Reduction of Calcium Interference on Barium Using the Nitrogen-Shielded Nitrous Oxide-Acetylene Flame in Atomic Absorption Spectroscopy†

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The interference effects of calcium on barium in atomic absorption spectroscopy, *i.e.*, background absorption and noise effect having been attributed to the CaOH green band were further studied. The behavior of the interfering calcium hydroxide radical and the barium atom itself was studied in relation to the distribution of natural species, OH and CN, using conventional and nitrogen-shielded nitrous oxide–acetylene flames. A remarkable reduction in the calcium interference was demonstrated using a nitrogen-shielded version of moderately fuel-rich flames. This effect was attributed to the suppression of CaOH formation which was brought about by an improvement in the reducing nature of the flame with shielding.

The calcium interference effects on barium, *i.e.*, background absorption and noise effect have been attributed to the molecular absorption and emission spectra of CaOH, and remain as major obstacles in the determination of this element in biological and geological materials, necessitating the removal of calcium in atomic absorption spectroscopy using nitrous oxide–acetylene flames.[1–3] Correcting for background absorption using a continuum source[4] appears impracticable due to the noisy signal of barium in the presence of calcium.[1] Gas-shielded burners have been used but with only limited information available on the behavior of the interferent.[5] It is difficult to meet the conditions for maximum barium absorbance and minimum calcium interference. The behavior of the barium atom in relation to the interfering CaOH radical in the nitrous oxide–acetylene flames does not appear to have been studied although the atomization of elements has often been discussed.[6–9]

Assuming that the oxides and hydroxides of alkaline earth elements in flames are in equilibrium with the oxidizing natural species,[10] making the flames more reducing may result in a reduction of the calcium hydroxide formation. In this paper, the distribution of barium atoms and CaOH radicals in the nitrous oxide–acetylene flames, as influenced by flame stoichiometry and inert gas shielding, has been studied as well as the distribution of OH and CN radicals. The CaOH population in a moderately fuel-rich nitrous oxide–acetylene flame has been clearly shown to be further suppressed by nitrogen shielding which results in a reduction in the calcium interference effects under optimum conditions for atomizing barium.

Experimental

A Perkin-Elmer Model 403 atomic absorption spectrophotometer was used. A barium hollow cathode lamp of maximum current 30 mA d.c. was operated at 26 mA as in previous work.[1] An Osram 64633 iodine-filled tungsten lamp was used at approximately 10 V a.c. with air cooling. A Perkin-Elmer nitrous oxide burner head was used with two types of laboratory-made gas shielding apparatuses, shown in Fig. 1. The first type (a) was fitted to the burner tightly covering the cooling fin and, in this way, the vertical holes encircling the head formed in the cooling block ensured laminar flow of the shielding gas. When the second type (b) was used, the burner head was removed from the cooling fin and fitted to this apparatus. Pure nitrogen or argon (99.9995% purity) was used as the shielding gas.

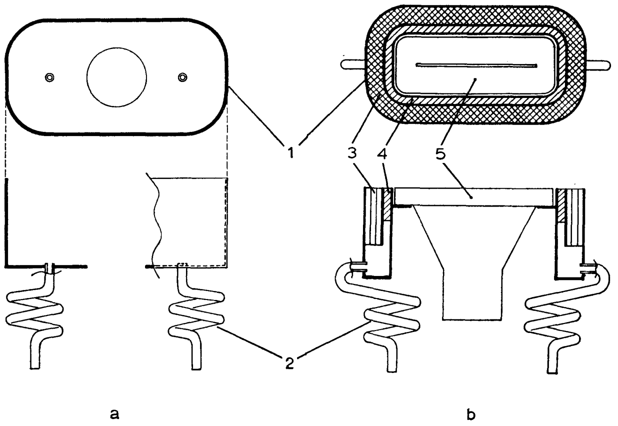

Fig. 1. Schematic diagram of burner with nitrogen shielding apparatus.
1: 1-mm thick brass box, 2: inert gas inlet, 4-mm diam. copper tube, 3: array of 2-mm diam. aluminum tubes 25 mm in length, 4: asbestos packing, 5: nitrous oxide burner head removed of cooling fin.

The position of the burner assembly was displaced manually by adjusting the installed racking mechanism stepwise by 2.5 and 0.43 mm in the vertical and horizontal directions, respectively. The flow rate of nitrous oxide was kept constant throughout the experiments, 13.2 dm^3/min (40.0 divisions of the flow meter reading at 30.0 psi). The acetylene flow rate was changed in seven steps from 7.36 to 8.33 dm^3/min (58.5 to 65.5 divisions at 8.0 psi). Thus, the nitrous oxide-to-acetylene flow ratio or molar ratio of the mixed gases as denoted by ρ[6] was lowered stepwise from 1.79 to 1.58. The setting of the flow meters was periodically checked during the course of measurements. Flow rates were read on the calibration graph revised by the manufacturer[11] neglecting possible small variations among flow meters of the same specification.

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The mask for the transmitting window on the right-hand side of the burner housing[1] was replaced with one having a 12-mm diam. circular aperture. When observing the spatial distribution of emission signal, another mask with a 4.5-mm diam. circular hole was attached to the window. Spatial resolution in the barium atom absorbance measurement was estimated as approximately 1.4 and 3.0 mm in the horizontal and vertical directions, respectively, measured at the focal plane close to the center of the burner slot. Spatial resolution in the emission study was estimated by viewing the filament of a small tungsten valve at the end of the slot nearer to the monochromator at 554 nm, as 1.3 and 4.7 mm in the horizontal and vertical directions, respectively.

The emission and absorption of CaOH was measured at 554 nm with a spectral band width of 0.4 nm, while 0.14 nm was used in recording the spectral profile. Flame background emission on aspirating distilled water at 554 nm, consisting of a C_2 band and continuum, was substracted.

The emission intensity of OH was measured using the 306.4 nm head with a spectral band width of 0.2 nm. The net intensity was obtained by substracting the contribution of the continuum, measured at 305 nm.

The OH and CN absorbances were measured using the Osram lamp by scanning each band with the head at 306.4 and 388.3 nm, respectively, employing a 0.07 nm spectral band width.

All emission and absorption measurements were carried out on aspirating either distilled water or salt solutions containing hydrochloric acid (0.1 mol dm^{-3}). Reagents used were of analytical grade, except for the Johnson Matthey "Specpure" barium carbonate and calcium carbonate.

Results and Discussion

Practically no difference was found between the two types of shielding apparatuses and between nitrogen and argon, with respect to the shielding effects on the CaOH emission intensity and flame stability. At a nitrogen flow rate of 13.5 dm^3/min, virtual suppression of the CaOH emission was achieved. Noise in emission and absorption measurements was found to increase above this flow rate.

Distribution of OH and CN in the Nitrous Oxide–Acetylene Flames as Influenced by Nitrogen Shielding. Spatial Distribution of the OH Emission Band: The distribution of the OH emission band in conventional and nitrogen-shielded flames of approximately optimum stoichiometry for barium atom absorbance ($\rho = 1.67$) is shown in Fig. 2. The emission intensity in the central part of the flame, corresponding to the interconal zone, was remarkably depressed with nitrogen shielding (Fig. 2b) while the red feather, about 15 mm in height in the conventional flame, was elongated to about 30 mm in the nitrogen-shielded version. In the outer zone, the OH emission grew more intense up the flame to form broad maxima on both sides of the flame at about 15 mm from the burner top in the non-shielded flame. The emission in this region was strongly suppressed with nitrogen shielding. The observed large reduction in the OH emission band intensity with nitrogen shielding in the interconal and outer zones, shows that the suppressed formation of OH at the boundary of the interconal zone and the suppressed diffusion of OH to the center of the flame[12] are caused by the depression in secondary combustion reactions due to the lack of entrained air. The persisting OH band emission in the primary reaction zone may be explained by the formation of the species and its strong chemiluminescence in

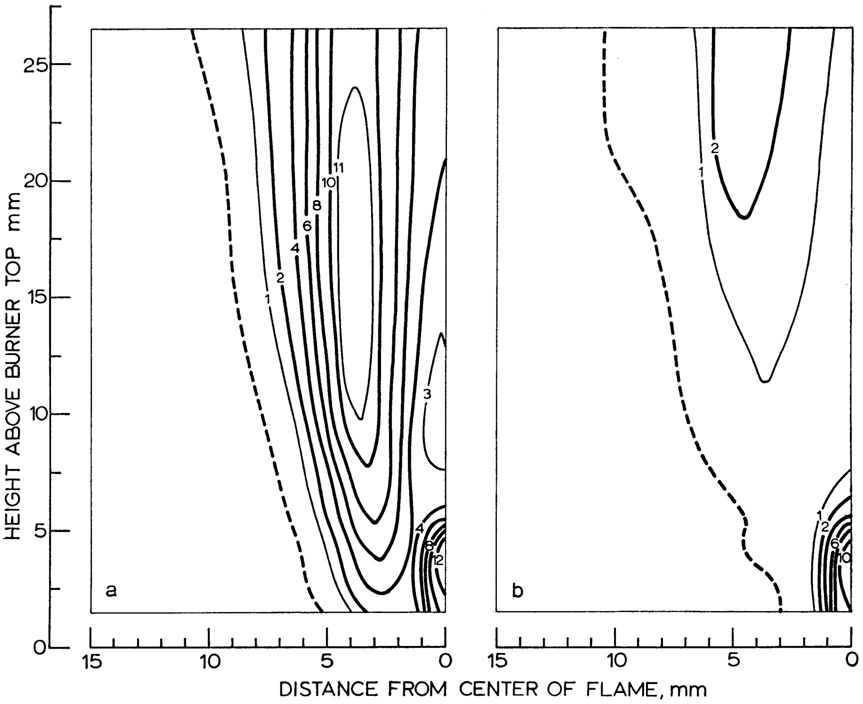

Fig. 2. Spatial distribution of OH emission intensity in the N_2O–C_2H_2 flames, of ρ 1.67.
a: Conventional flame, b: nitrogen-shielded flame.
——Flame envelope.
Figures on contour lines represent intensity in arbirary unit.

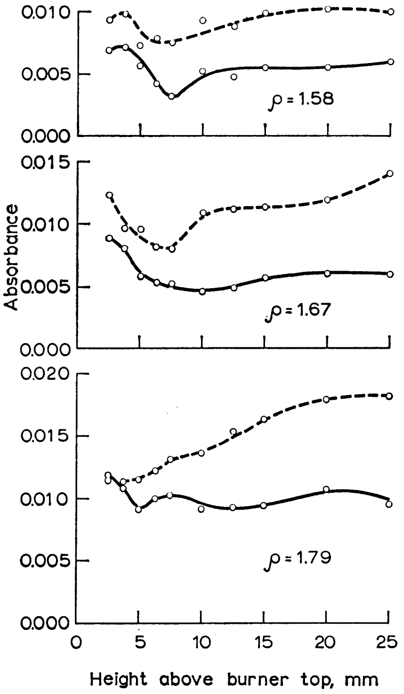

Fig. 3. Vertical distribution of OH absorbance in the N_2O-C_2H_2 flames.
----Conventional flame, ——nitrogen-shielded flame.

this region.[10)]

Vertical Distribution of the OH Absorption Band: The vertical absorbance profile of OH was studied. The results shown in Fig. 3 show the less pronounced effect of nitrogen shielding than that on OH emission. The absorbance was reduced by 57% at 10 mm when ρ= 1.67. A dip in absorbance just above the primary reaction zone was observed suggesting the presence of OH scavenging reactions involving carbon-containing species, 2C or C_2,[13)] and C_2 and CH.[14)]

Vertical Distribution of CN Absorption Band: The front of the CN absorbance profile moved up the flame along with decreasing ρ in the conventional and nitrogen-shielded flames as shown in Fig. 4. This approximately corresponded to the elongation of the red zone. A remarkable enhancement effect due to nitrogen shielding was observed above 5 mm, but hardly observable at 2.5 mm. The enhancement factor was 3 at 12.5 mm when ρ=1.67. The enhancement mechanism for CN absorbance is thought to be depression on shielding in the partial pressure of oxidizing species, O, OH, and H_2O[15)] which rapidly consume CN.

From the results of the distribution of OH and CN, it was confirmed that the reducing nature of the interconal region of fuel-rich nitrous oxide–acetylene flames could be further enhanced by nitrogen shielding.

Absorbance Profile of Barium Atom in the Nitrous Oxide–Acetylene Flames as Influenced by Nitrogen Shielding. The barium absorbance in the fuel-rich nitrous oxide-acetylene flames in the presence and absence of an ionization suppressor as influenced by ρ and nitrogen shielding was studied. The results at typical ρ values are shown in Figs. 5 and 6. The addition of potassium at a concentration of 1000 μg cm^{-3} caused a shift in optimum height due to build-up of neutral atoms which were otherwise depleted through ionization. The optimum ρ value in the conventional flames was

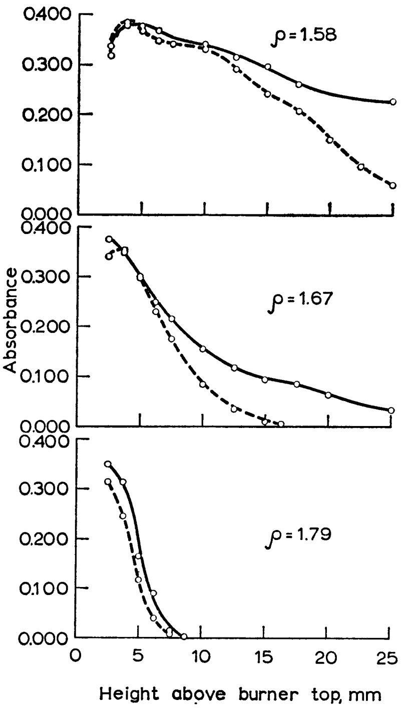

Fig. 4. Vertical distribution of CN absorbance in the N_2O-C_2H_2 flames.
----Conventional flame, ——nitrogen-shielded flame.

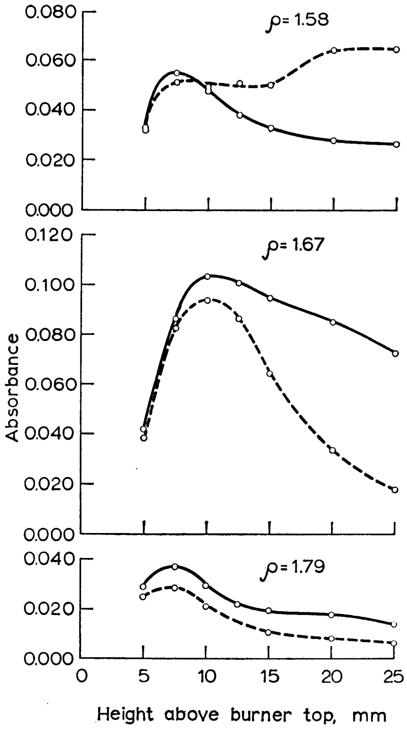

Fig. 5. Vertical absorbance profile of barium atom in the presence of an ionization suppressor in the N_2O-C_2H_2 flames.
5 μg cm^{-3} Ba+1000 μg cm^{-3} K.
----Conventional flame, ——nitrogen-shielded flame.

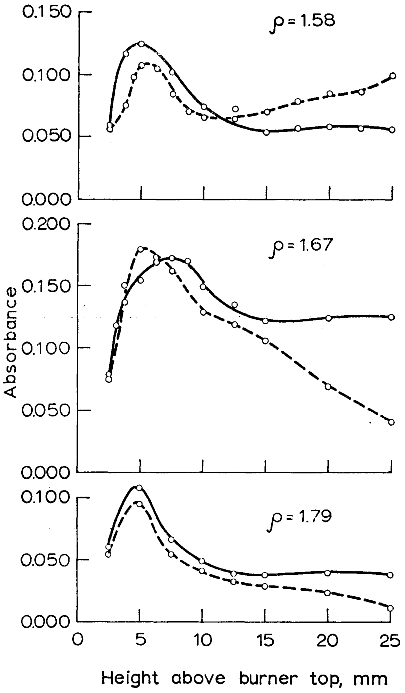

Fig. 6. Vertical absorbance profile of barium in the N_2O-C_2H_2 flames.
50 μg cm^{-3} Ba.
——Conventional flame, ——nitrogen-shielded flame.

1.66—1.67 on the ionization suppression. These results seem to differ from the published data.[6]

With the nitrogen-shielded flame of ρ 1.67, the rapid decrease of barium atom absorbance up the flame changed to show enhanced and markedly broader profiles. The optimum ρ was found to be slightly shifed to the lean side. These results suggest that free barium atoms are protected by the enhanced reducing atmosphere of the interconal zone of the shielded flames, in spite of a decrease in flame temperature on shielding reported in the literature.[16]

When the flame became extremely fuel-rich and slightly luminous with excessive carbon ($\rho=1.58$), the absorbance decreased and the vertical profile was found to be quite different from those at higher ρs. The absorbance increased again at higher positions above 12.5 mm in the conventional flame and this was found to disappear when the flame was shielded. In these flames, it was inferred that the flame temperature was too low to sufficiently atomize barium, due to deficiency of oxidant. Barium, mostly in the bound state under these conditions, may respond to changes in flame temperature rather than to the reducing nature of flames. A certain increase in temperature above the primary reaction zone between 15 and 25 mm has been reported in an unshielded fuel-rich nitrous oxide–acetylene flame while in the nitrogen-shielded counterpart, a sharp drop in temperature has been observed in the same region.[16] It is interesting to consider possible bound forms of barium in these conditions. Oxide and hydroxide cannot account for this since CaOH, having a similar energy of dissociation, 4.0±0.4 eV, to that of BaOH, 4.64±0.09 eV,[10] was suppressed according to the molecular absorption study described later. A possibility of incomplete solute vaporization due to the added potassium chloride was rejected since essentially the same phenomenon was observed in the absence of the potassium salt (Fig. 6, $\rho=1.58$). It may

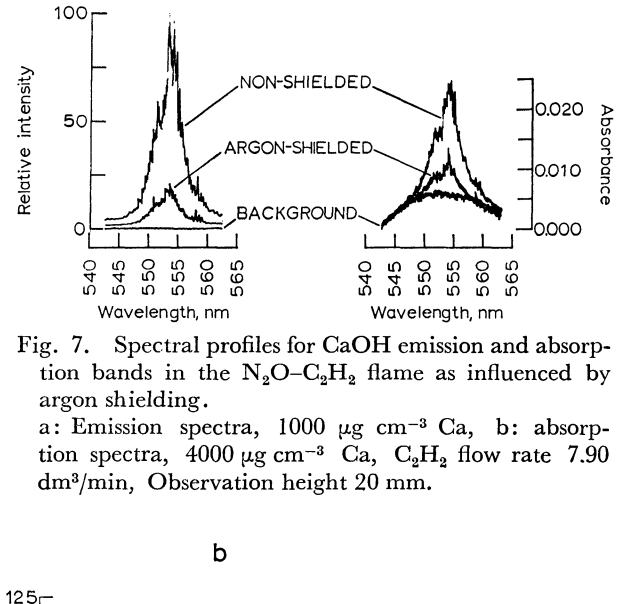

Fig. 7. Spectral profiles for CaOH emission and absorption bands in the N_2O-C_2H_2 flame as influenced by argon shielding.
a: Emission spectra, 1000 μg cm^{-3} Ca, b: absorption spectra, 4000 μg cm^{-3} Ca, C_2H_2 flow rate 7.90 dm^3/min, Observation height 20 mm.

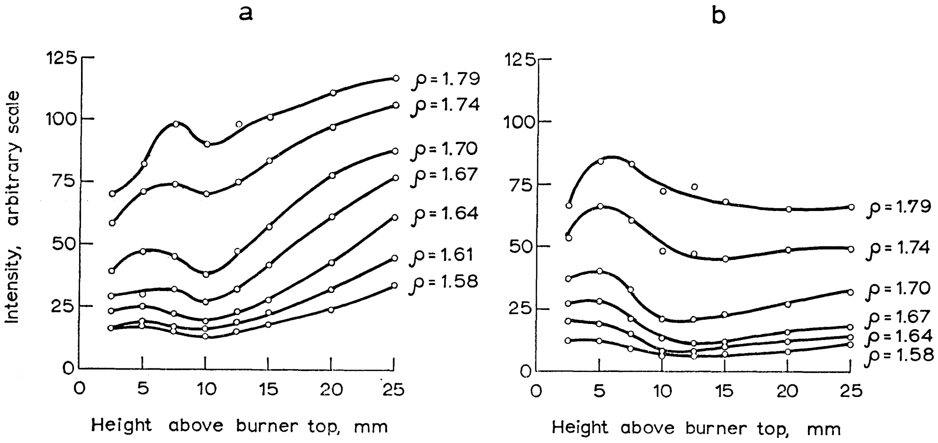

Fig. 8. Vertical distribution of CaOH emission intensity in the N_2O-C_2H_2 flames.
1000 μg cm^{-3} Ca.
a: Conventional flame, b: nitrogen-shielded flame.

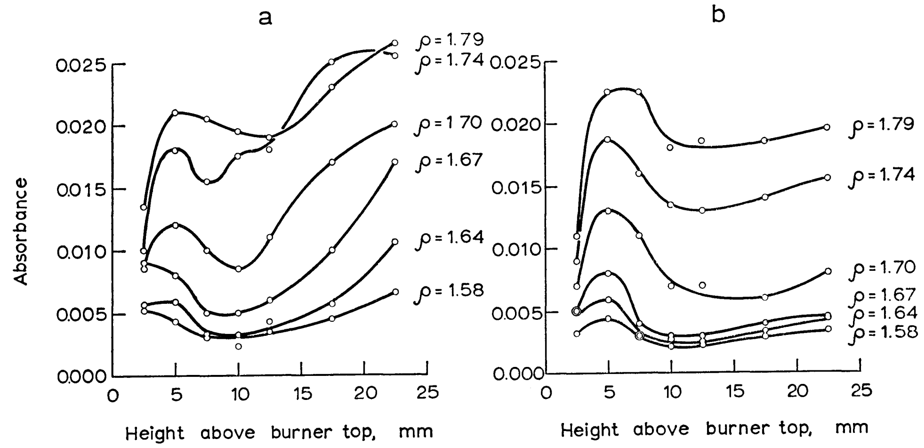

Fig. 9. Vertical distribution of CaOH absorbance in the N_2O–C_2H_2 flames. 4000 μg cm^{-3} Ca.
a: Conventional flame, b: nitrogen-shielded flame.

be inferred that carbon-containing barium compounds[6] are responsible for this phenomenon.

Distribution of CaOH in the Nitrous Oxide-Acetylene Flames as Influenced by Nitrogen Shielding. Vertical Profile of CaOH Emission Band: The emission band spectra of the CaOH green band in the fuel-rich nitrous oxide-acetylene flames as influenced by argon shielding are shown in Fig. 7a. The emission lines near 560 nm having been observed[1] were identified as the seven calcium atom lines lying between 558.2 and 560.3 nm the occurrence of which has been described in arc and spark;[18] this was proved by their distribution in flames and response to flame conditions.

As shown in Fig. 8a, the emission intensity of CaOH in the flames was gradually decreased when ρ was lowered. A small maximum between 5 and 7.5 mm and a minimum around 10 mm above the burner top was observed and the intensity was observed to remarkably increase further up the non-shielded flame. By shielding the flame with nitrogen, the CaOH emission was generally reduced, especially beyond 10 mm in height (Fig. 8b).

CaOH Absorbance Profile as Influenced by Flame Shielding: The suppressing effect of argon shielding on the CaOH absorption band in the flame is shown in Fig. 7b.

As shown in Fig. 9, the absorbance signal decreased as ρ was lowered. However, on shielding the flames, the absorbance was remarkably reduced further beyond 10 mm while being unchanged at 5 mm.

It may be concluded that the background absorption and noise effect due to calcium may be minimized by employing a moderate ρ value, *i.e.*, 1.67 required for maximum barium atom absorbance in the nitrogen-shielded flame.

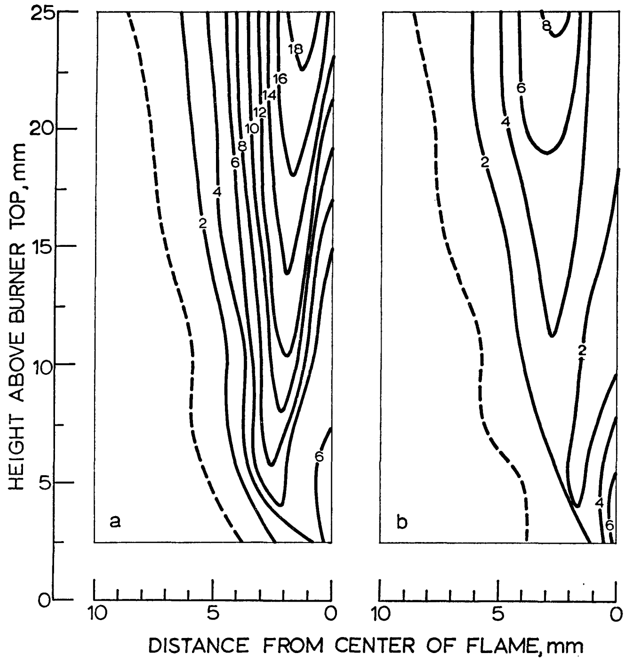

Fig. 10. Spatial distribution of CaOH emission intensity in the N_2O–C_2H_2 flames of ρ 1.67.
a: Conventional flame, b: nitrogen-shielded flame.
----Boundary of CaOH emission.
Figures on contour lines represent intensity in arbitrary unit.

Spatial Distribution of CaOH Emission Intensity: The distribution of CaOH emission intensity in the transverse section of the flames of ρ 1.67 was studied to investigate the occurrence of CaOH with respect to flame structure. The results are shown in Fig. 10. In the outer mantle of the conventional flame, a large build-up of the CaOH emission intensity was found up the flame (Fig. 10a). The central part of the flame up to 15 mm of weaker intensity was observed to correspond to a space inside the red feather, or the interconal zone. A small island-like region of strong CaOH emission was observed near the primary reaction zone. In the shielded flame, the emission band was suppressed throughout the flame, with the central part of weaker intensity being enlarged (Fig. 10b). The whole pattern of spatial distribution of the CaOH emission band may be compared with that of OH (Fig. 2).

These results suggest that CaOH, produced in the primary reaction zone, is markedly subjected to depopulation in the interconal zone of the nitrogen-shielded nitrous oxide-acetylene flames. This may be due to reactions with carbon-containing species, *i.e.*, C_2, CH, *etc.*, as well as the suppression of oxidizing species, *i.e.*, O, OH, and H_2O.

Effect of Nitrogen Shielding on the Background Absorption and Signal-to-Noise Ratio in the Barium Absorbance Signal in the Presence of Calcium. For the purpose of determining barium in the absence of calcium, an accord in conditions of the flame stoichiometry and height for maximum barium atom absorbance and those for minimum CaOH absorbance and emission intensity, is favorable. This may be due to the similarity in dissociation energies of the monoxide and hydroxide of barium and calcium.

TABLE 1. THE EFFECT OF NITROGEN SHIELDING ON BARIUM ATOM ABSORBANCE AT 553.6 nm IN THE PRESENCE OF CALCIUM OF VARIOUS CONCENTRATIONS IN THE NITROUS OXIDE–ACETYLENE FLAME

Calcium concn (μg/ml)	Conventional flame		N_2-shielded flame	
	Absorbance	Rel. S/N	Absorbance	Rel. S/N
0	0.073	1.00	0.147	1.00
500	0.079	0.84	0.132	0.90
1000	0.091	0.66	0.126	0.83
5000	0.102	0.30	0.143	0.82

10 μg cm^{-3} Ba+1000 μg cm^{-3} K. Observation height 17 mm.

The background absorption and relative S/N ratio in the presence of different concentrations of calcium were measured employing optimum flame stoichiometry, ρ 1.67, and the results are shown in Table 1. A height of 17 mm above the burner top was adopted for the purpose of comparison with previous work.[1] Using the nitrogen-shielded flame, the background absorbance due to calcium was substantially eliminated and the relative S/N ratio was found to be little affected by calcium in various concentration levels. This effect was also proved at an optimum height for the practical determination. As shown in Fig. 11, the interfering effects of calcium at concentrations of 2000 μg cm^{-3} were essentially eliminated.

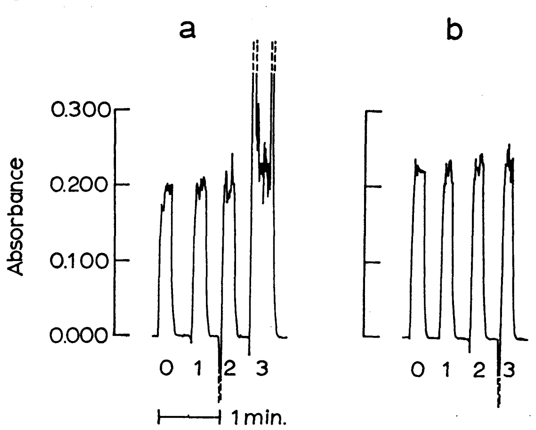

Fig. 11. Effect of nitrogen shielding on barium atom absorbance in the presence of calcium.
a: Conventional flame, b: nitrogen-shielded flame. Ca concn 0: None, 1: 500, 2: 1000, 3: 2000 μg cm^{-3}. 10 μg cm^{-3} Ba+1000 μg cm^{-3} K. Observation height 10 mm.

Conclusion

The nitrogen shielding of a fuel-rich nitrous oxide-acetylene flame remarkably reduced the spectral interference and the noise effect of calcium on the barium determination by atomic absorption spectroscopy. Spectroscopically, this was shown to be due to the suppression of CaOH radical formation by the enhanced reducing nature of the flame of an optimum oxidant-to-fuel flow ratio for maximum barium atom absorbance. By using this technique, the chemical separation of barium from calcium will be unnecessary or, at least, the time and tedious labor for perfect removal of calcium will be saved in the analysis of biological and geological materials of high calcium contents.

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