

SHORT COMMUNICATIONS

ON THE APPLICABILITY OF THE CARRIER-DISTILLATION AND BUFFER TECHNIQUES TO THE SPECTROGRAPHIC ANALYSIS OF LIGHTER REFRACTORY OXIDES LIKE Al_2O_3 AND MgO

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In the 1940s spectrographic analysis of nuclear grade uranium to determine B and Cd (nuclear poisons) at fractional parts per million, posed a serious problem. Then came the discovery of the well-known carrier-distillation (C-D) technique by Scribner and Mullin¹. In this ingenious technique the matrix uranium is converted to its refractory oxide (U_3O_8) and then mixed with a carrier material prior to spectrographic analysis. The function of the carrier is to achieve smooth distillation of the trace impurities into the arc column and to minimize the volatilization of uranium. The technique was subsequently extended to the analysis of refractory thorium oxide^{2,3}. In our laboratory we have attempted to use the C-D technique for the spectrographic analysis of the refractory oxides Al_2O_3 and MgO . In both the cases we have found that the C-D technique did not yield good precision (expressed in terms of coefficient of variation) and instead a buffer approach gave a better precision^{4,5} which is required in quantitative spectrographic analysis. With a view to understanding the reason for the unsatisfactory behaviour of the carrier in the case of Al_2O_3 and MgO , we have made a detailed study of the volatilization characteristics for the three matrices, U_3O_8 , Al_2O_3 and MgO since volatilization is the basis of the C-D technique.

In the present study we used AgCl as the carrier material since it is widely known for its carrier action. Gallium was incorporated in each matrix to represent the behaviour of the trace elements. Each matrix was ground with a mixture containing 5% AgCl and 100 ppm of Ga_2O_3 . Appropriate quantities of the ground mixtures were loaded separately in three C-D electrodes (ASTM type S-2). The volatilization spectra were taken on a Hilger's large quartz spectrograph in the wavelength region 226-285 nm. The spectra were excited in a 10 amp d.c. arc and recorded on Kodak's SA-I emulsion. The volatilization curves for Ga and Ag lines in each matrix are shown in figures 1, 2 and 3. In the case of U_3O_8 matrix, both Ga and Ag gave a single peak (figure 1) suggesting smooth distillation.

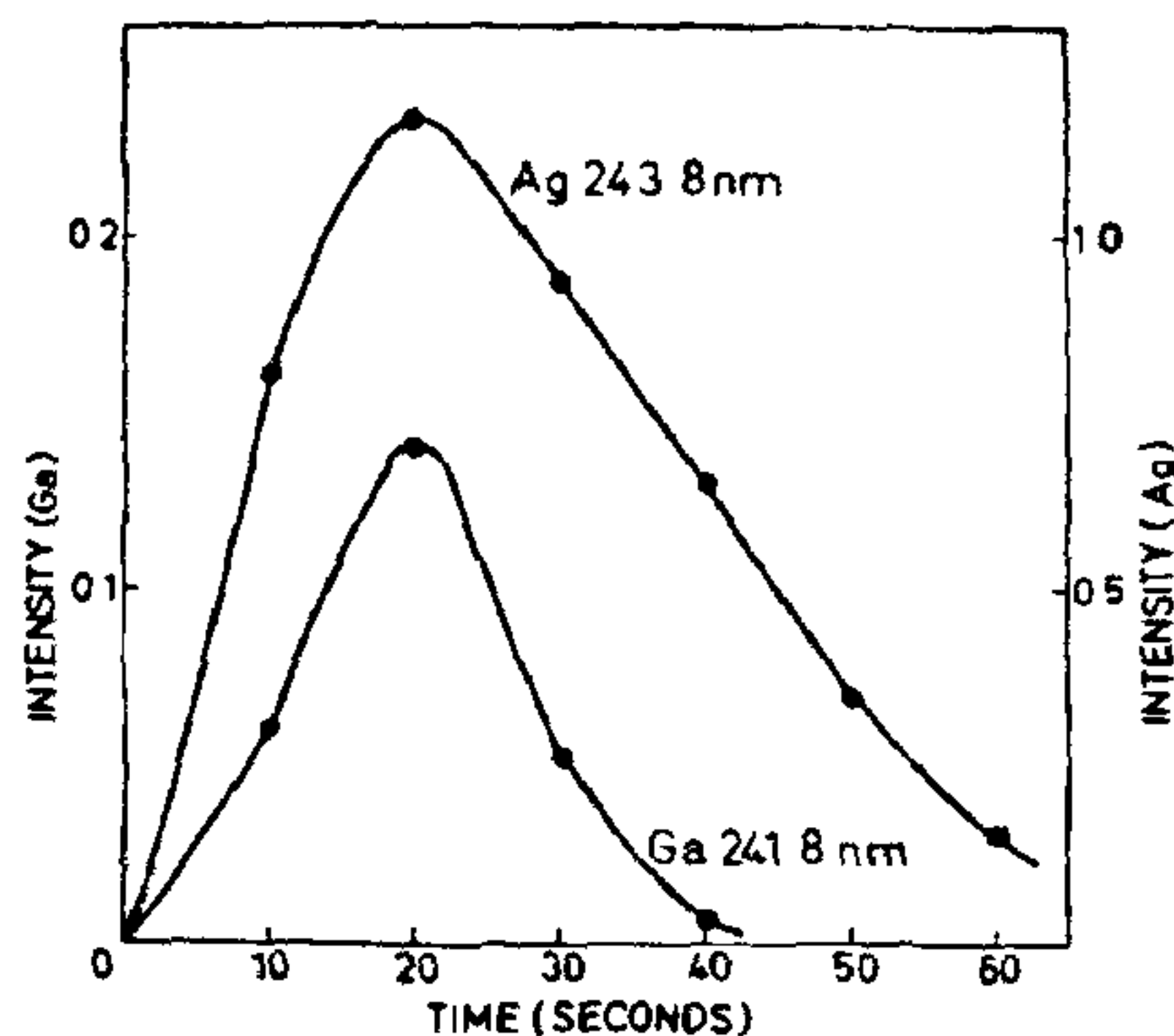


Figure 1. Volatilization curves for U_3O_8 + Carrier.

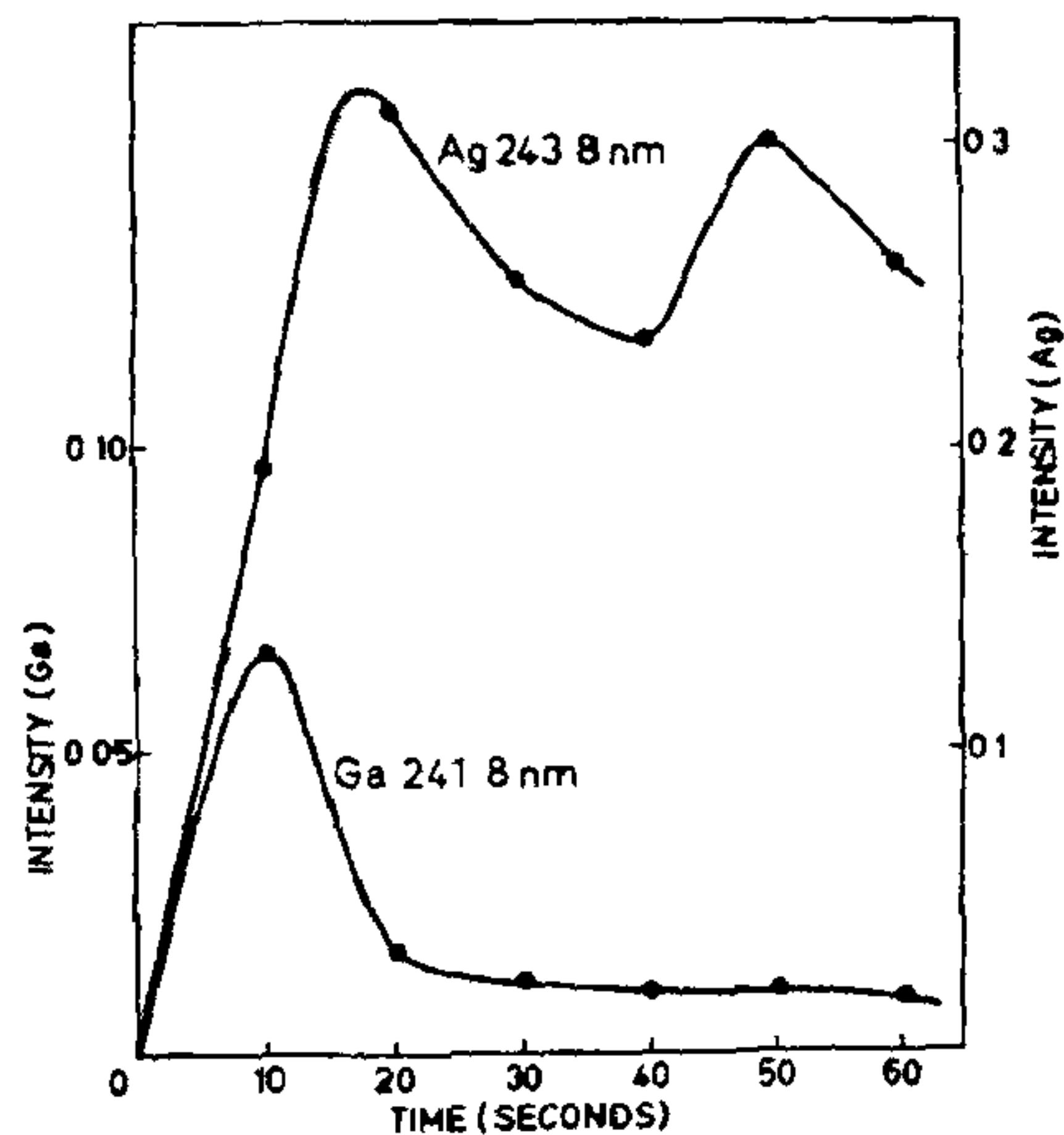


Figure 2. Volatilization curves for Al_2O_3 + Carrier.

In the case of Al_2O_3 the Ga line gave a peak at 10 sec, while the Ag line showed two peaks at 20 and 50 sec (figure 2). In the case of MgO , both Ga and Ag showed two peaks (figure 3). Such volatilization characteristics in Al_2O_3 and MgO suggest erratic volatilization of the trace element (Ga) and the carrier (Ag) into the arc column. Next, we took the volatilization spectra after mixing Al_2O_3 and MgO containing AgCl and Ga_2O_3 with pure conducting graphite powder which served as a buffer. Since our interest is to see the buffer action, the AgCl content was reduced to 500 ppm from 5%. Each mixture was loaded separately in gra-

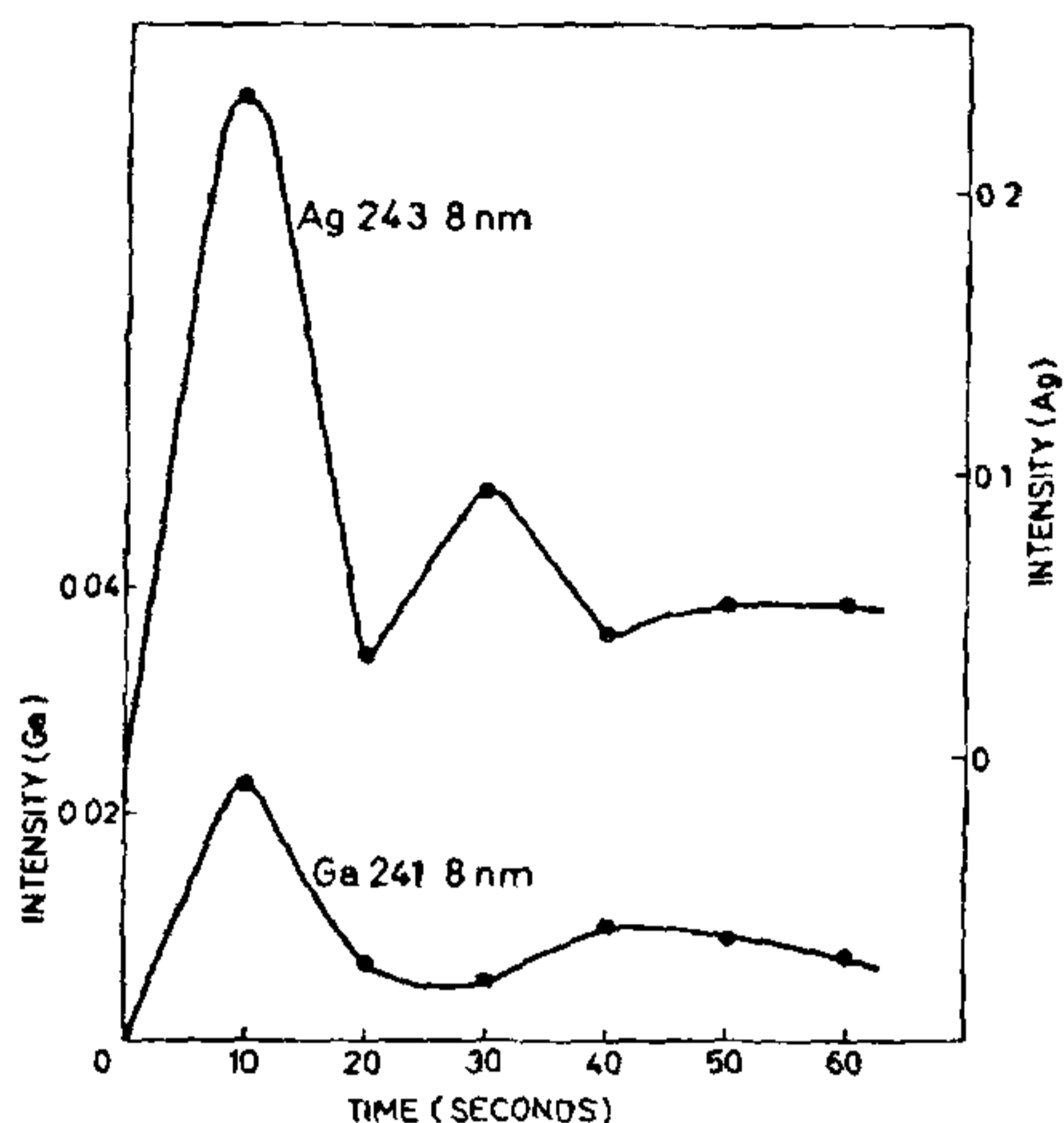


Figure 3. Volatilization curves for MgO + Carrier.

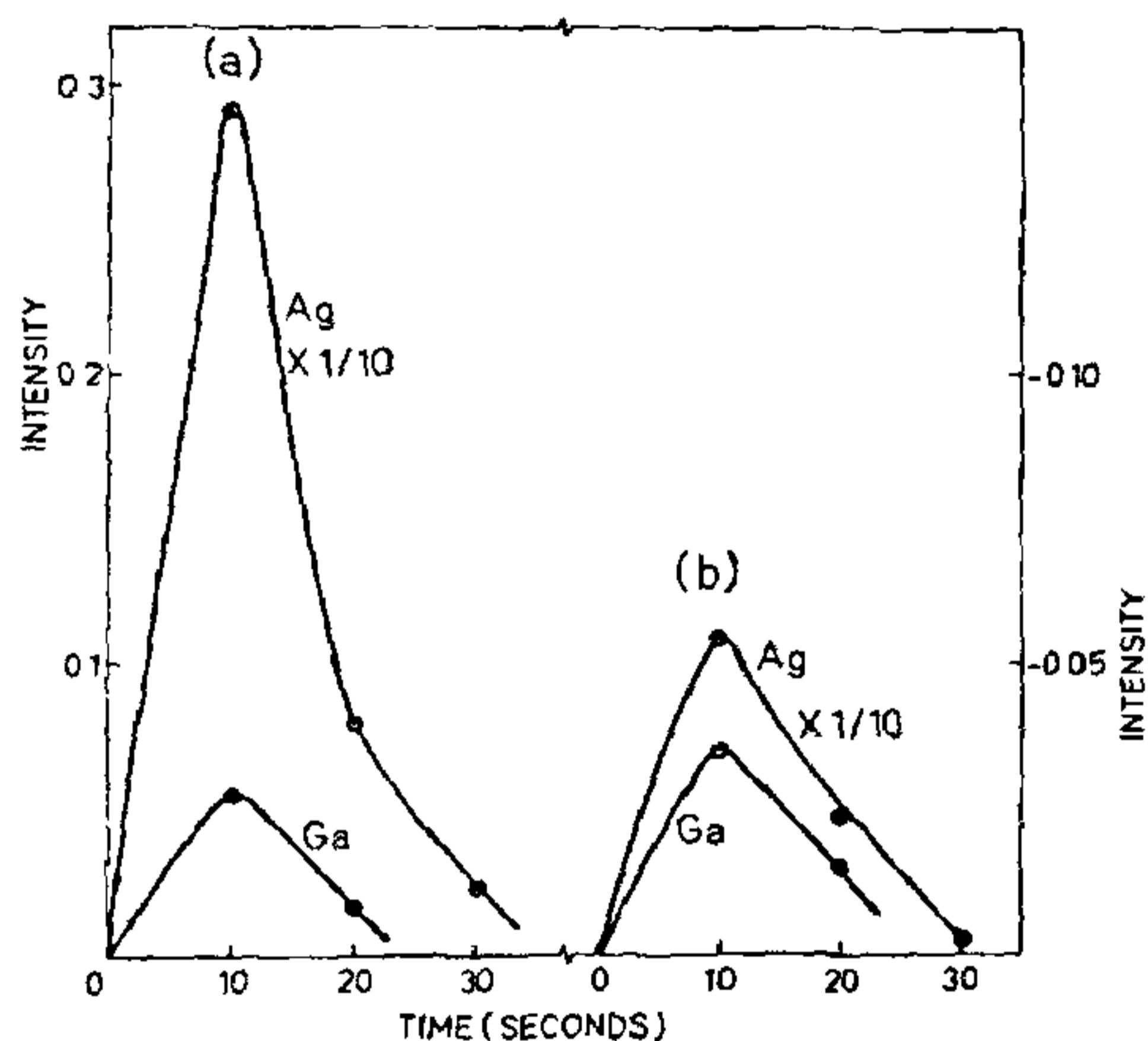


Figure 4. Volatilization curves for (a) Al_2O_3 + buffer & MgO + buffer.

phite electrodes (ASTM type S-8). The volatilization curves are shown in figure 4. Both Ga and Ag showed a single peak at 10 sec. Such a volatilization characteristic suggests smooth distillation of the elements into the arc column. Accordingly when the buffer approach was adopted better precision was obtained in the case of Al_2O_3 and MgO.

The superiority of the buffer action over the carrier action can be explained if we examine the electrode assembly¹ used in the C-D technique and also the density of the refractory oxide. The main functions of the two-piece electrode system are⁶. (1) to decrease the

temperature gradient existing in the electrode cavity; (2) to localize 100 mg of the sample at the bottom of the electrode and (3) to make a vent hole that facilitates smooth distillation of the trace elements and the carrier, but prevents the volatilization of the matrix element. These functions could be realised in the case of U_3O_8 and ThO_2 because of their higher density (8.3 g/cc and 9.86 g/cc). In the case of Al_2O_3 and MgO which are less dense (3.96 g/cc and 3.58 g/cc) compared to U_3O_8 and ThO_2 , the above functions could not be realized. Because of their lower density, only 20 mg of the sample was enough to occupy the volume occupied by 100 mg of U_3O_8 . Since the sample particles were less dense, it was difficult to make a vent hole which is essential for smooth distillation. Once distillation is not quantitative the trace elements and the carrier reach their peak intensities at different times (figures 2, 3). Thus the effect of the carrier is lost.

On the other hand when a buffer, like conducting graphite powder was added to Al_2O_3 and MgO and loaded in an ordinary electrode (ASTM type S-8) the volatilization was smooth and the spectra were highly reproducible in intensity, thus resulting in better precision^{4,5} than that achieved by carrier approach. Graphite by virtue of its higher ionization potential and better conductivity will be mainly controlling the arc temperature. Therefore, the matrix element and the trace elements volatilize smoothly. Thus graphite serves as a good spectroscopic buffer. The matrix element, Al or Mg, also comes into the arc, but as the spectra of these elements are simple, there is no spectral interference. From this study it can be concluded that although Al_2O_3 and MgO are refractory, because of their lower density compared to U_3O_8 , the C-D technique cannot be applied satisfactorily. A buffer approach seems preferable.

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1. Scribner, B. F. and Mullin, H. R., *J. Res. Natl. Bur. Stand.*, 1946, 37, 379.
2. Goleb, J. A., USAEC Report ANL-5000, 1953, 66.
3. Grampurohit, S. V., Saksena, M. D., Kaimal, V. N. P., Kapoor, S. K. and Murty, P. S., *Indian J. Tech.*, 1981, 19, 336., and the references therein.
4. Chandola, L. C. and Machado, I. J., *Indian J. Tech.*, 1975, 13, 471.
5. Murty, P. S., Dixit, R. M., Marathe, S. M., Subramanian, R. V., Khanna, P. P., Deshpande, S. S. and Geetha, N. S., *Proc. Int. Symp. Tr. Anal. Feb.*, 1981, 111.
6. Nachtrieb, N. H., *Treatise on principles and practice of spectrochemical analysis.*, 1950, p. 256