The Use of a Slotted Quartz Tube for the Analysis of Trace Metals in Fresh Water

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Abstract

With the growing awareness of the gradual build-up of trace metals in the marine and freshwater environments it has become increasingly necessary to monitor metal levels in water on a regular basis. Accordingly, fast and accurate analytical techniques are necessary. This paper describes the use of a slotted quartz tube (SQT) accessory to a conventional flame atomic absorption burner whereby significant increases in sensitivity and precision have been obtained to enable fourteen elements to be determined directly in a fresh water matrix.

Introduction

The importance of dissolved metals in potable water has been highlighted during recent years. While many metals are dietary necessities at trace concentrations, they may be toxic at higher levels and consequently prove health hazards. Most processes of sewage reclamation do not remove all metals and, with the increase in industrialisation, metal pollution of rivers and dams becomes a very important issue. It is therefore essential to monitor metal levels in water on a regular basis. This clearly represents a considerable undertaking in terms of analytical service and it is therefore essential to use an analytical method which is not only accurate and sensitive but is also fast and requires the minimum of sample preparation.

Of the great variety of instrumental techniques which have largely replaced wet chemical methods of metal analysis, atomic absorption spectroscopy has become the most popular. In addition, the recent development of non-flame atomisation (Massmann, 1968) has further emphasised the role which this technique can play by substantially increasing its powers of detection. Non-flame atomisation is, however, a slow process and as it is not always necessary to establish the levels of metals in water to the limits of which this technique is capable, flame methods are often preferred. In addition to this, the cost of a non-flame atomiser is not always within the budget of all laboratories.

This paper describes the advantages of the slotted quartz tube (SQT) (Watling, 1977), an accessory for a conventional burner, which has so far been shown to result in an increase in sensitivity and precision for fourteen elements. The technique is a direct modification of a conventional flame and because of this, analysis time is only slightly increased. In addition, the SQT is inexpensive and can be manufactured in most laboratory workshops.

Materials and Methods

A Varian Techtron AA6 atomic absorption spectrophotometer and BC-6 hydrogen background corrector were used throughout these experiments. Results were recorded both manually as direct absorbance values and graphically on an Hitachi flatbed pen recorder. The development of the SQT (Fig. 1) is the result

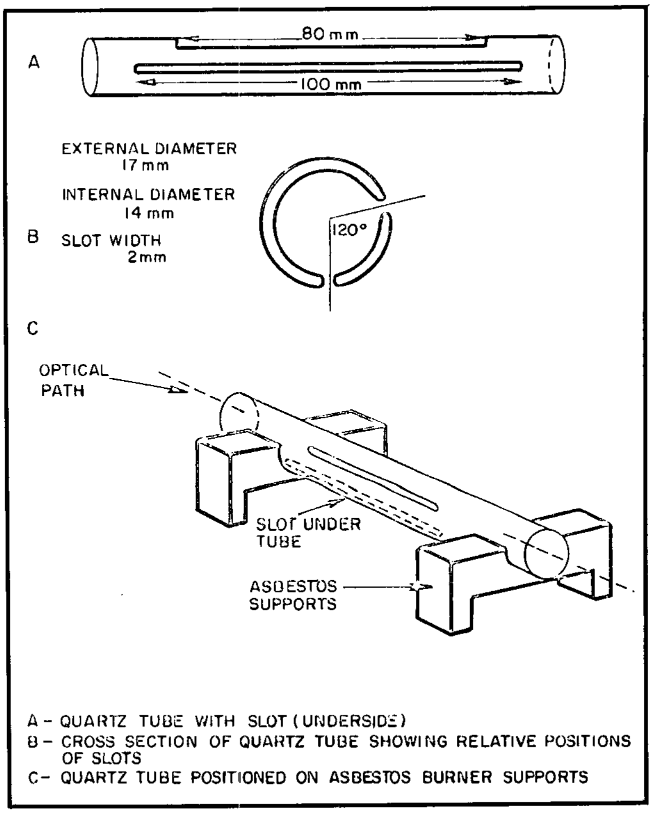

Figure 1
Diagram of slotted quartz tube

of research regarding methods of increasing the sensitivity of atomic absorption. The SQT is supported by asbestos blocks at a distance of 5 mm above the burner head. A portion of the flame is allowed to burn through a basal slot to the inside of the tube while the remaining gas burns around the outside of the tube. A second slot acts as an exhaust gas bleed-off reducing exhaust flame lengths at the ends of the tube and thereby eliminating lens misting problems. The optical path is along the axis of the tube and for its entire length the flame dimensions are critically controlled by the tube walls. This feature is extremely important when trying to overcome instrumental noise caused by flame flicker. The sample is nebulised directly into the flame but only the atomic population inside the tube gives rise to the absorbance signal. Flame speed through the tube is much slower than that of the original flame and the population of neutral atoms inside the tube is more stable, being isolated from entrained oxidising species normally present in conventional flames.

Standards

A series of multi-element standards was prepared in 10% HNO_3 to contain copper, lead, zinc, cadmium, cobalt, nickel, iron, manganese, bismuth, silver, mercury, arsenic, antimony and selenium in the concentration range 0,01-50,00 μg/mℓ of each element.

Results and Discussion

The absorbance values obtained for each standard of each element for the direct air-acetylene flame were compared with those for the same standards using this flame in conjunction with an SQT. In all cases, except that of iron, there was an increase in absorbance values. Table 1 gives values for the characteristic concentrations (that concentration of an element in solution which gives an absorbance reading of 0,004 (Gatehouse and Willis, 1961)).

TABLE 1

CHARACTERISTIC CONCENTRATIONS* OBTAINED USING AN AIR-ACETYLENE FLAME DIRECTLY AND IN CONJUNCTION WITH THE SLOTTED QUARTZ TUBE

Element	Flame (μg/mℓ)	SQT (μg/mℓ)
Zn	0,01	0,003
Cd	0,02	0,005
Ag	0,09	0,01
Co	0,15	0,08
Ni	0,10	0,08
Cu	0,10	0,05
Bi	0,40	0,10
Pb	0,25	0,08
Mn	0,10	0,06
Fe	0,25	0,25
As	2,00	0,20
Sb	0,50	0,10
Se	0,50	0,10
Hg	4,00	1,00

*Concentration of an element in solution which gives an absorbance reading of 0,004 (BM Gatehouse and JB Willis, 1961)

TABLE 2

COMPARISON OF RELATIVE STANDARD DEVIATION (RSD) PER CENT NEAR THE ANALYTICAL LIMITS FOR VARIOUS ELEMENTS USING THE AIR-ACETYLENE FLAME DIRECTLY AND IN CONJUNCTION WITH THE SLOTTED QUARTZ TUBE (SQT)

Element	Flame concentration μg/mℓ	RSD%*	SQT concentration μg/mℓ	RSD%*
Zn	0,01	18,0	0,01	5,2
Cd	0,05	14,4	0,05	1,9
			0,01	10,9
Ag	0,05	16,6	0,05	6,2
			0,01	28,3
Co	0,10	28,4	0,10	5,4
			0,05	18,0
Ni	0,10	11,1	0,10	9,6
			0,05	21,1
Cu	0,02	52,7	0,02	21,5
			0,01	37,1
Bi	1,0	9,1	1,0	1,9
			0,10	21,0
Pb	0,50	9,0	0,50	2,3
			0,05	27,0
Mn	0,05	23,4	0,05	13,2
Fe	0,10	17,9	0,10	13,1
			0,05	21,0
As	1,00	26,7	1,00	10,1
			0,10	32,0
Sb	0,50	14,6	0,50	5,8
			0,10	14,1
Se	1,00	17,9	1,00	4,5
			0,10	17,9
Hg	5,00	10,8	5,00	1,9
			1,00	14,7

*Average of twenty determinations

From this table it can be seen that up to a tenfold increase in sensitivity is achieved by using an SQT in conjunction with the conventional air-acetylene flame. In the case of arsenic and selenium, however, this comparison is somewhat biased as air-hydrogen is the analytical flame usually recommended. The characteristic concentrations of these two elements were therefore determined for this flame and found to be 0,8 and 0,4 μg/mℓ respectively. When the SQT is used in conjunction with the air-hydrogen flame, absorbance values are identical to those obtained with the air-acetylene flame. Nonetheless, there is still a fourfold increase in sensitivity over the most sensitive flame condition by using the SQT. Of the fourteen elements investigated, only iron shows no significant increase in sensitivity. This is probably because the height of the SQT above the flame is fixed and it is consequently not possible to sample the optimum flame zone for iron.

Precision

Analytical precision was considerably improved by the introduction of an SQT – the results are summarised in Table 2. In all cases there was an improvement in precision at low concentrations when the SQT was used, a tenfold improvement being observed for arsenic and selenium and a fivefold improvement for lead, cadmium, bismuth, mercury and antimony. All results were obtained using absorbance values on the linear portion of the calibration curve.

For elements, such as copper, nickel and iron, where very little enhancement of the absorbance signal was observed, the improved precision is probably due to the ability of the SQT to control flame dimensions and conditions along the length of the absorption path and hence increase the signal stability. From these results it is obvious that a considerable increase in both precision and sensitivity is obtained when the SQT is used, thus enabling at least an order of magnitude improvement in detection power for the majority of elements studied.

Interference studies

Three new series of standards were prepared for these studies; they contained 0,1, 1,0 and 25,0 μg/mℓ of each of the fourteen elements under investigation together with selected cations and anions in the concentration range 0-100 μg/mℓ. These compounds were sodium and potassium chloride, and the nitrates of sodium, potassium, calcium, magnesium and strontium. The effects that these solutions had on absorbance values were tested for each element and in the case of arsenic and selenium the experiment was repeated using an air-hydrogen flame.

This study indicated that there was little effect on any of the study elements by any of the potential interferents at concentrations below 100 μg/mℓ. The exception to this was copper where solutions of sodium and potassium chloride considerably enhanced the absorbance signal obtained using the SQT at concentrations as low as 10 μg/mℓ Na. Conversely, it was apparent that solutions containing calcium and magnesium gave reduced interference when using the SQT than when using a standard flame. In the case of arsenic, 1 000 μg/mℓ solutions of sodium and potassium chlorides enhanced the absorbance signal by 10% when using the SQT in conjunction with the air-acetylene flame. This interference can however be overcome by using either simultaneous background correction or the air-hydrogen flame with the SQT. No interference effects at all were observed for zinc, cadmium, silver, selenium, mercury or antimony.

In general, interferences are of equivalent magnitude in the flame and the SQT and are often within the normal variation of the signal and therefore do not present a serious threat to the usefulness of the SQT technique.

Conclusions

The application of the SQT technique to the analysis of trace metals in fresh water is obvious. Results obtained so far indicate that it is possible to achieve a significant increase in analytical sensitivity over conventional flame atomic absorption, often by at least an order of magnitude, for such elements as lead, zinc, cadmium, cobalt, silver, bismuth, manganese, arsenic, antimony, selenium and mercury. Because of the time factor, many of these elements are determined using conventional flame atomic absorption and often the water analyst has to be content with a "less than" figure. Using the SQT in conjunction with a standard air-acetylene flame, it is at least possible to lower this figure significantly and often to give actual values.

An improvement in the precision of the absorbance signal at very low element concentrations is also obtained even for those elements, such as copper, nickel and iron for which the use of the SQT does not provide significant signal enhancement. This improved stability near the analytical limit for the metal has obvious advantages.

Interference studies indicated that at concentrations below 100 μg/mℓ interferent, little or no effect on absorbance values could be observed. The exception to this was copper which was affected by dilute solutions of sodium and potassium chlorides, In general, however, concentrations of sodium, potassium, calcium, magnesium and strontium normally found in fresh water do not cause significant interference problems when using the SQT.

In addition, it must be pointed out that at an approximate cost of R5 each, the SQT provides a convenient and cheap method of increasing the detection power of flame atomic absorption analysis.

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