Spectrographic Analysis of Refractory Magnesium Oxide: A Buffer Approach

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Summary. A method has been described for the determination of eighteen trace elements in refractory magnesium oxide by optical emission spectroscopy. The main feature of the method is the use of a spectroscopic buffer instead of a carrier. When conducting graphite powder has been added as a buffer to the MgO sample prior to its excitation in a d.c. arc, there has been a smooth distillation of the matrix magnesium as well as the trace elements into the arc column. Addition of a carrier, however, does not either completely prevent the emission of Mg spectrum or result in smooth distillation. A Hilger large quartz spectrograph has been employed to record the spectra excited at 10 amp d.c. The Ga line at 265.99 nm has been used as an internal standard for the more volatile trace elements and the Mg line at 280.98 nm has been employed as an internal standard for the less volatile trace elements. The detection limits obtained range from 0.5–5 ppm. The mean relative standard deviation (RSD) of the method is ±14%.

1. Introduction

In the production of nuclear grade uranium metal high-purity magnesium finds its use as an alternative to calcium in the reduction of UF₄ to metal. Such high-purity magnesium needs to be analysed for several trace elements. The analysis of magnesium by OES can be conveniently done after its conversion to the refractory oxide (MgO). In the past Pevtsov et al. [1] and Degtyareva et al. [2] reported OES methods for the analysis of MgO. Pevtsov et al. [1] employed the well known carrier-distillation technique originally developed by Scribner and Mullin for the analysis of refractory U₃O₈ [3]. Degtyareva et al. [2] used a d.c. arc with two current settings (7 amp and 12 amp) and two exposure times (20 s and 45 s) to excite the MgO sample and estimate various trace elements. Recently Capdevila and Diaz-Guerra [4] reported a method which uses a carrier for the determination of many elements. But, they used the complete burn method for the determination of Al and Cr. Initially, in our laboratory also, the carrier approach was attempted [5]. However, the method did not yield good reproducibility with routine samples.

Magnesium oxide being much lighter than U₃O₈, a buffer approach seemed desirable for its analysis. Details of the method are presented below.

2. Experimental

2.1 Preparation of Standards

The eighteen trace elements were divided into two groups on the basis of the concentration range in which they were estimated. Group I included Ag, B, Bi, Co, Cr, Cu, Ge, Mn, Ni, Pb and Sn (11 elements) and Group II included Be, Cd, Fe, In, Sb, Ti and V (7 elements). Using Specpure grade MgO, a master standard was first prepared such that it contained 0.05 % and 0.5 % of Group I and II elements, respectively. All the trace elements, except boron were incorporated by adding their oxides (Specpure grade). Boron was added as metal. The master standard was successively diluted to obtain a set of seven standards in which Group I elements range from 0.5–50 ppm and Group II elements range from 5–500 ppm. A buffer mixture was prepared by grinding together pure conducting graphite powder and NaF in the ratio 9:1 by weight. 0.1 % of Ga₂O₃ was incorporated in the buffer mixture in order to use a Ga-line as internal standard. Each standard was mixed and thoroughly ground with the buffer mixture in the ratio 4:1 by weight.

2.2 Preparation of Samples

Samples were received mostly as Mg metal. 100 mg of the metal was dissolved in a minimum volume of (1:1) HNO₃ (Gr-grade) to obtain magnesium nitrate. The nitrate was converted to oxide by heating it over a sand bath, till NO₂.
fumes disappeared. The oxide thus obtained was ignited for 3 h at 500°C in a muffle furnace. The oxide was collected and ground with the buffer mixture in the ratio 4:1 by weight.

### 2.3 Procedure

Duplicate charges, each weighing 30 mg, of standards and samples were loaded in the cavity of ultra high-purity graphite electrodes. The electrode cavity should be just enough to accommodate the quantity of 30 mg (standard or sample) up to the brim. The loaded electrodes were thoroughly tapped and kept under an IR lamp till the time of arcing. The spectra were photographed on a Hilger large quartz prism spectrograph under the experimental conditions given in Table 1. The analytical lines chosen for constructing the working curves are listed in Table 2. The concentration ranges for which the working curves were linear for various elements are given in column 4 of Table 2.

### 3. Discussion

In order to effectively use the carrier-distillation technique for the analysis of refractory U₃O₈, Scribner and Mullin designed, specially, a two electrode system. One of the electrodes (ASTM type S-2) contains a very deep cavity and it sits on another electrode called pedestal (ASTM type S-1). The two main functions of such an electrode system are: (1) to keep the charge (100 mg of U₃O₈) at the bottom of the electrode and (2) to minimize the temperature gradient that normally exists along the length of the cavity of an electrode. In the case of refractory U₃O₈ the above functions could be realized to a high degree because of the high density of U₃O₈ (d = 8.3 g/cm³). The realization of the above two functions helps in smooth distillation of the trace elements from U₃O₈ along with the carrier into the arc column. However, in the case of MgO which is less dense (d = 3.4 g/cm³) compared to U₃O₈, it is difficult to achieve the above two functions for the following reasons. Due to the lightness of the MgO particles, operations such as tapping and venting would not help in keeping the charge at the bottom of the electrode. Only about 20 mg would occupy the volume occupied by 100 mg of U₃O₈. If the charge is increased so as to increase the intensities of the spectral lines, it would come up to the brim of the electrode, thus subjecting the sample to a high temperature and resulting in the emission of matrix magnesium. Our experiments with a carrier showed that the emission intensities of the lines due to trace elements as well as Mg were not reproducible from charge to charge. We, therefore, attempted the addition of a buffer. When high-purity conducting graphite powder was added to MgO in the ratio 4:1 by weight and a charge of 30 mg was loaded in an electrode that had a cavity depth just enough to bring the charge up to the brim, the spectra were highly reproducible. Both the volatile and less volatile elements came into the arc column uniformly during the exposure period. Although magnesium lines appeared along with those of the trace elements, they did not pose any problem because they were few in the spectral region of interest (241 – 340 nm). Further, a line due to Mg (280.98 nm) with those of the trace elements, they did not pose any problem because they were few in the spectral region of interest (241 – 340 nm). Further, a line due to Mg (280.98 nm)