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Atomiser, Source, Inductively Coupled Plasmas in Atomic Fluoresence Spectrometry (ASIA): A Study of Chemical and Ionisation Interference Effects

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Atomiser, source, inductively coupled plasmas in atomic fluorescence spectrometry (ASIA): a study of chemical and ionisation interference effects*

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Abstract—The effects of phosphate, aluminium, sodium and potassium on the atomic fluorescence of calcium at 422.7 nm and the ionic fluorescence at Σ393.4–396.8 nm have been studied. When the operating conditions are optimised for maximum fluorescence signal from a solution containing no interferents, interference effects are observed which may be interpreted in terms of stable compound formation, ionisation suppression and fluorescence quenching. These effects may be removed by optimising the operating parameters for minimum interference.

1. Introduction

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is clearly established as an excellent method for rapid multi-element analysis. It is a sensitive method with a long dynamic range and is relatively free from chemical matrix and ionisation interferences, but it is subject to spectral interferences. These spectral interferences arise from the complex nature of emission spectra and the problem is exacerbated by the high temperature of the plasma.

Atomic fluorescence spectra are far simpler and in the last few years a number of workers have attempted to use the ICP with atomic fluorescence in the hope of combining the best features of each. In these arrangements the ICP has been used as a source with the flame as an atomiser [1–5], as an atomiser with other devices as a source [6–19] and as both source and atomiser in the same system [20–28].

Work at this university has centred upon the use of a high power plasma as a source, and a low power plasma as an atomiser (in an arrangement which has been given the acronym ASIA) in order to demonstrate that atomic fluorescence is vastly superior to emission so far as freedom from spectral interference is concerned [21, 23, 25–28]. It has also been demonstrated that the detection limits attainable with ASIA are comparable with those obtained with ICP-AES.

The purpose of the work described in this paper is to demonstrate that the other desirable properties of ICP-AES, namely, long dynamic range and relative freedom from interferences other than spectral, are retained.

2. Experimental

The equipment used in the ASIA system has been adequately described elsewhere [23] and will not be discussed here.

2.1 Optimisation

The techniques used to optimise the operating parameters of the ASIA system, which numbered twelve in all, was that known as The Alternating Variable Search [29] in which a cyclic univariate search is carried out. This procedure takes approximately 45 min to complete when total signal is the response factor to be maximised.

2.2 Linear dynamic range

Standards were prepared by serial dilution of a stock calcium nitrate solution prepared from the AnalaR grade salt and a calibration curve obtained. The calibration curve covered the range from the detection limit to the point where self-absorption produced curvature of the graph. In this experiment the figure of merit chosen for the optimisation was the maximum fluorescence signal.

2.3. Chemical matrix ionisation effects

From the stock solution of calcium nitrate other solutions were prepared containing increasing quantities of phosphoric acid, aluminium, sodium and potassium. In all cases there was only one of these elements present along with the calcium. The solutions were prepared from AnalaR orthophosphoric acid, pure aluminium metal dissolved in AnalaR nitric and hydrochloric acids and solutions of AnalaR sodium and potassium chloride.

All these solutions were run on the ASIA instrument and the results obtained were recorded. The figure of merit used in the optimisation was the maximum calcium fluorescence signal. Where the results indicated a degree of chemical or ionisation interference the solutions were re-run with the instrument re-optimised for the figure of merit of minimum interference.

In all these studies cognisance was taken of the possibility of the calcium content of the reagents added, affecting the results and appropriate checks were made.

3. RESULTS AND DISCUSSION

Figure 1 shows the calibration curve for calcium at 422.7 nm in the fluorescence mode. It can be seen that the linear range is approximately six orders of magnitude, very similar to that obtainable by ICP-AES.

It has been shown [30] that the formation of refractory compounds between calcium and phosphate and calcium and aluminium, which causes a reduction of the emission of calcium in flames, is largely absent in the ICP when used in emission.

This satisfactory result arises from the high temperature of the plasma which dissociates any refractory compound which is formed. When the ICP is used as an atomiser in atomic fluorescence, a position is sought in the tailflame where it is cool enough to have a large population of ground state atoms. This condition may result in the formation of refractory compounds in the tailflame after they have been dissociated initially in the plasma. Figure 2 shows the results which were obtained with the calcium atom line at 422.6 nm when the phosphate and aluminium were added. It can be seen that phosphate is without effect up to a ratio of 10 000:1 phosphate to calcium. However, aluminium has a marked depressive effect.

If the instrument is re-optimised for minimum interference it is found that aluminium can be tolerated up to a ratio of 300:1, aluminium to calcium, as is shown in Fig. 3. In the re-optimisation the viewing height has been lowered as has the injector flowrate, as shown in Table 1. Thus a hotter portion of the tailflame is being observed with a consequent reduction in the formation of refractory compounds. This re-optimisation does of course lead to a worsening of the detection limits obtainable from a pure calcium solution.

The effect of adding an easily ionised element to a solution of an element whose atom is being measured by emission in a flame is to perturb the equilibrium by the addition of electrons to the system and thus enhance the emission of the atom line. This state of affairs is reduced in ICP-AES because the high temperature of the plasma means that there is already
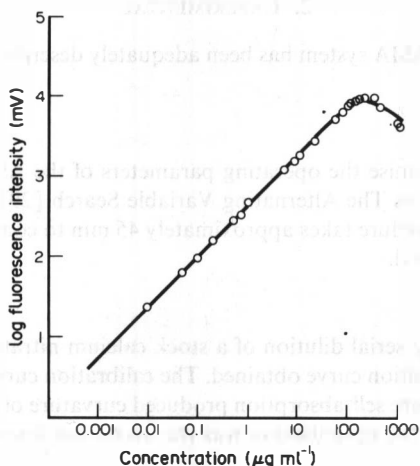

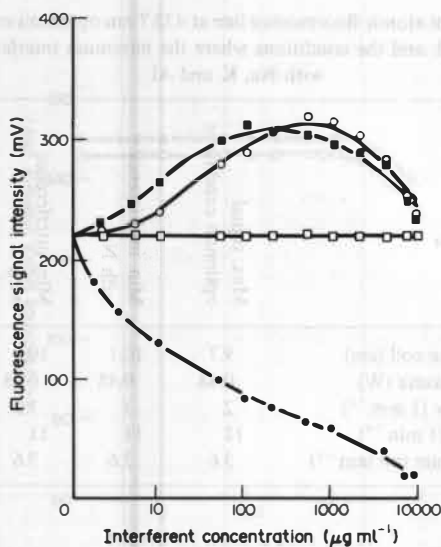Fig. 1. Calcium fluorescence calibration curve at 422.7 nm.

Fig. 2. The effect of increasing concentrations of Na, K, Al and PO$_4$ on the fluorescence signal at 422.7 nm from a 1 μg/ml solution of calcium under conditions optimised for maximum signal.
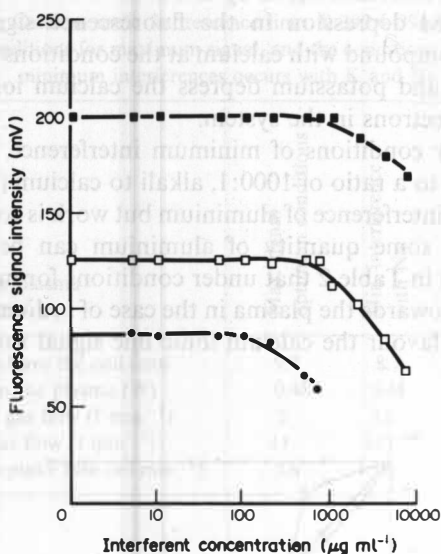■ $^+$Na, □ $^+$PO$_4$, ● $^+$Al, ○ $^+$K.

Fig. 3. The effect of increasing concentrations of Na, K, and Al on the fluorescence signal at 422.7 nm from a 1 μg/ml solution of calcium under conditions optimised for minimum interference.
■ $^+$ Na, □ $^+$Al, ● $^+$K.

a large population of electrons present and a relatively larger number must be added before an effect is noticeable.

In ASIA, as can be seen in Fig. 2, both sodium and potassium have a marked enhancing effect on the calcium atom line at 422.7 nm consistent with an ionisation effect. (The depression at higher concentrations of sodium and potassium is undoubtedly due to the quenching of the fluorescence by electrons). When the instrument is re-optimised for minimum interference, sodium and potassium can be tolerated by calcium up to a ratio of 300:1 and 100:1 respectively, alkali to calcium (Fig. 3). In this case the re-optimisation resulted in a higher observation point and a higher injection gas flow as shown in Table 1, consistent with a cooler position in the tailflame where the electron density would be lower.

Table 1. Calcium atomic fluorescence line at 422.7 nm optimum conditions for maximum signal, and the conditions where the minimum interferences occur with Na, K and Al

Atomiser plasma parameters	Max. signal optimum conditions	Min. interference with Na	Min. interference with K	Min. interference with Al
Height above the coil (cm)	9.7	10.1	10.9	9.2
Power in the plasma (W)	0.48	0.48	0.48	0.48
Injector gas flow (1 min^{-1})	2	3	3.2	1.8
Outer gas flow (1 min^{-1})	11	11	11	11
Liquid uptake rate (ml min^{-1})	3.6	3.6	3.6	3.6

Again this new set of operating parameters would give debased values for the detection limits.

The experiments were repeated using the sum of the calcium ionic lines at 393.4 and 396.8 nm. The results which were obtained (Fig. 4) were wholly predictable. Phosphate is without any effect on the fluorescence signal up to a ratio of 10 000:1, phosphate to calcium. Aluminium gives a marked depression in the fluorescence signal consistent with the formation of a refractory compound with calcium at the conditions optimum for the highest total signal. Both sodium and potassium depress the calcium ionic signal as one might expect with an excess of electrons in the system.

After re-optimisation for conditions of minimum interference, sodium and potassium were without any effect up to a ratio of 1000:1, alkali to calcium (Fig. 5). So far it has not been possible to reduce the interference of aluminium but work is continuing in order to find conditions where at least some quantity of aluminium can be tolerated at the ionic wavelengths. It can be seen in Table 2 that under conditions for minimum interference the observation height moves towards the plasma in the case of sodium and potassium. Since a higher temperature would favour the calcium ionic line signal this change in height is as
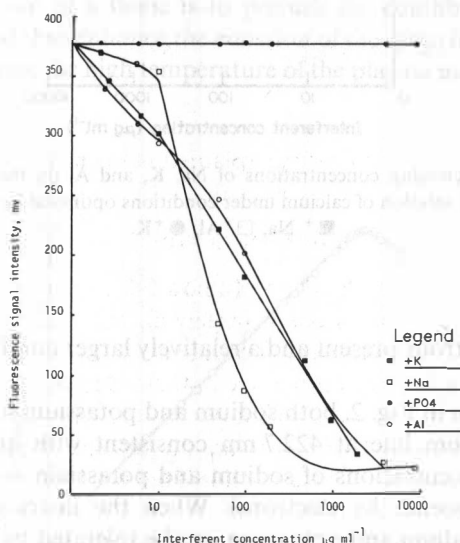

Fig. 4. The effect of increasing concentrations of Na, K, Al and PO$_4$ on the sum of the fluorescence signals at 393.4 and 396.8 nm from a 1 μg/ml solution of calcium under conditions optimised for maximum signal. ■ $^+$K, □ $^+$Na, ● $^+$ PO$_4$, O$^+$Al.
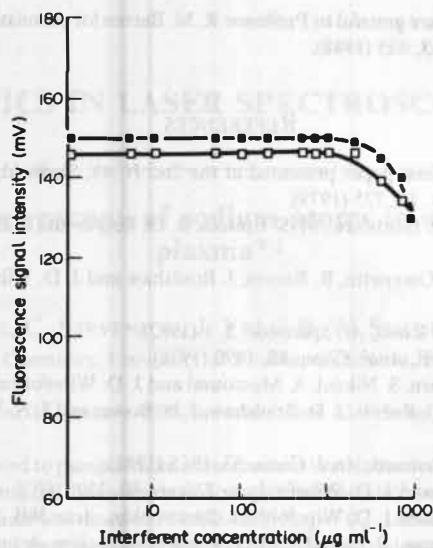
Fig. 5. The effect of increasing concentrations of Na and K on the sum of the fluorescence signals at 393.4 and 396.8 nm from a 1 μg/ml solution of calcium under conditions optimised for minimum interference. ■ Na, □ K.

Table 2. Calcium ionic fluorescence lines Σ 393.4–396.8 nm optimum conditions for maximum signal, and the conditions where the minimum interferences occurs with K and Na

Atomiser plasma parameters	Max. signal optimum conditions	Min. interference with Na	Min. interference with K
Height above the coil (cm)	9.7	8.7	9.2
Power in the plasma (W)	0.48	0.48	0.48
Injector gas flow (1 min⁻¹)	2	3.6 .	3.6
Outer gas flow (1 min⁻¹)	11	11	11
Liquid uptake rate (ml min⁻¹)	3.6	3.6	3.6

would be expected. What is not so easily explained is the marked increase in the required nebuliser flow rate.

4. CONCLUSIONS

In this paper it has been shown that the well-known depressive effect of phosphorus on the flame emission spectra of calcium, which is largely absent in ICP-AES, is largely absent in ASIA—for the atom line at 422.7 nm and the ionic lines at Σ 393.4 and 396.8 nm. This state of affairs applies if the working conditions are optimised for maximum fluorescence signal.

Aluminium has a marked depressive effect on both the atomic and ionic lines when the working conditions are optimised for maximum fluorescence signal. However, this depressive effect is reduced in the case of the atomic line if the working conditions are re-optimised for minimum interference.

The ionisation interference of the alkali metals is greatly reduced for both the atom and ionic lines of calcium when re-optimisation is carried out.

In all it is concluded that the effects described are of the same general order as those experienced in ICP-AES and much less than in FAAS.

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