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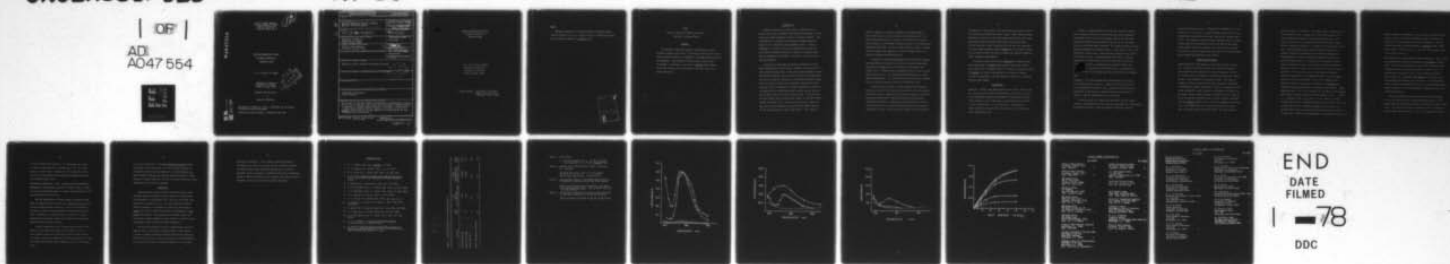
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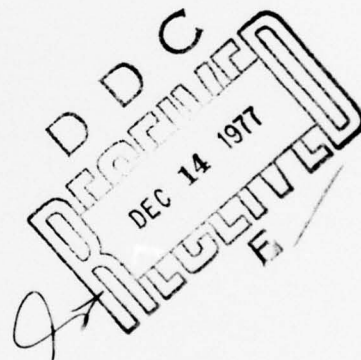
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MOLECULAR ABSORPTION SPECTRA
OF COMPLEX MATRICES IN
PREMIXED FLAMES

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BRIEF

Nonatomic absorption in premixed flames by untreated complex matrices (blood, milk, etc.) is shown to be low in magnitude and due only to molecular spectra of inorganic salts.

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Molecular Absorption Spectra of Complex Matrices in Premixed Flames

ABSTRACT

The question of molecular spectral interferences by undissociated inorganic matrix salts is inevitably raised when the direct atomic absorption analysis of digested or untreated complex materials is considered. Data presented in these studies indicate that the problem is not nearly as serious for premixed flame systems as has been reported for electro-thermal and total consumption burner atomization.

INTRODUCTION

Nonatomic absorption by matrix species represents one of the most severe and troublesome interferences encountered in direct trace level atomic absorption analysis of complex materials. This interference is correctable by techniques reviewed recently by Zander (1) if it does not exceed reasonable limits. However, Fernandez (2) and Culver (3,4) have indicated that the ability of correction schemes to handle this problem in flameless atomizers is exceeded by some samples if the matrix is not first oxidized by digestion.

Culver (4) has discussed the relative contribution to non-atomic absorbance of "smoke signals" caused by solid carbon scattering centers present early in the time variant atomization process when volatile elements such as arsenic and mercury are determined directly by carbon rod atomization of untreated biological samples. Culver and Surles (3) have also identified a heavily pronounced molecular spectral component of nonatomic absorption in carbon rod atomization due to undissociated matrix species such as diatomic and triatomic alkali and alkaline earth halides. These inorganic molecular spectra persist during later stages of transient electrothermal atomization (5) to interfere with the atomic spectra of many less volatile elements that would normally appear resolved in time from the earlier organic "smoke peak". This molecular

spectral component of nonatomic absorption was demonstrated by Culver and Surles (3) to be as high as 0.6 absorbance units in a carbon rod analyzer for as little as 5 microliters of 0.1% sodium chloride matrix. More complex matrices can easily drive the spurious absorbance much higher to a point where correction schemes no longer function properly (2), especially if the net readout scale is expanded for maximum analyte sensitivity.

In addition to the above mentioned carbon rod analyzer studies, data concerning the molecular band nature of nonatomic absorbance encountered in flame systems was presented by Koirtyohann and Pickett (6,7). A Beckman total consumption burner was used to spray sample and burn an $O_2 - H_2$ flame contained horizontally by a long path absorption tube. A 1% solution of sodium chloride was reported to give a spurious signal as high as 0.6 absorbance units.

A recent review by Zander (1) again presented the above mentioned data of Culver (3) along with the earlier data of Koirtyohann and Pickett (6) as a comparison of the relative amount of nonatomic absorbance encountered in flame and nonflame (electro-thermal) atomization techniques. Although the article presented a correct and thorough review of nonatomic absorption effects and correction techniques, the work of Koirtyohann and Pickett (6) was referenced

as appearing in 1975 instead of the actual publication year of 1965. The review also portrayed the data as simply "flame" spectra without mentioning or pointing out the specialized nature of the older total consumption, tubular enclosed flame system, leaving the reader with the incorrect overall impression that the data were generated on a more commonly employed modern premixed 10 cm slot burner system such as those currently available in present day standard commercial atomic absorption spectrometers.

In order to clarify the relative magnitude of nonatomic absorbance encountered in premixed flame systems, the present investigation deals with the characterization of molecular absorption spectra in premixed slot burner flame systems for a variety of complex clinical, environmental, and food samples in addition to individual inorganic salt spectra.

EXPERIMENTAL

Apparatus. Studies with samples below 5% salt content were carried out utilizing a Varian Techtron (Springvale, Vic., Australia) AA-5 single beam atomic absorption spectrometer including the standard Varian nebulizer with an added small volume sampling cone similar to that of Manning (8). A 10 cm Varian air - acetylene slot burner and Hewlett Packard (Palo Alto, Calif.) model 17501A strip chart recorder were used.

Studies on samples between 5% and 50% salt and solids content were carried out utilizing a second single beam atomic absorption spectrometer fitted with the flow through, high solids nebulizer recently developed for spectrochemical analysis by Fry and Denton (9) utilizing the Babington principle. This system included an Instrumentation Laboratories (Lexington, Mass.) "High Solids" 0.81 X 5 cm single slot nitrous oxide - acetylene burner head and a high solids 10 cm single slot air - acetylene burner head similar in design (except for the wider 0.81 mm X 10 cm "high solids" slot) to the 0.51 mm X 10 cm slot air acetylene Varian Techtron burner head. Varian Techtron and Jarrell Ash (Waltham, Mass.) H_2 continuum and neon filled hollow cathode lamps were utilized for all measurements.

Procedure. The hollow cathode lamps were operated at 15 ma and 5 ma respectively for H_2 and Cd. "Zero" and "100 %T" were reset at each wavelength utilized in the H_2 continuum for point by point assessments of the molecular absorption spectrum of each matrix studied. Spectral bandwidths of 0.6 nm were used.

To avoid burner slot clogging and gumming by the more complex clinical, environmental, and food matrices, measurements on these samples were made by the small volume cone method of nebulizer sampling

discussed by Sebastiani et.al. (10), Berndt and Jackwerth (11), and Manning (8). 0.2 mL and 1 mL sample volumes were utilized for the standard premix nebulizer and the new "high solids" systems respectively. This procedure yields transient recorder signals of concentration sensitivity and precision similar to that of the steady state response normally encountered with larger sampling volumes. All other less complex samples were aspirated until a normal steady state response was perceived at the readout.

RESULTS AND DISCUSSION

Premixed Molecular Flame Spectra of Polyatomic Inorganic Species.

Fig. 1 presents the earlier reported (1) review data (redrawn) of the molecular NaCl spectrum for carbon rod analyzer (curve a) and "flame" (curve b) atomization (redrawn) along with the "flame" (curve c) data observed in the present studies. The large discrepancy in the two "flame" curves arises from gross differences in the method of sample introduction. Curve b was generated on the "total consumption" tubular system of Koirtzmann and Pickett (6). The median aerosol droplet diameter introduced for such systems is 28 μm (12) whereas the median aerosol droplet diameter introduced into the premixed systems (Fig.1, curve C) is reported to be 8.6 μm (13). Since desolvation will be greatly delayed (14) for the total consumption burner (considering the ~ 3X larger starting

droplet diameter and therefore $\sim 27 \times$ larger droplet volume) and the tube temperature lower in comparison to the premixed system, the entire atomization sequence including droplet desolvation, salt crystal vaporization, and dissociation of molecular matrix species cannot be expected to be nearly as complete in the analytical viewing zone. Further droplets much larger (but normally rejected in a premixed system) than the median would enhance the presence of undissociated salt species further when viewed horizontally in a total consumption system. The tubular total consumption system should be expected to result in more heavily pronounced molecular spectra if the matrix salts are at all difficult to vaporize and/or dissociate. This (as well as the $4 \times$ path length difference) appears to account for the differences observed for the molecular spectra in the two flame systems. Fig. 2 gives expanded scale molecular spectra of CaCl_2 , NaCl , and MgSO_4 in the premixed air-acetylene flame for the purpose of wavelength identification. MgSO_4 decomposes above 1124°C which accounts for the absence of any measurable molecular spectrum (even at 20% salt content) in the 2250°C air - acetylene flame. CaCl_2 (mp 772°C , bp $> 1600^\circ\text{C}$) and NaCl (mp 801°C , bp 1413°C) produce wavelength maxima at 225 nm and 234 nm respectively which are in general agreement with the carbon rod analyzer data of Culver and Surles (3) and the calculations (NaCl) of Herzberg (15). Molecular band absorbance by undissociated matrix salts

therefore appears to predominate over scattering in premixed flame systems (as well as in total consumption systems and carbon rod analyzers) as the major cause of nonatomic absorbance. The magnitude of observed spurious absorbance in premixed flames is however actually $\sim 150 \times$ less (Fig. 1) than the "flame" spectra given in the earlier review (1).

Premixed Molecular Flame Spectra of Complex Materials. Fig. 3 gives the expanded scale molecular band spectra of untreated sea water, urine, whole blood, evaporated milk concentrate, and tomato sauce introduced directly (high solids system) as aerosols into a 10 cm premixed air-acetylene flame. It can be seen that samples (milk, blood, etc.) approaching 50% organic solids content give no measurable spectrum above the noise level. In sharp contrast to the electro-thermal atomization case (4), organic species appear readily degraded in the flame producing no measurable scattering or molecular spectra.

Only those samples with appreciable inorganic salt content such as sea water and urine produced measurable spectra in premixed flames (although greatly reduced in comparison to other atomizers). The spectra of urine and sea water of Fig. 3 compare well with the NaCl spectrum of Fig. 2. This is as expected since NaCl

is the principle dissolved salt ($\sim 1\%$ in sea water and $\sim 0.6\%$ in urine) in these matrices. The spectrum of KCl (3) is very similar to that of NaCl. Presence of KCl in addition to NaCl accounts for the slightly more pronounced absorbance than would be warranted by NaCl alone.

Concentration Dependence. Fig.4 demonstrates the concentration dependence of the molecular spectrum of triatomic CaCl_2 . A Beer's law type of relationship appears to govern the system below a solution concentration of $15\% \text{CaCl}_2$.

The high temperature environment present in premixed flames seems to suppress molecular spectra to a greater extent than cooler flames and electro-thermal atomizers, but this must ultimately be judged in terms of the predominance of atomic spectra as well. Table 1 therefore lists data pertaining to the ratio (line-to-background) of the atomic analyte (Cd) spectrum to the molecular matrix spectrum of sodium chloride.

The table demonstrates that, although electro-thermal atomization is analytically far more sensitive (owing to its reduced internal volume and reduced gas dilution of atomic vapor) as a sample introduction technique than aerosol generation, it does not dissociate polyatomic matrix species as well as the premixed flame.

It was also found that all untreated naturally occurring samples (sea water, urine, whole blood, milk, etc.) tested produced no measurable molecular spectra whatsoever in the premixed $N_2O-C_2H_2$ flame, thereby minimizing the need for correction schemes in those analyses of complex materials for which the atomic absorption analyte sensitivity in this flame is adequate.

CONCLUSIONS

Premixed flames exhibit molecular band spectra due to undissociated inorganic polyatomic species, however the predominance of such spectra is approximately 150 X less than the "flame" data reported in a recent review (1). In sharp contrast to electro-thermal atomization, no scattering or molecular spectra due to organic solids (up to 50% solids content) was detectable in pre-mixed flame systems. The spectra due to inorganic species are also greatly reduced compared to those reported in long path total consumption systems and electro-thermal atomization.

The fact that abnormally high salt concentrations had to be employed with a "high solids" premixed system in these studies in order to produce a molecular spectrum sufficiently pronounced (above the noise limit) to study, indicates that this interference is not nearly as serious for premixed flames as it is for other

atomization techniques. Actual samples (even though complex) are generally of lower salt content and can be directly analyzed by premixed flame atomic absorption spectroscopy with small or negligible levels of spectral interference that (even if pronounced enough to require correction) do not overwhelm the readout as would frequently be the case with electro-thermal techniques.

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Table 1. Line:Background Ratio in Several Atomizers.

Atomizer	Path (cm)	Cd Line (L) Atomic Absorbance/ppm	NaCl Background (B) Absorbance/% NaCl	(L/B) Ratio
Premixed $N_2O-C_2H_2$	5	0.06	0.00042	143.0
Premixed Air- C_2H_2	10	0.30	0.0035	84.7
Carbon rod (4)	1	147.	6.0	24.4
Total consumption system (6)	40	3.5	0.6	5.8

Figure 1. NaCl Spectra.

- a. 0.1% NaCl, carbon rod; b. 1% NaCl, long path total consumption; c. 5% NaCl, premixed flame.

Figure 2. Expanded Scale (10X) Molecular Spectra in Premixed Air - Acetylene.

20% MgSO_4 below noise limit at all wavelengths.

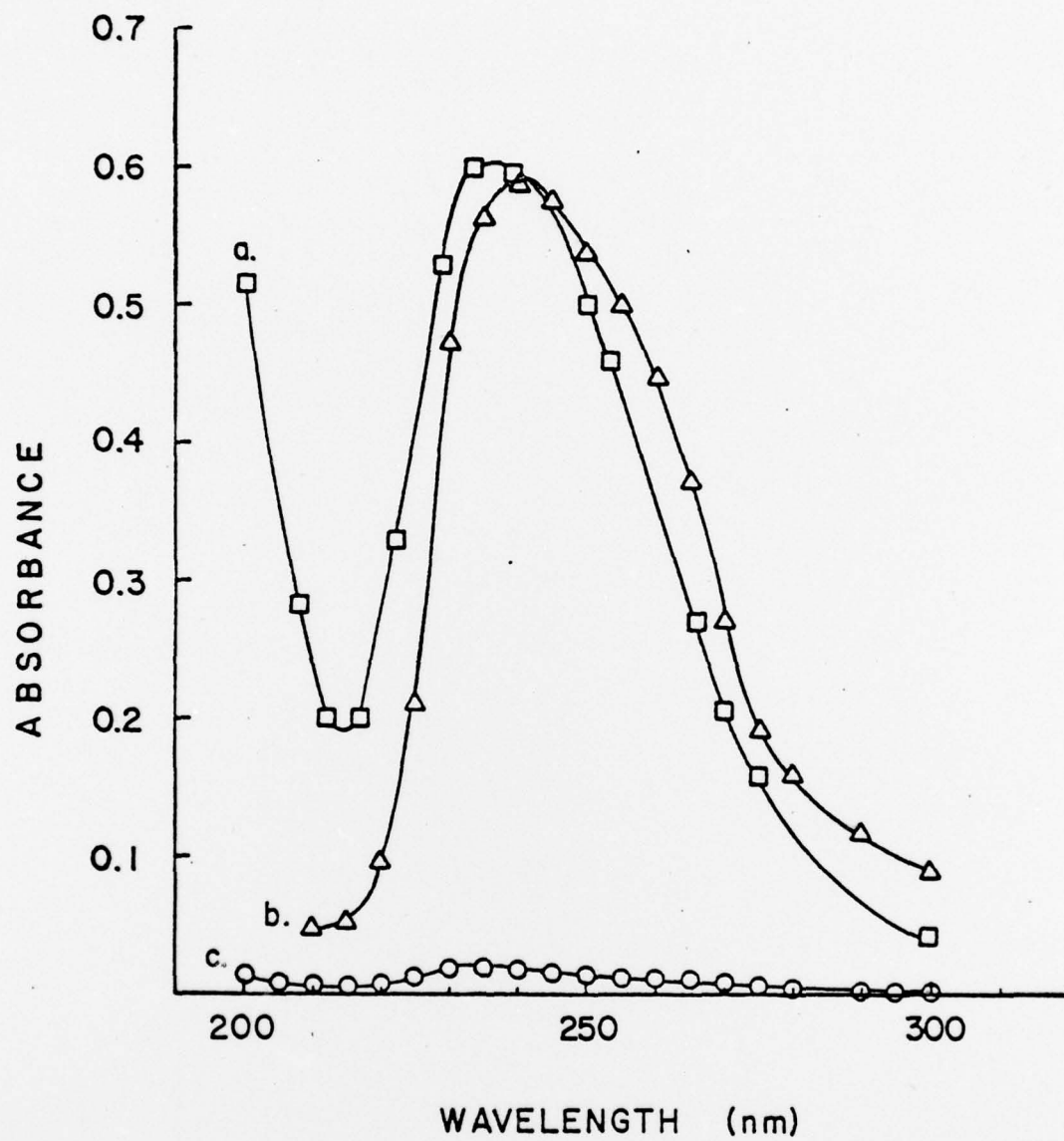
□ 5% CaCl_2 ; ○ 5% NaCl; -- Noise limit.

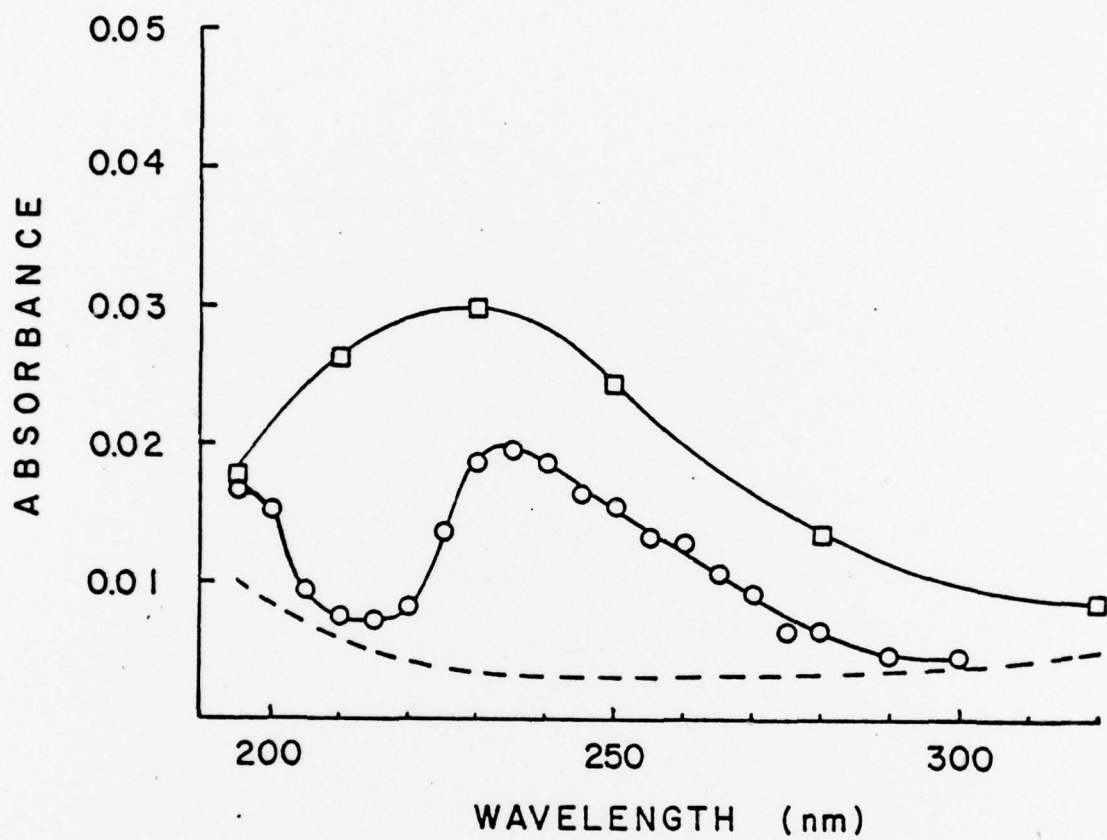
Figure 3. Expanded Scale Spectra of Untreated Complex Materials in Premixed Air-Acetylene Using High Solids System.

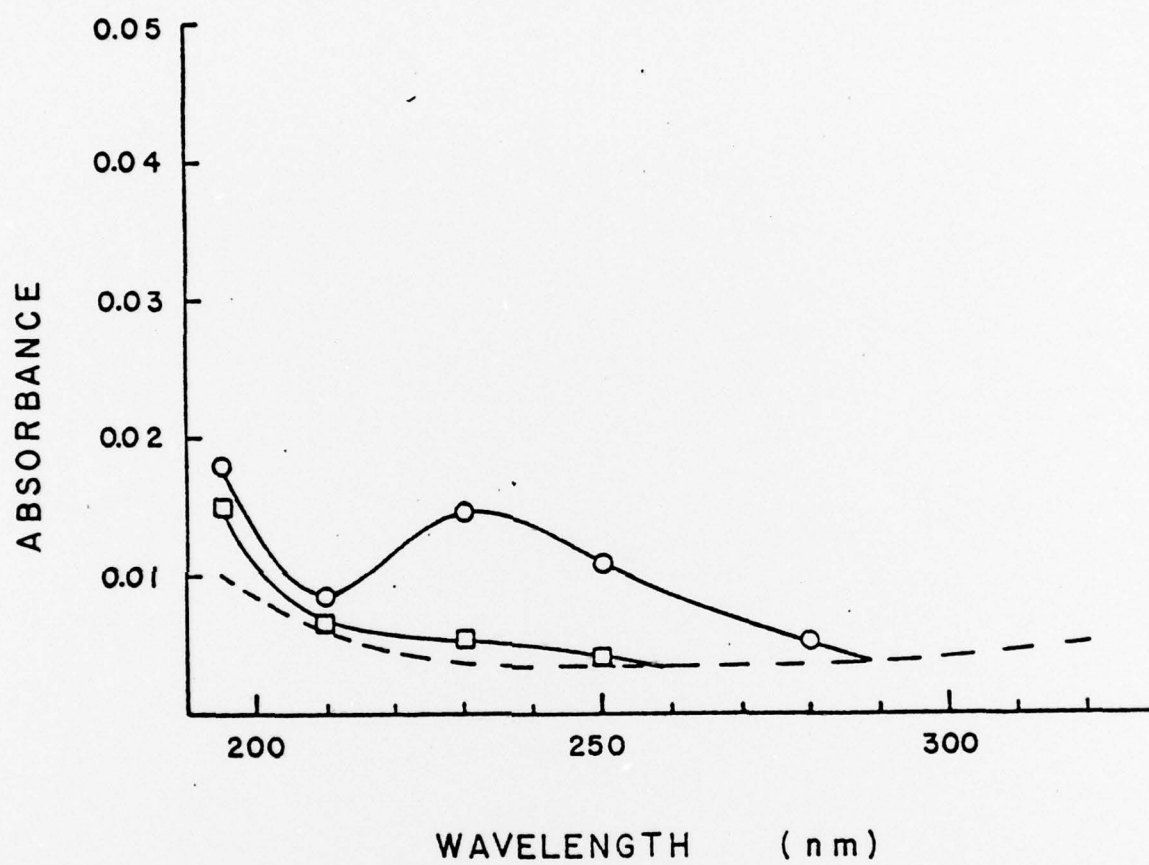
Whole blood, evaporated milk concentrate, and tomato sauce all below noise limit! ○ Sea water; □ Urine; -- Noise limit.

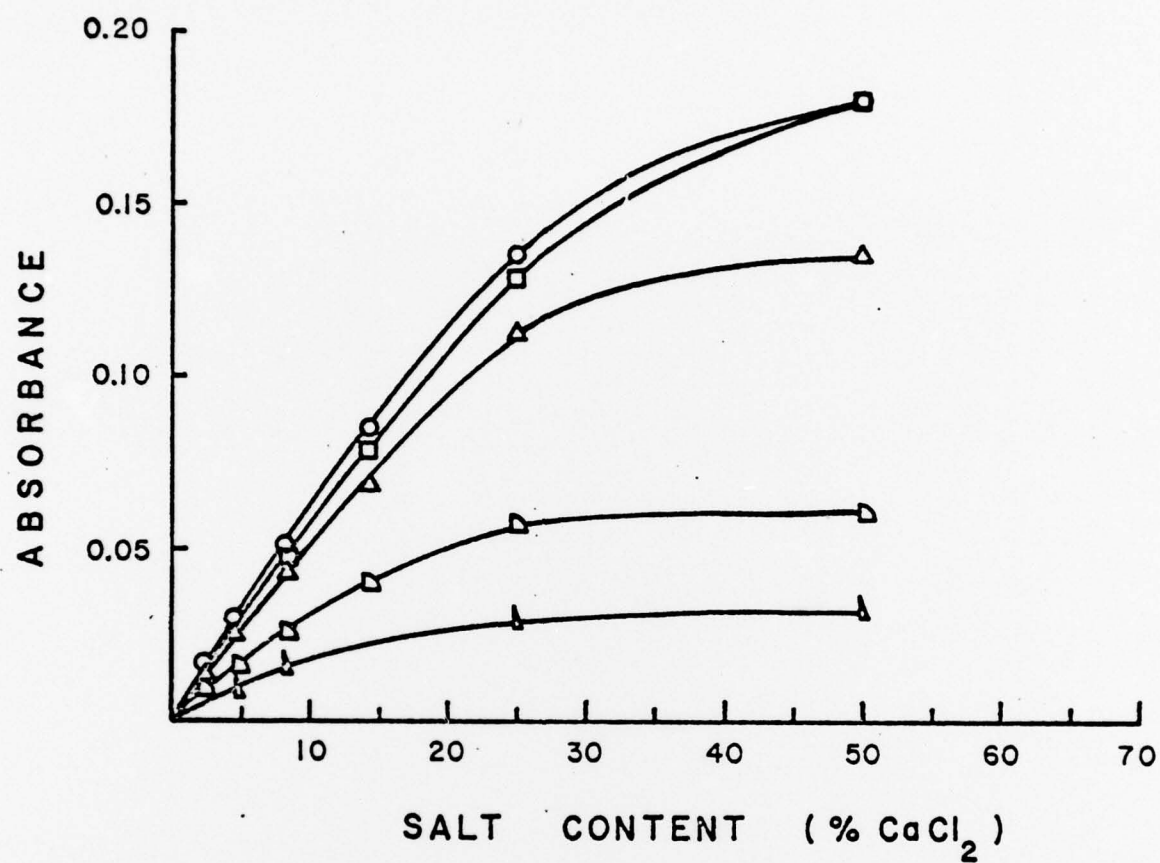
Figure 4. Concentration Dependence of Triatomic CaCl_2 Absorbance in Premixed Air-Acetylene Using High Solids System.

□ 210 nm; ○ 230 nm; △ 250 nm; ▢ 280 nm; ▵ 320 nm.









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