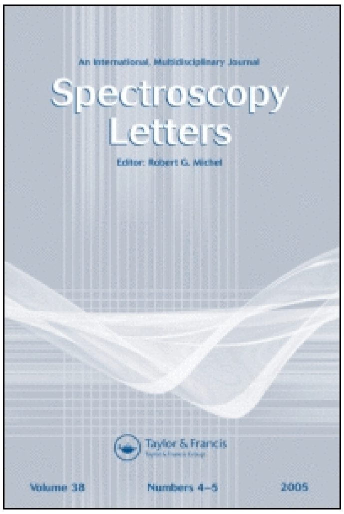

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THE INFLUENCE OF PHOSPHATE ON THE DETERMINATION OF CALCIUM BY FLAME METHODS OF ANALYSIS - A NEW APPROACH

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ABSTRACT

The depression of the analytical signal of calcium by phosphate ion when using turbulent (H_2/O_2 and H_2/A/entrained air) and laminar (C_2/H_2/air) flames in flame spectrometry is studied. Measurements of flame emission of calcium as a function of calcium to phosphate and pyrophosphate molar ratios for various flame heights in both turbulent and laminar flames are made. The phosphate interference when using turbulent flames is shown to be a result of a slow vaporization of the calcium phosphate particles. The phosphate interference when using laminar flames with chamber type aspirators is only important at high calcium and phosphate concentrations. The cause of the interference is probably a result of either slow vaporization of the calcium phosphate particles or a slow rate of change of the orthophosphate to pyrophosphate during the decomposition step.

The depression of the analytical signal of calcium by the phosphate ion is well-known both in flame emission (at 4227 Å or 5541 Å) and atomic absorption analysis (also at 4227 Å). The present views on the mechanisms of this interference have been summarised by Herrmann and Alkemade[1] and Elwell and Gidley[2], and two different hypotheses have emerged to explain this effect.

Schuknecht and Schinkel[3] and Alkemade and Voorhuis[4] have demonstrated the variation of the interference with height of observation. The interference is considerably reduced when measurements are made at greater distances from the burner tip. This, and other work[1,2,4] have led to the theory that the interference arises as a result of the very low volatility of solid particles of calcium phosphate at the temperature of the flame. A somewhat later theory[1] based on studies by Pungor[5] and supported by the observations of Yoffe et al.[6] attributes the interference to a gas-phase reaction in which calcium phosphate is first converted to the more refractory calcium pyrophosphate. The residual signal is then a consequence of the slow decomposition of the pyrophosphate.

Space does not permit a thorough review of the experiments which have led to the formulation of these hypotheses, but it must be mentioned that many of the experimental observations which have been reported by previous authors can be explained equally well by both theories. The purpose of this communication is to rationalize the current theory with regard to practice, and to attempt to settle an issue which is, by now, entirely academic.

APPARATUS

The apparatus was similar to that used by Mansfield et al.[7] for the observation of atomic fluorescence in flames, and differed from their experimental arrangement in that the light source was absent as observations were made of the calcium flame emission (at 4227 Å). A monochromator slit of restricted height was employed, which enabled a flame segment 0.3 cm high to be viewed. A total-consumption Beckman aspirator burner (medium bore capillary) was used with the hydrogen/argon/entrained air and hydrogen/oxygen flames. Gas flow rates were: H_2 10.0 ℓ min^{-1} and O_2 3.0 ℓ min^{-1}; H_2 10.0 ℓ min^{-1} and A 3.0 ℓ min^{-1}.

Observations of phosphate interference in laminar flames were carried out using a premixed acetylene/air flame, in conjunction with a chamber aspirator having a transfer efficiency (aspiration yield) of approximately 10%. The burner was provided with outer and inner flames, of which the aspirated aerosol was supplied only to the inner flame. This ensured a uniform temperature throughout the inner flame at any given height. Measurements of intensity against height were made using a 0.5 metre Ebert monochromator; a restricted area of flame, 0.4 cm in height, was observed; and gas flow rates were: C_2H_2 1.95 ℓ min^{-1} and air 18.3 ℓ min^{-1}.

PROPOSALS AND RESULTS

First, it is necessary to consider several fundamental processes which may occur on spraying a solution of calcium and sodium phosphate or phosphoric acid into a flame. Assuming that after evaporation of the solvent, the calcium is present in the form of a solid particle of calcium phosphate, the following changes could occur:

$$Ca(PO_4)_{2(s)} \rightarrow Ca_3(PO_4)_{2(g)} \qquad (i)$$

$$Ca_3(PO_4)_{2(g)} \rightarrow Ca_2P_2O_{7(g)} + CaO_{(g)} \qquad (ii)$$

These are the changes which form the basis of the theories mentioned above. It is, therefore, only necessary to distinguish between these reactions experimentally in order to elucidate the relative rates of the processes occurring in the flame. If process (ii) occurs in the solid phase rather than the gaseous phase, this would not influence the proposed mechanisms. Calculation of the equilibrium concentrations of calcium chloride-sodium dihydrogen phosphate solutions, using a published computer program[8], indicated the absence of the calcium phosphate complex[9] ($CaHPO_4$) at the concentrations employed and for the pH values of 1.0 to 11.0. Solubility data[9] (log $K_s \sim 25$) indicated the possible precipitation of $Ca_3(PO_4)_2$ at the concentration levels used, especially for alkaline solutions. Evidence from solution chemistry considerations, therefore, indicates that calcium is present as the orthophosphate which may be partially precipitated before aspiration.

It is, perhaps, surprising that no investigators have compared the depression of the calcium signal due to the presence of phosphate with that due to pyrophosphate. Inspection of equation (ii) shows that one mole of calcium oxide is liberated for every mole of calcium phosphate which undergoes decomposition to the pyrophosphate. This liberated oxide will dissociate and contribute to the analytical signal and in this way the relative effects of equations (i) and (ii) may be assessed.

(a) Experiments with Turbulent Flames. When the Beckman total-consumption aspirator burner was used to study the flame emission of calcium (4227 Å) in the presence of phosphate and pyrophosphate, the results summarised in Figure 1 were obtained with 10^{-4} M (4 ppm) calcium solutions and a hydrogen/oxygen flame. The curves are very similar to those reported by Alkemade and Voorhuis[1,4] for the interference of phosphate on the calcium emission in the laminar acetylene/air flame, although the concentrations are quite different. The results of Figure 1 indicate the well-known decrease of the degree of interference with height of observation as well as the sharp changes in slope corresponding to 3:2 and 2:1 stoichiometric ratios for calcium-to anion (PO_4^{3-} or $P_2O_7^{4-}$). The level of the plateaux in the curves from Figure 1 were plotted as a function of height and are summarised in Figure 2. The results in Figure 2, which were also confirmed by an independent experiment, indicate that in the hydrogen/oxygen flame, the degree of interference with excess amounts of phosphate and

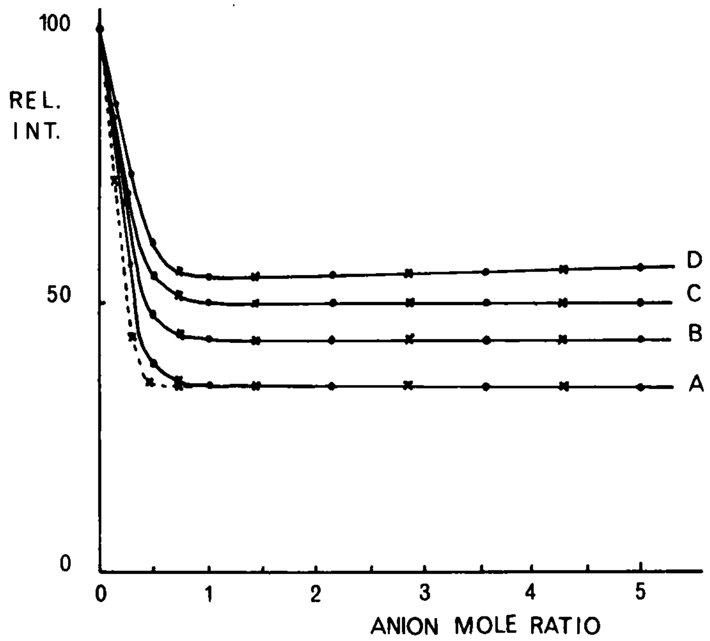

Figure 1

Relative emission intensity of calcium (10^{-4} M, 4 ppm) in the presence of ● phosphate, ✖ pyrophosphate; measured at A = 2 cm, B = 3 cm, C = 4 cm and D = 5 cm above the burner tip.

pyrophosphate is independent of the identity of the anion present. Results obtained with 2.5 x 10^{-3} $\underline{M}$ (100 ppm) calcium solutions gave the curves shown in Figure 3. The anomalous peak in the calcium pyrophosphate interference curves (Figure 3) has not been investigated further.

When 10^{-4} $\underline{M}$ (4 ppm) calcium solutions were sprayed into the hydrogen/argon/entrained air flame, the signal was depressed by both phosphate and pyrophosphate to zero. This was observed for measurements at all heights from 20 mm to 80 mm above the burner tip. The change in slope of the depression occurred at stoichiometric ratios of 3:2 and 2:1 for calcium to phosphate and pyrophosphate, respectively.

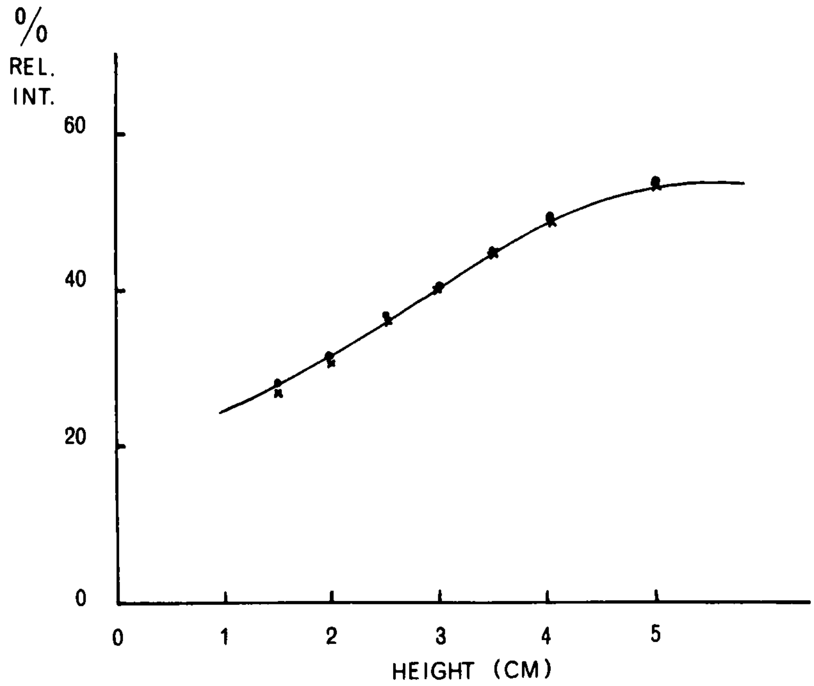

Figure 2

Relative emission intensity of calcium (10^{-4} M) in the presence of ● phosphate (3×10^{-4} M) and × pyrophosphate (3×10^{-4} M) as a function of height of observation.

(b) Experiments with Laminar Flames. On spraying the 10^{-4} M (4 ppm) calcium solutions into a premixed, laminar, acetylene/air flame, no depression of the signal could be detected in the presence of either phosphate or pyrophosphate. On aspirating the 2.5×10^{-3} M (100 ppm) calcium solutions, a depression could be easily detected and is shown in Figure 3. This interference was observed for measurements at a height of 10 mm above the burner (about 8 mm above the blue cones of the flame reaction zone) and could not be observed at a height of 20 mm.

DISCUSSION

The main differences occurring for the phosphate (and pyrophosphate) depression in turbulent and laminar flames are related to the rise

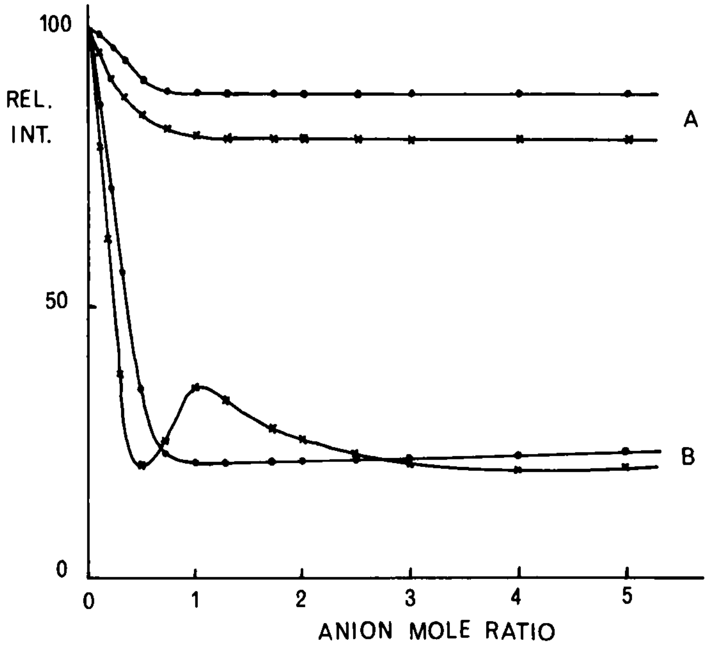

Figure 3

Relative emission intensity of calcium(2.5x 10^{-3} M, 100 ppm) in the presence of phosphate, pyrophosphate measured with A-laminar C_2H_2/air flame, B-turbulent H_2/O_2 flame.

velocity of the flame and the dimensions of the aspirated particles. The smaller, mean droplet diameter of the particles aspirated into the laminar acetylene/air flame make for a more complete decomposition of the calcium phosphorus compound. As a result, interference effects are considerably more apparent in turbulent than laminar flames having similar thermal temperatures.

From the results in Figure 2, the rate determining process for the interferences of phosphate and pyrophosphate is the slow volatilization of their calcium salts (i.e. equation (i)). The mechanism suggested by equation (ii) would be quite incapable of explaining these results, since the formation of calcium oxide would give a substantially higher signal for calcium phosphate than would be obtained with calcium pyrophosphate. The mechanism suggested by equation (i) also implies that the degree of interference is dependent on the concentration of calcium phosphate or pyrophosphate in the solution, as this directly determines the dimensions of the solid particles in the flame. The interference process represented by equation (ii) would, most probably, be less dependent on the solution concentration. In the light of these results, it is quite obvious that the older theory, which attributes the phosphate interference to a slow vaporization effect, is the only acceptable explanation for the influence of phosphate on calcium in turbulent flames. This conclusion also implies the existence of a calcium/phosphorus concentration, below which there is no depression of signal; that is, all the calcium phosphate particles entering the flame are completely vaporized at the height of observation. The location of this critical concentration is evident in the results of Schuknecht and Schinkel[3]. The existence of the phosphate decomposition through pyrophosphate is not disproved by this study; in fact, this reaction almost certainly occurs. The results only indicate that this is not the rate determining step.

The depression of the calcium signal to zero by phosphate and pyrophosphate in the hydrogen/argon entrained air flame, shows that under these latter conditions neither the calcium phosphate nor pyrophosphate particles undergo decomposition in the cooler flame.

In the experiments carried out in the laminar acetylene/air flame, the comparative freedom from interference can be attributed to the factors mentioned above. Interference effects were only important for high calcium and phosphate concentrations. It is possible that for a sufficiently small solid particle (as produced by a chamber type aspirator), the time required for vaporization is small compared with the time required for decomposition of the phosphate to the pyrophosphate. This may be the reason for the inequalities in the plateau levels for the interference of phosphate and pyrophosphate in the laminar flame. Alternatively, this could arise from differences in the time required for vaporization of the calcium phosphate or pyrophosphate particles. In view of the high calcium concentrations used in this latter study (2.5×10^{-3} M or 100 ppm), it appears unlikely that the rate of the reaction in equation (ii) has any importance in the practical analytical flame photometry of calcium.

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