

# Influence of Aerosol Drop Size on Signals and Interferences in Flame Atomic Absorption Spectrometry

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**Condensed-phase vaporization interferences (e.g., calcium/phosphate, magnesium/silicon, etc.) are examined for a number of elements and matrices in both the air/acetylene and nitrous oxide/acetylene flames. The performance of several nebulizers and spray chambers is examined, and a clear relationship is established between the drop size distribution of the tertiary aerosol entering the flame and the magnitude of the interference. Most interferences can be either totally eliminated or at least significantly reduced, by preferential elimination of large drops from the aerosol. This is achieved through the use of mixer paddles or impaction inserts in the spray chamber. Unfortunately, the decrease in interference severity is often accompanied by a corresponding decrease in analytical signal, resulting in a net loss of sensitivity. Conversely, signal increases achieved through the use of impact beads or nebulizers and spray chambers which pass large diameter (e.g., >10  $\mu\text{m}$ ) drops may lead to a significant worsening of condensed-phase interferences.**

Probably the most troublesome type of sample introduction interference in flame atomic absorption spectrometry (FAAS) is the *condensed-phase chemical interference*. Both Alkemade (1) and Kirkbright and Sargent (2) have attributed this type of interference to differences in the rate of release of metal atoms in the flame, determined by the chemical form or physical environment in which the analyte atom is present. In the air/acetylene flame, condensed-phase interferences inevitably appear as signal depressions. In the nitrous oxide/acetylene flame, by contrast, signal enhancements may also be observed (3-5). West et al. (3, 4) have suggested that such enhancements result from a reduction in the rate of lateral diffusion of atoms away from the flame central measurement zone.

Methods which have proved effective for the reduction of many condensed-phase interferences include (i) the use of the nitrous oxide/acetylene flame in place of the air/acetylene flame (5), (ii) the addition of large amounts of releasing agents to the sample matrix (6-8), and (iii) judicious control of the particle size distribution of solute introduced into the flame (9). In the course of a study of ultrasonic and pneumatic nebulizers, Stupar and Dawson (9) demonstrated that a relationship exists between the magnitude of certain condensed-phase interference effects and the size of particles remaining after solvent evaporation. They concluded, for example, that the signal depression of Mg by Al in an air/acetylene flame diminished as the size of solute particles in the flame was reduced by analyte dilution. Considering the broad implications of this early work, it is remarkable that no systematic investigation of particle size and interference effects has been carried out in the intervening 16-year period.

Earlier publications from this laboratory (10-12) have shown that the drop size distribution of an aerosol generated by a pneumatic nebulizer is significantly altered during its passage through the spray chamber. The interaction of the

primary aerosol with devices placed in its path, such as impact beads, mixer paddles, etc., leads to changes in the drop size distribution, mainly through the elimination of large drops from the primary aerosol (12). These processes finally give rise to the tertiary aerosol, i.e., the aerosol reaching the flame (12). In the present study, therefore, particle size in the flame was controlled by modifying the aerosol drop size through the use of aerosol-modifying devices, rather than through analyte dilution.

Based on the conclusions of Stupar and Dawson (9), it would be anticipated that the magnitude of most condensed-phase vaporization interferences would depend on the proportion of large diameter drops present in the tertiary aerosol. Consequently, in this study a number of the classical, condensed-phase interference effects were reexamined to determine the relationship between interference severity and tertiary aerosol drop size. It was found that several condensed-phase interferences reported in the literature were not present under experimental conditions typical of present analytical practice. Additionally, other reported interferences could either be reduced to a negligible level or be altogether eliminated, by suitable removal of large diameter drops from the aerosol.

## EXPERIMENTAL SECTION

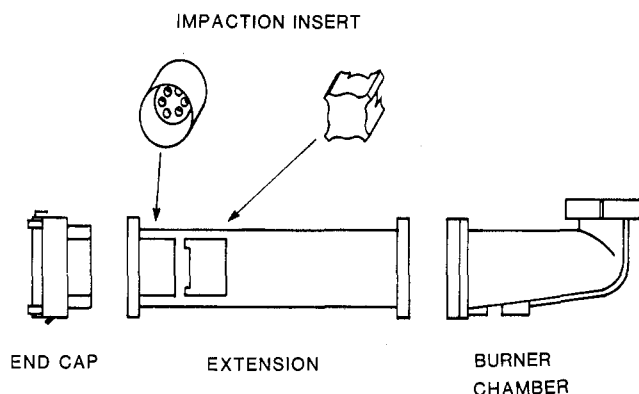
**Reagents.** Certified atomic absorption standards (1000  $\mu\text{g}/\text{mL}$ ) were obtained from Fisher Scientific (Atlanta, GA). Working standards of the various cation solutions were prepared by serial dilution of the certified standard solutions. Solutions with cation concentrations in excess of 1000  $\mu\text{g}/\text{mL}$  were prepared from analytical-reagent-grade nitrates or chloride. Standard solutions of sulfates were prepared from reagent grade  $\text{Na}_2\text{SO}_4$ , while phosphate standards were prepared by dilution of  $\text{H}_3\text{PO}_4$ . The deionized water used (Continental Water Conditioning Co., Atlanta, GA) has a rated specific resistance of 18 M $\Omega$ .

**Instrumentation.** Drop size distributions were obtained with an Andersen Model 2000 cascade impactor (Andersen Instruments, Atlanta, GA). The theory of the cascade impactor and its utility for such measurements have been discussed in previous publications from this laboratory (10, 12). Transport efficiency values were obtained by the direct method of Smith and Browner (13).

Atomic absorption measurements were made, under specified conditions, by using either a Perkin-Elmer Model 5000 atomic absorption spectrometer (Perkin-Elmer Corp., Norwalk, CT) or an IL Model 451 atomic absorption spectrometer (Instrumentation Laboratories, Andover, MA). The burner slot dimensions were as follows: air/acetylene, 105  $\times$  2 mm; nitrous oxide/acetylene, 54  $\times$  1 mm. Absorbance values quoted for the air/acetylene flame are the average of ten replicate 0.5-s integrations. Values quoted for the nitrous oxide/acetylene flame are the average of five replicate 3-s integrations. A normal AAS slit height was used, giving an optical viewing window in the flame of approximately 5 mm. With the Perkin-Elmer instrument, the standard adjustable concentric nebulizer was used. With the IL instrument, either Model J or Model K nebulizers were used.

In certain experiments, Teflon impaction inserts were placed in the aerosol path between the nebulizer and the burner head. These devices, constructed on the principles of cascade impactor design, were used as a means of removing larger drops from the aerosols produced by the various nebulizers. Typical inserts are illustrated in Figure 1. The first insert, which contains an array of holes, acts both as an initial aerosol impaction site for large drops and as a means of temporarily raising the axial velocity of

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**Figure 1.** Spray chamber impactor insert. Shown with extension for Perkin-Elmer spray chamber. See text for additional details.

the aerosol stream. The second impactor insert, placed close behind the first, acts as a secondary impaction site, collecting smaller droplets than those trapped by the first insert.

The first insert was designed to provide a smooth gas flow stream up to the drilled surface, but the precise depth of recess was found not to be critical. The dimensions of the first impactor inserts used in this study were as follows: (1) **Perkin-Elmer**. External diameter, 38 mm; diameter of drilled area = 25 mm; number of holes, 24; hole diameter, 2.6 mm. (2) **IL**. External diameter, 25.4 mm; diameter of drilled area, 18 mm; number of holes, 6; hole diameter, 2.6 mm. The dimensions of the inserts were selected to match the individual spray chambers. With the IL cylindrical spray chamber, direct insertion of the impactor was possible. In order to allow selective positioning of the impactor in the noncylindrical Perkin-Elmer spray chamber, however, a cylindrical aluminum extension to the spray chamber was constructed (Figure 1). This was placed between the spray chamber end cap and the spray chamber.

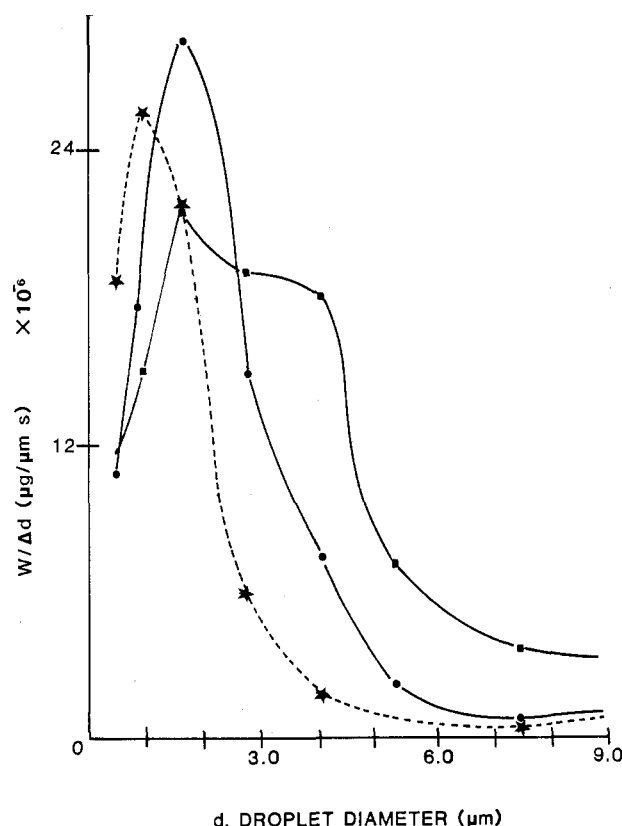
The second insert was designed so that a flat surface was presented to the aerosol stream passing through the first insert but so that the gas stream together with drops small enough to escape impaction could freely flow around it. The positioning of the second insert behind the first was not critical, and little difference in aerosol properties was observed for separations over the range 6–18 mm.

## RESULTS AND DISCUSSION

**Depression of Calcium by Phosphate in an Air/Acetylene Flame.** The depression of calcium absorption and emission signals in the presence of phosphates is one of the classical examples of a condensed-phase interference. Alkemade (14) and others (15, 16) have studied the interferences of phosphate- and sulfate-containing species on Ca signals and generally concluded that the interference increased with increasing anion concentration, until a plateau region was reached. The mechanism suggested by Alkemade (14) involves the formation of a low-volatility compound containing calcium, oxygen, and phosphorus, which inhibits the production of free atomic calcium.

If the action of phosphates on calcium is truly a kinetic effect, in which the effective vaporization rate of calcium in the flame is retarded by the formation of involatile phosphorus-containing compounds, certain conclusions follow. The observed interference will be related to the particle size of the desolvated aerosol and also to the height of observation in the flame. This assumes that parameters such as fuel flow, oxidant flow, etc. remain constant.

Drop size distributions obtained with a Perkin-Elmer concentric AAS nebulizer/spray chamber, operating with three different aerosol modification devices, are shown in Figure 2. Nebulizer operating parameters were optimized in accordance with manufacturers instructions. The distribution curves for an IL spray chamber, using Model J and Model K nebulizers, and a Model K nebulizer operated with an impaction insert, are shown in Figure 3. The distributions



**Figure 2.** Tertiary drop size distributions for Perkin-Elmer nebulizer/spray chamber. (★) Impaction insert; (■) bead; (●) paddle. Nebulizer gas flow = 10.4 L/min, aspiration rate = 8.0 L/min. Ordinate axis = analyte mass transport rate, normalized for unequal collection range of each stage of cascade impactor (see ref 14).

**Table I. Tertiary Aerosol Characteristics**

nebulizer model and spray chamber config	$W_{tot}$ , $\mu\text{g/s}$	$d_c$ , $\mu\text{m}$	% larger than 10 $\mu\text{m}$
Perkin-Elmer <sup>a</sup> with bead	5.8	4.6	51
Perkin-Elmer <sup>a</sup> with paddle	2.2	2.9	8
Perkin-Elmer <sup>a</sup> with impaction insert	1.6	2.0	0
IL Model J <sup>b</sup> with bead	3.6	4.4	51
IL Model K <sup>b</sup> with bead	1.2	2.7	18
IL Model K <sup>b</sup> with impaction insert	0.72	2.2	4

<sup>a</sup> Nebulizer gas flow = 10.4 L/min. Auxiliary oxidant flow = 2.0 L/min. Sample aspiration rate = 8.0 mL/min. <sup>b</sup> Nebulizer gas flow = 7.0 L/min. Sample aspiration rate = 6.0 mL/min.

labeled "impaction insert" arise from the use of the inserts shown in Figure 1. Table I provides a quantitative summary of the aerosol characteristics of all the nebulizer/spray chamber/insert configurations. In Table I, the parameter  $W_{tot}$  is a measure of the total analyte mass reaching the atomizer per second (13). The cutoff diameter,  $d_c$ , of the spray chamber (13) is the value of the drop diameter on a drop size distribution plot, where the ordinate mass transport term falls to 50% of its peak value. As such, it is a measure of the effectiveness of the spray chamber in removing large drops from the aerosol. A system with a low  $d_c$  value will only pass small drops, whereas one with a high  $d_c$  value will allow a coarser aerosol to reach the flame. Also shown is the percentage of tertiary aerosol collected in the preimpactor during the drop size distribution measurements. This percentage represents the portion of tertiary aerosol contained in droplets larger than 10  $\mu\text{m}$  diameter.

**Perkin-Elmer System. Pure Solution Studies.** The data in Table I, and the distributions shown in Figure 2, demonstrate that the width of the tertiary aerosol size dis-

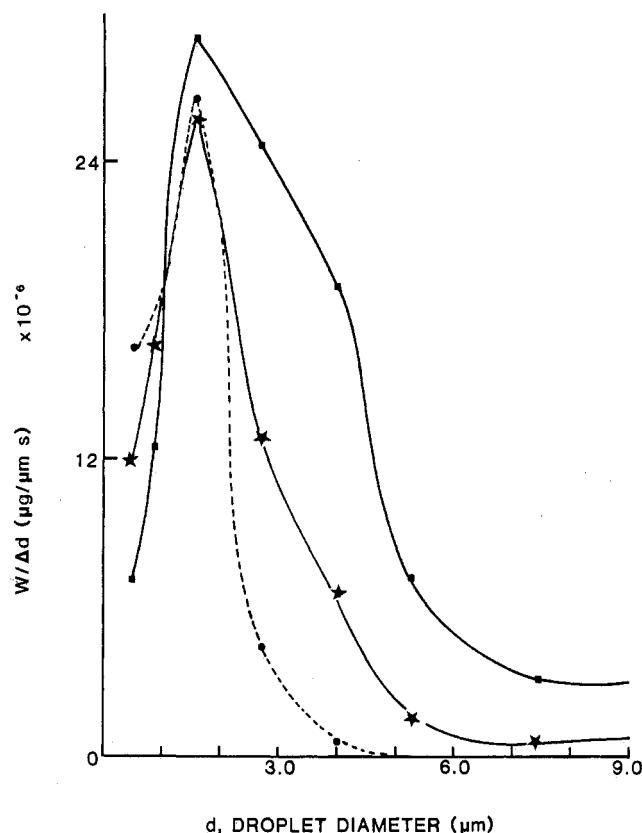


Figure 3. Tertiary drop size distributions for IL nebulizer/spray chamber. (■) Model J nebulizer; (★) Model K nebulizer; (●) Model K nebulizer + impactation insert. Nebulizer gas flow = 7.0 L/min, aspiration rate = 6.0 mL/min. Axis labels, as for Figure 2.

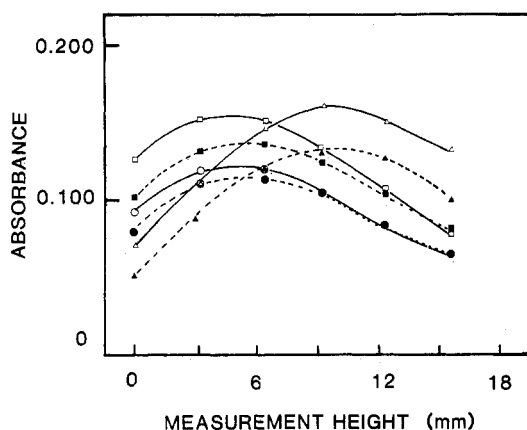


Figure 4. Absorbance vs. measurement height for Perkin-Elmer system. (■ □) Paddle; (● ○) Impactation insert; (▲ Δ) bead. (—) 5 μg/mL Ca; (---) 5 μg/mL Ca + 1000 μg/mL  $\text{PO}_4^{3-}$ . Nebulizer gas flow = 10.4 L/min.; aspiration rate = 8.0 mL/min.

tribution decreases in the order: spray chamber with bead > spray chamber with mixer paddle > spray chamber with impactation insert. It is significant that with pure  $\text{CaCl}_2$  solutions, absorbance vs. height profiles (Figure 4) show a clear correlation between the height for maximum absorption and the particle size distribution of the aerosol. The spray chamber/impactation insert system and the spray chamber/mixer paddle system, which produce a smaller percentage of large droplets, reach a maximum signal significantly lower in the flame than the spray chamber/bead system, which produces the highest percentage of large droplets.

**Interference Studies.** Figure 4 and Table II show the influence of 1000 μg/mL phosphate on 5 μg/mL Ca, for the Perkin-Elmer concentric nebulizer operating with the three different spray chamber configurations. The relative inter-

Table II. Interference of 1000 μg/mL  $\text{PO}_4^{3-}$  on 5 μg/mL Ca Solution, Using the Perkin-Elmer Spray Chamber and an Air/Acetylene Flame<sup>a</sup>

ht above burner, mm	% rel interference		
	bead	paddle	impactor
0	-28 (0.071)	-19 (0.126)	-13 (0.092)
3	-22 (0.111)	-13 (0.151)	-8 (0.119)
12	-15 (0.150)	-6 (0.108)	+4 (0.083)
20	-15 (0.115)	+4 (0.068)	+4 (0.052)

<sup>a</sup> Parentheses denote absorbance of 5 μg/mL Ca, without interferent. Nebulizer gas flow = 10.4 L/min. Aspiration rate = 8.0 mL/min.

ference values shown in this, and subsequent tablets, are ratios of the absorbance values of solutions containing both analyte and interferent to the absorbance of pure analyte solution. Negative values indicate signal depression; positive values indicate signal enhancement.

When the impact bead is used, the high proportion of large drops in the tertiary of the aerosol leads to significant interferences in the stoichiometric air/acetylene flame. The Ca analytical signal is depressed, even when measurements are made high in the flame. This indicates that the drop residence time in the flame is too short to ensure complete vaporization of the larger particles. When the mixer paddle is used, the depression is less than when using the impact bead, and interference-free measurements are observed at heights of 12–15 mm above the burner head. Least interference is found when the impactation insert is used. Interferences are negligible at measurement heights as low as 9 mm above the burner head.

For the various configurations of the Perkin-Elmer system, the cutoff diameter values,  $d_c$ , increase in the order: impactation insert < mixer paddle < impact bed. Clearly, there is a direct correlation between the proportion of large diameter drops reaching the flame and the severity of the calcium/phosphate interference, as the interference effect increases in the same order as the cutoff diameter.

**Limiting Drop Diameter.** The concept of a limiting drop diameter,  $d_{\max}$ , has been discussed in an earlier publication (12). The limiting drop diameter is defined as the drop size in the tertiary aerosol which contributes 10% or less to the analytical signal, and its value depends on the vaporization properties of each matrix/analyte combination. Consequently, this parameter relates vaporization effects in the atomizer to the tertiary aerosol drop diameter. The value of  $d_{\max}$  will also depend on the atomizer temperature. Generally, higher atomizer temperatures will cause a shift in  $d_{\max}$  to higher values. By definition, tertiary aerosols containing a substantial fraction of drops larger than  $d_{\max}$  will suffer from significant vaporization interferences. Few experimental values are available in the literature at present.

Based on the data obtained here, a  $d_{\max}$  value of 3.0 μm seems reasonable for  $\text{Ca}^{2+}/\text{PO}_4^{3-}$  depression in an air/acetylene flame, at the concentration levels described. A certain amount of subjective judgement is involved in assigning a value to  $d_{\max}$ , as measurement height in the flame is an important variable in the signal/particle vaporization relationship. In this study, removal of the interference at a measurement height <12 mm was used as a criterion for determining  $d_{\max}$ . Additionally, the aerosols used in this study did not have a continuously variable drop size, and so some signal vs. drop size extrapolation was necessary. Nevertheless, the  $d_{\max}$  values obtained in this manner should provide a useful way of comparing different analyte/matrix mixtures.

**Particle Size, Aerosol Transport, and Signal Magnitude.** Although the impactation system gives the lowest interferences, Table II shows that this gain is obtained only by sacrificing analytical signal. Both the mixer paddle and the

**Table III. Interference of 1000  $\mu\text{g/mL PO}_4^{3-}$  on 10  $\mu\text{g/mL Ca}$  Solution, Using the IL Nebulizer System and an Air/Acetylene Flame<sup>a</sup>**

ht, above burner, mm	% rel interference		
	Model J	Model K	K and Impactor
0	-44 (0.157)	-23 (0.224)	-11 (0.317)
3	-41 (0.332)	-18 (0.428)	-8 (0.399)
12	-30 (0.373)	-10 (0.364)	-2 (0.205)
20	-23 (0.220)	-6 (0.156)	+3 (0.089)

<sup>a</sup> Parentheses denote absorbance value of 10  $\mu\text{g/mL Ca}$ , without interferent. Nebulizer gas flow = 7.0 L/min at 40 psig. Sample aspiration rate = 6.0 mL/min.

impaction insert reduce mean drop size by removing larger drops from the aerosol. The direct result of this process is to decrease net analyte mass transport to the flame.

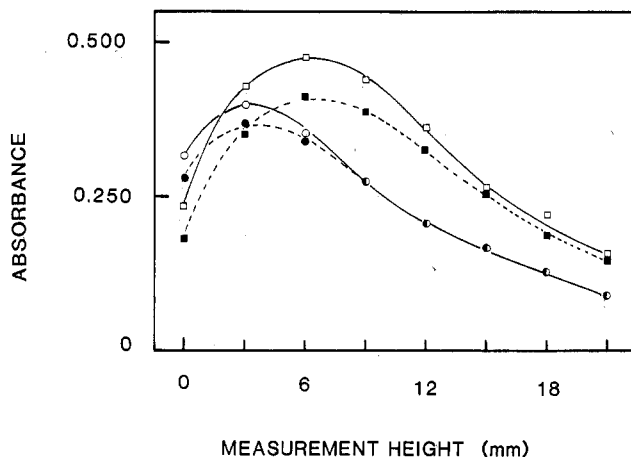
As shown in Table I,  $W_{\text{tot}}$ , the total aerosol mass reaching the atomizer per second, decreases in the order: bead > paddle > impactor. As expected, the magnitude of the analytical signal follows the same trend (Table II). The trade-off between analytical sensitivity, on the one hand, and interference freedom, on the other, is inherent in the concept of first generating a polydisperse aerosol, and then discarding the larger drops.

**Instrumentation Laboratory Nebulizers.** Similar interference studies were carried out by using a variety of Instrumentation Laboratory (IL) nebulizer/spray chamber arrangements. Figure 3 shows that the aerosol produced by the IL Model J nebulizer is very similar to the aerosol produced by the Perkin-Elmer nebulizer operating with an impact bead (Figure 2). The aerosol produced by the IL Model K nebulizer is very similar to that of the Perkin-Elmer system operating with a mixer paddle, except that with the IL system a larger percentage of the tertiary aerosol is contained in drops larger than 10  $\mu\text{m}$  (see Table I).

Table III shows the depressive effect of 1000  $\mu\text{g/mL}$  phosphate on 10  $\mu\text{g/mL Ca}$ , using the various IL nebulizer systems. Neither the Model J nor the Model K nebulizer was able to resolve the phosphate depression, even at measurement heights of 21 mm above the burner. However, addition of an impaction insert to the spray chamber of the Model K nebulizer allowed the interference to be resolved as low as 6 mm above the burner head. When the Model J nebulizer was operated with an impaction insert, the depressive effect was removed but only at the expense of a 90% signal drop. It appears that the Model J nebulizer produces a very high proportion of drops of >5  $\mu\text{m}$  in the primary aerosol. Subsequent modification of this primary aerosol during secondary and tertiary transport stages leads to a drastic reduction in the analyte mass per second reaching the atomizer.

Figure 5 is a plot of absorbance vs. height of measurement for the IL Model K nebulizer, operated with and without the impaction system. With the impaction insert, a downward shift in measurement height for maximum absorbance is observed. This again demonstrates the higher vaporization rates of smaller particles. Also, with the impaction system, the  $\text{Ca}^{2+}/\text{PO}_4^{3-}$  depression is removed 6 mm above the burner head. From these results, it is clear that the calcium/phosphate interference vs. drop size relationship is general and not merely an artifact of one experimental system.

**Depression of Mg by Al in the Air/Acetylene Flame.** From earlier discussion, it follows that the extent of condensed-phase vaporization interferences will be determined not only by drop size but also by the properties of the analyte and matrix. In order to test this hypothesis, a number of additional element/matrix combinations were studied. Tests were carried out by using only the Perkin-Elmer spray chamber systems. In light of the calcium/phosphate results,



**Figure 5.** Absorbance vs. measurement height for IL system. (■ □) Model K nebulizer; (● ○) Model K nebulizer + impactor. (—) 10  $\mu\text{g/mL Ca}$ ; (---) 10  $\mu\text{g/mL Ca}$  + 1000  $\mu\text{g/mL PO}_4^{3-}$ . Nebulizer gas flow = 7.0 L/min; aspiration rate = 6.0 mL/min.

it was felt that the general conclusions drawn from these tests would be valid for other systems.

The interference of Al on Mg has been classified as a condensed-phase interference effect. The mechanism suggested is that of mixed-oxide spinel formation between Mg and Al (17, 18). The magnitude of the interference is dependent on flame conditions, on the height of measurement (19), and on the particle size introduced into the flame (9). Wadlin and Harrison (19) found that the signal depression of a solution containing 0.8  $\mu\text{g/mL Mg}$  increased with increasing Al concentration. A plateau, corresponding to a 60% signal drop, was reached at an Al concentration of 50  $\mu\text{g/mL}$ .

In the present study, the Perkin-Elmer system was operated with the three spray chamber configurations. As expected, the interference decreased in the order: bead > paddle > impaction insert. Effective elimination of the interference (i.e., less than 5% signal depression) was observed when the impaction insert was used with a measurement height of 6 mm above the burner head. The interference effect could not be eliminated at any measurement height when either the mixer paddle or the impact bead was used. Hence, it appears that the limiting particle diameter for the Mg/Al interference is smaller than for the  $\text{Ca}^{2+}/\text{PO}_4^{3-}$  interference. The value  $d_{\text{max}}$  for the Mg/Al system is estimated to be <2.0  $\mu\text{m}$ .

**Depression of Mg by Ti in the Air/Acetylene Flame.** Titanium, like Al, forms magnesium spinels at high temperatures and has been shown to depress Mg absorption in both the air/acetylene flame and the nitrous oxide/acetylene flame (19). Other workers, such as Wilson (20), have observed enhancement effects due to Ti in the air/acetylene flame. Both Harrison and Wadlin (19) and Wilson (20) observed that by proper adjustment of the fuel-to-oxidant ratio and the height of measurement, the interference effect could be eliminated.

The results obtained for the air/acetylene flame in the present study followed the trends found earlier for Mg and Al. The impact bead and mixer paddle systems both showed significant depressive effects, even when the height of observation was increased. With the impaction insert, on the other hand, the interference effect was reduced to negligible levels throughout the height profile. The limiting drop diameter for interference-free measurements of Mg in the presence of Ti again appears to be <2.0  $\mu\text{m}$ .

**Depression of Mg by Si in the Air/Acetylene Flame.** A condensed-phase vaporization interference of Si on Mg has been reported (5, 15). It was also demonstrated that La- and Sr-releasing agents could remove the interference. However, in the present study, no detectable depression was observed, with or without added La, under any of the operating con-

ditions employed. Even when an impact bead was used, the absorbance of a 5  $\mu\text{g/mL}$  Mg solution was unaffected by the presence of 1000  $\mu\text{g/mL}$  Si, when measured in an air/acetylene flame. Apparently, the  $d_{\text{max}}$  value for this interference lies well above 10  $\mu\text{m}$ .

**Depression of Mn by Al in the Air/Acetylene Flame.** Sanzalone and Chao have shown (21) that Al solutions acidified with nitric acid produce a condensed-phase vaporization effect on Mn absorption in the air/acetylene flame. In the present work, a significant depressive effect was observed only with an impact bead and at low observation heights in the flame. The depression was reduced to <10%, when the height of measurement was increased to between 15 and 20 mm above the burner head. The use of the mixer paddle reduced the interference to a negligible level at measurement heights even as low as 3 mm above the burner top. The impaction inserts also resolved the interference but produced a severe reduction in the analytical sensitivity. Therefore, height measurements were not performed with the impaction insert. The  $d_{\text{max}}$  value for this interference is approximately 10  $\mu\text{m}$ .

**Depression of Mn by Si in the Air/Acetylene Flame.** Si has been found by various workers to give a negative interference with Mn (22, 23). In the present study the use of an impact bead resulted in significant depression of Mn by Si. The mixer paddle significantly reduced the interference but did not eliminate it, even at measurement heights of 20 mm. With the impaction insert, a signal enhancement was found in the presence of Si at observation heights of 9 mm or more. This was subsequently found to be the result of an ionization interference, as the Si was added as  $\text{Na}_2\text{SiO}_3$ . When an ionization buffer was added to the pure analyte solutions, interference with the impaction insert was less than 4% at a 9-mm measurement height. The value of  $d_{\text{max}}$  for this system is probably <2  $\mu\text{m}$ .

**Depression of Fe by Si in the Air/Acetylene Flame.** Only Si has been observed to interfere significantly with Fe in the air/acetylene flame (9, 23, 24). In the present study, interference effects were observed only when the impact bead was used. Interferences were negligible with both the mixer paddle and the impaction insert at measurement heights above 12 mm. The estimated value for  $d_{\text{max}}$  is 3  $\mu\text{m}$ .

**Vaporization Interferences with the Nitrous Oxide/Acetylene Flame.** Use of the high-temperature nitrous oxide/acetylene flame has eliminated many of the condensed-phase vaporization effects commonly found in the air/acetylene flame. Nevertheless, several instances of condensed-phase vaporization interferences in the nitrous oxide/acetylene flame are documented in the literature (5, 19, 25). Present studies have demonstrated, however, that some of these interference effects are no longer observed under normal experimental conditions. Furthermore, the magnitude of many of the remaining interference effects does not seem to be directly related to the tertiary aerosol drop size. This implies that these interference effects do not involve a vaporization mechanism.

**Interference of Ti on Mg in the Nitrous Oxide/Acetylene Flame.** Harrison and Wadlin (19) observed a 20% depression of Mg absorbance in the presence of 600  $\mu\text{g/mL}$  Ti, when measuring low in a nitrous oxide/acetylene flame. At greater measurement heights, they found that Ti enhanced the signal by as much as 15%. These studies were repeated, using the Perkin-Elmer system operating with an impact bead. Measurements were taken in a highly reducing flame and at measurement heights as low as 3 mm. No significant alterations were observed in the analytical signal under any conditions used. Although Ti produced a depression in the air/acetylene flame, Ti concentrations as high as 600  $\mu\text{g/mL}$  produced no effect in the nitrous oxide/acetylene flame.

Table IV. Interferences of Concomitants on 50  $\mu\text{g/mL}$  Mo with a Nitrous Oxide/Acetylene Flame<sup>a</sup>

spray chamber config	absorbance 50 $\mu\text{g/mL}$ Mo	% rel interference		
		1% $\text{HClO}_4$	1% HCl	200 $\mu\text{g/mL}$ Al
ht = 0 mm				
bead	0.166	+25	+1.2	+16
paddle	0.168	+4.2	-3.0	-3.6
impaction insert	0.142	+2.1	0	+6.3
ht = 3 mm				
bead	0.298	+52	+5.0	+14.0
paddle	0.257	+8.9	0	+5.8
impaction insert	0.222	0	-2.7	+1.0
ht = 12 mm				
bead	0.283	+80	+9.2	+12.0
paddle	0.182	+1.6	-8.8	-11.0
impaction insert	0.187	+1.6	-2.7	+2.7
ht = 20 mm				
bead	0.122	+87	+14	+16.0
paddle	0.100	+13	+6	0
impaction insert	0.129	+3.1	-1.6	-3.1

<sup>a</sup> Nebulizer gas flow = 10.4 L/min. Aspiration rate = 7.0 mL/min.

Apparently Mg/Ti particles resulting from drops as large as 10  $\mu\text{m}$  are adequately decomposed in the nitrous oxide/acetylene flame. We can only conclude that the nebulizer/spray chamber system used by Harrison and Wadlin (19) must have allowed a significantly greater fraction of large aerosol particles to reach the flame than the Perkin-Elmer systems used in this study.

**Interference of Al and K on Mg in the Nitrous Oxide/Acetylene Flame.** While the presence of Al may cause a negative interference for Mg in the air/acetylene flame (18, this study), it has been reported that the addition of a mixture of Al and K enhances Mg absorption in the nitrous oxide/acetylene flame (5). In the present work, a comparison was made between absorption signals of solutions containing 1  $\mu\text{g/mL}$  Mg and 1000  $\mu\text{g/mL}$  Na, 1  $\mu\text{g/mL}$  Mg and 1000  $\mu\text{g/mL}$  K, and 1  $\mu\text{g/mL}$  Mg and 1000  $\mu\text{g/mL}$  Al, using the Perkin-Elmer system with an impact bead. No significant differences between the signals for any of the solutions were found.

**Mo Interferences in the Nitrous Oxide/Acetylene Flame.** Kerbyson et al. (26) have shown that perchloric acid, hydrochloric acid, sulfuric acid, and Al all significantly enhance the absorption signal of Mo in the fuel-rich nitrous oxide/acetylene flame. They attributed the enhancement to competition between the concomitants and Mo for oxygen in the flame. West et al. (3) have also reported significant enhancements for a wide range of cations and anions and explained their results in terms of lateral diffusion effects. However, none of these authors considered the importance of drop size on interferences or made any attempt to characterize the tertiary aerosols generated by their systems. By contrast, data obtained in the present work (Table IV) support a strong drop size dependence of the interference effect. Significant enhancements occur at all measurement heights when the impact bead is used; a drastic reduction in enhancement occurs when the mixer paddle is used. The effect of the impaction insert is to further reduce the interference to a negligible level at most observation heights.

Kerbyson (26) also noted significant enhancement effects from  $\text{Na}_2\text{SO}_4$  and from sulfuric acid. In the present study, an enhancement of 60–90% was observed in the presence of

**Table V. Interferences of Concomitants on 100  $\mu\text{g/mL}$  Al Solution with a Nitrous Oxide/Acetylene Flame<sup>a</sup>**

	Ti	V	Cr	Mn	Fe	Co	Ni
ht = 0 mm							
bead (0.342)	+7.1	+14	-10.8	-24	-11.2	+3.1	-8.3
paddle (0.174)	+12	+10	-11	-6.5	-6.0	+3.5	-2.0
impaction insert (0.121)	+12	+11	+4	+2.5	0	+3.4	+2.5
ht = 3 mm							
bead (0.524)	+10.5	+10	-8	-3.8	-3.2	+3.0	-1.1
paddle (0.195)	+3	+4.5	-4.8	-2.6	-4.5	+1.0	-1.0
impaction insert (0.166)	-4.0	+2.4	+1.6	+0.8	0	-2.5	-3.3
ht = 12 mm							
bead (0.492)	+3.5	+2.7	-3.0	0	0	-1.0	+0.6
paddle (0.192)	-3.0	0	+1.2	+3.0	+5.0	-5.2	-5.0
impaction insert (0.121)	-6.6	+0.8	+2.5	+1.7	0	-1.7	+1.7
ht = 20 mm							
bead (0.308)	+1.9	+7.0	+1.6	+8.3	+7.6	-3.5	+7.6
paddle (0.178)	-0.6	0	-2.2	+3.0	+4.0	+1.1	+1.1
impaction insert (0.124)	-4.0	+2.4	+2.4	+2.4	+4.0	+4.8	+4.0

<sup>a</sup>Interfering metal concentration, 5000  $\mu\text{g/mL}$ . Relative percentage of interference reported by Marks and Welcher (25): Ti, +14; V, +21; Cr, +14; Mn, +11; Fe, +15; Co, +10; Ni, +26. Interferences observed with Perkin-Elmer systems. Concentration of cation interferents = 1000  $\mu\text{g/mL}$ . Nebulizer gas flow, 10.4 L/min. Aspiration rate = 8.0 mL/min. Parentheses denote absorbance values of 100  $\mu\text{g/mL}$  Al in the presence of 1000  $\mu\text{g/mL}$  K as KCl and 1.2 N HCl.

**Table VI. Interferences of Concomitants on 10  $\mu\text{g/mL}$  Cr with a Nitrous Oxide/Acetylene Flame<sup>a</sup>**

	Ti	V	Mn	Ni	Fe
ht = 0 mm					
bead (0.393)	-2.5	-0.3	+7.1	+1.8	+11
paddle (0.158)	-9.5	0	+0.6	-5.7	+7.2
impaction insert (0.093)	-8.6	+7.5	0	0	+1.7
ht = 3 mm					
bead (0.521)	-6.7	+2.3	+5.6	+3.8	+9.2
paddle (0.181)	-11.6	+2.2	-0.5	-6.1	+4.7
impaction insert (0.104)	-13.5	+2.9	-2.9	-5.8	-0.4
ht = 12 mm					
bead (0.457)	-12.1	+3.5	+3.7	+4.2	0
paddle (0.165)	-15.4	-0.6	-0.6	-4.2	-0.2
impaction insert (0.091)	-15.4	+1.1	-1.0	-6.6	+1.2
ht = 20 mm					
bead (0.370)	-15.7	+1.6	+1.4	+1.9	0
paddle (0.149)	-15.5	+0.7	0	-4.7	+0.6
impaction insert (0.081)	-21.0	-2.2	-1.3	-8.6	-1.4

<sup>a</sup>Interfering metal concentration, 5000  $\mu\text{g/mL}$ . Relative percentage of interference reported by Marks and Welcher (25): Ti, +36; V, +38; Mn, +27; Ni, +25; Fe, +9. Interferences observed with Perkin-Elmer systems. Concentration of cation interferents = 1000  $\mu\text{g/mL}$ . Nebulizer gas flow = 10.4 L/min. Aspiration rate = 8.0 mL/min.

1000  $\mu\text{g/mL}$  Na, using an impact bead. This enhancement was reduced to approximately 30% with the mixer paddle and to approximately 15% with the impaction insert. It is doubtful that the enhancement can be explained as a simple ionization interference, since Mo has an extremely high first ionization potential (7.35 eV) and the enhancement appears to be a function of tertiary aerosol drop size. No mechanism can be offered at the present to explain this enhancement effect. Sulfuric acid solutions caused a 10% depression in the Mo absorption signals, and the degree of depression was apparently not drop size related.

**Cationic Interferences on Al, Cr, and Ni in the Nitrous Oxide/Acetylene Flame.** Welcher and Marks have performed a comprehensive study of the interference effect of several cations on the absorption signals of Al, Cr, and Ni in the nitrous oxide/acetylene flame (25). They found that the magnitudes of some of these effects were dependent on the flame chemistry, as well as on the measurement height. Tables V–VII compare the results obtained by Marks and Welcher (25) to the results obtained in the course of this study. All of the stock solutions were prepared from the chlorides, and all test solutions were 1.2 N in HCl, and contained 1000  $\mu\text{g/mL}$  K as KCl, exactly duplicating the procedures of Marks and

**Table VII. Interferences of Concomitants on 40  $\mu\text{g/mL}$  Ni with a Nitrous Oxide/Acetylene Flame<sup>a</sup>**

	Ti	V	Cr	Mn	Fe	Co
ht = 0 mm						
bead (0.119)	+5.9	+7.6	+8.4	+4.2	+10.1	+14.3
paddle (0.055)	+3.6	0	0	-5.5	+1.8	+14.5
impaction insert (0.025)	0	0	0	0	0	0
ht = 3 mm						
bead (0.159)	+10.1	+2.5	+4.4	+0.6	+3.1	+13.8
paddle (0.055)	+5.5	0	+3.6	-3.7	+1.8	+14.5
impaction insert (0.025)	0	0	0	0	0	0
ht = 12 mm						
bead (0.130)	+1.5	+1.5	+3.1	+0.8	+0.8	+12.3
paddle (0.044)	+2.3	0	+2.3	-2.3	0	+9.1
impaction insert (0.025)	0	0	0	0	0	0
ht = 20 mm						
bead (0.120)	+0.8	+0.8	+1.7	-0.8	+0.8	+11.0
paddle (0.040)	+5.0	+2.5	+5.0	+2.5	+2.5	+12.5
impaction insert (0.025)	0	0	0	0	0	0

<sup>a</sup>Interfering metal concentration, 5000  $\mu\text{g/mL}$ . Relative percentage of interference reported by Marks and Welcher (25): Ti, +27; V, +7; Cr, +36; Mn, +78; Fe, +11; Co, +55. Interferences observed with Perkin-Elmer systems. Concentration of cation interferents = 1000  $\mu\text{g/mL}$ . Nebulizer gas flow = 10.4 L/min. Aspiration rate = 8.0 mL/min. Parentheses denote absorbance of 40  $\mu\text{g/mL}$  Ni in the presence of 1000  $\mu\text{g/mL}$  K as KCl and 1.2 N HCl.

Welcher (25). The literature values of absorbance given in the tables were obtained at the measurement height that gave the maximum absorbance value for the pure solution.

The presence of titanium or vanadium was found to give an overall enhancement of Al absorbance in the fuel-rich flame, while other cations examined caused a depression in the analytical signal. The largest degrees of interference occurred when use of the impact bead was coupled with low measurement heights in the flame. Increasing measurement height or using the mixer paddle or the impaction insert reduced the interference level to below 5%, although an associated decrease in the magnitude of the analytical signal was observed. Decreasing the fuel flow, and thereby making a leaner flame, also alleviated the interference effects, even when the impact bead was used. However, a severe decrease in sensitivity is experienced as the flame becomes leaner.

Table VI shows that Ti was the only element which produced a significant interference on the Cr absorption signal,

when using a fuel-rich nitrous oxide/acetylene flame. Here, the minimum interference was observed low in the flame and with the largest diameter drops. Thus, it would appear that the Ti depression was not a vaporization interference effect. Interferences in the analytical signal of Cr due to V, Mn, Ni, and Fe could be reduced to negligible levels either by using an impact bead and measuring high in the flame or by using a mixer paddle or impaction insert and measuring at any height.

The data in Table VII show that Co is the only element which produces any significant interference on Ni in the fuel-lean nitrous oxide/acetylene flame. All the other cationic interferences observed by Marks and Welcher (25) could be controlled either by using the mixer paddle or impaction inserts or through the use of large measurement heights, with the impact bead. The degree of Co interference on Ni was not related either to the drop size introduced into the flame or to the measurement height used. This is strong evidence against the likelihood of a condensed-phase vaporization effect.

### CONCLUSIONS

The ability to reduce condensed-phase vaporization interferences to negligible levels further enhances the analytical utility of atomic absorption spectroscopy, even at this late state in the technique's development. Many other important interferences, such as ionization and background scatter, may be controlled under most circumstances. Flame AAS cannot compete with the emission spectroscopy using the inductively coupled plasma (ICP) in many regards. Particularly, it cannot match the wider linear dynamic range possible with the ICP under simultaneous multielement conditions. Nevertheless, it appears that with suitable aerosol control, the performance gap in interference freedom between the two techniques may be significantly narrowed.

Nebulizers with impact beads, but no impaction devices, are not recommended for determination of elements in complex matrices with the air/acetylene flame. While improvements in sensitivity may result for some elements, the deterioration in accuracy that could occur should be carefully considered.

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**Registry No.** PO<sub>4</sub><sup>3-</sup>, 14265-44-2; Ca, 7440-70-2; Mg, 7439-95-4; Mn, 7439-96-5; Fe, 7439-89-6; Al, 7429-90-5; Cr, 7440-47-3; Ni, 7440-02-0; Mo, 7439-98-7; Ti, 7440-32-6; K, 7440-09-7; V, 7440-62-2; Co, 7440-48-4; Si, 7440-21-3.

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