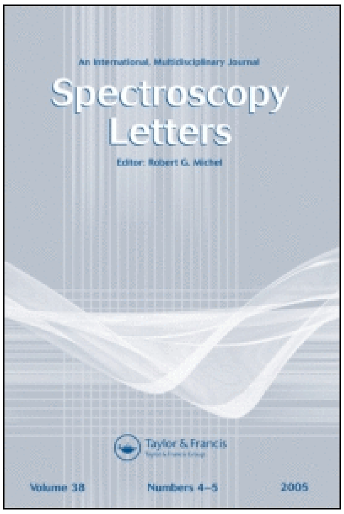

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Discrete Nebulization for Sample Introduction of High Salt Solutions in Flame Atomic Absorption Spectrometry

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DISCRETE NEBULIZATION FOR SAMPLE INTRODUCTION OF HIGH SALT SOLUTIONS IN FLAME ATOMIC ABSORPTION SPECTROMETRY

Keywords: Discrete Nebulization, Sample Introduction, Salt Solutions, Copper, Flame Atomic Absorption Spectrometry

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ABSTRACT

The detection of copper in high salt solutions using flame atomic absorption spectrometry with discrete nebulization of microliter volumes compared to conventional continuous nebulization for sample introduction was investigated. Using continuous nebulization, a decrease in absorbance signal and uptake rate with increasing salt concentration, a detection limit of 0.02 µg/mL for copper, and precision deteriorating with increasing salt concentration in the 1-3% range was found. Discrete nebulization showed similar trends with decreasing absorbance signal with increasing salt concentration, but had the advantage that the microliter volumes used prevented clogging of the burner. At low microliter volumes and high salt concentrations, the precision deteriorated to around 10% and detection limit to 0.3 µg/mL. The technique was rapid, simple and did not produce memory effects.

1. INTRODUCTION

Sample introduction approaches for atomic spectroscopy have been reviewed by Browner and Boorn[1] and Sneddon.[2] They concluded that the type of sample introduction technique used will depend on a number of interrelated variables including the physical state of the sample (solid, high dissolved solid solution, liquid, gas or mixture), amount of sample available, required analytical performance (accuracy, precision and level of analyte to be determined), and available atomic spectroscopic technique. Flame atomic absorption spectrometry (FAAS) with sample introduction by conventional pneumatic nebulization is still the most widely used atomic spectroscopic technique for quantitative trace metal determination despite the poor transport efficiency (2-10%), minimum volume of 0.5 mL required (due to uptake rate), some memory effects, and clogging of the system, particularly with high dissolved solid solutions which is potentially hazardous. The use of discrete or pulse nebulization for sample introduction has been investigated and reviewed by several workers.[3-6] Typical volumes of 0.2 mL were found to be optimum and were injected and aspirated for FAAS[3,4] or flame atomic fluorescence spectrometry.[5] Routh et al[7] investigated inductively coupled plasma-atomic emission spectrometry nebulization techniques for the analysis of microsamples.

In this paper we report the results of discrete nebulization versus conventional nebulization for sample introduction of high salt concentrations in the detection of copper by FAAS.

2. EXPERIMENTAL

2.1 Instrumentation

A Perkin Elmer, model 2380, FAAS equipped with deuterium arc background correction, conventional pneumatic nebulization sample introduction, and air-acetylene flame (40/20 ratio) was used. An American Scientific Laboratory copper hollow cathode lamp, operated at 18 mA and a wavelength of 324.7 nm was used. Signals were recorded digitally and on a Linear, model 0555-000, chart recorder.

2.2 Reagents

Deionized-distilled water was used in the preparation of all solutions. Serial dilution of 1000 µg/mL copper and 25% sodium chloride was prepared as required. All solutions were prepared with "Baker Analyzed" reagents.

2.3 Procedure

Cresser[5] has reviewed the systems used for discrete nebulization including injection into flowing liquid streams, free-falling droplet systems, and pipet-based systems. In this study, a similar arrangement as reported by Thompson and Godden[3] was used by inserting a shortened disposable pipet tip into the end of nebulizer uptake tube such that a tight fit existed. Volumes up to 400 µL could then be injected into this arrangement using a manual pipet. This arrangement was easily changed to prevent contamination. The uptake rate of the conventional nebulizer was measured by determining the volume/minute that the pneumatic nebulizer pulled into the flame with continuous sample aspiration and was the mean of at least three trials.[8] For discrete nebulization, peak height measurements were used. Peak area measurements were less precise. Results were the mean of at least three and in most cases ten trials. Background correction was used in this study.

3. RESULTS AND DISCUSSION

3.1 Conventional Pneumatic Nebulization

In this study, a constant concentration of 5.0 µg/mL of copper and salt concentrations in the 0-20% range were used.

3.1a

Absorbance Signal

The absorbance signal decreased with increasing salt concentration as shown in Figure 1. The maximum salt concentration used was 20% and showed a 60% drop in absorbance signal compared to a solution with 0% salt. Salt concentrations up to 4-5% did not significantly change the absorbance signal (at 5% salt concentration a drop of 8% in absorbance signal).

3.1b

Uptake Rate

The uptake rate decreased from 6.2 ml/min. at 0% to 2.4 ml/min. at 20% salt concentrations as shown in Figure 1.

3.1c

Analytical Figures of Merit

The detection limit (signal-to-noise ratio of 3) was 0.020 µg/mL at 0% and 0.044 µg/mL at 20% salt concentrations. Linearity of calibration extended to 1 to 2 orders of magnitude above the detection limit. Precision varied from under 1.0% at 0% to between 3-4% at 20% salt concentrations. The major concern was that at high salt concentrations the system would rapidly clog–creating potentially hazardous situations, causing memory effects, give spurious signals and need regular cleaning by flushing for many minutes with deionized water.

3.2 Discrete Nebulization of Microliter Volumes

3.2a

Absorbance Signal

The absorbance signal decreased in a similar manner as conventional nebulization with increasing salt concentration and is shown in Table 1 for several different microliter volumes.

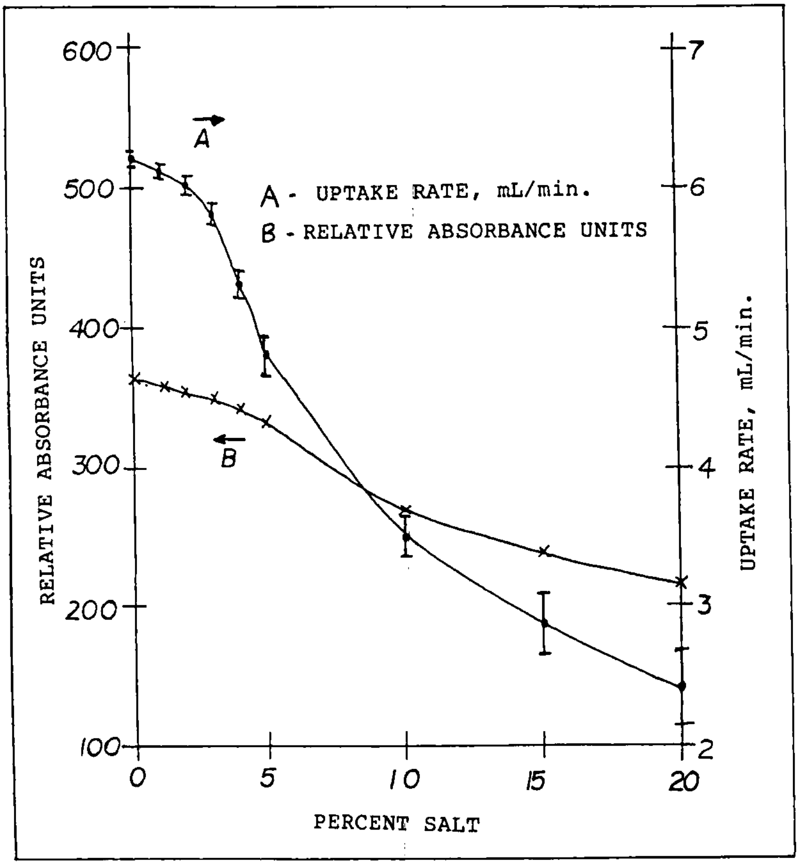

Figure 1. Effect of increasing salt concentration with constant copper concentration of 5 µg/mL on uptake rate and absorbance signal with conventional nebulization.

3.2b Volumes

A maximum volume of 400 µL and minimum volume of 10 µL was used in this study. The signals from volumes ≥ 100 µL were comparable to conventional nebulization. At volumes < 100 µL the signal was less compared to conventional nebulization, with the lowest volume of 10 µL giving a signal about six times lower.

Table 1

Effect of Increasing Salt Concentration and Decreasing Volume on Absorbance Signal and Selected Precision Values from 5.0 μg/mL of Copper

Volume μL	Salt Concentration % 0	2	4	10
400	280	-	-	
200	275 (2.0%)	-	251	255
150	-	-	-	255
140	269 (1.9%)	263	251	250
100	256	230	222	201
85	231	212	205 (4.9%)	183
75	211	191	190	169
70	195	187	180	162
50	169 (2.6%)	158 (2.1%)	158	149 (8.9%)
25	108 (2.8%)	118	103	86
10	45	50	38 (12.3%)	32 (10.9%)

Relative Absorbance Signal
(Precision in Brackets)

3.2c Analytical Figures of Merit

The detection limit (signal-to-noise ratio of 3) for 10 μL volumes was 0.2 μg/mL in 0% and about 0.3 μg/mL in 10% salt solution. The higher the salt concentration, the poorer the detection limit. Linearity was 1 to 2 orders of magnitude above the detection limit and is shown in Figure 2 for four different salt concentrations for 100 μL volumes. As noted previously, the higher the salt concentration the lower the signal. However, the higher salt concentration extends the upper concentration range. At 0% salt, there was some curvature in the calibration curve at high concentrations. Accuracy was assessed by determining two laboratory control standards (LCS) of copper concentration 0.4 and 0.8 μg/mL in a known salt concentration. The results

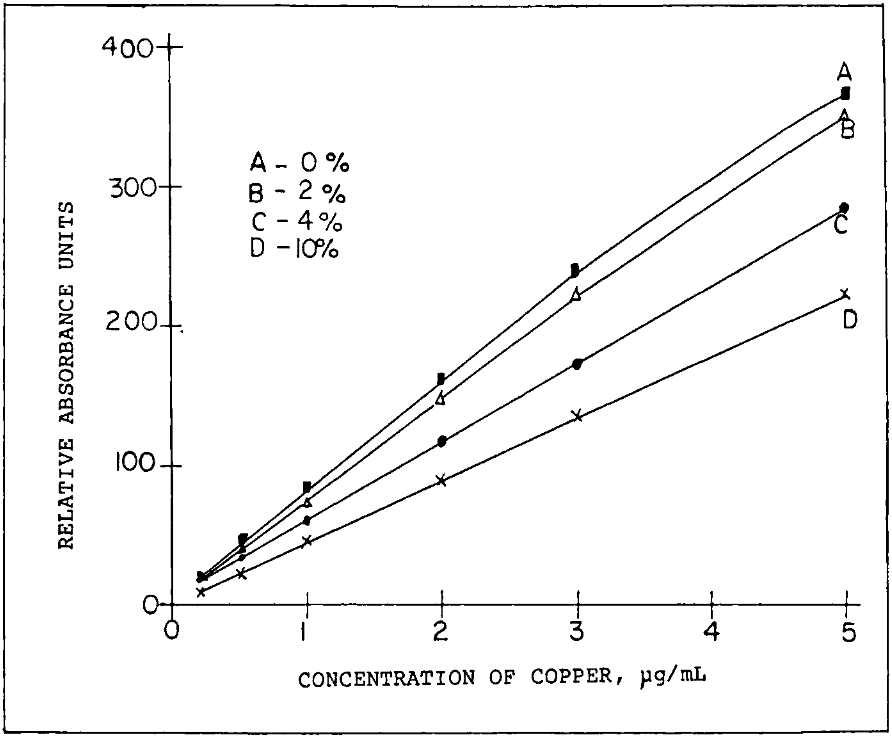

Figure 2. Effect of increasing salt concentration on copper calibration curves using discrete nebulization volumes of 100 µL.

are also shown in Figure 2, and while more diverse methods are required to fully characterize the accuracy, preliminary results were satisfactory. Selected precision values for peak height measurements are shown in brackets in Table 1 for several volumes and several different salt concentrations. In general, low volumes (≤ 50 µL) and high salt concentrations gave poor precision values (~10%). Peak shape for 100 µL volumes of 5.0 µg/mL of copper with different salt concentrations are shown in Figure 3. As noted previously, peak height will decrease with increasing salt concentration but at a given salt concentration, the precision is

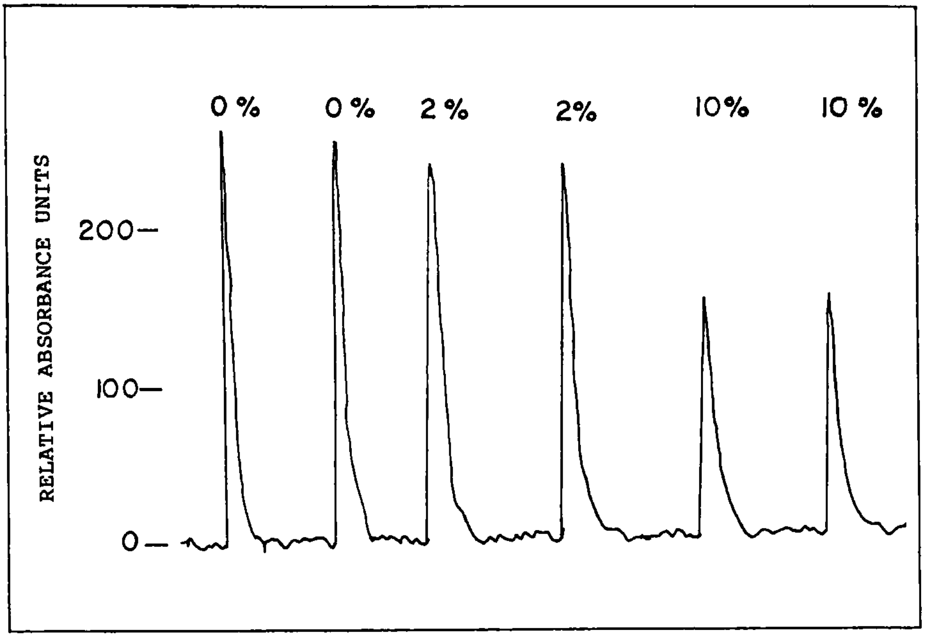

Figure 3. Effect of increasing salt concentration using a volume of 100 µL and constant copper concentration of 5.0 µg/mL on peak shape.

acceptable for many analyses. The peaks were sharp, gave no memory effect or tailing and were recorded almost instantaneously (< 1 second) from injection into the discrete nebulizer system. Some variation in peak shape was noted and was attributed to operator or manual dependence which could be eliminated with an automatic system.

3. CONCLUSION

This preliminary study has shown the potential of discrete nebulization of high salt solutions for flame atomic absorption spectrometry. Compared to the continuous nebulization, discrete nebulization is equally simple and rapid, prevents clogging of the burner by high salt solutions and gives acceptable precision. The signal is reduced with increasing salt concentration, but remains constant, and if standards contained salt concentrations would prevent no serious problems in accuracy in an analysis. The simple arrangement gave no dead volume and allowed the use of volumes of as low as 10 µL to be used. At low volumes, discrete nebulization gives a poorer detection limit of about an order of magnitude compared to continuous nebulization. Nevertheless, it has some merit, particularly for metal determination in the µg/mL levels of high salt solutions where limited sample volume is available. The application of the technique in clinical and biological samples is currently under investigation and will be in due course.

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