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September 1982**

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**PREPARATION AND EVALUATION
OF
SELF-REGENERATIVE
CARBON MONOXIDE
DETECTION GELS**

Bureau of Mines Open File Report 92-83

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FOREWORD

This report was prepared by The University of California at San Diego under USBM Contract number JO188159. The contract was initiated under the Minerals Health and Safety Technology Program. It was administered under the technical direction of The Pittsburg Mining and Safety Research Center with Dr. Emery Chilton acting as Technical Project Officer. Mr. J. E. Pettus was the contract administrator for the Bureau of Mines. This report is a summary of the work recently completed as a part of this contract during the period September 1, 1979 to June 30, 1981. This report was submitted by the authors on September 9, 1982.

PREFACE

The authors would like to thank David R. Hamm and Timothy Ross for their valuable assistance in the laboratory and Joanne Ashwell for her patient help in preparing this and previous reports. They would also like to thank the DuPont de Nemours Company for the generous donation of custom-made materials needed in the PTFE-entrained silica gel experimentation and Matheson, Coleman, and Bell (MCB) Manufacturing Chemists for supplying some proprietary organic binder used in the preparation of TLC plates.

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ABSTRACT

Continued development of an especially impregnated silica gel capable of reversible chemical detection of carbon monoxide (CO) was reported. The affects of changes in mine-related ambient conditions on the **detection catalyst's** response were explored. Temperature, humidity, and several **interfering gases** were found to affect the detection catalyst. The interferents include hydrogen sulfide, nitrogen dioxide, acetylene (and methylacetylene), and ammonia. High humidity decreased the detection catalyst's sensitivity to carbon monoxide for some formulations. Increasing temperature generally decreased the reaction time of the detection catalyst with carbon monoxide.

Badges and carriers for the visual presentation of the detection catalyst were constructed. Several variations of these devices included provisions for absorbants and filtering agents which help protect the detection catalyst from gaseous interferents.

A variety of catalyst support agents were tested in an effort to find the most suitable. Included were alumina, magnesium oxide, magnesium silicate, and several forms of silica gel. In addition to free-flowing forms of these sorbents, thin layer chromatography plates coated with cellulose, alumina, and silica gel and newly developed PTFE entrained silica gels were examined.

A limited physical, chemical, and mechanistic characterization of the detection catalyst and the materials used to prepare it has been carried out. Metal component ratio studies, spectral, analytical, pH, and rate measurements were done.

INTRODUCTION

The dangers present in mines and other enclosed-space environments are numerous. One of the recognized dangers is the possible presence of deadly carbon monoxide. A simple, inexpensive, and reusable detection device could greatly improve worker safety in areas where CO contamination can occur.

The development of such a device began in 1977, under a grant from the U.S. Department of the Interior (U.S. Bureau of Mines).¹ The detector is a badge-like device encapsulating a detection agent. The detection agent consists of silica gel impregnated with solutions of various metal salts. This detection agent or "catalyst" changes from yellow to blue when carbon monoxide is present and slowly returns to yellow when removed from a carbon monoxide contaminated atmosphere. Previous work established that the detection catalyst was sensitive to carbon monoxide above ~50 ppm in air and could be formulated to exhibit a rough "threshold" to carbon monoxide in the range of 50 to 500 ppm in air.

EXPERIMENTAL

Reagents

All chemicals used were Reagent Grade or better except were noted in reference #1 or below.

Palladium sulfate was prepared directly from the pure (99.9%, Martin Metals) metal^{2,3} or used as obtained from Alfa-Ventron Corp. ($\text{PdSO}_4 \cdot 2\text{H}_2\text{O}$) and Research Inorganic Chemical Corp. (10% aqueous solution). When a stock solution of palladium sulfate was prepared the most common formulation contained 0.013 grams PdSO_4 and 0.33 grams H_2SO_4 per milliliter.

A variety of silica gels and other chromatographic support materials were employed as catalyst support agents. In addition to those mentioned in reference #1 the following were used; Silica Gel: Research Inorganic Chemicals (SI-62, SI-64), E. Merck Reagents (7733 and 7754) Type 60, E. Merck Reagents (10181) Type 40, E. Merck Reagents (10185) Type 100 (35-70 mesh and 70-230 mesh); Alumina: MC/B AX611 alumina (80-325 mesh); Magnesium Silicate: J.T. Baker Florisil (60-100 mesh) (M368); Aluminum Oxide: A.R. magnesium oxide (6015).

12-Silicomolybdic acid was used as obtained from Climax Molybdenum or prepared from sodium molybdate (J.T. Baker 3764) and sodium silicate (MC/B SX750) according to the literature.⁴

Thin layer chromatography (T.L.C.) plates used were obtained commercially or prepared in the laboratory as described under "Methods" below. Commercial TLC plates included: Eastman Chromatogram Sheet #13181 (silica gel), E. Merck Silica Gel "60" (5506) plastic support, E. Merck Silica Gel "60" (5762) glass support, E. Merck Cellulose (5772) glass support, E. Merck Aluminum Oxide "60" (5500) plastic support, and E. Merck Aluminum Oxide "60" (5750) glass support.

Teflon^{®27}-entrained silica gel strips were obtained from E. I. DuPont de Nemours, Fabrics and Finishes Division. The base silica gel was from Davidson for the initial experiments but later tests involved custom preparations using E. Merck (Type 100) silica gel of 35-70 mesh entrained at a ratio of 90% silica gel to 10% Teflon[®]. Additional tests were conducted using discs containing from 25% to 75% Teflon[®] powder with the remainder being previously prepared detection catalysts on a variety of silica gels. These discs were prepared at UCSD as described later in this section.

Equipment

Test chambers, gas regulating equipment, and other preparatory and analytical equipment have previously been described in detail.¹ Additions and modifications are discussed below.

Test Chambers: Two photocell detectors were installed in the nonenvironmentally controlled plexiglass test chamber. The internal volume of this chamber was reduced from 1.5 liters to 0.3 liters. Four photocell detectors were mounted in the temperature and humidity controlled test chamber. This photocell chamber was first made of aluminum and polycarbonate, but later was replaced with a black anodized aluminum model with new photoresistors to minimize outside light interference during use.

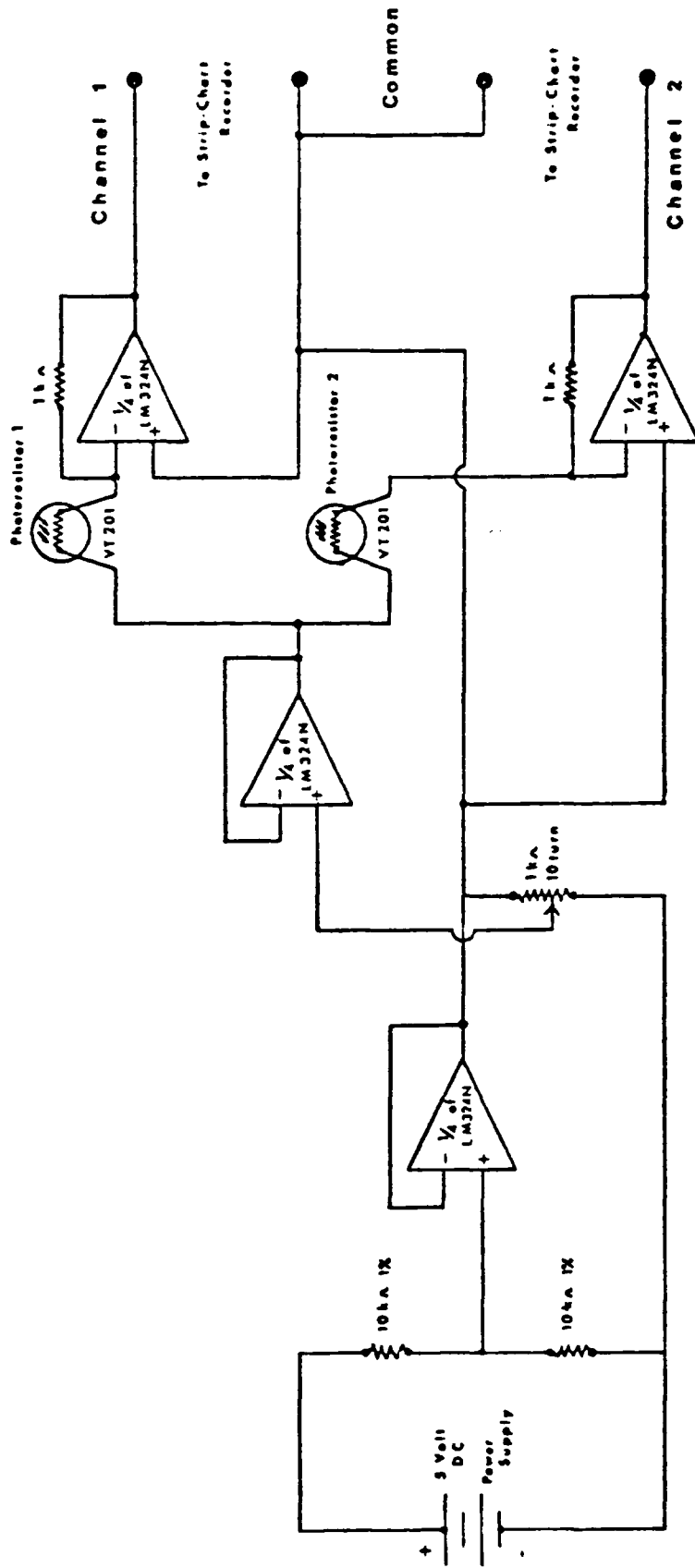
Photocell Detectors: These are photoresistive devices along with associated circuitry. They respond to visible light and when placed beneath a thin layer of detection gel with a light source above it, they emit a signal that changes with detection gel color and can be recorded on a normal strip chart recorder. A circuit schematic is shown in Figure 1.

Fluid-Bed Drying Chamber: A small volume "fluid-bed" device was constructed of plexiglass, Delrin, polyethylene, and stainless steel. It "fluidizes" the detection gel by means of a gas stream flowing in from the bottom of the chamber, which suspends the gel particles in a fluid-like mass and then exhausts through a frit at the top of the chamber. It is shown in Figure 2.

Karl-Fischer Apparatus: A Karl-Fischer titration apparatus was constructed for analytical water content determination. It is made of glass, platinum, polyethylene, and teflon with rubber serum cap seals. A diagram of its construction and the associated electronic schematic is shown in Figure 3.

Gas Handling Equipment: A four-tube Airco precision 150mm flowmeter was used for gas control and mixing. The fourth tube was used as the mixing chamber while a variety of calibrated tubes were used in the first three positions for carbon monoxide, air, and interferent gas control.

Modified Detection Equipment: In order to allow low level (ppm) detection⁵ of carbon monoxide a modification of the flame ionization detector's fuel supply line and the installation of an especially built predetector "catalytic converter" column was carried out on a Hewlett-Packard Model 700 Gas Chromatograph. These changes allowed the conversion of carbon monoxide to methane in the predetector column, which is then readily detected by the flame ionization detector. The predetector "catalytic converter" column is a 5" long section of 1/8" OD by 1/16" ID nickel tubing filled with nickel oxide on Anakrom C-22 (firebrick) 100/120 mesh. The nickel oxide on the firebrick support was formed by soaking the support material in a saturated nickel nitrate



Circuit Diagram of
Photocell Response Measurement System
(for CuO Detection Gels)

FIGURE 1

Fluid-Bed Drying Chamber

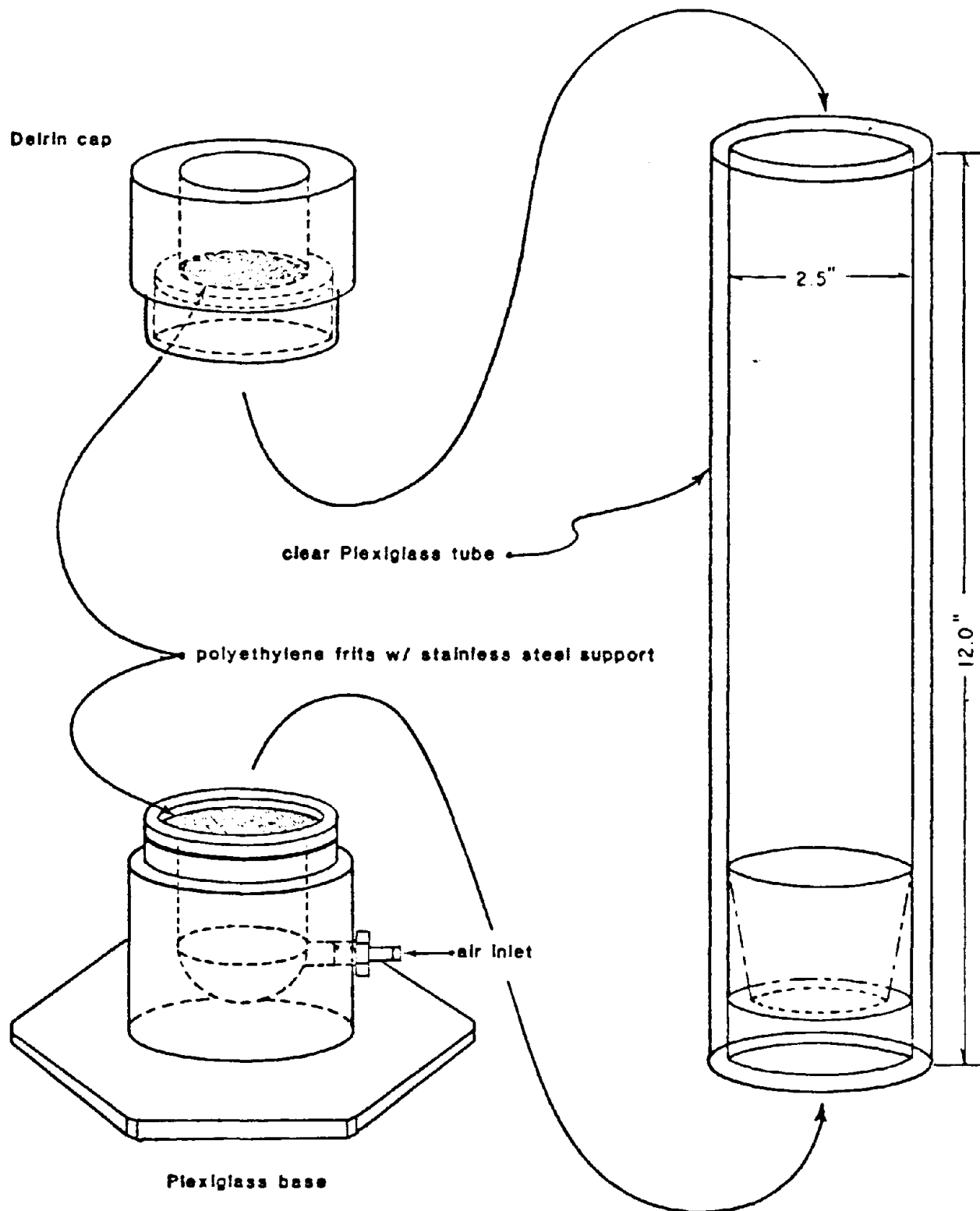


FIGURE 2

KARL-FISCHER
Titration Apparatus

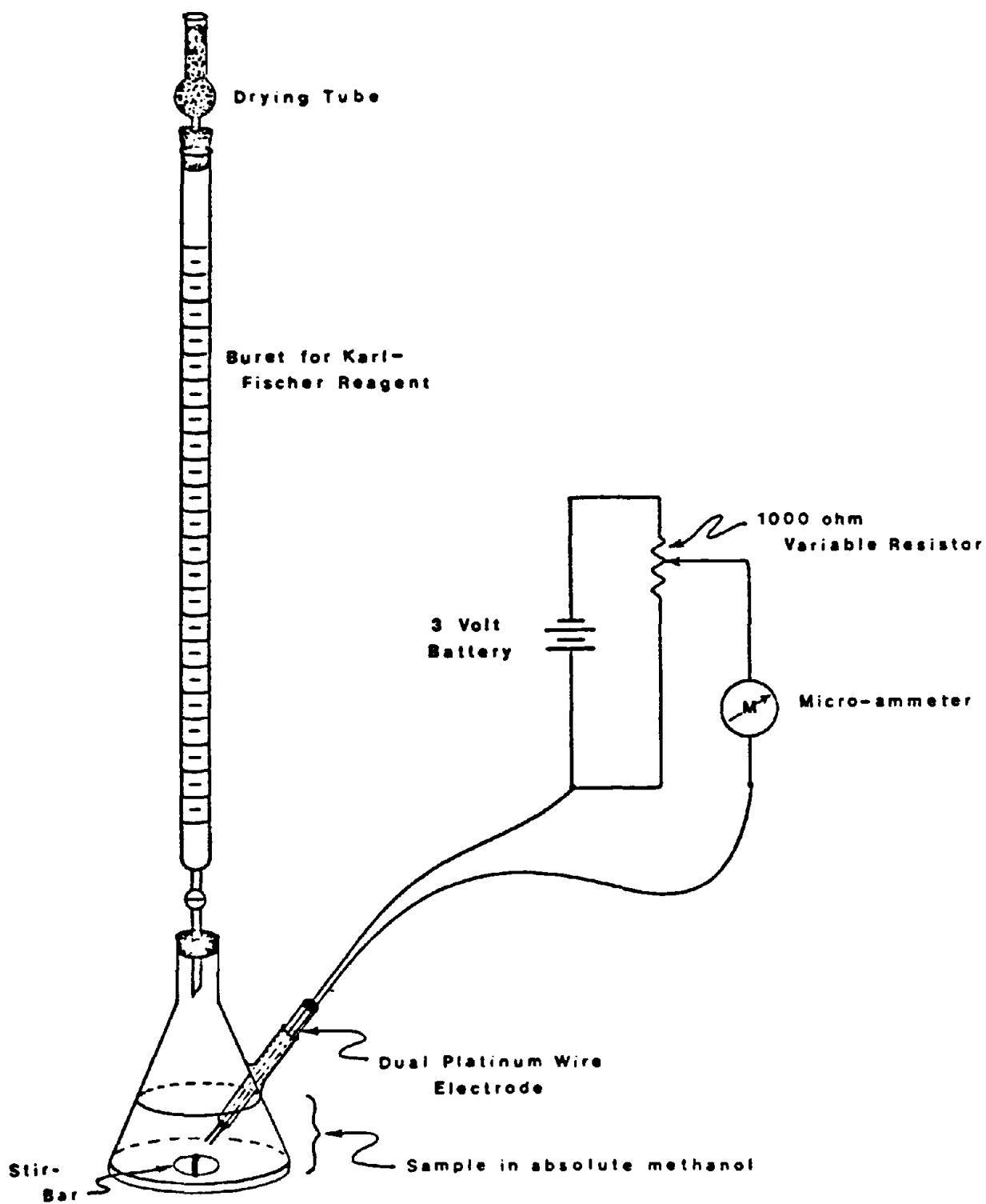
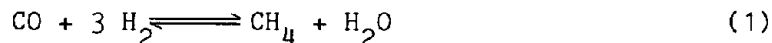


FIGURE 3

solution, drying overnight at 110°C, and roasting for 8 hours at 450°C in air. The predetector column is encased in an aluminum block which contains a heating cartridge controlled by means of a variable voltage supply, and a thermometer well.

Prior to use, the hydrogen fuel flow for the detector flame is diverted to the head of the predetector column, the predetector column is heated to $265^{\circ} \pm 3^{\circ}\text{C}$, and the system is allowed to equilibrate overnight. This allows a reduced nickel catalyst to form which allows the reaction of carbon monoxide with hydrogen according to equation #1.



Immediately after conversion the formed methane is swept into the detector and quantitatively monitored.

Due to the similar reaction of carbon dioxide with hydrogen over the nickel catalyst⁶, the normal gas chromatography column was chosen to separate carbon monoxide from carbon dioxide prior to their reaching the predetector column. When the detection of carbon monoxide was of interest, a 1 meter long 1/8" OD by 1/16" ID stainless steel column packed with 50/60 mesh molecular sieve 5 A was used because it retained carbon dioxide while passing carbon monoxide. A schematic of the modified equipment is shown in Figure 4.

Ancillary Equipment: A Curken (Model 250-3) three channel chart recorder was used for recording photocell output. The Buchi Model RE rotary flash evaporator with temperature controlled bath replaced the Model R. A Precision (Model 14510) mechanical convection oven supplemented the Blue M (Model OV-18A) mechanical convection oven. The Lab Line (Model 3625) vacuum oven was added for use in determining water content of the detection gels. Spectral measurements were made using a Beckman (Model DK-A) ratio recording (dual beam) U.V. -Visible Spectrophotometer and a Beckman (Model IR-33) Infrared Spectrophotometer.

A Beckman (Model 3500) pH meter was used to measure the hydrogen-ion content of the detection gel. Analytical measurements of copper, molybdenum, and palladium were done with a Perkin-Elmer (Model 373) Atomic Absorption Spectrophotometer.

A Desaga Heidelberg thin layer chromatography plate spreader was used to prepare samples of TLC plates using E. Merck type 100 silica gel for special tests involving TLC plates and binding agents. Plates prepared were from 0.25 mm to 1.00 mm in thickness.

A Carver Hydraulic Laboratory Press, Model C, was used in the preparation of Teflon®/detection catalyst discs. The discs were formed in a 1/2" diameter KBr pellet press, which yielded discs of approximately 0.5 to 1.0 mm in thickness.

**Modification of Gas Chromatograph
for Part per Million Carbon Monoxide Detection
(as Methane)**

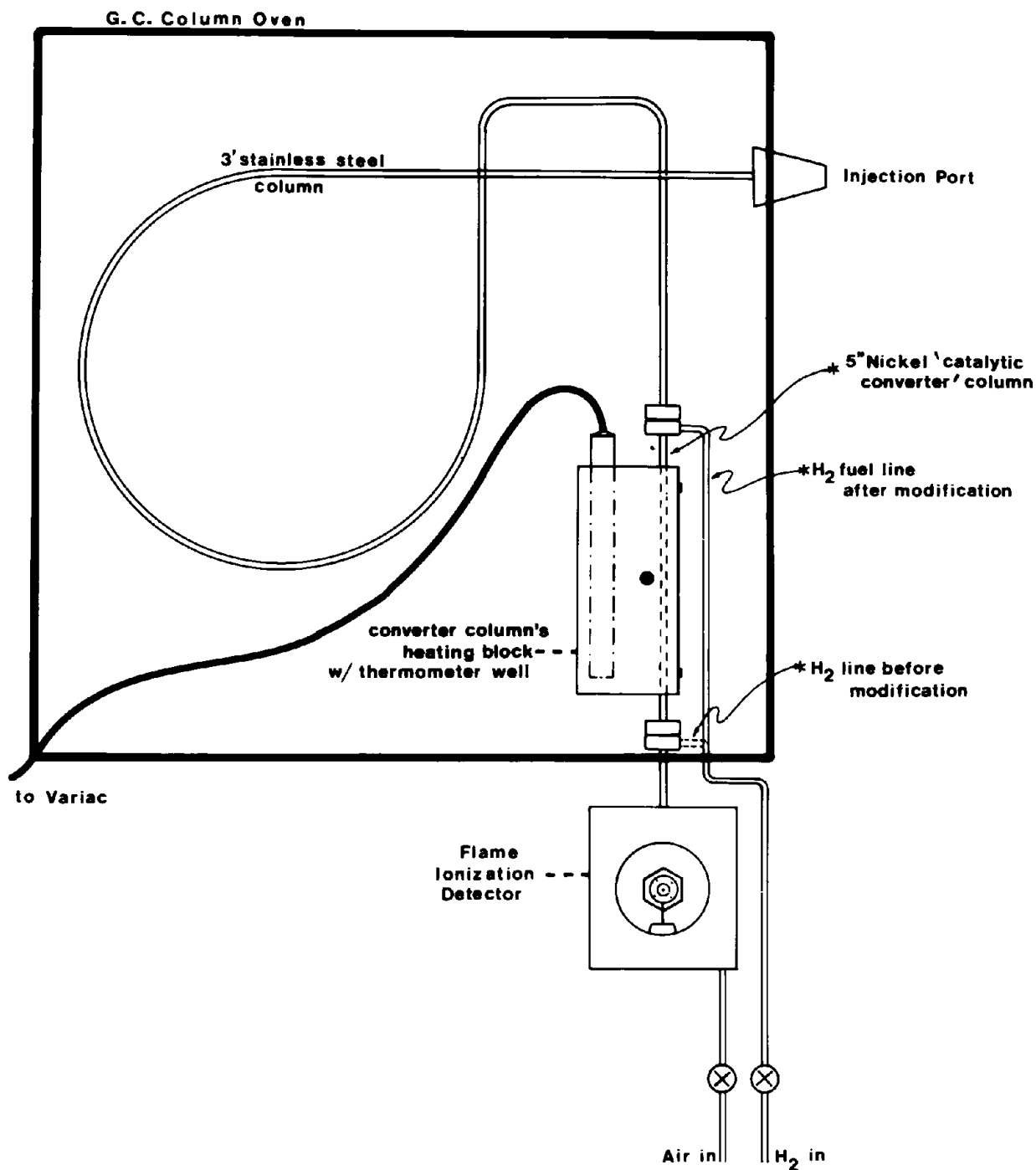


FIGURE 4

Methods

Changes in previously described¹ methods used for detection catalyst preparation, gas handling, detection gel characterization, and the procedure for response tests are noted below.

Method of Gel Preparation: The general technique used in detection gel preparation have previously been described. A modified drying procedure was adopted during the contract year. After treatment with hydrogen peroxide, the detection gel was added damp to a small fluid-bed chamber which was then connected to a source of dry, purified air or nitrogen and processed at room temperature until homogeneous and dry.

Preparation Involving Chromatography Supports Other than Silica Gel: The standard preparation procedure used for silica gel based detection gels was employed when using alumina, Florisil, and magnesium oxide. In place of the silica gel, an equivalent amount of the new support was used. A molybdenum-equivalent amount of 12-molybdosilicic acid (silico-molybdic acid) was substituted for ammonium molybdate in one series of tests.

Preparation of TLC plates with a variety of binders and E. Merck type 100 silica gel was carried out with accepted techniques from the literature⁷ in the majority of cases. Inorganic gypsum binder was used at levels of 8% to 18% of the binder/silica gel mixture. The manufacturer's suggestions were followed in preparing TLC plates with a proprietary organic binder supplied through Matheson, Coleman, and Bell (MCB) Manufacturing Chemists.

The preparation procedure for T.L.C. plates coated with alumina, cellulose, and silica gel involved mixing in aqueous solution containing appropriate amounts of 12-silicomolybdic acid⁸, cupric chloride, palladium sulfate, and acid and dipping or spraying the plates with the solution. Drying was done at 50°C in a mechanical oven. Hydrogen peroxide treatment was accomplished by spraying with a 5% aq. solution after the initial drying.

Impregnating the TLC plates and PTFE-entrained silica gel was accomplished through soaking, dipping, and spraying. Most impregnating solutions used in the tests involving these support materials were similar to normal impregnating solutions in component ratios but were from one to three times as concentrated. Several solutions contained silico-molybdic acid as the molybdenum source and a few solutions contained high levels of cupric sulfate.

PTFE (Teflon®)/detection catalyst discs were formed from a mixture of Teflon® powder and previously prepared detection catalyst. A small quantity of the mixture was placed in a die and the die was subjected to pressures of 500 to 5000 psi. Mixtures varied from 20% PTFE and 80% detection catalyst to 75% PTFE and 25% detection catalyst.

Water Content: Water content of the detection gels was measured by taking a one gram sample of gel in a tared vial and subjecting it to a given (15%, 20%, or 80%) relative humidity in a closed chamber, overnight, at room temperature. The vial plus gel were then accurately weighed dried four hours at 100°C in a vacuum (~15" Hg), and reweighed. The change in gel weight was then used to calculate the percentage water.

Gel Acidity: The relative acid content of the detection gels was determined by measuring the pH of a 10% (by weight) slurry of the gel in glass distilled water.

Detection Gel Component Analysis: Samples of prepared detection gels were carefully weighed, placed in a fritted glass funnel, and rinsed with distilled water until the silica gel remaining in the frit was colorless. The filtrate was then diluted to a known volume for use as a stock solution. Aliquots of the stock solution were diluted to concentrations in the working range of each element (palladium, molybdenum, and copper) and then run on a calibrated Perkin-Elmer Absorption Spectrophotometer.

Regulations and Analysis of Test Gases: Previously described methods¹ were used in most cases to introduce, regulate, and analyze gas mixtures. The concentration of carbon monoxide used in recent tests has been adjusted by using two 150mm rotameters, a premixed cylinder of carbon monoxide in air (Scott Environmental, ~1000 ppm), and a cylinder of air (Scott Environmental "Zero Gas"). Carbon monoxide levels between 0 and 1000 ppm could be delivered to the test chamber by using the rotameters as proportioners and keeping the total flow rate constant. An E.S.I. (Model 6000) Ecolyzer Carbon Monoxide Analyzer was used as a monitor of carbon monoxide test levels mixed as described above. A third 150mm rotameter was used to introduce various interferent gases during some tests.

Experimental Procedure for Response Tests: The details of general test chamber operation and control of experimental conditions have previously been reported¹ or are to be found in earlier pages of this report. Modifications in the test format due to the introduction of photocell detectors and a description of the response data currently being recorded will be presented here.

A small even layer of detection gel (0.05 grams to 0.10 grams) is placed on a test slide designed to position the gel sample(s) in the chamber, and the photodetector network, including the strip-chart recorder, is adjusted. The recorder is adjusted so that a 80%-90% deflection will occur when the detection gel's color changes from light yellow to dark blue. This is normally accomplished by setting the recorder pen to 90%-100% full-scale deflection, using the input voltage range controls while the yellow gel is in place and illuminated. The recorder zero is set prior to the slide being placed in the chamber, by either blocking light from the photoresistor or shorting the recorder

inputs and using the zero control to adjust the pen to 0%-5% of full-scale deflection. (This procedure approximates using an illuminated, dark blue detection gel over the photoresistor.)

A convenient chart speed is selected (usually from 20 cm/hr to 60 cm/hr), all experimental conditions are adjusted, and the challenge gas mixtures flow is started. Visual observations are recorded at several points during the test sequence including "first observable response time", "definite response time", and color designations at various times. A schematic representation of chart recorder response is shown in Figure 5. Note the chart recorder moves from full-scale deflection towards zero deflection during the course of a response experiment. A correlated visual account is as follows:

time = 0, detection gel is yellow/chart recorder is a ~95% of full-scale deflection;

"first observable response time", detection gel is light green/chart recorder has dropped to 75%-60% of full-scale deflection;

"definite response time", detection gel is green to blue-green/chart recorder is down to 60%-45% of full-scale response;

"final response time", detection gel is dark green to dark blue/chart recorder is at 25%-10% of full-scale deflection.

Note: 'Final response time' is taken to be the time necessary to reach 80% of the chart recorder's total recorded change during the course of the test.

Tests were usually terminated after the chart recorded response plateaued for more than five minutes, or after 45 minutes, whichever came first.

RESULTS AND DISCUSSION

Study of the Detection Gel's Physical and Chemical Properties

A variety of experiments were carried out with the purpose of better understanding the way in which the detection gel interacts with carbon monoxide and the way in which the atmospheric environment affects this interaction. Described in this section are studies of component ratios, pH, water content, spectral features, starting materials (purity and physical characteristics), and indirect reaction rate analysis. Recent work with special silica gels is reported here and the results of

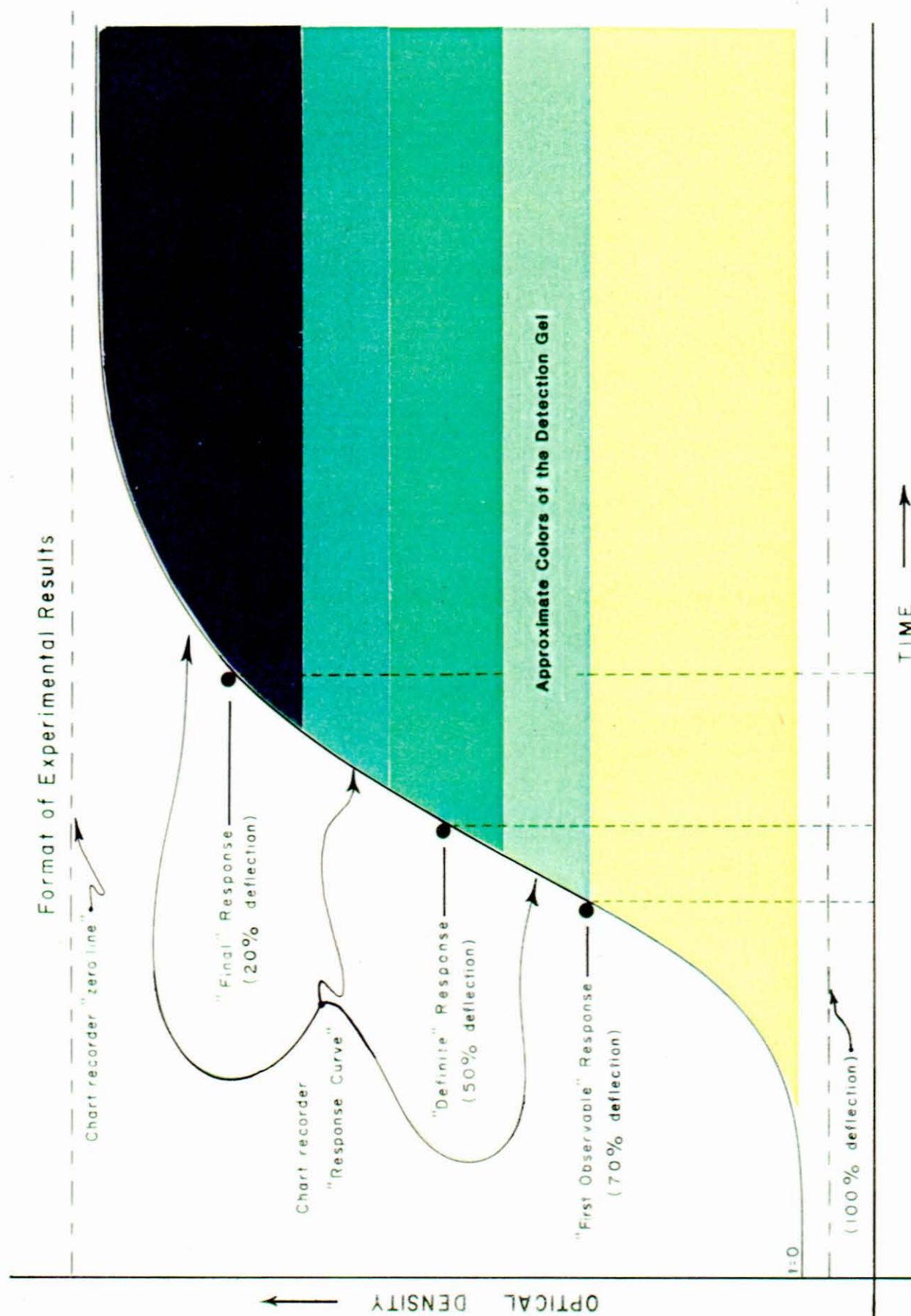


FIGURE 5

preliminary tests show that a detection gel can be formulated with reasonably stable response over a wide humidity range (<15% to >80% RH).

Metal Component-Ratio Studies: Three series of especially formulated detection gels were prepared to test the effects of changes in the molar ratios of the palladium, copper, and molybdenum used in the catalyst. The ratios used in the formulations are shown in Table 1.

The range covered for the composition variation in a given series was decided on by the examination of relative component composition found in previously prepared and tested detection gels. Only one component was varied at a time, keeping all other variables as constant as possible.⁹

The following assessments have been made from examining data from the tests at 510 ppm and 1009 ppm CO in air at 98% RH, 30% RH and dry (see Table 2 for qualitative results). In the Δ palladium series, gels #3 and #4 show the best response with #3 being significantly better than #4. In the Δ copper series, gels #2, #3, and #4 had reasonable response characteristics with #2 showing the best overall response to carbon monoxide. Looking at both the Δ Pd and the Δ Cu series results at once, the optimum copper to palladium ratio would lie in the range of 1:1 to 1:2. The results of tests on the Δ molybdenum series support data gathered from previous detection gels showing that good response to carbon monoxide occurs when Mo:Pd ratios fall in the range of 30:1 to 75:1.

Tests involving detection gels in which one of the metal components ("no Pd", "no Cu", and "No Mo" Table 1) was left out were conducted using pure CO and dry 510 ppm CO in air. The gel formulated with no molybdenum responded to pure CO within five minutes, turning to a brownish color. It regenerated to a yellowish buff color within a few hours. The gel without copper turned to a greenish-blue after four minutes exposure to pure CO, but it had not regenerated at the end of 36 hours. The gel lacking palladium did not respond to pure CO, even when exposed for over 10 minutes. The "No Cu" detection gel responded weakly to 510 ppm CO in air, but the other two incomplete gels did not respond at all.

It is apparent that the information obtained so far is very useful in defining narrow ranges of component ratios that show the best response to carbon monoxide. It has also furthered the understanding of the role each metal component in the gel plays. The data does not, however, show trends which are quantitative. This is due in part to the complex, multicomponent nature of the detection catalyst but other factors also contributed. Since optimum component ratios were not known before each series was formulated, a wide range had to be covered. This lead to a wide range of sensitivities (thresholds) to carbon monoxide, and for a number of the gels the thresholds are above 1009 ppm CO concentration maximum used so far. The fact that several gels failed to respond led to less clearly defined trends.

TABLE 1

Gram-Atom (Mole) Ratios for the Metallic Components
in the Test Series

Component Series	Molybdenum	:	Copper	:	Palladium
Palladium, "Δ Pd"					
#1	20	:	1	:	1.63
#2	20	:	1	:	0.98
#3	20	:	1	:	0.66
#4	20	:	1	:	0.33**
#5	20	:	1	:	0.16
#6	20	:	1	:	0.11
#7	20	:	1	:	0.07
"No Pd"	20	:	1	:	--
Copper, "Δ Cu"					
#1	20	:	0.3	:	0.66
#2	20	:	0.6	:	0.66
#3	20	:	1.5	:	0.66
#4	20	:	2.4	:	0.66
#5	20	:	3.3	:	0.66
#6	20	:	4.2	:	0.66
#7	20	:	5.2	:	0.66
"No Cu"	20	:	--	:	0.66
Molybdenum, "Δ Mo"					
#1	1	:	1	:	0.66
#2	16.66	:	1	:	0.66
#3	33.33	:	1	:	0.66
#4	50.00	:	1	:	0.66
#5	66.66	:	1	:	0.66
#6	83.33	:	1	:	0.66
#7	100.00	:	1	:	0.66
"No Mo"	--	:	1	:	0.66

** Calculated Composition = 2.07% Mo, 0.067% Cu, & 0.037% Pd.

TABLE 2

Qualitative Response Results for Tests Involving the Metallic-Component
Ratio Series

Component Series	Ratio (Mo:Cu:Pd)	Response at ~1000ppm CO in air
Palladium, "Δ Pd"		
#1	(20:1:1.63)	"slight"
#2	(20:1:0.98)	"good"
#3	(20:1:0.66)	"best"
#4	(20:1:0.33)	"very good"
#5	(20:1:0.16)	"slight"
#6	(20:1:0.11)	No Response
#7	(20:1:0.07)	No Response
"No Pd"	(20:1:--)	No Response; pure CO
Copper, "Δ Cu"		
#1	(20:0.3:0.66)	"poor"
#2	(20:0.6:0.66)	"best"
#3	(20:1.5:0.66)	"good"
#4	(20:2.4:0.66)	"fair"
#5	(20:3.3:0.66)	"slight"
#6	(20:4.2:0.66)	No Response
#7	(20:5.2:0.66)	No Response
"No Cu"	(20:--:0.66)	Good Response with pure CO, Incomplete Regeneration
Molybdenum, "Δ Mo"		
#1	(1:1:0.66)	No Data
#2	(16.66:1:0.66)	"fair"
#3	(33.33:1:0.66)	"best"
#4	(50.00:1:0.66)	"good"
#5	(66.66:1:0.66)	No Data
#6	(83.33:1:0.66)	No Data
#7	(100.00:1:0.66)	No Data
"No Mo"	(--:1:0.66)	Poor Response; pure CO

"Response" considers both the time taken to respond and the final color change.

TABLE 3

Commercial Silica Gels Used in the "A Gel" Series

"A Gel" #	Silica Gel Supplier	Product #	ASTM Mesh (as supplied)
#1	J.T. Baker	3404	80 Mesh
#2	J.T. Baker	3405	60-200 Mesh
#3	ROC/RIC ^a	SI-61	80 Mesh
#4	ROC/RIC ^a	SI-62	60-200 Mesh
#5	ROC/RIC ^a	SI-64	100-200 Mesh
#6	E.M. Reagents ^b	7733	35-70 Mesh
#7	E.M. Reagents ^b	7734	70-230 Mesh
#8	E.M. Reagents(extra-pure) ^b	7754	70-230 Mesh
"Type 40"	E.M. Reagents Type 40	10181	35-70 Mesh
"Type 100"	E.M. Reagents Type 100	10185	35-70 Mesh

Note: All "A Gel" Series gels used a Mo:Cu:Pd ratio of 20:1:0.66.

^aROC/RIC = Research Organic Chemical/Research Inorganic Chemical Corp.

^bE.M. Reagents #7733, #7734, & #7754 are all "Type 60" silica gels (with a mean pore diameter of 60A) produced by E. Merck, Darmstadt, Germany and supplied through their associate MCB Manufacturing Chemists, Inc. of Cincinnati, Ohio.

TABLE 4

Response Sampling for the Δ Gel Series

Conditions	Δ Gel #	Initial* (minutes)	Definite* (minutes)	Final* (minutes)	Height(Max.)
7/16/79 dry 23°C 1009 ppm CO ===== 40 cm/hr ~0.2 Volts	#1	11.7	13.2	17.3	180mm
	#2	12.0	16.5	26.3	165mm
	#3	19.1	21.8	24.6	
	#4	25.8	28.5	33.8	
	#5	12.3	15.0	28.2	
	#6	11.4	15.3	27.0	
	#7	10.7	12.0	16.8	
	#8	26.3	30.0	34.5	
7/19/79 98% R.H. 23°C 1009 ppm CO ===== 40cm/hr ~0.2 Volts	#1	8.3	11.6	22.8	150mm
	#2	13.8	23.3	36.8	125mm
	#3	slight response by 45 min. - - - -			
	#4	No Response			
	#5	14.6	16.5	25.8	165mm ^a
	#6	7.8	12.2	25.8	130mm
	#7	7.5	9.0	16.5	170mm
	#8	8.9	10.8	16.8	175mm

* Visual Response Times

^aThere was a chart-recorder malfunction during the testing of Δ Gel #5 which may have lead to inaccuracies in the data.

TABLE 5

pH Measurements for Several Detection Gels

"Gel"	1 st Measurement ("pH")	2 nd Measurement ("pH")
#1-3	2.97	3.06 (3.23, 2.94)
#1-4	2.28	2.26
#1-25	4.31	4.44
"Δ Cu" #1	1.04	--
"Δ Cu" #3	1.00	--
"Δ Cu" #5	1.16	--
"Δ Pd" #3	1.07	1.19
"Δ Mo" #3	1.10	--
"Δ Gel" #4	0.95	--
"Δ Gel" #6	1.07	--
"Type 40"	1.24	--
"Type 100"	1.23	--

Note: All measurements were done as a 10% (by weight) slurry of detection gel with distilled H₂O.

ammonium molybdate used affects the detection gel's pH. The amount of acid (H_2SO_4 or HCl) used in preparing the detection gels affects their pH, of course.

The Effect of pH on the Detection Catalyst

An experimental investigation of the way in which the detection catalyst's response and regenerative characteristics vary with pH (acid content) was undertaken. Preparation of a series of detection catalysts with final pH from below 1 to above 5 was carried out. Detection catalysts with final pH values outside the range mentioned had already been found unsuitable.

Catalyst with a final pH at the low end of the range (0.5 to 1.5 pH units) tends to be more sensitive to carbon monoxide, off-color in the oxidized state, and fair to poor in regenerative ability. Within the high pH range tested (3.5 to 5.0 pH units), the color of both the oxidized and reduced forms of the detection catalyst tend to be faded, the sensitivity is often decreased, and the regeneration tends to be moderate to rapid. The best over-all performance was found with detection catalyst having a final pH in the range of 1.5 to 3.5 pH units when E. Merck type 100 silica gel was used. The optimal pH varied for silica gel bases of different manufacture and pore diameter with some at as low as 0.9 to 1.2 pH units and others at as high as 4.2 to 4.4 pH units. The majority of type 100 detection catalysts measured for final pH follow a pattern of reduced sensitivity but increased regeneration at high pH (above ~3.0) and increased sensitivity but poorer regeneration at lower pH (below ~2.2). Reversals of this trend were found when several silica gels of varied manufacture were examined.

Experimental data revealed only qualitative trends as might be expected when the complex nature of the chemical interdependence of the detection catalyst components on hydrogen ion and each other is considered. In general there is a trade-off of sensitivity and regeneration over the tested pH range. The final pH value for a given detection catalyst will be dictated by what properties are most desired. Employing a range of pH values from ~1.5 to 3.5 should suffice for most purposes.

Special Development of New Supports

It was suggested by Dr. Emery Chilton of the U.S. Bureau of Mines¹³ that other chromatography sorbents might have better humidity stability than silica gel when used as the catalyst's support. At the time of his suggestion, little progress had been made in understanding and curing the "humidity problem". The experiments which ensued involved a variety of sorbents and several months' time.

The new chromatography supports tested were alumina, cellulose, magnesium oxide, and magnesium-silicate as the free sorbents and alumina, cellulose, magnesium-silicate and silica gel on commercial thin layer chromatography (T.L.C.) plates.

Earlier work done in this laboratory¹⁴ had indicated that silica was an essential part of the detection catalyst. The appearance and behavior of the detection gel during preparation indicated that silico-molybdic acid was being formed. The yellow color of the detection gel was taken as further evidence of this compound.

The first experiments involved the free sorbents and normal preparation techniques. As was expected from the above information, only very weak response (or no response at all) was found even when tested using pure carbon monoxide.

Silico-molybdic acid can be prepared from water soluble sodium silicate and sodium molybdate.⁴ It appeared that this compound was necessary for proper detection gel response, so molybdenum equivalent amounts were added to the new sorbents in place of the ammonium molybdate normally used in the preparation of the gel. The results were somewhat encouraging and are summarized below.

Free Sorbents:

Alumina	-pure CO, color changed from lime green to white, regenerated. 1009 ppm CO, weak response from green to grey.
Cellulose	-pure CO, no response.
Magnesium Oxide	-pure CO, no response.
Magnesium Silicate	-pure CO, color changed from light yellow to mauve, regenerated. 1009 ppm CO, no response.

T.L.C. Plates:

Alumina	-pure CO, color changed from yellow to greenish blue, regenerated.
Cellulose	-pure CO, color changed from white to translucent pale blue, regenerated. 1009 ppm CO, no response (30 minutes).
Silica Gel	-pure CO, color changed from pale yellow to blue, rapid regeneration (< 1 hour). 510 ppm CO, color changed from pale yellow to pale blue (10 minutes, 20% RH and 8 minutes, 98% RH), regenerated (~30 minutes).

Alumina and silica gel T.L.C. plates have shown the best response to date. Studies involving the free sorbents will be curtailed, but the continuing study of T.L.C. plates is planned. The T.L.C. plates offer some advantages over the normal silica gel support used in the detection catalyst. The plates exhibit both rapid response to carbon monoxide and a quick regeneration when exposed to clean air. Additionally, the plates are very easy to handle, especially when used with plastic backing rather than the normal glass backing.

TLC Plates as Detection Catalyst Supports

Silica gel and alumina TLC plates had been suggested earlier¹ as logical detection catalyst supports. It was felt that the plates would offer an acceptable and convenient medium for detection catalyst preparation since they are easily handled and can be obtained in a large selection of adsorbents and backing materials.

Thin Layer Chromatography, or TLC, is a well-known analytical technique used to separate complex mixtures and/or identify individual compounds on a very small scale. Typically a solid sorbent (adsorbent material) such as alumina or silica gel is layered or bound on a stiff backing material as a thin layer. The classic backing material is glass plate, but plastics and aluminum metal are gaining in acceptance. The combination of dry sorbent on a stiff backing is referred to as a "plate". It is the backing material which allows the sorbent to be easily manipulated. Plastic and aluminum backing allow additional utility in that they can easily be cut to appropriate size and shape for special applications.

The way in which TLC plates were prepared and used is described above in the "EXPERIMENTAL" section. It was found that aluminum backed plates were unsuitable for use as detection catalyst supports because the acid contained in the impregnating solution reacted with the aluminum metal. The majority of experiments involving TLC plates employed glass backed samples because of their availability in a wide variety of sorbents and because of their proven chemical inertness. Several tests were conducted using commercially available plastic backed plates to allow evaluation of detection catalyst impregnated samples in badges.

Alumina TLC plates can be used as a catalyst support medium, as long as silico-molybdic acid is included in the impregnating solution¹. The minimum response threshold obtained with alumina supported detection catalyst has been ~900 to 1200 ppm CO in air; and even at this relatively "high" level, the response is extremely weak. The color change observed is from pale yellow to very pale blue-green. Regeneration does take place in clean air - usually in 3 to 10 hours after exposure to ~1000 ppm CO in air. A few preparations have taken over 24 hours to regenerate or have failed to regenerate completely. The detection catalyst, when prepared on alumina TLC plates, does not appear to be entirely stable to ambient humidity changes.

Experiments conducted using silica gel TLC plates impregnated with detection catalyst components provided promising results. The maximum sensitivity was below 400 ppm CO in air. Humidity changes did affect the response times and threshold sensitivities of detection catalyst prepared on most commercially available TLC plates. TLC plates especially prepared using E. Merck (type 100) silica gel provided reasonably reliable results through a humidity range of 10% to 80% RH, but the sensitivity limit for the formulations prepared was just below 500 ppm CO in air (changes could be detected at concentrations as low as ~250 ppm CO in air, but not reliably).

Reasonable sensitivity was not the only encouraging feature of the detection catalyst when prepared on silica gel TLC plates. It was also found that the speed of detection of CO and of regeneration of the catalyst after detection were greatly improved. Times as short as 1 to 3 minutes were observed for initial response time to concentrations of CO at or below the 500 ppm level. Regeneration would often take less than three hours and sometimes less than one hour when silica gel TLC plates were used as catalyst supports. This is likely due, at least in part, to the thin cross-section of the silica gel on the TLC plates used in testing.

The biggest drawbacks encountered in using TLC plates as supports for the detection catalyst were mechanical stability and, more seriously, the tendency of the plate/catalyst system to auto-darken after storage over periods as short as two weeks. Both deficiencies appear to result from what is used to "bind" the sorbent to the backing material. Organic binders, the kind most commonly employed in commercial plates, increase the mechanical stability of sorbent binding but apparently cause or contribute to the auto-darkening phenomenon. The use of calcium sulfate as a binding agent provided detection catalyst TLC plates which could be stored for periods of at least two to three months without auto-darkening but had a very low degree of mechanical stability.

Special Catalyst Support

The idea of preparing the detection catalyst on an easily handled support medium was attractive from a packaging/protection standpoint. Using TLC plates held promise, but difficulties in mechanical stability and chemical compatibility would have to be overcome. During a discussion of the detection catalyst with a representative of a commercial chemical firm (Dr. Lautenberger; DuPont), the availability of a new support material was mentioned. The material consists of silica gel entrained in a PTFE (PolyTetraFluoroEthylene; Teflon®) matrix. The matrix is a very open "spider web" of PTFE which traps the silica gel (or other granular material) in its strands. This matrix offers high gas permeability, reasonable aqueous "wettability", and excellent flexibility plus other desirable physical properties for use in badges. It theoretically contains only Teflon® and silica gel when properly prepared, which should make it compatible with the detection catalyst. Formulations which contain as high as a 9 to 1 ratio of silica gel to PTFE "binder" can be produced.

Due to the unique properties of the PTFE-entrained silica gel, it appeared to merit testing as a detection catalyst support. Procedures analogous to those used with TLC plates¹⁵ were employed because of the similarity of TLC plates and PTFE-entrained silica gel.

The first samples tested were "strips" containing 80% Davidson silica gel and 20% Teflon® and prepared by soaking in impregnating solution at an elevated temperature to increase "wetability". Initial results with these strips revealed they did indeed respond to carbon monoxide in air with several samples responding at less than ~1000 ppm CO in air. The color change was from light yellow to light blue or light green for most of the strips.

Additional strip samples were obtained with compositions of 80% Davidson silica gel to 20% Teflon®; 90% Davidson silica gel to 10% Teflon®; and a custom preparation of PTFE-entrained silica gel by DuPont using 90% E. Merck type 100 silica gel to 10% Teflon®. The custom preparation was carried out in an effort to keep variation to a minimum in comparative testing of the new support with previous systems and to minimize the humidity sensitivity of the detection catalyst when prepared on this material. Samples in which the silica gel to Teflon® ratio was 9 to 1 could be soaked in room temperature impregnating solution because they exhibited an increased "wetability". Spraying of the impregnating solution onto support strips was also used in several instances.

In this preliminary investigation of PTFE-entrained silica gel support material, the maximum sensitivity attained was ~400 ppm CO in air. The mechanical stability of the support was good and it was easily cut to any size and shape desired. Test results varied with impregnating solution composition and silica gel used to prepare the support samples.

Long term stability and regeneration of the more sensitive formulations (response at or below ~1000 ppm CO in air) proved to be a problem for the new support material. The response color was more grey than blue (blue being the "normal" color) and regeneration would often not go to completion. Additionally, if sensitive formulations were left unexposed to carbon monoxide and in storage, they would auto-darken in one to four weeks in most cases. The off-color response and poor regeneration can be signs of reducing impurities in the support material; and although some of the samples were subjected to various cleaning procedures before impregnation, the presence of organic or metallic impurities appears to be the most likely explanation. Preparations of the detection catalyst on the new support with higher than normal copper content do appear to regenerate and store properly but they respond only to high levels of CO in air (>1%).

The presence of off-white samples of PTFE-entrained silica gel strips and strips containing what appear to be small metal particles or flakes have been noted. Abnormalities in the behavior of test batches of the detection catalyst both during and after impregnation appear to have some relationship to the presence of either particulate metal

impurities or the organic impurities assumed to be responsible for the off-white color of the support material. During impregnation by soaking, it was noted that in a number of cases support samples with particulate impurities would locally turn the impregnating solution from yellow to blue. This type of reaction has been noted before when the impregnating solution was put in contact with a number of different metals. It is likely that what occurs is reduction by the contact metal of the palladium and molybdenum in the acidic impregnating solution.

New samples of the PTFE-entrained silica gel support material and more extensive precleaning procedures will be used to reduce or eliminate the problems involving organic and metallic support impurities.

Extensive humidity tests have not as yet been conducted with detection catalyst prepared on the PTFE-entrained silica gel support. A few tests with support material containing 90% E. Merck type 100 silica gel were conducted at humidities of 30% and 80% RH and show a variation in response time of about 12% at 1000 ppm CO in air. The response curves are very similar at both levels of relative humidity. Further humidity tests with more sensitive formulations would be required before any definitive statement could be made about the stability towards humidity variations of catalyst prepared on the new support.

Overall the new support material seems to be the most impressive alternative to loose silica gel investigated to date. Results appear to indicate the PTFE-entrained silica gel support could offer sensitivities at or below 250 ppm CO in air, that reasonable humidity stability would result from the use of large pore silica gel (E. Merck type 100 or similar material), and that the mechanical properties are ideal for a wide variety of applications. The problems to be overcome appear to be involved with reducing the level of impurities in the new PTFE-entrained silica gel support.

Another possible form of the detection catalyst worth mentioning in this section is that of the PTFE/detection gel disc. Formed under pressure from a mixture of Teflon® powder and prepared detection gel, the disc is more delicate than the PTFE-entrained silica gel support material but less so than a TLC plate prepared with gypsum binder.

The idea of examining the disc format for the detection catalyst evolved from Teflon®-catalyst compatibility tests conducted during the PTFE-entrained silica gel experimentation. The compatibility tests were being run to insure that Teflon® was chemically inert with respect to detection catalyst, a point in question because of storage problems associated with detection catalyst prepared on the PTFE-entrained silica gel. Mixtures of prepared detection catalyst and Teflon® powder were to be stored in closed containers for several weeks to insure compatibility; and in an effort to assure intimate contact with the detection catalyst, a few samples were pressed into discs. None of the samples, including the discs, gave any visual indication of chemical interaction after periods as long as 8 weeks. The disc samples, being the easiest to handle, were subjected to a flow of pure carbon monoxide

to insure that the detection catalyst was still reactive. The samples did indeed respond to carbon monoxide, although most showed an inhomogeneous (mottled) appearance due to the high Teflon® content. Tests run at 1000 ppm CO in air also gave rise to response in most disc samples and regeneration occurred for the majority of samples responding.

The preparation of these PTFE/detection catalyst discs is outlined above in the "EXPERIMENTAL" section. It should be noted that the discs' response and regeneration characteristics depend on the amount of Teflon® used in the mixtures and the amount of pressure used to form them. If too much Teflon® is used, the tendency for the Teflon® to "cold flow" entirely around the catalyst particles weakens the response and regenerative properties of the discs. It is assumed that this is due to gas permeation (carbon monoxide and oxygen) difficulties. If too little Teflon® and/or pressure is used, the disc's mechanical strength is greatly reduced.

Both the PTFE-entrained silica gel and the PTFE/detection catalyst discs appear to warrant further study.

Humidity Related Detection Catalyst Experimentation

Humidity moderated response (threshold) changes were noted in early development of the detection catalyst. Since certain detection gels showed greater sensitivity to variations in humidity than did others, a search was made for factors which seemed to strongly influence the catalyst's behavior under conditions of varying humidity. On examining technical data available through the distributor of one commonly available brand of silica gel, it was found that the amount of water which a silica gel absorbs at a given temperature and relative humidity is a function of the mean pore diameter of the silica gel. Silica gel with a large mean pore diameter was shown to have a nearly constant water content over a broader range of relative humidity than silica gel with a small mean pore diameter. Tests involving a silica gel (E. Merck type 100) with a comparatively large mean pore diameter (100Å) were conducted and show fair consistency in response over a wide range of humidity. The results of this testing on "free-flowing" sorbent are discussed below. Additional relevant information can be found under the section titled "Water Content Measurements".

Tests involving response times at various concentrations of carbon monoxide at 98% RH, 30% RH, and under dry conditions were run to compare the silica gels. A sample of the data is recorded in Table 4. As can be seen from the data, there is a considerable range of response characteristics for the silica gels. It is important to note that while some of the gels showed increased and decreased response times on going from dry to humid conditions others showed little or no humidity variations. One of the silica gels in this series, Δ gel #3, was used in a few of the more closely studied formulations found in the previous report.¹ As is apparent from the data, this particular silica gel can show significant humidity variations.

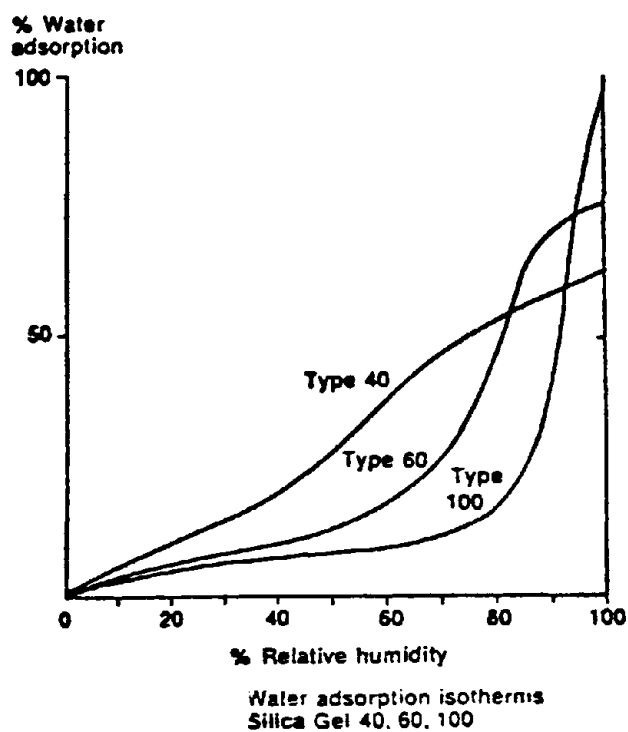
The results of the water content measurements done using the Δ gel series are suspect due to a lack of proper equipment. Some silica gels are capable of humidity equilibrating within seconds, so all accurate measurements must be done in an enclosed humidity chamber containing an analytical balance. However, even when the inaccuracy is allowed for, significant variations in both absolute water content at a given relative humidity and the way in which the water absorption isotherm varies from silica gel to silica gel appear to be present. Changes in relative humidity can exert a strong influence on detection gel response. This is likely to be due to a water related change in the gel, so a literature examination of water absorption data for silica gels was started. Some useful information was encountered in a product brochure put out by the E. Merck Company. A graph (see Figure 6) illustrated the relationship between the mean pore diameter of three silica gels and their water absorption isotherms. As the graph indicates, there is a marked difference in the water content of the gels as a function of relative humidity. There are, however, regions of relative humidity where little change in the water content occurs.

One proposal for minimizing humidity related response variations involved preparing a "high humidity" and a "low humidity" detection gel. The E. Merck Type 40 and Type 100 silica gels appeared well suited to this proposal. Type 40 shows only a slow water content change in the range of high humidities (70% RH to 95% RH) while Type 100 silica gel's water content remains virtually unchanged in the low to intermediate humidity range (10% RH to 70% RH). E. Merck Type 60 silica gel, with a mean pore diameter of 60Å, is the only one normally supplied as a chromatography sorbent. It had been the only one tested for suitability as a detection catalyst support. Samples of Type 40 and Type 100 silica gels (with mean pore diameters of 40Å and 100Å, respectively) were obtained and used in the formulation of test quantities of detection gels.

The results of some initial tests with the detection gel prepared on Type 100 silica gel are shown in Table 6. There is a striking stability in response time over the entire range of humidities examined. Even a test at 98% RH had a consistent response time. There may be no need to develop two detection gels for "high" and "low" humidity conditions. The Type 100 detection gel was found to respond to concentrations of CO in air below 200 ppm.

Humidity stability experiments with E. Merck type 100 silica gel were generally carried out at 30%, 50%, and 80% RH. Several additional tests were conducted at 98% RH, 90% RH, 15% RH, and under "dry" conditions.

There were some experiments in which either the detection threshold or the response time varied but for the most part the results were consistent from 80% RH down to 15% RH. Variations were generally less than 22% ($\pm 11\%$) in first response time throughout this range of relative humidities. The maximum deviation noted in first response time was 56% (8 minutes at 98% RH and 12.5 minutes at 15% RH; 500 ppm CO in air) for a detection catalyst that responded below 500 ppm CO in air.



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FIGURE 6

TABLE 6

Results of Initial Tests with "Type 100" Silica Based Detection Gel
(Silica Gel with ~100A Mean Pore Diameter)

Conditions (room temp. & 500 ppm CO)	t-initial (minutes)	t-final (minutes)
Dry	9:38	27:--
30 % RH	3:00	20:--
80 % RH	2:20	18:--
95 % RH	3:33	20:--
Dry	5:00	24:--
Dry	3:00	22:--

The maximum deviation noted for detection threshold was 33% (~500 ppm CO in air under dry conditions and ~375 ppm CO in air at 98% RH). When type 100 silica gel was employed it was noted that if deviations occurred, they generally occurred towards higher detection threshold and/or longer response time at lower relative humidities (dry or nearly dry conditions). Long exposure (>24 hours) to humidities above 80% RH did delay response and/or raise the detection threshold in a few cases.

A range of typical response times for a variety of type 100 detection gels is given for reference purposes:

Carbon Monoxide Level (in air)	500 ppm	300 ppm	100 ppm ^a
first response time	4-13 minutes	10-21 minutes	24-33 minutes
final response time	12-28 minutes	14-36 minutes	32-45+ minutes

^aresponse weak - difficult to prepare this sensitive
a catalyst with Type 100 silica gel.

Interferent Gases; Protection of the Detection Catalyst

The detection gel's response to carbon monoxide was found to be adversely affected by five gaseous interferents; hydrogen sulfide, nitrogen dioxide, ammonia, acetylene, and methylacetylene. (see Table 7). The results of tests involving the interferent gases, the behavior of the detection catalyst in their presence, and methodology for protecting the detection catalyst from their effects follows.

Earlier work¹⁶ had suggested that the detection catalyst might be susceptible to interference by inorganic and organic reducing agents and compounds which directly interact with catalyst components.

Gases known to be present at times in mine environments were screened for possible incompatibility with the detection catalyst. Included were acetylene, ammonia, carbon dioxide, ethylene, hydrogen sulfide, methane, methylacetylene, nitric oxide, nitrogen dioxide, and sulfur dioxide.

Hydrogen sulfide (H₂S) reacts rapidly with the detection gel, yielding a blue-gray to dark brown gel which does not regenerate completely. The darkening renders the gel useless for the detection of carbon monoxide. The color change is most likely due to a reduction of one or more of the metal salts present and/or the conversion of the metals into sulfide forms. Reduction of palladium (II) to the metal and molybdenum (VI) to "molybdenum blue" is possible as is the formation of a number of metal sulfides such as PdS and MoS₃.¹⁷

Nitrogen dioxide (NO₂) appears to function as a competitive inhibitor of carbon monoxide, blocking the detection gel's response to CO at concentrations as low as ~5 ppm in air but within minutes of removal from the gas stream the gel returns to its normal response.

TABLE 7

The Effects of Some Interferent Gases on a CO Detection Gel

Interferent	Concentration* (ppm in air)	Test Conditions**	Observed Response
1. Acetylene (C ₂ H ₂)	100	Static (dry)	Normal Response ^a
	200	Dynamic (wet & dry)	Slight darkening of the detection gel without CO present.
2. Ammonia (NH ₃)	~2	Dynamic (dry)	Normal Response ^a
	50	Dynamic (dry)	Faded response with CO present
3. Carbon Dioxide (CO ₂)	2000	Dynamic (dry)	Normal Response ^a
4. Ethylene (C ₂ H ₄)	225	Dynamic (dry)	Normal Response ^a
5. Hydrogen Sulfide (H ₂ S)	~5	Dynamic (wet & dry)	Slight discoloration w/o CO present, incomplete regeneration.
	12	Dynamic	Gel turned blue-grey w/o CO present, incomplete regeneration.
6. Methane (CH ₄)	50,000 (5%)	Dynamic (dry)	Normal Response ^a
7. Methylacetylene (C ₃ H ₄)	200	Dynamic (dry)	Slight darkening of the detection gel without CO present.

-Continued-

TABLE 7

-Continued-

The Effects of Some Interferent Gases on a CO Detection Gel

Interferent	Concentration* (ppm in air)	Test Conditions**	Observed Response
8. Nitric Oxide (NO)	15	Dynamic (wet & dry)	Washed out final response color when CO is present.
9. Nitrogen Dioxide (NO ₂)	~3	Dynamic (dry)	Pale response with CO present.
	~5	Dynamic (dry)	Inhibited response to CO.
	10	Dynamic (wet & dry)	"Totally" inhibited response to CO; removal of NO ₂ during test allowed normal detection gel response to CO.
10. Sulfur Dioxide (SO ₂)	~17	Dynamic (wet)	Normal Response ^α
	40	Dynamic (dry)	Normal Response ^α
	100	Static (dry)	Normal Response ^α

Note: All tests employed Gel 1-4 at 22°C & [CO] ~500ppm in air.

* Concentration values given are approximate (generally ±20%).

** Dynamic tests were done with a total flow of gases of ~1.0 liter/min.

Static tests were done in a serum bottle (~1000cc).

Dry ↔ ≤10% R.H.

Wet ↔ ~80% R.H.

^α Normal response for the detection gel is a change in color from yellow to blue within 10 minutes when CO is present; and regeneration from blue to yellow within 16 hours after CO is "removed".

Nitrogen dioxide can react with copper (under special conditions)¹⁸ but the detection gel's behavior in its presence would indicate an association with palladium or molybdenum sites. In fact, an easily reversed association of NO_2 with palladium is known¹⁹ and would account for the behavior of the detection gel in the presence of the gas.

Nitric oxide (NO), another tested interferent, does tend to have a washing out effect on the detection gel's response color, but this is likely to be due to the presence of small amounts of NO_2 formed from the facile reaction of nitric oxide with oxygen.¹⁰

Acetylene (C_2H_2) interferes with the detection gel's function beginning around 200 ppm in air, a concentration unlikely to be encountered in normal mine operations. It is probable that the interaction of acetylene occurs with the palladium, even though interactions are also known for copper and molybdenum. The well-known "Wacker Process" involves both palladium (II) and copper (II) in the oxidation of olefins²¹ and such interactions are likely with the detection gel. The detection gel can be recovered, if exposed to acetylene, by heating to $\sim 80^\circ\text{C}$ under humid conditions. The acetylene is probably oxidized and lost at the higher temperature, since this is known to occur with propylene.²²

Methylacetylene (C_3H_4) reacts more slowly with the detection catalyst than does acetylene but can cause interference and darkening of the catalyst when present above concentrations of ~ 200 to 250 ppm in air. The reaction with the detection catalyst appears to be reversed when the catalyst is gently heated in moist air or oxygen.

Ammonia (NH_3), when present in concentrations above 1.0% in air, can nearly decolorize the detection catalyst and render it unsuitable as a carbon monoxide indicator. Tests run at ~ 50 ppm NH_3 in air showed a significant reduction in color intensity, especially if ammonia exposure had been in progress for a considerable period of time prior to introduction of carbon monoxide to the gas stream. At levels of ~ 1 to 3 ppm NH_3 in air, no significant response variations were observed.

Methodology for protecting the detection catalyst from interferents was investigated. Of prominent importance was to maintain "near-normal" response to carbon monoxide while decreasing or eliminating the interferent's effect on the detection catalyst.

Several approaches to the problem of protecting the detection gel from interferent gases have been explored. They involve the use of chemical compounds known to react with the interferent gas but not with carbon monoxide. The approaches include the direct addition of protection agents both homogeneously and heterogeneously, and the use of these agents as gas filters, first in their powdered or granular form, and second in the form of impregnated cloth or paper filters soaked in aqueous solutions of protection agents.

Direct addition of such compounds was tried two ways: adding a soluble "adsorbent" compound during the detection gel preparation, or intimately mixing the substance with a completely prepared and dried detection gel. Direct mixtures of powdered zinc oxide, sodium bicarbonate, lead acetate and other similar materials with the detection catalyst were found to be inadequate protection against interferents. Similar tests in which powdered "protectants" were mixed with the binding agent used to prepare thin layer chromatography (TLC) plates (which were subsequently impregnated with a solution of detection catalyst components) showed more uniform but still incomplete protection against hydrogen sulfide and nitrogen dioxide. Both the homogeneous and heterogeneous addition of adsorbent compounds failed to completely protect the detection gel from the effects of hydrogen sulfide or nitrogen dioxide.

Protection of the detection gel through the use of an encapsulating device or "badge" was then attempted. Several such devices employing filter compartments for interferent gas adsorbents are described in a previous report.¹ This approach does effectively protect the detection gels from interferents but suffers from a delay in response to carbon monoxide and slow regeneration times for the gels.

External filters placed in especially constructed badges were examined for use as selective "gas adsorbents". The three approaches to this concept involved direct placement of a powdered adsorbent in the path of gaseous molecules moving towards the detection catalyst, the use of filter paper impregnated with adsorbents, and the use of charcoal "cloth" impregnated with sodium bicarbonate. Current tests have shown that combinations of zinc oxide and Mallcosorb (a commercial acid-gas adsorbent) along with charcoal cloth are sufficient to protect the detection gel from at least 20 ppm hydrogen sulfide, 15 ppm nitrogen dioxide, and 250 ppm acetylene (for short periods of time). An experiment in which the charcoal cloth filter was soaked in solutions of various acid-gas adsorbents at concentrations of 0.05M to 1.00M was carried out. The treated filter could be used in the filter compartment of the detection catalyst badge and did allow more rapid carbon monoxide permeation and response by the catalyst.

The badge found to offer the least deviation from non-enclosed response times was one with a flow-thru design in which filters could be placed both in front of and behind a thin layer of detection catalyst. It was this type of badge that was used in the majority of interferent tests that included a protective filter or agent.

The direct use of powdered and granular adsorbents did afford a great deal of protection to the detection catalyst from interferents, but when used in sufficient amount to provide this protection, the response to carbon monoxide was delayed or impaired. Using adsorbent impregnated filter paper and charcoal "cloth" was satisfactory in terms of carbon monoxide response time and appeared to function properly as interferent adsorbents. The charcoal "cloth" showed the best results in that it was effective against hydrogen sulfide, nitrogen dioxide, and acetylene. Although none of the filter arrangements appeared to

completely negate the effects of 50 ppm NH_3 , the sodium bicarbonate impregnated charcoal "cloth" did seem to alleviate its bleaching effects.

Measurements to Elucidate the Detection Catalyst's Chemical Mechanism

At the recommendation of the U.S.B.M. technical supervisor for the project, additional work in the understanding of the mechanistic properties of the catalyst was initiated.

Spectral Analysis: One logical approach to understanding the mechanism by which the detection gel acts is to look for likely intermediates spectrophotometrically. Visible and infrared (IR) spectroscopy were suggested as plausible techniques for this task. Visible spectroscopy was suggested due to the detection gel's color change from yellow to blue upon interaction with carbon monoxide. It was believed that the spectral changes might reflect changes in the oxidation state and/or ligand environment of the transition metals present in the detection gel. IR spectroscopy was logically chosen because carbon monoxide is oxidized to carbon dioxide in the presence of the detection catalyst. If detectable quantities of metal carbonyls were formed during the interaction they might be identified by their characteristic IR absorption bands.

1. Visible Spectroscopy: Attempts to obtain visible absorbance spectra for the detection gel failed to give decisive results, despite repeated efforts. The difficulties were chiefly experimental in nature. Silica gel, used as the catalyst support, disperses incident light too widely to obtain absorption spectra. Even if an absorption spectrum could have been obtained for the yellow detection gel it is doubtful that one could have been recorded for the reacted "blue state" due to its intense light absorptivity.

The second approach to acquiring visible spectra was rinsing a small quantity of detection gel with water and using the filtrate for normal solution absorption spectroscopy. A spectrum was obtained for the yellow form of the catalyst in this manner. The yellow filtrate shows an absorbance maximum at ~400 nm. "Reduction" of the catalyst with carbon monoxide followed by rinsing failed to give a "blue" solution suitable for absorption spectroscopy.

Another more recent approach employed a catalyst impregnating solution (metal salts, acid, and water) made with silico-molybdic acid in place of ammonium molybdate. The visible spectrum of this yellow solution shows an absorbance maximum at ~400 nm, similar to the one mentioned above. Reduction of the solution using carbon monoxide, sodium borohydride, or dithionite produced an intensely absorbing unstable blue solution. The solution quickly forms a colloidal precipitate and changes in color towards a greyish-blue. When the colloidal suspension is present in low concentration a spectrum cannot be obtained. Filtering the solution or diluting it carefully to a pale blue does allow a crude spectrum to be recorded, if done quickly.²³ When properly

recorded, the blue solution's spectrum exhibits a broad maximum at approximately 750 nm.

Results of the experiments described above are somewhat limited, but chemically reasonable explanations do exist for most of the spectral features. The absorbance spectra of the yellow solutions obtained from the special impregnating solution or as a result of rinsing a prepared detection gel bear a close resemblance to the solution spectrum of palladous ion (Pd^{+2}). The molar absorptivity at 400 nm is $\sim 200 \text{ M}^{-1} \text{ cm}^{-1}$, reasonable for a "d-d" transition and close to that found for palladous ion. The colloidal precipitate formed upon reduction of the impregnating solution is most likely due to elemental palladium being formed. Reduction of a palladous chloride solution gave similar results. The "blue" color of both the solution and the detection gel is probably due to the formation of reduced heteropoly-molybdates which are closely related to "molybdenum blue" species. A recent report²⁴ of the reaction of molybdenum trioxide on hydrated silica shows a "broad absorption band at λ ca. 700 nm", which is similar to that found for the reduced impregnating solution. The visible spectra for reduced heteropoly-molybdates (such as silico-molybdic acid) have long been attributed to intervalence charge transfer bands.²⁵ Their presence would account for the high molar absorptivity exhibited by the "blue" solution and detection gel.

2. Infrared Spectroscopy: The use of infrared to directly examine the course of the catalyst's reaction with carbon monoxide has proved fruitless. As in the case of visible spectroscopy, the use of silica bound catalyst led to too great a dispersion of the incident energy in the infrared spectrophotometer. Even the use of the gel's particles failed to give a meaningful spectrum.

The demonstration of the presence of metal carbonyls in the detection gel's interaction with carbon monoxide would be of great significance in mechanistic research. The highly distinctive infrared absorption bands of metal carbonyls should give insight into the nature and strength of the metal-CO interaction. It is hoped that a way will be found to record infrared spectra of the detection gel in the near future.

Mechanistic Information from Gas Chromatography: The rates of carbon monoxide uptake and release of carbon dioxide by the catalyst were measured using gas chromatography (G.C.). Highly oxidizing formulations were used in place of standard detection gel formulations. Oxidizing gels are similar to detecting gels but they employ higher metal salt concentrations and oxidize carbon monoxide much faster. The low sensitivity of the G.C. necessitated the use of high carbon monoxide concentrations. Detection gel formulations were incapable of oxidizing the high levels of CO at a reasonable rate.

The experiments were carried out using 1.0 gram of catalyst in a 38 ml serum vial. Pure carbon monoxide was introduced at "t=0" using a syringe. Samples (0.25 ml) of headspace gas were taken at 30 second intervals for the first 5.0 minutes and at 2.0 minute intervals thereafter. The samples were then injected into the G.C. and the amounts of carbon monoxide, carbon dioxide, and oxygen were determined.

Three oxidizing gel formulations were used in the experiments; and although their rates varied considerably, the same qualitative pattern emerged for all:

- a. The decrease in CO concentration is rapid and reasonably constant until the CO level drops to between 0.25 and 0.10 of the initial concentration (~15% CO in air). Under normal conditions the CO level is reduced to less than 5% of its original value in less than 5 minutes.
- b. The increase in the amount of CO₂ present over the catalyst is directly related to the decrease in CO concentration, with no apparent lag in time.
- c. The rate at which O₂ is taken up by the catalyst is slow compared with the rate at which CO is oxidized by it, normally taking over 20 minutes to reach ~95% of the theoretical value.
- d. When CO in nitrogen is used in place of CO in air, the rate of CO decline and CO₂ release is nearly as rapid as when oxygen is present.

The catalyst's color change from yellow-green to blue seems to be closely associated with the rate of CO decline, while the rate of reversal (regeneration) appears more closely associated with the rate of oxygen uptake. Results of the experiments with no oxygen present show that the catalyst initially supplies the oxygen necessary in the oxidation of carbon monoxide to carbon dioxide.

After the modifications to the gas chromatograph were completed (see "Experimental" section), several kinetic parameters of the **detection catalyst** (as opposed to the **oxidation catalyst** just discussed) were examined by gas chromatography in an attempt to more fully understand its functioning. This endeavor proved to be rather difficult both from the standpoint of experimental design and due to the complexity of the detection catalyst system. A portion of the data has been examined in the light of previous work and interpreted with respect to what is believed to occur chemically in the detection catalyst. Most experimental data was collected using a gas chromatograph equipped with the modified flame ionization detector (FID) described above in the "EXPERIMENTAL" section.

The results of tests done with the modified gas chromatograph agree with those of similar tests done earlier with the less sensitive thermal conductivity detector. With highly oxidizing catalyst and ~15% concentration of CO in air, there is a rapid and nearly constant rate of decrease of CO, followed by a gentle slowing of the rate of decrease as the absolute level of CO in air falls below 2%. No sharp breaks in the rate of decrease of carbon monoxide were observed and a good portion of the data appeared to fit reasonably well to a rate equation with a first order dependence on carbon monoxide.

When detection catalyst is used and the initial level of CO is ~15% in air, the pattern observed is generally one of rapid initial decrease, but the decrease nearly ceases within a few minutes at most. Once the rate of CO decrease has fallen off there remains a slow but discernible decrease in the concentration of CO which continues over a long period of time.

The actual times and rates varied among the detection catalysts tested. One discernible trend proved to be the correlation between the regeneration rate of the catalyst and the rate of decline of CO after the break-point of initial rapid decrease. The time it took to reach the break-point in decline also showed some correlation to the time it took for the detection catalyst to show a visual color change (slow visual response often concurred with a late break-point), but this was not as clearly defined as it had been when oxidation catalyst was used. The CO concentration at which the break-point occurred was also dependent on the amount of detection catalyst used in the test. A schematic on the appearance of raw kinetic data is shown in Figure 7.

An explanation for the observed data is that the initial rate of reduction of CO represents a CO binding or CO oxidation process and that after all readily accessible binding sites are "filled" or after the system is reduced to a certain level, a secondary process becomes rate determining. The second "apparent" rate could be CO oxidation and release from the binding site as CO₂ or the reoxidation of the system by a copper catalyzed reaction. In light of data obtained with the highly oxidizing catalyst which shows little or no delay between reduction in CO level and an equivalent increase in CO₂ level, the secondary process would more likely be associated with system reoxidation.

Experiments at low levels of CO were hampered by slow leaks in the reaction containers and high background noise during measurements on the gas chromatograph. No sharp changes in the rate of CO decline were noted when initial levels of CO were 5000 ppm and 1000 ppm in air. The decrease did not appear to be completely linear initially and measurements of CO level beyond the first 15 to 20 minutes were too unreliable to use.

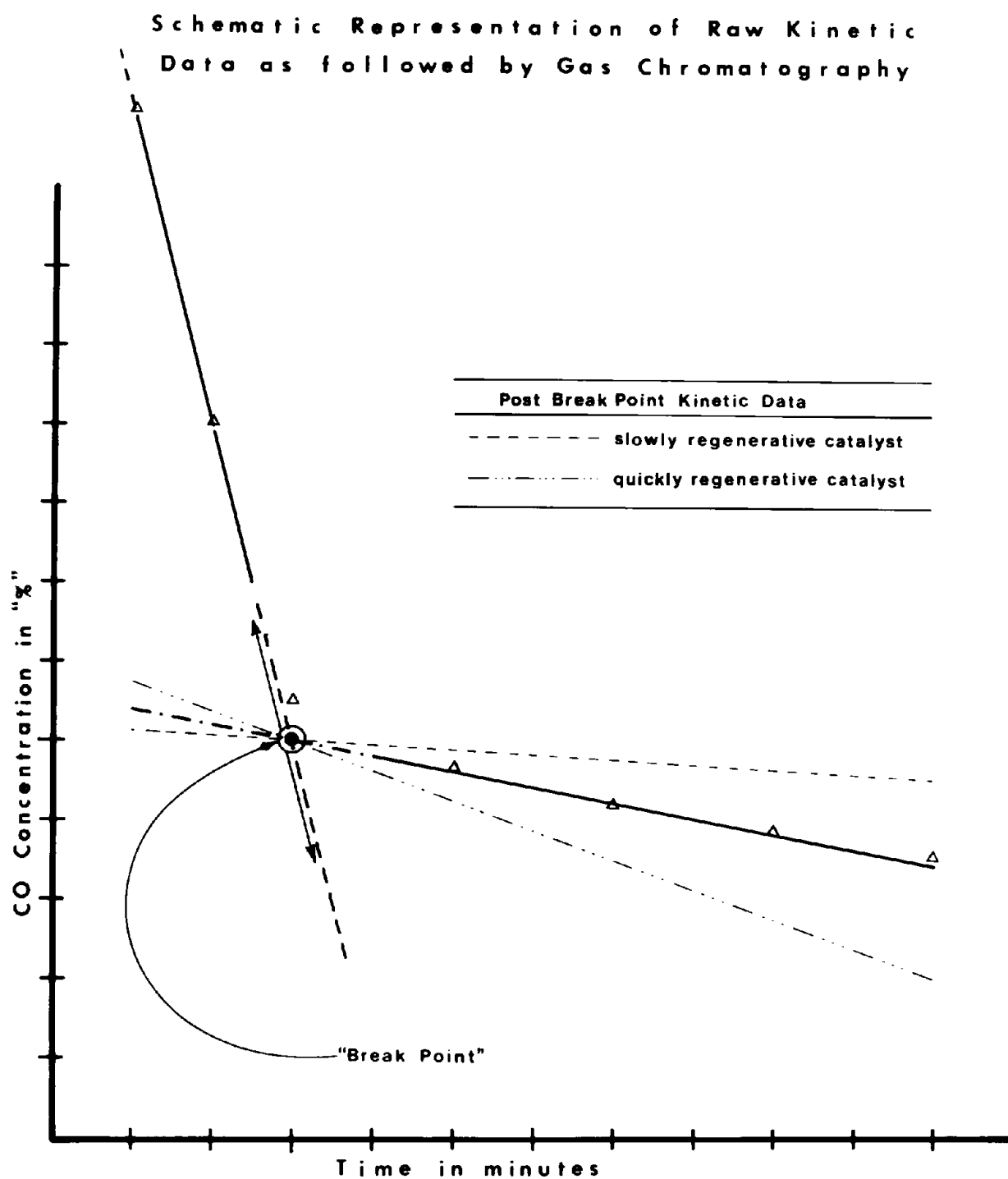


FIGURE 7

Materials To Be Used in Producing the Detection Gel

The preparation of the normal silica gel based detection gel had previously been carried out using commercially available reagents that had not undergone any formal suitability tests. Preparing a detection gel involves the use of silica gel, cupric chloride, palladium sulfate, ammonium molybdate, sulfuric acid, hydrochloric acid, hydrogen peroxide, and water. The results of some investigations dealing with these reagents are reported here.

Glass distilled water is normally used in preparing detection gel, but deionized water ($10^{-6}\Omega$) has also been found suitable. No difficulties were presented by the use of reagent grade cupric chloride, ammonium molybdate, hydrogen peroxide, and acids obtained from various suppliers. The source of palladium sulfate and the type of silica gel used were found to have profound effects on the detection gel's properties.

The silica gel must be a highly purified grade (most "Chromatography Grade" silicas are sufficient). Lower purity silica gels often contain reducing impurities (often organic) which were found to interfere with the function of the detection catalyst and are difficult to remove after preparation. The average particle size of the silica gel should be around 0.3 mm (~59 mesh ASTM) as a practical consideration of future encapsulation. Trace metal contamination should be as low as possible, preferably below 0.01% for most transition metals. Particular attention should be paid to the amount of copper present. Levels as high as 0.10% have been found listed on lot analysis of chromatography grade silica gels. Copper, an important ingredient of the catalyst, is rarely added in concentrations above 0.10% and so even small amounts of contaminant copper can cause problems. Current studies indicate that the mean pore diameter of the silica gel should also be considered.

The palladium sulfate used should be free from chloride and highly water soluble. Previously, palladium sulfate had been obtained from Research Inorganic Chemicals, Inc. as a 10% aqueous solution. During the contract period it became necessary for this laboratory to produce palladium sulfate directly from high purity palladium metal for economic reasons. A comparison of the visible spectrum of the "home-made" solution to that of some recently purchased commercial solution revealed some disturbing differences. The commercial preparation was shown to be contaminated with chloride (halide) through further spectral and chemical (silver nitrate) testing. Similar tests using the laboratory prepared solution showed it to be free of chloride. Empirical tests using detection gels prepared with palladous chloride in place of palladous sulfate have shown improper color response on interaction with carbon monoxide and very poor regeneration properties.²⁶ Problems with solid palladium sulfate obtained from Alfa-Ventron have also been experienced. It is suggested that the palladium sulfate for the detection catalyst be prepared directly from the metal to insure purity. Additional experiments involving the replacement of cupric chloride with

cupric sulfate and ammonium molybdate with silico-molybdic acid were carried out. The use of silico-molybdic acid was found to improve response colors and slightly decrease the response time of normal detection gel. A gel prepared using cupric sulfate fared worse in response and regeneration than those with cupric chloride.

The molybdenum, copper, and palladium contents of three prepared detection gels were analyzed by atomic absorption spectroscopy. There were only minor inconsistencies between the amounts of metal added in preparation and the amounts found in the analyses.

SUMMARY AND CONCLUSIONS

Changes made in the equipment used to prepare and test the detection gels greatly facilitated this work. The installation of photocell detectors in the test chamber also allowed semi-quantitative measurement of response characteristics. A modification of an FID equipped Hewlett-Packard 700 gas chromatograph was carried out to allow the detection of small amounts of carbon monoxide (through conversion to methane). New equipment was acquired for the preparation and handling of custom TLC plates. Standard techniques were employed in preparing the new TLC plates.

Interferent gases were found to include the following: hydrogen sulfide (~5ppm); nitrogen dioxide (~3ppm); acetylene and methylacetylene (~175-200ppm); and ammonia (~35-45ppm after extended exposure). The study of the effects of interferent gases has shown hydrogen sulfide, nitrogen dioxide, and ammonia to be the only gases to pose a serious threat to the proper response of the detection gels. Their removal from the gas stream can be affected through the use of simple chemical adsorbents. The most practical protection against the majority of interferent gases was provided by "charcoal cloth" impregnated with 0.2M sodium bicarbonate. The carrier badge configuration found to impede the detection process the least was a flow-thru design with interferent filter material on both sides of the detection catalyst.

Component concentration studies have revealed the (approximate) optimum molar ratios for the metal salts used in the detection gel's preparation. Palladium was shown to be necessary for the detection of carbon monoxide by the gel. Molybdenum's presence serves to improve response colors and aid in the regeneration of the catalyst. The absence of copper severely reduced the detection gel's capacity for self-regeneration. The way in which the detection gel's acid content affects its response is currently being investigated. Additional studies involving component-ratios and catalyst loading appear to be necessary.

A test series involving eight different silica gels has shown that the silica used greatly affects the response characteristics of the detection gel. Differences in physical characteristics, impurity levels, and water content are felt to be responsible for most of the response variations. Two additional silica gels, with unusual mean pore diameters and published water absorption isotherms, were tested as

catalyst supports. One of these gels, with a mean pore diameter of 100Å, behaved with remarkable consistency over a wide range of relative humidities. It responds to carbon monoxide concentrations as low as 200 ppm in air.

Humidity was found to exert a small but noticeable influence on detection catalyst prepared on E. Merck type 100 silica gel. In the range of 15% RH to 80% RH the deviations in first response time were less than 22% for the majority of type 100 detection catalysts tested. This amounts to a deviation of about ± 1 minute in 1st response time for a detection catalyst that responds with an average time of 9 minutes.

Spectral analyses aimed at elucidating the detection gel's mechanism have been only marginally useful. The blue color attained by the detection gel after exposure to carbon monoxide appears to be due to reduced silico-molybdic acid (a heteropoly-molybdate). Investigations using infrared spectroscopy, which could yield key mechanistic information, have been thwarted so far by technical difficulties.

Examining the pH dependence of the detection catalyst revealed a trade-off of sensitivity for regenerative ability in varying the pH from low values (~ 1 pH unit) to high values (~ 4 pH unit). For most purposes, a range of 1.5 to 3.5 pH units should be adhered to.

Gas Chromatography has been used to measure the rate of disappearance of carbon monoxide and oxygen, and the rate of formation of carbon dioxide above the catalyst. An **oxidizing catalyst**, chemically very similar to the detection gel, was first employed in the experiments. It was demonstrated that carbon monoxide was initially oxidized by the catalyst much faster than oxygen was taken up. This suggests that the oxygen necessary in the oxidation of carbon monoxide is initially supplied by the catalyst. The uptake of atmospheric oxygen appears to be connected mainly with the catalyst's regenerative properties. The color change from yellow-green to blue correlated with the disappearance of CO while the regeneration from blue to yellow-green followed the uptake of oxygen. Some carbon monoxide was oxidized to carbon dioxide even when oxygen was excluded from the reaction vial but the catalyst failed to regenerate under these conditions.

Kinetic examination of the **detection catalyst's** reaction with CO followed the preliminary work with oxidizing catalysts. It was carried out using a modified gas chromatograph with a flame ionization detector. When high initial levels (15%) of carbon monoxide were used the rate of decline of CO appeared to undergo an abrupt change after only a brief period of exposure. The possibility of a CO binding capacity or reduction capacity for the catalytic system is felt to be the most likely explanation of the sharp reduction in rate. No sharp changes in rate of CO decline were seen when highly oxidizing catalyst was tested or when initial levels of carbon monoxide were low (5000 ppm and 1000 ppm in air). Further modification of the gas chromatograph may allow more information to be obtained at low initial CO levels.

Experiments in which alumina, cellulose, and other chromatography supports were substituted for silica showed only a few weakly positive results. The detection catalyst prepared on supports which did not contain silica would only respond to carbon monoxide when silicomolybdic acid was used in the impregnating solution. Treated alumina and silica gel thin layer chromatography plates could detect carbon monoxide at concentrations below 1000 ppm. The response rate is fast and the regeneration rate is very good for the silica T.L.C. plate supported catalyst, but the colors are pale compared with the standard detection gel. Preparation and handling were considerably easier with the T.L.C. supports. Drawbacks were found to be auto-reduction if organic binders were used and mechanical instability if calcium sulfate was employed to bind the silica gel to the backing material. If the proper binding agents can be found or formulated, TLC plates would be well suited for use as detection catalyst supports.

A promising method of detection catalyst support is the use of PTFE-entrained silica gel. This material, theoretically consisting of only polytetrafluoroethylene and silica gel, offers desirable mechanical and physical properties (moderate strength, high gas permeability, and facile size and shape modification) and can be prepared with relatively humidity insensitive silica gel. Sensitivity to CO below 500 ppm in air has already been obtained with detection catalyst prepared on this support. Difficulties with detection catalyst auto-reduction on storage occurred with this support. Pressure produced PTFE/detection catalyst discs may offer some of the advantages of the PTFE-entrained silica gel and do not appear to undergo auto-reduction on storage.

Should the auto-reduction problem be found to result from a removable impurity in the PTFE-entrained silica gel; it would be the support of choice for the detection catalyst.

Most constituents of the detection gel were found to be suitable as the commercially available reagent grade chemical. As previously mentioned, appropriate silica gels were found in the commercial market, but purity and physical characteristics had to be closely screened. Two commercial sources of palladium sulfate were found to be unsuitable. It is currently prepared in the laboratory from palladium metal.

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11. At present, of the factors known to affect a detection gel's water content, the most prominent is the silica gel used to prepare it.
12. This does not mean that the response of a particular detection gel formulation fails to correlate with water content.
13. Dr. Chilton (U.S.B.M.) is the technical advisor for the project.
14. Unpublished results, this laboratory. In 1973 a number of these supports (alumina, magnesium oxide, etc.) were examined. They were abandoned shortly afterward when it became apparent that silica actually plays a chemical role in the detection gel's response mechanism.
15. The use of silicomolybdic acid in place of ammonium molybdate was found to be necessary with all supports except silica gel. In the case of silica gel T.L.C. plates, the use of silicomolybdic acid improved their performance. See the "EXPERIMENTAL" section in this report.

16. a. The presence of an off yellow color in the detection gel is an indicator of interference. Colors such as gray, brown, or blue-gray often occur when an interferent has poisoned the detection catalyst.
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26. The contaminated palladium sulfate might explain some recent problems with catalyst regeneration experienced at the U.S. Bureau of Mines Experimental Station, Pittsburgh.
27. Teflon is a registered trademark of the E. I. DuPont de Nemours Company. The use of the trade name is only for the purpose of clarity; please see the note on the inside of the front cover.

