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THE IDENTIFICATION OF TRENDS IN OUTGASSING TECHNOLOGY

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ABSTRACT

A large amount of chemical analysis data involving identification of outgassing products from spacecraft, experiment modules, and support equipment has been accumulated at the Goddard Space Flight Center over the past ten years. In order to gain some insights into significant trends in the occurrence of outgassing problems and to assist in the implementation of meaningful materials selection policies, these data have been reduced to a computer compatible format and subjected to a variety of relevant program operations. From these data a list of the most troublesome outgassing species has been compiled and several useful and interesting materials' correlations have been developed.

INTRODUCTION

It has been recognized for a long time that outgassing of organic materials and subsequent condensation of the products on critical surfaces of flight hardware can be a serious problem. Detrimental effects include attenuation of optical signals in instrument systems, alterations of alpha/epsilon ratios of thermal control surfaces, corona discharge effects in high voltage electronics, and various detector malfunctions.

In order to guard against the occurrence of such problems, Goddard maintains a system of surveillance of outgassing levels in its thermal vacuum test facilities. This system involves operation of a liquid nitrogen-cooled cold finger to trap outgassed species in each vacuum facility during hardware testing. At the conclusion of each test, the condensed organic residues are washed from the cold finger and taken to the analytical organic chemistry laboratory for quantification and identification. These chemical analyses are performed using advanced instrumental methods including infra-red spectrophotometry and mass spectrometry. The results of these analyses are used routinely to indicate the acceptability of flight hardware or to flag down problem materials and track down outgassing sources.

In addition to this surveillance activity, an extensive materials' outgassing evaluation program has been conducted through the years by the Materials Control and Applications Branch. Through this effort, polymeric materials are subjected to a standard test condition (24 hours at 125^{o}C in vacuum with a room temperature (25^{o}C) collector plate) resulting in determination of total weight loss and total volatile condensable material (CVCM). This test has been accepted as ASTM-E-595-77, and thousands of materials have been evaluated. This information is being used as a basis for recommending materials for space flight use in order that the incidence of problems related to outgassing might be reduced. All spacecraft projects are required to include in their design requirements, a materials review, which contains an evaluation of outgassing potential. The effectiveness of this materials engineering effort can be shown both by the degree of success of our flight programs and by reductions in the occurrence of time and money-consuming problems during the test and integration phase of spacecraft preparation.

An effort has now been made to develop more specific and technical information concerning the effectiveness of our programs by computerizing all of the analytical chemistry data accumulated over the last ten years of outgassing residue analysis. Pertinent data describing the test item, test facility, and the amount and composition of each sample were entered in the data bank. Computer operations were then developed and employed in order to generate data which might show significant events and trends in the occurrence of outgassing problems through the years. By finding specific changes in the frequency of occurrence of individual outgassed species and correlating them with known materials' usage practices, the impact of previous materials' decisions can be estimated. Also, an assist in making logical materials selections and establishing meaningful policies for future spacecraft projects may be obtained.

CHEMICAL ANALYSIS DATA

The scope of the analytical data used to form this study has been restricted somewhat in the hope of keeping it consistent and compatible. Analytical results of cold finger residues from thermal vacuum facilities at Goddard and some of its contractors have been included as well as witness mirror residues and wipe samples from various flight hardware which either had contamination problems or potential problems. However, analytical data from known materials, suspected sources, micro-CVCM tests, and contamination problems not related to outgassing have been excluded. The total number of analytical reports used was 1294 and covered the time period from 1970 through 1979.

Procedures for obtaining good analytical samples of thermal vacuum outgassing products have been developed and remained essentially unchanged throughout this period. The cold finger is a small cylindrical device (Figure 1) installed in the thermal vacuum facility and cooled with liquid nitrogen during part or all of a thermal vacuum operation in order to condense any volatile species which might be present. This scavenger process results in accumulation of sufficient sample for chemical analysis. The cold finger is warmed to room temperature during the back filling phase which results in maximum retention of condensables while avoiding condensation of water vapor from the air. The residue is then washed from the cold finger with spectrograde 2-propanol and the solution sent to the chemistry laboratory for analysis.

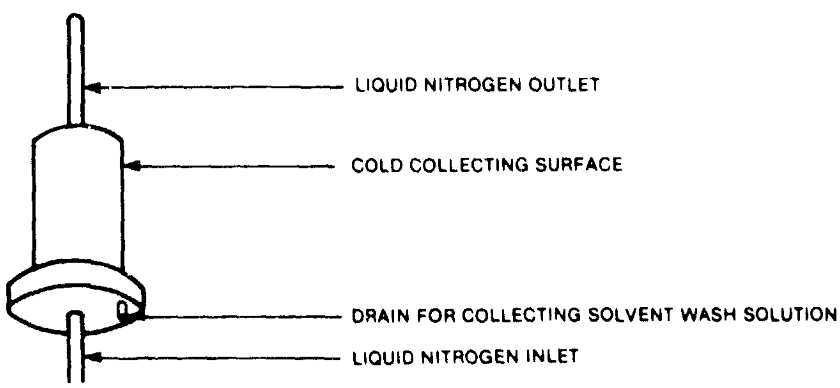

Figure 1 Diagram of Chamber Cold Finger

The cleanliness profile of spacecraft surfaces can be determined by taking wipe samples. The procedure involves the use of precleaned cotton swabs dampened with alcohol to wipe areas from 25 to 50 square inches. In order to obtain sufficiently clean cotton swabs, it is necessary to extract them in a Soxhlet extractor for 24 hours with chloroform followed by 24 hours with alcohol. This process removes all traces of wood resins, cotton seed oil, and adhesive which would interfer with the analysis. It is also important to make certain that the surfaces to be wiped are not affected by the alcohol solvent, ie., metallic sufaces, Kapton, Teflon, anodized, etc.

Although there have been a number of significant advances in our analytical technique and capability through the years, the basic procedure has been somewhat constant. The first step for a cold finger analysis is the gentle removal of the solvent by warming on the steam bath. The residue is weighed and is then ready for infra-red analysis. Wipe sample residues must be extracted from the swabs using hot alcohol and rinsing techniques and subsequent solvent removal on the steam bath.

The infra-red spectrum of one of these samples is most efficiently obtained using the technique called "cating a film". The sample is dissolved in a few drops of chloroform and applied to a polished potassium bromide (KBr) disc. Evaporation of the chloroform leaves a thin film of the sample. The fingerprint absorption spectrum is then obtained by scanning from 2½ to 20 microns with a research grade IR spectrophotometer. Interpretation of IR data can provide good identification of homogenous samples, the prominent constituents of simple mixtures, and at least the more significant functional groups in complex mixtures.

When required, more specific identifications can be obtained using advanced mass spectrometric techniques. With this method the sample is ionized by electron bombardment in the mass spectrometer and the mass fragmentation pattern of the resultant positive ions is recorded. This pattern is very specific for each chemical species and results in unique chemical identification for each compound. Moreover, by the use of the combination gas chromatograph/mass spectrometer (GC/MS) a complex mixture can be separated and identification obtained for each of its components. Cold finger condensables are especially amenable to this technique since the very properties which allow mobility in a vacuum system also make the material suitable for chromatographic separation. If the GS/MS data does not account for all of the features shown by the infra-red scan, then a batch-type mass spectrum must be obtained using the direct insertion probe. Some of the materials which require this treatment are organic acids, amines, and higher molecular weight compounds.

A COMPUTER FORMAT FOR THE ANALYTICAL DATA

A computer format was developed to allow formation of a data bank containing the maximum amount of self-consistent information from chemical analysis reports from log books spanning a ten year period. These reports represent the work of different chemists using an evolving analytical capability and advancement in instrumentation and, therefore, contain some inherent inconsistencies. In addition, there have been some variations in thermal vacuum facilities' operating procedures and policies. In spite of these possible sources of inconsistencies and the fact that the reports were never intended to be suitable for computerization, the data format shown below was established. Eighty-entry Fortran coding card were used-one for each analytical report-with the following number assignments:

TABLE I. CODING CARD FORMAT

	Column Numbers
Analysis report number	1-5
Analysis date	6-11
Job order number	12-14
Project name	15-19
Test item name	20-29
Type of test	30-31
Facility identification	32-34
Type of sample	35-36
Sample weight	37-39
Type of analysis	40
Materials identified	41-45, 46-50, 51-55, 56-60, 61-65, 66-70
Were there more?	71

Abbreviations and numbers were used where required in order to fit this format. The "Type of test" refers to the hardware testing program being monitored while the "Type of sample" refers to the method of sample collection, i.e., cold finger, wipe sample, etc. Facility identifications are the chamber numbers for the Goddard units and arbitrarily assigned numbers for contractor facilities as shown in TABLE II. Sample weights are applicable only to cold finger samples and are listed in milligrams. The "Types of analysis" includes infra-red spectrophotometry, direct insertion mass spectrometry, and gas chromatography/mass spectrometry and combinations of these techniques which are number coded as shown in the table (TABLE II).

TABLE II. CODE NUMBERS AND ABBREVIATIONS

I Type of Analysis

	Number
Infra-red only (IR)	1
Mass Spectrometer - direct probe (MS)	1
Gas Chromatography/Mass Spectrometry (GC/MS)	3
IR + MS	4
IR + GC/MS	6
MS + GC/MS	7

II Facility Identification

	Number
Goddard Thermal Vacuum Chambers	236-245
Solar Environmental Simulator (GSFC)	290
University College London (UCL)	300
RCA Hightstown, N J	301
MSDS (England)	302
Jet Propulsion Laboratory (JPL), CA	303
Honeywell Radiation, Lexington, MA	304
Ford Aerospace, CA	305
ITT, Fort Wayne, IN	306
Fairchild, MD	307
Lewis Research Center, OH	308
General Electric, Valley Forge, PA	309
Gulton Ind., CA	310
Santa Barbara Research Center, CA	311
Cape Kennedy	312
RFI Clean Room (GSFC)	313
Wallops Island Flight Center, VA	314
Lockheed Missiles & Space, CA	315
Sperry Flight Systems, AZ	316

Computer operations on this data bank were designed to list data, sorting according to different categories such as test item, project, primary material, or frequency of occurrence of a material using various control parameters. Attempts were then made to illustrate interesting and informative materials' correlations, trends in types of occurrences, and technology areas in which improvement has been made or in which further study must be concentrated.

RESULTS AND DISCUSSION

In order to attempt to identify the kinds of materials which have most often been responsible for the observed outgassing problems at Goddard and significant trends in their rates of occurrence, programs for data sorting were written with the following kinds of parameters:

- -Count the number of times each material occurred as either the primary or secondary material.
- -List the count in quarter year increments.
- -Limit data to include only samples with ten or more milligrams weight.

Identification of Materials

From this listing, which disregards all samples where the amount of outgassing was less than 10 milligrams and includes only the predominant two species identified in each sample, a table of the most often reported problem materials was generated (TABLE III). It should be pointed out that many of these names used for identification are for generic classes and include large numbers of materials, for instance, aliphatic hydrocarbons, esters, and silicones, while others are for specific individual compounds such as di(2-ethyl hexyl)phthalate (DEHP or DOP), dibutyl phthalate (DBP), hydroxy methoxy benzophenones (HMBZP), and 2,6 ditertiary butyl p-cresol (BHT). Thus, we have shown that the most often found individual species is DEHP.

TABLE III. MATERIALS FOUND IN COLD FINGER RESIDUES

(Samples v 10 mg - April, 1970 Through December 1979)

Material Code	Number of Occurrences
1. ALHYD	196
2. MESIL	131
3. DEHP	118
4. ESTER	100
5. PHEST	29
6. DBP	27
7. ARMHY	23
8. MPHSI	19
9. HMBZP	19
10. UPETH	18
11. BHT	16
12 DC704	16
13. RTV56	13
14. ORGAC	10
15. TCEPH	8
16. DEHAZ	6
17. TPP	6
18 DTAMQ	5
19. PCB	5
20 DEHAD	4

Trends in Occurrences of Generic Classes

In TABLE IV these individual materials have all been incorporated into the appropriate generic classes and the number of occurrences and their percentages calculated. This listing shows that esters (36%), aliphatic hydrocarbons (23%), and methyl silicones (16%) account for 75% of the outgassing problems observed during the last ten years of thermal vacuum testing at Goddard.

TABLE IV. PRINCIPLE MATERIALS BY GENERIC CATEGORIES

Category	Number of Occurrences	Percentage
1. All Esters	298	36
2. Aliphatic hydrocarbons	196	23
3. Methyl silicones	132	16
4. Aromatic silicones	48	5.7
5. Antioxidants	40	4.7
6. Aromatic hydrocarbons	23	2.8
7. Polyurethane derivatives	18	2.2
8. Organic acids	10	1 1
9. Other materials	73	9

An attempt was made to show possible trends in the rates of occurrence of these classes of compounds by plotting the number of times they were found in samples over ten milligrams as a function of calendar year. Immediately it was discovered that the large differences in the numbers of reports issued from one year to the next resulted in discontinuities in all frequency curves for certain years. This was corrected by calculating a normalizing factor for each year (TABLE V) in order to weight results according to the total amount of analytical activity that year.

TABLE V. CALCULATION OF ANNUAL FREQUENCY NORMALIZATION FACTORS

Year	Total Number of Reports	Fraction of Average	Normalizing Factor
1970	29	129/29	4.4
1971	59	129/59	2.2
1972	164	129/164	0.79
1973	190	129/190	0 68
1974	115	129/115	1.12
1975	61	129/61	2.1
1976	184	129/184	0.70
1977	215	129/215	0 60
1978	102	129/102	1 3
1979	131	129/131	0 98
TOTAL	10 √1294		
AVERAGE	129		

Using these factors and the quarterly count data from the computer sorting, rate curves were plotted for the three major classes of contaminants, namely, esters, aliphatic hydrocarbons, and methyl silicones (Figure 2). From the curves it can be seen that real progress in reducing the instances of serious outgassing was made between 1970 and 1975. This time period correlates well with the initiation and acceptance of materials engineering practices dictating the incorporation of low outgassing materials only, into flight hardware. However, from 1975 to the present, little additional improvement

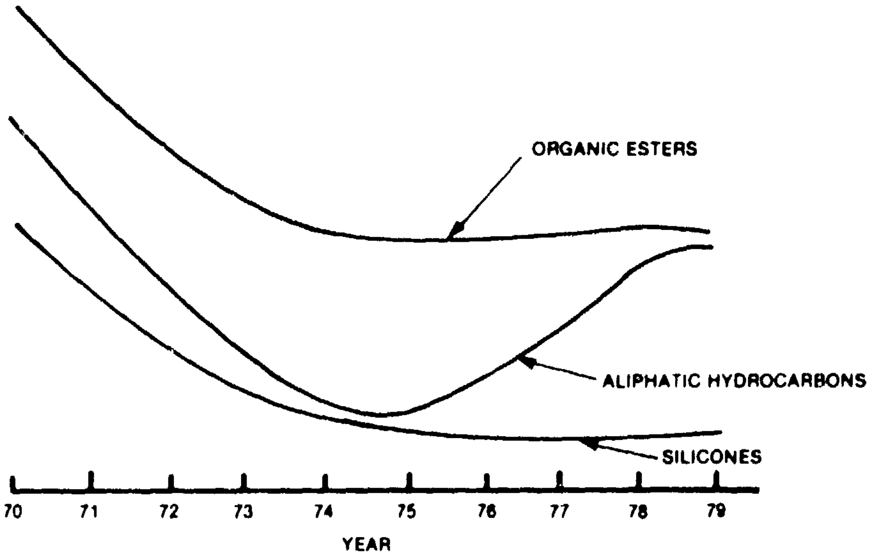

Figure 2 Normalized Frequency of Occurrence of Excessive Outgassing by Chemical Class

can be shown, and, in fact, the occurrence of serious outgassing due to aliphatic hydrocarbons has risen significantly. These facts indicate that increased research into possible sources and differentiation of outgassed aliphatic hydrocarbon species should be intitated and that schemes for more effective materials control and cleanliness procedures should be developed.

Outgassing from Solar Panels

A dramatic correlation between materials selection and outgassing was shown in the case of solar panel bakeouts. Historically, these have been one of the largest sources of condensable outgassing material and have resulted in excessive expenditures of time and money to perform repetitive thermal vacuum bakeouts in order to reduce the outgassing rates to acceptable levels. Some of the high outgassing solar cell adhesives used over the years have been Sylgard 182 and 184, RTV 511, and RTV 560/RTV 580. TABLE VI shows the number of thermal vacuum tests performed on solar panels at Goddard for various projects along with the number of

TABLE VI OCCURRENCE OF SERIOUS OUTGASSING FROM SOLAR PANELS

Project	Test Year	Number Over 10 mg	Total Tests
RAE-B	1970	4	55
IMP-I	1970-73	8	8
SSS-A	1970-71	2	2
OAO	1970-72	10	10
IMP-J	1973	7	9
IEU	1974-75	12	2
ISEE-A	1976-77	1	11

these tests which resulted in cold finger residues over ten milligrams. The dramatic improvement for ISEE-C, indicating only one bad outgassing event out of eleven tests (9%) as compared to 91% bad for all previous projects, is a direct result of changing from RTV 511 to RTV 566 solar cell adhesive. Incidently, the one occurrence was not due to the cell adhesive but was shown to be caused by the use of an improperly cured polyurethane material used elsewhere on the panel.

Outgassing from Thermal Blankets

A similar improvement in outgassing performance has been shown for thermal blankets (TABLE VII). In 1972-1974 eight out of nine thermal blanket bakeouts resulted in excessive outgassing, whereas, in 1977-1979, only three of twenty were in the excessive range. In this case, however, no clear-cut materials' correlation could be found and it is likely that the improvement can best be explained as due to the institution of better cleanliness procedures during fabrication and handling.

TABLE VII OCCURRENCE OF SERIOUS OUTGASSING FROM THERMAL BLANKETS

Project	Test Year	Number Over 10 mg	Total Tests
SAS-B	1972	5	5
ERTS	1972-73	2	3
ATS-F	1974	1	1
AEM-A	1977-78	1	3
IUE	1977	1	4
MMS	1978	1	4
SMM	1978-79	0	9

Antioxidant from Wire Insulation

The appearance of a unique material in many cold finger residues since 1976 has caused an interesting and enlightening investigation. This material, known as hydroxy, methoxy benzophenones, has originated from certain electronics packages and a large number of cable bakeouts. Eighteen out of twenty two samples where it was found were in the excessive range, i.e., over ten milligrams. A little research has shown that this substituted benzophenone is the antioxidant/uv stabilizer in Raychem "Spec 44" wiring insulation. Our previous outgassing test data of Spec 44, done in 1976, showed this material to be acceptable and repeat tests this year also support this conclusion. However, it appears that the antioxidant is marginally condensable and can be expected to cause problems only on surfaces cooled below room temperature. The appearance of large amount of this material in cold finger residues seems to be caused by the fact that there were very large amounts of wire used and the borderline condensable material was collected on cold surfaces. For future space flight use, Raychem has agreed to produce their "space grade" Spec 44 wire without this additive.

Miscellaneous Materials' Outgassing Trends

Other attempts to correlate materials' usage with outgassing results have not been so unequivocal. For instance, tracking of the rate of occurrence of four interesting specific compounds is shown in Figure 3.

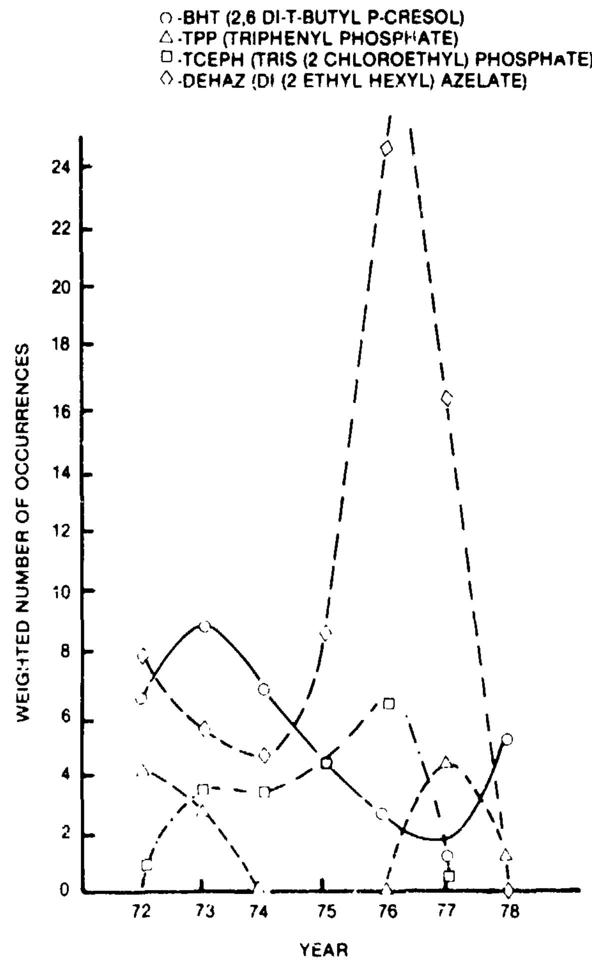

Figure 3 Normalized Rates of Occurrence of Some Unique Compounds

The appearance of the volatile antioxidant, BHT(2,6 ditertiary butyl p-cresol), has declined somewhat in recent years, perhaps as a result of better materials screening practices, but has not yet been eliminated. This material is commonly used in synthetic rubbers and plastics, but its specific sources in aerospace hardware are still uncertain.

The compound triphenyl phosphate, which is a fire retardant plasticizer, was detected in 1972-1973 and then not again until 1977. Studies of the hardware and projects associated with the appearance of this material were inconclusive with the only correlation being that it appeared mostly in samples which also contained significant amounts of aliphatic esters such as azelates and adipates.

The frequency of occurrence of another fire retardant, tris(2-chloroethyl) phosphate, seems to have been more well-behaved. Its occurrence, which was associated with polyurethane foams, increased through 1976, and since then has virtually disappeared from samples of collected outgassing products. An even more dramatic shift in frequency, but again not well explained, is the case of di(2-ethyl hexyl)azelate, a plasticizer used for its low temperature effectiveness. The rate of appearance of this compound increased radically in 1976 and 1977 and then, for no obvious reason, dropped to almost nothing.

Thermal Vacuum Tests of Whole Spacecraft

Although there are not enough data from equivalent tests to provide any accurate statistical trends, the outgassing results from whole spacecraft are never-the-less of considerable interest and demonstrate some important materials' correlations. Some of the results which can reasonably be compared are presented in TABLE VIII.

TABLE VIII. OUTGASSING FROM THERMAL VACUUM TESTS OF WHOLE SPACECRAFT

Facility	Year	Spacecraft	Amount of Residue	Primary Products
238	1971	IMP-H	20 mg	Methyl silicones
238	1973	RAE-B	32 mg	DEHP/RTV-560
238	1978	AEM-A	1 mg	ALHYD
238	1978	AEM-A	1 mg	ALHYD
290	1975	CTS	38 mg	DBDAC (Anti-oxidant)
290	1975	CTS	2 mg	ALHYD
290	1975	NRL	9 mg	RTV-560
290	1975	NRL	6 mg	RTV-560
290	1977	ISEE-A	4 mg	ALHYD
290	1977	IUE	4 mg	ALHYD
290	1977	IUE	9 mg	ALHYD
290	1977	IUE	3 mg	ALHYD
290	1977	IUE	1 mg	ALHYD
290	1979	SMM	12 mg	ALHYD/DEHP
290	1979	SMM	1 mg	ALHYD

From facility 238, a dramatic reduction in amount of outgassed residue was observed between the early 70's and the AEM-A(HCMM) tests which were run in 1978 and resulted in only one milligram of collected material. For the IMP-H in 1971, the large amount of outgassed residue (20 mg) was shown to consist of methyl silicones from the solar cell adhesive (Sylgard). In 1973, excessive outgassing from the RAE-B(32 mg) was attributed to plasticized vinyl (probably wire insulation material) and to the solar cell adhesive system, RTV-560/580. Both of these outgassing sources have now been eliminated from all flight hardware materials lists.

Tests conducted in the Solar Environment Simulator (SES), facility 290 provide less dramatic results because the collected cold finger residues are always smaller due to the extremely unfavorable geometry (the facility is gigantic compared to the cold finger surface area, and to the fact that there is tremendous pumping capability, ie., high through-put per unit volume. However, there have been some notable occurrences such as in the case of the CTS in 1975. The first thermal vacuum test resulted in 38 milligrams of collected condensable residue which was shown by mass spectrometry to consist of a single chemical species with the ponderous chemical name of ditertiary butyl dimethylamino para-cresol. This material, also known as "Ethyl Antioxidant 703", is comparatively volatile and was completely absent from the subsequent cold finger sample where the amount of residue was only two milligrams.

Most of the other spacecraft tested in this facility have produced only moderate amounts of outgassing products. It has been demonstrated, especially in the case of the IUE, that continued thermal vacuum operation can be an effective final clean-up technique. Thus, the last two cold finger amounts were about one milligram, which is the amount expected when the chamber is operated with no payload at all. The exact same sequence was observed with the SMM spacecraft in 1979.

CONCLUSIONS

Computerization of chemical analysis data has been used successfully to identify several important trends in the occurrence of outgassing problems in aerospace programs. The frequency of occurrence totals show that di (2-ethyl hexyl) phthalate (DEHP) is the most often found individual species in outgassing samples and that esters are the leading generic class of compounds. The effectiveness of this data bank has been demonstrated by the good correlations between materials and their outgassing products for solar panel bakeouts and cable bakeouts. However, trends in frequency of occurrence of many compounds have been demonstrated where no correlation could be established. In the case of the class of compounds called aliphatic hydrocarbons, it was shown that the number of instances of significant outgassing due to these materials is increasing. If this trend is to be reversed, more knowledge concerning the sources and chemistry of the compounds included in this classification will have to be derived by intensified research in this area.