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DEVELOPMENT OF CHEMICAL ANALYSIS TECHNIQUES FOR ADVANCED MATERIALS RESEARCH PROGRAM

Third Quarterly Progress Report

covering the period
June 1, 1965 to August 31, 1965

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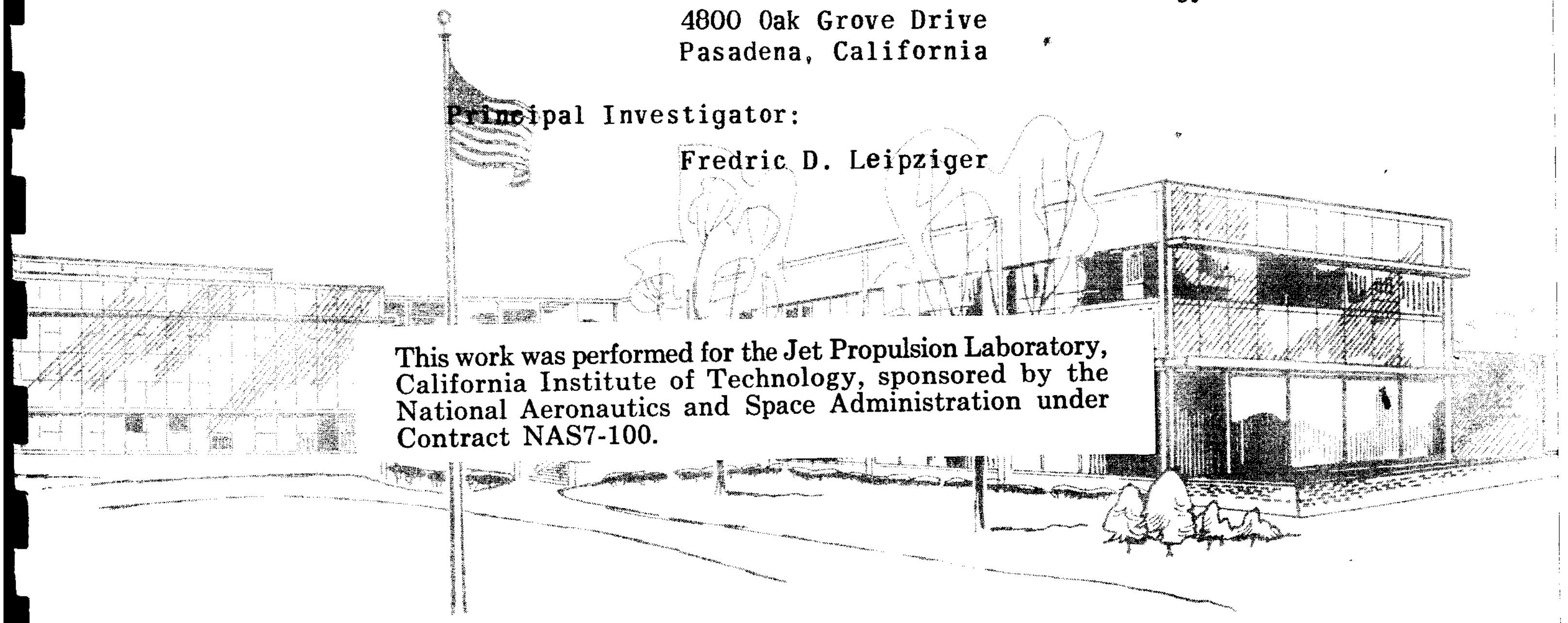
Prepared for: Jet Propulsion Laboratory
California Institute of Technology
4800 Oak Grove Drive
Pasadena, California

Principal Investigator:
Fredric D. Leipziger



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Development of Chemical Analysis Techniques
For
Advanced Materials Research Program

I. SUMMARY

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The period covered by this report has been devoted to the analysis of MgO powders and compacts. These analyses include mass spectrographic impurity analyses, emission-spectrographic checks of metallic impurity levels, and hot extraction hydrogen analyses.

Several problems have arisen with respect to mass spectrographic analyses. Briefly, these involve surface contamination and difficulties in the analysis of insulating compacts. The surface contamination problem has been resolved by a combination of baking and presparking. The method used for the analysis of compacts is not yet in reliable condition. In order to obtain any analyses for these materials we have had to resort to grinding techniques.

II. ACTIVITY DURING THE REPORTING PERIOD

A. Mass-Spectrographic Analysis of MgO Powders.

Techniques for the mass-spectrographic analysis of MgO powders have advanced to the point where we consider this a reliable and accurate analysis. A surface contamination problem has been successfully resolved and we have obtained excellent checks on the level of metallic impurities by means of emission spectrography. Details of the procedure for powders follow.

A weighed portion of the MgO is intimately mixed with two parts by weight of pure silver. The mixture is then pressed at 12000 psi to form electrodes. These electrodes are split lengthwise before being inserted into the mass spectrograph to avoid surface contaminants. The specimen is baked overnight at about 150°C and a prespark exposure of 3×10^{-8} coulombs is recorded prior to the analytical exposures. The analytical exposures consist of a series covering the range 1×10^{-13} coulombs to 3×10^{-8} coulombs. These steps lead to the following accomplishments:

1. The insulating powder is converted to a solid conducting shape suitable for use as an electrode in the mass spectrograph. The intimate weighed mixture allows us to make quantitative estimates of impurity levels since known amounts of silver and MgO are present in the spectrum.

2. Splitting the electrodes avoids surface impurities introduced by the die. Attempts to remove these impurities by etching and scraping have not yet met with complete success. The fresh surface exposed by splitting the electrode seems to give results most representative of the sample composition.

3. Baking and presparking also aid in the removal of surface impurities. When the spectrum of the prespark is examined we often see impurities that are not present in the bulk of the sample. Figure 1 shows an extreme example of surface impurities recorded in the prespark spectrum and their subsequent removal. The baking step also allows us to estimate nitrogen levels in these samples.

B. Emission Spectrographic Checks of Mass Analyses.

The accuracy of the mass spectrographic analysis of metallic impurities has been substantiated by emission spectrography. Emission

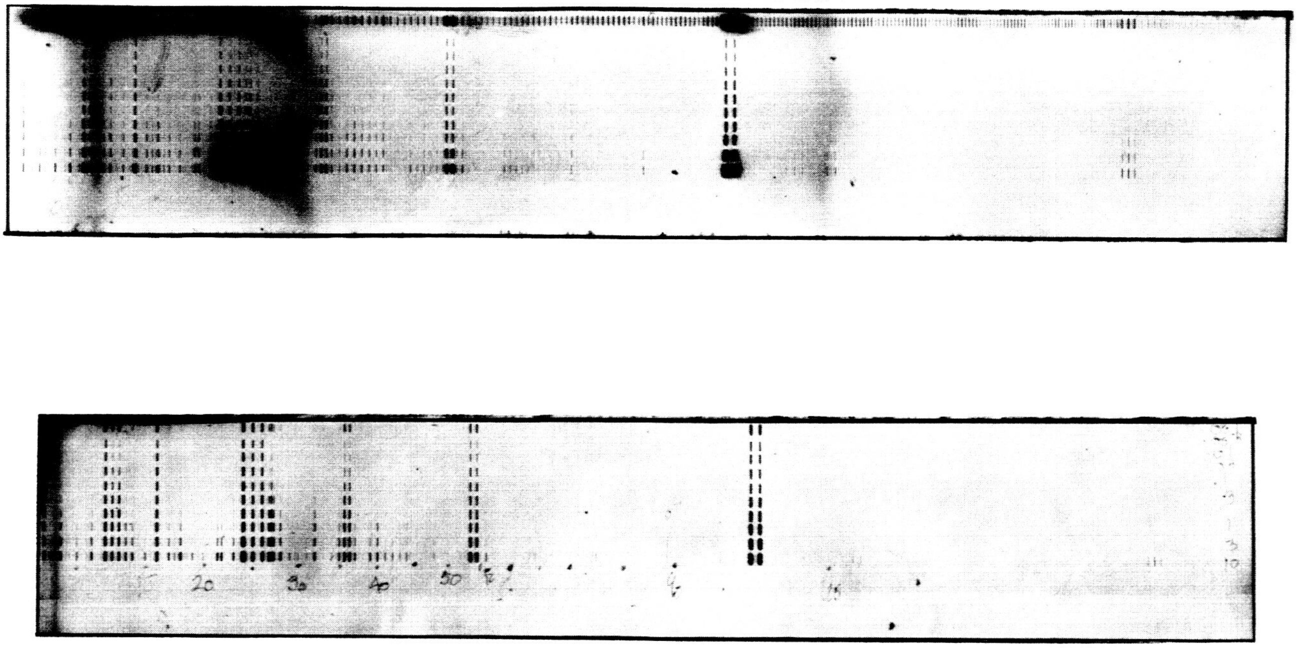

FIG. 1 Mass spectra of MgO compacts. In the upper plate, lines attributable to hydrocarbon impurities are clearly visible. These lines have been eliminated from the lower plate by a combination of baking and presparking treatments.

analyses have been conducted with the aid of a series of MgO materials with known impurities in the range 1-1000 ppm. These materials provide us with working curves to relate intensity to concentration for unknown MgO samples. Working conditions for the emission analyses are as follows:

Table I. Condition for emission-spectrographic analysis of MgO.

Baird 3-meter spectrograph
dc arc
15 amperes
25 mg sample
10 μ slit width
3 μ slit height
45 second exposure
Argon atmosphere
Wavelength range - 2400-3600 Å, 2nd order
Eastman SA-1 plates

Sensitivity limits have been determined for the method and these are listed below for the elements of interest.

Table II. Detection limits for impurities in MgO by emission spectrography. (ppm weight)

Boron	5 - 10
Sodium	0.01
Aluminum	1
Silicon	1
Potassium	0.01
Calcium	1
Titanium	1
Chromium	1
Manganese	1
Iron	1
Copper	0.05
Cobalt	1

Problems involving very poor sensitivity were encountered early in this work. These problems have been resolved by using second-order spectra, and also by the use of an argon atmosphere. The use of argon for the arc atmosphere gives a marked reduction of background on the plate with a consequent increase in sensitivity.

The sensitivity and accuracy of the emission method for metallic impurities appear to be quite satisfactory. However, this still leaves a small group of impurity elements such as phosphorus and fluorine which will need to be checked by other methods. A brief investigation will be made during the fourth quarter to find check methods for these elements.

Agreement between mass and emission methods for metallic impurities has been unusually good. The techniques used to evaluate plates from the mass spectrograph are probably the prime sources of error in the analysis. The present state of mass-spectrographic analyses for materials without standards will lead to errors of at least ± 50%. Most of the emission spectrographic checks fall within these limits. A comparison of mass and emission results for two MgO powders and a magnesium metal sample follow.

Table III. Comparison of mass and emission spectrography for selected elements in magnesium and magnesium oxide (ppm atomic).

	Fisher M-300		JPL-8		Magnesium Metal	
	Mass	Emission	Mass	Emission	Mass	Emission
B	3	< 10	2	< 10	3	5
Na	100	500	<1	< 30	5	-
Al	75	50	35	50	5	15
Si	2400	> 1000	75	65	9	15
K	<1	< 1	<1	< 1	40	-
Ca	150	350	30	20	3	5
Ti	10	< 10	<1	< 10	3	< 5
Cr	5	< 5	3	< 5		
Mn	2	< 5	<1	< 5		
Fe	85	65	15	15		
Ni	10	< 5	<1	< 5		
Co	10	5	<1	< 5		
Cu	5	< 5	2	5		
Zn	11	5	10	10		
Ba					1	ND

C. Mass-Spectrographic Analysis of MgO Compacts.

Analysis of pressed specimens of MgO has been the most difficult problem encountered so far. A common technique which involves the use of a metallic counter electrode has not lived up to its promise. This method uses gold or silicon as a counter electrode at the rf side of the source. Claims in the literature state that the contribution from the metallic electrode is less than 5% of the total ion beam.

The major source of our trouble with this technique is illustrated in Fig. 2. Examination of the gold line at mass 197 indicates that the contribution is both greater than 5% and also uncontrollable. This would indicate that while appreciable quantities of MgO are being ionized, the gold is also making a major contribution to the spectrum. The varying gold content of the spectrum makes quantitative interpretation of the plates impossible because the amount of MgO in a given exposure cannot be estimated. A comparison of this technique with the powder method further illustrates the problems of plate interpretation, using a counter electrode.

In the powder method, we have intimately mixed weighed portions of MgO and silver. This allows us to calculate the exact amount of MgO in each exposure and then make quantitative estimates of impurity levels. In the counter-electrode technique, with the amount of MgO varying by an unknown amount in each exposure, we are able only to make qualitative estimates.

Analyses have been obtained from several pressed MgO specimens by grinding and then treating the specimens as a powder. This is definitely an expedient to allow us to estimate the purity of the samples. However, the results appear quite acceptable.

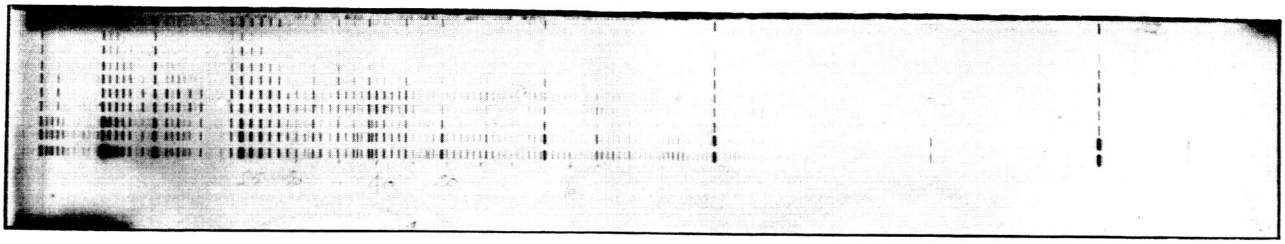

FIG. 2 Mass spectra of compacted MgO specimen with a gold counter electrode. Note the varying amount of gold in the spectra as well as the varying hydrocarbon impurity.

The pressed specimens were ground in a boron carbide mortar to about 300 mesh. Then the powder was mixed with silver, pressed into electrodes and treated in the normal manner. Considerations of the hardness of the specimen and the mortar indicate that there should be little or no contamination introduced in the grinding step. Hardness of boron carbide is 9.5, while estimates for the hardness of MgO are about 5.5. This has been borne out in our examination of the mass spectra of materials analyzed by the grinding technique. Various JPL MgO powders show from 1 - 5 ppm atomic boron content and this value has not been exceeded in our analyses. The contamination level will be strongly dependent on the hardness of the MgO sample, and some materials may not be amenable to this treatment.

The results of three analyses on pressed MgO are shown in Table IV, on the following page.

The most promising solution to the problem of mass analyses for compacted MgO specimens would seem to be direct sparking of two MgO electrodes. Materials of surprisingly poor conductivity ($CaWO_4$, UO_2) can be analyzed in the mass spectrograph with excellent results. In the hope that the same would be true for MgO, in spite of its insulating properties, we have made some preliminary experiments to ascertain how much ion current is available from a pair of MgO electrodes.

While it has not yet been possible to obtain sufficient ion current to be useful analytically, sparks were obtained between the two insulating electrodes. The electrodes projected about one-half inch beyond the holders, so there is no doubt that sparks were drawn between the electrodes and not between the holders. The sparking was erratic and was not confined to the area between the two electrodes.

Table IV.
Analysis of MgO Compacts

OP 125	
B	10 (contam. ?)
F	< 1
Na	< 1
Al	1000 +
Si	8
P	< 1
S	4
Cl	15
K	< 1
Ca	5
Fe	3 ?
N	65
OH	3

OP 141	
B	3
F	3
Na	< 1
Al	12
Si	40
P	10
S	3
Cl	65
K	3
Ca	40
Fe	4
N	50
OH	3

OP 144	
B	3
F	2
Na	< 1
Al	6
Si	20
P	5
S	8
Cl	35
K	5
Ca	10
Fe	3 ?
N	300
OH	1

If the sparking rate can be increased it should be possible to get enough ion current to be of analytical value. One possible mechanism for this process would involve strong local heating effects which would cause the resistivity to fail enough so that sparking occurs. This would seem contrary to the exceptional thermal conductivity of MgO, but from our observations during mass-spectrograph analyses it still appears plausible. In many analyses we have seen severe local heating of electrodes, probably due to electron bombardment in the sample area. Therefore, it would seem that the major barrier to this type of analysis, i.e., obtaining a spark, has already been surmounted. It remains for us to increase the sparking rate to the point where we can obtain useable ion beams. If the sparking area could be confined to a small area on the electrode, reasonable ion currents could be obtained.

Methods for increasing ion current from an insulating electrode pair are being investigated. The most promising of these involves sharpening one electrode to a point. This will result in increased temperature and conductivity which should aid in ionization of the sample.

The advantages to be gained from the direct sparking of two MgO electrodes are obvious. All the ion current obtained is useable and there is no interfering spectrum from conducting additives such as silver or gold. If this method can be developed into a routine accurate analytical technique it will solve almost all of our problems with MgO impurity analysis.

D. Evaluation of Mass-Spectrograph Photoplates.

The determination of impurity concentration from line density on a photoplate has always been a contributing factor to errors in mass-spectrographic impurity analyses. The fact that there is no universal or accepted method for plate interpretation is indicative of the general lack of agreement among spectrographers on data analysis.

Visual estimation and microdensitometry are two common methods in use today. Visual estimation is simple and rapid and is normally restricted to semi-quantitative work. The microdensitometric method is much more time consuming but is also potentially more accurate and precise. In an effort to evaluate the two methods for our purposes we have analyzed a number of plates by both techniques.

We have found that visual estimation is giving equivalent results with a fraction of the investment of time necessary for densitometry. The major gain of the densitometric method is an increase in precision without necessarily a concurrent increase in accuracy. We feel that weekly checks on emulsion sensitivity are all that are required to make the method of visual estimation competitive in accuracy with densitometric procedures at the present time.

E. Hydrogen Determination.

After many minor problems, the first analyses for hydrogen in standards are being performed. The National Bureau of Standards titanium samples, certified for hydrogen, are being analyzed. The first sample to be analyzed gave results which were within 10% of the 0.02 weight percent hydrogen value.

Since gas analyses will be necessary on the MgO samples, a laboratory to do these must be located.

In recognition of the difficulties encountered in the analysis of the interstitial elements in refractories, the National Academy of Sciences is sponsoring a round-robin on the analysis of carbon, nitrogen, hydrogen, and oxygen in refractory metals. We have been asked to participate in this study on the basis that the spark-source mass spectrograph is a new tool for these analyses. The materials involved are niobium, tantalum, tungsten, and molybdenum, and this will give us another chance to check the mass spectrograph against classical techniques such as vacuum fusion and hot extraction.

III. PLANS FOR NEXT QUARTER

Plans for the next quarter include continuation of the effort to obtain ion currents of useful magnitude from MgO electrodes. This technique, if successful, will give us accurate and reliable analyses for MgO compacts without resort to grinding or counter-electrode methods.

A literature survey will be made to find methods for checking the accuracy of mass spectrographic analyses for elements such as fluorine, chlorine, and phosphorus, which cannot be checked by emission methods.

Hydrogen analyses of NBS standards and MgO samples will continue.

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