RESEARCH REPORT

[redacted]

GPO PRICE $ ______

CFSTI PRICE(S) $ ______

Hard copy (HC) 1.00

Microfiche (MF) .50

ff 653 July 65

N65-30537
(ACCESSION NUMBER)

(THRU)

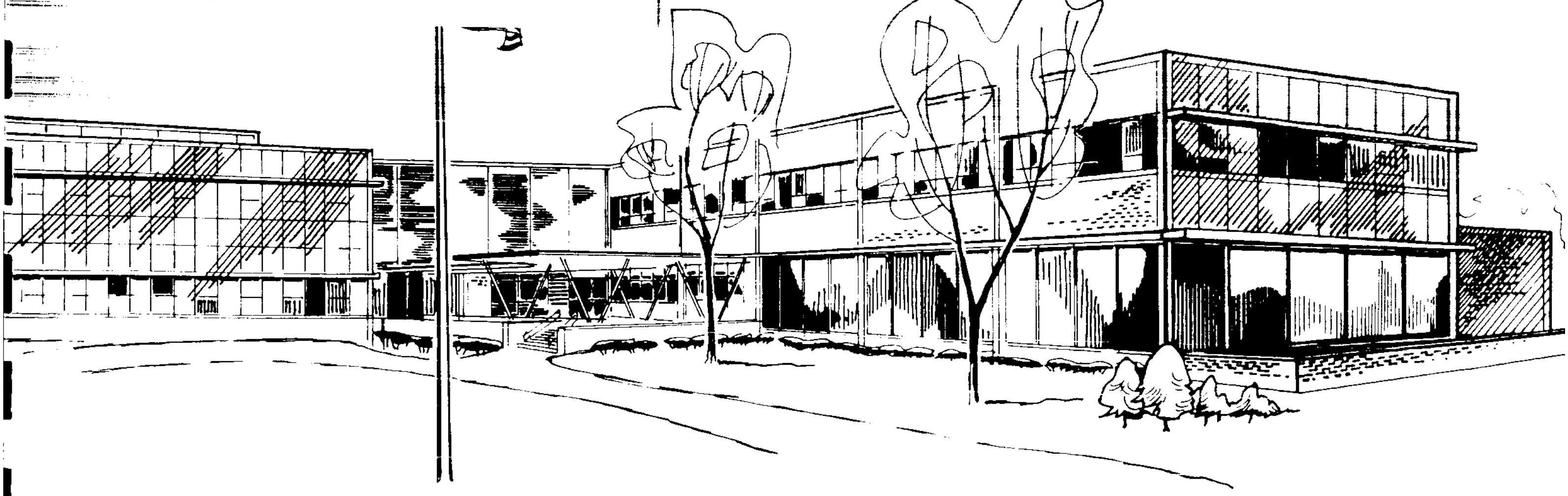
15
(PAGES)

1
(CODE)

CR 64230
(NASA CR OR TMX OR AD NUMBER)

06
(CATEGORY)

FACILITY FORM 602



SPERRY RAND RESEARCH CENTER

SUDBURY, MASSACHUSETTS

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SRRC-RR-65-21

DEVELOPMENT OF CHEMICAL ANALYSIS TECHNIQUES FOR ADVANCED MATERIALS RESEARCH PROGRAM

First Quarterly Progress Report

covering the period
December 1, 1964 to February 28, 1965

JPL Contract No. 950992

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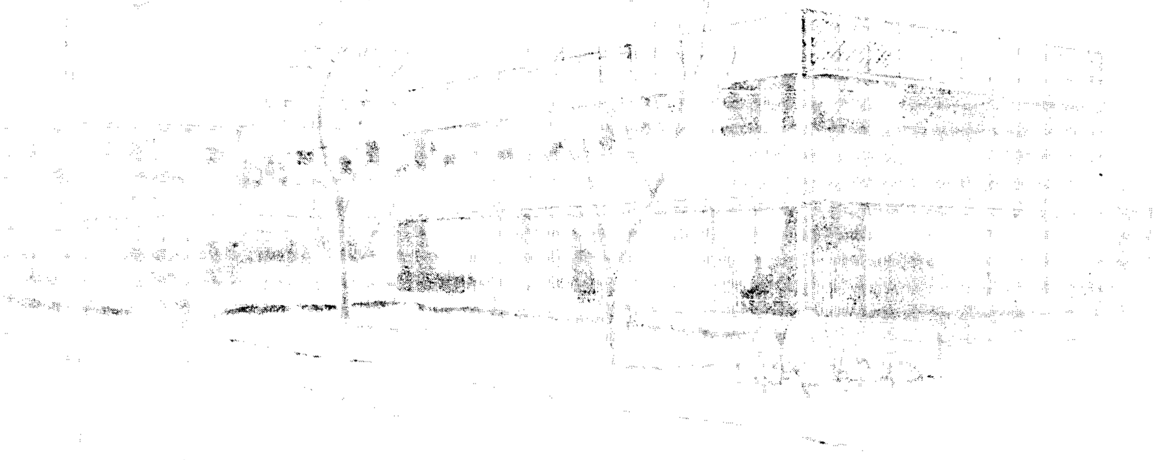

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This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

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Development of Chemical Analysis Techniques
For
Advanced Materials Research Program

I. SUMMARY

The objective of this program is the elucidation of standard analytical techniques for refractories in the Jet Propulsion Laboratory, Advanced Materials Program. Analyses of stoichiometry, impurities, and the chemical state of the interstitial elements are of principal interest.

The initial phase of this work has been concerned with the evaluation of existing analytical techniques for accuracy, sensitivity, and applicability. Several conclusions may be drawn from this literature survey. For example, the subject of impurity analysis is covered so comprehensively that it is solely a question of picking the most appropriate method. However, for some analyses, such as deviations of oxides from stoichiometry, there is very little to be learned from the literature. The status and evaluation of literature methods have been tabulated in Letter Reports 1 and 2 (see Table 1.). The only change in this tabulation is the recommendation of the use of mass spectrography for the analysis of interstitials. This method is being successfully used for the elements carbon, nitrogen, and oxygen, at Batelle Memorial Institute.

Literature methods were evaluated for their sensitivity, accuracy, size of sample required, and element coverage. For example, if a method was found which could analyze many elements simultaneously it was given consideration, even though the precision might be poorer than the optimum

for an individual analysis.

With these criteria in mind, we have searched the literature for methods applicable to the Jet Propulsion Laboratory's materials problems. Also, we have discussed these problems with other advanced analytical laboratory groups. There is very little disagreement regarding analytical methods in the literature and among laboratories we have visited. Emission spectroscopy is almost universally used for impurity analysis, while vacuum fusion, or some modification of vacuum fusion, is used for hydrogen and oxygen determinations. Nitrogen in metals is analyzed either by vacuum fusion or the classic Kjeldahl method. The widespread use of the Kjeldahl method lends some validity to the statements that vacuum fusion is an inadequate technique for nitrogen.

It appears obvious from the literature search that the two areas requiring the most development are concerned with the determination of small deviations from stoichiometry in oxides and the chemical state of the interstitial elements. These two problems will require a considerable amount of laboratory effort before methods are available which are capable of the required accuracy.

II. ACTIVITY DURING THE REPORTING PERIOD

A. This section gives a detailed account of the various established techniques for the four major analytical categories: impurities, interstitials, state of combination of interstitials, and stoichiometry.

i. Impurity Analysis

The problem of impurity analysis is best handled by an instrumental method. Wet chemical or colorimetric techniques of high accuracy are available, but these are suitable for only one element at a time and therefore are not considered. The choice of instrumental methods is between emission spectroscopy, x-ray spectroscopy, and mass spectrography.

By far, the bulk of impurity analyses is now being done by the emission technique. This method is considered to be capable of an accuracy of ± 20%, when standards are available. This accuracy is subject to matrix effects so that standards must be identical to unknowns in every respect. Sensitivity varies depending on the impurity and the nature of the matrix, but 10 ppm is a reasonable figure for metallic impurities. The biggest advantage of the emission method is the small sample size required for an analysis. A few milligrams are sufficient sample in a routine, well-established procedure. The biggest disadvantage of the method is in its inability to analyze interstitials, anion-type impurities (F, Cl, P, B) and elements which do not have a decided metallic character. Since many of these elements are of critical importance, the method can be recommended only as a technique to check metallic impurity analyis.

X-ray fluorescence suffers from the same disadvantages as the emission method but has much less sensitivity. With properly prepared standards the attainable accuracy is probably ± 10%. Matrix effects are a major problem with x-ray spectroscopy, and because of this many x-ray techniques deal with solutions rather than solids. Sensitivity varies with the element and matrix, the sensitivity being partly dependent on the atomic number. Sample size requirements are somewhat greater than for emission spectroscopy. A major disadvantage of x-ray fluorescence is the lack of sensitivity for low-atomic number elements. Elements below magnesium in atomic number are difficult or impossible to determine by x-ray methods. The x-ray spectrograph is best suited to the role of a check method for those elements which it is capable of analyzing.

Mass spectrographic impurity analyses at this time are relatively new. Instruments have been available commercially for only three or four years. Their most common use, so far, has been in the analysis of semiconductor materials where part-per-billion sensitivity is of prime importance. However, the instrument has several assets which recommend it highly for refractory analyses. Elements such as sulfur, carbon, nitrogen, oxygen, and the halogens can be estimated on the same basis as metallic impurities. These elements are examples of impurities which may have a profound effect on the properties of magnesium oxides, yet are of questionable reliability when analyzed by emission techniques. Reproducibility is another advantage of the technique. Our experience with mass-spectrographic analyses has shown that duplicates are always reproducible to ± 50%. The major disadvantage of the method, at present, lies in the lack of accuracy. A factor of two seems to be the best attainable accuracy without the use of a standard. However, relative numbers should be within ± 50%.

ii. Analysis for Interstitials

The analysis for hydrogen, nitrogen, oxygen, and carbon presents a more complex picture. There are numerous chemical and instrumental methods available, but only the most common or useful will be discussed.

Hydrogen is the simplest analytical problem of all. It is currently determined in all cases as either an adjunct to vacuum fusion or by a hot extraction technique. Hydrogen differs from the other gaseous elements in being relatively loosely bound. In solid samples, hydrogen may be present in solid solution, as hydrogen gas in voids, as vapor in voids in the form of water, or as a hydride. Simple heating under reduced pressure is sufficient to decompose all metallic hydrides, and the same is true of hydrogen solid solutions. In general, therefore, no drastic treatment of the sample is necessary to release the hydrogen. Hydrogen diffuses readily through metals and high temperatures are not normally required. This is the basis for the hot extraction procedure for hydrogen analysis.

The sample is heated in a vacuum system and the pressure of the gases driven off are measured in a standard volume. These gases may be diffused through heated palladium, first to separate them from CO, CO_2, or other gaseous impurities. This is probably the most sensitive, precise method available to us. The technique has a sensitivity of 1 ppm with an accuracy of ± 10%. Of all the methods investigated during the literature search, hot extraction is the most suitable to JPL problems.

Carbon analyses are most commonly done by combustion procedures with varying claims for accuracy and sensitivity. Assessment of these claims is difficult, but a recent paper demonstrates a sensitivity of 10 ppm and an accuracy of ± 12% by modifications of the standard LECO combustion technique.

These modifications include the use of a platinum disk susceptor, avoidance of combustion accelerators, extreme care in blank determinations, and careful calibrations. The platinum disk is used as a bath to aid in liberating carbon so that it may react with oxygen to form

Co_2, which is measured in a conductometric cell. Combustion accelerators (iron, tin) which are normally used must be avoided because their carbon content is of the order of 10 ppm and also varies.

Recent developments in mass spectrography indicate that carbon may be analyzed satisfactorily as long as there are no mass interferences. MgO is the only compound of interest where there is a mass interference in the carbon determination, $Mg^{24}{++}$ obscuring $C^{12}{+}$. Mass spectrography has a sensitivity of 1 ppm atomic and an accuracy of ± a factor of two.

Nitrogen analyses are done by vacuum fusion or chemically by the Kjeldahl method. Of the three elements normally analyzed by vacuum-fusion techniques (hydrogen, oxygen, nitrogen), nitrogen is least accepted. Apparently there is incomplete liberation of the gas since vacuum fusion results are often lower than those obtained by chemical methods. The area of uncertainty is small, but neither of these techniques is well suited to JPL problems. Stated sensitivity is 10-20 ppm with an accuracy of ± 20%, but both of these figures seem optimistic.

The alternate to these two methods is mass spectrography. The use of this instrumental technique for interstitial analysis is very recent but shows great promise. It also has the great advantage of producing an impurity analysis along with analyses for nitrogen, oxygen, and carbon. Thus, a single small sample may be used for impurities and interstitials with only a slight sacrifice in accuracy. The sensitivity for nitrogen is 1 ppm atomic and the accuracy is ± a factor of two.

Oxygen analyses are also the subject of a good deal of speculation. Vacuum fusion and inert-gas fusion are by far the most widely used methods, but activation analysis and chemical methods find some acceptance. The situation is analogous to the state of nitrogen analyses. Oxygen levels below 50 ppm are suspect, and a claimed accuracy of ± 20% is probably optimistic.

Early in the literature search, the emission-spectroscopic method appeared to be a promising technique for the analysis of nitrogen, oxygen, and hydrogen simultaneously. This is, in essence, an inert-gas-fusion method with spectroscopic detection. The sample is arced in the spectrograph in a platinum lined graphite electrode. Thus the chemistry of the gas extraction is the same as in fusion techniques. The gases are liberated and excited to emission by the temperature of the arc, and their spectra are recorded photographically. Originally, this appeared to be a very promising method. It was capable of high accuracy and apparently gave complete nitrogen recoveries. This is not the case in vacuum fusion. However, a blank problem severely limits the sensitivity. Recently, modifications to the method have been made which entail the use of a chromatographic detector in place of the photoplate. This change has not appreciably improved the sensitivity which is still of the order of 50 ppm. This is not adequate for JPL problems and the method cannot be recommended in its present state.

The only remaining method with any promise is mass spectrography. Sensitivity and accuracy are the same as for mass spectrographic analyses of nitrogen and carbon, i.e., 1 ppm and ± a factor of two.

iii. State of Combination of Interstitials

This area is only lightly covered in the literature. The only directly applicable information concerns the separation of graphite in refractory carbides These differentiation methods involve dissolution of the matrix and subsequent analysis of the graphitic residue. For example, graphite in hafnium carbide is determined by dissolving the carbide in HF, HNO_3, and KHF_2. The insoluble graphite residue is then analyzed by standard combustion techniques. Obviously, this type of analysis leaves much to be desired. The sample size must be large and the sensitivity (50-100 ppm) is inadequate.

Similar analyses have been done for nitride phases in steel and aluminum alloys and could possibly be applied to refractory metals. This is a very difficult problem and will require extensive investigation before adequate methods are available.

iv. Stoichiometry of Oxides

Again, this is a problem which has received very little attention. An oxygen deficient compound of Al_2O_3, with an approximate formula corresponding to $Al_2O_{2.96}$, has been reported by several authors. There have also been reports of a similar zirconium compound, but no mention of non-stoichiometry in magnesium or calcium oxides. Methods are available for the determination of oxygen deficiency in TiO_2 or CuO, but these are not applicable to Al_2O_3 or MgO. One possible and attractive method would involve measuring the oxygen taken up by oxygen-deficient compounds in a vacuum system. Since a large amount of oxygen is required to return a compound such as $Al_2O_{2.96}$ to stoichiometry (44 standard cc/gram), a technique which involves measurement of changes in oxygen pressure could possibly detect deviations as small as 0.01%. A method similar to this could probably be developed in a matter of eight to ten weeks.

B. This section contains information concerning laboratory work done during the reporting period (1 December, 1964 - 1 March, 1965).

If mass spectrography is chosen as the general analytical tool, we will use other more classical methods to ascertain the reliability of the mass spectrograph. To this end, we have been setting up several classical procedures. The first of these is the LECO inert-gas-fusion apparatus for the determination of oxygen. This equipment does a reliable job on oxygen from 50 to 500 ppm, with an accuracy of ± 20%. We have made some small modifications to the accepted procedure for this instrument. The equipment is normally calibrated using weighed (1-5 mg) samples of Ag_2O. This is not considered a stoichiometric compound, thus introducing an extra area of uncertainty into the calibration procedure. In place of the silver oxide we have been using U_3O_8. This material is available from the National Bureau of Standards and is definitely more reliable than Ag_2O.

The procedure for inert-gas-fusion oxygen analyses involves heating a sample in contact with carbon in a pure argon stream. Oxygen is liberated and reacts with the carbon to form CO, which is swept into a $Ba(OH)_2$ solution where conductometric measurements are made and related to the oxygen content of the sample. Composition and stability of the $Ba(OH)_2$ solution are important in the precision of the measurement. We will most likely replace the $Ba(OH)_2$ with NaOH. This produces a much more reproducible solution and should give a noticeable increase in precision.

Another area where modification is needed is in the use of a platinum bath for refractory materials. Steels and other relatively low-melting metals may be dropped directly into the heated graphite crucible with acceptable gas liberation. However, the refractory metals will not entirely release their gas content under these conditions. By wrapping samples in platinum foil, complete liberation of oxygen is obtained.

X-ray and emission spectroscopic standards for impurity analyses have been started and will continue. These are made by adding known quantities of impurity to pure matrix materials. Analysis of these artificial standards will produce standard curves which are used in the analysis of unknown materials.

The design of a hot extraction vacuum system for the determination of hydrogen in refractories has been started. This system should be capable of determining hydrogen down to 1 ppm with an accuracy of ± 10%.

The results of mass spectrographic analyses on two JPL tungsten samples (Table II) follow. A list of pertinent literature references is appended.

III. PLANS FOR NEXT QUARTER

We intend to concentrate our efforts on oxides and carbides, with particular emphasis on magnesium oxide and tantalum carbide. The utility of the mass spectrograph for both impurity and interstitial anayses will be determined. Analyses will be checked using emission and x-ray spectroscopy, wet chemistry, and other classical techniques.

Since the bulk of the work will involve nonconducting materials, an evaluation of techniques for producing ions in the spark source will be necessary. Two methods are available. The first uses a counter electrode of pure material, such as gold or silicon. The second involves mixing the nonconductor with graphite. Both methods introduce small impurities, but the analysis tends to be more accurate when graphite is added. When the counter electrode is used, the contribution from the gold or silicon is not a steady amount. The graphite mixture, if properly prepared, will have a constant ratio of graphite to sample. The use of graphite obviates a carbon analysis, and calls for the possible evaluation of other conducting binders.

IV. OTHER ACTIVITY

Several trips to laboratories have been made during this first quarter. These included the Pratt & Whitney Nuclear Aircraft Engine Laboratory in Middletown, Connecticut, the General Electric Company in Schenectady, New York, the Norton Company in Worcester, Massachusetts, and the Picker X-Ray Corporation in White Plains, New York where there was a mass spectrograph meeting devoted to spark-source instruments. In general, discussions at these laboratories bore out information obtained from the literature. In a few cases, interesting procedures or modifications were cited and these are being used where applicable.

TABLE I

Determination	Emission Spectrography	Mass Spectrography	Vacuum Fusion	Hot Extraction	Combustion
Refractory Metal Carbides					
Carbon (free)	4 E	4 E	-	-	1 C
Carbon (combined)	3 E	3 B	-	-	1 C
Hydrogen	2 E	3 B	1 C	1 A	-
Nitrogen (free)	4 E	4 E	-	-	-
Nitrogen (combined)	2 E	2 D	1 C	-	-
Oxygen (free)	4 E	4 E	-	-	-
Oxygen (combined)	2 E	2 D	1 C	-	-
Metallic impurities	1 C	3 B	-	-	-
Metal Oxides					
Carbon (free)	4 E	4 E	-	-	1 C
Carbon (combined)	3 E	2 D	-	-	1 C
Hydrogen	2 E	3 B	1 C	1 A	-
Nitrogen (free)	4 E	4 E	-	-	-
Nitrogen (combined)	2 E	2 D	1 C	-	-
Stoichiometry	-	-	3 C	-	-
Metallic Impurities	1 C	3 B	-	-	-
Refractory Metals					
Carbon (free)	4 E	4 E	-	-	1 C
Carbon (combined)	3 E	2 D	-	-	1 C
Hydrogen	2 E	3 B	1 C	1 A	-
Nitrogen (free)	4 E	4 E	-	-	-
Nitrogen (combined)	2 E	2 D	1 C	-	-
Oxygen (free)	4 E	4 E	-	-	-
Oxygen (combined)	2 E	2 D	1 C	-	-
Metallic Impurities	1 C	3 B	-	-	-

Symbols:

1 - Technique is applicable with laboratory check.
2 - Technique will be satisfactory with refinement.
3 - Technique requires extensive work.
4 - No applicable technique available.

A - Sensitivity to 1 ppm and accuracy better than ± 20%.
B - Sensitivity to 1 ppm and accuracy greater than ± 20%.
C - Sensitivity to 10 ppm and accuracy better than ± 20%.
D - Sensitivity to 10 ppm and accuracy greater than ± 20%.
E - Sensitivity to 100 ppm and accuracy better than ± 20%.
F - Sensitivity to 100 ppm and accuracy greater than ± 20%.

More precise information on sensitivity and accuracy is to be found in the text of the report.

TABLE II

Tungsten Analyses

PPM (wt.)

	G.E. Powder Met.		Electrowon
Li	<0.1		<0.1
B	0.06		0.2
F	0.3		5
Na	0.2		18
Mg	0.5		2
Al	14		20
Si	35		400
S	2		4
Cl	8		75
K	1		2
Ca	0.2		15
V	<0.1		0.3
Cr	0.4	Probable	3
Fe	0.4	dye	95
Ni	0.5	contamination	8
Zn	-		0.5
Mo	-		7

References

Impurity Analyses

1. KAPL A-SM-1 OTS, Department of Commerce, Washington, D. C., 1965.
2. McKaveney, J. P., Anal. Chem. 35, 2139 (1963).
3. PWAC 340 OTS, Department of Commerce, Washington, D. C., 1961.
4. Reed, J. F., Anal. Chem. 33, 1337 (1961).

Interstitial Analyses

1. Beeghly, H. F., Anal. Chem. 21, 1513 (1949).
2. Carson, C. C., Anal. Chem. 32, 936 (1960).
3. Feick, G., and Guistetti, W., Anal. Chem. 36, 2199 (1964).
4. Gordon, W. A., et al., Anal. Chem. 36, 1396 (1964).
5. Green, I. R., Still, J. E., and Chirnside, R. C., Analyst 87, 530 (1962).
6. Harris, W. F., Talanta 11, 1376 (1964).
7. LA 2306 OTS, Department of Commerce, Washington, D. C., 1959.
8. Lesser, R., Trans. 8th National Vacuum Symposium (Pergamon Press, New York, 1961), Vol. 2.
9. MacDonnel, R. L., et al., Anal. Chem. 35, 579 (1963).
10. Mallett, M. W., Talanta 9, 133 (1962).

General Analysis of Refractories

1. ARL 180 OTS, Department of Commerce, Washington, D. C., 1961.
2. DMIC Memo 49 OTS, Department of Commerce, Washington, D. C., 1960.
3. MAB 178-M, National Academy of Sciences, Washington, D. C., 1961.
4. TID 3560 OTS, Department of Commerce, Washington, D. C., 1961.