Turk J Chem
26 (2002) , 263 – 270.

Determination of Zinc in Aerosol Samples by Discrete Nebulization Flame Atomic Absorption Spectrometry

Deniz Yurtsever SARICA*
TÜBİTAK/ATAL, Besevler, 06530 Ankara-TURKEY
e-mail: dsarica@tubitak.gov.tr
Dilek AKIM
Double Major Senior Student at Chemistry Dept, METU Ankara-TURKEY
Tuncel ÖZDEN
TÜBİTAK/ATAL, Besevler, 06530 Ankara-TURKEY

Received 12.04.2001

A well-known analytical method, "discrete nebulization", which is suitable for samples having a limited amount like body fluids, high solid content or salt solutions, and less volatile metals, has been further developed for zinc determination in aerosol samples.

The effects of injection volume and nebulizer aspiration rate on absorbance and precision were studied. A calibration graph was obtained linearly up to 1.75 mg/L Zn with a 0.9988 correlation coefficient and 3.09% RSD using 50 μL injection volume, values comparable to conventional continuous nebulization. The detection limit (3S) achieved by the method was calculated to be 1.09 ng or 0.020 mg/L for 50 μL injection volume. A hydrophobic PTFE micro sampling cup was used.

Aerosol samples were collected between January 1996 and December 1998 in Mersin, Turkey, using polycarbonate filters. Collected samples were digested in the presence of HNO_3 and HF. Digested samples were analyzed for zinc using discrete nebulization flame atomic absorption spectrometry (FAAS).

The validity of the proposed method was established by evaluating the accuracy of analyses of BCSS-1 (Marine Sediment Reference Materials for Trace Metals and Other Constituents) CANADA. For the given true value of 119.0 ± 12 mg/Kg zinc, a value of 118.98 ± 0.26 mg/Kg zinc was found with a precision of 0.22% RSD. As a further check on accuracy, recoveries from aerosol samples were examined and found to be 94-102% , again testifying to the reliability of the proposed method.

Key Words: Discrete nebulization, FAAS, zsinc, aerosol samples, flame micro sampling.

Introduction

Zinc has a key role in the maintenance of the body's nervous, reproductive and immune systems. It is required for the senses of taste and smell, is an integral part of insulin and is required for the control of blood sugar levels. It helps wound healing, normal growth, good vision and maintenance of healthy skin. It is also known to reduce symptoms of the common cold and shorten recovery time[1].

*Corresponding author.

Zinc is an essential trace mineral, which, next to iron, is the second most abundant trace mineral in the body. Zinc is stored primarily in muscle but is also found in red and white blood cells, the retina of the eye, bones, skin, kidneys, liver, and pancreas. In men, the prostate gland contains more zinc than any other organ[1].

Zinc is one of the metals most frequently determined by atomic absorption spectrometry (AAS), as it was found that AAS was superior to all other methods[2].

Flame atomic absorption spectrometry (FAAS) with sample introduction by continuous nebulization is still the most widely used atomic absorption spectroscopic technique for quantitative trace metal determination despite the poor nebulization (transport) efficiency (2-10%), minimum volume of 0.5 mL required (due to uptake rate), some memory effects, and the clogging of the system, particularly with high dissolved solid solutions, which is potentially hazardous. The transient display responses that result have similar precision and sensitivity to those obtained with normal larger (1-5 mL) samples by atomic absorption studies. This sample introduction was found to be less susceptible to system clogging than normal steady state aspiration (continuous nebulization) techniques since less of the sample is aspirated. FAAS with discrete nebulization has been studied by many researchers and applied to several different practical analyses[3−12].

The aim of this study was to optimize the experimental conditions for determining trace elements using discrete nebulization FAAS, which is very rapid and simple and has been overlooked lately. Zinc determination in aerosol samples via hydrophobic PTFE microsampling cup was chosen for this purpose.

Experimental

Sample collection

Daily aerosol samples were collected in Mersin / METU between January 1996 and December 1998, on pre-weighed polycarbonate filters. Filters were divided into parts. A quarter of it was re-weighed and treated with an HNO_3-HF mixture for dissolution. Blanks were prepared exactly the same way and all were sent to our laboratory after diluting to a final volume in PET bottles.

Reagents and apparatus

All chemical products and solvents were of analytical grade (CARLO ERBA and MERCK). Standard working solutions were prepared from zinc stock solution (Fisons), 1000±0.5% mg/L, immediately before use. Deionized water was obtained via the MILLIPORE water system (Elix-10 followed by Milli-Q 185 Plus and 0.22μm filtering unit).

A 22x14x12 mm PTFE Microsampling cup was coupled directly to the nebulizer capillary. Injections were carried out with Brandt and Jencons micropipettes. All glassware was soaked in nitric acid bath (10% v/v) for 24 hours and rinsed with deionized water several times before use.

All experiments were carried out with an ATI-UNICAM 929 Atomic Absorption Spectrometer, equipped with deuterium arc background correction.

Instrumental parameters

Absorption measurements were carried out at 213.9 nm in the instrumental conditions that provide the best sensitivity. These conditions were 5cm burner head, at 0.5 nm spectral bandwidth, with 1.2 L/min C_2H_2 flow, and 5.0-mL/min aspiration rate.

The sample was manually injected with a micro pipette into a PTFE funnel (i.e., microsampling cup) connected to the nebulizer by a small length of capillary.

Results and Discussion

Starting with the results obtained by Cresser, M.S. and Berndt, H. [5,10−12], the applied method is an adaptation of the one used by D. Yurtsever Sarıca in her M.Sc. thesis [13].

Optimization of the working parameters

Injection Volume

In order to select the optimum injection volume, the absorbance values versus injected volume are plotted for 0.5 mg/L and 1 mg/L Zinc in Fig. 1. The signal height increases with injected volume up to about 80 μL, and thereafter the signal intensity remains the same as that obtained by continuous aspiration.

There is obviously a greater degree of fragmentation of larger droplets occurring at the impact bead in the discrete nebulization mode. Therefore, one would not obtain one-fifth of the sensitivity of a 250 μL sample, for a 50 μL sample. The loss of sensitivity by reducing the volume from 250 μL to 50 μL is compensated by the increase in nebulization efficiency.

The calibration plots for zinc obtained with different sample volumes are shown in Fig. 2.

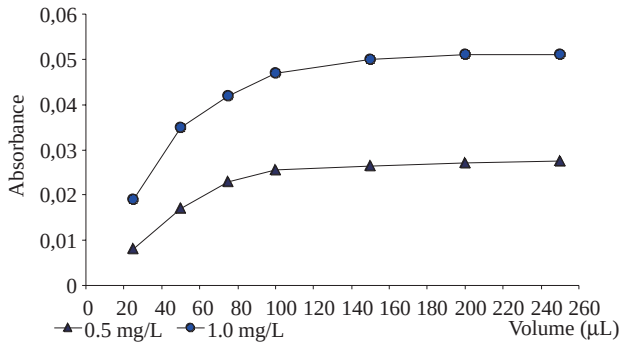


Figure 1. Effect of Injected Solution Volume on Signal Height.

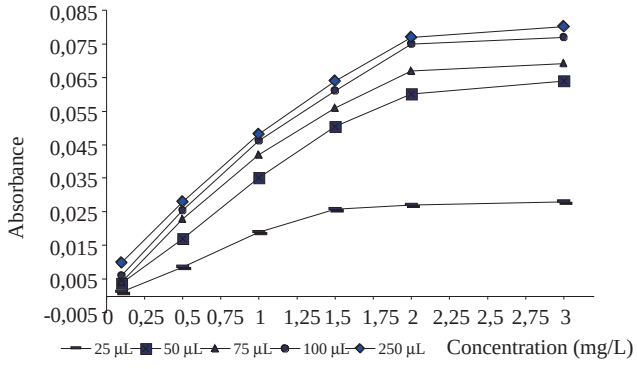


Figure 2. Calibration Plots for different volumes of aqueous zinc solutions.

The curves obtained with 100 μL and 75 μL sample volumes were almost identical to those observed in continuous aspiration and were linear up to 1.90 mg/L. With a 50 μL sample volume the responses were also comparable with continuous nebulized signals up to 1.75 mg/L and even 25 μL, and the graph was linear up to 1.5 mg/L. Analytical sensitivity was not much less for the 75 μL sample than for the larger volumes.

A summary of the properties of the calibration plots is given in Table 1. The use of a micro sampling technique, even with a 25 μL injection volume, does not impose a great penalty in terms of loss of precision.

Table 1. Some of the properties of calibration plots obtained with different sample volumes.

Volume	Reproducibility (% RSD)	Correlation Coefficient	Slope	Upper Limit of Linear Range (mg/L)
25	6.11	0.9858	0.0147	1.50
50	3.09	0.9988	0.0322	1.75
75	2.47	0.9992	0.0365	1.75
100	1.96	0.9939	0.0389	1.75
250	1.52	0.9997	0.0406	1.90

According to the data obtained in Figure 2 and Table 1, a sample volume of 50μL has been chosen for further studies, since it gave an acceptable reproducibility, and the loss of sensitivity compared to continuous nebulization was at an acceptable level. Comparatively poor precision of 25 μL sample volume is due partly to pipetting difficulties with small volumes. The precision worsens below 50 μL but does not exceed 10% RSD. Fry et al.[7] had similar results.

If one works with defined small volumes, i.e., 50 μL instead of relatively large amounts such as 1000 μL used with continuous nebulization, then the volume sensitivity of flame atomic absorption will be higher at identical concentration sensitivity since the nebulized part of the sample can be transferred to the flame almost at once. This is very important because in this way a limited time is required to form a dynamic equilibrium in the flame, since the sample reaches the flame in a transient mode, and a peak shape signal is obtained.

Nebulizer aspiration rate

Once the sample volume is chosen, optimization of the aspiration rate becomes important in order to obtain large, reproducible signals[14]. With increasing aspiration rate, the signal height passes through a maximum; at high uptake rates reproducibility gets poorer and sensitivity drops. This dependence is shown in Table 2 for signals of a zinc solution of relatively high concentration (0.8 mg/L).

In this case, the precision is mainly limited by the influence of aspiration rate; since at this concentration of zinc, the signal to noise ratio is high enough to neglect the effect of base line noise on precision.

The signal increased with the sample volume of solution to a saturation value determined by the aspiration rate of the system. The peak height response is better for smaller volumes at lower aspiration rates. A sample aspiration rate of 5.0 mL/min was chosen for further studies.

Table 2. Effect of aspiration rate on absorbance and precision of zinc (0.8 mg/L aqueous solution, 50 μL injection volume)

Aspiration Rate (mL/min)	Peak Height (Absorbance unit)	Relative Standard Deviation (% RSD) N=19
1.5	0.187	2.09
2.2	0.232	2.86
5.0	0.327	3.11
9.5	0.355	3.20

The experimental results show the superiority of the PTFE cup, which was used throughout this study. A comparison between discrete nebulization and continuous nebulization techniques for zinc is given in Table 3.

Table 3. Comparison of discrete and continuous nebulization techniques for zinc.

Parameters	Discrete Nebulization	Continuous Nebulization
Injection volume (μL)	50	250
Absolute Detection Limit (ng)	1.1	2.9
Concentration Detection Limit (mg/L)	0.02	0.01
Reproducibility (% RSD) for N=19	3.1	1.5
Correlation Coefficient	0.9988	0.9997
Upper Limit of Linear Range (mg/L)	1.75	1.90
Aspiration rate (mL/min)	5.0	9.5

Absolute detection limits are improved by micro sampling when 50 μL of sample is nebulized. In the literature similar results have been obtained[8]. It is easy to observe deterioration in concentration detection limits when discrete nebulization (micro injection) is employed, because of the smaller volumes used and the smaller signals thus obtained.

Since the ratio of the signals from 250-μL to 50-μL samples is less than five, better absolute limits with discrete nebulization are obtained, as expected.

Having an rsd value of approximately 3%, microinjection is comparable with conventional continuous nebulization, which has 1.5% rsd.

Accuracy Test

The validity of the proposed method was established by evaluating the accuracy of analyses of BCSS-1 (Marine Sediment Reference Materials for Trace Metals and Other Constituents) CANADA.

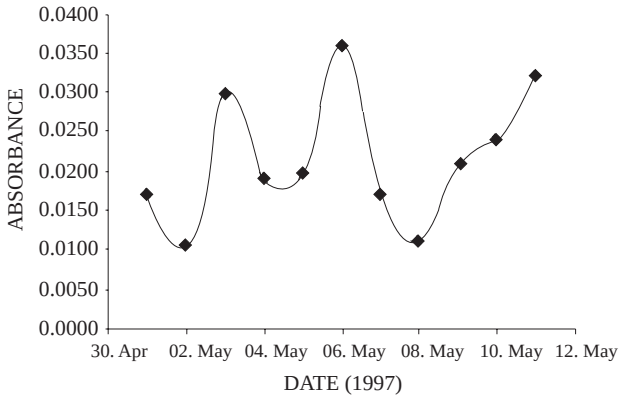
The standard addition method was carried out with five replicate measurements. For the sampling and analyzing procedures, the optimum conditions were employed, which were obtained experimentally and are mentioned in the Figures and Tables. The mean (x) and its standard deviation (SD) for five replicate measurements was 118.98 ± 0.26 ppm (w/w) with 0.218% RSD. Precision, i.e., the reproducibility of the technique, is good enough, as shown in Table 4. The analytical results agreed well with the certified values.

Table 4. Accuracy Test Results of Zinc Determination in Standard Reference Material, namely BCSS-1.

	Concentration Zn, mg/Kg	True Value
	118.70	119.0 ± 12 mg / Kg
	119.20	
	118.90	
	119.30	
	118.80	
x:	118.98	
SD:	0.2588	
RSD:	0.218 %	

Determination of Zinc in Aerosol Samples Collected on Polycarbonate Filters with Discrete Nebulization FAAS

It was attempted to investigate the results of the optimized technique by applying the whole method to real samples. For this purpose, the aerosol samples collected on polycarbonate filters between January 1996 and December 1998 in the Mersin area / METU were used. A major problem encountered when AAS is used in environmental analysis is the choice of a suitable matrix for standards because particulate matter aerosol samples are complex. In addition, viscosity, relative density, drop-size distribution, exothermic or endothermic processes in the flame, flow rates, and chemical interferences have to be considered. The analysis of such samples therefore requires calibration by the standard additions method. Typical experimental results are given in Fig. 3



Figue 3. Zinc determination in aerosol samples using discrete nebulization FAAS.

Blanks were determined in exactly the same way. The sample-to-blank ratio was about 37 and according to the studies of Tunçel et al.[15] above 3 is acceptable.

As a further check on accuracy, recoveries from pooled aerosol samples were examined. Recoveries of zinc ranged between 94 and 102%, again testifying to the reliability of the proposed method

Aerosol samples contain several other anions and cations [15]. Among the cations present in aerosol samples, the ones most likely to form chloride salts, namely, $CaCl_2$, KCl, $MgCl_2$, and NaCl, were chosen to study the interference effects. Solutions containing high excess amounts of chlorides were prepared such that the zinc concentration was always 1mg/L. The results indicated that there was no suppression in the signal when electrolyte concentrations were at their normal aerosol levels. The results of our study also confirm that the presence of chlorides at even values well above the normal levels in aerosol does not cause a suppression in discrete nebulization flame analysis unless there are synergistic effects in real samples.

Conclusion

Flameless AAS systems do accept sufficiently small volume samples, but such methods are generally more time-consuming, expensive and interference-prone, although they provide higher sensitivity.

The micro sampling cup used for discrete nebulization represents a technique of similar concentration sensitivity, improved absolute sensitivity, similar precision, improved sample size requirements, improved analysis time, reduced memory problems, and improved tolerance to high solid content materials in comparison to normal steady-state (continuous nebulization) aspiration approaches. As Mitchell et al.[16]concluded,

the micro sampling cup procedure is exceedingly rapid and yields the same results regardless whether aqueous standards or standard additions are used for calibration.

As Sneddon et al.[17] observed, at low volumes, discrete nebulization gives a poorer detection limit of an order of magnitude compared to continuous nebulization.

The precision of the micro sampling (discrete nebulization) technique is satisfactory (3.1% RSD). The accuracy of the method is also satisfactory, with recoveries of 94% to 102%. The discrete nebulization technique has other advantages, such as being rapid and simple, requiring small volumes of sample and having no clogging problems.

Consequently, whenever the sensitivity associated with flame nebulization techniques is sufficient for determination, the discrete nebulization technique offers an inexpensive, simple, efficient and superior alternative that can be applied over a wide range of analyses and is suitable for multielement analysis.

Acknowledgments

We would like to thank to Assist. Prof. Nilgün KUBİLAY/METU for providing us with the aerosol samples.

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