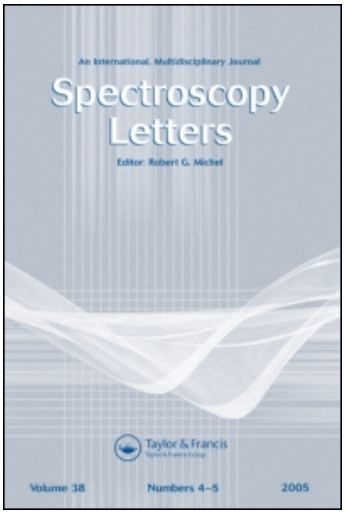

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Determination of Chloride by Flame molecular Absorption Spectrometry with Continuum Source and Self-Reversal Background Correction

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DETERMINATION OF CHLORIDE BY FLAME MOLECULAR ABSORPTION SPECTROMETRY WITH CONTINUUM SOURCE AND SELF-REVERSAL BACKGROUND CORRECTION

Key Words: chloride determination; nitrous oxide/acetylene flame; continuum source background correction; self-reversal background correction.

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ABSTRACT

The use of continuum source and self-reversal background correction were investigated for flame molecular absorption spectrometry (MAS). Chloride was

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determined by MAS using the aluminum monochloride molecule in a conventional flame atomic absorption spectrometer. Absorbance of this molecule was monitored in a lean nitrous oxide/acetylene flame at 261.4 nm using a lead hollow cathode lamp as the excitation source. Characteristic masses of 210, 260, and 820 mg/L were observed for no background correction, continuum source correction, and self-reversal correction, respectively. The ability of the techniques to correct for interferences caused by high concentrations of fluoride and sodium was investigated. The self-reversal technique was shown to remove interferences at concentration levels up to 10,000 mg/L. Chloride was determined in chloroacetic acid using calibration with chloride standards; continuum source correction had the best recovery value. These results suggest that both correction methods should be investigated for practical applications of flame MAS to obtain optimum analytical performance.

INTRODUCTION

Flame atomic absorption spectrometry (FAAS) is a widely accepted method for the determination of metals at low parts-per-million concentrations because of its high sensitivity and selectivity [1, 2]. However, halides are difficult to determine by AAS because their resonance lines are in the vacuum UV region, requiring an evacuated spectrometer. Halides also have high electronegativity, and form very stable molecules which interfere with AAS determination [3]. An alternative method for halide determination is molecular absorption spectrometry (MAS), involves formation of a diatomic molecule between the halide and a

reagent metal [3-6]. The analytical signal is the light absorbed by this diatomic molecule from a hollow cathode lamp (HCL) or a continuum source, such as a deuterium arc lamp.

A number of reports have discussed the determination of chloride by MAS. Tsunoda et al. [7] determined chloride using the aluminum monochloride molecule at 261.4 nm in a nitrous oxide/acetylene flame and a carbon rod furnace. A continuum source was used for excitation with a two channel background correction method, in which measurements were alternately made at the peak of the molecular band (261.4 nm) and away from the band (260.1 nm). The characteristic mass for the carbon rod system was 120 pg. No analytical data were reported for the flame analysis. Chloride was determined in a National Institute of Standards and Technology (NIST) orchard leaves standard reference material (SRM) and in organochlorine compounds. The accuracy of the analyses was within 15 % of the recommended (SRM) or added (organochlorine compounds) values.

Dittrich et al. [6] determined chloride with AlCl at 261.4 nm in a graphite tube furnace with a continuum source and a two channel method for background correction similar to that of Tsunoda et al. [7]. An extraction method was employed to separate and preconcentrate chloride. A detection limit of 1.5 ng chloride was reported and the extraction procedure was shown to reduce interferences.

Parvinen and Lajunen [8, 9] determined chlorine in a graphite tube furnace. The AlCl molecule was excited by a lead HCL at 261.4 nm, and a continuum

source was used for background correction. The technique was used to determine chlorine in organic compounds and α-pinene products. The analyses were within 10 % of the expected value for the organic compounds. For the α-pinene products, the accuracy was within 15 % of the value obtained by a gravimetric procedure.

Butcher [10] determined chloride by flame MAS with no background correction using the excitation system described by Parvinen and Lajunen [10]. The addition of sodium, fluoride, and strontium ions was shown to severely affect the size of the flame MAS signal. Chloroacetic acid was determined with accuracy of 10 % of the expected value, but no signals were obtained for the analysis of mouthwash and a NIST milk powder SRM.

Fender and Butcher [11] determined chloride as the AlCl molecule using a lead HCL in a graphite tube furnace. Self-reversal background correction was compared to continuum source background correction. Characteristic masses of 0.6 and 1.0 ng were obtained for the two background correction methods. The self-reversal technique was shown to provide better accuracy than continuum source correction for the determination of chloride in a NIST simulated rain water SRM.

The purpose of this study was to investigate the use of background correction for chloride determination by flame MAS. Aside from the early two channel method reported by Tsunoda et al. [7], background correction has not been used for this technique. No background correction, continuum source background correction, and self-reversal background correction were employed in

this study. The effect of various ions upon the analytical signal was evaluated. The suitability of each background correction system to do real sample analysis was investigated by the determination of chlorine in the form of chloroacetic acid.

EXPERIMENTAL

Flame MAS measurements were performed with a Thermo Jarrell Ash AA Scan-1 spectrophotometer equipped to do continuum source and self-reversal background correction.

All stock solutions were prepared from high-purity reagent salts (Aldrich, Milwaukee, WI) using distilled, deionized water. Aluminum solutions were made from aluminum nitrate nonohydrate and chloride solutions were prepared from ammonium chloride. All standards were prepared by the daily, serial dilution of the above stock solutions. All chloroacetic acid sample solutions were made 1,000 mg/L in chloride and 10,000 mg/L in aluminum.

Solutions containing 10,000 mg/L aluminum and various concentrations of chloride were aspirated at a rate of 5 $mL \cdot min^{-1}$. A 3 second integration period was employed for all measurements. Due to the high aluminum concentration, the burner head had to be cleaned between measurements.

RESULTS AND DISCUSSION

Method Optimization

Earlier work from our group included the optimization of instrument parameters for chloride determination by flame MAS using the AlCl molecule [10].

The conditions employed for this work are identical to those in our previous study except for the aluminum concentration. We employed 10,000 mg/L, rather than 13,500 mg/L, in order to reduce the incidence of clogging the burner. A summary of conditions for chloride determination is given in TABLE 1.

Analytical Figures of Merit

Calibration plots were prepared for the AlCl system with no background correction, continuum source background correction, and self-reversal background correction, and the results are given in TABLE 2. The calibration sensitivity (slope) was highest for no background correction, which is expected since some sensitivity loss is expected in any background correction procedure. The continuum source sensitivity was 80 % of the uncorrected sensitivity. Continuum source background correction generally causes minimal degradation of the sensitivity. The slope of the self-reversal corrected graph was only 25 % of the uncorrected signal, indicating that a significant signal loss occurred in the background correction process. We [11] proposed in our graphite furnace MAS work on chloride that the HCL is only partially self-reversed, leading to a significant loss in sensitivity. We suggest that this process is also occurring in this work. The sensitivity values result in characteristic concentration values of 210, 260, and 820 mg/L for uncorrected, continuum source corrected, and self-reversal corrected measurements, respectively. Linear dynamic ranges of the methods were similar for the methods, with values of 1.4, 1.6, and 1.1 orders of magnitude, respectively.

TABLE 1. Conditions for Flame MAS

Reagent Concentration	10,000 mg/L aluminum (as $Al(NO_3)_3 9H_2O$)
Wavelength	261.4 nm
Light Source	Lead hollow cathode lamp
Spectral Bandpass	1 nm
Flame Conditions	Nitrous oxide (15 L/min)/acetylene (13 L/min)
Sample Aspiration Rate	5 mL/min

TABLE 2. Analytical figures of merit for flame MAS

Background correction	**Calibration sensitivity**	**Characteristic concentration, mg/L**	**Linear dynamic range**
Uncorrected	0.000021	210	1.4
Continuum Source	0.000017	260	1.6
Self-Reversal	0.0000054	820	1.1

Interferences

One disadvantage of MAS for real sample analysis is its susceptibility to interferences due to cations and anions [3]. For example, in our previous flame MAS work for chloride without background correction [10], significant interferences were observed from sodium and fluoride ions.

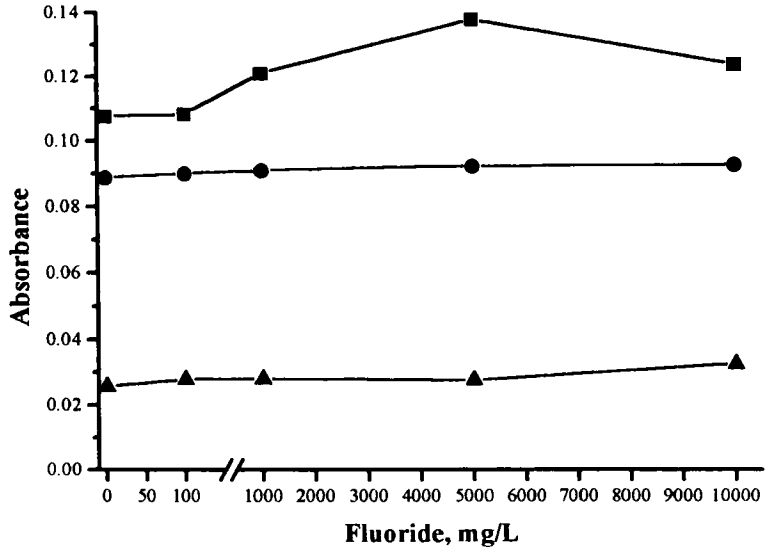

FIG 1. Effect of fluoride (as ammonium fluoride) upon the flame AlCl signal at optimized conditions: (■) no background correction; (●) continuum source background correction, (▲) self-reversal background correction.

FIG. 1 shows the effect of fluoride concentration upon the flame MAS signal with no background correction, continuum source background correction, and self-reversal background correction. Although an positive interference (enhancement) was observed for the uncorrected signal, no effect was observed with either continuum source or self-reversal background correction. These data seem to indicate that background correction may be necessary for accurate flame MAS analyses.

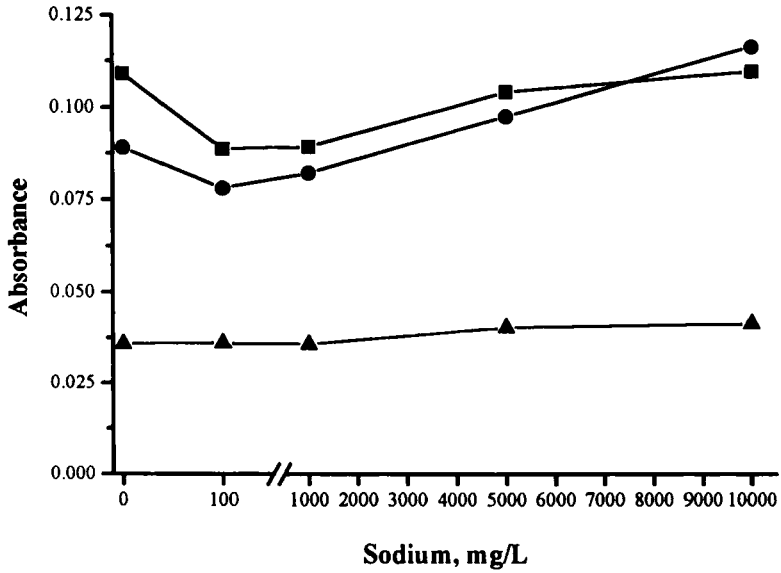

FIG 2. Effect of sodium (as sodium nitrate) upon the flame AlCl signal at optimized conditions: (■) no background correction; (●) continuum source background correction, (▲) self-reversal background correction.

The effect of sodium concentration upon the AlCl signal is shown in FIG. 2. For no background correction and continuum source background correction, a signal suppression was observed from 100-1000 mg/L sodium. The continuum source also showed a small signal enhancement at 10,000 mg/L sodium. However, the self-reversal signal was not significantly affected by sodium concentrations up to 10,000 mg/L. These results seem to indicate that self-reversal background correction may correct for some backgrounds that the continuum source method cannot. The limitations of continuum source background correction have been

TABLE 3. Determination of chloride (0.100 % introduced as chloroacetic acid) by flame MAS (n = 3)

	No Correction	Continuum Source Correction	Self-Reversal Correction
Flame MAS, %	0.15 ± 0.03	0.090 ● 0.01	0.130 ± 0.004
% Recovery	150	90	130

discussed extensively in the atomic absorption literature [1, 2, 12, 13], including its inability to correct for large background levels and background whose level varies across the monochromator bandpass (structured background).

Real Sample Analysis

The utility of flame MAS for real sample analysis was investigated by the determination of chlorine in the form of chloroacetic acid with the three background correction methods (TABLE 3). Chloride standards were used for calibration. The percent recovery of the analyses was 150 % for no correction, 90 % for continuum source correction, and 130 % for self-reversal correction. For this sample, the continuum source method gave the best accuracy. These results are consistent with the accuracy (approximately 10-15 %) previously reported by MAS for chloride determination [7, 9-11]. Better accuracy would probably be obtained by the use of organochlorine standards. These data also suggest that both continuum source and self-reversal background correction should be investigated

with flame MAS to determine which method gives more accurate correction for a particular analysis.

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