

Ultramicroanalysis of Metals by Means of an Integrating Atomic Absorption Spectrometer and a Carbon Filament Atom Reservoir

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ABSTRACT

A fast reacting atomic absorption spectrometer in combination with a carbon filament atom reservoir was used for ultramicroanalysis of calcium and magnesium. The analysis of 1×10^{-12} mole of magnesium gave a variation coefficient of $\pm 3\%$ and analysis of 2×10^{-11} mole of calcium gave one of $\pm 5\%$. The effect of adding various common biological substances to the samples in great excess was tested. No interference could be observed.

INTRODUCTION

During the last 5 years, interest in atomic absorption (AAS) and atomic fluorescence spectroscopy (AFS) has focused on the development of more efficient atomisers. The atomisation of metals by flames is still the most used and the most convenient way for most analyses by means of AAS. The flames, however, have several disadvantages such as low efficiency, seldom more than 15%, and poor reproducibility. Furthermore they often have interfering and quenching radicals which may reduce the analytical signal.

Several attempts have been made to circumvent these disadvantages, e.g. by atomising the samples placed on reducing material like graphite (Lvov, 1969; Massman, 1965, 1967). The reduction by the carbon is used in order to prevent the formation of refractory oxides of the metal. The metal samples are atomised by electrical heating. By using these methods, small samples of zinc, antimony, iron, copper could be analysed. The volumes used were about 30 μl .

West & Williams (1969) described the use of a carbon rod as an atom reservoir for AAS. Small volumes of about 1 μl were evaporated on the rod, followed by the atomisation of the metal by means

of passing a current of 100 A through the rod, which was surrounded by an inert gas. The analytical signal was complete in about 5 sec. However, the measurements were not very accurate. The variation coefficient was found to be about 30%.

In the present communication, results are presented from the use of a carbon filament as an atom reservoir in combination with a rapidly integrating spectrometer. In previous reports (Danielson & Ulfendahl, 1969; Danielson & Öberg, 1974) the equipment used has been described. The spectrometer has been used with a hydrogen/air flame into which the samples to be analysed were inserted by means of small platinum loop, but the studies have now been extended to the use of the carbon filament.

EXPERIMENTAL AND PROCEDURE

Fig. 1 illustrates the principal construction of the spectrometer. A monochromatic light from a hollow cathode lamp (Varian Techtron or Westinghouse) passes through a quartz lens condenser system, through an electronic light beam chopper, through the atom reservoir, to a monochromator. A photomultiplier is used for light detection. The output from the PM-tube is fed to the electronic integrating system.

The main features of the equipment are the same as described before (Danielson & Öberg, 1974) except for the light beam chopper and the atomising device, which is the carbon filament cell.

The chopper previously used by us has been changed to an electronic one which consists of an electronic turning fork, which is fed from a special 24 V a.c. source. From its drive circuit a signal is fed to the electronic integrator, the signal starting the measurement. The light beam chopper (Bulova Inc., USA) has a frequency of 400 Hz and a maximal amplitude of 5 mm. The chopper is completely stable and does not give any electronic noise.

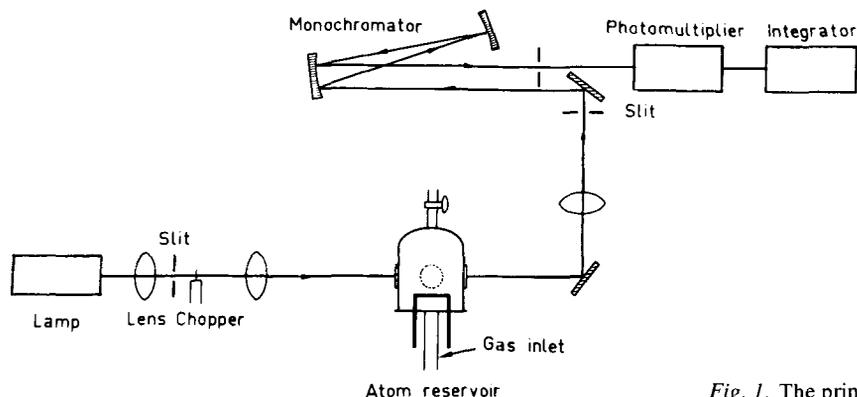


Fig. 1. The principle of the equipment used.

The carbon filament atom reservoir

The design is illustrated in Fig. 2. Two cylindrical electrodes made of stainless steel (diameter 9 mm) are mounted on a brass plate (diameter 68 mm). The steel electrodes are movable, enabling the carbon filament to be moved in relation to the light beam. The electrodes have at their upper ends two plates each, between which the carbon filament (diameter 1–2 mm) can be fixed in a groove. Good electrical contact is obtained by means of two clamping screws. The brass base plate has an edge, to which an O-ring is attached in order to provide a tight seal between the plate and the glass cone which is put on top of the base plate. The steel electrodes are connected to two leads from a transformer, which can provide 100 VA at 7

or 10 V. This transformer is connected to a variable transformer in order to be able to regulate the primary voltage of the former transformer. The steel rods contain copper tubes through which cooling water can circulate (see Fig. 2) providing a rapid cooling of the carbon filament and the electrodes. This means that a new sample very soon can be put onto the filament.

Between the steel rods there is an inlet for argon, which prevents the formation of refractory oxides and carbon oxides.

The glass cone is painted black to prevent reflection of light in to the monochromator. The glass cone has three quartz windows, enabling this type of reservoir to be used both for AAS and AFS. When used for AFS the

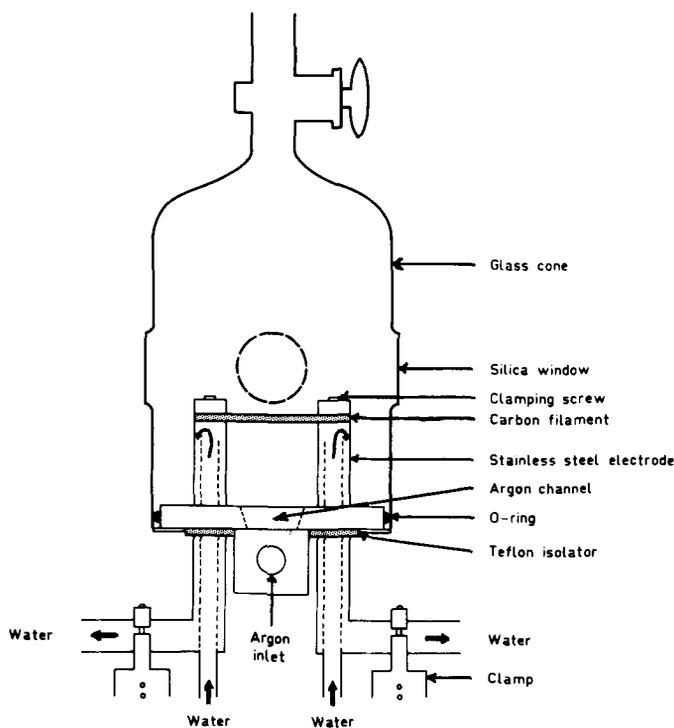


Fig. 2. The carbon filament atom reservoir.

fluorescence light has to be measured perpendicularly to the main optical path, i.e. the mono-chromatic light entering the glass cone through one window and the recording of the fluorescence being performed through a window perpendicularly to the first one.

The carbon filament is usually 5 cm long but the effective length has usually been 24 mm. The carbon filaments used had a diameter of 1–2 mm (Link WWS, Morganite Ltd., England). The length and the diameter of the filament as well as the current which is passed through the filament can be varied in order to change the filament temperature, which is not the same for all elements to be analysed.

The design of the atom reservoir is a modification of a reservoir described by Maines, Andersson and West (personal communication). The glass cone is placed on the optical axis of the spectrometer. The length axis of the carbon filament should be just below the optical axis and the entrance slit of the monochromator. The location of the filament in relation to the light beam is dependent of which element is to be analysed.

The argon flow through the glass cone is regulated by a special gas valve (TRAS 100, AGA, Stockholm, Sweden) and measured by a flowmeter.

Handling of the samples

The samples were put on the carbon filament by means of an Agla micrometer syringe (Burrhoughs Wellcome, England), by a Hamilton syringe, by so-called constant volume pipettes or by other microglass capillaries previously described.

RESULTS

Analysis of magnesium

Procedure. A high intensity lamp (Varian Techtron) fed with a 10 mA current gives a stable light intensity. The light beam is adjusted so that it is located a few mm above the carbon filament. The sample is dried on a marked spot on the filament. The evaporation of the water or other solvent can be done by using a small current. The glass cone is put on top of the base plate and adjusted to the correct position followed by the gassing of the glass cone with argon for 1 min.

After the gassing of the glass cone and adjusting the spectrometer to give no signal, the carbon filament is heated by passing current through for 5 sec. The filament is then heated to about 2000–2500 K. The analytical signal is most often complete in less than 5 sec, often in 1 sec. The duration of the signal is dependent on the temperature of the heated filament and the size of the sample and the gas flow through the glass cell.

No signal is obtained until a sample is placed on the filament. If the filament is contaminated, it may be heated for a longer period, 15–30 sec, thus usually abolishing the signal. A repeated run without sample should give no analytical response. Sometimes the filament is so contaminated that it has to be discarded. If the filament has been heated too much, carbon stuff can be detached from the filament on reheating. If these small particles pass the light, they will cause a false analytical signal. In this case too the filament has to be discarded.

After cooling of the filament for 2 min by passing argon through the cell, the glass cone can be removed, and a new sample can be placed on the filament and analysed following gassing of the cell.

For the analysis of calcium, zinc, copper, iron and other elements the procedure is similar, but the carbon filament has to be adjusted in relation to the light beam in order to achieve an optimal analytical signal. The gas flow too must be adjusted for each element separately in order to obtain the optimal analytical signal.

The rate of gas flow through the glass cell. In order to prevent to oxidation of the carbon filament an inert milieu is necessary in the glass cone. The gas also prevents the formation of fumes and background radiation. Any inert gas will serve this purpose, but argon was found to be the most convenient.

The described reservoir is designated in such a way that it can be used either with a gas flow or under static conditions. For elements analysed in the present communication a low gas flow was used in order to produce a greater analytical signal. It is advisable to have a slightly positive pressure inside

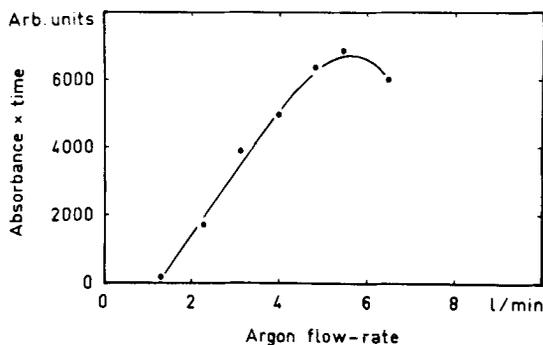


Fig. 3. The relation between argon flow rate through the atom reservoir and the signal, when samples containing 1×10^{-11} mole of magnesium were analysed. Each dot is the mean of two determinations.

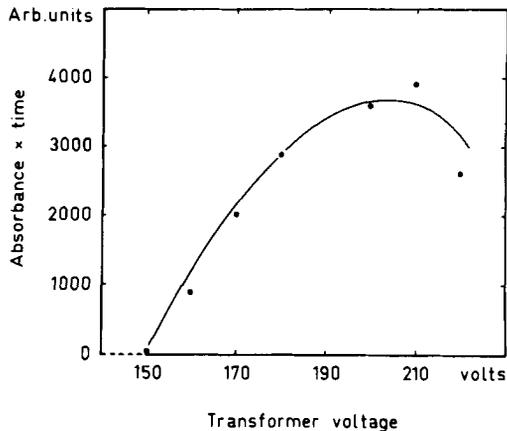


Fig. 4. The relation between transformer voltage of the first transformer and the analytical signal, when samples containing 2×10^{-11} mole of magnesium were analysed.

the glass cell in order to prevent air to leak into the cell. Since the diffusion rate for the atom vapour away from the heated carbon filament is dependent on the gas pressure and the flow rate, it is necessary to determine the optimal gas flow rate in order to get a good analytical response. The optimal gas flow rate is not the same for all elements and has to be determined for each element to be analysed.

Fig. 3 illustrates the dependency of the analytical response on the gas flow rate, when magnesium is analysed. Samples containing 1×10^{-11} mole of magnesium were analysed at different flow rates of argon. It will be seen that the analytical signal increases with increasing flow rates up to a maximal value about 5.5 l/min followed by decreasing responses. The fading of the analytical signal at high flow rates is easily explained, as the atom vapour then passes the light beam very rapidly, resulting in a weakening of the signal.

At very low gas flow rates the argon flow is of great importance too, since the gas prevents water vapour and other gases formed from condensing on the quartz windows, which may cause a reduced analytical signal and an impaired reproducibility.

The temperature of the carbon filament. With an optical pyrometer the temperature of the heated carbon filament can be determined. An optimal temperature can be found empirically by studying the analytical signal at different temperatures. The temperature can easily be varied by changing the primary voltage which feeds the low voltage transformer, the secondary current of which is used to heat the filament.

Fig. 4 illustrates the analytical signal at various primary transformer voltages, when identical samples of 2×10^{-11} mole of magnesium were analysed. The secondary voltage of the second transformer was 7 V. It will be seen that there is an optimal voltage of about 200 V followed by a decline in response, which also is explained by the fact that at very high temperatures of the carbon filament the atom vapour passes very rapidly through the light beam. For each element it is necessary to ascertain the optimal temperature of the filament.

Analytical curves for magnesium. Samples containing various amounts of magnesium from 1×10^{-10} to 5×10^{-14} mole have been analysed with this method. Fig. 5 shows an analytical curve for samples containing from 0 up to 10^{-10} mole of magnesium. The first part of the curve is linear, but further up the curve deviates from the straight line.

Fig. 6 illustrates an analytical curve, where samples from 0 up to 6×10^{-12} mole were analysed. The calibration curve in this region was quite linear. The samples had a volume of $1 \mu\text{l}$. The linearity of the curve is dependent on the location of the filament in relation to the light path. If the carbon filament is not in or near the optimal location, hyperbolic analytical curves are obtained, as shown in Fig. 7. The variation coefficient for ten identical samples of 1×10^{-12} mole of magnesium (sample volume $1 \mu\text{l}$) was found to be $\pm 3\%$. No exact determination was made of the minimal amounts of magnesium which could be analysed with this method.

Interferences. An investigation of interferences was performed. No interference with the analytical response was observed from phosphate, chloride,

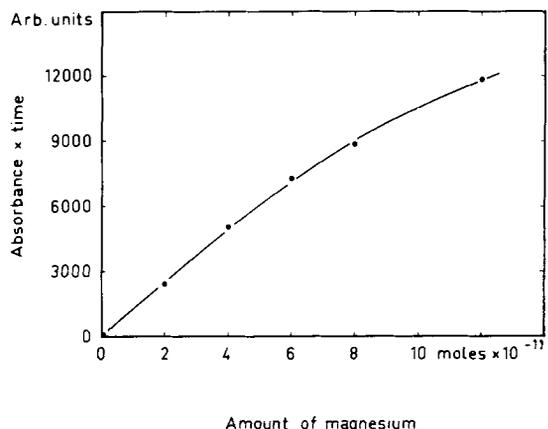


Fig. 5. An analytical curve for magnesium.

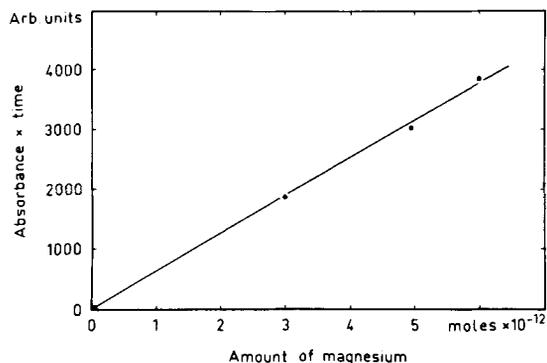


Fig. 6. An analytical curve for magnesium when the carbon filament is optimally adjusted.

nitrate, nor from calcium, copper, sodium, potassium among others, when these elements were added in great excess.

This was not unexpected because the analysis is run in an inert atmosphere and on a reducing support material (the carbon filament). This is consistent with Lvov's results (1969) using the graphite furnace. Nor was any interference obtained from the light of the heated filament; this was because of the glass cell being painted black and the monochromator light being chopped and also because the monochromator excluded light of wavelengths not desired.

Analysis of calcium

The same procedure as for magnesium was adopted for the analysis of calcium. The optimal voltage to the primary of the transformer was found to be about 180 V at an argon gas flow rate of about 4.8 l/min.

The location of the carbon filament in relation to the light pathway was more critical for the analysis of calcium than for magnesium. Fig. 8 shows an analytical curve for the analysis of calcium in the region from 0 to 10×10^{-12} mole. The sample volume used was 1 μ l. Each point is the average of 4 determinations for each concentration. In this curve, correction for background was not done, which explains why the curve does not pass through zero. Usually no signal was obtained when the filament was heated without a sample, but sometimes a small response could be seen, as in this case, especially when a high sensitivity of the electronic recording system was used.

The variation coefficient for 5 determinations of

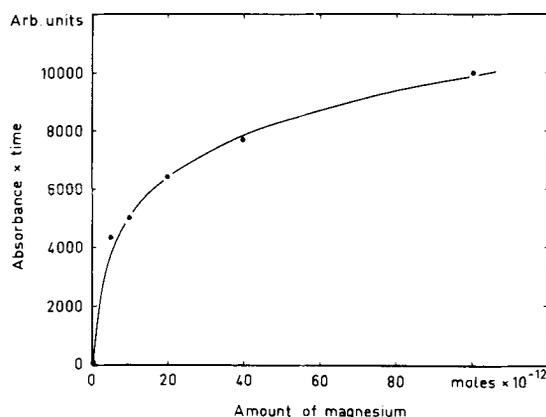


Fig. 7. An analytical curve for magnesium when the carbon filament is non-optimally located.

samples of 2×10^{-11} mole calcium was found to be $\pm 5\%$.

No interference of magnesium, calcium, phosphate, chloride, nitrate or sodium was found, which was consistent with the results for magnesium.

Other elements studied

In order to test whether elements other than calcium and magnesium could be analysed with the described method, small samples of copper, zinc, lead, iron and mercury were run and found to give good analytical signals. The analysis of these elements will be subject to further study.

DISCUSSION

The described atomic absorption spectrometer was designed and constructed to enable us to analyse

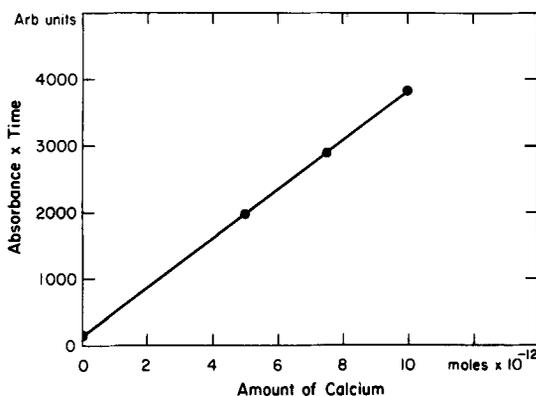


Fig. 8. An analytical curve for calcium.

microsamples of metals, preferentially calcium and magnesium in samples obtained by micropuncture from kidney. As shown under Results, the method can be used for the analysis of very small samples of magnesium and calcium and probably also for other elements, as found in preliminary studies.

The equipment described can also be used for integrating atomic fluorescence measurements. The sensitivity of AFS can easily be increased far beyond the sensitivity of AAS because the analytical signal increases with increasing intensity of the monochromatic light.

Handling of the samples

The handling of the samples is of great importance in the analysis. The sample had to be put on exactly the same spot every time—otherwise the results were not reproducible. This is explained by the fact that the temperature varies along the heated filament, with the highest temperature in the middle of the filament. When the sample was placed on the filament at different locations the temperature and then also the atomisation varied, causing a variation in the analytical signal. It is therefore recommended that the sample volume should not exceed 5 μl in order to get good results. This was valid for all elements studied. It is also recommended that the samples are put exactly on the same spot on the filament each time.

The temperature of the filament

The current through the filament has to be very accurately regulated in order to obtain reproducible results. One source of error is the formation of carbon oxides, which reduce the thickness of the carbon filament, as the oxides formed evaporate. This will result in poor contact between electrodes and filament and alter the temperature of the filament, due to the poor contact and the changed filament thickness. This then will impair the reproducibility. These errors can easily be avoided by waiting until the filament is cool again following an analysis. It is therefore recommended that the clamping screws are checked frequently in order to ensure good contact between filament and electrodes.

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