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DEVELOPMENT OF CHEMICAL ANALYSIS TECHNIQUES FOR ADVANCED MATERIALS RESEARCH PROGRAM

by

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44

TABLE OF CONTENTS

Section		Page
	ABSTRACT	1
I	INTRODUCTION	1
II	RESULTS	2
	A. Literature Survey	2
	B. Mass Spectrography as an Analytical Tool	3
	REFERENCES	21
	APPENDIX A	
	APPENDIX B	
	APPENDIX C	
	APPENDIX D	
	APPENDIX E	

Development of Chemical Analysis Techniques
for
Advanced Materials Research Program

ABSTRACT

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A series of spark source mass spectrographic procedures have been developed in an effort to specify reliable analytical techniques for the determination of bulk impurities in refractory oxides. These include the determination of gases and bulk impurities in both solid and powdered specimens. The accuracy of the mass spectrographic methods has been checked by emission spectrography, wet chemistry, and vacuum methods.

I. INTRODUCTION

The objectives of this program have been the specification of reliable analytical techniques for bulk impurities and gases in refractory materials (e.g., magnesium oxide and tantalum carbide). This program of study was initiated because of the inaccuracy of analytical results obtained from commercial laboratories, due in part to a lack of experience in analyzing the materials of interest, and also to the wide diversity of methods used to characterize their impurity contents. Commercial analytical laboratories handle a great many different materials; their major concern is speed rather than accuracy, which has lead to a tendency to handle all materials in the same manner.

The analyses of interest to the Jet Propulsion Laboratory have included bulk impurities, both metallic and nonmetallic, and the interstitials. In commercial laboratories this entails the use of at least five different methods: emission spectrography for metallic impurities, wet chemistry or combustion techniques for nonmetallic impurities, vacuum fusion or inert gas fusion for oxygen, Kjeldahl technique for nitrogen, and extraction for hydrogen. This diversity of technique, coupled with the problem of standardization, makes intralaboratory comparisons of results difficult.

With these problems in mind, we have developed a series of analytical methods for detecting all impurities in refractory materials. The spark source mass spectrograph is the tool, and the methods used meet all JPL requirements concerning sample size, accuracy, and reproducibility.

II. RESULTS

In the sections which follow, we describe briefly the spark source mass spectrographic techniques which have been developed and applied to refractory materials of interest to JPL. Detailed procedures are compiled in a series of appendices which appear at the end of this report. The choice of mass spectrography, as the most useful analytical tool, was made after an extensive literature search.

A. Literature Survey.

As the first step in this study, a systematic survey of the literature was made in order to ascertain the accuracy, sensitivity, and usefulness of commonly available analytical methods. Since the reliability of analytical data for refractory materials is a common problem, a great many pertinent references were found.[1-18] The ordinary and most widely used techniques were found to be almost exactly the same for all refractory systems — metals, oxides, and carbides. The problem of metallic impurities is generally solved by using either emission or x-ray spectroscopy. The interstitial elements (carbon, nitrogen, oxygen, and hydrogen) are also analyzed by using a minimum of methods. Gases are normally done by either vacuum or inert gas fusion, although other methods of analysis are available. Nitrogen is also handled by the Kjeldahl wet chemical method, and an alternate method for hydrogen is the hot extraction technique. The nonmetallic elements such as sulfur, phosphorus, and boron are determined by wet chemical and colorimetric methods.

These techniques all have a common fault: at the lower end of their sensitivity limits, they become inaccurate. Since the impurity levels expected in JPL materials are in the 1-100 ppm range, many of these common methods are inadequate. This loss of accuracy and the problems encountered in trying to compare analytical results for the same element but from different techniques led us to consider the spark source mass spectrograph for analyses of all impurities in refractory oxides and carbides.

B. Mass Spectrography as an Analytical Tool.

Spark source mass spectrographs have been available commercially for only five years. The extreme sensitivity of the spectrograph has prompted its primary use in the analysis of dopants in semiconductor materials. However, the instrument has some attractive features which make it useful for this type of study, namely, excellent sensitivity (1 ppb) and coverage of all elements.

The spark source mass spectrograph uses an rf spark between two conducting electrodes to ionize the matrix and impurity content of the sample. The ions formed in the spark are accelerated into the first of two analyzing sections. The first section is an electrostatic analyzer which is necessary because of the energy spread imposed on the ion beam by the energetic rf spark. Then, after the ions have been energy selected, they pass into the magnetic analyzer where they fall upon a photographic plate which is placed at the focus of the magnetic sector. Thus, the only restrictions placed on the sample are those of electrical conductivity and ability to withstand high vacuum.

In actual practice, it has been found possible to ignore the electrical conductivity requirement for many samples. The vacuum requirement imposes problems on the materials of interest since they are uneffected by the vacuum. The only restriction, in practice, is sample size. There must be enough material available for two electrodes 1/16" diam by 1/2" long. If this requirement can be met, it is then possible to analyze a refractory oxide for metallic, nonmetallic, and interstitial impurities down to a level of 1 part-per-billion-atomic with an accuracy of ± 50%. The problem which immediately arises is adapting this method for the handling of powders.

i. Powder methods.

Since a pair of electrodes 1/16" x 1/2" are required for mass spectrographic analysis, some method for converting powders to appropriate electrode shapes must be considered.

A standard technique for handling powders,[19] developed by workers in the field, has been modified for this particular problem. This method involves adding a weighed amount of high-purity graphite or silver powder to a weighed amount of the powdered sample. Graphite and silver are chosen because of their ease of compaction as well as for their electrical characteristics. The powders are mixed thoroughly by shaking and then pressed into an appropriate shape at a pressure of approximately 12,000 psi. This should produce a conducting electrode with the sample homogeneously dispersed in a noninterfering matrix.

The major problem we have had with this technique has been concerned with high levels of impurities from the die contaminating the surface of the compact. Figure 1 shows an extreme example of this contamination and its subsequent removal. The walls of the die are undoubtedly the source of this contamination, since high levels of iron, nickel, and chromium can subsequently be removed. Apparently, hydrocarbons also come from the die, although it is not oiled. The treatment we have found successful for removal of the surface contamination involves physical removal of the surface and subsequent baking in the mass spectrograph. After the electrodes are removed from the die, the surface is scraped with a platinum or tantalum tool, after which the electrodes are split lengthwise. The electrodes are placed in the source in such a manner that the freshly cleaved surfaces are opposed so that sparking occurs between clean surfaces.

Next, the source is evacuated and baked for twelve hours at a temperature of 150°C. The last step in the cleaning procedure is a prespark exposure of 100×10^{-9} coulombs.

Figure 1 shows a major hydrocarbon. The contaminant in the upper plate of Fig. 1 is hydrocarbon which predominates in the prespark exposure. The second plate, which was treated by the procedure described above, shows no hydrocarbon contaminant and markedly reduced levels for fluorine, water, and iron. Checks with well-known materials have verified the efficiency of this cleaning procedure.

Table 1 illustrates the magnitude of contamination possible if the cleaning treatment is omitted. The material is JPL-8 MgO, mixed with

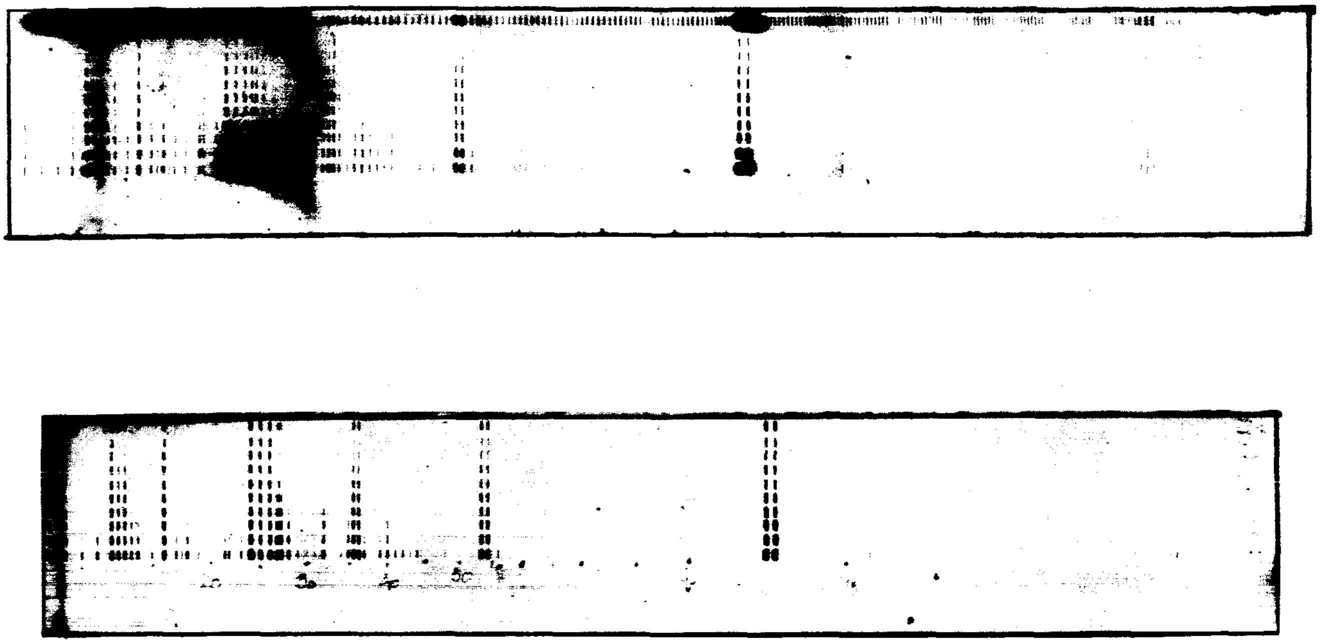

FIG. 1 Mass spectra of MgO samples. The upper plate has been presparked but not baked. The lower plate has been baked overnight and extensively presparked.

two parts by weight of pure silver powder, and analyzed mass spectrographically with and without surface cleaning.

Table 1. Effect of cleaning procedure on mass spectrographic analysis of JPL 8 (ppm A).

Without Surface Treatment		With Surface Treatment
1	B	2
-	N	50
3000	F	40
< 3	Na	< 1
470	Al	35
1700	Si	75
38	P	< 1
360	S	115
570	Cl	75
60	K	< 1
150	Ca	30
< 1	Ti	< 1
3	Cr	3
< 2	Mn	1
45	Fe	15
10	Ni	< 1
12	Co	< 1
10	Cu	10
15	Zn	2

Also of interest is the analysis of commercially-available high-purity MgO. A sample of Fisher M-300 MgO has been analyzed by the technique described above and the results of this analysis are shown in Table 2, using JPL-8 as a comparison.

During the contract period, all work on powders has involved the use of a high-purity silver powder obtained from L. Light Co., Ltd., Colnbrook, England. This material was analyzed prior to its use and was found to make no significant impurity contribution at the 1 ppm level. Silver has proved superior to graphite for this use for two reasons. The electrodes produced from a 2 to 1 silver-to-MgO mixture are much stronger and easier to handle than the comparable graphite mixture.

Also, interferences in the mass spectrum of silver are nonexistent since multiply charged species fall at fractional masses, while graphite gives rise to a series of polymeric ions at masses 24 and 25, 36 and 37, 48 and 49, etc.

Table 2. Mass spectrographic analysis of Fisher M-300 and JPL-8 (ppm A).

Fisher M-300		JPL-8
3	B	2
100	N	50
110	F	40
100	Na	< 1
75	Al	35
2400	Si	75
130	P	< 1
510	S	115
285	Cl	75
< 1	K	< 1
150	Ca	30
10	Ti	< 1
5	Cr	3
2	Mn	< 1
85	Fe	15
10	Ni	< 1
10	Co	< 1
5	Zn	2
-	Cu	10

ii. Mass spectrographic analysis of bulk impurities.

Mass spectrographic analysis of both metallic and nonmetallic bulk impurities in MgO has been straightforward. The problem of abnormal sensitivity coefficients which occasionally gives rise to spurious results has not bothered us in either MgO or TaC matrices.

The procedure for the analysis of bulk impurities involves a graded series of exposures on the photoplate which range from 0.0001 to 10×10^{-9} coulombs. Each exposure differs from adjacent exposures by a factor of three so that impurity lines can be read on at least two exposures.

Analysis of the photoplate data has been performed by two methods: visual and microdensitometric. The visual method is simple and rapid and has been used for the majority of the data analysis. The method is based on visual estimation of the exposure necessary to produce a "barely detectable" line for an impurity element, E_i. An estimate is also made of the exposure necessary to produce a barely detectable line for an internal standard, E_s, which is usually a major constituent.

From these estimates, the impurity concentration has been calculated with the aid of the following expression:

$$\frac{E_s}{E_i} \times \frac{x}{100} \times \frac{I_s}{I_i} \times \frac{S_s}{S_i} \times 10^6 = \text{ppm A} \qquad (1)$$

where x is the concentration of the internal standard, I_s is the abundance of the isotope of the standard upon which the estimate is based, I_i is the corresponding quantity for the impurity element, and S_s and S_i are relative sensitivities of the standard and impurity. In this analysis, the assumption has been made that ion intensity is linear with concentration. This assumption has proven valid for a large number of analyses.

Early in this study, the microdensitometric method was used. Measurements of line density were made in a manner similar to that used for emission spectrographic plates. The line density so obtained was reduced by a graphical technique to a value of E_s (or E_i), and substituted into Eq. (1). Since results from the two methods were comparable, the visual method has been used in the interest of speed.

Because of the high purity of the JPL materials, we have normally been concerned with only twelve to sixteen impurities, all in the low-mass range. There have been no unusual problems of plate interpretation. The values reported for sodium, potassium, and calcium are based on the doubly ionized lines at masses 11.5, 19.5, and 20, respectively. This is a normal procedure for elements which have high-thermal-ionization efficiencies. Since local heating of the electrodes in the spark area is unavoidable, the first stage of these elements is almost wholly due to thermal ionization. However, it is impossible to form doubly ionized species, such as Na^{2+}, by thermal modes. Therefore, the doubly ionized species are the result of ionization in the spark and, as such, may be used for analysis. A factor of five reduction of intensity has been used for the second stage of ionization so that for an element with an apparent concentration of 1 ppm derived from a doubly ionized line the concentration is actually 5 ppm.

The only case of mass interference encountered during this work has concerned the determination of carbon in magnesium oxide. The doubly-ionized Mg_{24} line completely obscures C_{12} while Mg^{2+}_{26} obscures C^{+}_{13}. These interferences have made the mass spectrographic analysis for carbon impossible with the resolution available in our instrument.

A series of MgO materials have been analyzed in an attempt to locate steps in the production process which may be introducing impurities. Figure 2 is a schematic diagram of the steps in the JPL process for producing high-purity MgO from magnesium metal. Samples of material from steps 2, 3, 4, 5, 10, 11, and 13 have been analyzed by mass spectrography and the results are shown in Table 3. Powdered materials were mixed with silver and pressed into electrodes, while the solid materials were analyzed by a technique to be described in part iv. of this section. Two samples of the magnesium metal starting material have also been analyzed and these results are shown in Table 4.

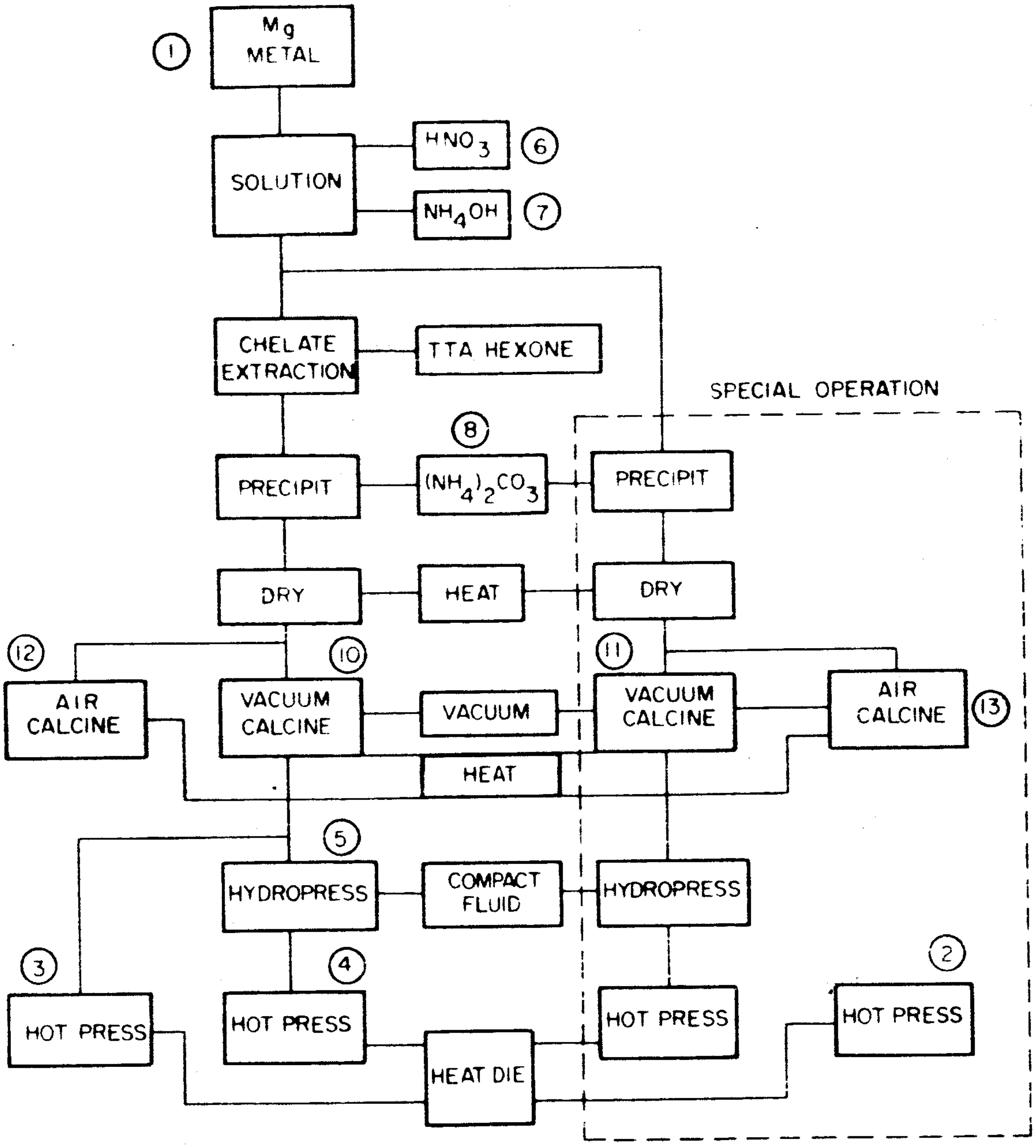

FIG. 2 Jet Propulsion Laboratory process for production of high purity magnesium oxide.

Table 3. Mass spectrographic analyses of JPL MgO (ppm A).

Sample No.	2	3	4	5	10	11	13
B	3	1	5	5	3	8	< 1
F	17	>200	>125	>250	>250	30	50
Al	*	*	*	30	15	5	30
Na	< 1	1	1	< 1	< 1	1	< 1
Si	190	175	115	170	75	65	80
Ca	12	75	60	30	40	30	30
Cl	65	125	110	95	45	35	55
Fe	8	3	20	8	20	14	10

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* Aluminum sample holders have masked Al impurity in these cases.

* * *

Table 4. Mass spectrographic analyses of JPL magnesium (ppm A).

#1		#2
3	B	< 1
15	N	30
1000 *	F	1
5	Na	1
5	Al	13
9	Si	18
< 5	S	< 5
40	Cl	> 1000 *
4	K	5
3	Ca	6
3	Fe	7
1	Ba	1

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* Etch

The most obvious conclusion to be drawn from these analyses is the effect of the extraction step using TTA and hexone. Samples which have not been through the extraction step are noticeably cleaner than those which have been extracted, particularly with regard to the volatile impurities. Fluorine levels in the unextracted samples are much lower. Also of interest in this connection is the analysis of JPL #49, a sample of MgO received early in 1966. This material had not been through the chelate extraction step and anhydrous ammonia was used in place of NH_4OH as a precipitating reagent. Table 5 shows the analytical results obtained from the normal powder technique.

Table 5. Mass spectrographic analysis of JPL #49 (ppm A).

B	< 1
N	65
F	8
Na	< 1
Al	11
Si	40
K	< 0.1
Ca	13
Cl	45
Fe	3

JPL #49 is also obviously a clean material, but the expected advantages of using anhydrous ammonia have not been demonstrated in this one sample.

iii. Analysis of interstitials.

Analyses for carbon, nitrogen, oxygen, and hydrogen are difficult for many reasons. The widespread occurrence of these elements and the ease with which they can be adsorbed on a sample surface are the major problems associated with their analysis. The marked effect these elements have on the properties of materials, even at low levels, makes their analysis critically important.

At the present time, there is a great deal of interest in high-purity materials. These materials often have interstitial element concentrations too low to be reliably measured by standard techniques. For example, oxygen concentrations below 50 ppm wt. approach the sensitivity limit of the vacuum fusion technique. Emission spectrographic analysis of gases also suffers from a blank problem and a sensitivity problem.

In an effort to avoid the dual problems of using techniques at the limit of their sensitivities and using four different techniques for the four elements, we have developed a mass spectrographic method for the analysis of these elements. The method is fully described in Appendix A.

Quantitative analyses of gases by the spark source mass spectrograph have been difficult because of the presence of nitrogen, oxygen, and hydrogen in the residual vacuum of the instrument. Another complicating factor was the possibility of gases remaining in the spark area, which would lead to abnormally high sensitivity coefficients. Studies at Battelle Memorial Institute indicated that the surface condition of the samples was also of prime importance.

With these considerations in mind, we have developed a procedure to analyze gases in metals as well as nonmetals using the spark source mass spectrograph. The most important point in the procedure is careful attention to the surface condition of the sample. A combination of etching, baking in the instrument source, and presparking leads to removal of adsorbed surface layers. As a deterrent to readsorption of gases, the analytical exposures are taken in the reverse of their normal order. The prespark exposure is taken first (30 to 100 × 10^{-9} coulombs), then the longest analytical exposure, followed by successively shorter exposures. This

16

procedure tends to keep the sample hot and to prevent readsorption of the gases present in the source.

The levels of gas present in the source probably give rise to a low-level blank which is strictly dependent upon the vacuum in the source. In an attempt to evaluate this blank, we have run several materials which should have very low gas contents. Figure 3 is the low mass spectrum of a gold sample showing small amounts (1 ppm A) of nitrogen, oxygen, and carbon. It is impossible to distinguish between blank and actual gas content of the gold at this level, but the plate demonstrates the feasibility of the method at least to the 1 ppm A level.

At the start of this study, hydrogen analyses by mass spectrography were considered to be unusually difficult because the magnet pole pieces had been hydrogen annealed. This supposedly would lead to a low-level source of hydrogen and a high blank. In practice, this has been proven to be untrue. By using the etching, baking, and presparking technique we have been able to conduct analyses for hydrogen below 1 ppm wt. for refractory metals.

The first step in the development of a method for interstitials was a study of the effects of etchants. It was suspected that HNO_3 etches might lead to high nitrogen values and possibly to high oxygen values because of the formation of oxides on the surface of the sample. However, the baking and presparking steps apparently remove all traces of oxide because we have been able to duplicate National Bureau of Standards values for nitrogen and oxygen in HNO_3-etched steels.

The available NBS gas standards are steels, certified for nitrogen and oxygen. Table 6 lists the results of mass spectrographic analyses on four of these samples and a comparison with the certified values.

17

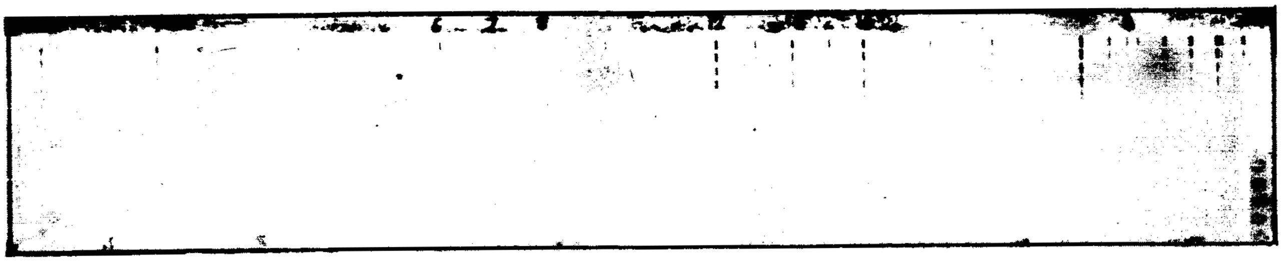

FIG. 3 Low mass region mass spectrum of gold showing low levels of carbon, nitrogen and oxygen.

Table 6. Mass spectrographic analyses of
NBS Certified Steels (ppm wt.).

Sample No.	O_2 certified	O_2 found	N_2 certified	N_2 found
1041	170	117	40	25
		179		17
		95		21
		avg. 130		avg. 21
1042	170	245	140	70
		210		115
		115		95
		avg. 190		avg. 93
1044	90	90	40	14
		65		28
		55		22
		avg. 70		avg. 21
1045	70	55	40	35
		140		65
		140		62
		avg. 110		avg. 54

Some of the samples and some of the runs used HF-HCl etches, while the remainder used HNO_3 etches with no discernible difference in results.

As another test of the mass spectrographic method, we participated in a round robin concerning the analysis of interstitials in refractory metals sponsored by the National Academy of Sciences. Only one other mass spectrograph laboratory (Bell and Howell) participated. All the other participating laboratories used standard techniques such as vacuum fusion, inert gas fusion, hot extraction, and the Kjeldahl method for nitrogen. Table 7 lists the results of both mass spectrographic analyses and the average of the other methods used. Table 7 indicates that the accuracy of the method is at least adequate. A compilation[20] of the analyses by classical methods indicates that the spread among the twenty participating laboratories makes mass spectrography a competitive method. Since these materials were not highly purified, the levels of the interstitials were not unusually low. The sensitivity of the mass spectrograph is of the order of 0.01 ppm wt., a figure which could not be approached by any of the classical techniques.

Table 7. Comparison of mass spectrograph with standard methods for interstitials in refractory metals (ppm wt.).

	Tantalum		Niobium		Molybdenum		Tungsten	
	MS	Classical	MS	Classical	MS	Classical	MS	Classical
Carbon	20	19	28	18	215	228	27	22
Nitrogen	7	31	12	48	6	14	11	13
Oxygen	16	25	34	53	33	14	46	9
Hydrogen	40	26	1.8	2.0	0.7	1.0	1.8	0.9

iv. Direct analysis of nonconductors.

The analysis of solid insulating materials by spark source mass spectrography has always been a difficult problem. Materials with very low conductivity, such as silicon and uranium dioxide, can be sparked and analyzed successfully, but insulators, including MgO, have been more difficult. There are several techniques available for the analysis of insulators but each has a severe drawback. The most common method is to reduce solid pieces to a powder by grinding and then using the technique described in Appendix A. This leads to contamination of the powder from materials picked up from the mortar and pestle. In high-purity materials analysis these impurities tend to overshadow the actual impurity content.

An alternative technique uses metallic electrodes to which the nonconductors are physically bound. A spark is drawn between the conducting electrodes and is then transferred to the insulator. The obvious

20

disadvantage of this method is the appearance of the metallic electrodes in the mass spectrum of the material of interest. The method is useful only in a qualitative analysis.

A third possibility is a method which has recently been developed at Bell and Howell Research Center. This technique entails the use of a high-purity metal counter electrode. For example, a piece of MgO would be one electrode while the electrode on the rf side of the circuit would be high-purity gold. It is claimed that the contribution from the rf side can be kept to 3-10% of the total ion current. Since gold is available in extremely high purity, contributions of up to 10% in the mass spectrum should not interfere in the impurity analysis of the MgO. This seemed to be a reasonable approach to our problem with solid MgO pieces, so it was tried in this laboratory with the results shown in Fig. 4. Examination of the plate shown in Fig. 4 reveals that the gold line at mass 197 is varying and is also greater than 3-10% of each exposure. This indicates that while appreciable amounts of MgO are being ionized, the gold is also making a major contribution to the mass spectrum. The varying gold content of each exposure makes quantitative interpretation of the plates impossible because the amount of MgO in a given exposure can only be estimated.

Since all of the above techniques exhibit some disadvantage, we decided to try direct sparking of two insulating electrodes. A private communication[21] from the laboratories at Associated Electrical Industries informed us that this has been done with small single crystals of MgO. This would be the most direct and satisfactory technique because it would avoid the inconvenience of conducting additives and the resultant interference in the mass spectrum.

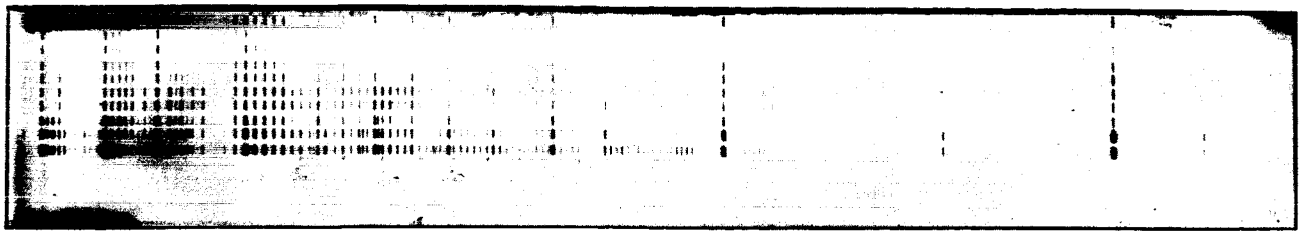

FIG. 4 Mass spectra of compacted MgO specimen with a gold counter electrode. Note the varying amount of gold in the spectra.

The first attempt at direct sparking of two pieces of MgO was encouraging. High-spark voltages were used and some intermittent sparking was observed. Local heating and crumbling of the electrodes were the major problems. Since all impurities of interest are at the 1 ppm level or higher, a great deal of ion current is not necessary for the analysis of MgO. The technique finally evolved uses 60 kV of spark voltage with the two electrodes held in aluminum clamps to ensure good electrical contact. Instrument parameters are described in Appendix C.

A typical mass spectrum from two MgO electrodes is shown in Fig. 5. The solid pieces were supported in aluminum clamps and a spark voltage of 55 kV was used. The spectrum is clean and normal plate interpretation techniques are used except for elements susceptible to thermal ionization. Due to the severe local heating, we get a marked enhancement of thermal ionization. The elements of interest which are affected are sodium, potassium, and calcium. Use of the doubly ionized lines at 11.5, 19.5, and 20, respectively, leads to reasonable analyses, although there is a slight loss of sensitivity. A factor of five for the ratio M^{+}/M^{++} has been found to give the best results.

v. Check analyses.

As part of this program, checks have been made, using classical techniques, on the reliability of the mass spectrographic method. Metallic elements have been determined using the emission spectrograph; oxygen has been checked by inert gas fusion, and hydrogen by hot extraction. The impurity levels in all cases have been high enough so that the sensitivity of the classical technique has not been pushed to the limit.

The details of the emission spectrographic method are given in

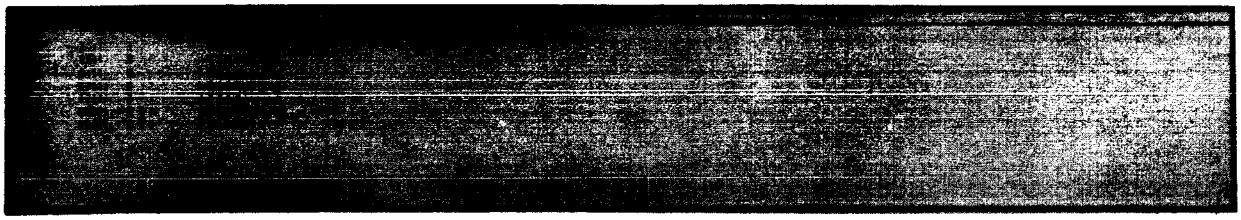

FIG. 5 Mass spectrum produced from two MgO electrodes. Spark voltage 5.5 kV. The high aluminum content is from aluminum holders.

(17-1)

Appendix D. After some preliminary difficulties with sensitivity we were able to get good checks on mass spectrographic values. The sensitivity problem has been solved by using second-order spectra for analytical purposes. Table 8 shows detection limits for impurities of interest.

Table 8. Detection limits for impurities in MgO by emission spectrography (ppm wt.).

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

Table 9 shows a comparison of mass and emission spectrographic results for two MgO powders and one sample of JPL magnesium metal. The agreement between the two methods for these samples is excellent.

Table 9. Comparison of mass and emission spectrographic analyses (ppm A).

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

ND - not detected.

As a further check on the accuracy of the mass spectrographic method, a series of MgO samples from the JPL process (Fig. 2, Table 3) have been analyzed by emission spectrography and a comparison of the results is shown in Table 10. With the exception of silicon most of the values agree reasonably well.

Check methods for the gases have included inert gas fusion for oxygen and hot extraction for hydrogen. Oxygen has been determined in a series of National Bureau of Standards materials, both by mass spectrography and inert gas fusion. The results of oxygen analyses are shown in Appendix B. Inert gas fusion analyses of the same samples agreed to within ± 30% of the certified values.

Hydrogen analyses have been performed using the classical hot extraction technique. The apparatus for this analysis is shown in Fig. 6. Results from this system have been somewhat disappointing in that values by hot extraction have been higher than mass spectrographic values for the same samples. The normal procedure for hot extraction hydrogen analyses involves a mass spectrometric gas analysis of the evolved gas to determine its hydrogen content. Since a gas mass spectrometer has not been available to us we have not been able to ascertain the hydrogen content of the gases extracted from MgO samples.

Table 11 shows the results of mass spectrographic and hot extraction analyses for hydrogen in a group of MgO samples. The reproducibility of the hot extraction system has been poor compared to the mass spectrographic technique. Variations of 100% have been observed for hot extraction, while ± 30% is typical for mass spectrography.

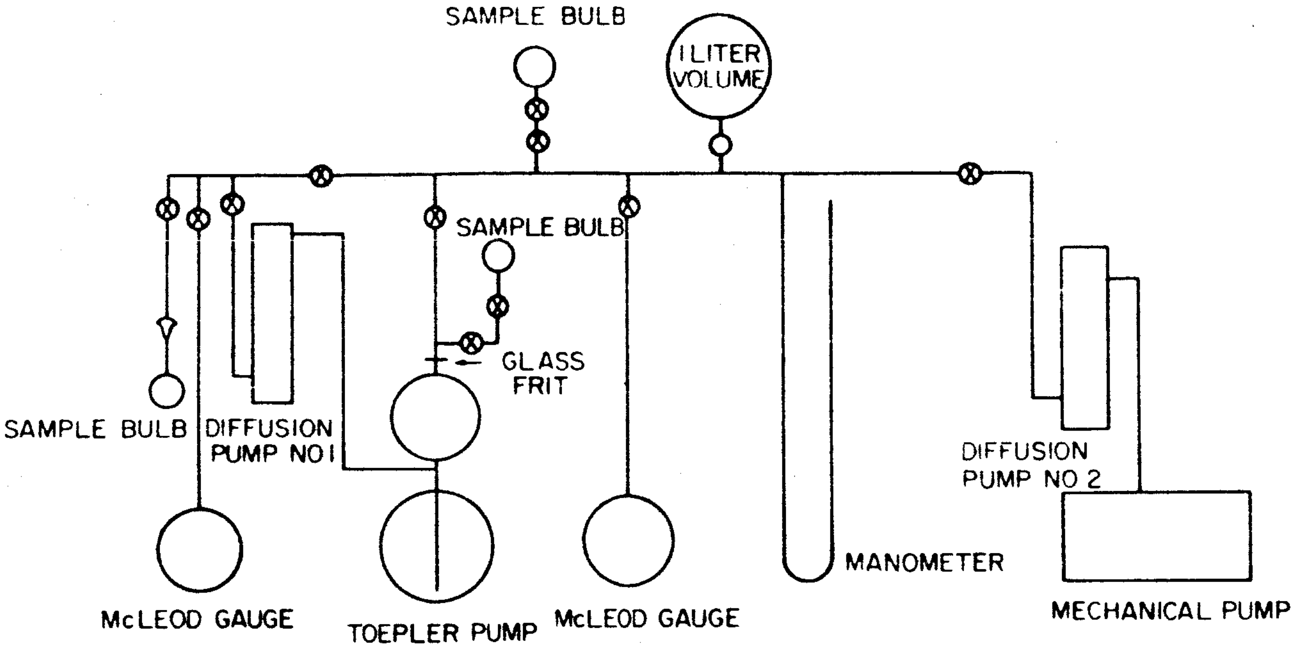

FIG. 6 Hot extraction system for hydrogen.

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Table 10. Comparison of mass and emission spectrographic analyses (ppm A).

Sample No.	2		3		4		5		10		11		13	
	M	E	M	E	M	E	M	E	M	E	M	E	M	E
Boron	3	1	1	1	5	1	5	1	3	1	8	3	<1	1
Aluminum	10	3	10	7	20	15	30	30	15	20	5	5	30	5
Silicon	190	30	175	10	115	20	170	7	75	15	65	30	80	30
Calcium	12	5	75	10	60	15	30	5	40	10	30	25	30	15
Iron	8	2	3	2	20	2	8	2	20	2	14	7	10	5

M = mass

E = emission

* * *

Table 11. Hydrogen analyses by mass spectrography and hot extraction (ppm wt.).

Sample No.	Mass. Spec.	Hot Extraction
OP 125	75	200
OP 128	25	185
OP 111	35	300
OP 14	15	175

Because of the excellent checks obtained from mass spectrographic analyses of hydrogen standards using refractory metals (Table 7), we would tend to reject the hot extraction values.

An interesting feature of hydrogen analyses by mass spectrography is the correlation of the peaks at mass 1 (hydrogen) and mass 17 (OH^+). The intensities of the two peaks vary together, which suggests that hydrogen in MgO is present, at least partly, as hydroxyl.

vi. Reproducibility and accuracy.

It is difficult to assess the reproducibility and accuracy of the mass spectrographic methods we have used for the analysis of magnesium oxide.

The complete absence of standard MgO materials makes any value a guess. However, by using metal systems where standards are available, we can make some estimates of these parameters. In systems of refractory metals we feel that both reproducibility and accuracy for mass spectrographic methods are better than ± 50%. In cases where standards are available before analysis, this figure can probably be reduced to ± 30%. In a long-term series of analyses relative values are probably also good to ± 30%.

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3

APPENDIX A

The mass spectrographic analysis of insulating and conducting powders is a straightforward procedure. Conducting powders need only to be pressed into a shape which is suitable for use as an electrode. The insulating powder requires the addition of a conducting material such as graphite or silver. The major problem encountered in our work has been contamination of the compact with material from the die. A reliable method for removal of this contamination has been developed. The procedure described below is for insulating powders.

A weighed sample of the insulating powder is mixed with twice the weight of pure silver powder in a Wig-L-Bug for 1 minute. The silver powder is 99.999% pure and is available from L. Light Co., Ltd., Colnbrook, England. The two-to-one ratio for silver to magnesium oxide is necessary to form strong electrodes. Many other powders require less silver. After mixing has been accomplished, two electrodes are prepared using the Ringsdorff Powder Moulding Die (Ringsdorff Carbon Corp., East McKeesport, Pa.). This die will produce electrodes 1/16" x 1/16" x 5/8" which can be inserted directly into MS-7 electrode holders.

The surface cleaning procedure, which is extremely important, consists of physical removal of the surface of the compact. After the compact is removed from the die the surface is scraped with a tantalum tool. Next, the piece is split lengthwise to expose the interior. The two electrodes are mounted in the instrument so that sparking will occur on interior surfaces. The last step in the cleaning is a long (30 to 100×10^{-9} coulombs) prespark exposure. This procedure has been successful for the removal of surface contaminants insofar as we have been able to judge.

Silver has been used exclusively for our work with powders because it produces a strong electrode which withstands the stresses of the cleaning procedure. Graphite is the alternative conducting additive. We have avoided using graphite because the electrodes produced are much weaker, structurally. However, graphite is available in very high purity and may be needed if an impurity of interest is present in the silver powder.

APPENDIX B

The Analysis of Nitrogen, Oxygen and Hydrogen
by
Spark Source Mass Spectrography

F. D. Leipziger and R. J. Guidoboni
(Sperry Rand Research Center Report, SRRC-RR-65-102)

The Analysis of Nitrogen, Oxygen, and Hydrogen
by
Spark Source Mass Spectrography*

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ABSTRACT

A procedure for the determination of nitrogen, oxygen and hydrogen by spark source mass spectrography is described. The reduction of instrument blank levels is an important consideration in this analysis. Factors which influence the blank level include vacuum, choice of sample etch, and baking of the source. A pre-spark of 100 to 300 nanocoulombs is considered an integral part of the procedure, since it apparently removes the last traces of surface impurities. Blanks below 1 ppm atomic have been observed. The procedure can also be applied for the determination of carbon.

INTRODUCTION

The use of the spark source mass spectrography for low-level impurity analyses is a well-established procedure (1,2). One of the advantages of the instrument is its ability to ionize all elements with equivalent sensitivity. However, while analyses of some nonmetallic impurities, such as sulphur, boron, and phosphorous are routine, analyses of the permanent gases have always been more difficult. Carbon has been traditionally grouped with hydrogen, nitrogen, and oxygen as being difficult to analyze by this technique.

There are several reasons for the difficulties encountered with these analyses. The major problem lies in the widespread occurrence of these elements, especially in the residual gases present in the source of the instrument, even at pressures as low as 10^{-8} torr. A second problem is the ease with which these elements are adsorbed on the surface of a sample.

Indeed, an etch which is meant to clean a sample surface may, instead, introduce large amounts of carbon, nitrogen, hydrogen, and oxygen.

As an indication of the apparent concentration of these elements, when no effort has been made to reduce the blank, we might find carbon and hydrogen to appear to be 1% and nitrogen and oxygen to appear to be 0.1% in a typical sample, even with a source pressure of 5×10^{-8} torr. These values are strictly an indication of the blank level. When appropriate steps are taken we find blank levels ranging from 0.3 to 1 ppm atomic for carbon, nitrogen, oxygen, and hydrogen.

It was originally feared that blank levels for hydrogen would be much higher than for nitrogen or oxygen because of large steel surfaces which had been hydrogen annealed (3). However, it has been possible to detect hydrogen below 1 ppm wt. in refractory metals. By baking, presparking, and the judicious choice of etching reagents, we have been able to hold blanks for H, N, and O to reasonable levels and perform analyses for these elements within the capabilities of the spark source mass spectrograph.

EXPERIMENTAL

We are reporting the results of a series of analyses for nitrogen and oxygen in NBS steels. These materials were chosen because they have been certified for nitrogen and oxygen content.

Also reported are analytical results for low levels of nitrogen, oxygen, and hydrogen in platinum, gold, and some refractory metals. The refractory metals were analyzed during a round robin sponsored by the National Academy of Sciences, and mass spectrographic values are compared with the mean of all other methods. However, the technique to be described below has also been found applicable to other metals and to many insulators. Although analyses for carbon in these same materials appear to give reasonable results, there are no certified samples available.

Sample Preparation

The three factors which are most important to the analyses of these elements are: good vacuum to remove surface layers; baking to remove adsorbed gases from the source and sample, and presparking to present a clean surface for analysis. The use of oxidizing acids was avoided in this study. HF and HCL were used to etch the steel samples, although extensive presparking and baking after an etch with HNO_3 were sufficient to give reasonable values for oxygen and nitrogen.

After a relatively large amount of material was removed by the etchant, the samples were rinsed and placed in the mass spectrograph. Once a suitable vacuum had been attained (5×10^{-8} torr or better) the source was baked overnight, at a temperature of 175°C. Prior to making the analytical exposures, a prespark exposure of 300×10^{-9} coulombs was made. Then the analytical exposures are made in the reverse of the normal order, i.e., the longest exposure is made first with subsequent shorter exposures. We have found that this procedure keeps the sparking area free of re-adsorbed gases.

A pair of electrodes, each 1/8" x 5/8", were cut from the center of all samples. These were etched in HF-HCL and placed in the mass spectrograph. After baking and presparking, a series of analytical exposures ranging from 100×10^{-9} to 0.001×10^{-9} coulombs were taken.

Plate interpretation was made using both visual and densitometric techniques. The analytical lines used were at masses 14 and 7 for nitrogen, 16 and 8 for oxygen, and 1 for hydrogen. A factor of ten was used for the ratio M^{+}/M^{++}.

Instrumental parameters were: spark voltage 30%; repetition rate 100 cps; pulse length 200 microseconds.

RESULTS AND DISCUSSION

The results of our analyses are shown in Tables 1 - 3. While the accuracy of the results is not good when compared to chemical methods, it is nevertheless well within the accuracy of the instrument. It is interesting to note that all analyses were performed assuming a sensitivity coefficient of unity. This is in marked contrast to the work of Harrington et al. (4) who found an experimental sensitivity factor of 6.4 for nitrogen and 7.9 for oxygen in standard iron samples. There are two major advantages of the technique: sensitivity (1 ppm atomic or less) and the wide variety of materials to which it can be applied.

Table 1. Oxygen and Nitrogen Analyses of NBS Certified Steels (ppm wt.).

Sample No.	O_2 Certified	O_2 Found	N_2 Certified	N_2 Found
1041	170	117	40	25
		179		17
		95		21
		Avg. 130		Avg. 21
1042	170	245	140	70
		210		115
		115		95
		Avg. 190		Avg. 93
1044	90	90	40	14
		65		28
		55		22
		Avg. 70		Avg. 21
1045	70	55	40	35
		140		65
		140		62
		Avg. 105		Avg. 54

Table 2. Oxygen and Nitrogen Analyses of Gold and Platinum (ppm wt.).

	O_2	N_2
Gold "A"	0.08	0.07
	0.08	0.11
	0.13	0.08
Gold "B"	0.70	0.18
	0.62	0.11
	0.79	0.10
Platinum	4.1	0.85
	6.0	0.60
	3.7	0.66

Table 3. Hydrogen Analyses of Refractory Metals (ppm wt.).

Material	Hydrogen, Certified	Hydrogen, Found
Molybdenum	1.0	0.7
Niobium	2.0	1.8
Tantalum	26	40
Tungsten	0.9	1.8

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APPENDIX C

Because of the problems associated with the analysis of solid insulators, which have been outlined in Sec. II. B. iv. of this report, we have made attempts to avoid using conductors as an aid in the ionization of insulators. A private communication from laboratories in England stated that they had been able to achieve direct sparking of small MgO single crystals. Since this type of technique would be of direct aid to us, we attempted a similar technique.

There has been no real problem with the direct sparking of two MgO electrodes. Unusually high-spark voltages are necessary and the ion currents produced are feeble, but enough integrated current is available in a reasonable time to obtain 1 ppm A sensitivity easily. Table 1 lists mass spectrograph settings for sparking of insulators. The problem of electrical contact between the sample and the holder has necessitated the use of a soft metal clamp for holding the sample. If the MgO samples are inserted directly into the holder, the sparking is both weak and erratic. Since high temperatures are developed in the sample rods, the holder material must have a fairly high melting point. Aluminum has proved to be the most useful material, although some aluminum from the holder appears in the spectrum.

Thermal ionization of sodium, potassium, and calcium is enhanced by the heat generated in the samples during sparking. Use of the doubly ionized lines at 11.5 for sodium, 19.5 for potassium, and 20 for calcium makes analysis for these elements possible with only a small loss in sensitivity.

There apparently is some correlation between the pressure at which the MgO is compacted and the ease of sparking. MgO samples of the highest density sparked with the least trouble while friable materials were most difficult to spark.

Table 1. Instrument settings for analysis of insulators.

Spark voltage	55-65 kV
Pulse length	100 μsec
Repetition rate	30-300 cps

Average time for 1×10^{-9} coulomb exposure is 15 min.

APPENDIX D

Spectrographic Analysis of MgO

Principle.

A method has been developed which provides for the determination of impurities in high-purity MgO. The samples are weighed directly into necked-cup electrodes and excited with a dc arc in an argon-oxygen atmosphere. The resulting spectra are recorded on a photographic plate and the transmittances of the analytical and internal standard lines are measured and Δ log I values are calculated. The percent concentration of the various impurities is determined from previously prepared analytical working curves.

Preparation of Standards.

Standards were prepared to cover the concentration range of .001 to .1 percent. These standards were synthesized by the preparation of a mixture of Johnson Matthey "specpure" reagents and the subsequent addition of varying amounts of high-purity magnesium oxide to obtain the desired impurity levels. All powders used were ground to pass a 200-mesh sieve with a boron carbide mortar and pestle to ensure homogeneous mixing in a ball mill. The standards prepared in this manner were then diluted with graphite in a 1:1 ratio and placed in a ball mill for homogeneous mixing.

41

Sample Preparation.

All samples are ground to pass a 200-mesh sieve in boron carbide (as were all reagents used for standards). An equal weight of graphite was added to the samples, which were then placed in a ball mill for mixing.

Procedure.

Duplicate 25 mg charges of both standards and samples were weighed directly into necked-cup electrodes and ignited with a dc arc in an atmosphere of 70% argon and 30% oxygen (to eliminate cyanogen-band formation) using the operating parameters listed in Table 1. After the spectra are recorded the plate is developed, the transmittances of the analytical and internal standard lines are measured, and Δ log I values are calculated using the Seidel function. The percent concentration is determined on an analytical working curve thus prepared.

Table 1. Operating parameters for the analysis of MgO.

Wavelength range	2400-4400 Å
Excitation	dc arc
Amperage	12 ± .5 A
Preburn	none
Exposure	45 sec
Analytical gap	3 mm
Slit width	10 μ
Slit height	2.5 mm
Atmosphere	70% argon/30% oxygen
Emulsion	Kodak SA-1

APPENDIX E

Listed below are the results of analyses of various materials submitted to the Sperry Rand Research Center by the Jet Propulsion Laboratory for mass spectrography.

Table 1. Tantalum carbide analyses for oxygen.

Sample No.	Oxygen (ppm wt.)
3-4	180
2-4	500
3-3	5500
3-2	2200
3-1	1800
2-5	4500
2-3	280
2-2	750

* * *

Table 2. Mass spectrographic tungsten analyses (ppm wt.)

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

● Probable die contamination

Table 3. Mass spectrographic copper analyses (ppm A).

Sample 157-69	
C	75
N	10
0	15
Al	1
Si	7
P	< 1
S	< 1
Cl	1
K	1
Fe	2
Ag	2

Sample 157-72		
C	110	
N	75	
0	95	
B	5	
F	5	(etch)
Mg	3	
Al	10	
Si	30	
P	3	
S	5	
Cl	15	(etch)
K	8	
Ca	20	
Fe	10	
Ag	18	

Sample 157-73	
C	90
N	5
0	12
Al	25
Si	30
Fe	1
Ag	1

Sample 157-74	
C	25
N	5
0	30
Si	10
Fe	8
Ga	2
Ag	20

Sample 157-77		
C	70	
N	10	
0	30	
B	1	
F	300	(etch)
Na	1.5	
Al	2	
Cl	1100	(etch)
K	6	
Si	10	

* * *

Table 4. Mass spectrographic niobium analyses (ppm A).

MRC-ANN-2		MRC-UA
2	F	5
10	Mg	5
65	Al	200
185	Si	450
2	S	5
5	Cl	15
3	K	3
35	Ca	80
5	Cr	10
30	Fe	30
25	Zr	45
25	Mo	35
30	Ta	50