A Method to Perform Direct Oxygen Analysis on Lunar Simulants and Other Complex Oxide Materials

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A Method to Perform Direct Oxygen Analysis on Lunar Simulants and Complex Oxide Materials

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ABSTRACT

An essential requirement for making space travel and long term missions more efficient and affordable to NASA includes finding innovative ways to supply oxygen for life support and propulsion. In this experiment, carrier gas hot extraction was investigated as a possible method for measuring the oxygen from samples of lunar soil simulants before and after oxygen extraction. The determination of oxygen using the RO600 Oxygen Determinator is usually limited to oxides with low oxygen concentrations, but after the manipulation of certain furnace operating parameters such as analysis time and ramp rate, the RO600 was used to determine the oxygen content of high concentration oxides such as Fe_2O_3, Al_2O_3, and SiO_2.

INTRODUCTION

Currently, three types of reduction processes are being investigated as possible methods for extracting oxygen from oxygen rich lunar soil. The three processes under investigation include hydrogen reduction, carbothermal reduction, and molten oxide electrolysis. All of these processes reduce the metal oxides found within lunar soil to pure metals or alloys and the gaseous by-products are further processed to produce oxygen (except in the case of molten oxide electrolysis that produces oxygen in one step). The amount of oxygen produced must be measured for each process. In the past, indirect oxygen measurement has been performed by determining the oxidation state of the metals. However, for this study a LECO RO600 Oxygen Determinator (RO600) was purchased in order to directly measure the oxygen content of the processed by-products. Other objectives included identifying specific oxides in lunar soil simulant and determining which oxides are reduced more than others.

Table 1

Oxide	**Oxygen Percentage**
Al_2O_3	47.1%
CaO	28.5%
Fe_2O_3	30.4%
SiO_2	53.3%
TiO_2	40.1%

EXPERIMENTAL

Materials

Five high concentration pure oxides were investigated with theoretical oxygen contents ranging from 29 to 53% oxygen as shown in Table 1. Mixtures of Fe_2O_3 and SiO_2, JSC-1A lunar soil simulant (JSC-1A), and hydrogen-reduced samples from Lockheed Martin were also investigated. While lunar soil was not used during any parts of this study, the composition of JSC-1A is comparable to the composition of actual lunar soil found in Mare regions. As shown in Table 2, JSC-1A served as an adequate substitute and has only minor differences in composition compared to lunar soil.

■ Lunar Soil	■ JSC-1A
■ 47% SiO_2	■ 47% SiO_2
■ 2% TiO_2	■ 2% TiO_2
■ 15% Al_2O_3	■ 18% Al_2O_3
■ 3% Fe_2O_3	■ 0% Fe_2O_3
■ 7%FeO	■ 11%FeO
■ 9% MgO	■ 10% MgO
■ 10% CaO	■ 11% CaO

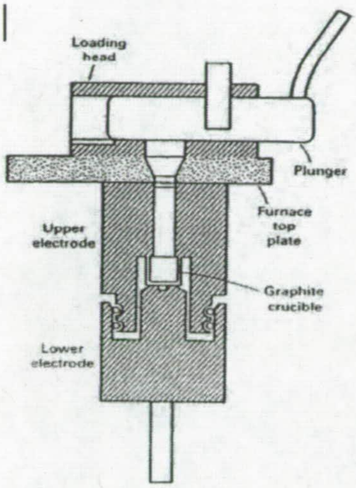
Table 2
Composition of
Lunar Soil vs. Lunar Soil Simulant JSC-1A

All samples of high concentration oxides were in the form of powders and had at least a 99.9% purity. Helium, with a purity of at least 99.9%, was used as the carrier gas, and nitrogen was the gas used for purging of atmosphere. A combination of tin capsules, nickel baskets, and high-temperature graphite crucibles were used in order to provide a more uniform rate of heating.

Apparatus and Procedure

Before analysis began, powder samples weighing approximately 0.02 grams were placed into tin capsules which were crimped closed. Next, tin capsules were placed tightly into nickel baskets. Once the samples were prepared, the loader button of the RO600 was pushed and the nickel basket with tin capsule was placed into the loading head, as indicated in figure 1. Analysis began by placing an empty, high-temperature graphite crucible on the lower electrode. The electrodes closed once the loader button was pressed again and atmosphere was purged from the crucible. Gasses that were trapped in the graphite were driven off as high current passed through the crucible. A sample was then dropped from the loading head into the graphite crucible The crucible was electrically heated either at fixed power ranging from 1000 to 5000 W with a minimum analysis time of 60 seconds, or with a power-time-program in the ramping mode with varying powers and times in order to determine the best parameters for oxygen measurement. Again, high current passed though the crucible increasing the temperature. Carbon from the crucible reduced the sample forming carbon monoxide and carbon dioxide.

Figure 1



Gasses released from high oxygen content samples, the type of samples investigated in this study, passed from the furnace to the carbon monoxide and carbon dioxide detectors, whereas gasses released from low oxygen content samples passed through heated rare earth copper oxide which converted carbon monoxide to carbon dioxide.

The RO600 measured the oxygen content of the sample by using an infrared (IR) detection system as shown in figure 2. The IR source radiated visible energy as well as all of the wavelengths in the infrared spectrum. As the sample gasses passed through the IR cells, they were analyzed at wavelengths specific to each gas.

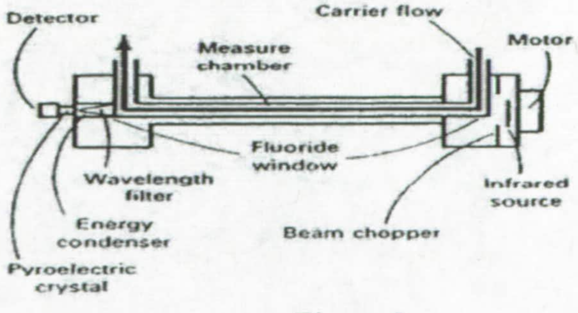


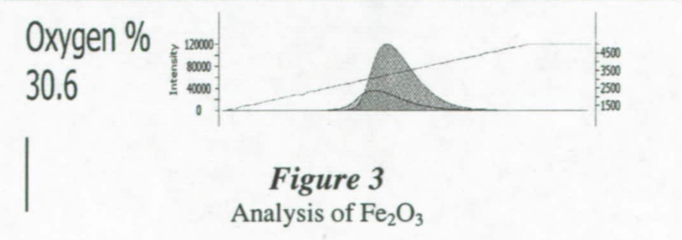
Figure 2

Once the analysis was complete, a graph of the specific oxide was displayed onto the attached computer monitor. Each graph showed the measurement of oxygen as a peak or series of peaks with an area representative of the oxide's measured oxygen percentage based upon molecular weight. Information displayed above the graph also included the specific name of the sample, total weight in grams, date and time at which analysis began, method used for analysis, and total time of analysis in seconds. The normal view of the graphs depicted peak formations, time of analysis, intensity, and power or temperature at which the oxygen was measured. Two types of software known as OxSep and Peak Find, included with the RO600, were also available in order to view the oxygen percentage of each peak for graphs with multiple peaks. Before a new analysis began, both electrodes were cleaned with a brush and vacuumed in order to prevent contamination of later analysis.

RESULTS AND DISCUSSION

Pure oxides

In order to identify the specific oxides in lunar soil simulant, pure oxides were investigated. Based upon the power level and time at which the peak of pure oxides occurred, the same oxide could be identified using lunar soil simulant. Accurately determining the power level and time at which peaks occurred for easily reduced pure oxides, including Fe_2O_3 and TiO_2, required minimal manipulations of furnace parameters such as analysis at low and high power, minimum analysis time, and ramp rate. As shown in figure 3 and figure 4 below, the peak formations for easily reduced pure oxides were reproducible and the measured oxygen percentages were exceptionally close to the theoretical values shown in table 1 above. For example, the results of numerous sample runs showed that the necessary furnace parameters needed to produce the most accurate and repeatable results for Fe_2O_3 were at a power level of approximately 1800 W and its peak occurred between 20 and 30 seconds. However, harder to reduce pure oxides such as Al_2O_3 and SiO_2 required numerous manipulations of furnace parameters in order to observe relatively similar peak formations and oxygen percentages close to theoretical values. One of the problems faced during the analysis of Al_2O_3 included saturation of the IR cells. Results were improved after lowering the mass from 0.04 grams to 0.02 grams in order to stay within detection limits. There were also discrepancies between the theoretical 47% of oxygen for Al_2O_3 and the maximum 45% of oxygen measured. Even after increasing and decreasing the ramp rate, the theoretical percentage of oxygen for Al_2O_3 was never obtained. As shown in figure 5 and figure 6, first manipulations of furnace parameters for hard to reduce oxides were unsuccessful. While later manipulations helped to improve the measured oxygen percentages, furnace parameters that produce repeatable peak formations have yet to be found.


502-138

Name	Mass	Analysis Date	Method
502-138	0.0271	6/4/2007 11:02:35 AM	Med-High Oxygen Conc

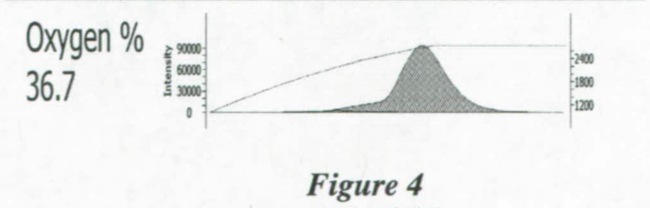
Oxygen %
30.4

502-138

Name	Mass	Analysis Date	Method
502-138	0.0294	6/4/2007 11:07:36 AM	Med-High Oxygen Conc

Oxygen %
30.6

Figure 3
Analysis of Fe_2O_3


TiO2

Name	Mass	Analysis Date	Method
TiO2	0.0216	7/10/2007 4:16:07 PM	Med-High Oxygen Conc

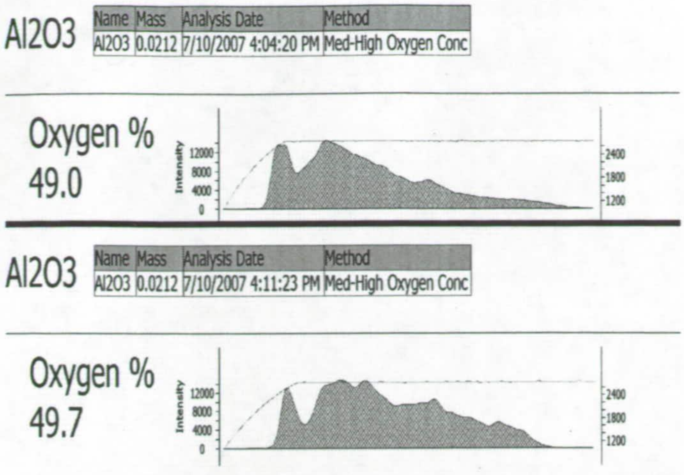
Oxygen %
36.3

TiO2

Name	Mass	Analysis Date	Method
TiO2	0.0210	7/10/2007 4:21:00 PM	Med-High Oxygen Conc

Oxygen %
36.7

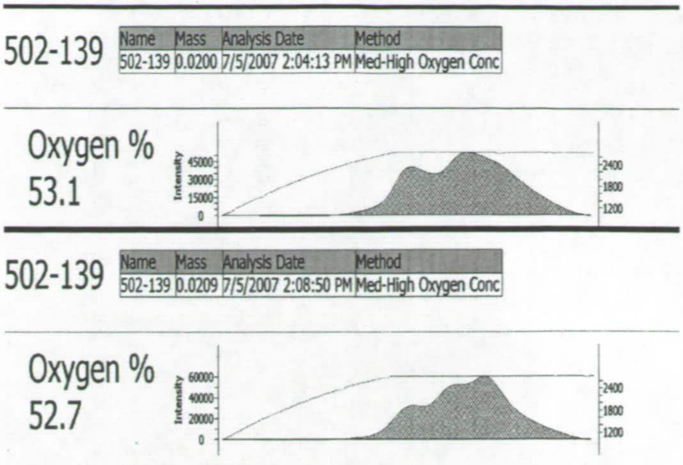
Figure 4
Analysis of TiO_2



Name	Mass	Analysis Date	Method
Al2O3	0.0212	7/10/2007 4:04:20 PM	Med-High Oxygen Conc

Name	Mass	Analysis Date	Method
Al2O3	0.0212	7/10/2007 4:11:23 PM	Med-High Oxygen Conc

Figure 5
Analysis of Al_2O_3



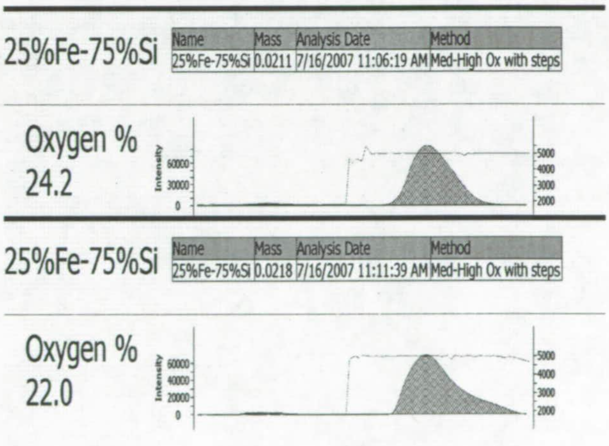
Name	Mass	Analysis Date	Method
502-139	0.0200	7/5/2007 2:04:13 PM	Med-High Oxygen Conc

Name	Mass	Analysis Date	Method
502-139	0.0209	7/5/2007 2:08:50 PM	Med-High Oxygen Conc

Figure 6
Analysis of SiO_2

Mixtures of Fe_2O_3 and SiO_2

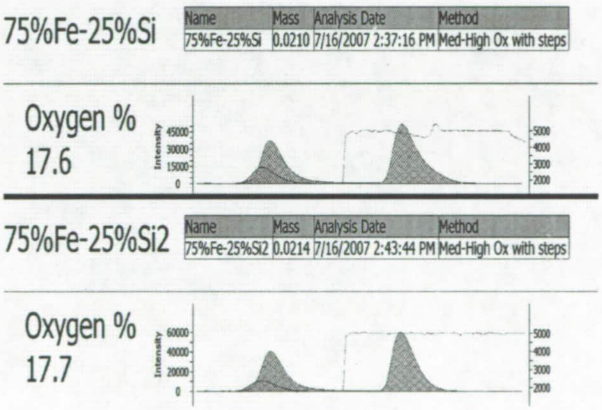
Two mixtures of Fe_2O_3 and SiO_2 were made with compositions of 75% Fe_2O_3 and 25% SiO_2 as well as 25% Fe_2O_3 and 75% SiO_2. Based upon the power level and time at which peaks occurred for pure Fe_2O_3 and SiO_2, a step method was created to ramp the furnace to 1800 W and held for 45 seconds in order to identify Fe_2O_3 followed by a step to 5000 W and held for 50 seconds to identify SiO_2. As shown in figure 7, the first peak formation of the 75% Fe_2O_3 and 25% SiO_2 mixture compares to the peak formation observed for pure Fe_2O_3 just as the second peak compares to the peak formation observed for pure SiO_2.



Name	Mass	Analysis Date	Method
25%Fe-75%Si	0.0211	7/16/2007 11:06:19 AM	Med-High Ox with steps

Name	Mass	Analysis Date	Method
25%Fe-75%Si	0.0218	7/16/2007 11:11:39 AM	Med-High Ox with steps

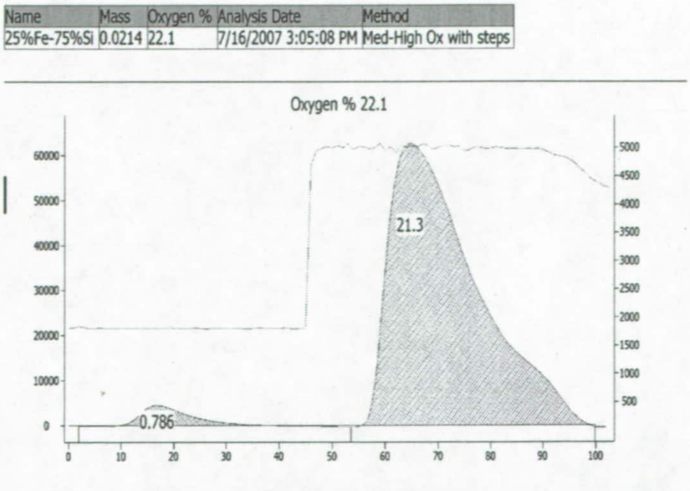
Figure 7
Analysis of $25\%Fe_2O_3$-$75\%SiO_2$



Name	Mass	Analysis Date	Method
75%Fe-25%Si	0.0210	7/16/2007 2:37:16 PM	Med-High Ox with steps

Name	Mass	Analysis Date	Method
75%Fe-25%Si2	0.0214	7/16/2007 2:43:44 PM	Med-High Ox with steps

Figure 8
Peak find view of the
Analysis of $25\%Fe_2O_3$-$75\%SiO_2$



Name	Mass	Oxygen %	Analysis Date	Method
25%Fe-75%Si	0.0214	22.1	7/16/2007 3:05:08 PM	Med-High Ox with steps

Figure 9
Analysis of 75% Fe_2O_3-$25\%SiO_2$

Lunar Soil Simulant

Based upon the successful peak formations observed in the two mixtures of Fe_2O_3 and SiO_2, the oxygen content of JSC-1A lunar soil simulant was also measured using the exact same furnace parameters. The peak formations were comparable to those of pure Fe_2O_3 and SiO_2 with the Fe_2O_3 peak occurring between 20 and 30 seconds and the peak occurring after 60 seconds. Based upon the results received, the separation of easily reduced oxides from harder to reduce oxides proved to be possible.

Lockheed Martin samples
Lockheed Martin has been working on the hydrogen reduction process to produce oxygen from lunar soil. The samples received from Lockheed Martin (a total of 4 samples) were produced during reduction reaction using JSC-1A at different reaction temperatures. Because the samples were reduced (oxygen extracted), caution was taken to minimize the exposure of the samples to air. Therefore, all the sample handling was done in a glovebox under a nitrogen environment. The hydrogen reduction process is believed to be selective to reduce iron oxide, which composed approximately 10%wt of the composition of JSC-1A. In theory, if all the iron oxide in the simulant would have been reduced the samples should have lost approximately 2.5% oxygen. The results on these samples showed an oxygen percent reduction of 1.2% - 2.4%. At this point, specific information on the experimental conditions is not available to make any conclusions on the results of the analysis.

Using OxSep to determine the percentage of oxygen for oxides with several peaks proved to not be promising for high concentration oxides based upon the comments of researchers at LECO Corporation, the manufacturer of the RO600. While investigations are still underway, the Peak Find software appeared to be a possible method for studying samples with mixtures of oxides such as lunar soil simulant.

CONCLUSIONS

After numerous manipulations of various furnace parameters such as analysis at low and high power, minimum analysis time, and ramp rate, it was concluded that easily reduced material such as Fe_2O_3 and TiO_2 can produce peak formations and oxygen percentages in a reproducible manner. Hard to reduce oxides such as Al_2O_3 and SiO_2 require further manipulations in order to produce more accurate and reproducible results. In accordance with the second objective of identifying oxides in lunar soil, the results from the analysis of the Fe_2O_3 and SiO_2 mixtures and the lunar soil simulant proved that the technique is promising in its ability to separate easily reduced oxides from harder to reduce oxides. No method was found to separate individual peaks. The analysis of the Lockheed Martin samples correlated to the expected value based on experimental results.

ACKNOWLEDGEMENTS

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