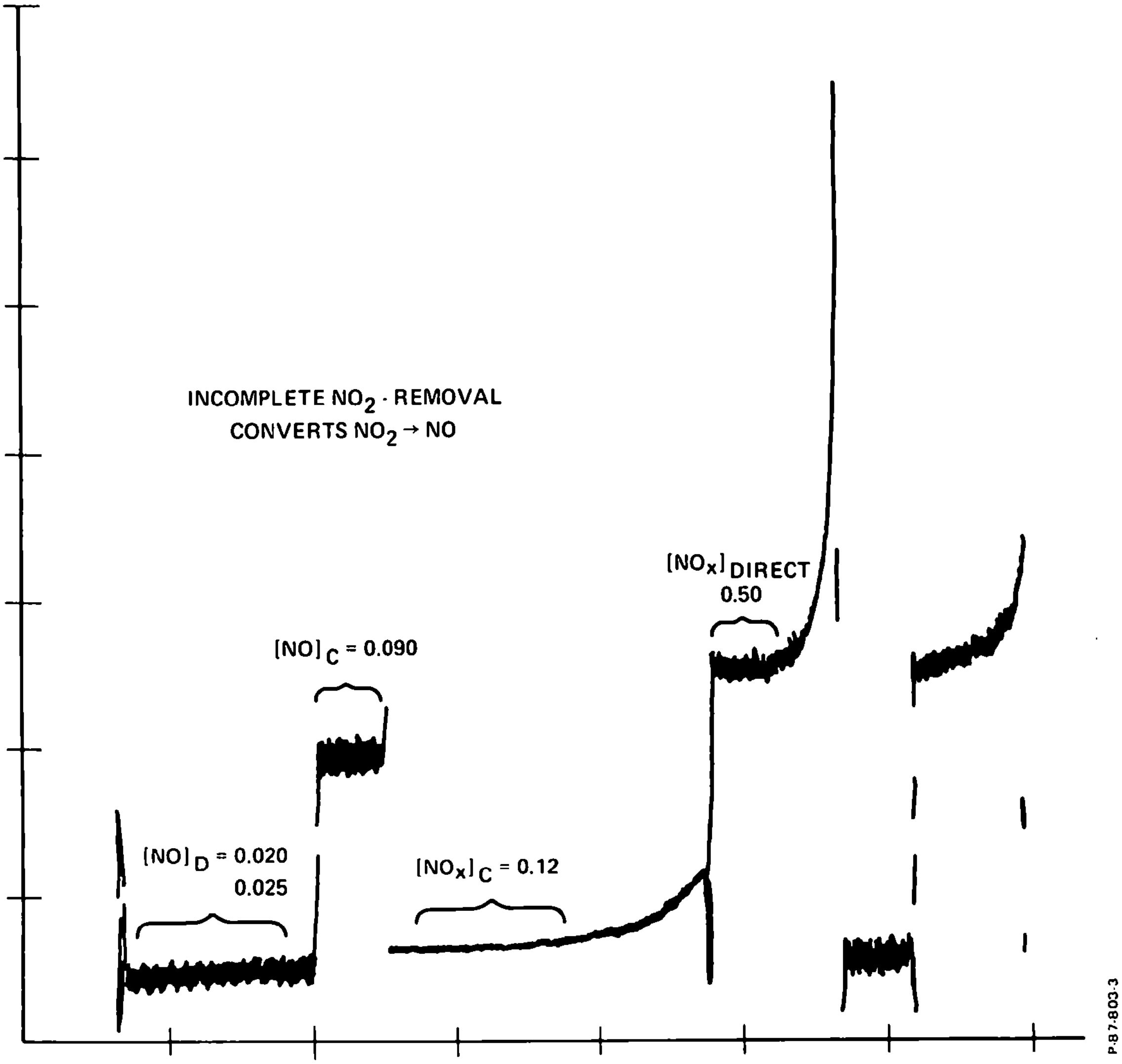

Figure 11 - TEA/Chromosorb AW DMCS

Since,

$[NO]_D = 0.025$ ppm, $[NO_X]_D = 0.50$ ppm,

$[NO]_C = 0.09$ ppm, $[NO_X]_C = 0.12$ ppm

$$[NO_2]_D = [NO_X]_D - [NO]_D = 0.50 - 0.025 = 0.475 \text{ ppm}$$

$$[NO_2]_C = [NO_X]_C - [NO]_C = 0.12 - 0.09 = 0.03 \text{ ppm}$$

Therefore

$$\Delta\ NO_2 = [NO_2]_D - [NO_2]_C = 0.475 - 0.03 = 0.445 \text{ ppm}$$

$$\Delta\ NO = [NO]_C - [NO]_D = 0.090 - 0.025 = 0.065 \text{ ppm}$$

Thus

$$\%\ [NO_2]_{removal} = \left(\Delta\ NO_2/[NO_2]_D\right) \times 100 = (0.445/0.475)\ 100 = 93.7\%$$

$$\%\ [NO_2 \rightarrow NO] = \left(\Delta\ NO/[NO_2]_D\right) 100 = (0.065/0.475)\ 100 = 11.6\%$$

$$\%\ [NO_2]_{absorption} = 82.1\%$$

For the injection mode of operation, the same basic calculations are used, except that the areas of the generated peaks are used. Each area is obtained by triangulation of a given peak.

In the quantitative recovery study, the elution of the oxides of nitrogen from the collector is also in the form of a peak. For the percent recovery estimate, the peak area of the eluant from the collector is counted as $A_{recovery}$. The average area of the peaks obtained by injecting the same sample through the direct path is calculated as $\overline{A}_{direct}$. The ratio $A_{recovery}/\overline{A}_{direct}$ denotes the effectiveness in recovery. When this ratio is equal to 1, a 100% recovery is achieved. The analytical accuracy of the approach was somewhat limited by the triangulation method; however, it should suffice for the present application. An electronic integrator would definitely increase the accuracy of analysis.

3.3 EVALUATION OF CANDIDATES

3.3.1 Triethanolamine and Supports

The recent report by Levaggi et al. on the superior performance of triethanolamine (TEA) on Celite-22 fire brick prompted us to attempt to reproduce their work. Unfortunately, we observed persistent NO_2 to NO conversion. Since Celite washed with concentrated nitric acid exhibited extensive conversion of NO_2 to NO (Figure 12), we decided to

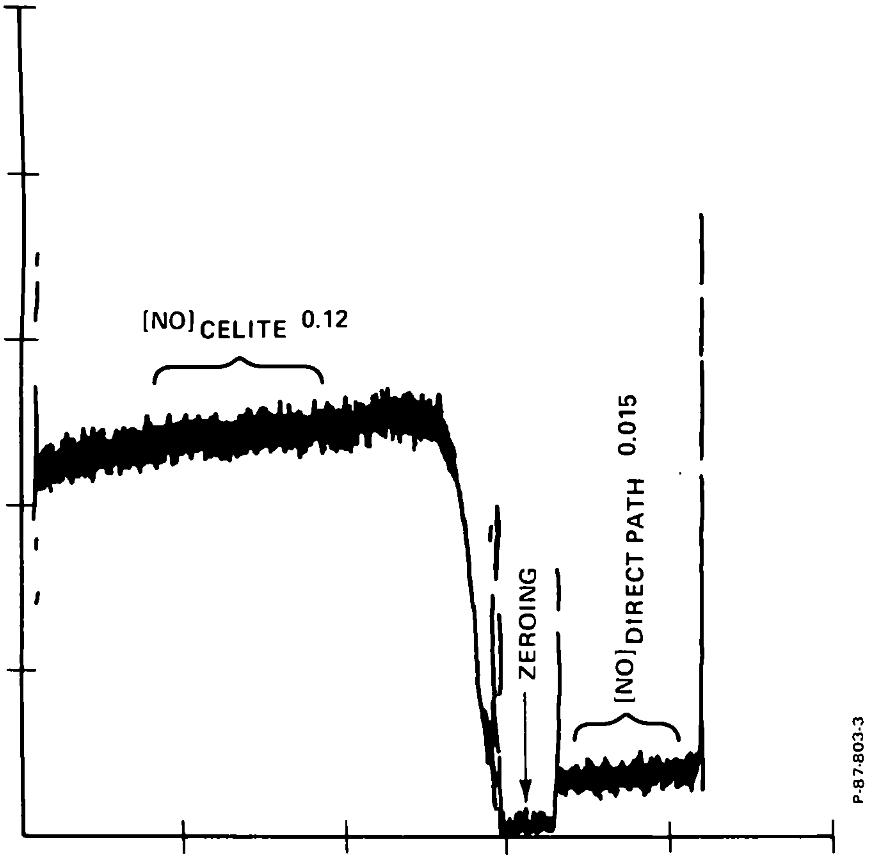

Figure 12 - Celite (AW)

study other support materials: Corning special textured glass beads; Chromosorbs G and W, both of which are AW-DMCS (acid washed and silane treated); Chromosorb T (Teflon); and Regis Gas Pak FS (Teflon-coated diatomaceous earth). Absorbent packing made by coating TEA on these supports activated the conversion of NO_2 to NO, despite the fact that the supports themselves were found to be inert. These puzzling results are illustrated in Figures A-1 through A-5 of Appendix A.

We speculated that evaporating the methanol solution of TEA during the coating of the support might have introduced impurities or damaged the inert surface of the support. Finally, after repeated failure to obtain an inert packing on any of these supports (including an attempt to coat TEA onto the support without solvent), it occurred to us that TEA itself might be impure. This postulation was later confirmed by the observation that TEA itself, without a support, gave a 10% conversion of NO_2 to NO (Figure A-6).

A pure sample of TEA (clear liquid) was then obtained and stored in the dark. A packing was made by dissolving 5 g of this sample in methanol and evaporating the solution onto 20 g Chromosorb G AW DMCS 80/100 mesh. After conditioning at 80°C for 4 hr with 40 cc/min helium flow, this packing was then evaluated in a polypropylene tube. As illustrated in Figure 13(a) and (b), this packing completely and selectively absorbed NO_2 and was inert to NO.

In this experiment, the original sample concentration was:

$$[NO_X]_D = 1.2 \text{ ppm}$$

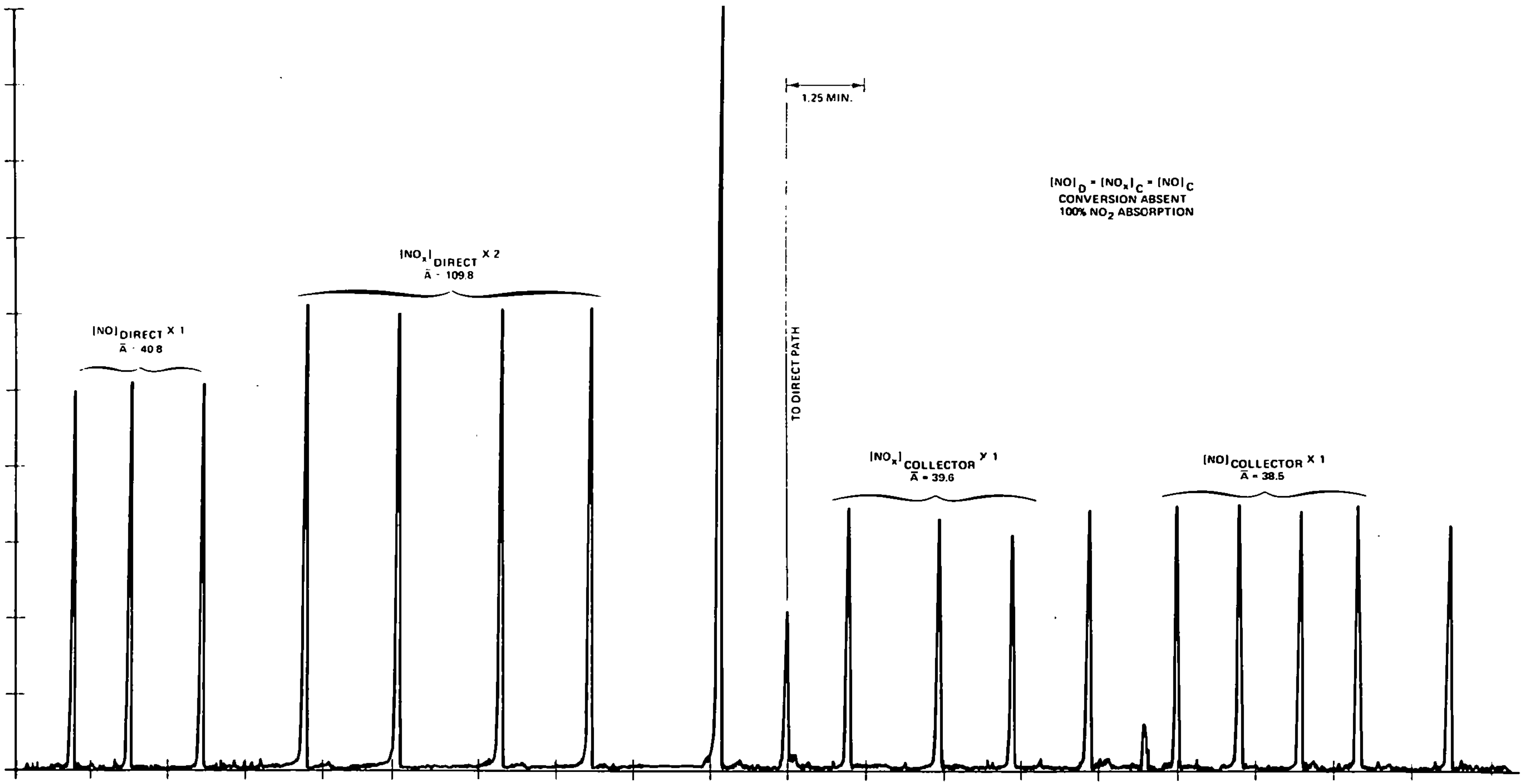

Figure 13(a) - Pure TEA/Chromosorb G DMCS - Injection Mode

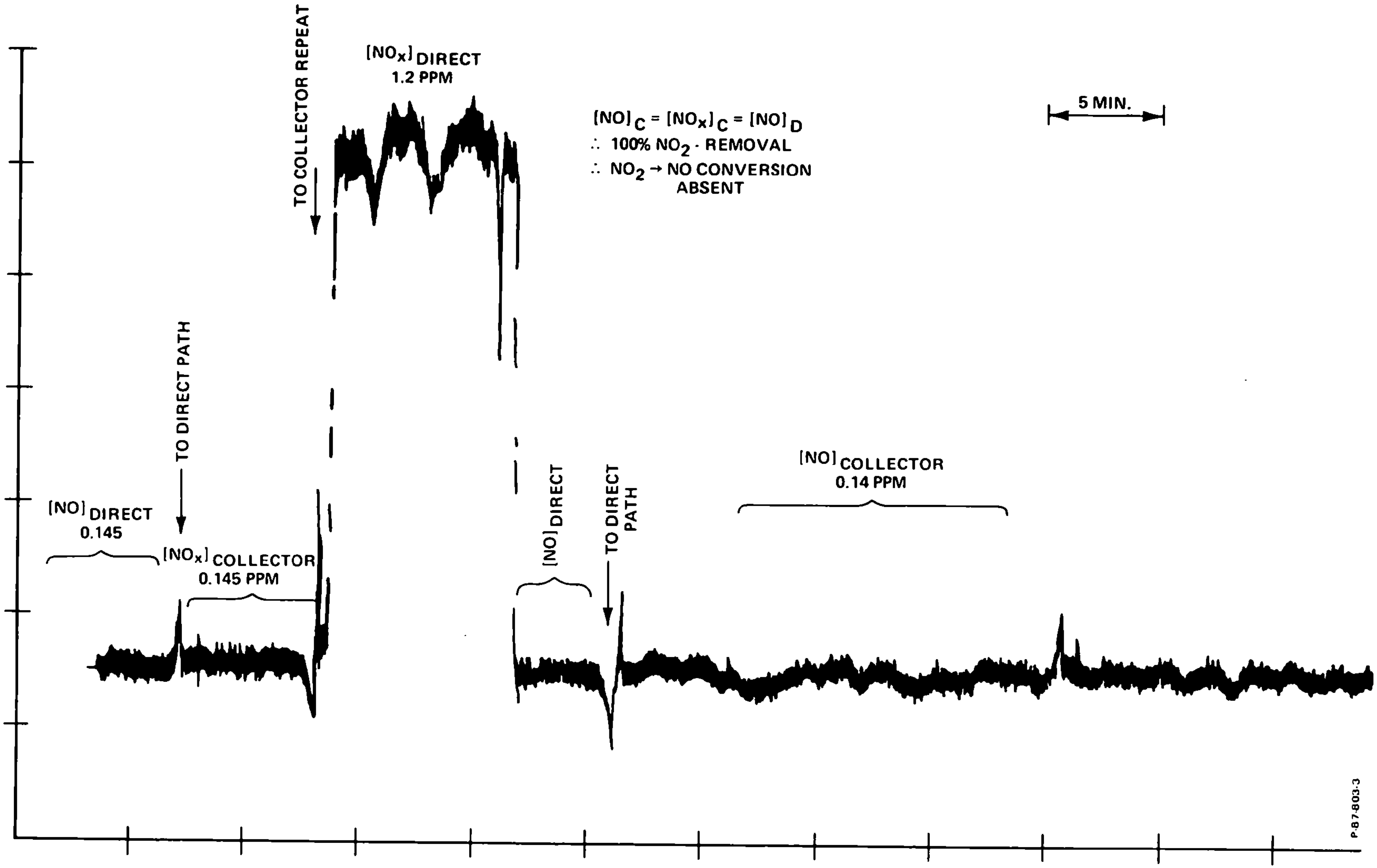

Figure 13(b) - Pure TEA/Chromosorb G DMCS - Continuous mode

$$[NO]_D = 0.14 - 0.145$$

After passing the collector,

$$[NO_X]_C = 0.14 - 0.145$$

$$[NO]_C = 0.14 - 0.145$$

That is,

$$[NO_X]_C = [NO]_C = [NO]_D, \text{ or}$$

$[NO_2] = 0$ after passing the collector.

These values indicate 100% NO_2 removal and no $NO_2 \rightarrow NO$ conversion.

Similarly, for the injection mode,

$$\bar{A}_{[NO_X]_D} = 109.8;$$

$$\bar{A}_{[NO]_D} = 40.8;$$

$$\bar{A}_{[NO_X]_C} = 39.6;$$

$$\bar{A}_{[NO]_C} = 38.5 \quad .$$

That is,

$$[NO_X]_C \doteq [NO]_C \doteq [NO]_D$$

which represents 100% NO_2 removal and no $NO_2 \rightarrow NO$ conversion.

3.3.2 Thermal Instability of TEA Packings

The recovery of the absorbed NO_2 from the TEA/Chromosorb G collector by elution into the NO_X analyzer was attempted using thermal methods. Evaporation of TEA occurred above 80°C, and the color of the packing changed to orange above 150°C, thus indicating possible decomposition of the packing. An NO_X elution peak was obtained, however, at this temperature. This heat-treated packing subsequently converted NO_2 to NO and had lost its capability for NO_2 removal. A new collector was made by packing the TEA/Chromosorb G into a stainless tubing which was then subjected to gas chromatographic evaluation for bleeding. Persistent bleeding occurred at and above 75-80°C, despite extensive conditioning at this temperature.

These results clearly indicated that materials having higher boiling points or melting points than TEA should be sought to improve thermal stability. Solid candidates were particularly attractive. Most of the candidates shown in the amines, alcohols, and amino-alcohol column of Table 2 were chosen on the basis that their chemical structure resembled that of triethanolamine and their melting points were higher. Triethanolamine hydrochloride (m.p. 177-179°C), and Bis-Tris (m.p. 103-104°C) are typical examples of this kind.

3.3.3 Amino-Alcohol Screening

Quite extensive but rapid screening of the available amino-alcohols resulted in the identification of triethanolamine hydrochloride (TEA•HCl) as a potentially reusable NO_2 collector material. All the other amino-alcohols either converted NO_2 to NO or failed to absorb NO_2 or NO. Figure A-7 to A-9 in Appendix A are recordings from tests of some of the amino-alcohols. Because of the time constraint, each material was rapidly screened for its affinity for NO_2 and/or NO, and its surface activity toward NO_2 to NO conversion. Although not every recording trace was presentable, the necessary data were recorded for calculation. The results of the evaluation for all materials are summarized in Table 3.

3.3.4 Triethanolamine Hydrochloride (TEA·HCl)

The TEA·HCl was a fine white powder, fluffy in texture. It was physically mixed with Chromosorb G AW-DMCS 80/100 mesh in a 1:1 ratio by volume, and then packed into a Pyrex tube for evaluation. The performance of TEA·HCl/Chromosorb G AW-DMCS, illustrated in Figure 14(a) and (b), showed 100% NO_2 removal and the absence of NO_2 to NO conversion

$$[NO_X]_C = [NO]_C = [NO]_D = 0.14 - 0.15;$$

$$\bar{A}_{[NO_X]_C} \doteq \bar{A}_{[NO]_C} \doteq \bar{A}_{[NO]_D}$$

The preparation of TEA·HCl/Chromosorb G packing was somewhat difficult due to the fluffy nature of TEA·HCl. Moreover, although TEA·HCl is very soluble in water, Chromosorb G, W, T, etc. are all hydrophobic. Therefore, some other support should be sought. TEA·HCl can be transformed into larger particles. Cold-pressing at 21×10^6 kg/m^2 for 20 min produces a cake that will break into chips. These chips, however, did not have adequate mechanical stability, since they gradually broke down into a powder.

Table 3 - Materials Evaluated (1 of 2)

	Material	Results and Remarks
Support	1. Celite 22	Specially acid washed and fired sample absorbs NO_2, is inert to NO at room temp., gives off absorbed NO_2 above 150°-200°C, chosen for TEA·HCl support.
	2. Corning textured glass bead	Inert to NO, NO_2, has low surface area and capacity for coating material.
	3. Chromosorb G AWDMCS	Inert to NO_2 and NO, hydrophobic; Chrom. G 45/60 mesh can be best mixed with the Co_2O_3 powder to afford a decent gas flow, chosen for Co_2O_3 support.
	4. Chromosorb T (Teflon)	
	5. Chromosorb W AWDMCS	
	6. Regis Gas Pack FS (Teflon coated diatomaceous earth)	
	7. Silane treated glass wool	Inert to NO_2, NO
Container	1. Pyrex glass	Inert to NO, NO_2, chosen for both lab test and collector cartridge construction.
	2. Aluminum	After going through heating cycle to 200°C, converts $NO_2 \rightarrow NO$
	3. Teflon coated aluminum	Inert to NO_2, NO
Absorbent Candidates (Inorganic)	1. Co_2O_3/Chromosorb G	Absorbs NO_x completely up to 350°C. Releases the absorbed quantitatively above 390°C.
	2. $NiSO_4$	Does not absorb NO_2, converts $NO_2 \rightarrow NO$
	3. CuO (wire)	Slightly absorbs NO_2. Slightly converts $NO_2 \rightarrow NO$ (<4%)
	4. Cu_2O/Chromosorb G	Converts $NO_2 \rightarrow NO$. Does not absorb NO_2.
	5. $CoSO_4$	Converts $NO_2 \rightarrow NO$.
	6. CoO	100% NO_x removal

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Table 3 - Materials Evaluated (2 of 2)

	Material	Results and Remarks
Absorbent Candidates (Organic)	1. 1,5-pentanediol/Celite	61% NO_2 removal, 11% NO removal
	2. THEED/Chromosorb W	<10% NO_2 removal, 50% $NO_2 \rightarrow NO$ conversion
	3. Quadrol/Chromosorb W	Does not remove NO_2 to any significant extent Significantly converts $NO_2 \rightarrow NO$ (70%).
	4. Polyoxyethylene(8)ethylene diamine/Chromosorb T	Does not remove NO_2
	5. TEA·Borate	80% NO_2 removal, converts 13% $NO_2 \rightarrow NO$
	6. 2-(2-butoxyethoxy)ethanol/ Celite	78% NO_2 removal, slightly converts $NO_2 \rightarrow NO$.
	7. 1,1',1"-nitrilo-tri-2-propanol/Celite	100% NO_2 removal Converts $NO_2 \rightarrow NO$ (∿50%)
	8. Impure TEA coated on	
	a. Chromosorb G	4% $NO_2 \rightarrow NO$ conversion
	b. Chromosorb W	16%
	c. Chromosorb T	17%
	d. Regis Gas Pak FS	40%
	e. Without support	10%
	9. Pure TEA/Chromosorb G	0% conversion, 100% NO_2 removal Poor in thermal stability
	10. Triethanolamine hydrochloride (TEA·HCl)	0% conversion, 100% NO_2 removal, chosen NO_2 absorbent
	11. Bis-Tris	Inert at room temp.
	12. N,N'-Bis-(2-hydroxyethyl)-piperazine	NO_2 removal up to 62%, converts $NO_2 \rightarrow NO$ slightly
	13. N,N'-Bis-(2-hydroxyethyl)-p-toluenesulfonamide	Does not absorb NO_2
	14. Phenyldiethanolamine succinate (Hi-EFF 10B)	Inert at room temp.
	15. Tris-(hydroxymethyl)-aminomethane	<10% NO_2 removal, 2% conversion $NO_2 \rightarrow NO$.
	16. 1,1-tris-(hydroxymethyl)-ethane	<10% NO_2 removal, 2% conversion $NO_2 \rightarrow NO$.

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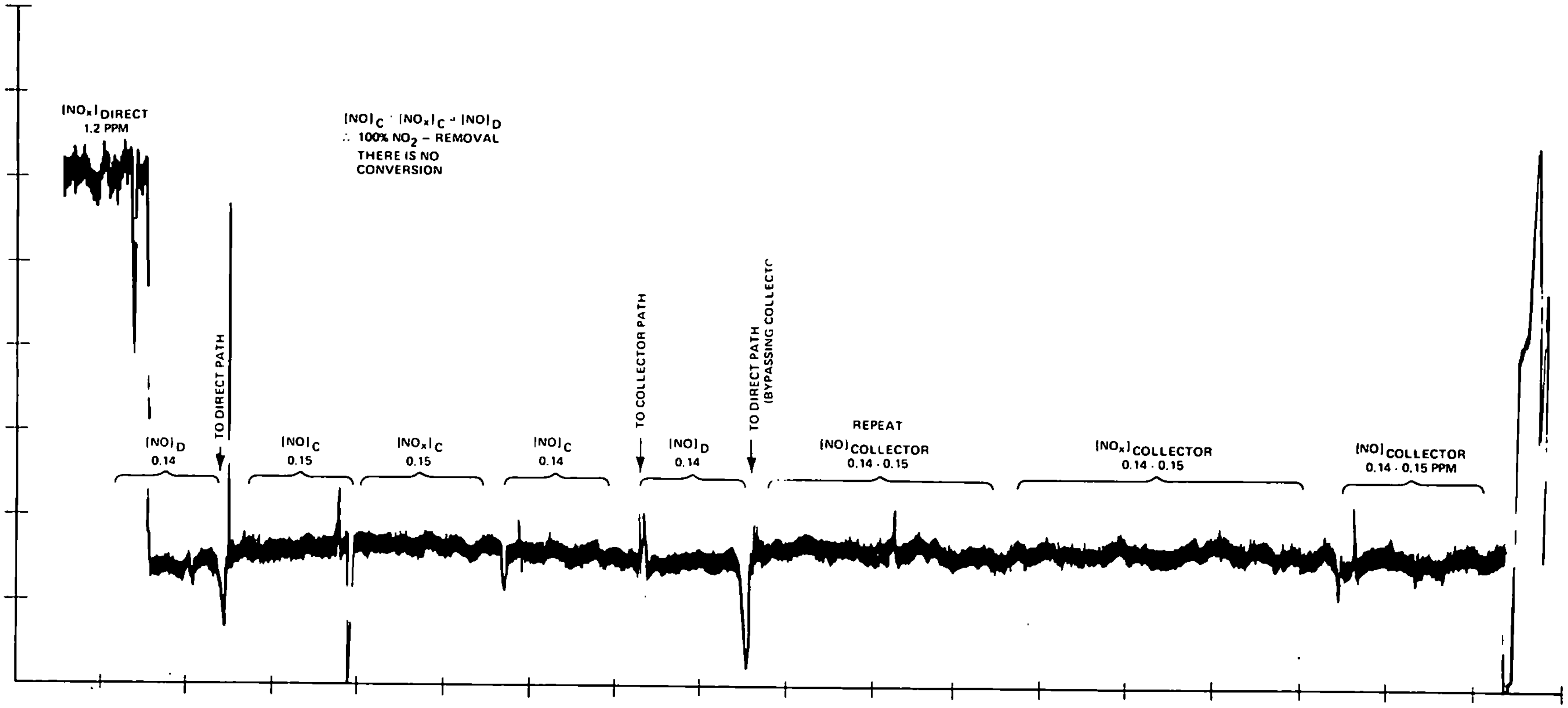


Figure 14(a) - TEA•HCl/Chromosorb G AW DMCS - Continuous Mode

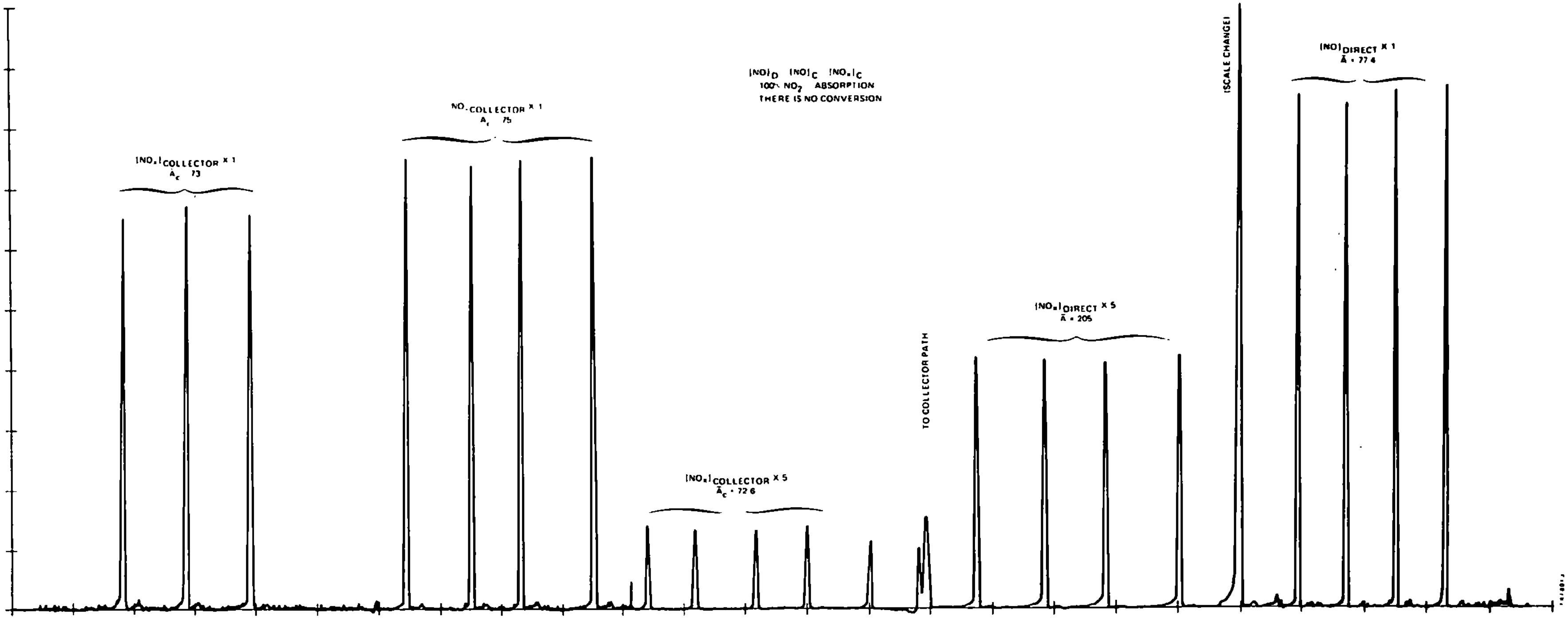


Figure 14(b) - TEA•HCl/Chromosorb G AW DMCS - Injection Mode

3.3.5 Further Work with Celite

Since Celite was the only available support that was not hydrophobic, we decided to re-examine it as a possible support. The previous acid treatment used concentrated HNO_3 and a short soaking time. In the retest, Celite 22 firebrick (from Johns Mansville) was soaked in concentrated HCl for over 72 hr, washed with distilled water until neutral to litmus paper, dried at 80°C, heated to 250°C for 2 hr, and fired at 1200°C for 48 hr. Figure 15 shows that Celite treated in this manner was inert to NO and absorbed NO_2 at room temperature up to 45%. The absorbed NO_2 was released at 150-200°C.

3.3.6 Recovery by Thermal Method (TEA•HCl/Celite)

Blank

TEA•HCl was tested to determine whether it would decompose to give off NO_X. For this test, a tube was packed with TEA•HCl and silane-treated glass wool. Figure 16 indicates that the TEA•HCl did give off some NO_X at a temperature of 160-170°C. The evolution was most likely the NO_2 absorbed by the TEA•HCl, since another heating cycle up to 200°C did not cause further evolution.

TEA•HCl/Celite

TEA•HCl was weighed and dissolved in distilled water. Pre-weighed, acid-treated Celite was added and the solution was allowed to stand an hour. The water was then evaporated at 80°C with occasional stirring; the dried packing was then transferred into the Pyrex cartridge. Prior to evaluation, this collector cartridge was conditioned at 100-120°C for 4 hr with 120 cc/min air flow, then heated to 170°C to check for

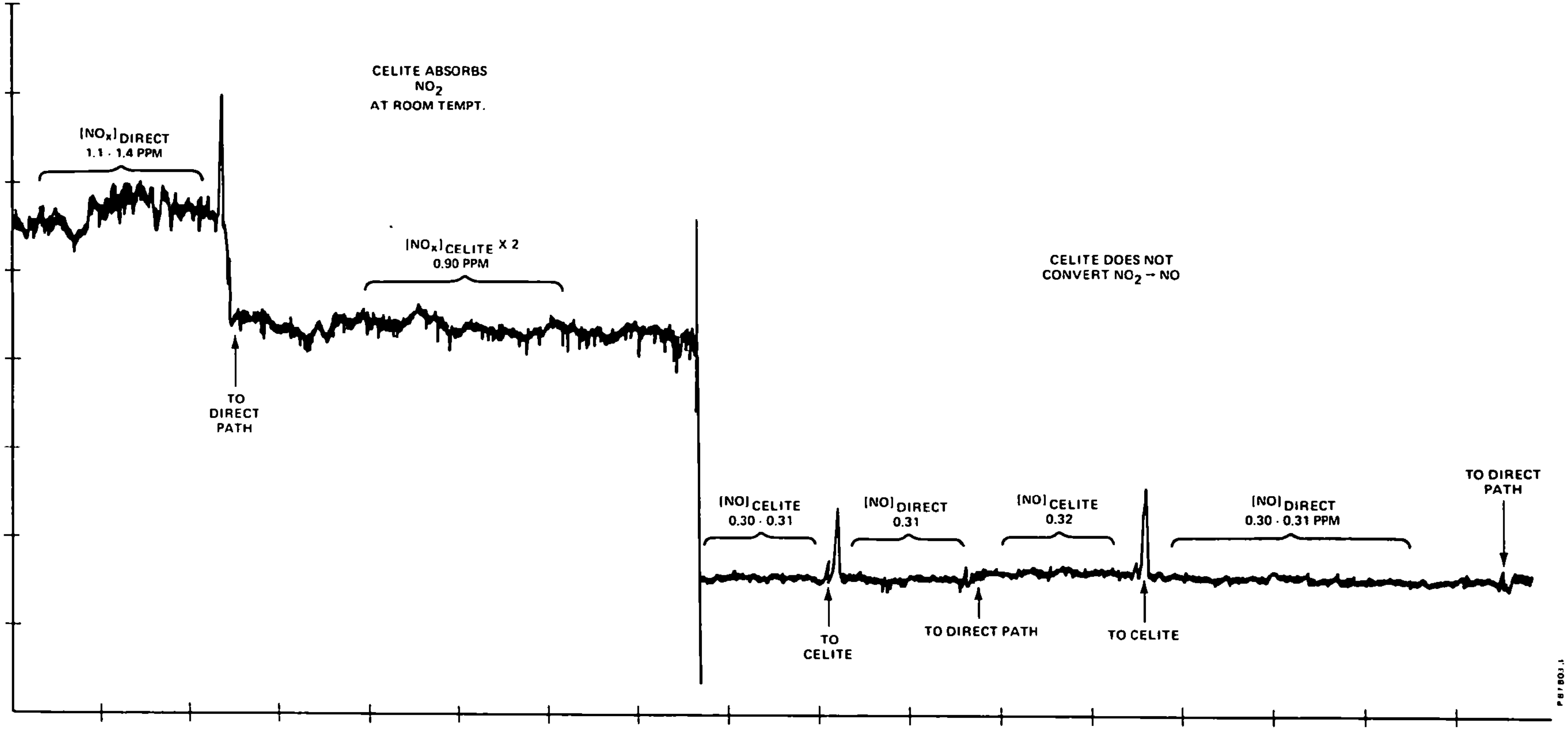


Figure 15(a) - Celite, Specially Treated (Acid-Washed, Neutralized with Distilled H_2O, Dried and Fired at 1200°C for 48 hr): Inert to NO, absorbs NO_2 at Room Temperature

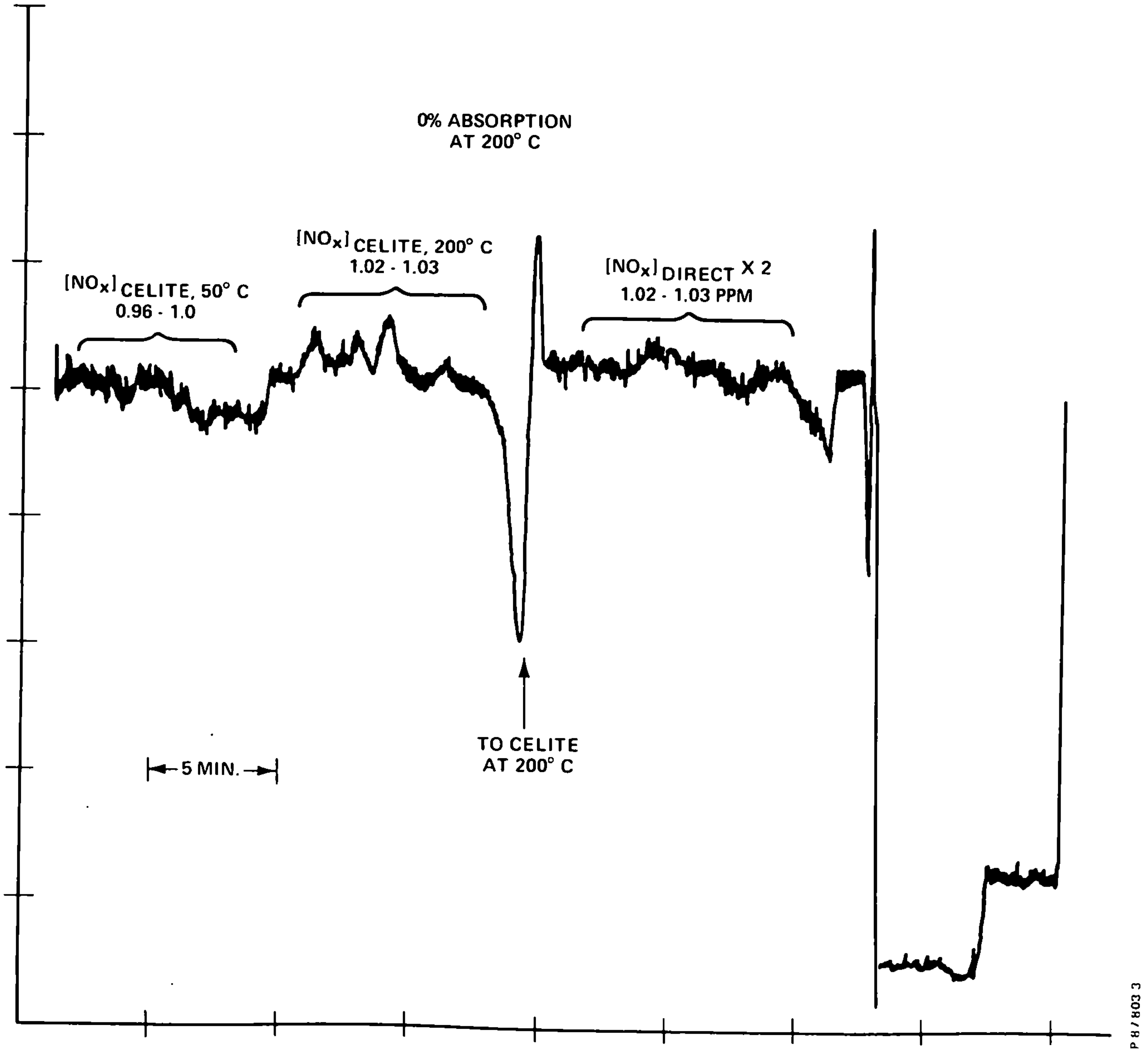


Figure 15(b) - Celite, specially treated (Acid-washed, neutralized with distilled H_2O, Dried and Fired at 1200°C for 48 hr): at 200°C, does not absorb NO_2

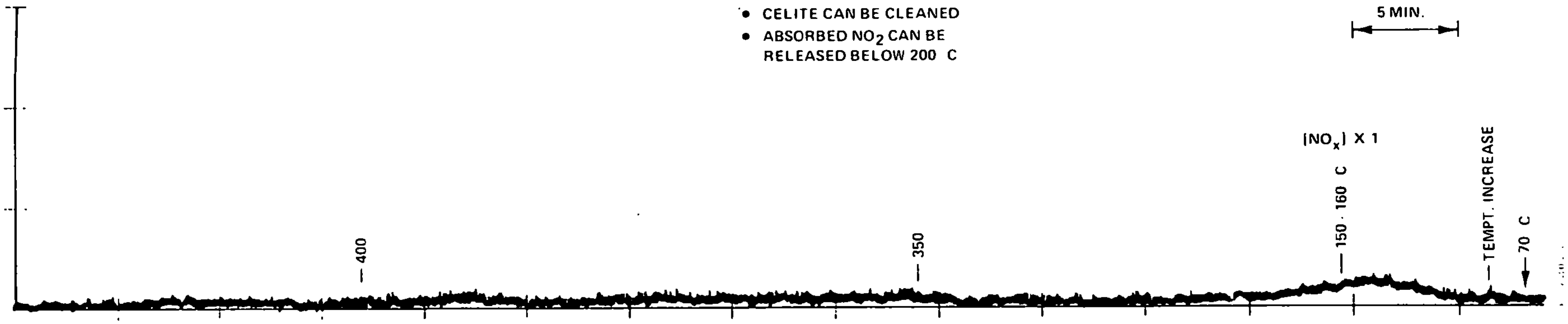


Figure 15(c) - Celite, Specially Treated (Acid-Washed, Neutralized with Distilled H_2O, Dried and Fired at 1200°C for 48 hr): Releases Absorbed NO_x When Heated

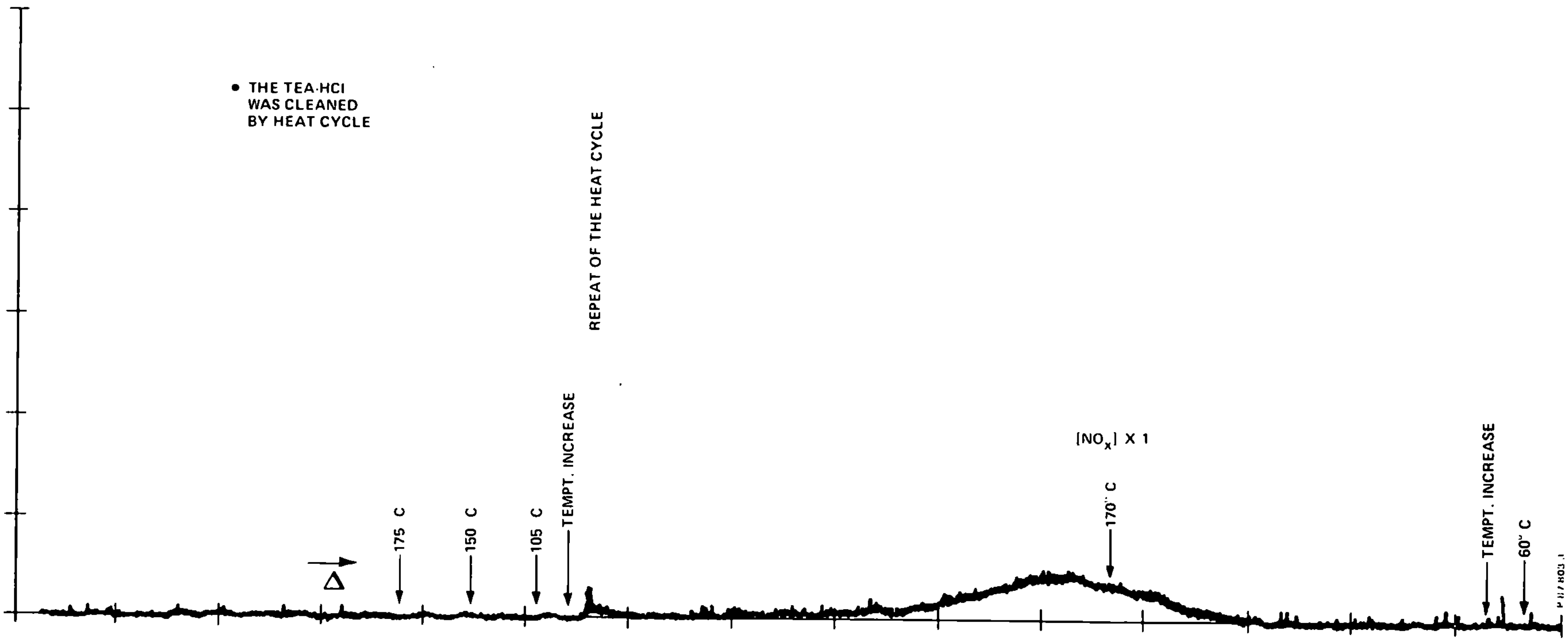


Figure 16 - Blank, TEA•HCl/Glass Wool (by Heat)

release of NO_X. Its performance at room temperature is given in Figure 17(a). TEA·HCl absorbed no NO_X at 165-170°C as indicated in Figure 17(b).

3.3.7 The NO_2 Collector: TEA·HCl/Celite

That TEA·HCl/Celite was a true NO_2 collector was further confirmed by the test results given in Figure 18. This figure shows clearly that the packing not only removed NO_2 from the sample air without disturbing NO at room temperature, but also completely released the NO_2 at an elevated temperature. This experiment utilized the injection mode; the volume used for each injection was 5 cc. The collection efficiency was estimated:

$$\bar{A}_{[NO_X]_D} = 355$$

$$\bar{A}_{[NO]_D} = 32$$

Therefore

$$A_{[NO_2]_D} = 355-32 = 323$$

$$\bar{A}_{[NO]_C} = 31.5$$

$$\bar{A}_{[NO_X]_C} = 33.5$$

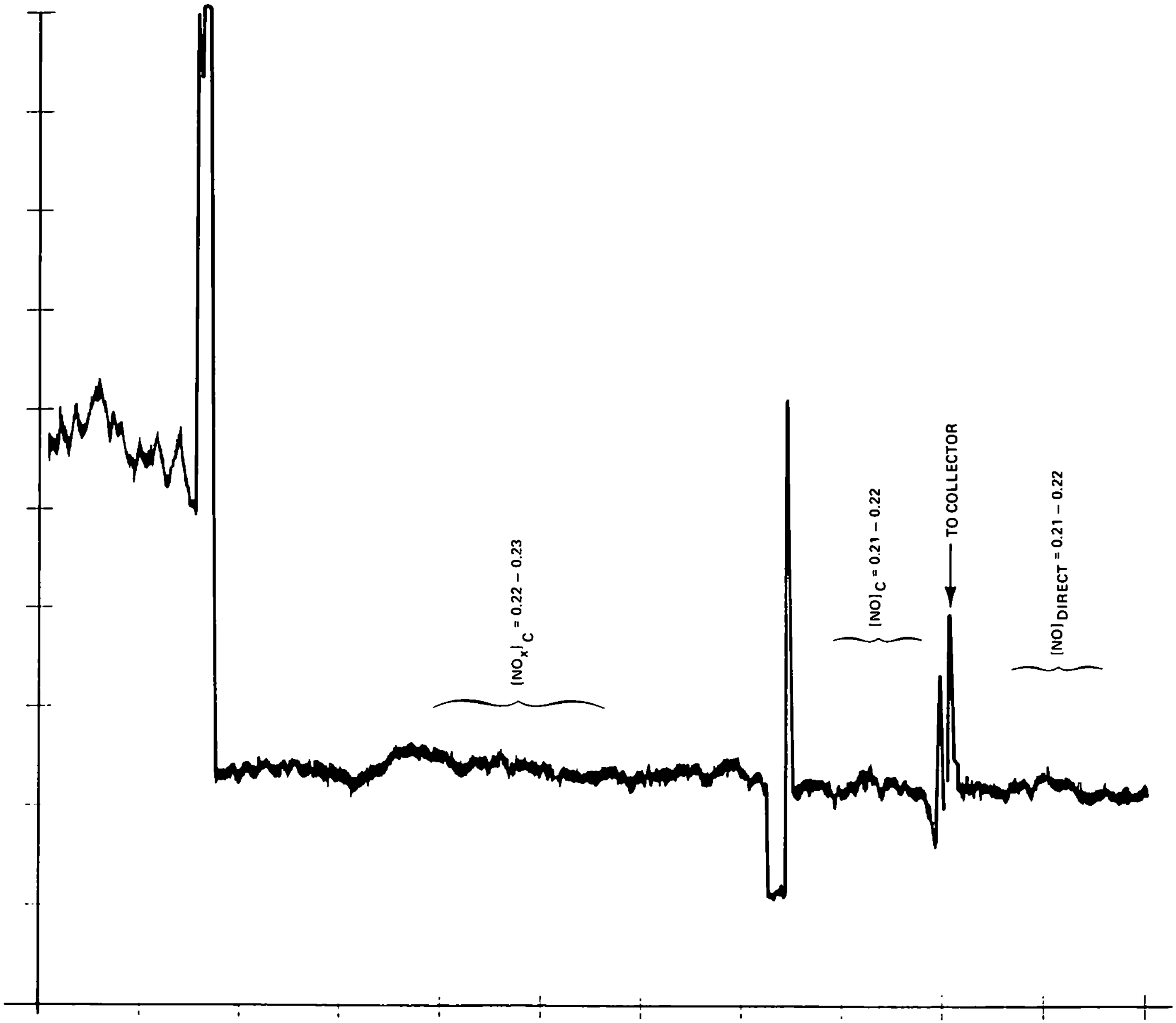


Figure 17(a) - TEA·HCl/Celite at room temperature, inert to NO, absorbs NO_2 completely

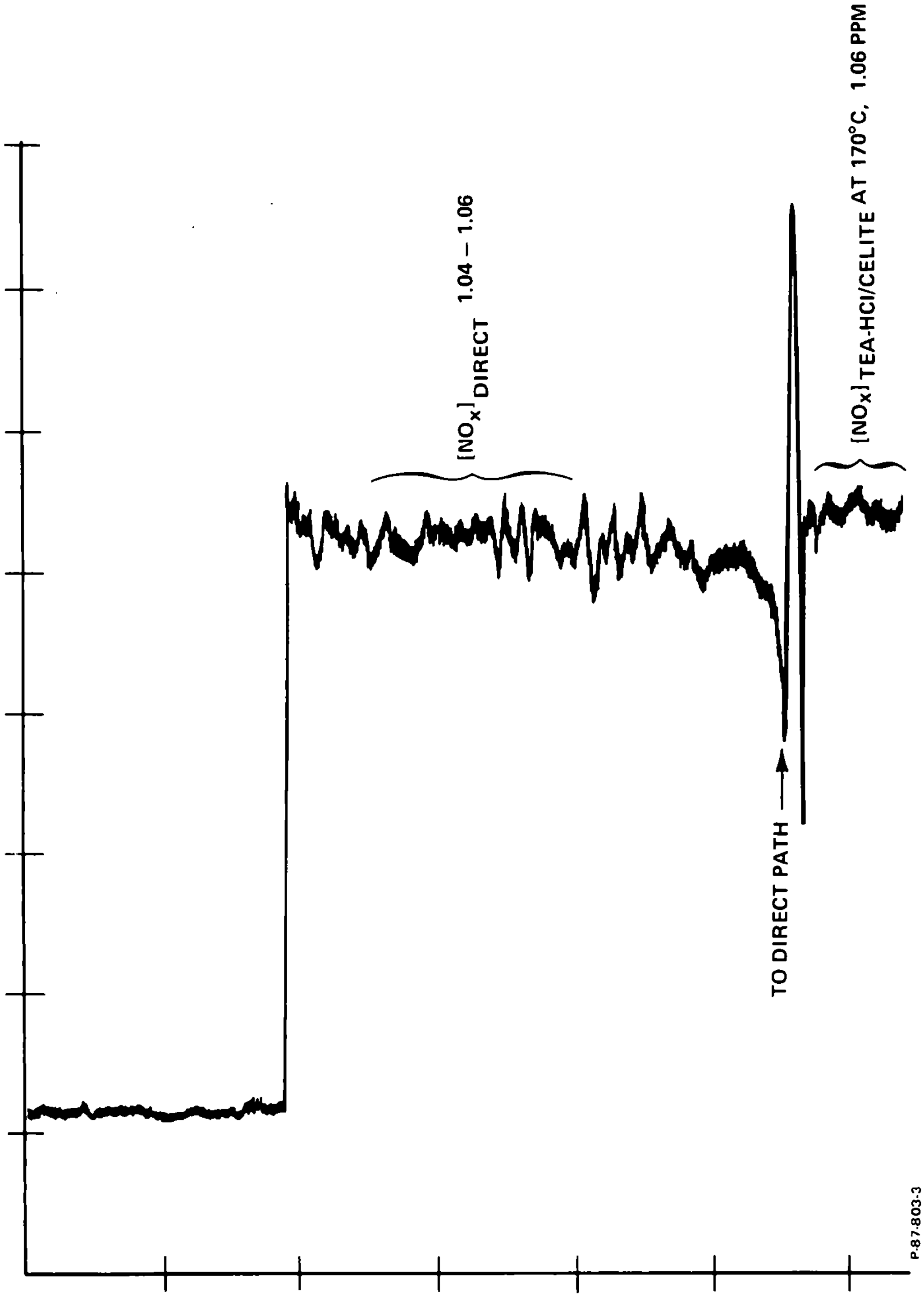


Figure 17(b) - TEA•HCl/Celite at 165-170°C, NO_2 completely passes through

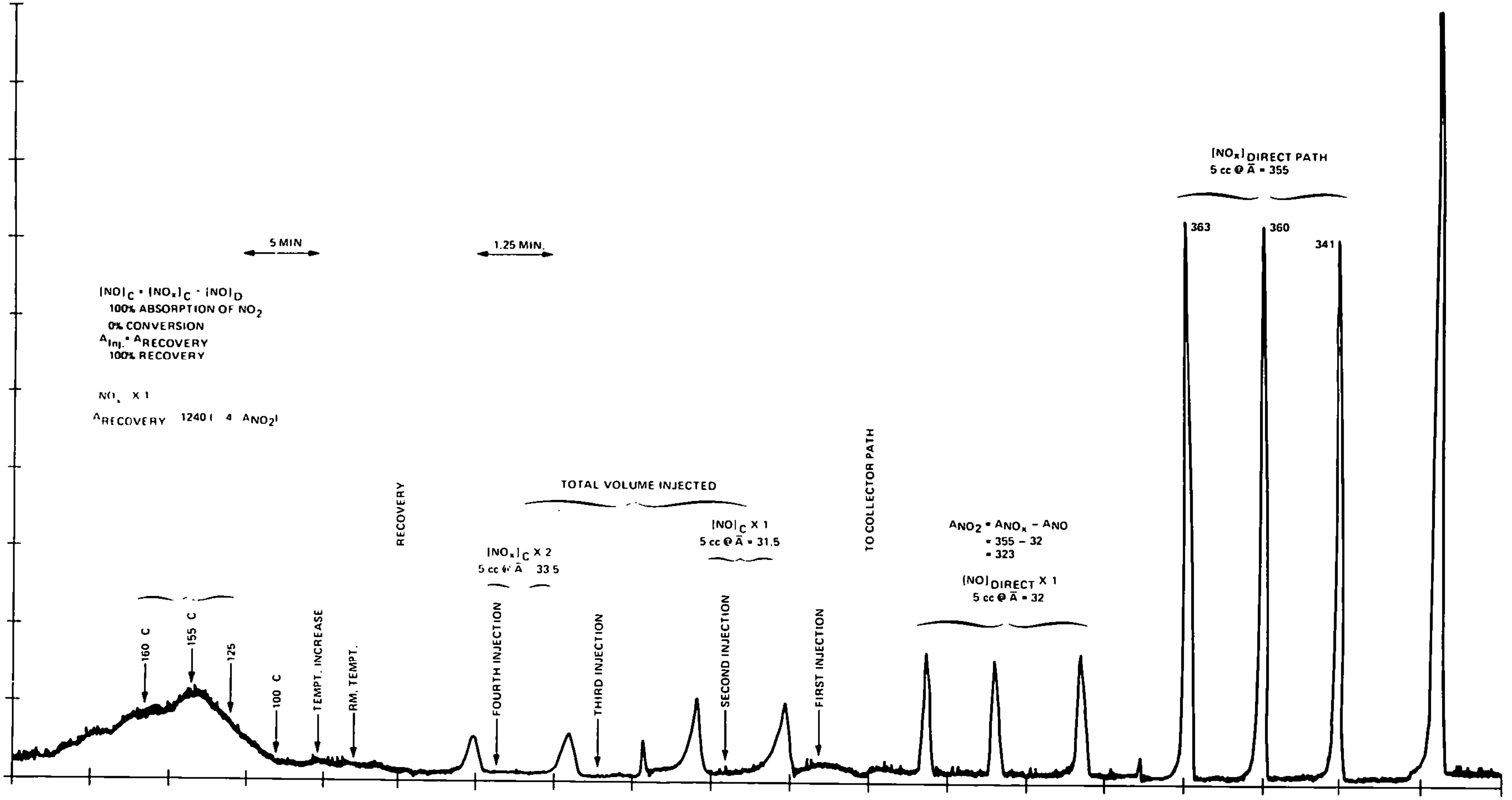


Figure 18 - Performance of NO_2 Collector TEA•HCl/Celite (SO_2-Treated, 1000 ppm SO_2/Air, 1 ℓ/min for 20 min)

Thus,

$$\overline{A}_{[NO_2]} \sim 0 \quad \text{and} \quad [NO]_C \sim [NO_X]_C \sim [NO]_D$$

A total of 20 cc was introduced into the collector in 4 sequential injections. The recovery peak between 120-170°C had a calculated area of 1240 counts, that is, about 4 times the area for each 5 cc injection of NO_2. In other words, TEA•HCl/Celite released its absorbed NO_2 completely:

$$A_{recovery} = 1240 \doteq 4\ A_{[NO_2]_D} = 4 \times 323$$

The above collector material went through many temperature cycles before these measurements [Figure 17(b) for example] and it also underwent an SO_2 treatment in which 1000 ppm SO_2 in air was passed through the collector for 20 min at 1 ℓ/min flow rate. Furthermore, the ambient air carrier used in these experiments contained up to 95% humidity. Nonetheless, the material retained its performance as a good NO_2 collector.

3.3.8 NO Absorbent

An effort was made to identify an NO absorbent or a total NO_X absorbent to complement the NO_2 absorbent TEA•HCl/Celite.

Since it was known that inorganic oxides can interact with NO_X (for example, PbO_2 forms a nitrate with nitrogen oxides), the following inorganic compounds were chosen for further study: CuO, Cu_2O, $CoSO_4$, Co_2O_3, CoO, $NiSO_4$. The cobaltous and cobaltic oxides proved to be excellent total NO_X absorbents, whereas the other salts evaluated showed negative results. Figures A-10 to A-13 show the results obtained from some of these oxides.

The capability of cobaltic oxide to absorb NO_X is clearly depicted in Figures 19 and 20. In these experiments the sample NO_X was quantitatively injected into the collector where it was completely absorbed and later released without loss at 395-420°C. The packing was prepared by first heating Co_2O_3 (grayish-black powder) in a Pyrex tube at 500-550°C with air flow for 48 hr. When cool, the oxide was physically mixed with Chromosorb G AW-DMCS 80/100 mesh (or 45/60 mesh) in 1:2 ratio by volume, then packed into a Pyrex tube or an aluminum collector cartridge. Prior to evaluation, the collector was conditioned at 420°C overnight or until it was free from any pre-absorbed NO_X. During the evaluation of the collector with an NO_X analyzer, the ambient air carrier gas contained 92% humidity.

As shown in Figure 20(a), the cobalt oxides completely absorbed the NO at 250°C. The area count for each injection was established by injecting samples into the collection system with the absorbent at 390-400°C at which temperature no absorption occurred.

$$\bar{A}_{[NO]_{injected}} = 97$$

$$A_{1[NO]_{recovered}} = 100$$

$$A_{2[NO]_{recovered}} = 104$$

These values indicate 100% recovery.

Figure 20(b) depicts the quantitative recovery of NO_X as follows:

$A_0 = A_{[NO_X]_{injected}} = 1224$ (for each injection at 405-410°C)

A_1 (recovery from 1 injection) $= 1360 \sim A_o$

A_2 (recovery from 2 injections) $= 2640 \sim 2A_o$

A_3 (recovery from 3 injections) $= 4468 \sim 3A_o$

A_4 (recovery from 4 injections) $= 5472 \sim 4A_o$

and,

$$A_2/A_1 = 1.94,\ A_3/A_1 = 3.28,\ A_4/A_1 = 4.02 \quad .$$

Results represented in Figure 21 were obtained on the collector Co_2O_3/Chromosorb G AW-DMCS 45/60 contained in an aluminum cartridge. This figure also demonstrates that the collector absorbed and released NO_X quantitatively as shown below:

(a) For each 1 cc injection of NO_X sample, the average area count was $\overline{A}_1 = 545$ (1 cc through a direct path).

(b) Injection of a 1 cc sample into a hot collector at 430°C afforded an area count of $A_2 = 560$

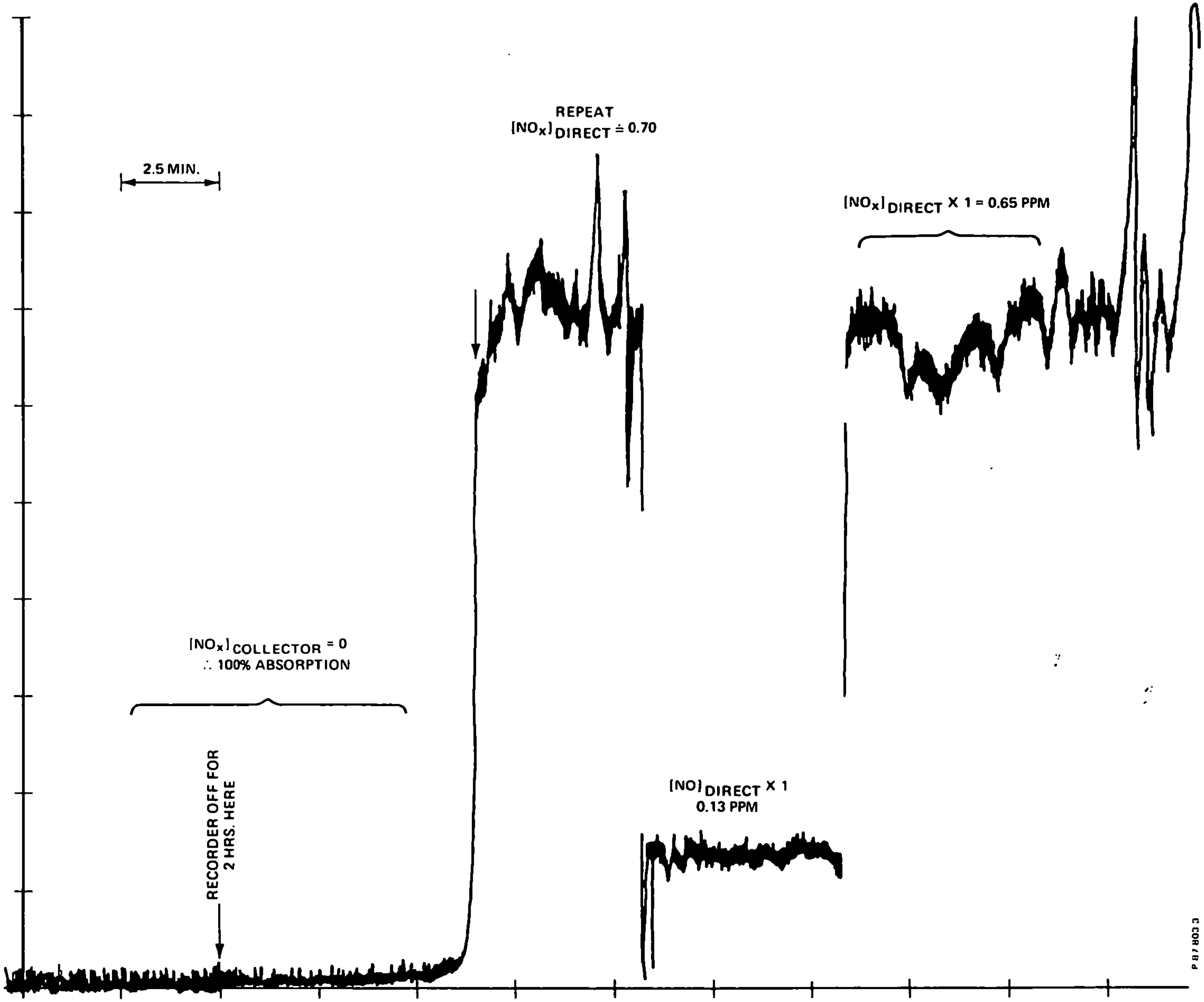


Figure 19 - Total NO_X Collector (Aluminum cartridge), Co_2O_3/Chromosorb G

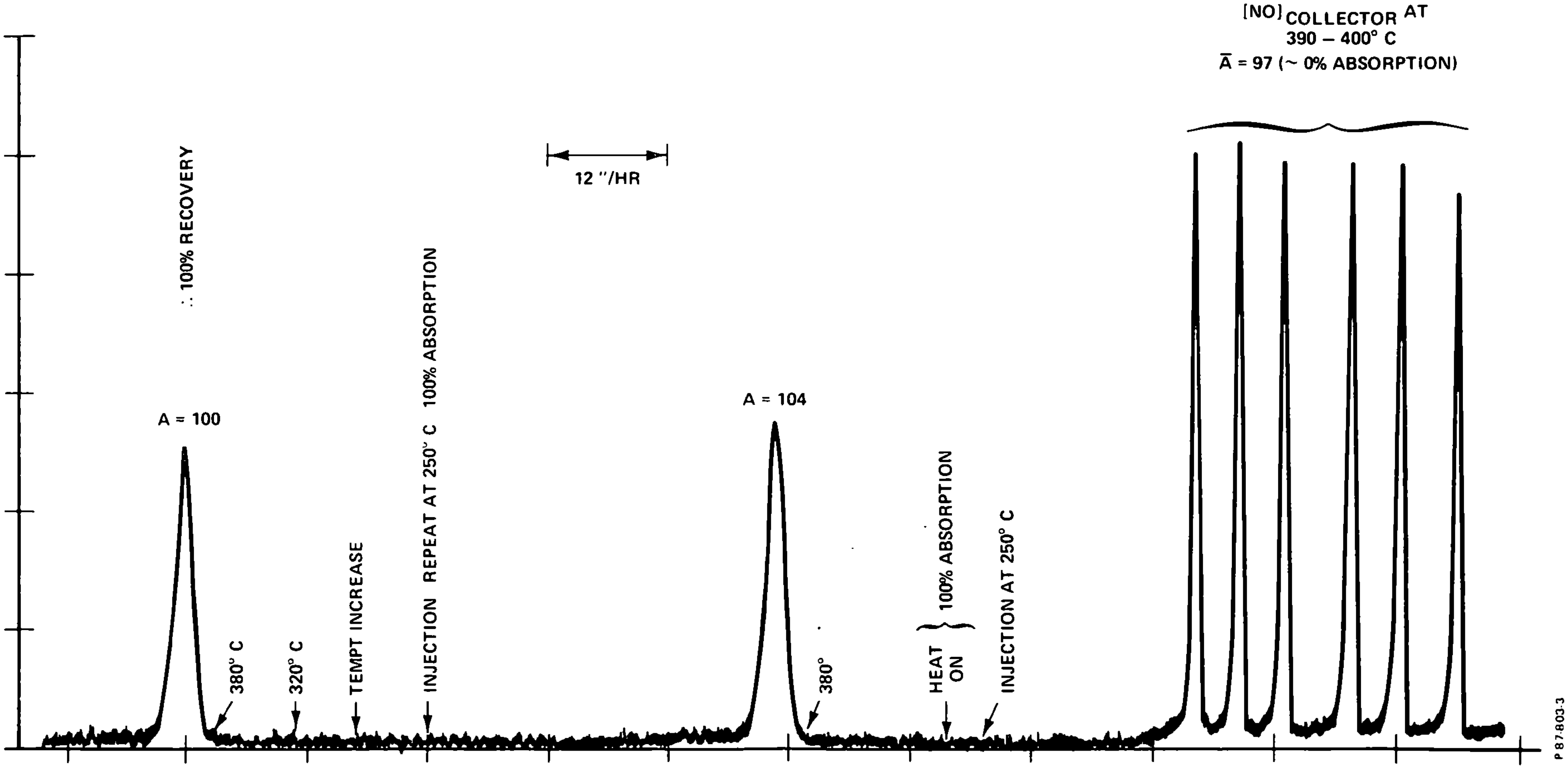


Figure 20(a) - NO$_X$ Collector, Co_2O_3/Chromosorb G 80/100 mesh - Quantitative Collection and Recovery of NO

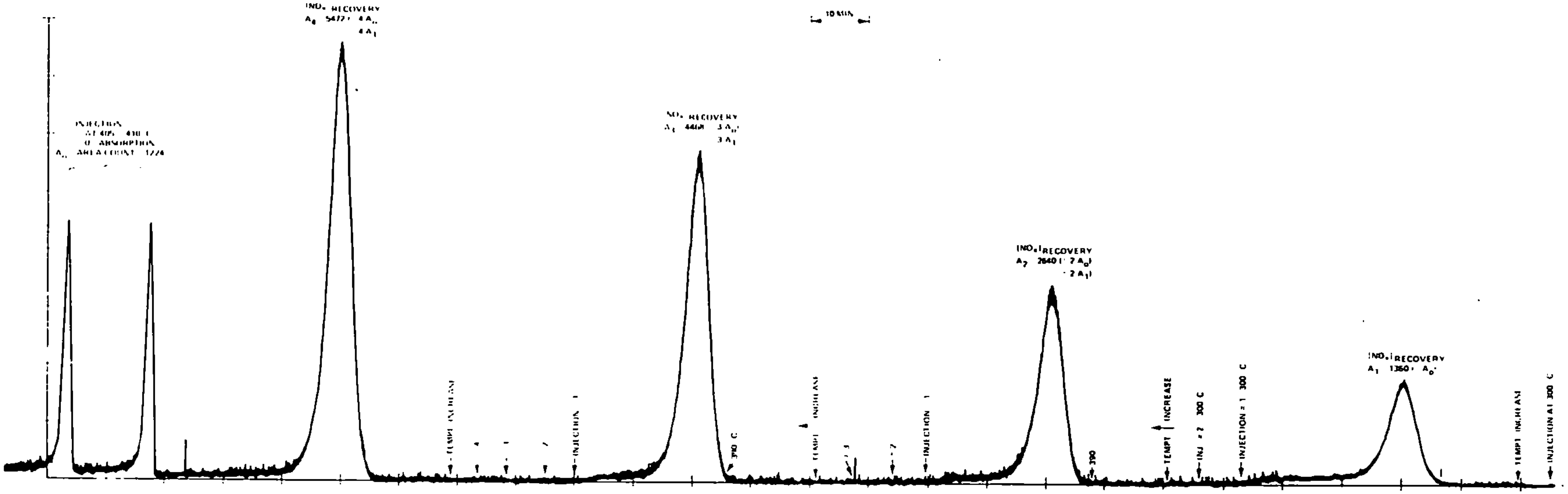


Figure 20(b) - NO$_x$ Collector, CO$_2$O$_3$/Chromosorb G 80/100 Mesh - Quantitative Collection and Recovery of NO$_x$

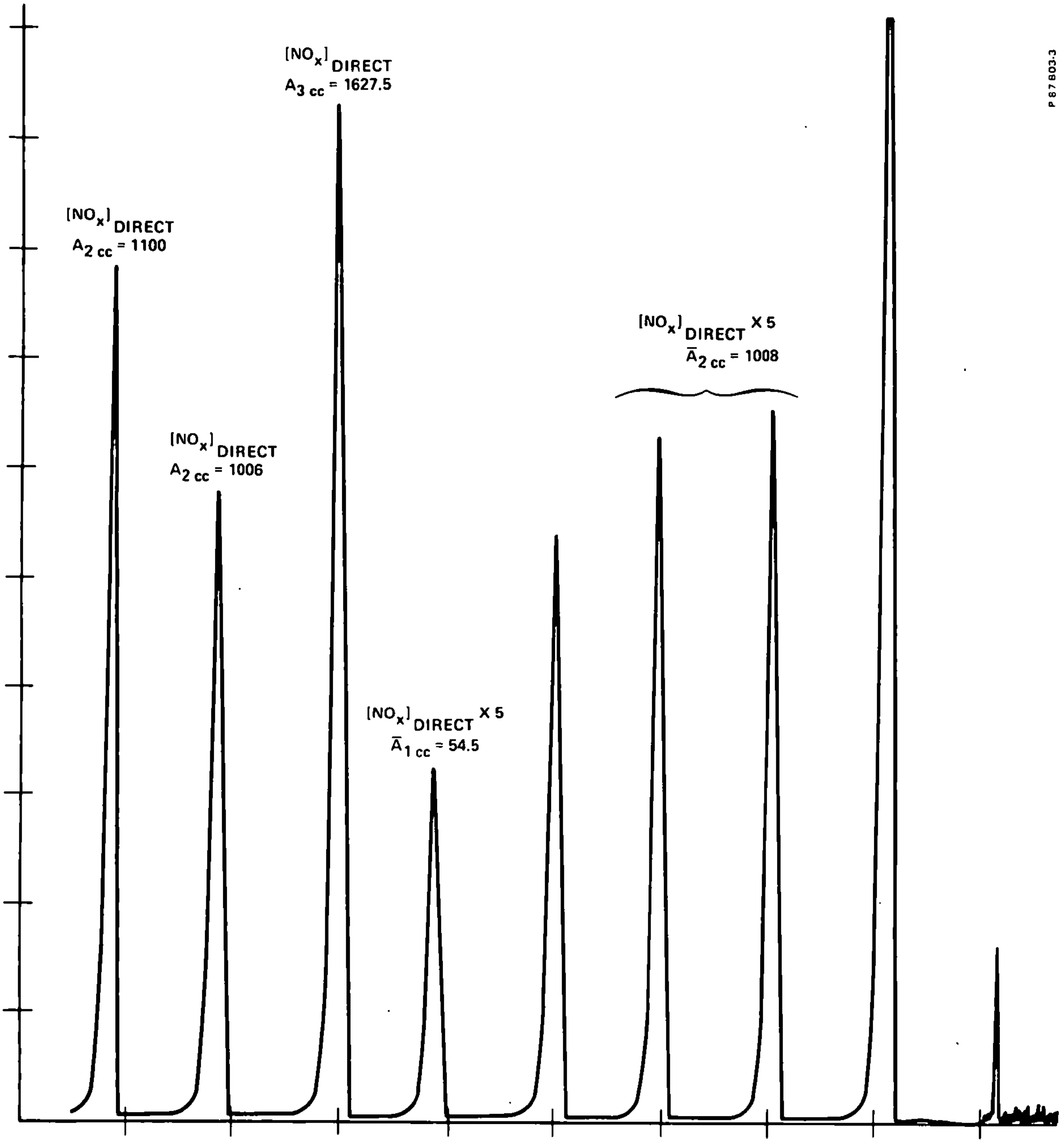


Figure 21(a) - NO_X Collector (Aluminum Cartridge, Co_2O_3/Chromosorb G 45/60 mesh) - Area Estimate of Sample Injected, Carrier Air Contains 92% Humidity

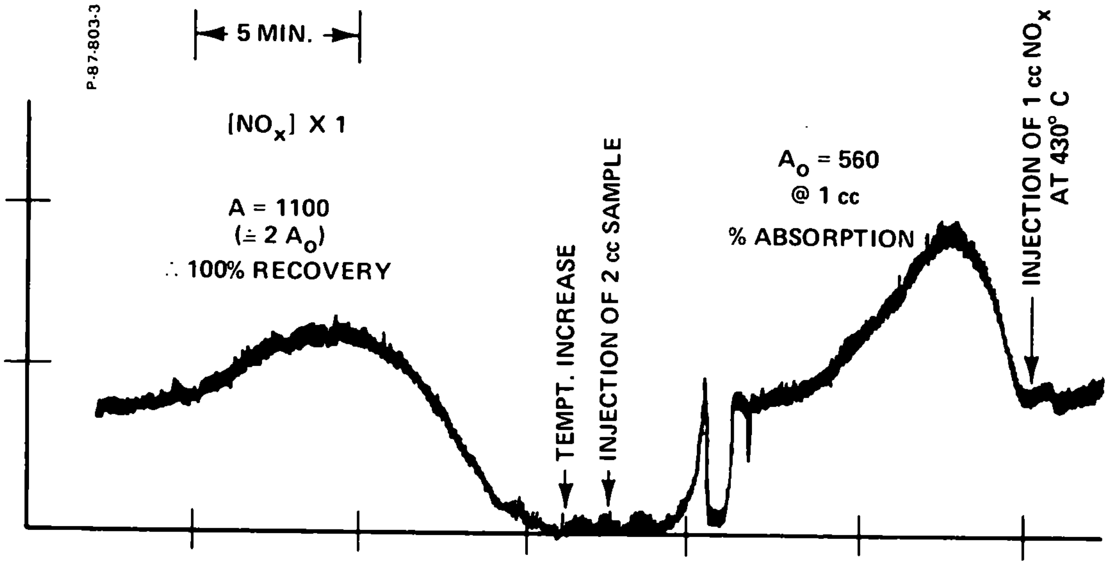


Figure 21(b) - NO$_X$ Collector (Aluminum Cartridge, Co_2O_3/Chromosorb G 45/60 mesh) - Quantitative Recovery of 2 cc Sample Injected

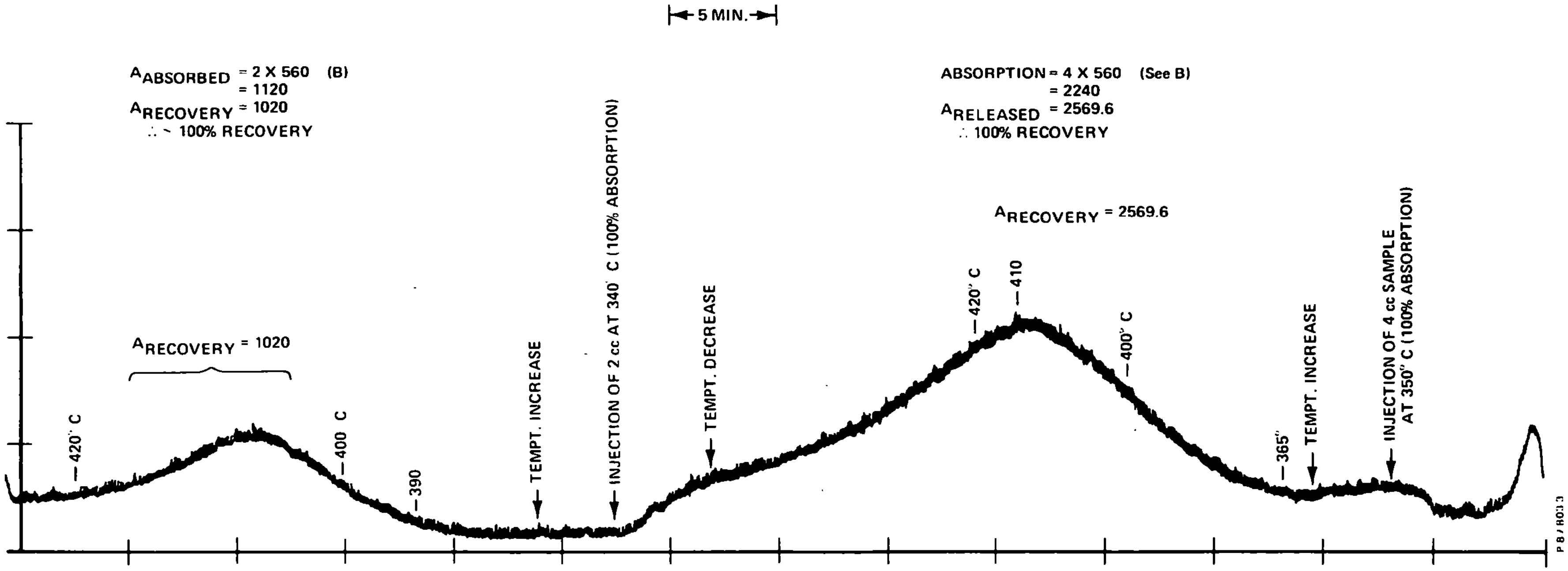


Figure 21(c) - NO_X Collector (Aluminum Cartridge, Co_2O_3/Chromosorb G 45/60 mesh) - Quantitative Recovery of 2 cc and 4 cc Sample Injected

(c) A 2 cc sample injected into the collector at ∿300°C was totally absorbed; when the collector temperature was raised to 430°C, a peak was obtained with an area count of

$$A_3 = A_{\text{recovery from 2cc}} = 1100 \doteq 2\ \bar{A}_1 = 2\ A_2$$

$$A_3/\bar{A}_1 = 2.0;\ A_3/A_2 = 1.96$$

(d) $A_4 = A_{\text{recovery from 4cc}} = 2569.6 \sim 4 \times A_2$

$$A_5 = A_{\text{recovery from 2cc}} = 1020 \doteq 4 \times A_1$$

It was therefore clear that an NO_X absorbent had been identified. Moreover, this cobalt oxide could serve as an NO absorbent with a precolumn such as TEA or TEA•HCl to first remove NO_2. This tandem arrangement was therefore chosen for the design of the NO_2, NO collection unit.

3.3.9 Calibration of Peak Areas

A calibrated sample of 1.1 ppm NO (Matheson Gas Products, Inc.) was used for the area/mass equivalent calculation. Various volumes of this sample were injected to establish an average area count.

Each cubic centimeter of calibrated sample containing 1.4 ng produced an area count of 4, (Figure 22) making each area count equivlent to 0.35 ng NO. Based on the calculation, each cubic centimeter of sample prepared by the laboratory test setup contained on the order of 10^{-7} g. This sample size was injected into collectors being evaluated to test their absorption efficiency.

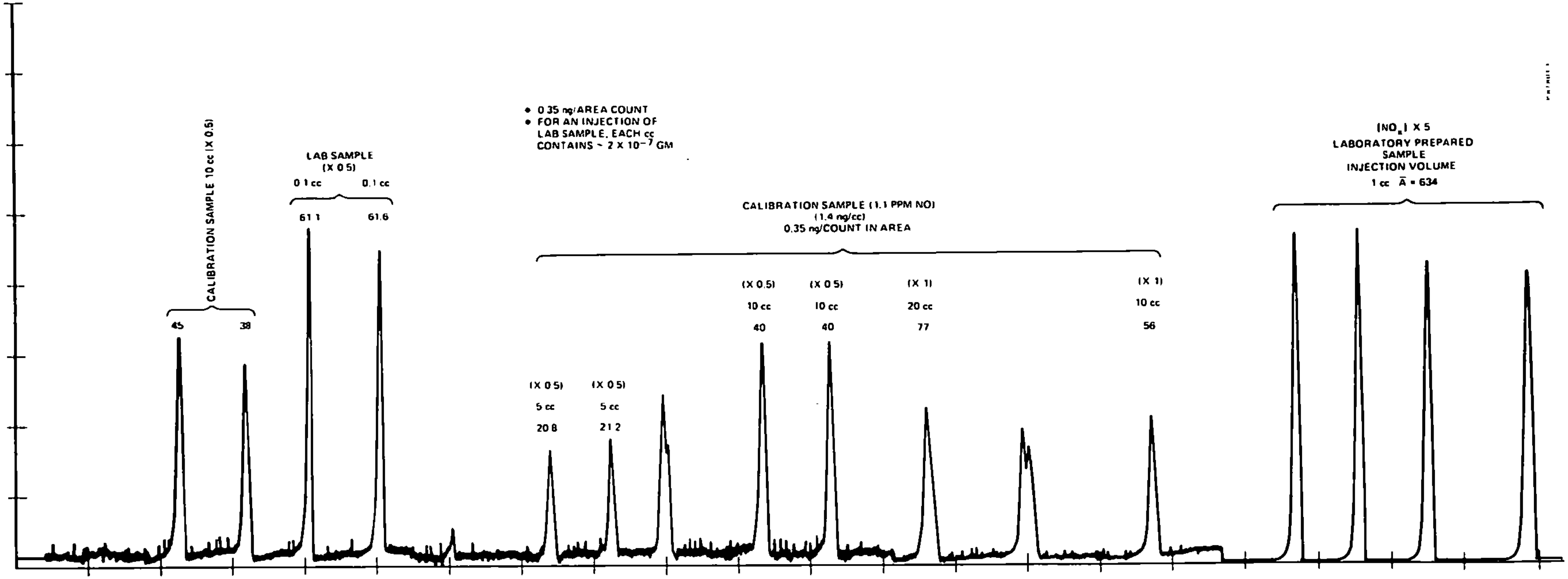


Figure 22 - Estimation of Quantity of Sample Injected with Calibration Sample Mixture

3.4 INTERFERENCE STUDIES

The effects of moisture, hydrogen sulfide (H_2S), and sulfur dioxide (SO_2) on the performance of the collectors were investigated. Moisture alone up to 92% did not affect the performance of the cobalt oxide and TEA·HCl/Celite. Likewise the combination of H_2S (20.2 ppm in N_2 from a permeation tube) and up to 96% humidity had no synergistic effect on TEA·HCl/Celite (see Figure 23). Passing 1000 ppm SO_2 in air at a flow rate of 1 ℓ/min for 20 min through the TEA·HCl/Celite had no effect. The support retained its superior performance. The presence of SO_2 and moisture did not change the concentration of [NO] or $[NO_X]$ in the absence of TEA·HCl/Celite. However, an effect was noted when $[NO_X]_C$ and $[NO]_C$ were compared with or without the presence of both moisture and SO_2. A 6 to 30% reduction of NO passing through the collector was noted in the presence of both 1000 ppm SO_2 and moisture (see Figure 24). Thus NO might have been converted to NO_2 which was in turn absorbed. However, this effect was produced by SO_2 in a concentration 100 times that of the nitrogen oxide in the sample (1 cc NO_X sample with an area count about 90 was equivalent to about 3×10^{-8} g, while 1 cc of 1000 ppm SO_2 contained about 3×10^{-6} g). This high a concentration is unlikely to be encountered in actual field conditions.

Figure 25 shows the recovery from the SO_2-treated TEA·HCl/Celite collector which had been injected with 20 cc NO_X (see Figure 18 for area count), then stored in the lab drawer for 48 hr prior to thermal release. The area count of the recovery peaks obtained from this collector was more than equivalent to the 20 cc injection. ($A_{recovery} = 1596$. $A_{20\ cc} = 4 \times 323 = 1292$ per Figure 18), indicating a 100% release from the collector.

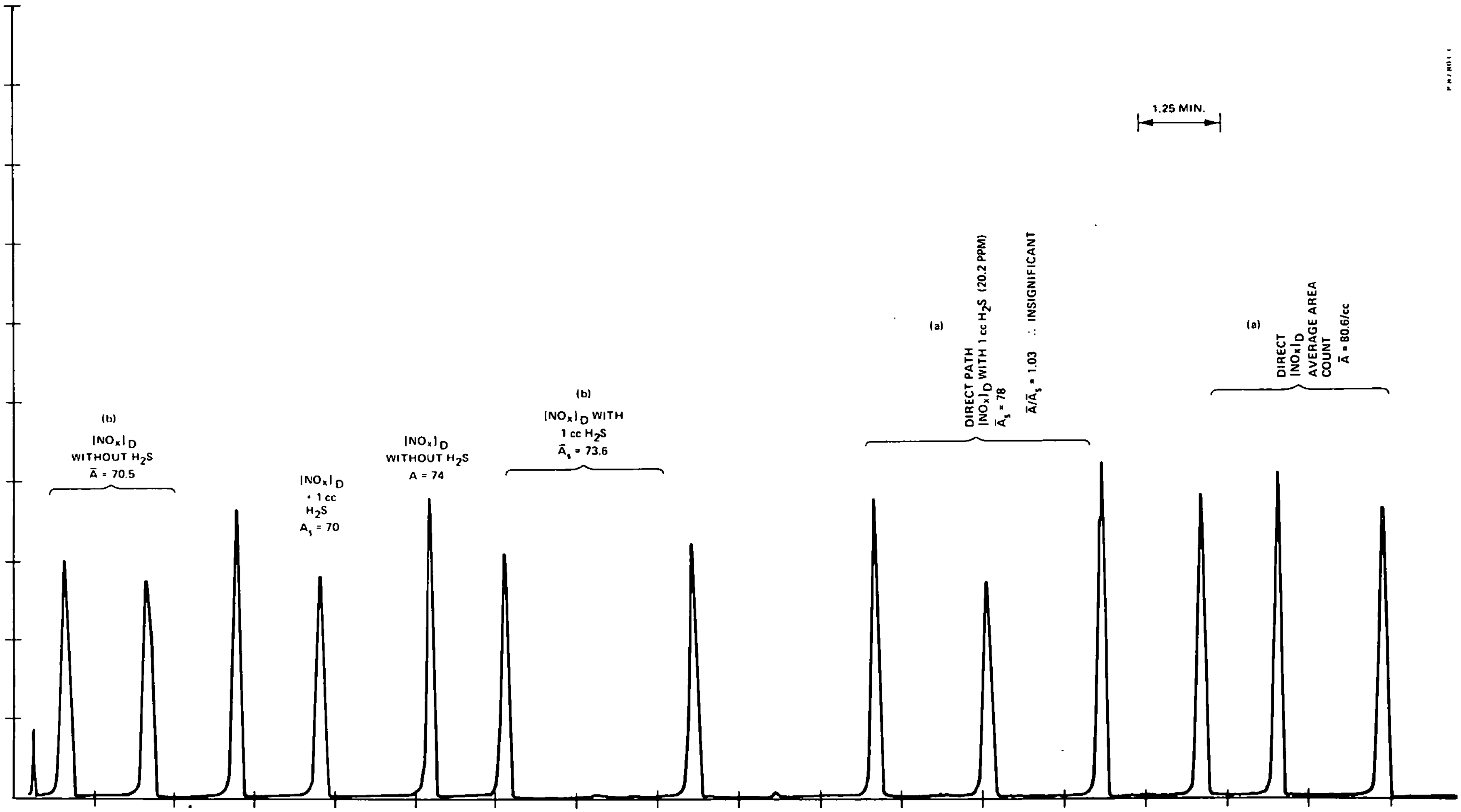


Figure 23(a) - Effect of H_2S (20.2 ppm) on TEA·HCl/Celite, Carrier Air Contains 96% Humidity - Direct Path (Bypassing Collector), Injected Volume: 1 cc NO_x

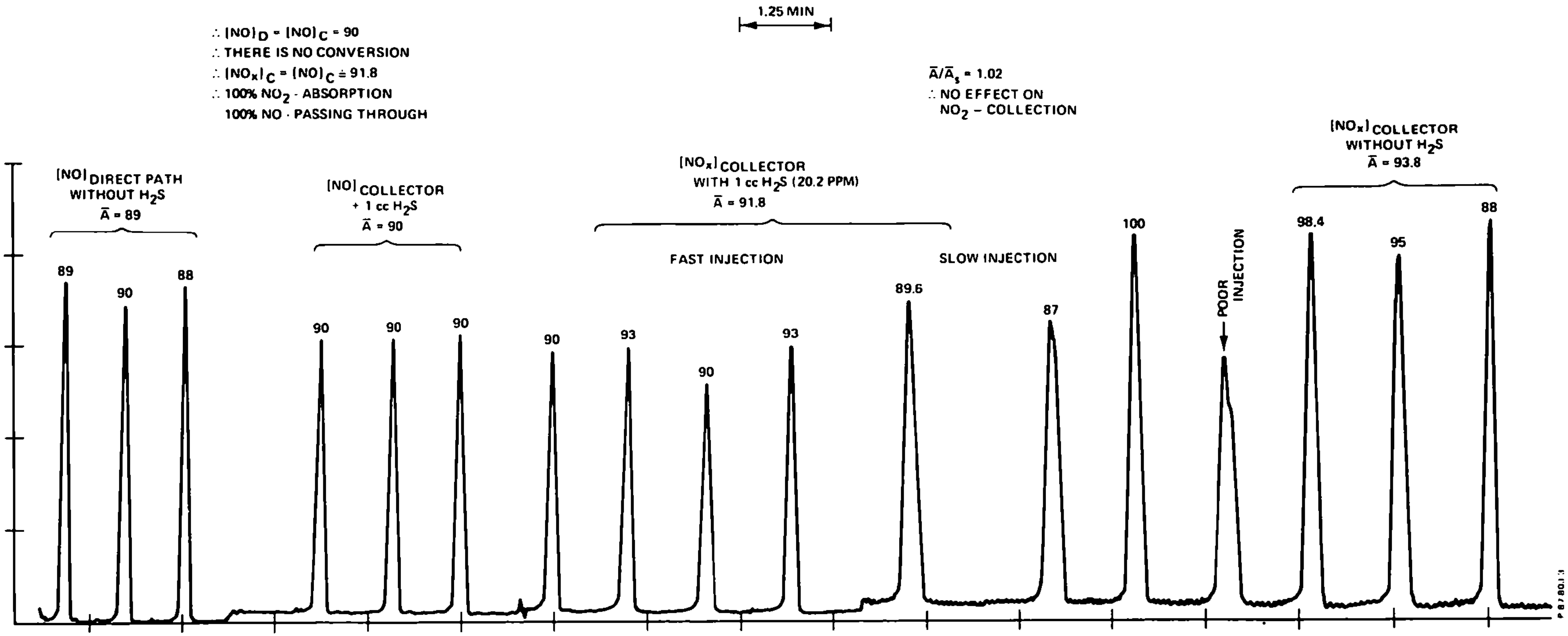


Figure 23(b) - Effect of H_2S (20.2 ppm) on TEA•HCl/Celite, Carrier Air Contains 96% Humidity - H_2S Does Not Affect the Performance of the Collector

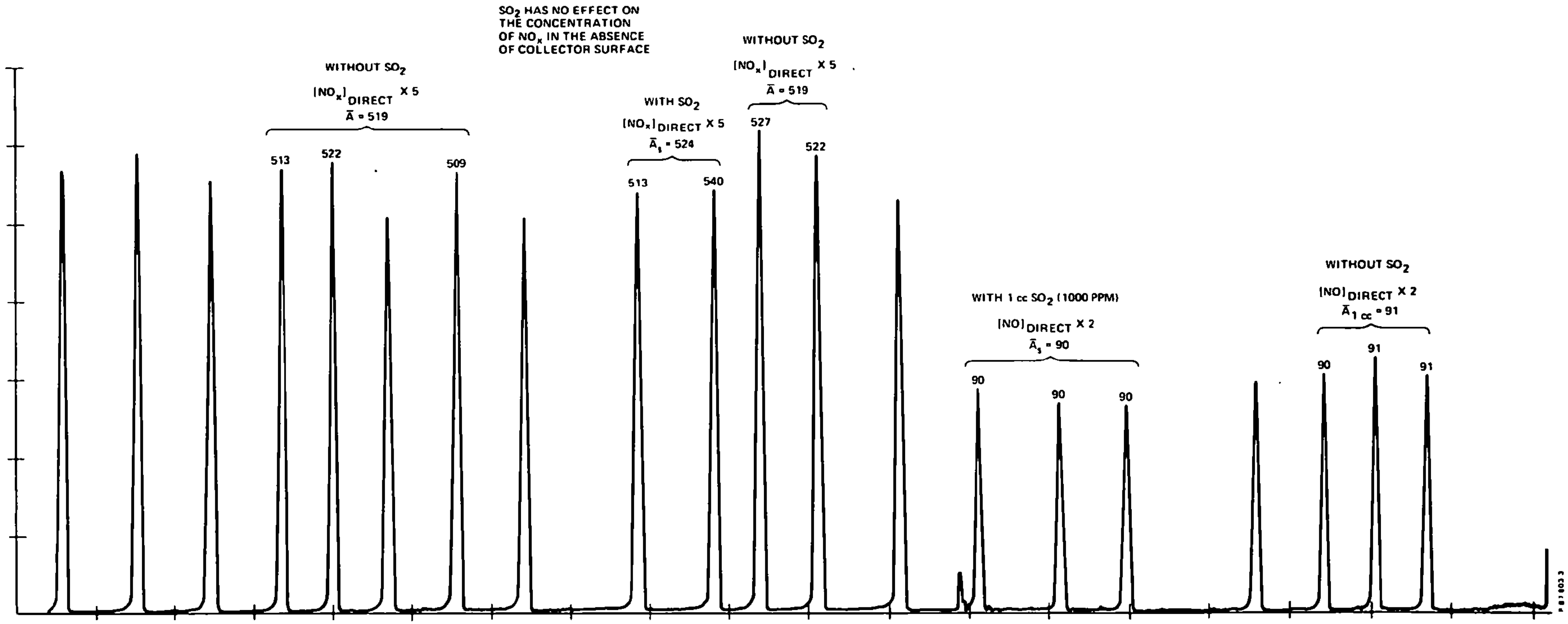


Figure 24(a) - Effect of SO_2 (1000 ppm/air) on TEA•HCl/Celite, Carrier Air Contains 90% Humidity - Direct Path

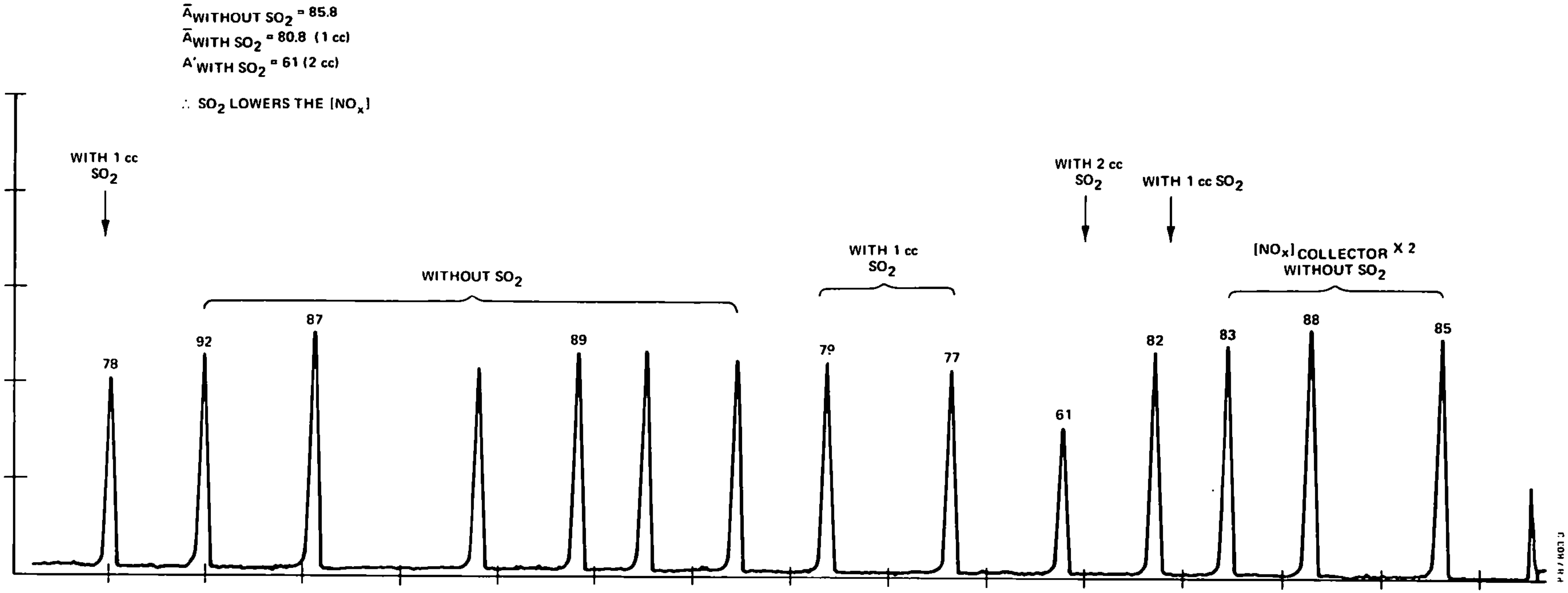


Figure 24(b) - Effect of SO_2 (1000 ppm/air) on TEA•HCl/Celite, Carrier Air Contains 90% Humidity - [SO_2] Lowers [NO_x] Passing Through the Collector

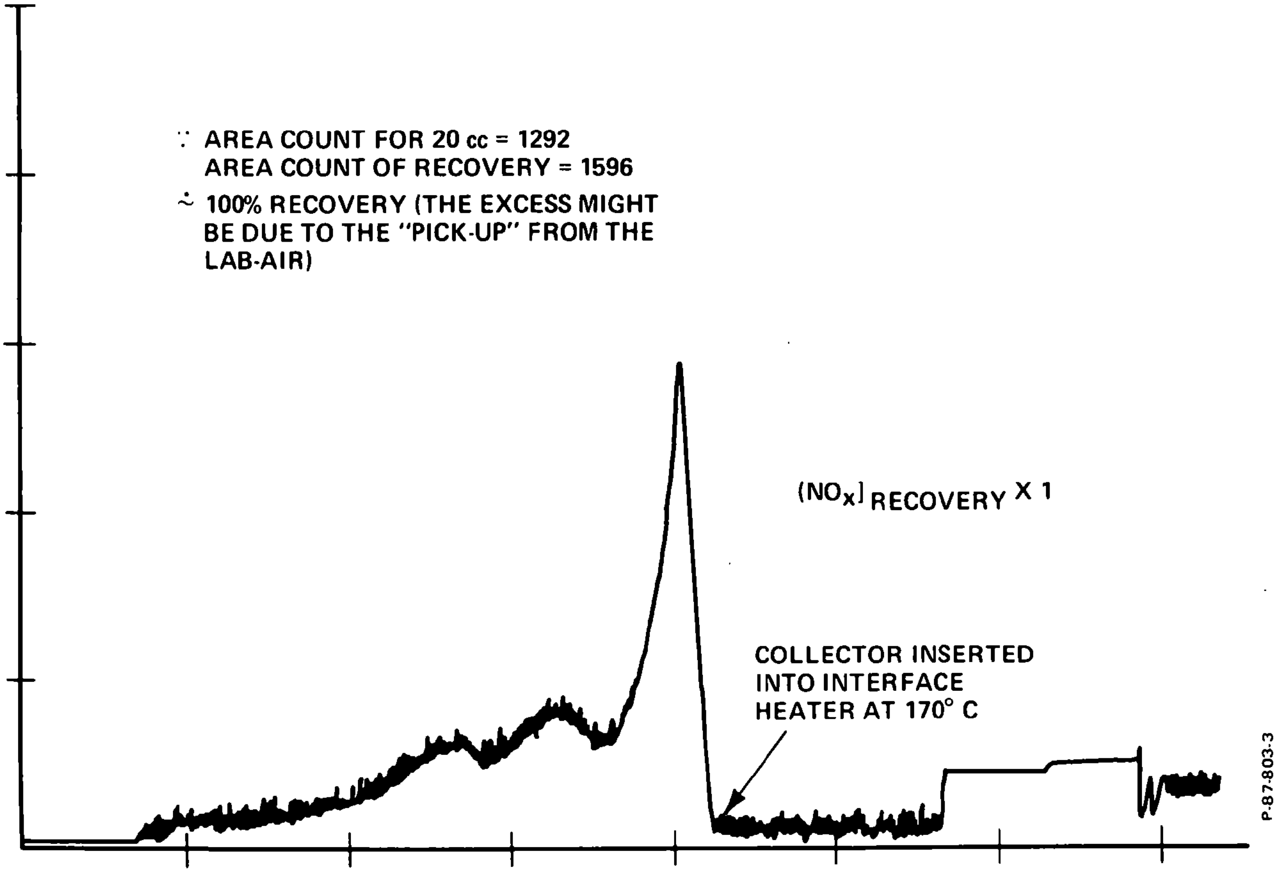


Figure 25 - Recovery from NO_2 Collector, TEA•HCl/Celite (SO_2-treated), which was injected with 20 cc NO_X (see Figure 18 for area count), stored in a lab drawer for 48 hr.

3.5 DEVELOPMENT OF COLLECTOR SYSTEM

3.5.1 First-Generation Collector Cartridge and Field Collection System

The collector cartridge is required to be: (a) rugged, (b) lightweight, (c) good in heat transfer, (d) easily packed and unpacked, and (e) able to interface with a suitable analytical instrument for analysis.

The first three requirements can be easily satisfied by choosing an aluminum shell for the cartridge. The last two are met by having a Luer-Lock terminal on the cartridge for syringe needle adaption (to a gas chromatograph, for example), and a stem that can be easily opened at one end for charging and discharging the cartridge. Such a design is shown in Figure 26. In this first-generation cartridge, the barrel can be opened near one end. A V-clamp holds the barrel tight. This clamp is tightened by an Allen-head screw. Both terminals are tapered to allow Luer-Lock connection. As shown in Figure 26(b), one of the Luer terminals is made by inserting a specially made Luer-end screw into the barrel.

The inside surface of the cartridge was coated with Teflon to ensure its inertness, because inertness was essential for selective NO_2 collection. The surface was evaluated for its catalytic activity in converting NO_2 to NO before and after the Teflon coating. The results showed that bare aluminum catalyzed conversion, whereas the Teflon-coated surface was inert (Figures A-14 and A-15 in Appendix A). For NO_X collection, however, the conversion is not a problem. Therefore, two identical aluminum collector cartridges were made, one of which was internally Teflon-coated for the NO_2 collection absorbent, and the other uncoated for the total NO_X absorbent.

Parallel or dual-path collections could be employed, with one collector for NO_2 and the other for NO_X. The difference between the two would represent the concentration of NO. This concept is reflected in Figure 27 which illustrates the dual-path collector/pump assembly. The collector cartridge was supported by an aluminum tube lined with soft padding. A filter was located in front of the cartridge and another behind

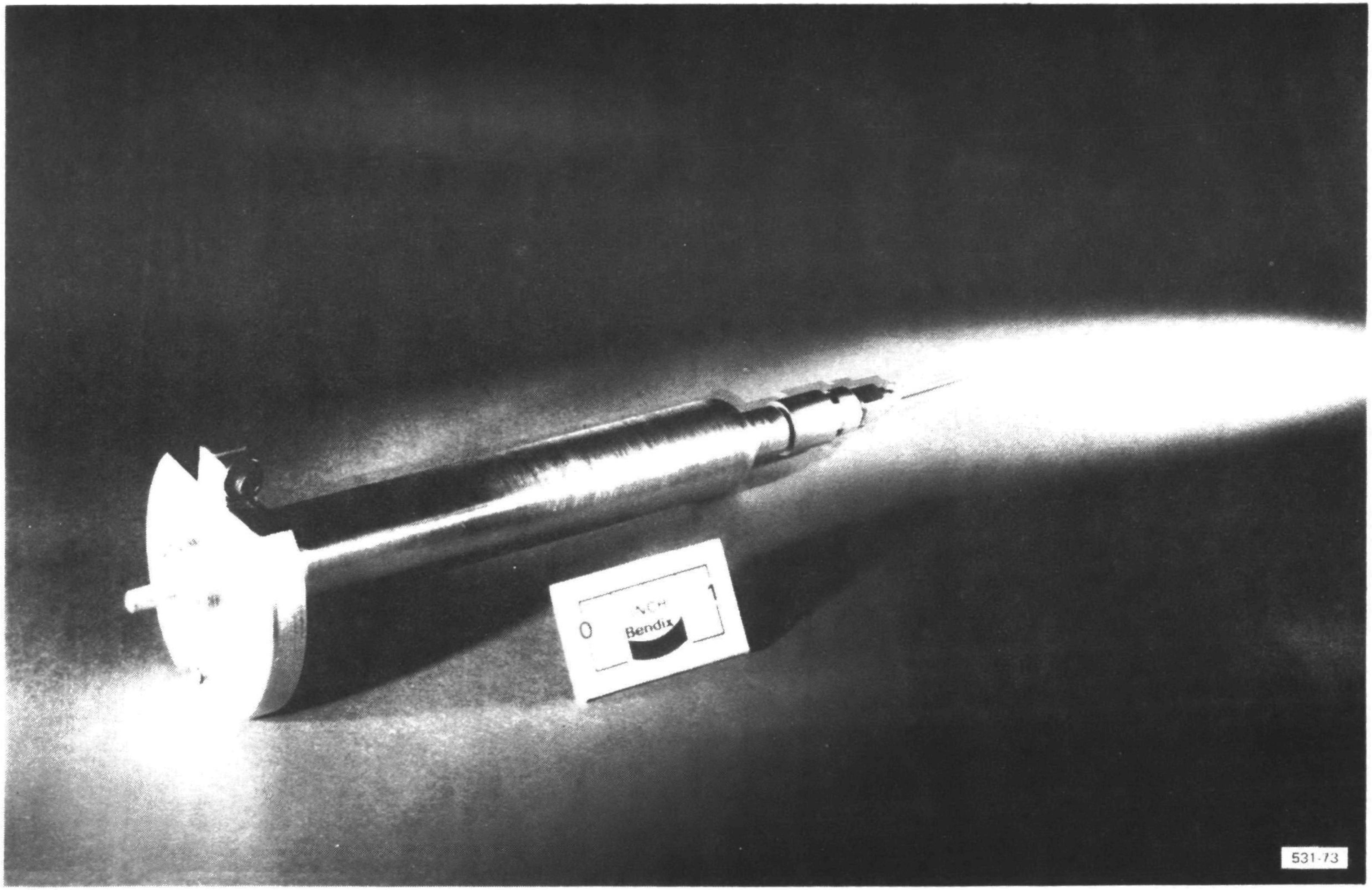

0
INCH
Bendix
1
531-73

Figure 26(a) - First-Generation Collector Cartridge - Aluminum Cartridge

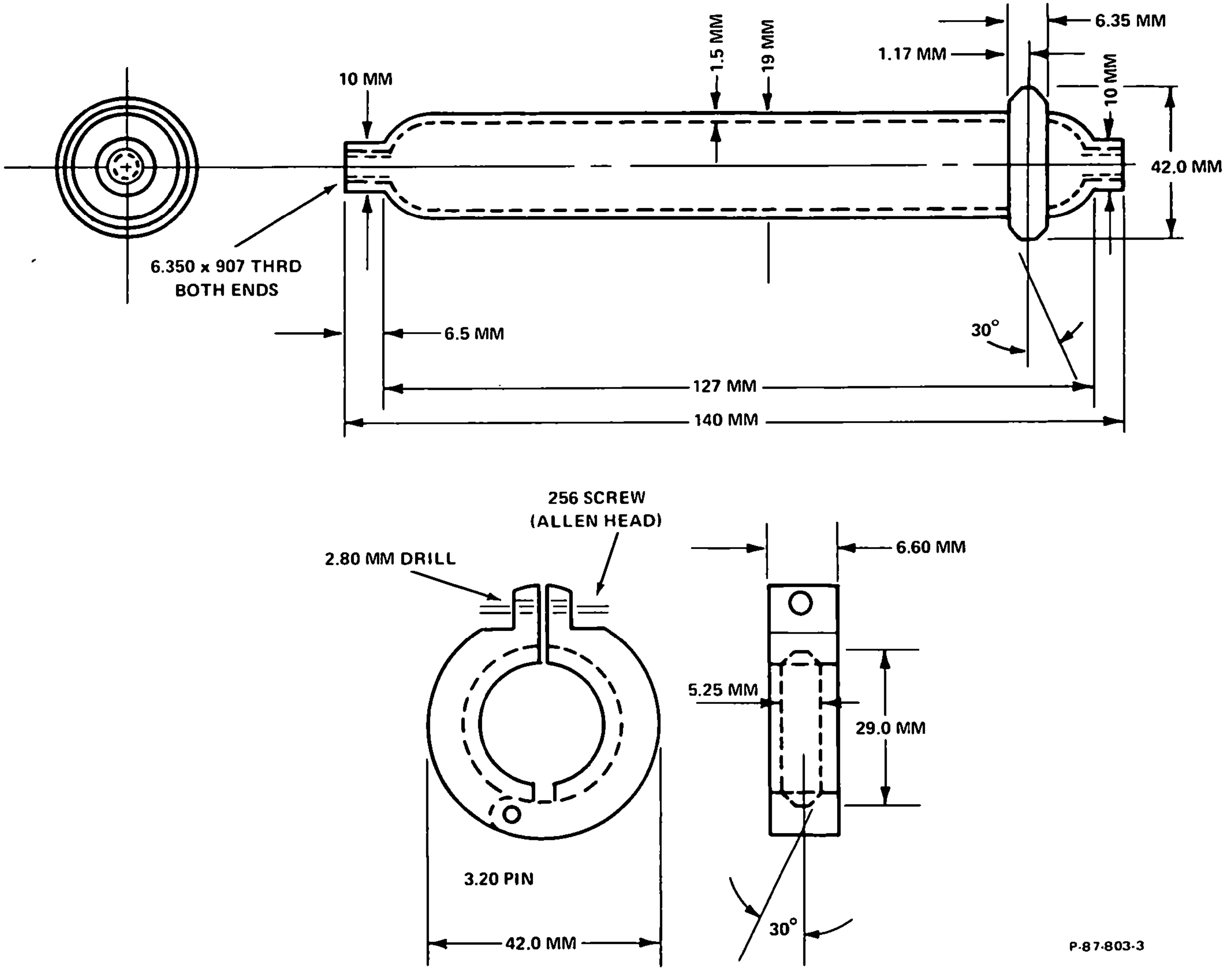

10 MM
1.5 MM
19 MM
1.17 MM
6.35 MM
10 MM
42.0 MM
6.350 x 907 THRD
BOTH ENDS
6.5 MM
30°
127 MM
140 MM
256 SCREW
(ALLEN HEAD)
2.80 MM DRILL
6.60 MM
5.25 MM
29.0 MM
3.20 PIN
42.0 MM
30°
P-87-803-3

Figure 26(b) - First-Generation Collector Cartridge - Details of the Cartridge

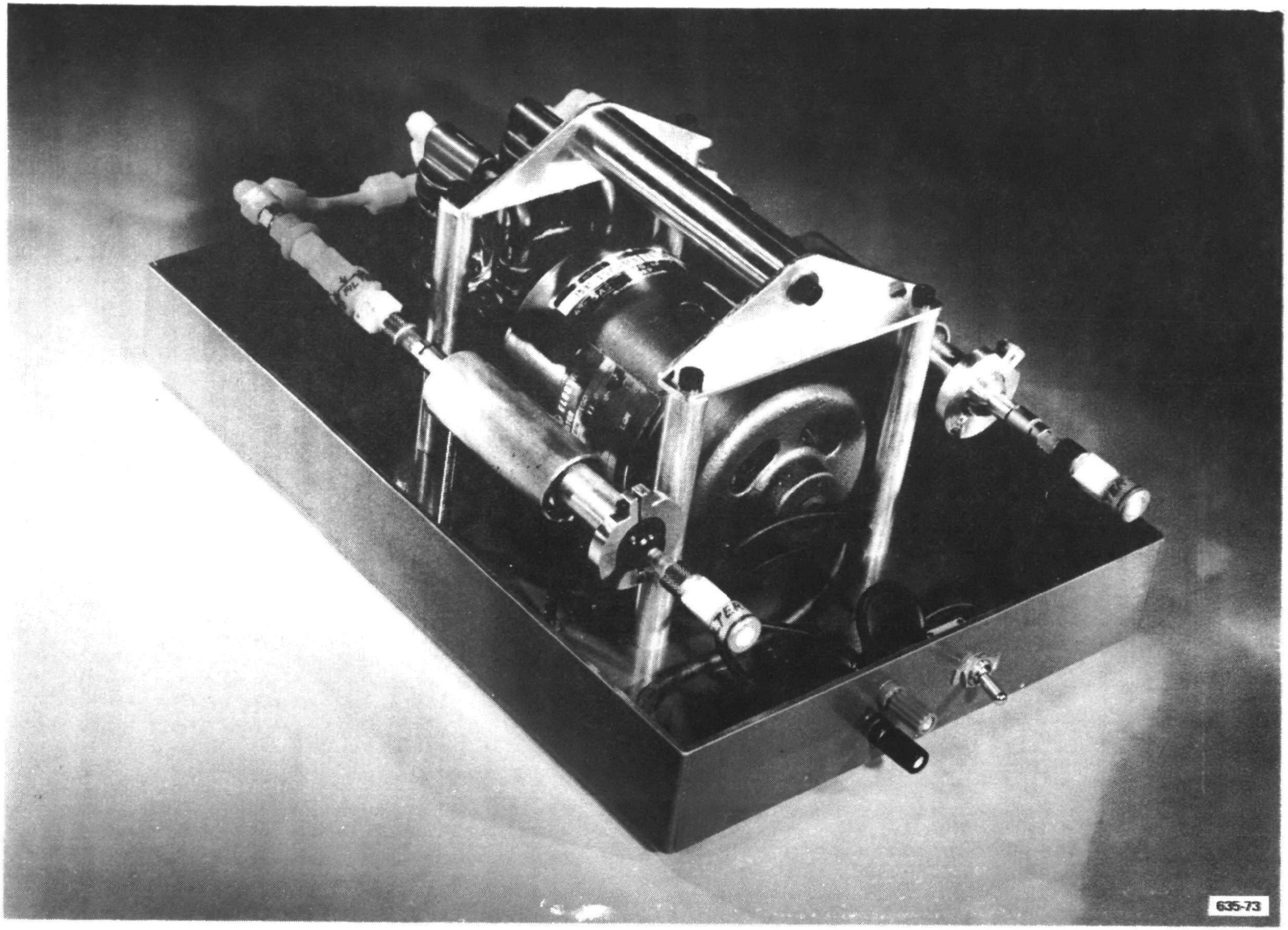


Figure 27 - First-Generation Dual Path Collector/Pump Assembly

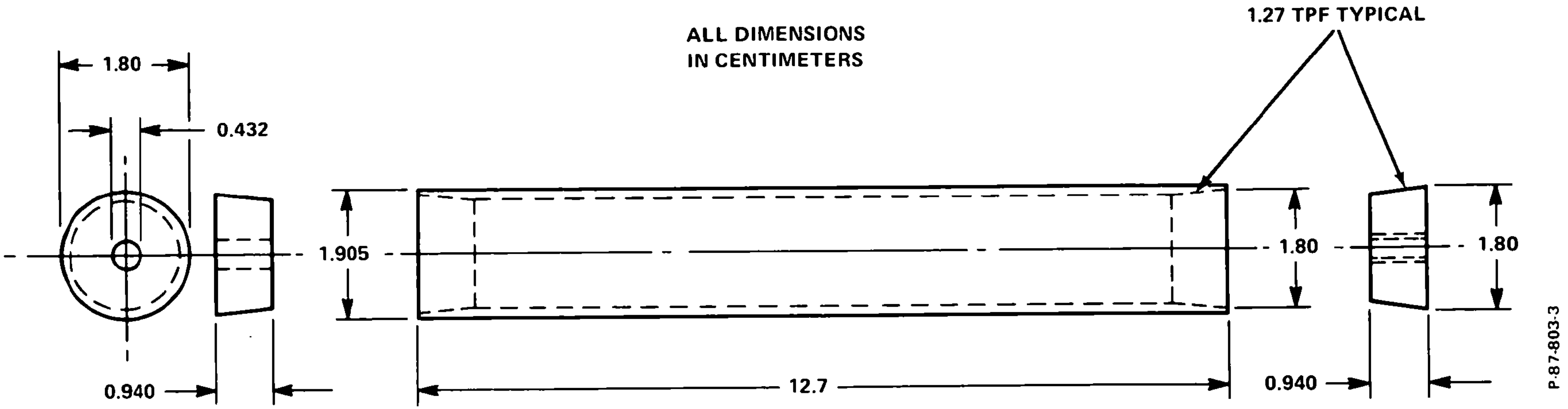
it. The filters were actually Beckman Teflon Connectors (#504) containing a piece of Gelman Type-A glass filter paper cut to size. A terminal cut from a Hamilton female/female Luer connector was inserted into the Teflon connector to enable the filter to be attached onto the cartridge. A limiting flow critical orifice was located between the pump and the filter.

The drawback to this approach is that the NO concentration is found indirectly by subtraction, and two collector units are required each time. A more direct method is desirable.

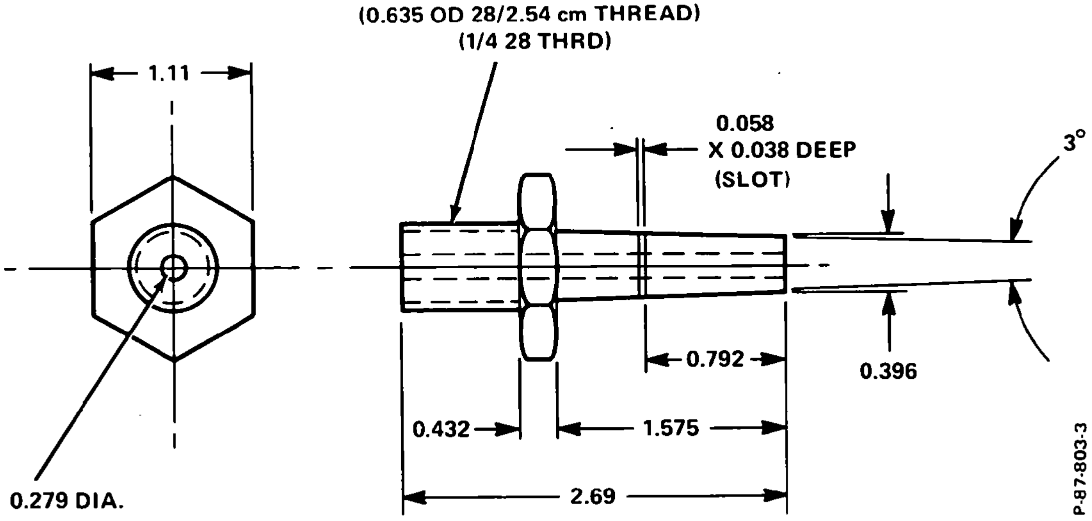
3.5.2 Development of Collector Unit

The development of a collector unit was based on a tandem arrangement of an NO_2 collector and an NO_X collector, with the former serving as the precolumn. When air is being sampled, the first collector removes NO_2, leaving the NO to be taken up by the NO_X collector. This arrangement thus afforded a direct method of sampling NO_2 and NO. Only one collection unit was necessary when these two collectors were packaged in tandem.

This collector unit should house the two collector cartridges sturdily, should be easily assembled or disassembled, and should be easily attached to the pump for field collection. Figures 28 to 31 represent a design possessing such features. In this design, the NO_2 collector cartridge is a disposable Pyrex tube (for the non-reusable TEA), which has an 0.63 OD inlet on one end, and a Luer groundglass taper (Kontes Glass Co, Vineland, N. J. #K-663500-0244) on the other. The glass taper readily fits into the aluminum cartridge (containing Co_2O_3) through the inlet hole in its end.


ALL DIMENSIONS
IN CENTIMETERS
1.27 TPF TYPICAL
1.80
0.432
1.905
1.80
1.80
0.940
12.7
0.940
P-87-803-3

(a) CARTRIDGE BODY AND END PLUGS


(0.635 OD 28/2.54 cm THREAD)
(1/4 28 THRD)
1.11
0.058
X 0.038 DEEP
(SLOT)
3°
0.792
0.396
0.432
1.575
2.69
0.279 DIA.
P-87-803-3

(b) LUER – END SCREW

Figure 28 - Second-Generation Aluminum Cartridge (Co_2O_3)

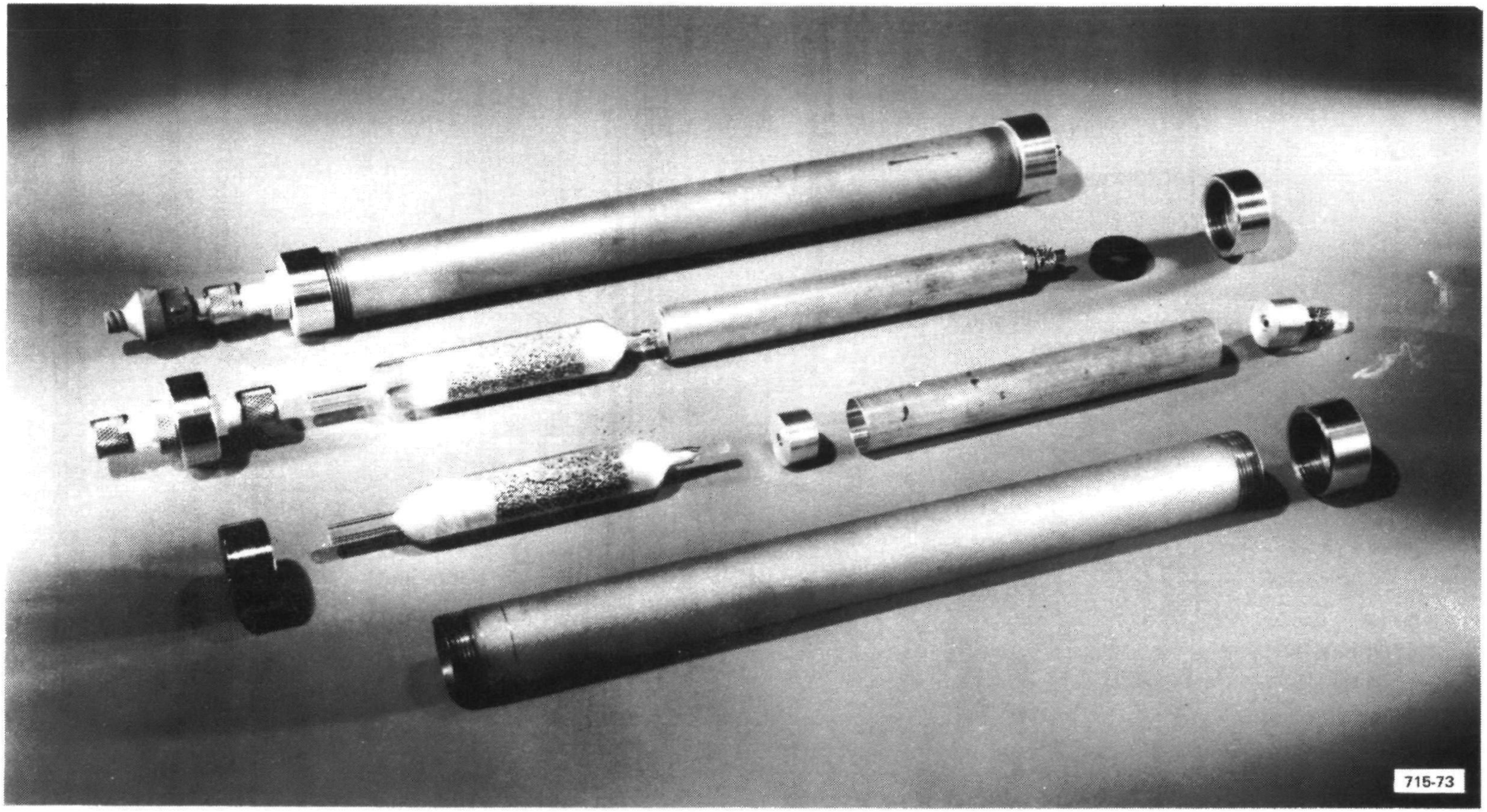


Figure 29 - Second-Generation Pyrex NO_2 Collector Cartridge shown with aluminum cartridge and collector unit subassembly

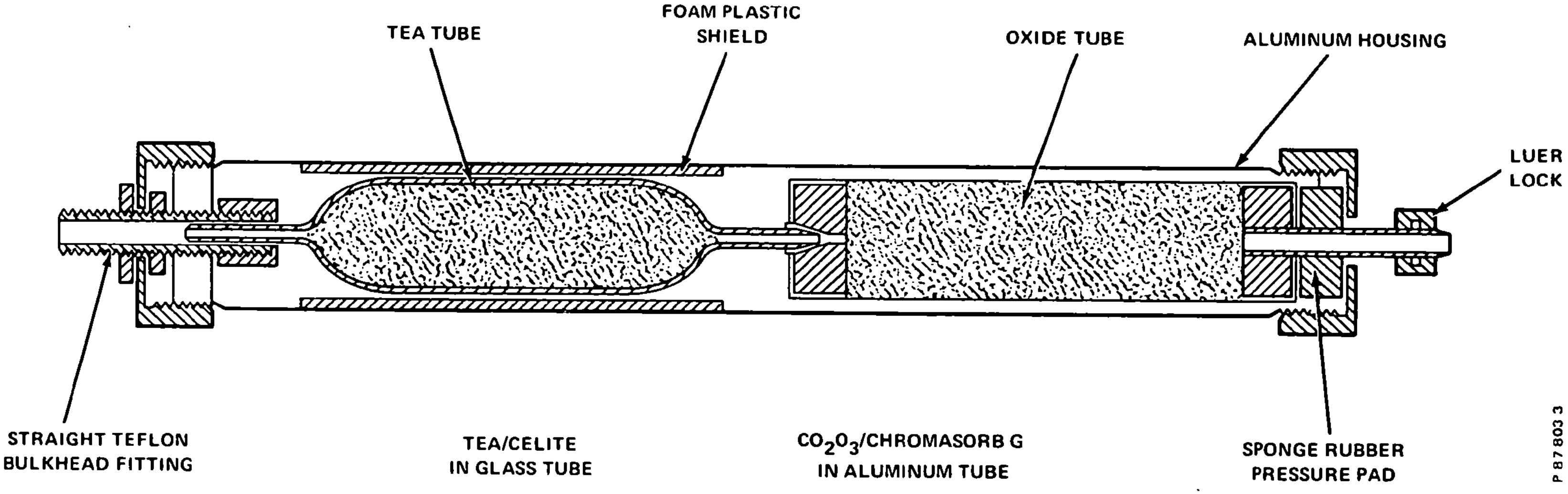
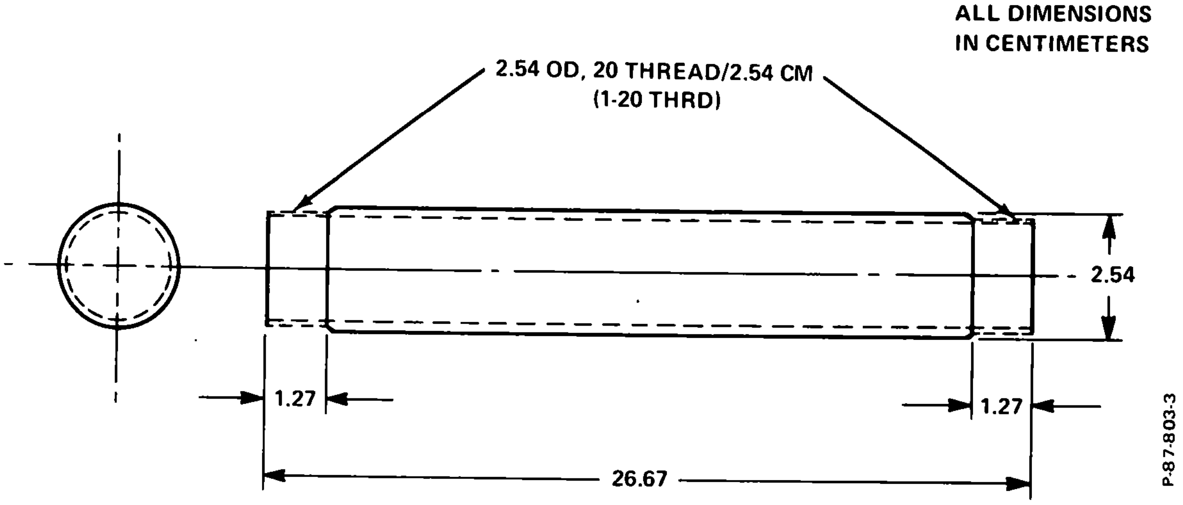
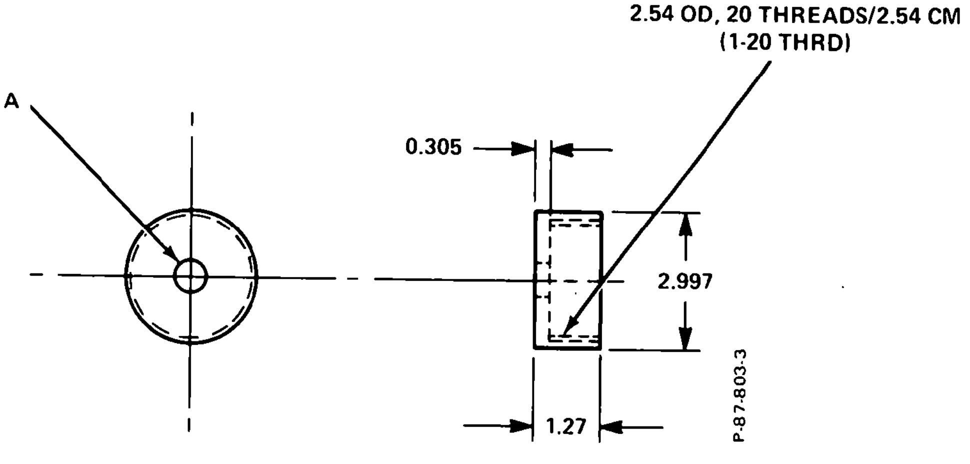

TEA TUBE
FOAM PLASTIC SHIELD
OXIDE TUBE
ALUMINUM HOUSING
LUER LOCK
STRAIGHT TEFLON BULKHEAD FITTING
TEA/CELITE IN GLASS TUBE
CO_2O_3/CHROMASORB G IN ALUMINUM TUBE
SPONGE RUBBER PRESSURE PAD
P 87803 3

Figure 30 - Collector Unit Assembly with Glass NO_2 collector and aluminum collector cartridges.


ALL DIMENSIONS
IN CENTIMETERS
2.54 OD, 20 THREAD/2.54 CM
(1-20 THRD)
2.54
1.27
1.27
26.67
P-87-803-3

(a) ALUMINUM TUBE


2.54 OD, 20 THREADS/2.54 CM
(1-20 THRD)
A
0.305
2.997
1.27
P-87-803-3

A =	
	0.953 OD, 24/2.54 CM THRD
	1.27 DRILL

(b) END-PLATE

Figure 31 - Details of the collector unit tube

The aluminum cartridge with Co_2O_3 packing is assembled by pressing the end plugs into the tube. These end plugs are removable. The outlet of the aluminum cartridge has a Luer-Lock terminal provided by the Luer-end screw (Figure 28). Though not shown in the sketch, the Luer-end screw has a Luer-Lock ring attached onto the slot cut for it. In assembly, the Pyrex tube is first inserted into the Beckman bulkhead Teflon connector on the end-plate and tightened; this then attaches to the aluminum cartridge via the Luer ground taper. The resulting subassembly is then carefully placed into the collection tube and the end-plate is tightened. The assembled unit has the Luer-Lock end of the NO_X collector as one of the terminals.

For analysis, the unit is disassembled, and the cartridges are inserted separately into the interface device for recovery of the collected nitrogen oxides. A special Luer coupler shown in Figure 32 is designed for the aluminum cartridge. This coupler readily goes into the hole at one end of the cartridge and serves as the terminal for analysis.

Although this design appears to be very attractive, the glass Luer taper unfortunately restricts the sample flow and introduces mechanical weakness because of its thin, narrow, fragile neck. To alleviate these problems, a design with two identical Pyrex tubes joined by Beckman Teflon connectors fitting into a unit housing is recommended. This design has been described in detail in Section 2. One unit of such design was mailed from Bendix to EPA and arrived at the destination safely.

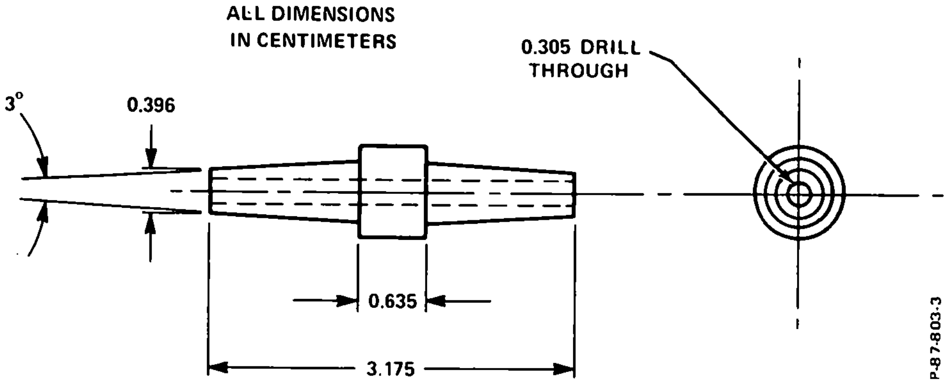


Figure 32 - Luer-coupler (for interfacing the second-generation Co_2O_3 collector cartridge to the analyzer)

3.6 SAMPLING PUMP

Since the sampling pump is one of the key components of the sampling system, currently available pumps were surveyed. Desirable features for this pump are: (1) low power DC- or 110V AC-operated; (2) capability for continuous 24 hr unattended operation; (3) capability for providing high air flow rates, greater than 10 ℓ/min if possible.

Literature was requested from over thirty manufacturers of pump and air samplers. The majority do not make DC motors for the pump. Most of the DC-operated vacuum pumps on the market are low in air flow rate (less than 10 ℓ/min) and are not designed for continuous operation with any restrictions other than particle filter paper (<100 mm Hg). The most promising pumps that can most closely meet the requirements are Model 107C DC20 from Thomas Industries Inc. (Sheboygan, Wisc. 53081) and Model 1531 from Gast Manufacturing Corp. (Benton Harbor, MI 49022). Both pumps deliver 35-42 ℓ/min free air flow, and remain operative against 500-600 mm Hg vacuum; they both can be powered by 12V DC source.

The Gast pump was chosen for the present program since its manufacturer had a better delivery time than Thomas Industries. This Gast Rotary Vane Pump weighs 8 lb., has a 1/10 HP power requirement, and draws 11.3 A for operation. A 12V battery or 12V battery charger (12 amp-rate) can serve as power supply for this pump.

3.7 COLLECTION SYSTEM (AIR SAMPLER)

The system is required to collect samples continuously up to 24 hr in the field with either DC or AC power. This capability is provided by the installation of an interval timer, and 12V battery charger to serve as power supply and rectifier, or a 280 amp hr truck battery.

The development effort was concentrated on the design of a portable, weatherproof and tamper-proof housing for the collection unit, vacuum pump, interval timer, power supply (battery charger) and battery. This has been accomplished with a housing made of aluminum; it contains three shelves for respectively the collector unit and pump; timer and battery charger controls; and battery. Locks are provided for the housing. For disassembly and transportation, the housing can be easily detached and folded. The details have been given in Section 2.

3.8 INTERFACE DEVICE

When thermal release was established as a satisfactory means of recovering the trapped oxides from the collectors for analysis, the interface design became a relatively simple matter. Two approaches were tried.

The first approach utilized an aluminum tube to serve as the oven body which readily accepted the collector cartridge. Thermal power was supplied from a thin integral heater/sensor foil (Thermofoil heater) manufactured by Minco Products, Inc. The Thermofoil heater was easily wrapped around the aluminum heating tube with pressure-sensitive adhesive. The heater took either DC or AC power source; its heating power was limited by the resistance of the heater foil, the power supplied, and the mass and geometry of the heat sink. Repeated trials, however, failed to produce an oven capable of bringing the collector to the desired temperatures. Custom manufacturing would be necessary to accomplish the task and was too expensive to pursue.

The second approach resulted in the interface design depicted and described in Section 2. This device had a variable temperature setting ranging from ambient to 500°C; this range was made possible by a proportional temperature controller and platinum sensor.

3.9 PRELIMINARY FIELD COLLECTION AND ASSAY OF NO_2 with TEA•HCl

This was only a preliminary and limited experiment. It was designed to check the performance of the collection material under a more realistic field condition. A continuous chemiluminescence NO_X-monitor, and a continuous Saltzman NO_2-monitor (Technicon Autoanalyzer) were used for comparative study.

3.9.1 Experimental Procedure

This experiment was conducted at Wayne County Department of Health, Air Pollution Control, Detroit. Air sample was taken from a sampling manifold leading into the laboratory from the rooftop. One manifold line was led to a Bendix chemiluminescence NO_X monitor, and another to a Technicon Wet Chemistry Analyzer for comparative, continuous NO, NO_2 monitoring. From the same manifold, air samples were drawn into the collector by a small diaphragm pump for 24 hours continuous NO_2-collection. The collectors were tubes packed with Triethanolamine hydrochloride mixed with Chromosorb G AWDMCS (45/60 mesh) in 1.5/1 ratio. Approximately 6 grams of packing was used for each collector. For assay, the same elution/area count technique as previously described was used as in the screening tests with a Bendix NO_x-analyzer. The experimental results are summarized in Table 4. Table 5 gives the hourly $[NO_2]$ average read outs by Technicon and chemiluminescence analyzers.

3.9.2 Discussion

The experimental results indicate that the present ambient and assay method with solid absorber is promising when the flow rate is kept around 100 cc/min. The comparison data were obtained by a continuous Saltzman technique using a Technicon Autoanalyzer, and by a chemiluminescent analyzer running at the same time on the same sample. As shown by the attached Table 5, the hourly averages of the two techniques do not agree satisfactorily and neither do the 24 hr averages. The present collection and assay technique show consistently higher results than both other methods. While it is possible that these preliminary data contain systematic errors due to variations in flow, the lack of agreement of the two other techniques suggests the presence of inadequacies in the methods employed. The possibility definitely exists that the present collection and assay technique gives correct results, in which case the other two techniques would give results seriously in error on the low side. It would be worthwhile to remove these uncertainties and obtain consistent results both in controlled laboratory conditions and in the field.

Table 4 - Summary of Experimental Results

Collector Number	Flow Rate	Collection Time	Daily Average [NO_2] (By Technicon and Chemiluminescence)	Measured Collected Quantity	Quantity To Be Collected (Calculated from Daily Ave.)
2	1 lit/min.	24 hrs.	0.035 ppm	11.99 μg	90.7 μg
3	1 lit/min.	24 hrs.	0.025 ppm	4 μg	64.8 μg
16	105 cc/min.	24.2 hrs.	0.032 ppm	(a) by area count 12 μg (b) by weighing 13.85 μg	8.8 μg
17	80 cc/min. for 4 hrs. 75 cc/min. for 20.2 hrs.	24.2 hrs.	0.032 ppm	(a) by area count 7.6 μg (b) by weighing 7.4 μg	6.29 μg

Table 5 - Comparison of Ambient NO_2-Concentration by
Technicon and Bendix Monitor~~s~~ (Date: 12-8-73)

Time (hr.)	Technician ppm	Bendix ppm	Tech:Bendix Ratio
0-1	0.050	0.035	1.43
1-2	0.050	0.035	1.43
2	0.040	0.030	1.33
3	0.040	0.030	1.33
4	0.030	0.020	1.50
5	0.030	0.020	1.50
6	0.030	0.025	1.20
7	0.040	0.030	1.33
8	0.040	0.030	1.33
9	0.030	0.025	1.20
10	0.030	0.025	1.20
11	0.030	0.020	1.50
12	0.020	0.015	1.33
13	0.020	0.020	1.00
14	0.020	0.015	1.33
15	0.020	0.015	1.33
16	0.020	0.020	1.00
17	0.030	0.025	1.20
18	0.030	0.025	1.20
19	0.030	0.020	1.50
20	0.030	0.025	1.20
21	0.030	0.020	1.50
22	0.030	0.020	1.50
23-24	0.030	0.020	1.50

SECTION 4
SUMMARY AND RECOMMENDATIONS

4.1 SUMMARY

Simple collection and assay of NO and NO_2 using solid chemical absorbents was proven feasible. The selective collection of these oxides is possible with a tandem arrangement of two absorbent cartridges: The first, containing triethanolamine hydrochloride packing, completely absorbs NO_2 from the air sample without affecting the NO concentration. The second, filled with cobalt oxide packing, quantitatively removes NO. These collected oxides are later eluted and analyzed separately.

The interface device developed to transfer the sample for analysis accepts one collector cartridge and heats it to a temperature which releases the nitrogen oxide. At 160-170°C, the absorbed NO_2 is quantitively released from the TEA·HCl collector as NO; cobalt oxide gives up its captured NO completely at 400-420°C. When the collector is coupled via this interface to a suitable instrument, such as a chemiluminescence NO_x analyzer, the NO and NO_2 are easily measured. When cooled, the collector cartridges are ready for reuse in sample collection.

For convenient handling, a special collector unit was developed. This unit is easy to assemble and to install in a collector system; moreover, it is easy to disassemble. Its rugged, lightweight construction enables its safe and inexpensive transportation within the postal system.

A simple weatherproof collection system was built for field collection, based on the concept of a collector unit containing the solid chemical absorbents. Its Gast vacuum pump and interval timer enable the sampler to operate up to 24 hr continuously without attention. This operation can be powered either by a 12V DC high capacity battery or by a 110V AC power supply with a 12V DC output.

Although the collectors developed under this contract met the performance requirements in the laboratory, extensive field testing may lead to possible design improvements. The major effort of the program was in the screening and evaluation of chemical absorbents, so the collector unit represents an experimental prototype. Additional work will be required to rigorously test and further improve the designs. Recommendations for further work are detailed in the following subsections.

4.2 RECOMMENDATIONS

4.2.1 NO_2 Collector With TEA·HCl

TEA·HCl (m.p. 177-179) selectively collects NO_2 and is inert to NO at room temperature. At higher temperatures, its affinity for NO_2 decreases and it catalyzes the conversion of NO_2 to NO. Its desirable property as an NO_2 absorbent, however, returns when the temperature is decreased. In use, the TEA·HCl cartridge is heated to 160-170° to recover the absorbed NO_2, thereby regenerating the absorber. If the temperature exceeds 170°C, however, some discoloration of the absorbent occurs, after which NO_2 to NO conversion is noted with the cartridge at room temperature. Limiting the temperature to 170°C, therefore, is a necessary precaution with this cartridge.

The ultimate lifetime of the TEA•HCl absorbent should be determined. Laboratory tests confirmed its performance up to ten heating cycles, but more extensive cycling should be evaluated. If the absorbent has a long lifetime, it can be encased in a more permanent material, such as Teflon-coated aluminum instead of the present disposable Pyrex. The metal case has the obvious advantage of nonbreakage.

Absorbent capacity also should be further evaluated. The present collector cartridge was designed in a size convenient to pack and handle without regard to the ultimate absorbent capacity. When the absorbent's maximum capacity has been determined, the optimum size for the cartridge can be established.

4.2.2 Cobalt Oxide

Since both cobaltous and cobaltic oxides absorb NO_x completely, conversion of NO_2 to NO is not a problem. The total absorption capacity of each oxide should be measured, however, to design an optimum collection cartridge.

Preliminary tests indicate that cobaltic oxide quantitatively absorbs and releases NO independently from the NO_2 absorption. If this is true, one could use cobaltic oxide alone for the collection and assay of the nitrogen oxides. The analyzer, such as a gas chromatograph, would have to differentiate the NO_2 from NO, since they would evolve simultaneously from the collector. Further investigation of this phenomenon could lead to a single absorbent collector.

The extensive and combined effects of possible interfering species, such as moisture, SO_2, peroxide, and CO_2, on collector performance could be examined. It has been established that moisture present in air up to 96% humidity does not affect the performance of the collectors. The TEA•HCl absorbent was subjected to 1000 ppm SO_2 at a flow rate of 1ℓ/min for 20 min and still retained its performance. Nonetheless, evaluation of collection efficiency in the presence of both moisture and SO_2 in more common concentrations should be systematically investigated. The preliminary data indicated that the presence of highly concentrated SO_2 and moisture (96%) did lower the concentration of NO passing through the TEA•HCl. This may be caused by the conversion of NO to NO_2, the latter then being absorbed. The conversion may be attributed to the combined effect of SO_2, moisture, and the surface of the absorbent. In the absence of the absorbent, no change in concentration was observed. This indicates the need for a systematic study of the effect of interferences on both absorbents under realistic field conditions.

The nature of bonding of the nitrogen oxides to the absorbent surface was not studied for either absorbent. This phenomenon should be investigated using IR and DTA techniques to determine what inherent properties of the absorbents might degrade their performance. Such an investigation might also reveal what other types of compounds could serve as NO and NO_2 absorbers.

4.2.3 TEA•HCl Packing

This absorbent is a fine, white powder which, when used by itself as a collector packing, introduces great flow restriction and results in a poor flow rate. Physical mixing of such a fine powder with an inert support such as Chromosorb G AW DMCS 45/60 does not produce an especially good packing. The best packing is produced by solution-coating the TEA•HCl (in distilled water) onto a support such as Celite. This technique gives a high-capacity packing with desirable flow characteristics.

Two points with respect to this collector packing are worth further consideration. First, the Celite surface should always be completely covered by the absorbent. Celite absorbes NO_2 at room temperature and, although it gives up the captured NO_2 at 170-200°C, the efficiency of the absorbent is better preserved and controlled when no extra foreign surface is present. Second, the collection efficiency of this absorbent at flow rates higher than 120 cc/min has not been evaluated. Since field collection may involve flow rates > 1ℓ/min, the absorbent efficiency under such conditions should be determined.

4.2.4 Cobalt Oxide Packing

Commercial cobalt oxide is a grayish-black fine powder (∿200 mesh). This powder must also be mixed with some inert, more coarse support (Chromosorb G, 45/60) to afford a reasonable flow rate. Other means of making packings of lower flow restriction that should be further investigated are

- Hot-pressing or cold-pressing the oxide into a cake, firing the cake at high temperature, then crushing the cake into chips for packing.
- Solution-coating $Co(NO_3)_3$ onto a support such as Celite, drying, then coverting to Co_2O_3 at 200-250°C in air.

With the first method, the packing's capability of retaining its shape without breaking down to a powder is the major question. Moreover, the firing temperature chemically converts the Co_2O_3 into CoO and Co_3O_4, which may affect the desirable properties as an absorber. The second method gives good flow characteristics as evidenced by its use with the TEA•HCl/Celite packing; however, removing the residual nitrate from the packing is quite difficult. In fact, conditioning of packing prepared by this method for over a week at 450°C in air did not result in a clean absorbent. A systematic evaluation of these packings should be undertaken.

4.2.4 Collector Configuration

The present design of the collector unit contains two Pyrex cartridges. Although these cartridges are ruggedly constructed, they can be broken during assembly or disassembly. When the necessary tests are performed and the reusability and lifetime of the absorbents are fully established, a nonbreakable cartridge design can be considered. Experimental work showed that aluminum cartridges coated inside with Teflon did not affect NO_2 collection. The Teflon coating is required for the TEA•HCl/Celite cartridge, since any NO_2 to NO conversion results in analytical error.

The final cartridge design will still require a precaution with respect to overheating, since extremes of temperature will induce decomposition of the packing and the coating. A longer range program may prove worthwhile, therefore, to develop a collection material of higher thermal stability.

APPENDIX A

TYPICAL RECORDINGS OF COLLECTOR MATERIALS EVALUATION

APPENDIX A

TYPICAL RECORDINGS OF COLLECTOR MATERIALS EVALUATION

This appendix contains a collection of recordings representing the evaluation of various absorbents and container materials. These recordings are given in Figures A-1 through A-15.

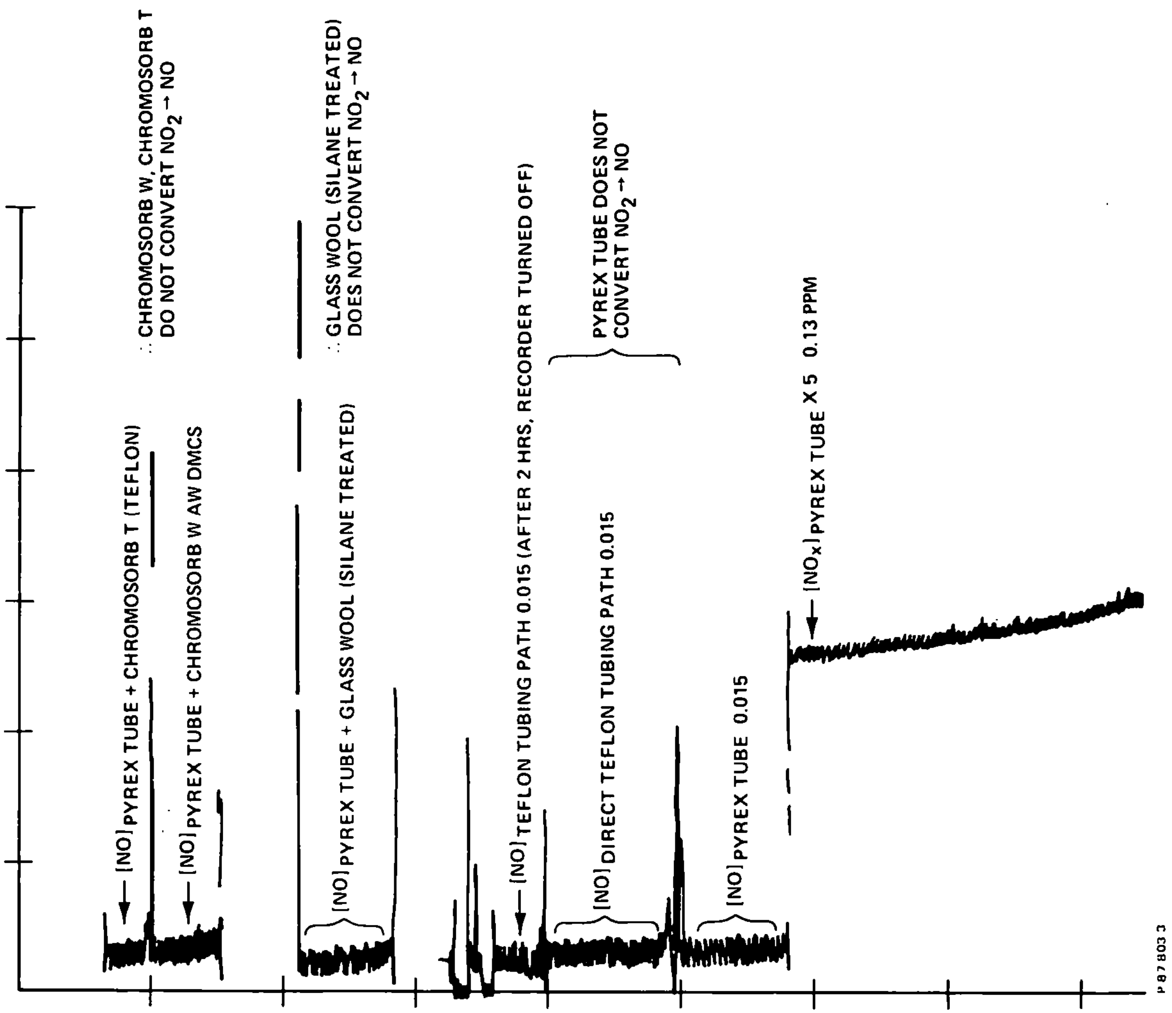


Figure A-1 - General material evaluation, showing the inertness of (1) Pyrex tube, (2) silane-treated glass wool, (3) Chromosorb T, and (4) Chromosorb W AW DMCS

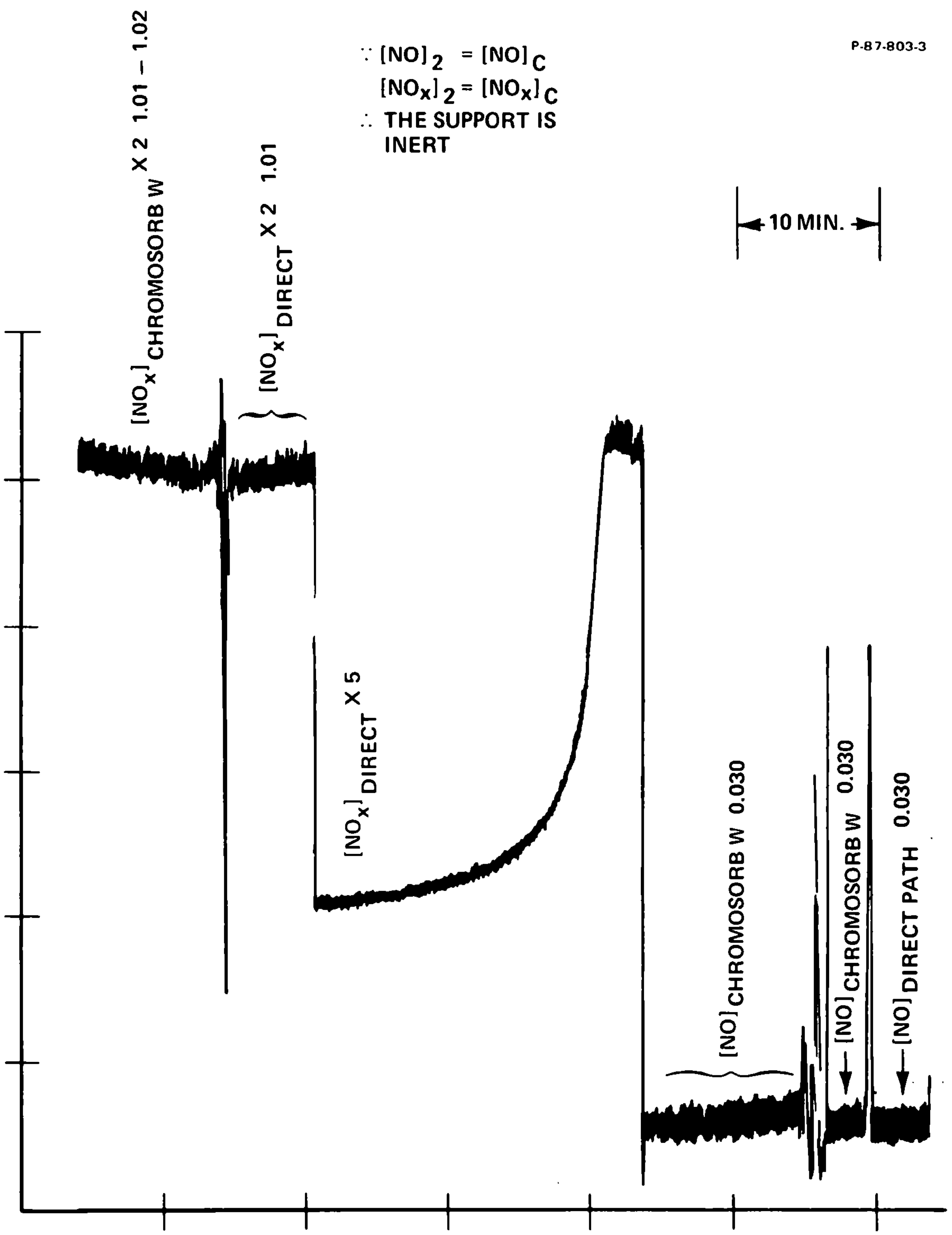


Figure A-2 - Chromosorb W AW DMCS

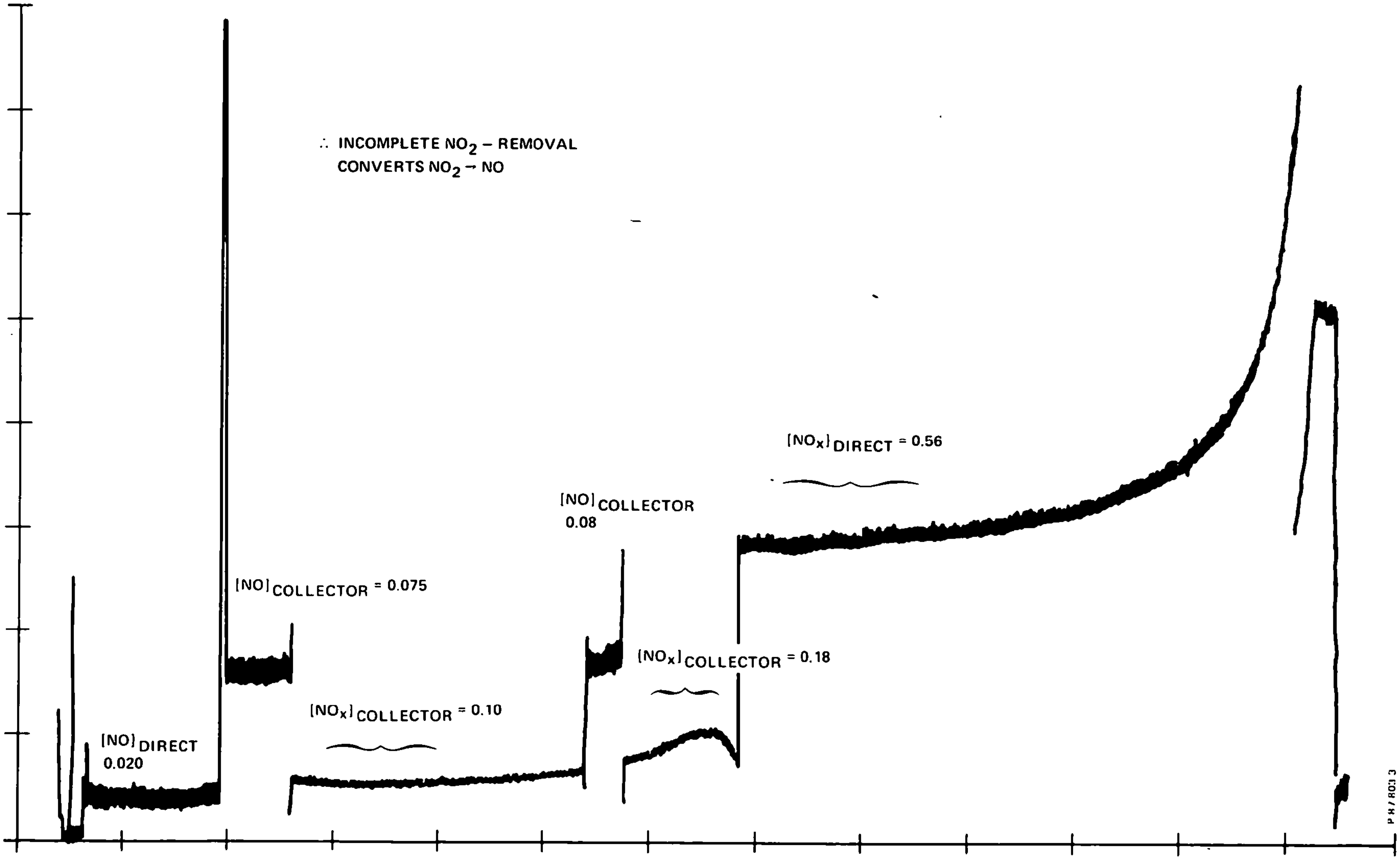


Figure A-3 - TEA/Chromosorb W AW DMCS

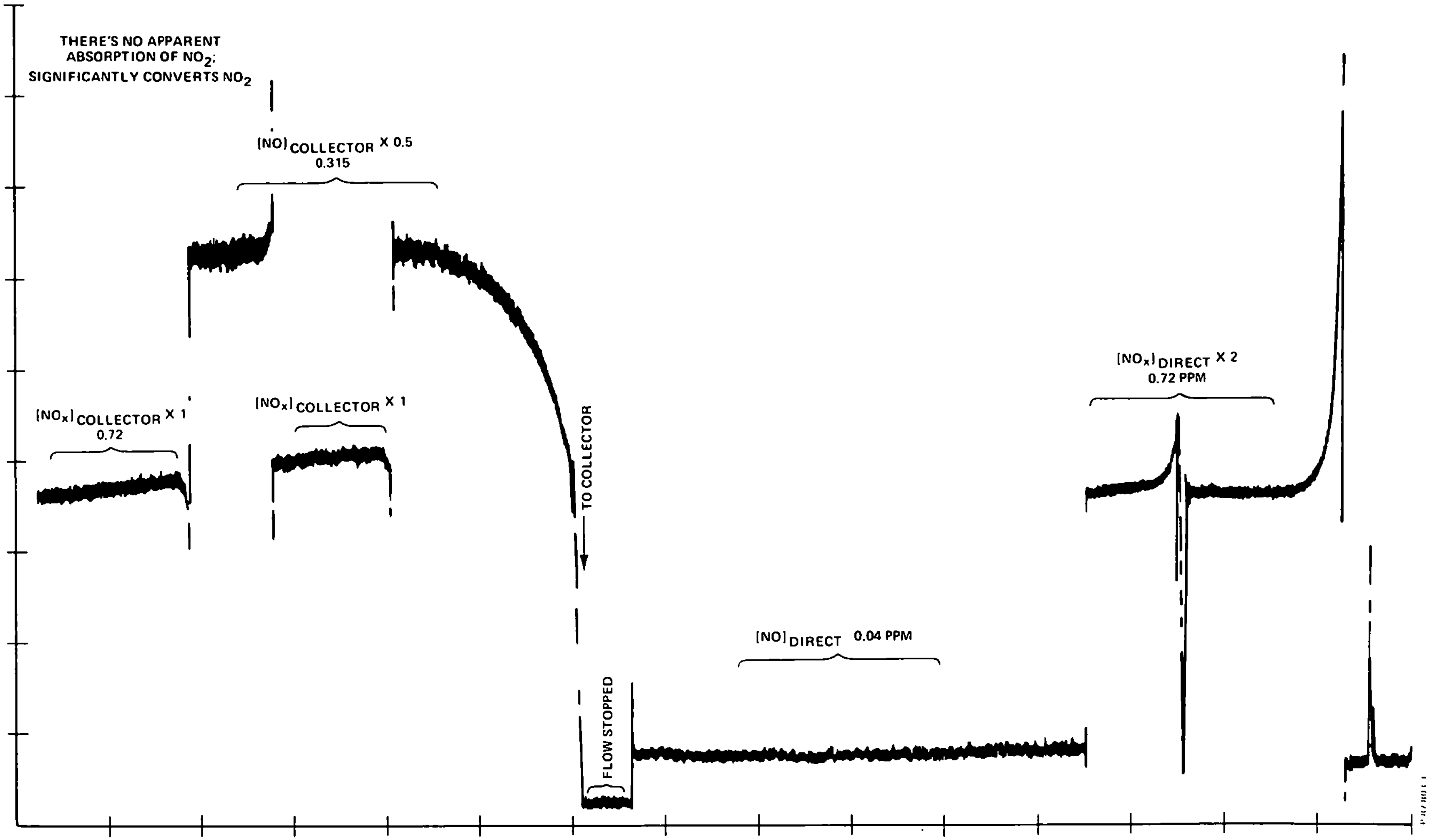


Figure A-4 - TEA/Regis GasPak FS

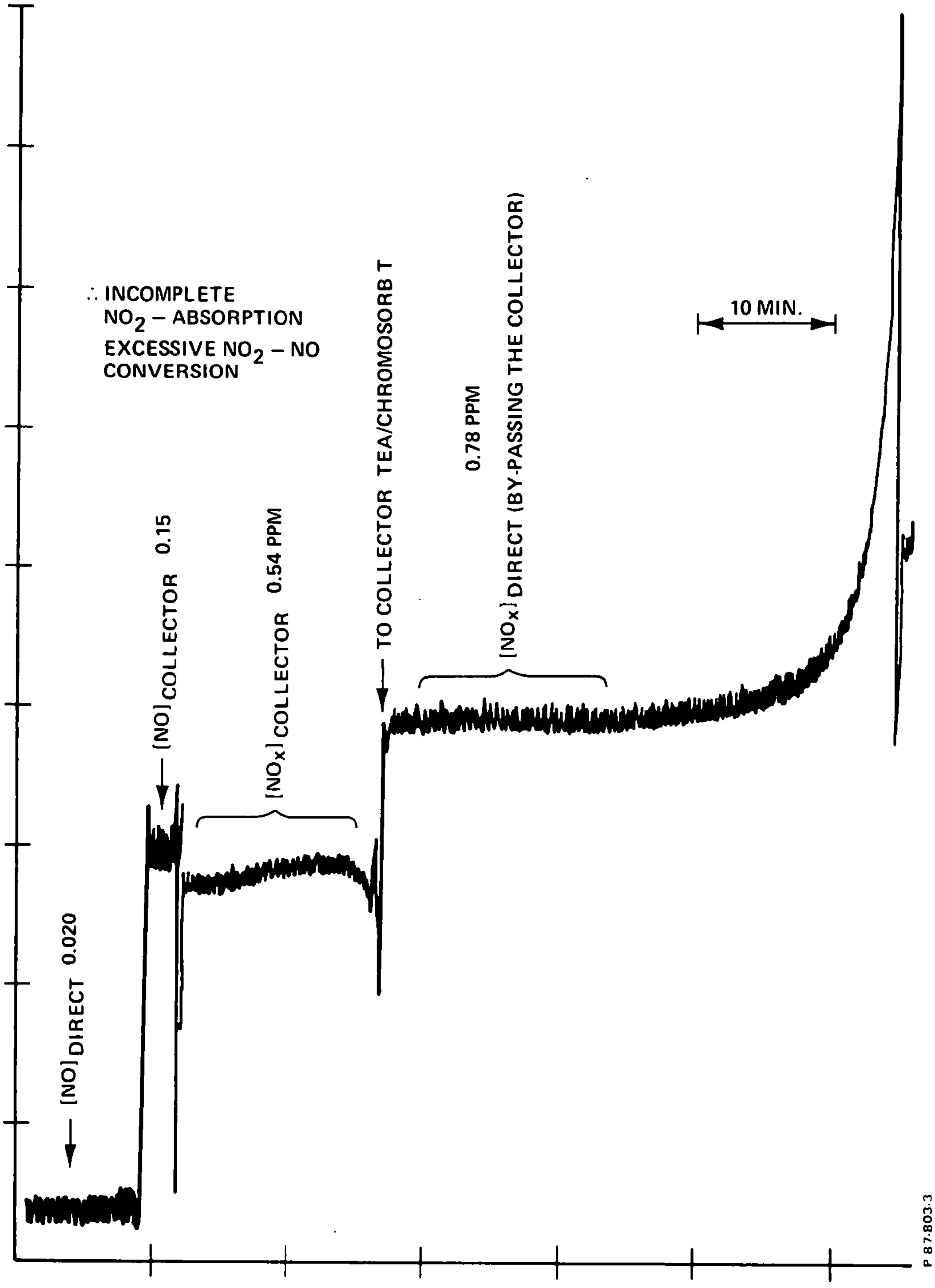


Figure A-5 - TEA/Chromosorb T

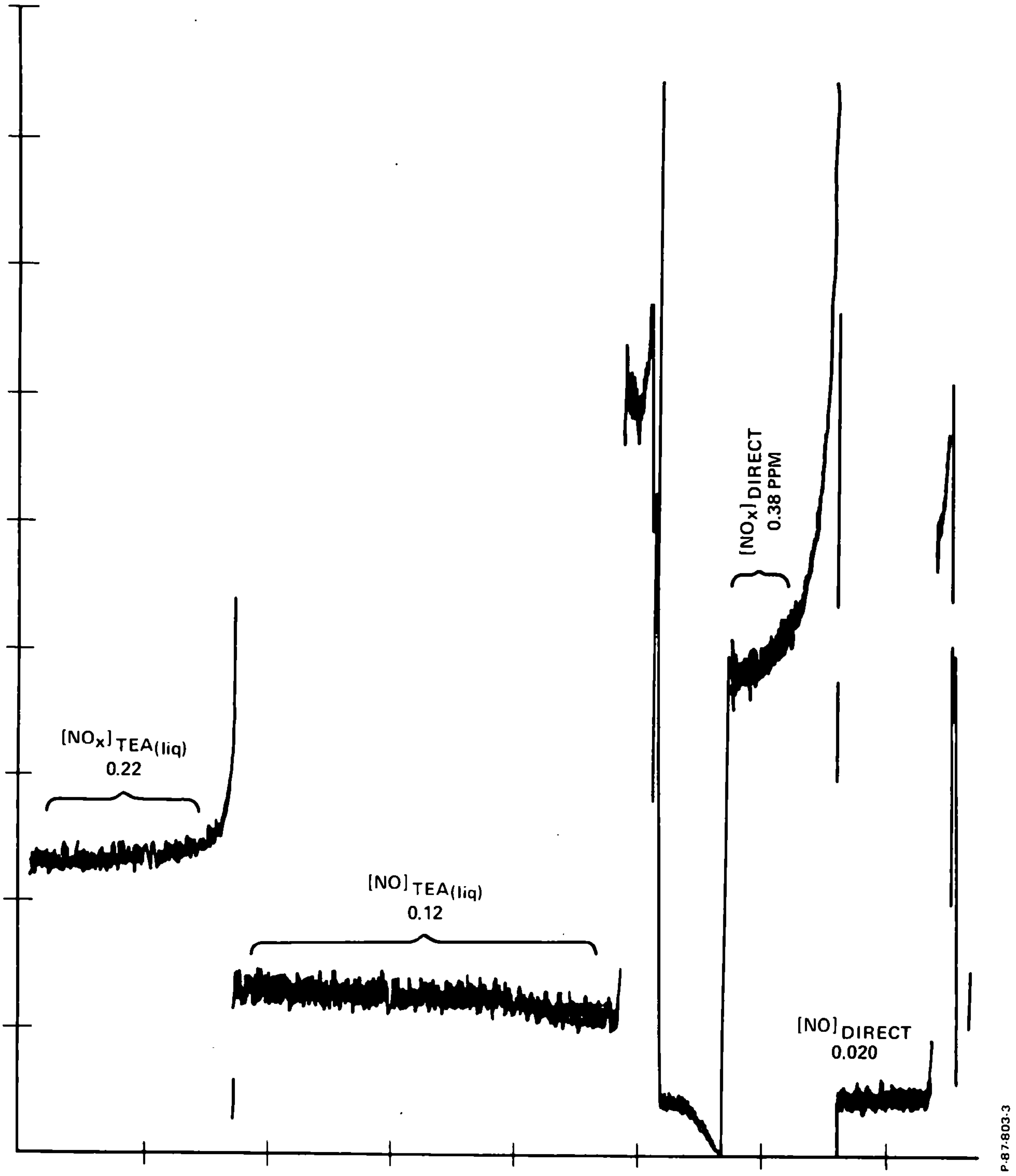


Figure A-6 - TEA/NEAT (liquid)

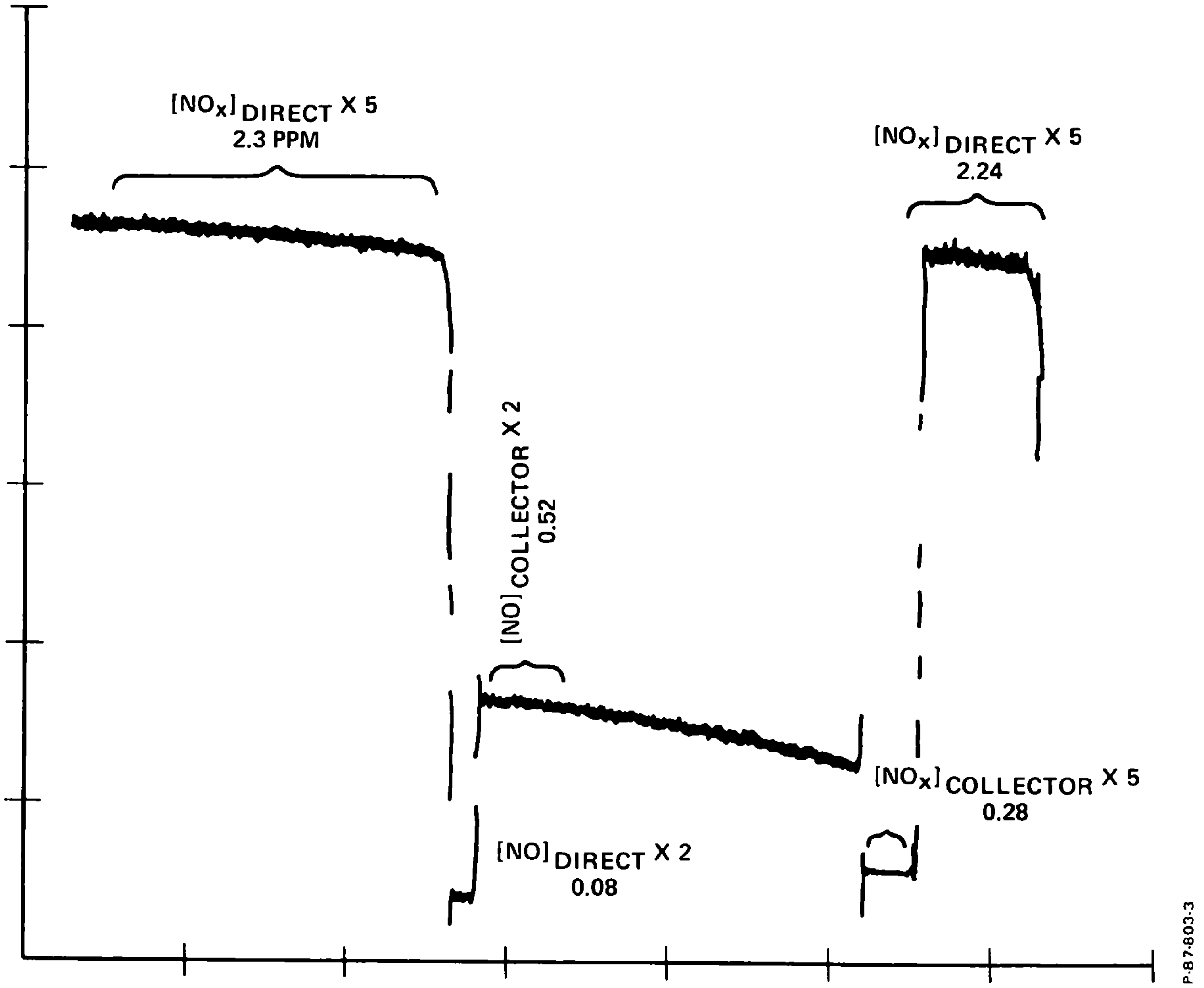


Figure A-7 - TEA Borate

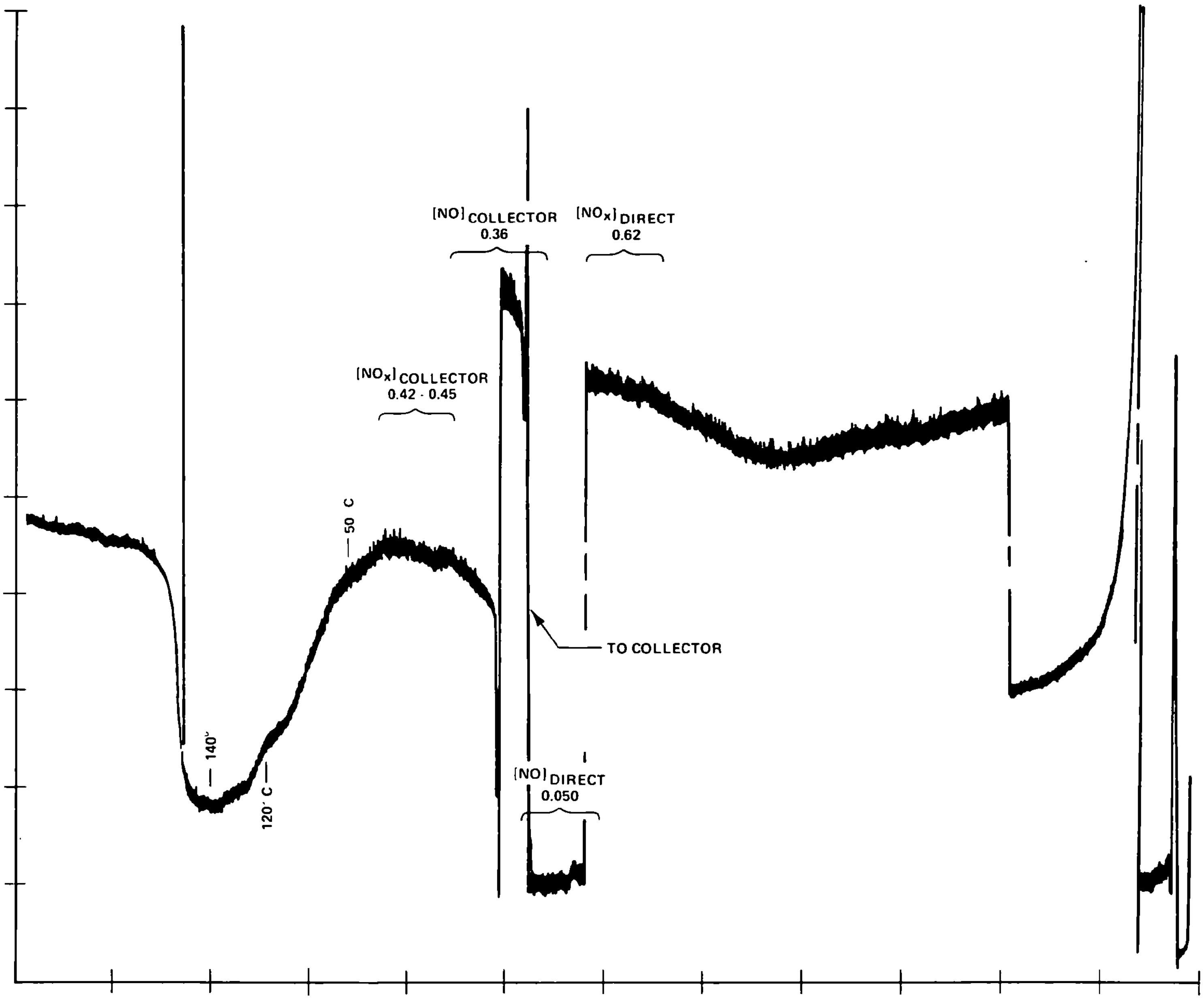


Figure A-8 - THEED

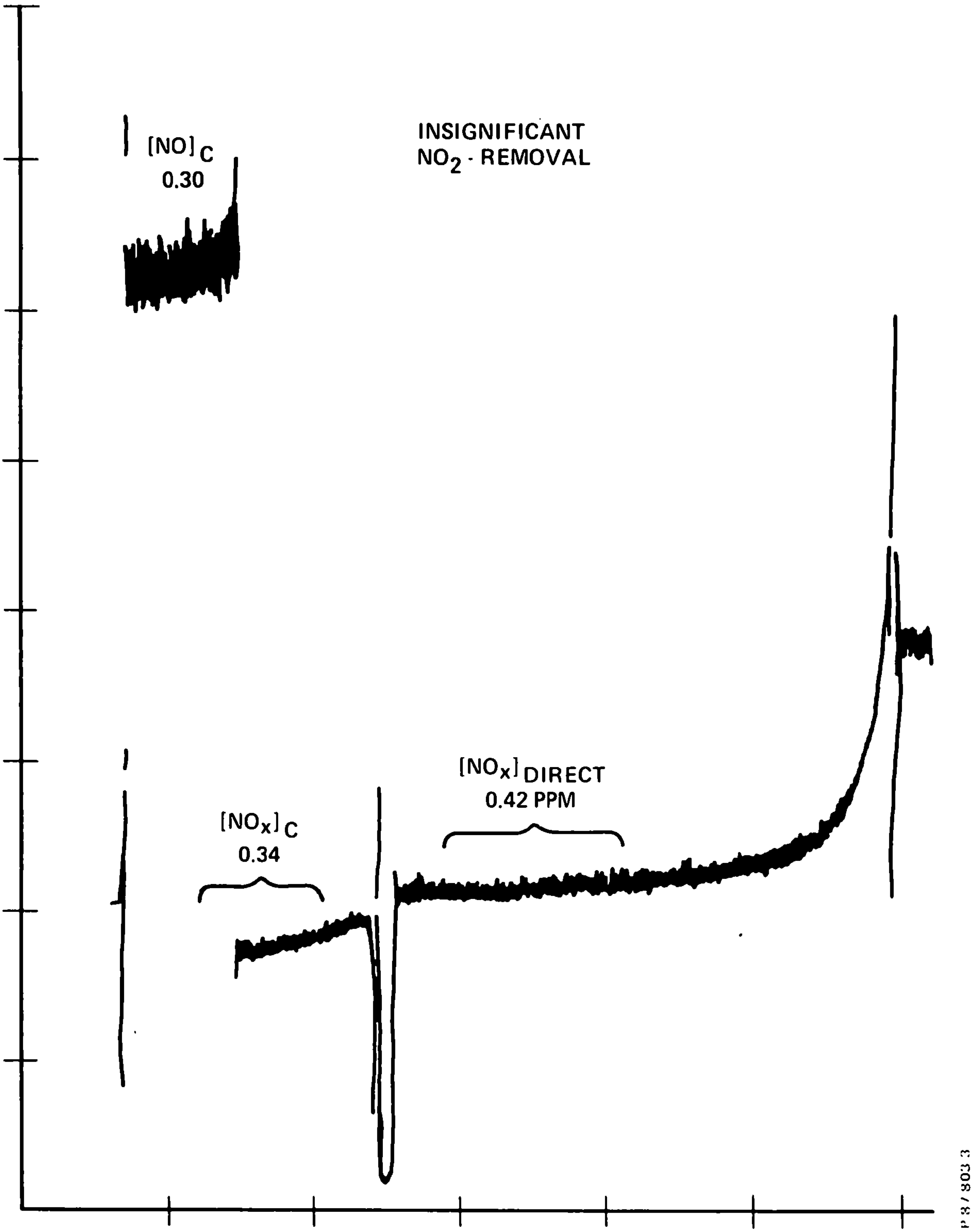


Figure A-9 - Quadrol/Chromosorb W AW DMCS

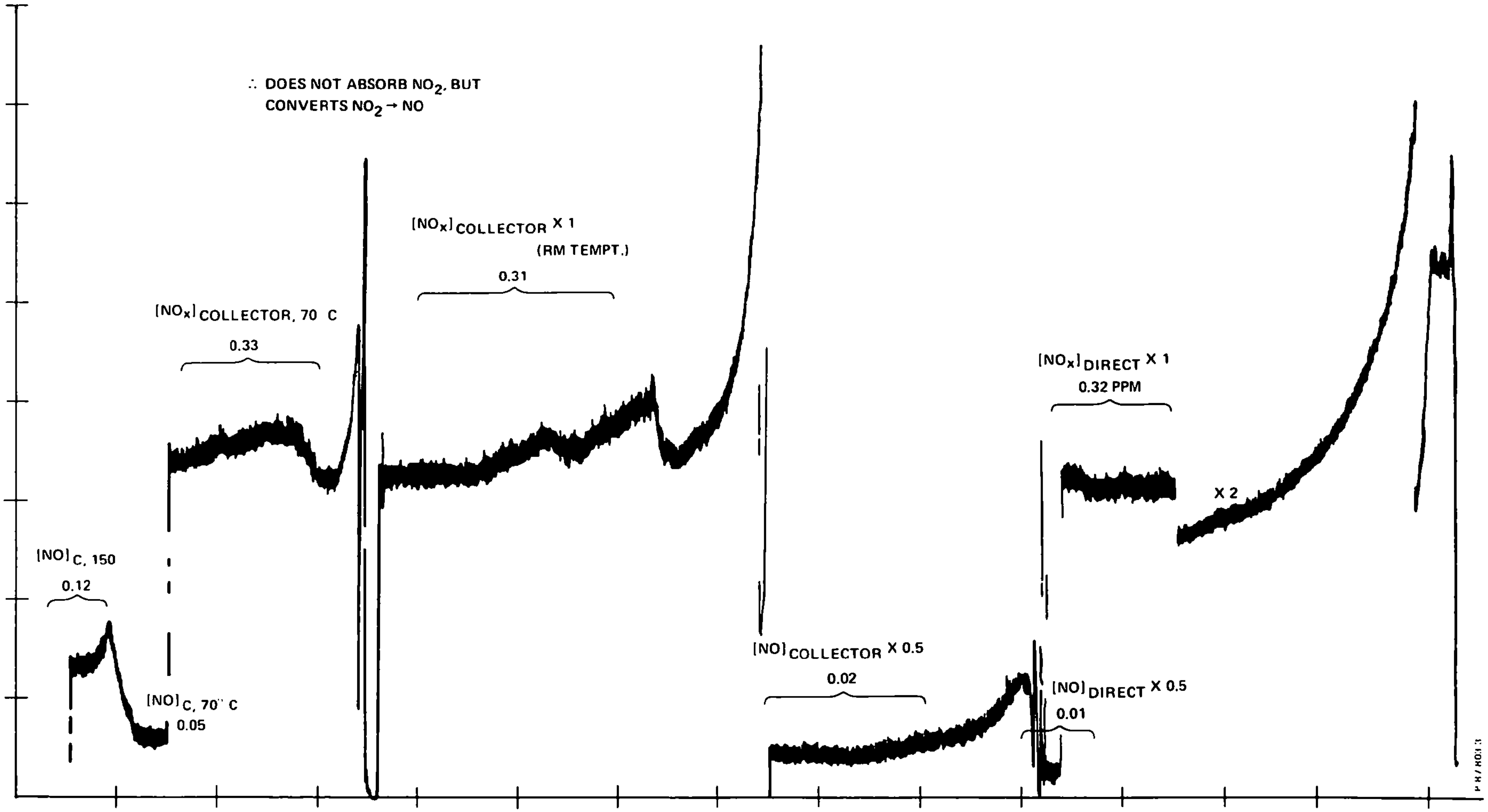


Figure A-10 - $NiSO_4$

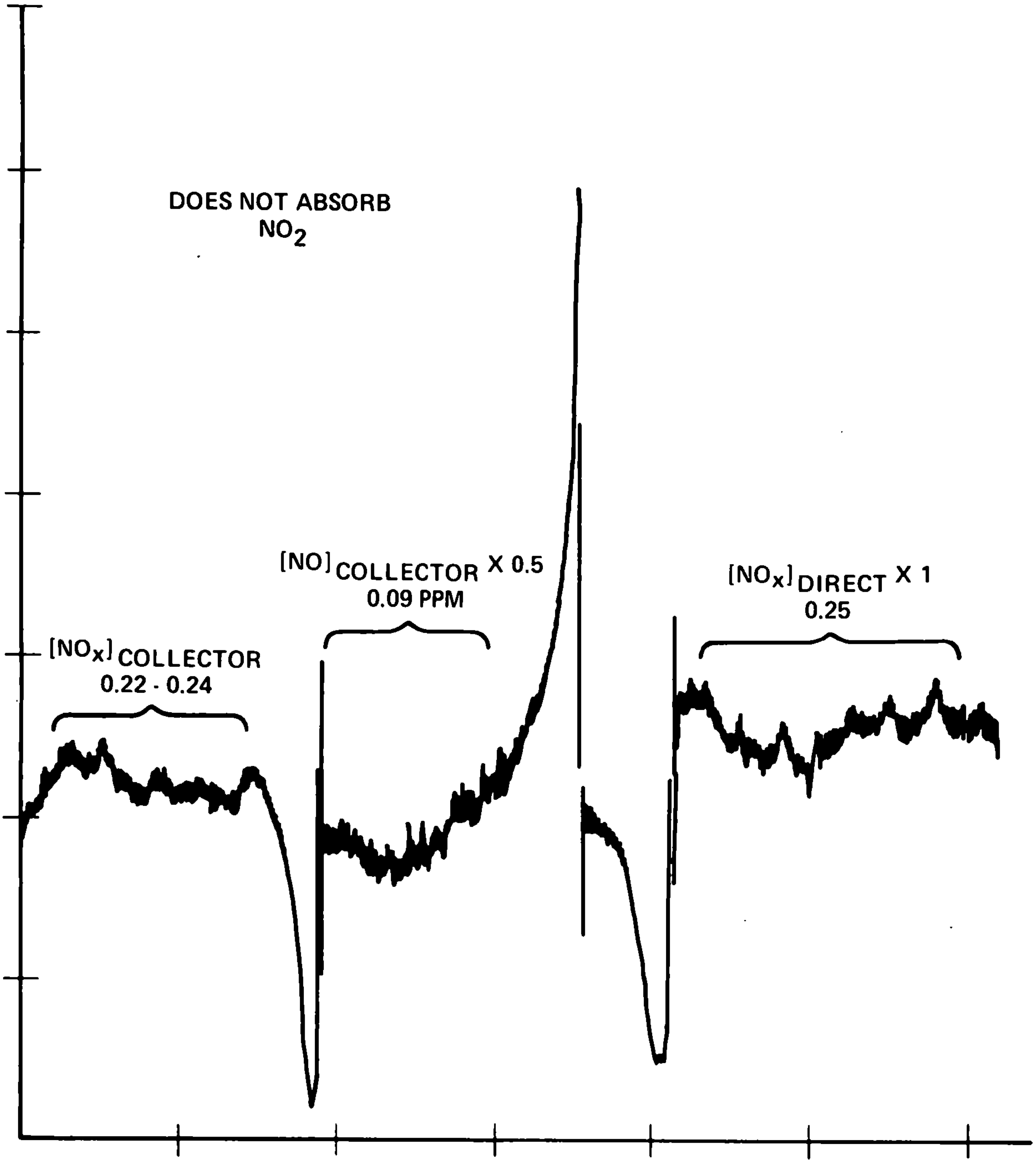


Figure A-11 - $CoSO_4$

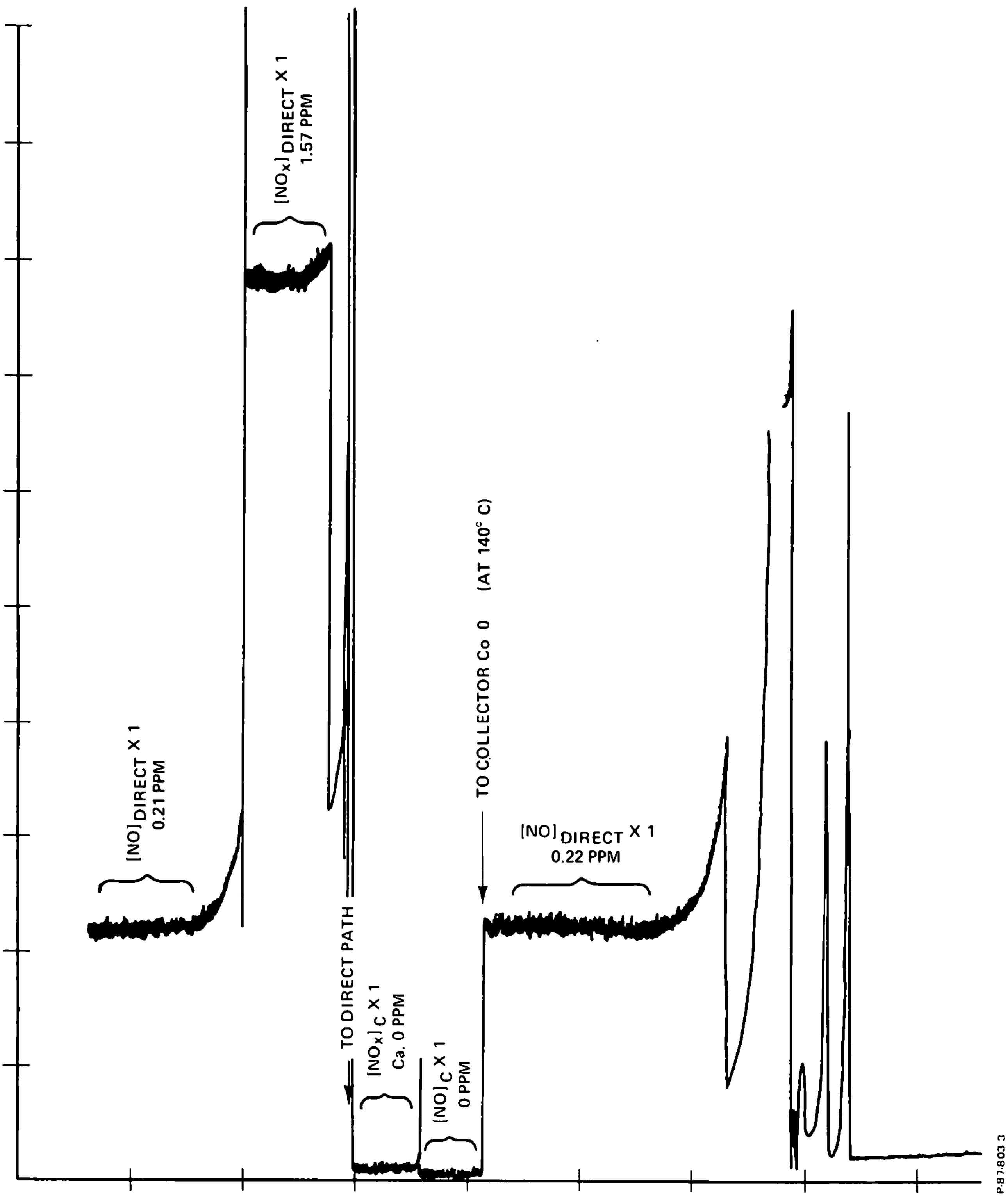


Figure A-12 - CoO

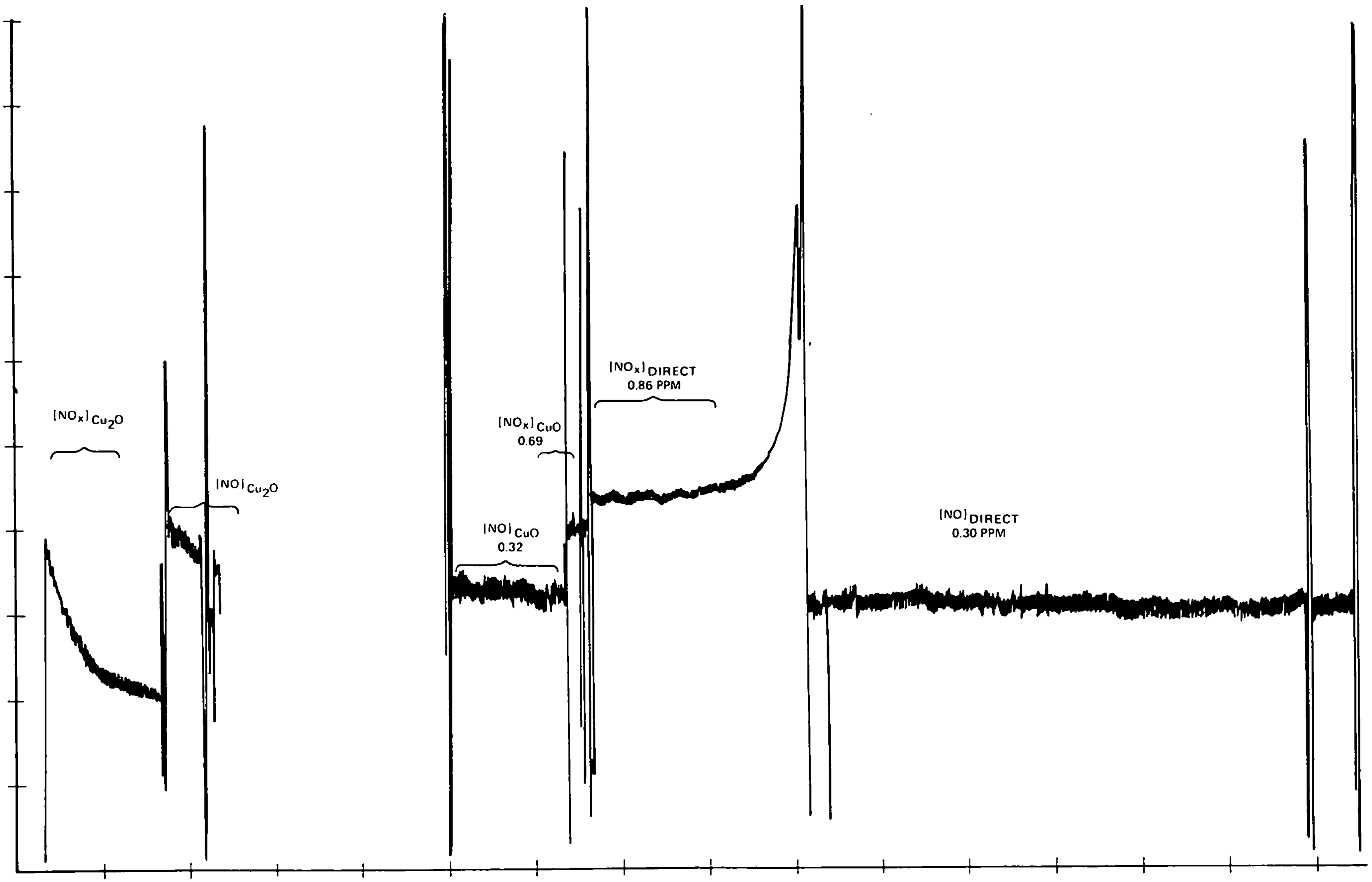


Figure A-13 - CuO

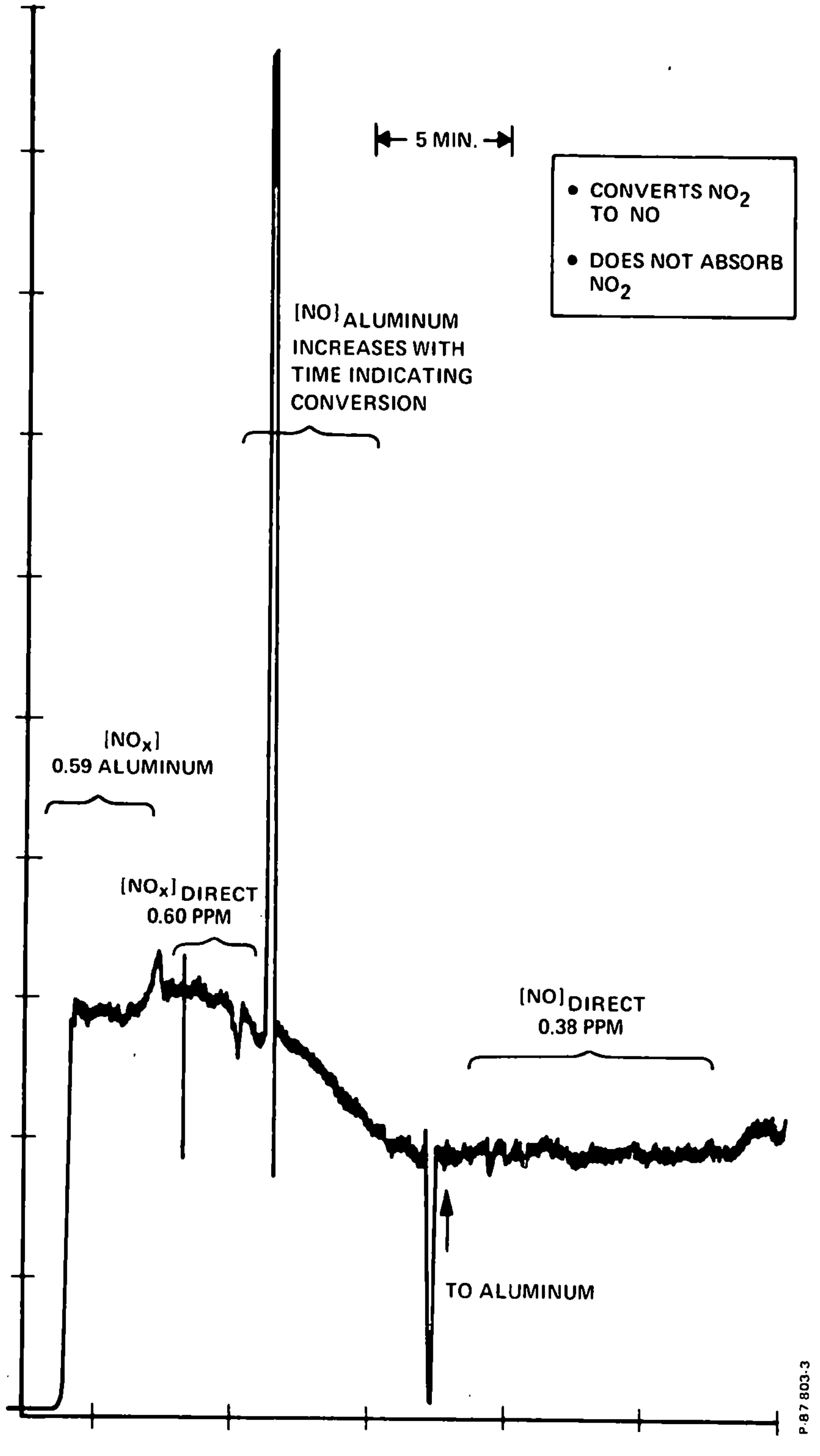


Figure A-14 - Aluminum cartridge (after heating cycle to 200°C and cooled down to room temperature)

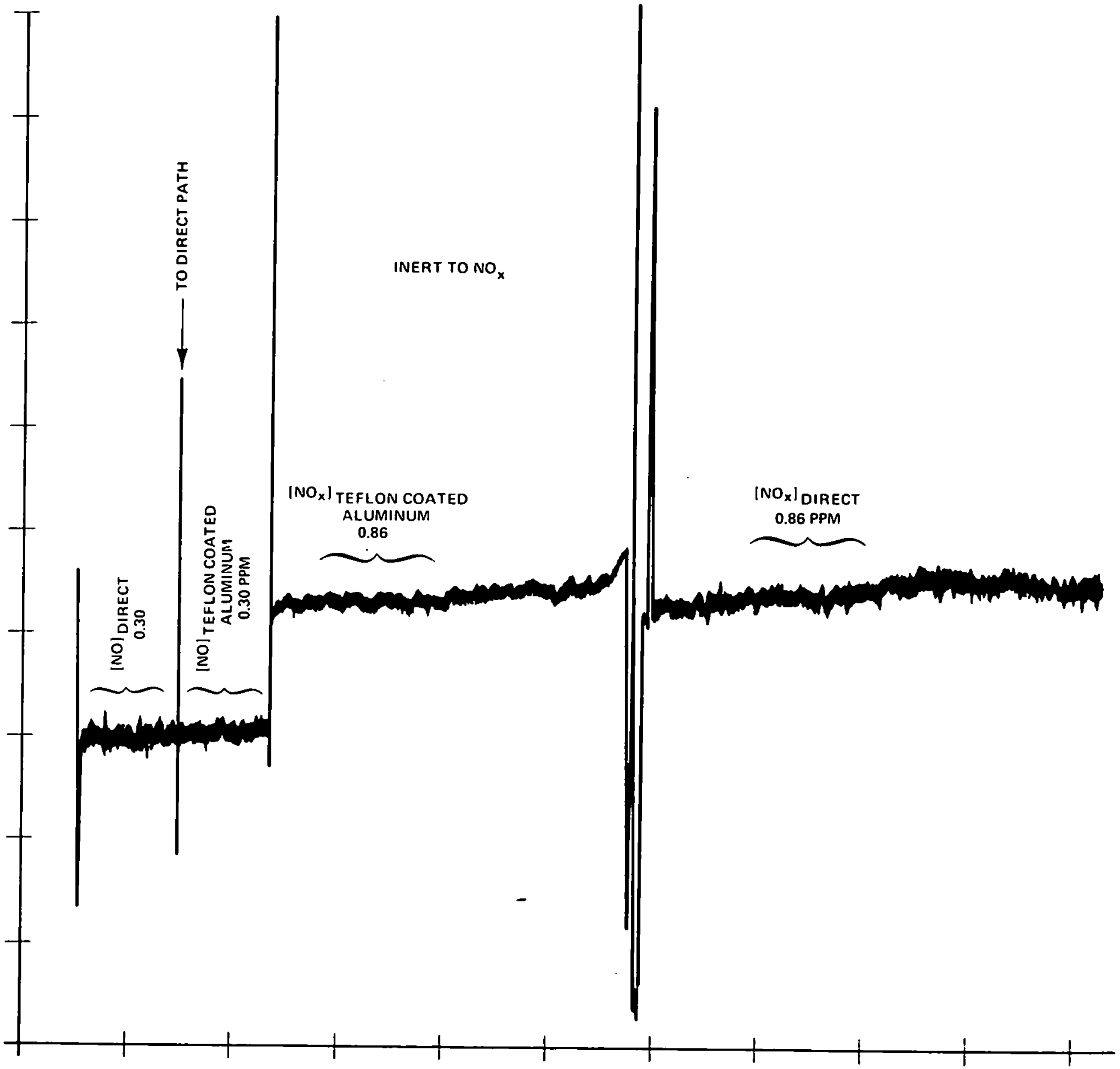


Figure A-15 - Teflon-coated aluminum surface

APPENDIX B

DIRECTIONS FOR ASSEMBLING COLLECTOR FIELD HOUSING

(1) Place folded housing in flat position with back side down (large door with hasp up).

(2) Open door and remove legs.

(3) Close door and turn unit over (front down).

(4) Remove wing nut and screw holding cover in folded position.

(5) Unfold housing by pulling upper section so it swings upward and toward bottom.

(6) Stand housing upright with cover in full open position.

(7) Remove five remaining wing nuts holding sides in folded position

(8) Swing sides into position running studs into appropriate holes and fastening with wing nuts.

(9) Lay the housing on one side and install legs on the other side with 1/2" long 1/4-20 bolts; match one leg with clearance hole to stud head.

(10) Turn housing onto other side and install remaining two legs.

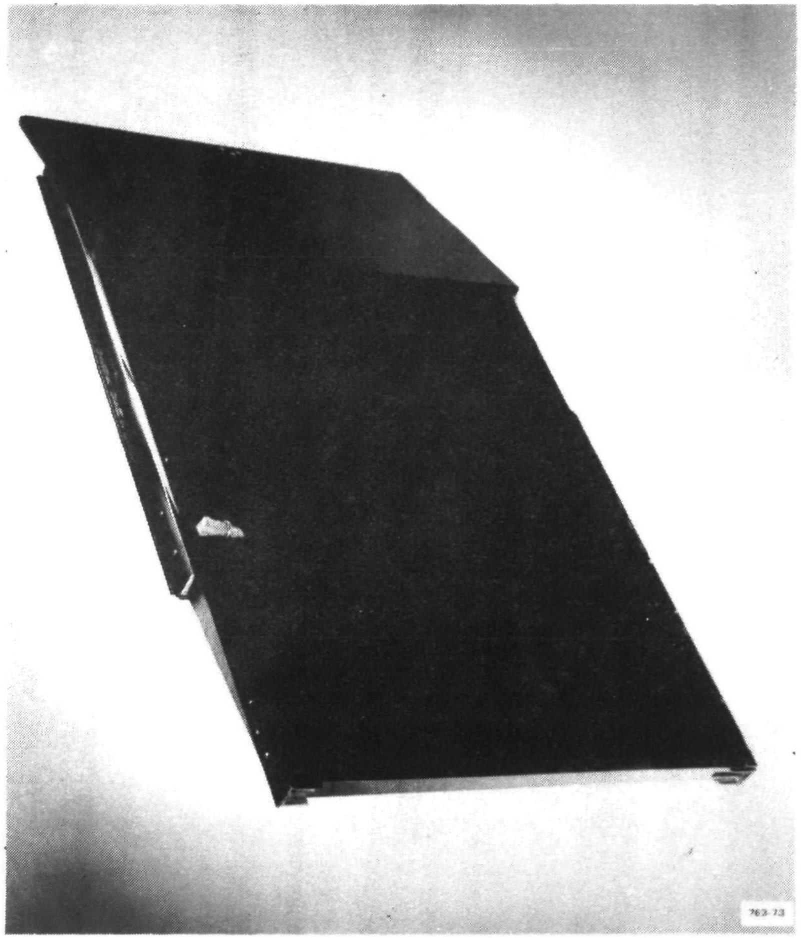


Figure B-1 - Folded View of Collector System Housing

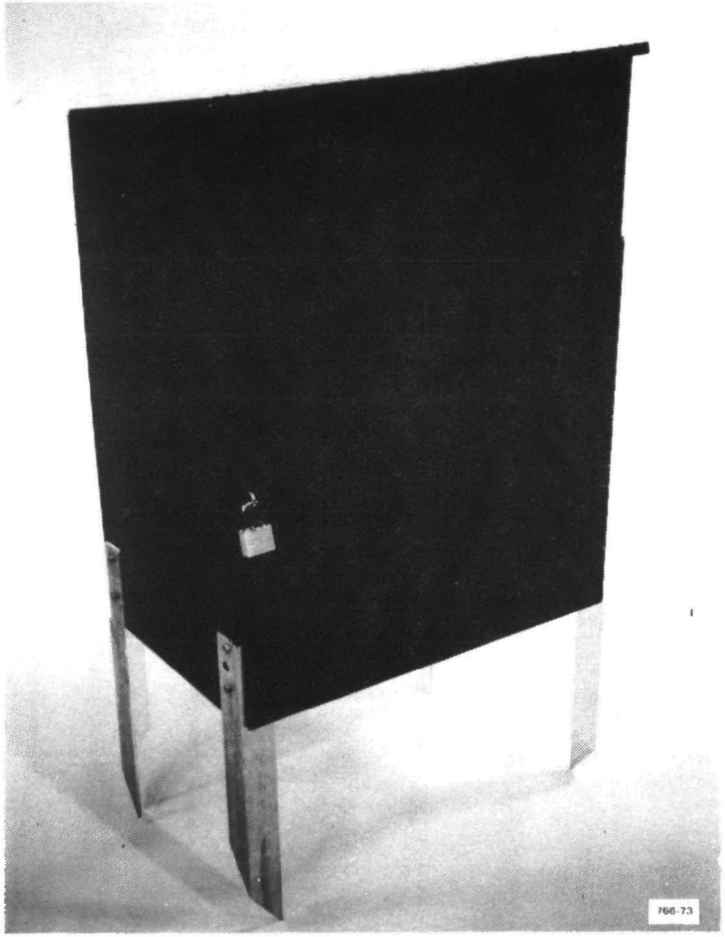


Figure B-2 - Assembled Collector Unit