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ARLI Report No. 3006-S

DEVELOPMENT OF SPACECRAFT TOXIC GAS REMOVAL AGENTS

December 1974

ANALYTICAL RESEARCH LABORATORIES, INC.
160 Taylor Street
Monrovia, California 91016

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December 1974

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APPROVED:

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ABSTRACT

Spacecraft air purification media used in past missions have exhibited less than optimum performance in the management of CO, NH_3, NO_2, and SO_2. With emphasis on the first two toxic agents, the present effort was directed to the development of agents suitable for the removal of these toxic gases and, hopefully, other spacecraft contaminants. An extensive technology review was conducted, yielding a large number of potentially useful materials and/or concepts. Because the two toxic gases of greatest interest, CO and NH_3, suggested the use of catalysis principals, emphasis was placed on the investigation of transition metals on various supports. A number of other material types should, however, be investigated.

Forty-three materials were prepared or obtained and 25 put into test evaluation. Using gas chromatographic techniques, seven candidates were found that effectively managed various combinations of the 4 toxic gases; none managed all. The materials so identified included 6 transition-metal containing preparations and a supported LiOH material. Three commercial charcoals showed some efficacy for the toxic gases and may constitute candidates for enhancement by doping with transition metals.

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RESULTS

Of the 25 candidate agents test evaluated on the present program, 15 were found to be inadequate for the management of any of the four toxic gases of interest - - CO, NH_3, NO_2, and SO_2. The remaining 10 candidates showed various efficacies for one or more (but not all) of the toxic gases. Two of the transition-metal containing agents converted CO to CO_2. This effect was quantitative for only one of the two agents, a commercial product, Purafil, offered by the company of the same name. Three other of the 10 candidates exhibited some retention for CO. The best retention, probably involving chemisorption, was on Ni-doped charcoal; this agent's capacity may require optimization. One of the CO-retaining materials was a commercial charcoal, Nuchar WVL. Performance, however, was marginal.

Six of the candidate agents were effective in managing NH_3. Four operated by adsorptive mechanisms, the other two by chemical conversion processes. In the first category, two agents containing transition metals performed impressively, while the other two materials, both commercial charcoals, were considerably less effective. The two materials that converted NH_3 (to unknown products) required elevated temperature (150°C) in order to produce quantitative results. These agents were Purafil and a permanganated silica gel.

The last two agents cited were also effective in converting NO_2 quantitatively, again to unknown products and at elevated temperature (150°C). The only other agent effective for NO_2 management was Barnebey-Cheney VG charcoal, but retention was marginal.

Sulfur dioxide was reversibly retained by only two agents, the superior of the two being LiOH supported on charcoal. One undoped charcoal, Nuchar WVG, retained SO_2 but not adequately.

In Table 1, the performance of the 7 doped materials and 3 commercial charcoals that were found to be variously effective are itemized. The data pertain to test conditions involving a 10 to 15 cm bed thickness, slug addition of the contaminant gas, and gas velocities, within the packed bed, of about 10 cm/sec.

TABLE 1. PERFORMANCE SUMMARY OF EFFECTIVE MATERIALS

Removal Agent	Contaminant Removed	Temp.	% Conversion or Adsorption	Retention Time	Species Eluted	Suspected Operating Mechanism	Process Regenerable
2% Re on AC charcoal	CO	390°C	~7% Conversion	-	CO_2 & CO confirmed	Catalytic	unknown
60% $NiCl_2$ on AC charcoal	CO	Room	30% Adsorption	>36 min (adsorbed portion)	CO confirmed	Chemisorptive	unknown
70% $NiCl_2$ Exchanged 13X Mole Sieve	(a) CO	Room	100% Adsorption for CO≤ 0.02%	2 min on fresh column	not identified	Adsorptive	yes
	(b) NH_3	230°C	100%	hours	NH_3 confirmed	Adsorptive	yes
3% Permanganated alumina (Purafil)	(a) CO	150°C	100% Conversion	-	CO_2 confirmed	Chemical Conversion	unknown
	(b) NH_3	150°C	100% Conversion	-	Unidentified & NH_3 absent	"	unknown
	(c) NO_2	150°C	100% Conversion	-	Unidentified & NO_2 absent	"	unknown
3% Permanganated Silica gel	(a) (CO ?)	150°C	None at ≥1% levels. Unknown at lower levels	-	CO confirmed	-	-
	(b) NH_3	150°C	100% Conversion	-	Unknown & NH_3 absent	Chemical Conversion	unknown
	(c) NO_2	150°C	100% Conversion	-	Unknown & NO_2 absent	Chemical Conversion	unknown

TABLE 1. PERFORMANCE SUMMARY OF EFFECTIVE MATERIALS

Removal Agent	TG Contaminant Removed	Temp.	% Conversion or Adsorption	Retention Time	Species Eluted	Suspected Operating Mechanism	Process Regenerability
SK500 Mixed $RE_2^*O_3$ Exchanged Mole Sieve	NH_3	Room	100% Adsorption	Hours for fresh column	-	Adsorption	yes
	"	263°C	100% Adsorption	Hours for fresh column 3.75 min. for equilabrated column	NH_3 indicated via titration	Adsorptive	yes
10% LiOH on AC charcoal	SO_2	Room	100% Adsorption	54 min for fresh column; 10 min for equilibrated column	SO_2	Chemical Conversion	yes
Nuchar WVL**	CO	Room		0.3 min	unknown	Adsorptive	yes
Nuchar WVG**	NH_3	190°C	100% Adsorption	>10 min	"	"	"
	SO_2	190°C	"	0.2 min	"	"	"
Barnebey-Cheney VG**	NH_3	Room	"	>35 min	"	"	"
	NO_2	Room	"	2 min	"	"	"

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*RE = Rare Earth

**Candidates for possible enhancement by doping.

CONCLUSIONS

1. Barnebey-Cheney AC charcoal, which has been used as a toxic gas removal agent in Apollo, Skylab and other missions, is less than optimum for the management of CO, NH_3, SO_2 and NO_2. It is, however, the best all around charcoal adsorbent. Three other charcoals have unexpected capacities for CO, NH_3, SO_2, and NO_2. These are Westvaco's Nuchar WVL for CO and Nuchar WVG for NH_3 and SO_2 and Barnebey-Cheney's VG for NH_3 and NO_2. This does not mean that these charcoals should replace AC, but they should definitely be considered for doping with selected agents for the specific toxic gases for which they have shown superior adsorption.

2. The use of transition metals on three different types of substrates definitely results in efficacious systems for the management of various of the contaminants studied. In conclusions No. 3 through 7, these systems are individually considered.

3. Chemical conversions of CO, NH_3 and NO_2 to innocuous effluents or irreversibly retained species can be achieved at an apparent 100% efficiency using 3% permanganated alumina (Purafil).

4. Chemical conversions at the 100% level and with the formation of innocuous or irreversibly retained products is achieved when NH_3 and NO_2 contact 3% permanganated silica gel.

5. Molecular Sieve (Linde 13X), exchanged to 70% of stoichiometric with $NiCl_2$, furnishes strong retention of NH_3 and moderately strong retention of CO.

6. Linde SK500 Molecular Sieve, exchanged with mixed rare earths (MRE), is a strong sorbent for NH_3 but not CO.

7. Barnebey-Cheney AC charcoal, doped to 60% with $NiCl_2$ provides moderately strong retention of CO. Considering Conclusion No. 5, the dopant (Nickel) may prove to be effective on any high surface area support.

8. Essentially complete removal of SO_2 can be achieved using AC charcoal loaded to 10% with LiOH. This agent is regenerable with respect to

SO_2 but to an extent as yet undetermined. Conclusions as to the comparative performance of LiOH thus supported and the neat form used in spacecraft also cannot yet be drawn.

9. Study of the potentially useful materials, processes, and systems that were identified in the technology survey of the present program will require a commitment considerably exceeding the level-of-effort of the present program. Because of this situation, it was concluded that the most cost effective approach would be to bring as many candidates as possible to a preliminary level of evaluation even if the deferment of ultimate system selections resulted.

RECOMMENDATIONS

1. More detailed test work (See below) is required before promising agents can be subjected to scaled-up performance evaluations in spacecraft-rated design configurations. While the agents identified on the present program appear promising, some 30 other promising candidates (those selected in the preliminary screening) should undergo further evaluation before ultimate selection is made. Their evaluation should be pursued in the same manner as was observed in identifying the promising agents described herein. After that has been done, only the two or three best materials should be taken into the more detailed test evaluations.

2. Four classes of materials considered on the present program because of the constraints imposed by the research and preparation requirements are recommended for future study. They include: (1) polymeric materials for the removal of low molecular weight organic and inorganic vapors, as well as higher molecular weight but volatile Freons; (2) zirconium (IV) phosphate substituted with Cu; (3) transition metal oxides on highly porous supports, such as the new preparations of silica beads, alumina, and zirconia now being manufactured; (4) clays swollen and exchanged with transition metals and quaternary ammonium salts.

3. Two of the more promising agents that would be identified in following the foregoing recommendations should be subjected to detailed performance characterizations. This should include the following:

a. Determine removal capabilities down to a level of 1 ppm inlet concentration, as well as the ultimate loading capacity at low and high concentration levels, in order to provide assurance of quantitative effectiveness.

b. Establish in greater detail the chemical composition of the products normally eluted and vacuum/thermally desorbed from the agents during and after the processing of the inorganic toxic gases, respectively.

c. Determine the behavior and ultimate fate of models representing each of the eleven classes of organic compound types that require management.

d. Where appropriate, evaluate the regenerability of the agents by testing under conditions of prolonged cycling with appropriately contaminated air streams.

INTRODUCTION

A. PROGRAM OBJECTIVES

The NASA task requirements for the present program were four in number. These are paraphrased below, each being designated with the corresponding Task Requirement Number as required by the covering DRD.

Task 2.1 - An investigation would be conducted to determine the present and developing state-of-the-art of the techniques of airborne trace contaminant control and removal agents and their feasibility for use in NASA programs. Included in this technology survey would be the consideration of both regenerable and nonregenerable removal agents.

Task 2.2 - The formulation and preparation of agents determined to be appropriate for laboratory study would be pursued.

Task 2.3 - Conduct lab investigations of the agents formulated and prepared under Task 2.2. Considered in the design of the agent testing procedures would be such spacecraft compatibility factors as toxicity, flammability, gravity dependence, etc. Additionally, consideration would be given to bulk density, removal efficiency, trace gas capacity, power requirements, longevity, etc. The sorptive properties of the agents, such as displacement of one gas by another, catalytic decomposition of gases, catalytic conversion of gases, and other factors which may be effective in the adsorption process would also be considered. From these investigations, ARLI would then develop a final listing of candidate agents for further evaluation under Task 2.4.

Task 2.4 - Evaluation of the final candidate agent(s) to determine removal capacity and efficiency for CO, NH_3, NO_2, SO_2, and suitable representatives from a list of 76 organic compounds compiled by the NASA. The gases of primary concern would be CO and NH_3; the gases of secondary concern would be NO_2 and SO_2. The organic compounds would be of least concern, although consideration would be given to the applicability of the agent(s) for the dual purpose of removing both the inorganic gases cited as well as the organic contaminants. The control levels sought would be at 10% or less of OSHA maximum allowable concentrations (MAC's). The latter values are 50 ppm for CO and NH_3, 5 ppm for NO_2 and SO_2.

B. ATTAINMENT OF OBJECTIVES

Task 2.1 - Machine and/or manual searches were conducted on such information sources as Air Pollution Abstracts, NASA-STAR, Air Pollution Translations, Chemical Abstracts, etc. The Crerar National Translation Center was visited by the Principal Investigator. Searches in the pertinent fields were also run for the program by the National Technical Information Service and Smithsonian Institute Scientific Information Exchange. Over 700 novel processes, concepts, or materials were identified as potentially worthy of study on the program.

Task 2.2 - From the technology review conducted on the present program, three categories of materials and/or concepts were identified as having potential for substantial payoff. Category I materials were so typed as falling within the purview of the present program. The number of items falling within Category I were too numerous to be individually considered. Thus the arbitrary elimination of many candidates resulted.

Category II materials, although offering the potential for securing a significant advance in the state-of-the-art of air purification were excluded from consideration as requiring materials research and preparation beyond program scope.

Category III materials and concepts involve bacteriological and/or biochemical processes. These are reported herein for the benefit of technologists of the appropriate disciplines.

From the Category I group, 32 materials were formulated and prepared for laboratory evaluation. An additional 10 materials were obtained that were to be tested without further modification.

Task 2.3 - All of the materials collected in Task 2.2 were considered to be compatible with spacecraft applications. Screening of these materials involved a battery of some 324 tests, which far exceeded the level of effort that could be committed. Certain agents were therefore eliminated, reducing the battery to 120 tests. This grouping was further screened with emphasis being placed on CO and NH_3 management. Some 66 experiments were then selected for performance in the subsequent task.

Task 2.4 - Candidate agents were tested for their efficacy in managing CO, NH_3, SO_2, and NO_2. Because of relative program priorities, tests with organic contaminants were not attempted. The materials evaluated included 6 commercial charcoals, 2 modified charcoals, 4 doped charcoals, 4 doped Zeolites, and 2 other doped minerals. Successful results were obtained with a number of these agents, as are itemized in the Conclusions and Results sections which appear earlier.

C. ORGANIZATION OF REPORT

In the six sections that follow, the overall work performed on the program are considered in logical sequence. This arrangement of material does not necessarily conform with the actual chronology of events, since new ideas and materials were brought into consideration even up to the last few months of the program.

The first section describes the technology review that was conducted for the identification of materials and concepts that could have potential application. Section II presents the results of the technology survey, including a review of a key area covered - - transition metal systems. Section III enumerates the systems that were considered for evaluation on the program and furnishes general information on the methods used to prepare those materials that were selected for evaluation. Section IV develops a justification for the approach that was observed in planning the experimental work. The next section describes the test system design actually employed in evaluating the various candidates selected. Section VI details the scope and results of the test work performed on the program.

I. TECHNOLOGY REVIEW

A. INFORMATION SOURCES SEARCHED

The primary information sources reviewed on the present programs were as follows:

- Scientific and Technical Aerospace Reports (NASA-STAR)
- Air Pollution Abstracts - EPA Air Pollution Technical Information Center (APTIC)
- National Technical Information Service (NTIS)
- Smithsonian Science Information Exchange (SSIE)
- Chemical Abstracts
- EPA Translations
- The 167th National Meeting of the American Chemical Society (ACS)
- Crerar Library - National Translation Center

The manner and scope of the searches conducted varied. Where machine searches were available, these were purchased and conducted for a fairly broad period if the performing agency could furnish that capability. In order to limit the amount of material that would be output, search descriptors were carefully selected and specified. Where manual searches were conducted by the project staff, the period covered was necessarily restricted to recent years to conserve labor. The reviews performed on the various information sources are described in the following paragraphs.

1. NASA-STAR

A machine search was conducted by NASA's Western Research Application Center (WESRAC) located at the University of Southern California. The period covered was from 1962 through 1973 and was limited to three NASA Subject Categories: Biosciences, Biotechnology, and Chemistry. A manual search was also made of the STAR's for the years 1972 and 1973.

2. Air Pollution Abstracts

An APTIC machine search was made of the entire series. The Subject Fields were restricted to: Control Methods, Measurement Methods, and Basic Science and Technology. A manual search was also made of the issues for the years 1971 and 1972.

3. NTIS

The U. S. Government Research Reports were machine searched by NTIS from the inaugural date of the file in 1964 up through 1973. Search constraints were mutually developed between the project staff and that of the NTIS.

4. SSIE

A "custom" search was conducted by the Smithsonian on its current file of summaries of ongoing R&D work sponsored by the Government. The search constraints were the same as used by NTIS, which agency also called for the SSIE search.

5. Chemical Abstracts

A machine search of Condensate Tapes was conducted by WESRAC. Because of the scope of this information system, a carefully organized listing of objectives and descriptors was prepared. The search period was from 1970 through 1973, although the starting year was initially called out as 1967. WESRAC's failure to cover the years 1967 through 1969 left a three year gap, since the manual search conducted by project personnel was set from 1962 through 1967.

6. EPA Translations

Manual searches were made of Volumes 3 and 4 of Air Pollution Translations and the 1973 output of the Monthly Translations List and Current Contents. Both publications are produced by the Information Services Division of the EPA

7. The 167th National Meeting of the American Chemical Society

This meeting was attended by the Principal Investigator because of the large number of titles that suggested relevance to program objectives.

8. Crerar Library

A list of some 168 foreign-language publications was prepared. This library was then visited by the Principal Investigator over a reading period of three days.

B. RESULTS OF THE SURVEY

The topical treatment of the information obtained on the survey is presented in Section II. The comparative productivity of the various elements of the survey is discussed in the following paragraphs.

1. Machine Searches

a. NASA-STAR

The machine search of the STAR's produced 371 "hits". About 75 of these abstracts were sufficiently relevant and furnished a state-of-the-art perspective. Only one item was adequately novel to justify study on the present program.

b. Air Pollution Abstracts

Machine search of these abstracts produced 144 hits. Forty of these proved of value in defining the state-of-the-art. Another 27 appeared to be relative to program objectives; many of these were foreign-language items.

c. NTIS-SSIE

The searches performed by these two agencies produced some 120 hits. Seventy of the NTIS reports were obtained on microfiche of which 20 were studied in some detail. Fifteen of the SSIE hits were of interest.

d. Chemical Abstracts

The Condensate Tapes yielded WESRAC 120 hits. Twenty-five were of only background value, while 14 were of sufficient interest to acquire the entire publications. Eleven of the 14 were unavailable in English.

2. Manual Searches

The manual searches proved more fruitful than the machine searches. From Air Pollution Abstracts, Air Pollution Translations, and Chemical Abstracts, over 700 titles were identified as worthy of screening. About half of these items, including some 168 foreign-language references which could only be read in abstract form, were studied.

3. Other Sources

a. The 167th National ACS Meeting

This meeting, which was held in nearby Los Angeles, proved a valuable source of information. Of 50 papers identified as being germane to program objectives, 21 were heard and discussions held with 7 of the authors.

b. Crerar Library

During this visit, translations of some 168 titles of foreign-language papers and patents were sought. Because of fund limitations, the Crerar has reduced its translation activities significantly in recent years. Partially because of this, only 28 translations were found, none of these being for the 30 patents of interest.

II. FINDINGS OF THE TECHNICAL SURVEY

A. OVERVIEW

A great deal of information was obtained, the comprehensive review of which would pose a burdensome task to the reader. The material has accordingly been organized to lay stress on the areas that become focal during the testing performed on the present program.

In Section II. B, which immediately follows, systems are presented which, if selected for investigation, could be pursued within the constraints of the present program. Because of their number, descriptions have been arranged in tabular form. References are largely given as Chemical Abstract accession numbers to reduce the length of an already bulky bibliography.

Thereafter, in Section II. C, systems are presented which, for various reasons, could not be investigated on the present program. Many require extensive fundamental work and others, considerable preliminary investigative effort to even prepare the materials of interest. Still others involve disciplines that were not represented on the contractor's staff. These systems, however, are felt to have potential of affording significant advances in the air purification technology. For this reason, complete titles of the references are provided in the tabulations.

In Section II. D, a topical review is presented. It has, however, been restricted to a specific area that was of particular interest on the present undertaking. It deals with transition-metal containing systems and materials that may be enhanced through the addition of these metals. Confining the review to this selected but highly promising area was done for the reason given in the first sentence of this Section.

B. SYSTEMS FALLING WITHIN PROGRAM PURVIEW

Tables 2 through 5 itemize the various systems that may be appropriate for the management of CO, NH_3, NO_2, and SO_2, respectively. As pointed out above, evaluation of these systems was considered practical

TABLE 2. CANDIDATE SYSTEMS FOR THE MANAGEMENT OF CARBON MONOXIDE

MATERIAL	REFERENCES
Charcoals, doped/undoped	
Coconut and coal-derived	65:17732f, 19333C, & 1419g
Graphon	65:19616e & 19338h
Carbosieves	65:19339c & 19339f; 59:10816h
Zeolites, doped/undoped	
Linde Mole Sieves - TM* Exchanged	65:4694f, 4695b, & 17733d
Type "Y" - TM-exchanged or -loaded	65:4697d; 64:7403c, 10437h, & 18464d; 63:3930g; 62:4929a & 8420h; 58:5425h, 9650h, & 9651d; Crerar TC-6405 & TT 65-63512
Other Type Adsorbents	
Calcined bloated clays	64:10895a & 5786g
Irradiated metal oxides	65:196a; 64:4296d, 4298g, & 4297a
Ga_2O_3 & Li_2O doped ZrO_2	63:6348h, 1077b, & 12363h
Amine & quat** swollen clays	58:9649g; 65:19339e
Chemical Conversion Media	
TM oxides	65:19767c; 63:12669b & 10771b; 62: 64a & 304d; 59:361g & 9866a; 58: 5511f,
Getters, Ta & Ti (improved)	58:12185d; 59:9653b
Cross-linked polymers	
UV-irradiated	65:3210g & 19767d
Silent-discharge irradiated	63:17266h & P4414b
Amine resins	57:8413 & 12377h
Polyvinylols	59:810c & 2967c; 60:14418f
Carbonyls	57:P2077i & 11080g
Epoxies	65:PC13350d & P8767f
Complexation Media	
Clathrates (β - quinol)	64:4452a; 58:982a & 9863d
TM-polymer chelates	63:12369c; 60:14418f
Carbonyls	57:11080g
TM oxides	65:17759c; 63:3930g; 58:10759h; ACS 121INOR
Catalytic Media	
Promoted Fe & Co catalysts	Crerar NTC 72-11482

TABLE 2. CANDIDATE SYSTEMS FOR THE MANAGEMENT OF CARBON MONOXIDE (cont.)

MATERIAL	REFERENCES
Mineral Catalysts	
$ZrOCl_2$ impregnated vermiculite	65:P5363e
Noble & other TM promoted magnesite	65:16108e & 1418a
Reduced Mn ore	65:1478f
Noble & other TM's, salts, & oxides	65:335h, 5443, 16107c, 16117e, 16117b, 1410d, 9788h, 15183b, & 17733b; 64:2784h, 2785a, 167d, 15026d, 12476d, & 13425d
Metal Alloys	
Co/Co Oxide Mixtures	59:5823a
Fe/Cr & Cu/Co	59:10742g; Crerar NTC 72-11482
Special Reactions for Detector Development	65:6535c & 12833e; 62:1242d
Misc (TM-chelate polymers, Pt/Pd photocatalysts, TiO_2 Solid Solutions with W & Fe oxides, etc.)	63:2416c, 12363h, 9195d, 12364e, 12369c, 12370c, 12369c, 14611c, 15985f, 15755f, & 17197a

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*TM = Transition Metal(s)

**quat = Alkyl quaternary ammonium compound(s)

TABLE 3. CANDIDATE SYSTEMS FOR THE MANAGEMENT OF AMMONIA

MATERIAL	REFERENCES
Macroreticular Resins	
TM exchanged	Kogyo Kagaku Zasshi, 73, 1083 (1970)
K & Na exchanged	60:2026e
Zeolites	
TM exchanged	Z. Chem, 10, 228 (1970)
$KAlO_2$ exchanged	56:P6692f, 60:1139e
Complexation Media	
Ni treated charcoal	U. S. 3,436,352, April 1969
Graphites	57:5558b
Silicas	
Co (II) doped	62:5922c
$Mn(OH)_2$ modified	57:5723c
K, Fe, & Al modified	56:10968i
γ - irradiated	57:1778c
Misc	
TM impregnated vermiculite	61:11766h
Fe_2O_3	57:11884i
Semiconductor systems	60:3591f
Promoted magnetites	65:16108e

TABLE 4. CANDIDATE SYSTEMS FOR THE MANAGEMENT OF NITROGEN DIOXIDE

MATERIAL	REFERENCES
Adsorbents	
Charcoals/porous coals	62:9958c
Chemical Conversion Media	
$PbO(OH)_2$	58:5040e
Polymeric N-vinylcarbazole	59:11669d & 810d
Chemisorptive & Catalytic Media	
Alkali metal oxides on charcoal	Japan 47-50982, Dec. 1972
TM oxides	NASA CR-1388, July 1969

TABLE 5. CANDIDATE SYSTEMS FOR THE MANAGEMENT OF SULFUR DIOXIDE

MATERIAL	REFERENCES
Adsorbents, Alkali Treated	
Zeolites	65:19338f
Porous clays	64:5786g
Chemical Conversion Media	
Polymeric structures containing amino alcohols, aromatic amines, or carbonyls	65:3990e; 64:868f & 15990f; 63:13025f & 9082f; 62:6583h; 60:P1859b; 61:P5813f; 59:810e & 2312d; 58:6252c; 56:P13708d
Fe doped charcoals	NASA CR-1388, July 1969
Catalytic Media	
TM doped charcoals	Crerar NTG-R3813
TM oxides	64:15026d

in terms of program constraints. These systems were accordingly brought into the selection process, which is described in the next section.

All references given in Tables 2 through 5 are Chemical Abstract Accession Numbers, unless otherwise specified. Items from the 167th National Meeting, Los Angeles, April 1974 are designated simply as "ACS". Items from the National Translation Center are designated "Crerar". The abbreviations TM and RE represent "transition metal(s)" and "rare earth(s)". Patents are so designated by the country of origin.

C. SYSTEMS FALLING OUTSIDE PROGRAM PURVIEW

1. Chemical or Physical Process Systems

A number of processes were identified in the literature search which appeared to have good potential for application development but could not be studied on the present program. As stated earlier, this was because the amount of effort to pursue these particular systems was considered to be in excess of what could be reasonably committed on any component of a balanced program. In many of these systems, inadequate information existed as to the techniques that should be used in preparing the materials of interest. In other cases, ancillary processes or components would first have to be developed in order to make the system compatible with application constraints. It is felt, though, that these systems, which are briefly described below, have considerable potential merit.

a. Copper Substituted $Zr_3(PO_4)_4$

Dudukovic and coworkers (Reference 1) evaluated various ion exchange compounds as catalysts for automobile exhaust treatment equipment. They prepared crystalline Cu-substituted $Zr_3(PO_4)_4$ by a dry, solid-solid reaction and a wet method. The material was found to be more efficient than other known catalysts for the conversion of CO to CO_2 in the presence of O_2. Additional work is needed, however, to increase the surface area and reduce the Δp of the catalytic packing.

b. Mixed Cu/Cr Oxides on Alumina

Shatrov et al (Reference 2) report on materials intended for the same application as described in the preceding paragraph. Using alumina as a support, Cu and Cr are coprecipitated on the support to produce catalysts that promote the oxidation of CO and the conversion of NO_2 to N_2. Yao (Reference 3) describes similar results using oxides of Co carried on the same report. The Cu/Cr systems appear more attractive, although the proper proportions of the oxides furnishing optimum performance needs to be worked out.

c. n-type Mixed TM Oxides on Porous Supports

Other TM systems for the catalytic conversion of CO to CO_2 have been reported by Artyukh (Reference 4) and Freeman (Reference 5) and their coworkers. The reaction is promoted using n-type transition metal oxides on highly porous supports. Candidates for the latter function are a new silica bead material offered by PPG Industries, Inc. and new high porosity alumina and zirconia products manufactured by ICI America, Inc.

d. Modified Clays and Micas

Micas and clays show only moderate adsorptive and catalytic activity. When swollen with $ZrOCl_2$, however, Magee and his co-inventors (Reference 6) demonstrated that vermiculite can be used for the oxidative elimination of CO and hydrocarbons. It is believed that other transition metals will show similar if not enhanced behavior. Also, percolation of organic quartenary ammonium salts into clays (Reference 7, 8, and 9) produces structures capable of absorbing several fold more benzene vapor than the untreated clay. Thus, when the details of preparation are found and a selection of clays minerals is made, this type of candidate may provide two different materials: one for the catayltic gas phase decomposition of contaminants and a second for the adsorption of CO and/or organic vapors in the bound quartenary organic layers exchanged into the mineral structure.

e. Fuel Cell Devices

Several interesting systems have been described in which CO is oxidized in apparently reversible electrochemical processes. These involve gas-solid and gas-liquid configurations. Dell and Wheeler reported (Reference 10) such a system involving oxides of uranium; Zazonov and Logrimenko discuss (Reference 11) the use of rare earths (-Gd, Sm, Ce, Yb, La, Nd, and Dy). Noskova and her coworkers used Fe (III) and Cu (II) systems, incorporating a Pd promoter. If used in fuel-cell configurations, the electrode geometry, composition, and fabrication requirements would require study and the reversibility of the processes carefully evaluated.

f. Liquid-Phase TM Reactions

Several interesting reactions promoted by TM's and TM salts in nonaqueous media have been reported. Reed and Eisenberg (Reference 13), for example, discuss the coupled reduction-oxidation of NO_2 and CO in dimethyl sulfide using $Rh(PO_4)_2$. Kaiser and Saillant (Reference 14) described the use of Rh and Ir addition compounds of cis-octadienyl biimidazole for the complexation of CO. If such systems could be properly configured, say, through the use of permselective membranes, they would perhaps be rendered practical for spacecraft use.

g. Liquid Alkali Metals

Ottolenghi and Linschitz (Reference 15) have demonstrated that the well known anhydrous formation of metal amides from NH_3 and the liquid metal can be usefully exploited. Ultraviolet irradiation of the formed amide disproportionates NH_2^- to form N_2 and H_2. Room temperature liquid alkali metals, such as NaK eutectic would probably be suitable. The principal problem of course would be to isolate the reaction from other air components, such as through the use of permselective membranes.

2. Biological and Biochemical Process Systems

In the technology survey conducted, it was inevitable that many systems would be identified that involved biotechnology. This occurred despite the fact that no effort was exerted to examine the literature serving the various biological and biochemical professions. In any case, although such systems were not explored on the present program, they should be mentioned here. It is recognized of course that a search within the proper bio-fields would doubtless have produced a far greater number of pertinent titles than were found on this project.

Of the most interesting papers found, References 16 through 18 stand out. These deal with the enzymic oxidation and protein-complexation of CO. References 19 through 21 describe enzyme systems that variously convert NH_3 to innocuous products.

Utilization of such systems in practical configurations is of course within the province of the bio-engineer. It is obvious, however, that the new techniques (e. g. Reference 22) of immobilizing enzymes on inorganic supports to which they are chemically or physically bound, would be applicable.

D. REVIEW OF THE PERTINENT TECHNOLOGY INVOLVING THE TRANSITION METALS (TM'S)

1. Carbon Monoxide Effective Systems

Among early workers, Tsitsishvilli and Andronikashvili (References 23 and 24) demonstrated an improved adsorption of hydrocarbons on Ag zeolites. Later, these same workers (Reference 25) reported irreversible retention of CO on X type Ag zeolite, although capacity was not discussed. They also found (Reference 26) that the retention of CO on A type Ca zeolite was increased from seconds to 4 min after the Ca was exchanged with Ag. Similar results were observed by Neimark and his coworkers (Reference 27) for the same type of zeolite with CO and olefins when Co was used as the exchanging metal.

Extension of these studies to other TM's is also found in the work of Rabo et al (Reference 28) and Kavtaradze (References 29 and 30) for CO and by Stach et al (Reference 31) as well as Kamada and Tashiro (Reference 32) for NH_3. Breck, Castor, and Milton (U. S. Pat.

3, 185, 540) use Fe, Ni, or Co exchanged A type Na zeolite to remove traces of CO and O_2 from other gases.

While the above work is all in terms of TM-modifications of zeolites, other workers have published results showing enhanced CO and NH_3 adsorption, catalysis, and noncatalytic conversion on TM oxides, salts, and alloys, both unsupported as well as on a variety of substrates. Rojek (Reference 33) demonstrated CO adsorption and catalytic conversion on Co/Co oxide mixtures. Mueller and Koltermann (Reference 34) studied sepiolite clays with respect to CO and SO_2 adsorption and concluded that these minerals behave as molecular sieves having 0.6 to 0.8 nm dia. channels. Barrer (Reference 35) made an in depth study of the factors affecting the specificity of physical adsorption for a variety of minerals, natural and synthetic, as well as charcoals, silica gel, alumina and others. He determined the effect on specificity by modifying such materials by chemical treatment, cation exchange, and decationization. Sinyak, et al (Reference 36) experimentally determined the oxidation efficiencies of several TM catalysts for CO, as well as NH_3, CH_4, and H_2S.

Valuable contributions were made by Krylov (Reference 37) on the correlations and comparisons of experimental activity data and electronic, structural, surface properties, and electronic distributions of solid binary catalysts. Equally important correlations for TM alloys were made by Artyukh et al. (Reference 38), who studied the catalytic activities of alloys and their electronic structure. In a similar vein, comparative studies for graphites, charcoals, hydroxides, oxides, and chemically modified surfaces were carried out by Kiselev (Reference 39) and Dubinin (Reference 40).

Numerous workers (e.g. References 41 through 57) have investigated the nature of CO adsorption and catalysis on various forms of Ni, W, and Mo. Alloy catalysts for CO oxidation were also investigated by several groups (e.g., References 52 and 53), most of which involved Fe/Cr, Cu/Co, or Fe/Cu. Other supported metal and alloy systems are represented by the work of Sokol'skii (Reference 54) and Tajbl (Reference 55) and their coworkers who studied Pt, Pd, and Pt/Pd on clays and Pd on alumina for CO oxidation.

A considerable range of supported and unsupported, single and mixed TM oxides has been investigated for CO adsorption or oxidation. Variations of ZnO compositions for CO oxidation have been studied by Molinari, et al (Reference 56), Arnberg and Seanor (Reference 57), and Semenova and Markina (Reference 58). Solid solutions of WO_3 and Fe_2O_3 in TiO_2 have been examined by Mikhailova, et al (Reference 59) for CO adsorption and oxidation. Materials incorporating V_2O_5 and MoO_3 were studied by Tarama, et al (Reference 60). Combined reduction of NO and oxidation of CO on reduced Mn ores was reported by Chkhubinishvili, F. V. and E. H. Chagunova (Reference 61). The mechanism of CO oxidation on thoria was elucidated by Claudel, et al, and confirmed by kinetic measurements (Reference 62).

2. Ammonia Effective Systems

Although not nearly as voluminous as the work reported on CO adsorption and catalysis, many interesting and valuable studies have been made of the behavior of NH_3 with TM-containing materials. Voelter and Schoen (e. g. Reference 63) have determined the heat of activation for NH_3 on Co, Ni, Cu, and Zr. They found the NH_3 decomposition rate at 850°C on the 111 face of some metals to be as much as 12 times greater than that on the 100 face. Boyle, et al (Reference 64) determined isosteric heats of adsorption of NH_3 on silica Xerogel with and without Co and other TM compounds added. IR reflectance spectra of the TM impregnated materials indicated that the NH_3 surface bending was partly physical and partly chemical.

Complete oxidation of NH_3 in air at 600°C on V_2O_5 has been reported by Morekin, et al (Reference 65). The adsorption rates and heats of activation for NH_3 decompositions on various catalytic materials has been reviewed by Artyukh, et al (Reference 66). Other TM oxide formulations effecting the oxidation of NH_3 are reported by several investigators. Kynev, et al, (Reference 67) used a mixture of 87% Co_3O_4, 10% Al_2O_3, and 3% CuO from 20 to 700°C. Magyar (Reference 68), on the other hand, achieved catalytic decomposition of NH_3 on a material containing 87.9% Fe_2O_3, 7.2% Cr_2O_3, and 0.05% K_2O. The heat of activation was measured at 8.9 Kcal/mole, with chemisorption prevailing at around 450°C. Other Fe compound catalysts effective around that temperature have been described by Matsui and Toyoshima (Reference 69).

Breck and Acara (Reference 70) have developed specially treated zeolites for the adsorption of NH_3. Krejcar (Reference 71) prepared an ion exchange resin material to furnish the same function. Roessler disclosed in a 1963 Belgian patent (Reference 72) a method for achieving the reversible sorption of NH_3 in a molten salt mixture of 10 parts $NaHSO_4$, 13 parts K_2SO_4, and 0.6 parts of Na_2SO_4. Another salt system was patented by Halley and Halawaty in a U. S. patent (Reference 73). In this case, it is claimed that solid phase H_3BO_3 absorbs NH_3 at temperatures up to 150°C to weights 10 times that of the absorber. The NH_3 can be recovered in an inert gas carrier at tmperatures above 180°C.

Four interesting reactions involving NH_3 have been reported. Den Besten and Qasim (Reference 74) have observed the photocatalytic oxidation of NH_3 on Zr oxides using UV light. Hata and Kinumaki (Reference 75) reported the reaction of NH_3 and aliphatic amines with SO_2 to form solid thionylimides. Bhatnagor (Reference 76) suggests that Ni cyanide complexes are stabilized through the formation of clathrate compounds with NH_3. Even more interesting, Varlamov (Reference 77), et al, observed the acoustic promotion of NH_3 reactions with NO_x at low concentration levels.

3. Sulfur Dioxide Effective Systems

In many of the citation's made in the foregoing subsections, mention has been made of systems that are apparently effective for SO_2 and NO_2. These systems and reactions have also applied to CO or NH_3 and have therefore been considered under those headings, since those toxic gases were given priority. Because it would be redundant to discuss these systems again here, the present section deals only with those systems which were either ineffective for CO and/or NH_3 or were not tested with those gases. Consequently, a relative few systems require review and, in the case of NO_2, none at all.

In the matter of SO_2 management, Davtyan and Ovchinnikova (Reference 78) tested TM oxides as catalysts. They found the catalytic activity at room temperature to be: Pt > charcoal > V_2O_5 > graphite > Cr_2O_3 > Fe_2O_3. Mars and Maessen (Reference 79) found that V_2O_5 dissolved in $K_2S_2O_7$ oxidized SO_2 when O_2 was present. The chemisorption rate of the latter appeared to be the rate determining step. Keier (Reference 80) has shown that TM chelate polymers possess high catalytic activity. This activity can be influenced over several orders of magnitudes depending on the choice of ligand for a given TM.

III. SELECTION AND PREPARATION OF CANDIDATE TOXIC GAS REMOVAL AGENTS

A. MATERIALS SELECTION

As a result of the survey described in the previous two sections and considering certain approaches originally proposed to the NASA, a listing of potential candidate systems was developed. This listing included far more items than could possibly be tested on the program. Since many of the candidates involved the same materials but with different loadings of dopant, a single composition was selected on best judgement, while the others were culled. To further reduce the test group to a manageable group, additional candidates were eliminated, again using best chemical intuition. The overall list of candidates and the selections made are shown as Table 6.

As discussed later, the evaluation of an agent requires three tests per toxic gas used. Each of these tests required a minimum of 2.5 hrs, exclusive of data reduction etc. Some tests actually had to be run much longer. Of the 25 materials that were brought into test evaluation, 219 tests were indicated, of which 177 were actually completed. Because of the substantial test time required, it can be understood why a material selection process became necessary.

B. MATERIALS PREPARATION

A number of the materials listed on Table 6 that were selected for evaluation were commercial products that of course required no preparation. This is true of all of the undoped charcoals, RE/SK 500, and Purafil. The other materials on Table 6 were prepared in accordance with the pertinent literature instructions or, where this was not explicit or available, by best chemical judgement.

Doped charcoals were prepared using a 40 to 100 mesh charcoal wetted with a quantity of a solution of the dopant calculated to furnish the desired loading. The solvent was then removed using a rotary vacuum evaporator and IR lamp heat.

TABLE 6

LIST OF REMOVAL AGENT CANDIDATES

Removal Agent	Toxic Gas Targets					Min. No. of Tests Req'd per agent	Selection Result*
	CO	CO_2	NH_3	NO_2	SO_2		
I. Undoped Charcoals							
Barnebey-Cheney							
AC	X	X	X	X	X	15	S
VG	X	X	X	X	X	15	S
GI	X	X	X	X	X	15	S
Witco Nuchar							
WV-G	X	X	X	X	X	15	S
WV-L	X	X	X	X	X	15	S
WV-H	X	X	X	X	X	15	S
WV-W	X	X	X	X	X	15	E
Special Charcoals							
Carbosieve "B"	X	X	X	X	X	15	S
Graphon	X	X	X	X	X	15	S
Porous Coals	X	X	X	X	X	15	E
II. Doped AC Charcoals							
1% LiOH				X	X	6	E
10% LiOH				X	X	6	S
10% KOH				X	X	6	E
15% KOH				X	X	6	E
10% $NiCl_2$	X		X			6	E
20% $NiCl_2$	X		X			6	S
60% $NiCl_2$	X		X			6	P
10% $FeCl_3$					X	3	P
0.5% $RuCl_3$	X			X		6	P
1% $RhCl_3$	X					3	P
2% $ReCl_5$	X					3	P
5% $ZrCl_4$	X					3	P
2% $PdCl_2$	X					3	P
5% $SmCl_3$	X					3	P
1% $CuCl_2$	X					3	P
III. Doped Zeolites (Linde)							
Type 13X							
70% Ni(II) exchanged	X		X			6	S
Type "Y"							
SK41, NH_4 Zeolite 70% Ni(II) exchanged	X		X			6	E

TABLE 6

LIST OF REMOVAL AGENT CANDIDATES

(cont.)

Removal Agent	Toxic Gas Targets					Min. No. of Tests Req'd per agent	Selection Result*
	CO	CO_2	NH_3	NO_2	SO_2		
SK40 modified by 4% Al extracted & exchanged with $Ru(NH_3)_4(OH^-)(Cl^-)$	X			X		6	P
SK500 rare earth mixture exchanged	X		X	X		9	S
SK120 single rare earth exchanged	X		X	X		9	E
Specially activated Linde 5A Mole Sieves	X					3	S
IV. <u>Doped Macroreticular</u>							
Dowex-50-W							
Fe(II) exchanged	X		X			6	E
CO(II) "	X		X			6	E
Ni(II) "	X		X			6	P
Mn(II) "	X		X			6	P
Cr(II) "	X		X			6	E
Pd(II) "	X		X			6	P
Zr(II) "	X		X			6	E
Sm(III) "	X		X			6	E
Cu(II) "	X		X			6	P
Ag(I) "	X		X			6	P
Zn(II) "	X		X			6	E
V. <u>Powdered Metal Alloys</u>							
Co - Fe Alloy (1:1)			X			3	E
VI. <u>Other Doped Adsorbents</u>							
3% permanganated alumina (Purafil)	X		X	X	X	12	S**
3% permanganated Silica gel.	X		X	X	X	12	S**

---

*S = Selected & Tested; P = pending (selected but not tested); E = eliminated

** of 12 tests required, only 9 could be completed

Doped zeolites were prepared by effecting the required number of sequential passes of the dopant solution, which was of the proper concentration to produce the desired loading. In some cases, higher TM loadings were effected by digesting the zeolite with the chosen TM solution. This was followed by drying, extrusion, and calcining. The dopant was then reduced to the metallic form by flowing H_2 through the bed at a selected elevated temperature.

Alloys were prepared by mixing C.P. metal powders in the desired proportions and melting the mixtures in a helium atmosphere in a Lindberg induction furnace. The homogenous melt was then broken up, pulverized, and sieved.

TM exchanged macroreticular resins were prepared using conventional ion-exchange procedures and appropriate TM salt solutions containing the desired equivalents of TM ion. The columns were rinsed with water, following which the resins were dried in vacuo at a temperature below 100°C.

The materials prepared or procured in commercial forms are those itemized in Table 6 with the designations "S" or "P" in the right-hand column. Most of the materials were made up in quantities of less than 10 g.

IV. EXPERIMENTAL APPROACH

A. OVERVIEW

The effects selected agents might demonstrate in controlling the materials of interest to this program are well known. They can be broadly grouped within three categories: (1) physical adsorption; (2) chemisorption; and (3) catalytic or chemical conversion accompanied by some effect undergone by the product of catalysis or chemical reaction that may again involve the other two processes.

Parameterization of physical adsorption, which can involve solution, occlusion in microreticular structures, and related processes, is best approached using GC techniques.

Chemisorption processes can be measured similarly but, in the case of strong or almost irreversible Van der Waal bondings, for different reasons. Where weak chemisorptive energies are involved, the situation can be treated almost like physical adsorption. Systems involving high bond energies between the active surface and the solute vapors behave quite differently but can still be observed by GC techniques. Instead of a partition effect, the adsorbent must be completely saturated prior to breakthrough to the GC detector.

The observed difference between the two processes is predicated on the concentration of the sorbate. Under subcritical and otherwise fixed conditions, a physical process will release the sorbate at the same time from the bed of adsorbent, regardless of its concentration in the carrier. In a strongly chemisorptive process, elution of the sorbate will be largely determined by its concentration in the carrier. These are of course broad generalizations but, in either case, both processes are nicely observed using GC methodology.

The third case, which involves catalysis or chemical reaction, is also amenable to measurement using GC techniques. Whichever prevails, the analyte or contaminant to be controlled, will be catalyzed or reacted to a specie that will exhibit its own behavior to the sorbent, whether involving secondary reactions, physical adsorption, chemisorption, or complete indifference. The rate of catalysis or reaction can have a decided effect on the observer's ability to measure the process, but this only constitutes a qualitative property of the experiment. The main jist intended in this overview is that the GC technique does comprise the proper approach for evaluating future generation spacecraft air purification media.

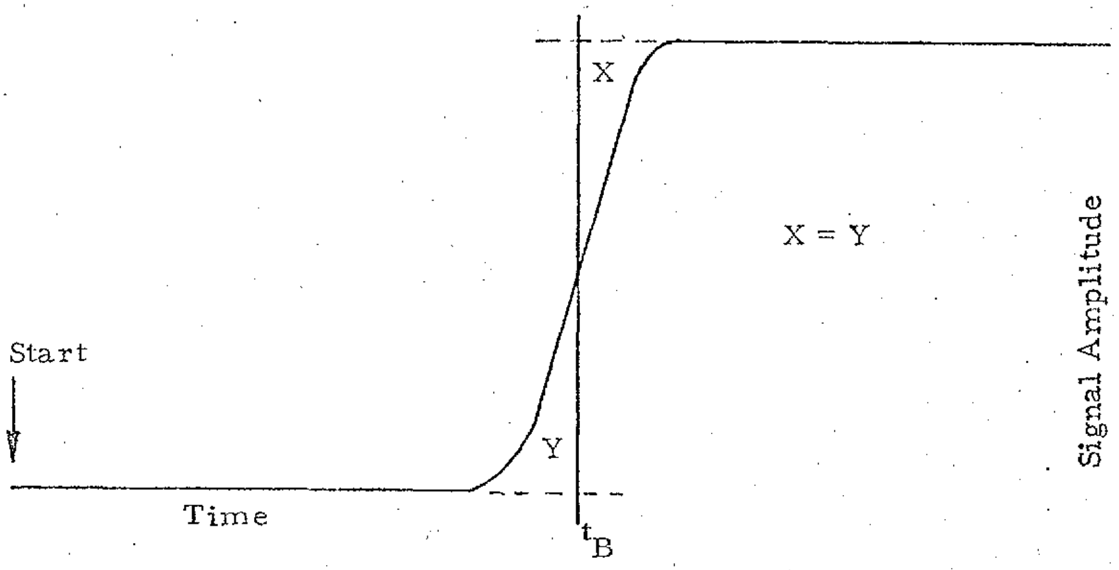
B. CANDIDATE SCREENING APPROACH

1. Alternatives

On the present program, energetic chemisorptive processes were avoided in that they implied the use of nonregenerable sorbents. The present discussion thus points to laboratory procedures that are based on consideration of physical adsorption effects as being predominant, with or without the involvement of catalytic or chemical conversions. From this perspective, two approaches, as defined below, were possible; both involve GC methods.

2. Evaluation of Candidates under Continuous Contaminant Loading Conditions

An obvious approach to conducting evaluation tests of candidate adsorbents would be to pass contaminant-containing gas through them until breakthrough occurs. This is essentially a simple form of frontal analysis. If the tests are conducted within the linear portion of the adsorption isotherm and since irreversible adsorbents would be deemphasized, contaminant concentration would not be important. Thus the capacity of each candidate could be related to the breakthrough volume, V_B, or the air flow-rate times the time to breakthrough, t_B. The latter is usually graphically defined as the vertical intercept of the breakthrough signal front that furnishes equal area segments formed by the intercept, the signal, and tangents to the baseline and plateau of the signal, viz:

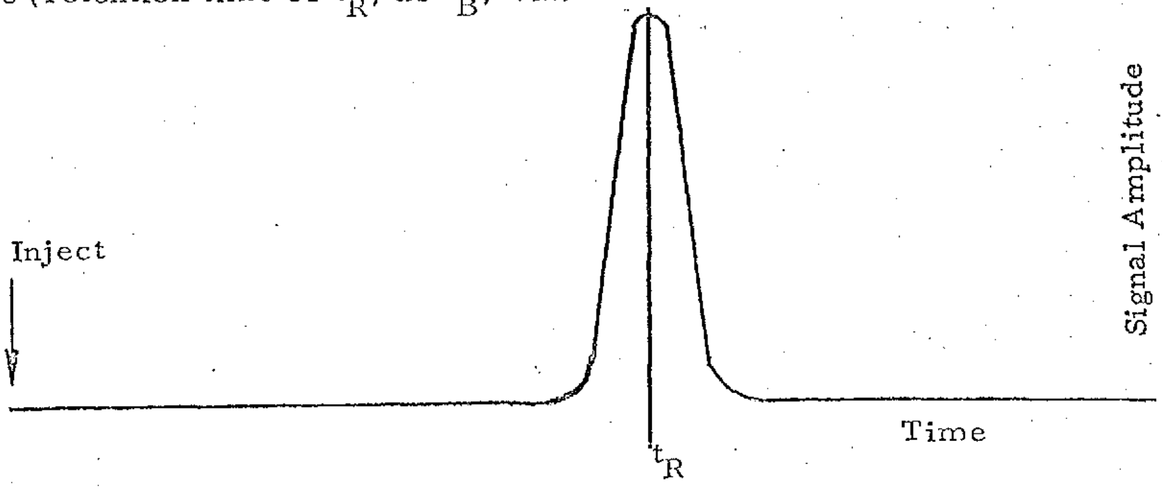


FRONTAL ANALYSIS BREAKTHROUGH POINT

If, at breakthrough, the analyte were eliminated from the input gas, it would take in excess of an additional t_B for all of the analyte remaining on the adsorbent to come off. Although the stripping process can of course be expedited, frontal analysis is not a convenient approach.

3. Evaluation of Candidates under Plug Loading Conditions

For screening purposes, one need only inject a small volume of the contaminant-containing gas that would have been used for frontal analysis. If the carrier flow rate is the same, the signal for the discretely injected sample will, under ideal conditions, occur at the same time (retention time or t_R) as t_B, viz:



This is to say that retention volume, V_R, which is flow rate times t_R, is equal to V_B. This equivalence, which is well known to gas chromatographers and has been mathematically derived from basic principles, is conditional. The factors that can introduce offsets are not important in the present context, particularly if one demphasizes irreversible processes.

4. Experimental Approach

Using CO_2 as a reference material and the four contaminants of interest (CO, NH_3, SO_2, and NO_2), one of these was injected as a slug onto a short column of the candidate agent. The latter was held at an appropriate temperature, usually room in initial testing. The next type of toxic gas was then injected after an interval of 0.5 to 1 hr, unless the preceding slug had already eluted, in which case the next type gas was injected immediately after the recorder had returned to base line.

After all five test compounds had been added and any elutions had been noted, the temperature of the adsorbent was increased at a moderate rate to stripping temperature (260 - 360°C). Evidence of elution was then again checked. After reaching stripping temperature, the adsorbent was usually held there for 16 or more hours with the helium flow maintained. The adsorbent was then cooled to 5 or 10°C below the lowest temperature above ambient where evidence of desorption was noted. Those gases that exhibited significant retention at room temperature were then injected again onto the adsorbent.

Sequential testing of the test gases at this first elevated temperature was continued and the elution data recorded. Any test gas failing to elute at this first elevated temperature stage was then reapplied after column reactivation and resetting to the next higher temperature where elution occurred in the initial temperature program.

The object in the approach chosen was to establish as rapidly as possible whether substantial retention had occurred and to find the temperature region in which all five test gases are resolved using a time scale that is compatible with the large number of samples that had to be screened. This approach furnished a rough figure of merit or index that allowed an immediate, if tentative, ranking of the removal agents tested. This thus permitted timely decisions to be made as to the worthiness of candidates for more detailed characterization. In the interest of expediency, retention times were applied to the recorded elution data, whether obtained during a programmed temperature run or on an isothermal run, and whether obtained from a single injection onto a newly activated column or from one from which the elution of several other TG's had already occurred. By operating the beds at the same exit (atmospheric) flow rates, retention times were adequately comparable for runs involving the same thermal conditions. On the program, just over a thousand tests of the type described above were conducted.

V. LABORATORY TEST SYSTEM

A. FLOW ARRANGEMENT

The schematic of the system used for the evaluation of toxic gas removal agents is shown in Figure 1. The system is basically a gas chromatograph, except that in lieu of conventional columns, short (10 to 15 cm) sections of adsorbents were used.

Samples can be inlet through either valve V2 or the septum between V1 and the 6-port linear sampling valve. When inlet at V2, the sample gas can be flowed in continuously or as a sample loop slug. Although continuous flow addition was never actually required, a permeation tube oven and flow system was also provided. A septum was installed on the reference side of the system to permit checking of the system while material is still adsorbed on the test column.

Column stripping at elevated column-oven temperature can be performed by either back purging with helium (using valves V1, V9, V10, and FC-2) or vacuum. Trapping can be done on either side of the flow system at the points indicated. IR cells and cold traps were actually used. In the former case, a bypass arrangement was employed, so that, based on detector signal, the sample slug could be trapped at the proper instant.

B. TEST SYSTEM COMPONENTS

The test system was built up from components available in the laboratory. A photograph of the test system is shown in Figure 2. The cabinet at the left with attached manometer and valve array is disgrammed in Figure 1. This system is pictured in Figure 3, showing the opened column oven and detector oven module. The two variacs are used to control the temperature of the column oven and the reference-side septum inlet, respectively.

The detector oven temperature controller is located in the cabinet to the right (Figure 2) of the GC cabinet. The former, a module from a Hewlett-Packard (HP) Model 5750 gas chromatograph, also houses

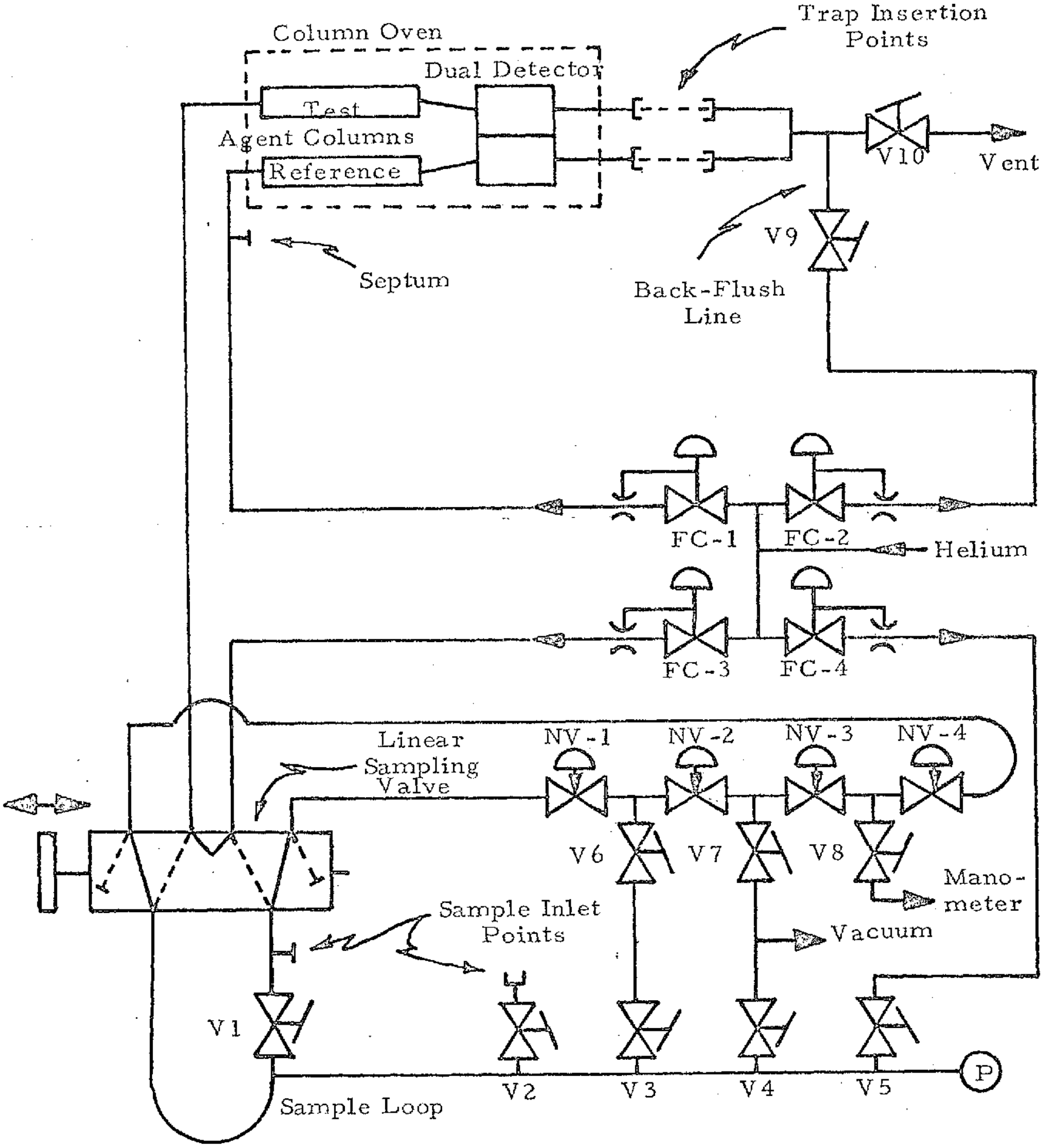


Figure 1. Flow Diagram of Laboratory Test System

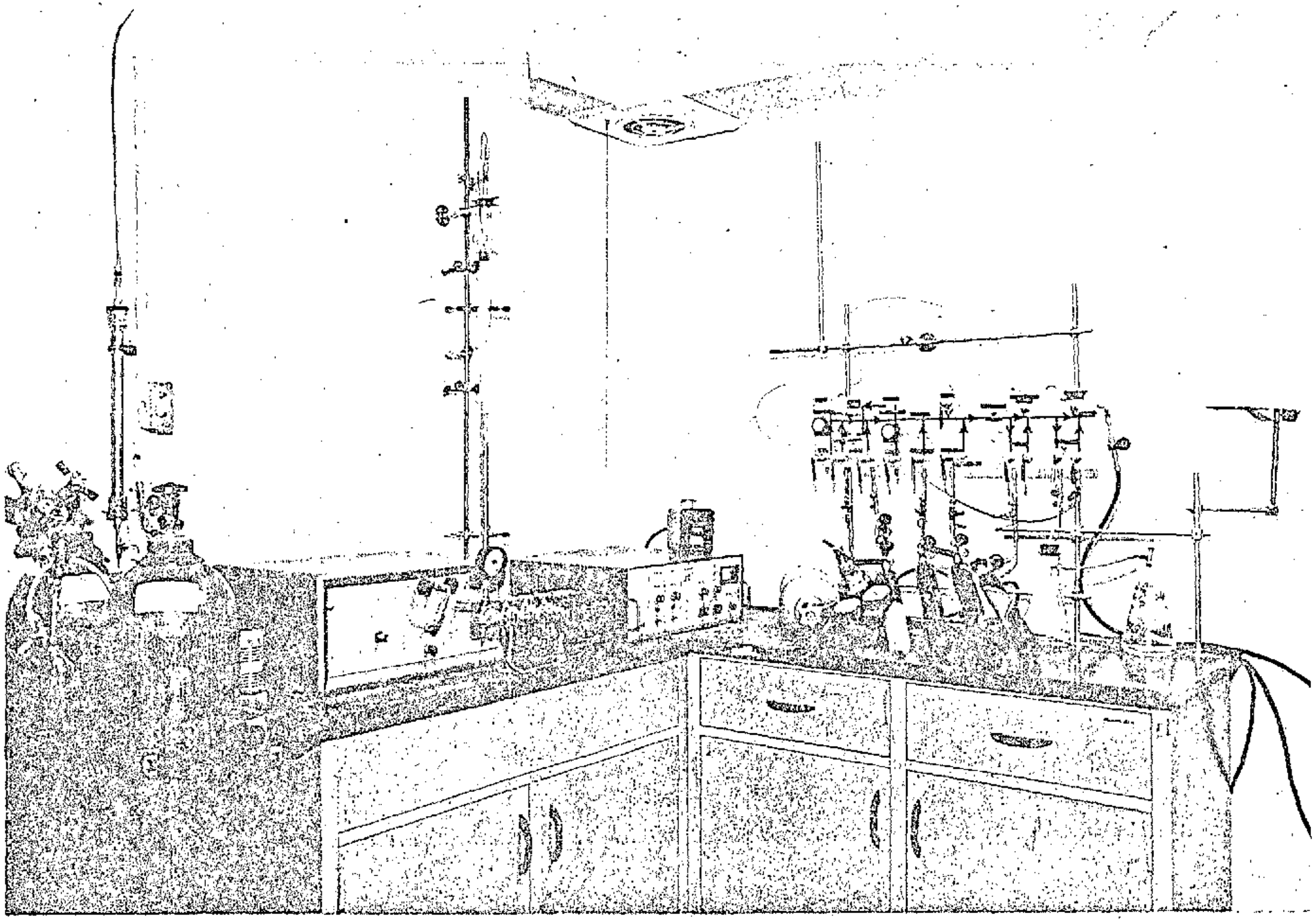


Figure 2. Photograph of Laboratory Test System

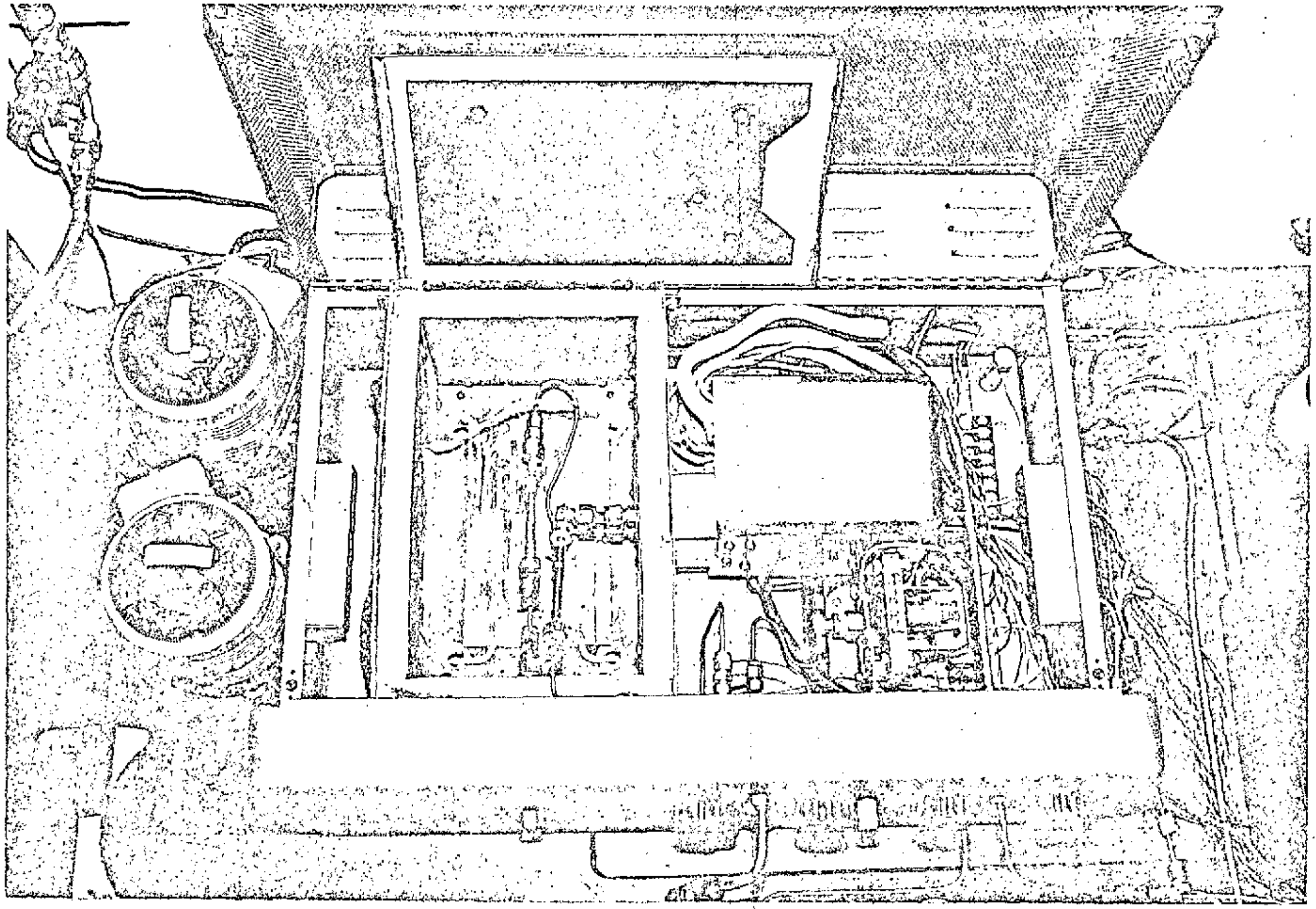


Figure 3. Photograph of Interior of GC Cabinet

the detector electronics. The detector (thermal conductivity) and detector oven were also obtained from the same H-P system. Atop the H-P cabinet is the pyrometer (Thermo Electric Co. Mini Mite Model 70296) used to readout the temperature of the column oven. The temperatures of the detector oven and heated septum-inlet were fixed and needed to be verified only occasionally.

At the far right of Figure 2 is the gas sampling apparatus, which is not shown in Figure 1. With this component, the gases of interest could be flowed to vent in discrete sections of the apparatus. Each of these sections is fitted with a septum to permit syringe removal of the gases for transfer to the GC system. The sampling arrangement could also be used to dilute the gases of interest with an appropriate diluent.

The plumbing used in the test system incorporates both 0.25 and 0.125 in. tubing, largely 316 SS. The 6-port linear sampling valve is a Wilkens Instrument & Research, Inc. Model XA-203. The carrier gas regulation valves (FC-1, -2, -3, and -4) are Brooks Instrument Division Emerson Electric Co. Model 8744. The needle valves located in the sample loop (NV-1, -2, -3, and -4) are Robbins Aviation, Inc. Model INS736S-4D. With the exception of V1, the diaphragm toggle valves are Hoke, Inc. Model C 416K. Valve V1 is a Hoke, Inc. Model T 139-1-8/B2P.

C. DATA ACQUISITION AND REDUCTION

The output of the TC detector and attenuator/amplifier was input to a 10 in. strip chart recorder (Leeds & Northrup Speedomax Model S) and, a computer integrator (Autolab Division Spectra-Physics System I).

D. EXPERIMENTAL CONDITIONS

Each of the candidates tested was loaded in about 1 g quantity into a 10 to 15 cm section of SS tubing (0.25 in.). Flow rate was maintained between 40 and 50 cc/min. Outlet was at atmospheric, where flow rate could be determined by a bubble buret.

Column temperature was initially set at room. Isothermal operation at elevated temperatures was controlled by the Variac, which introduced small but acceptable temperature variations. When temperature programming was practiced, the oven was merely turned on, using a high Variac setting. This furnished a reproducible and nearly linear temperature ramp.

VI. EXPERIMENTAL RESULTS

A. UNDOPED CARBON MATERIALS

Because of its role in the space program, Barnebey-Cheney AC charcoal was tested on the present program to provide reference data. Additionally, however, other charcoals which have been variously suggested for air purification applications were also tested. These, materials are discussed first, since they comprise some of the best media now available off-the-shelf for toxic gas removal.

The conditions for the tests under which the following data were obtained are described in Section V. D, immediately preceding.

1. Barnebey-Cheney AC Charcoal

The average results of the tests with AC charcoal are presented in Table 7. These data justify the studies performed on the present program. Retention of CO and NO_2 was minimal. Room temperature retention of NH_3 and SO_2, on the other hand, was significant. In these cases, the tests were abandoned without elution of NH_3 or SO_2 after 16 and 67 min, respectively. Retention of CO_2 was modest.

2. Barnebey-Cheney GI Charcoal

The results obtained with this material are given in Table 8. Like the AC grade charcoal, GI provides insignificant retention of CO. The GI charcoal appears to furnish better hold-up for NH_3, CO_2, and NO_2. Its retention of SO_2 is less than that of AC charcoal.

In the case of NO_2, a small portion is apparently decomposed soon after column contact. Other decomposition products result when the adsorbent is taken through a temperature ramp.

It was found that the behavior of NO_2 on Barnebey-Cheney GI charcoal is highly dependent upon the activation temperature and conditioning of the adsorbent following activation. GI Charcoal activated up to 360°C for several hours, that had not been exposed to other test gases or NO_2, will retain the latter for more than 120 minutes during a temperature program ranging from 140°C to 320°C. The same column, after exposure

TABLE 7. RETENTION CHARACTERISTICS OF BARNEBEY-CHENEY AC CHARCOAL

(40 to 100 Mesh)

			Elution Temperature, °C	
Test Gas	Vol., cc	R_t, min.	Isothermal Tests	Temperature Programmed Tests[a]
Carbon Monoxide	0.10	0.35	20	-
	0.080	0.16	200	-
	0.075	0.10	340	-
Ammonia	0.10	16.[b]	20	-
	0.10	83.	-	167 (20-420)
	0.080	0.28	260	-
	0.10	0.19	340	-
Nitrogen Dioxide	0.10	0.33	20	-
	0.080	0.15	200	-
	0.075	0.09	340	-
Sulfur Dioxide	0.10	67.[b]	20	-
	0.080	0.9	200	-
	0.10	86.	-	136 (20-420)
	0.080	0.2	340	-
Carbon Dioxide	0.10	3.1	20	-
	0.080	0.15	200	-
	0.050	0.10	340	-

Footnotes: a) Program Range shown in parentheses
b) Test aborted at this time w/o elution

TABLE 8. RETENTION CHARACTERISTICS OF BARNEBEY-CHENEY GI CHARCOAL (60 to 80 Mesh)

Test Gas	Vol., cc	R_t, min.	Elution Temperature, °C Isothermal Tests	Elution Temperature, °C Temperature Programmed Tests[a]
Carbon Monoxide	0.040	0.3	25	-
	"	0.2	80	-
	"	<0.1	260	-
Ammonia	0.050	120[b]	30	-
	"	20[b]	80	-
	"	47	-	170 (80-305)
Nitrogen Dioxide	0.080	13[c]	80	-
	"	120[b, d]	-	- (80-360)
Sulfur Dioxide	0.10	25	-	129 (80-150)
Carbon Dioxide	0.10	21	-	117 (70-160)

Footnotes: a) See Table 7
b) See Table 7
c) Activated column previously exposed to other test gases
d) Previously unused, activated (360°C) column

to and elution of other test gases, will furnish substantial elution signals attributable to NO_2 and/or its decomposition products after 5 to 6 minutes at 80°C.

3. Barnebey-Cheney VG Charcoal

Table 9 displays the results obtained with this charcoal. Again, CO retention is seen to be slight, while the hold-up for CO_2 is less than that of AC charcoal, which only feebly retains either gas. The retention of NH_3, NO_2, and SO_2 on VG charcoal is superior to that of AC charcoal but not GI charcoal. As on the latter, these three test gases are chemically decomposed at the temperatures which produce desorption signals.

4. WestVaco Nuchar WV-L Charcoal

The performance of this charcoal with respect to the five test gases (Table 10) resembles that of Barnebey-Cheney AC charcoal. The latter, however, does afford a somewhat better retention of SO_2. As all the other charcoals tested, the WV-L material does not appear to release NH_3, NO_2, and SO_2 without chemical conversions occurring.

It is recognized of course that in the event of chemical conversion of an adsorbed specie, the process is thermally controlled and R_t may largely pertain to the behavior of the formed species. In the case of temperature programmed tests, R_t may well have represented the time to reach activation energy levels. This appears to be the situation with the AC, GI, and WV-L charcoals with respect to NH_3 and SO_2. Although the long R_t's vary considerably (the program ranges differ), the elution temperatures fall in a fairly narrow range for all 3 materials. Yet, at only moderately higher (isothermal experiment) temperatures, R_t becomes so short as to suggest an induction rather than a gradient sorption process. Again, however, the GC term, R_t, is useful for comparison purposes even if not always correctly utilized as a term.

5. WestVaco Nuchar WV-G Charcoal

With the exception of the unusual behavior of NH_3, this material furnishes about the same performance as does the WV-L charcoal (Table 11).

TABLE 9. RETENTION CHARACTERISTICS OF BARNEBEY-CHENEY VG CHARCOAL

(60 to 80 Mesh)

Test Gas	Vol., cc	R_t, min.	Elution Temperature, °C: Isothermal Tests	Elution Temperature, °C: Temperature Programmed Tests[a]
Carbon Monoxide	0.050	0.32	40	-
	0.025	0.20	180	-
	0.025	0.12	260	-
Ammonia	0.060	35[b]	40	-
	0.075	1.1	180	-
	0.025	0.13	260	-
Nitrogen Dioxide	0.060	30[b]	45	-
	0.10	2	50	-
	0.10	0.24	180	-
	0.10	0.14	330	-
Sulfur Dioxide	0.10	71[b]	45	-
	0.075	0.45	180	-
	0.10	0.46	320	-
Carbon Dioxide	0.060	0.18	40	-
	0.025	0.13	180	-
	0.025	0.05	260	-

Footnotes: See Table 7

TABLE 10. RETENTION CHARACTERISTICS OF NUCHAR WV-L CHARCOAL

(40 to 100 Mesh)

Test Gas	Vol., cc	R_t, min.	Elution Temperature, °C Isothermal Tests	Elution Temperature, °C Temperature Programmed Tests[a]
Carbon Monoxide	0.080	0.28	30	-
	0.070	0.17	200	-
	0.080	0.13	360	-
Ammonia	0.10	45[b]	30	-
	0.10	66	-	186 (30-360)
	0.070	52	200	-
	0.10	0.25	330	-
	0.10	0.18	360	-
Nitrogen Dioxide	0.080	0.27	30	-
	0.070	0.17	200	-
	0.60	0.13	360	-
Sulfur Dioxide	0.080	28[b]	30	-
	0.080	38	-	154 (30-360)
	0.080	0.5	200	-
	0.10	0.17	360	-
Carbon Dioxide	0.080	1.33	30	-
	0.070	0.20	200	-
	0.060	0.15	360	-

Footnotes: See Table 7

TABLE 11. RETENTION CHARACTERISTICS OF WESTVACO NUCHAR WV-G CHARCOAL

			Elution Temperature, °C	
Test Gas	Vol., cc	R_t, min.	Isothermal Tests	Temperature Programmed Tests[a]
Carbon Monoxide	0.10	0.3	25	-
	0.10	0.17	190	-
	0.10	0.13	340	-
Ammonia	0.10	21[b]	25	-
	0.10	10[b]	190	-
	0.20	148	-	510 (340-510)
Nitrogen Dioxide	1.00	0.25	25	-
	0.20	0.17	190	-
	0.20	0.13	340	-
Sulfur Dioxide	0.10	39[b]	25	-
	3.0	3.2	25	-
	0.20	0.75	190	-
Carbon Dioxide	0.10	1.6	25	-
	0.10	0.17	190	-
	0.060	0.13	340	-

Footnotes: See Table 7

In the tests with SV-G charcoal, SO_2 was introduced at two widely different levels so as to detect saturation. The results obtained indicate that while chemisorption probably operates, the number of sites are limited.

6. Cabot Graphon

The test results for this material are shown in Table 12. For all practical purposes, this modified charcoal behaves as if inert to all of the test gases.

7. Supelco Carbosieve B

The behavior of this material with the five test gases is shown in Table 13. In general, Carbosieve B and AC charcoal appear to be of about the same efficiencies for the gases they can hold up (NH_3 and SO_2).

B. NICKEL DOPED MATERIALS

1. Nickel Chloride Doped (70%) 13X Molecular Sieves

This material, representing the first attempt on the program to achieve superior air-purification media, produced encouragement. As seen in Table 14, it does, unlike all the carbon materials discussed earlier, retain CO, if only slightly. The effect, however, does tend to vindicate the decision to place emphasis on TM-doped materials.

The performance of the 70% $NiCl_2$ doped 13X molecular sieves with NH_3 was very good and apparently reversible. However, a low level bleed occurred during the temperature programmed tests. In one case, this was seen 3 min (93°C) after the program was initiated.

The undoped form of the adsorbent is also effective with respect to NH_3 but, it is believed, nowhere to the extent demonstrated by the doped material.

2. Nickel Chloride Doped (70%) AC Charcoal

This material furnished very interesting results with CO. The R_t data in Table 15 pertain to only the unretained portion of the CO.

TABLE 12. RETENTION CHARACTERISTICS OF CABOT'S GRAPHON

(60 to 80 Mesh)

Test Gas	Vol., cc	R_t, min.	Elution Temperature, °C Isothermal Tests	Elution Temperature, °C Temperature Programmed Tests
Carbon Monoxide	0.020	0.11	35	-
	0.020	0.11	100	-
	0.020	0.06	290	-
Ammonia	0.020	0.10	35	-
	0.040	0.10	100	-
	0.020	0.12	290	-
Nitrogen Dioxide	0.025	0.13	61	-
	0.040	0.07	100	-
	0.020	0.01	290	-
Sulfur Dioxide	0.025	0.20	50	-
	0.020	0.12	100	-
	0.020	0.07	290	-
Carbon Dioxide	0.020	0.11	35	-
	0.020	0.13	100	-
	0.020	0.06	290	-

TABLE 13. RETENTION CHARACTERISTICS OF SUPELCO CARBOSIEVE B

(60 to 80 Mesh)

			Elution Temperature, °C	
Test Gas	Vol., cc	R_t, min.	Isothermal Tests	Temperature Programmed Tests[a]
Carbon Monoxide	0.100	0.27	35	-
	0.075	0.13	200	-
	0.050	0.14	300	-
Ammonia	0.100	25[b]	35	-
	0.075	0.25	200	-
	0.050	0.18	300	-
Nitrogen Dioxide	0.100	0.23	35	-
	0.050	0.15	200	-
	0.050	0.17	300	-
Sulfur Dioxide	0.100	32[b]	35	-
	0.075	0.45	200	-
	0.050	0.23	300	-
Carbon Dioxide	0.100	0.93	35	-
	0.075	0.11	200	-
	0.050	0.12	300	-

Footnotes: See Table 7

TABLE 14. RETENTION CHARACTERISTICS OF NICKEL CHLORIDE DOPED (70%) 13X MOLECULAR SIEVES

Test Gas	Vol., cc	R_t, min.	Elution Temperature, °C	
			Isothermal Tests	Temperature Programmed Tests[a]
Carbon Monoxide	0.10	2.0	25[c]	-
	0.60	0.25	25[d]	-
	0.10	0.13	230	-
Ammonia	1.0	19[b, c]	25	-
	7.6	2.2[d]	25	-
	6.0	32[b, c]	25	-
	6.0	49	-	301 (25-515)
	0.60	44[b]	230	-
	0.60	68	-	457 (230-515)

Footnotes: [a] See Table 7

[b] See Table 7

[c] Freshly activated bed

[d] Column previously exposed to test gas

TABLE 15. RETENTION CHARACTERISTICS OF NICKEL CHLORIDE DOPED (60%) AC CHARCOAL

(60 to 100 Mesh)

			Elution Temperature, °C	
Test Gas	Vol., cc	R_t, min.	Isothermal Tests	Temperature Programmed Tests[a]
Carbon Monoxide	1.0 to 23.0	0.2[e]	25	-
	1.0	0.2[e]	260	-
Ammonia	2.0	167[b]	25	-
	20.0	6[d]	25	-
	5.0 to 20.0	2.2[d]	263	-

Footnotes: a) through d); See Table 14
e) Partial elution of test gas

In the room temperature tests, only about 70% of the CO came off the bed. Removal of the balance required temperatures near 200°C. It is obvious from this that the material does sorb CO strongly but the number of available sites is limited. This problem may be corrected by developing alternative preparation techniques.

The performance of the $NiCl_2$ doped charcoal was also very impressive for NH_3. Although a bleed was noted (19 minutes after room temperature injection), the material slowly eluted was probably N_2.

In the two 25°C isothermal tests, the widely different R_t's obtained result from preconditioning of the column. In the case where no elution had occurred after 167 min into the run, the column was freshly activated and had not been previously exposed to the test gas. In the second case, the column had already been saturated with 66 cc NH_3, yet retained an additional 20 cc for 6 min. The material thus suggests excellent potential.

C. PERMANGANATED MATERIALS

1. Permanganated (3%) Alumina - Purafil

Because of the success ARLI workers had had in the removal of NO_2 with MnO_2-treated silica gel,[*] testing of the related (commercial) material, Purafil, was suggested. At room temperature, it was found to have no effect on CO (2.0 cc), either retentive or catalytic. At 150°C, however, 10 cc of CO is quantitatively converted to CO_2, as demonstrated by IR spectra of the eluates. The CO_2 eluted in 1.33 min from a 40 to 100 mesh column.

The results with NH_3 were also impressive. At 180°C, injections of 1.0 to 10.0 cc of NH_3 resulted in 100% conversion of the test gas, in most but not all runs. The product formed was found to be transparent over the IR range from 2 to 6 μm. It was therefore assumed to be N_2.

Although Purafil does appear to be highly promising, some caution should be exercised. It actually behaves very similarly to

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[*] In work done in the mid-fifties involving rocket propellants.

hopcalite, also a Mn-containing material. Hopcalite, however, is counterindicated for spacecraft use because of other unfortunate characteristics. It catalytically converts certain innocuous organic compounds to highly toxic species. An example of this is the dehydrohalogenation of halocarbons. In the case of trichloroethylene, this would lead not only to the formation of HCl but of dichloroacetylene.

2. Permanganated (3%) Silica Gel

The NO_2-removal agent that had inspired the testing of Purafil was itself also tested. The product prepared was 28 to 200 mesh silica gel permanganated to 3%.

This material proved completely ineffective with respect to CO. One to ten cc injections at isothermal test temperatures ranging between room and 177°C produced neither retention or conversion.

In tests with NH_3, more encouraging results were obtained. Using 10.0 to 20.0 cc injections of NH_3 at room temperature, a major part eluted immediately. Up to 40% of the gas did not elute, however, and this required a temperature program up to 204°C to remove. The gas eluted was shown to be NH_3 by its IR spectra. This overall behavior strongly suggests limited-site chemisorption.

Runs with NH_3 made at elevated temperatures resembled those with Purafil. At 121°C, a 5.0 cc sample of NH_3 was almost quantitatively converted to N_2 (as determined by IR transparency). The small amount of NH_3 that was not converted was very difficult to elute. This occurred only after 33 min at 121°C, followed by a temperature ramp taking an additional 25 min to reach the elution temperature of 400°C.

Finally, the permanganated silica gel was tested with NO_2, a procedure that time did not permit in the case of Purafil. The test gas (2.0 cc) was completely converted to unidentified species at both room and 124°C. Most of the reaction products eluted immediately (0.2 min), although a small fraction required heat to remove. In the case of the NO_2 adsorbed and unconverted in the room temperature run, this fraction was thermally released at 204°C, after 17 min at room temperature and 8 min into the ramp.

D. OTHER CANDIDATES

1. Rhenium Doped (2%) AC Charcoal

This material proved to be of questionable value, although it was only tested for its effectiveness for CO. Room temperature retention of the latter test gas was insignificant, or about the same as obtains on the undoped support. When tests were run at 389°C, about 7% of the 10 cc of CO injected was converted to CO_2. While this is unimpressive in itself, one can speculate that catalytic efficiency might be significantly enhanced using higher dopant loadings or more appropriate operating parameters.

2. Lithium Hydroxide Doped (10%) AC Charcoal

Although the individual components in this candidate are materials already used in spacecraft, potential benefits may result by combining them to increase the surface area and thus the effectiveness of the alkali metal hydroxide. The results of this experiment are shown in Table 16.

Of the two acid gases tested, NO_2 was retained very little, while SO_2 appeared to be nicely managed by the system. In the first 25°C test listed, the amount of SO_2 represented about 50% of the amount required to saturate the bed. In the second test, the same amount was injected but onto a column that had been saturated with SO_2. In the 3rd and 4th tests, it was found that performance would be lost if the column had previously been exposed to NO_2. This is a very curious phenomenon, since the system does not retain NO_2. In the 5th of the room temperature tests, the column had been thermally reactivated. The R_t, however, was considerably shorter than that for a fresh column. Also, some type of low level bleed was noted from the reactivated bed after 2.6 min into the room temperature run.

3. Mixed Rare Earth (RE) Oxide Exchanged Molecular Sieves (Linde SK500)

This material (extruded 20 mesh) proved ineffective with both CO and NO_2 in terms of either retention or conversion of these

TABLE 16. RETENTION CHARACTERISTICS OF LITHIUM HYDROXIDE DOPED (10%) AC CHARCOAL

Test Gas	Vol., cc	R_t, min.	Elution Temperature, °C Isothermal Tests	Elution Temperature, °C Temperature Programmed Tests[a]
Nitrogen	0.10	0.2	25	-
Dioxide	0.10	0.05[d]	220	-
Sulfur	20.0	54	25	-
Dioxide	20.0	10[d]	25	-
	2.0	0.2[d]	25	-
	0.60	1.0	25	-
	17.5	29	25	-
	2.5	1.6	230	-
	1.1	8[b]	230	-

Footnotes: a) through d); See Table 14

test gases. In the case of CO, 1.0 cc slugs were run at 25 and 263°C. In the case of NO_2, 1.0 to 5.0 cc injections were run, but only at room temperature.

The behavior with NH_3 was another matter. Five tests (1 to 10 cc) were run at 263°C and in four, no recovery was made after waiting as long as 72 min. In the 5th test 20 cc of NH_3 was injected after the column had been previously loaded with 36 cc of NH_3. The test gas (verified by titration) then came off in 3.75 min.

4. Ruthenium Exchanged (4%) Molecular Sieves (Linde SK40)

Like the previous material, this candidate proved a failure with respect to both CO and NO_2. Again, however, the extruded 20 mesh agent was tested at 3 temperatures (25, 150, and 370°C) with CO, but only at room temperature with NO_2. This should be extended to include higher temperatures where catalytic effects may be induced.

5. Specially Activated Linde 5A Molecular Sieves

The undoped molecular sieves had been specially activated by Applied Science Labs, Inc. It was tested on the present program because it was reported to have unusually good retention characteristics for CO. The material was found to be essentially identical in performance with the 5A molecular sieve column (activated by project personnel) used in the reference column of the experimental apparatus.

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