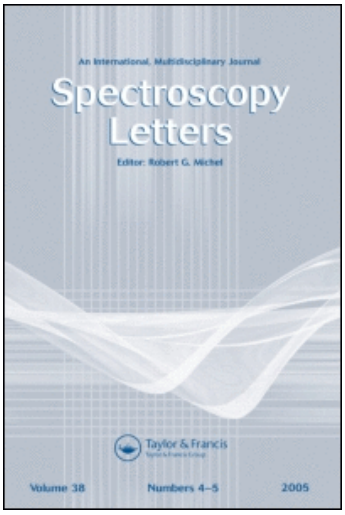

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Preatomization Losses in Flameless Atomic Absorption Spectroscopy

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PREATOMIZATION LOSSES IN FLAMELESS ATOMIC ABSORPTION SPECTROSCOPY

Key Words: atomic absorption, graphite furnace, preatomization losses

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ABSTRACT

A preatomizing (charring) step is customarily used in flameless atomic absorption spectroscopy. Experiments were carried out to investigate the effect of the charring temperature on the final response and to determine at what temperature significant losses were occurring. Four elements of environmental significance (Pb, Cd, Be, V) were investigated in three matrices obtained from air pollution studies.

It was found that Pb and Cd were lost in charring above 500°C and 330°C, respectively, and that the loss rate differed for the different matrices. The maximum charring temperatures for Be and V were 900°C and 1280°C, respectively. Preatomization losses were also examined for Co, Ni, Fe and Cu in aqueous solution. Several effects which could

be explained by a change in atomization rate were noted at low charring temperatures.

INTRODUCTION

Flameless atomic absorption spectroscopy is gaining widespread use as a highly sensitive and relatively simple method of trace analysis. When applied to environmental samples, a preatomizing (charring) step is incorporated into the analysis sequence to destroy the generally quite complex sample matrix. Care must be taken in this step so that trace substances of interest are not lost before atomization.[1]

In air pollution studies, the measurement of metals present in airborne particulates generally entails the collection of the particulates on a filter medium with subsequent extraction or digestion of the filter. Filters may be inorganic (glass fibre) or organic in nature (cellulose, TFE, PVC, etc.). The filter digest therefore contains a matrix which is often complex and has certain elements present in large concentrations. Some of the metals of interest from a pollution point of view, such as lead and cadmium, have low boiling points and the range of possible charring temperatures to destroy the matrix is therefore limited.

This paper compares the effect of the charring temperature on the response obtained from an atomic absorption spectrophotometer with a heated graphite atomizer. Samples of four metals (Pb, Cd, V, Be) were examined in two filter digests and in water. It was found that the dependence on

charring temperature was different for each metal and also differed for the three matrices in some cases.

EXPERIMENTAL

The experiments were carried out with a Perkin-Elmer 403 spectrophotometer equipped with an HGA-70 graphite furnace and power supply. The furnace temperature was measured with a thermocouple and found to be somewhat lower than the manufacturer's calibration; details of the investigation of temperatures in the graphite furnace are given elsewhere.[2] A deuterium lamp background corrector was used for all the measurements.

Two filter digests were investigated and compared with standards made up with distilled water. A glass fibre matrix was obtained by digesting two unexposed discs of Gelman A glass fibre filter, 36 mm diameter, in the conventional manner.[3] This involves dissolution of the filter material with hydrofluoric acid, treatment with nitric acid, filtering and making up to volume with water. The digest contains several elements in fairly large concentrations, i.e. (in µg/ml) Na--400, Al--200, Si--400, Ba--300, Zn--150, Ca--200, K--150. The second filter investigated was an organic Millipore filter composed of mixed esters of cellulose. One filter disc of 37 mm diameter was dissolved in 5 ml nitric acid, digested at low heat for several hours and made up to volume (25 ml). The resulting digest does not contain large concentrations of any cations but does contain an organic residue which is not destroyed by the digestion.

The samples for the experiments were prepared by adding

known amounts of metal to the filter blanks. For the cases of Pb and Cd in the glass fibre samples, the small amount of Pb and Cd already present[3,4] in the blank was taken into account. Measurements were made at concentrations which were in the upper half of the linear response range of the instrument. The atomizing temperature was nominally 2700°C for V and Be and 2400°C for Cd and Pb; charring times were 30 seconds. The peak height was used to measure the response in all cases.

Lead. Figure 1 shows the results for lead, for which the concentration in all three media was 0.5 µg/ml. Losses of the metal occurred above 500°C and could be detected by the instrument response during the charring step. The glass fibre matrix resulted in almost total loss of lead at 680°C.

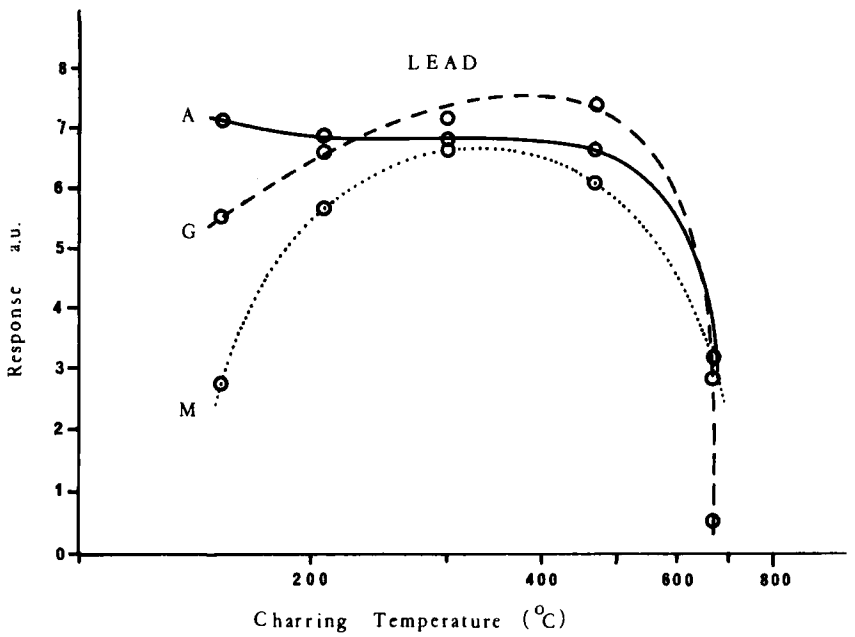

Fig. 1

Response of lead in aqueous (A), glass fibre (G) and Millipore (M) media as a function of charring temperature

Of interest is also the variable response obtained at low charring temperatures. The aqueous curve is nearly flat, while the glass fibre and Millipore curves show an initial increase in response for increasing charring temperatures. This increase was attributed to a change in the rate of atomization, at least for the Millipore case. It was found that the peak areas at 162°C were the same for the aqueous and Millipore samples even though the peak heights differed considerably.

Cadmium. The cadmium samples contained 0.04 µg/ml cadmium and showed charring losses already above 300°C (see Figure 2). Losses were highest for the aqueous medium and lowest for the glass fibre matrix. All curves are relatively flat until 300°C. The difference in response for the three media at low charring temperatures could not be attri-

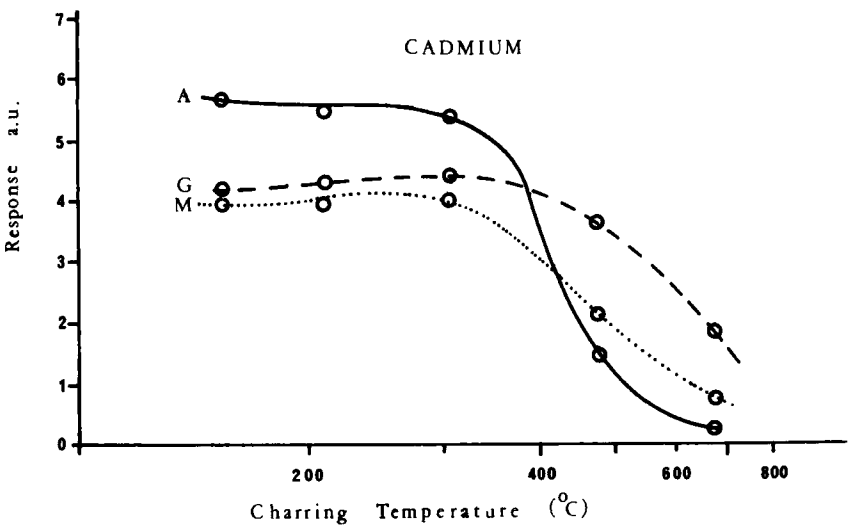

Fig. 2

Response of cadmium in aqueous (A), glass fibre (G) and Millipore (M) media as a function of charring temperature

buted to different atomization rates since peak heights and areas were found to be proportional.

Vanadium and Beryllium. Figures 3 and 4 show the results for vanadium and beryllium and neither metal gave any loss during charring up to 700°C. For beryllium, the aqueous and Millipore samples gave virtually identical responses; the concentration used was 0.06 μg/ml Be. The glass fibre matrix suppressed the beryllium signal to the extent that no response resulted. (The reasons for this are presently being investigated.) The results for vanadium show small changes in peak height for changing charring temperatures. The glass fibre sample behaved like the Millipore sample at low charring temperatures and like the aqueous sample at higher charring temperatures. The concentration of vanadium in all samples was 0.5 μg/ml.

Experiments were also carried out to determine at what

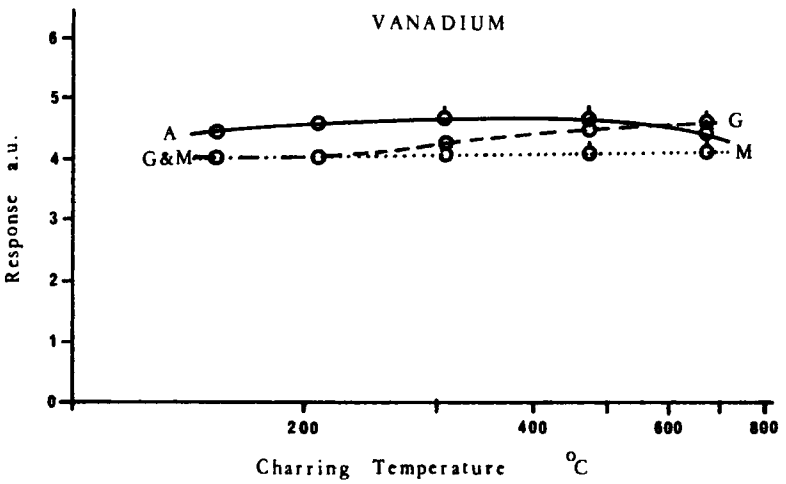

Fig. 3

Response of vanadium in aqueous (A), glass fibre (G) and Millipore (M) media as a function of charring temperature

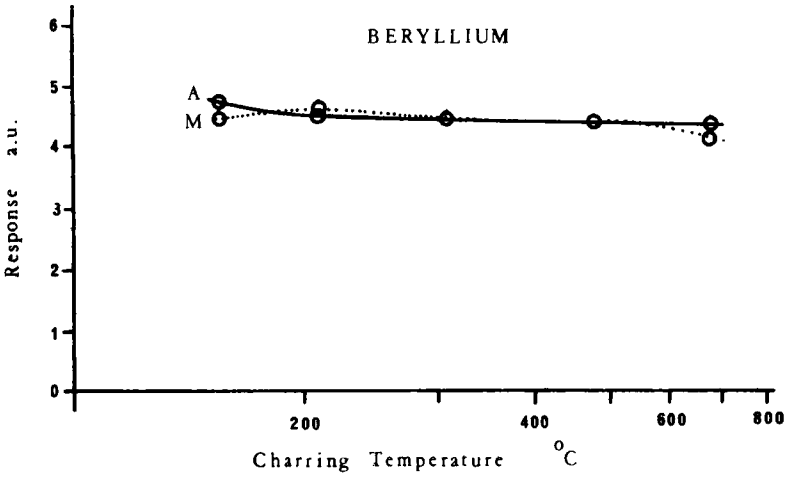

Fig. 4

Response of beryllium in aqueous (A) and Millipore (M) media as a function of charring temperature

temperatures vanadium and beryllium would begin to be lost. To obtain higher charring temperatures on the instrument, the atomization setting was used twice in each analysis sequence, once for the charring temperature and then again for the atomization step. The results are given in Table 1, which also include results for Ni, Fe, Co, Cu, Pb and Cd.

TABLE 1

Maximum Charring Temperatures (°C)

Element	This work	Other*	Melting Point
Cd	330 ± 20		321
Pb	500		327
Cu	720	650	1083
Be	900		1277
Ni	900	890	1453
Fe	900		1536
Co	900		1495
V	1280		1710

*see Reference 1

All these experiments were done using aqueous solutions. The maximum charring temperature is defined as that temperature at which less than 5% of the metal is lost on charring (30 sec charring times). Table 1 also includes the melting points of the pure metals and some results obtained by Fuller.[1]

DISCUSSION

The results shown in Figures 1-4 indicate that charring temperatures can affect the response in several ways. Perhaps most importantly, high charring temperatures can lead to losses of the metal, either as the metal itself or through a volatile compound. In our experiments, lead and cadmium were lost as the metal at the higher charring temperatures because an atomic absorption signal was noted during charring.

A second possible effect of charring temperatures is a change in peak height response which cannot be attributed directly to a loss of the metal. An example is lead, where a decreased response at low charring temperatures could be attributed to a slower rate of atomization, at least for the Millipore case. Apparently the presence of a matrix can retard atomization by chemical or physical means. This may also be the reason that losses are often less at high charring temperatures when a matrix is present, as for cadmium in Figure 2.

The above observations serve to show that the atomization step in the furnace is complex. Atoms can be formed by a volatilization and dissociation of metal compounds

directly, or by a reduction of the metal on the carbon surface with subsequent vaporization of the metal atoms. Probably both processes take place to a greater or lesser extent depending on the element and the matrix present. Fuller[1] found that for copper, losses were independent of the copper compound used. He suggested that in all cases the copper oxide was formed first and that reduction to metallic copper occurred on the graphite. The experiments discussed in this paper were not carried out to answer questions of this nature. It is interesting to note, however, that the maximum charring temperatures bear some similarity to the melting points of the metals (Table 1). The oxides of the metals studied have melting points considerably higher.

The results indicate the errors which may arise when a charring step is used in the analysis. If at all possible, charring temperatures and times should be kept to a minimum so that no measurable losses occur. In principle, one could work in a region where some charring loss is taking place, but in practice it is found that reproducibility is much poorer in such cases. Calibration is also a problem and the results would indicate that the safest approach is to make up standards in the matrix or use the method of additions.

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