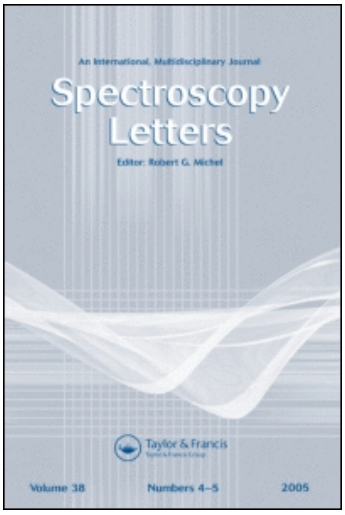

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Determination of Chlorine by Aluminium Monochloride Molecular Absorption Spectrometry Using Lead Atomic Lines

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DETERMINATION OF CHLORINE BY ALUMINIUM MONOCHLORIDE MOLECULAR ABSORPTION SPECTROMETRY USING LEAD ATOMIC LINES

Key words: aluminium chloride molecular absorption spectrometry: electrothermal vaporization, chloride, determination

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ABSTRACT

In earlier studies the methods for determination of chlorine by aluminium monochloride molecular absorption spectrometry have been based on the use of the continuous light sources.

In this study we investigated the molecular absorption of AlCl in a carbon rod furnace for determination of chlorine, by using the lead atomic line at 261.418 nm emitted from a Pb-hollow cathode lamp. A deuterium lamp was used for simultaneous background correction.

INTRODUCTION

Molecular absorption spectrometry at a high temperature has been developed for the determination of nonmetallic elements (Fuwa et al, 1969 and Haraguchi et al, 1976). These elements are difficult to determine by conventional AAS methods because their resonance lines lie in the vacuum ultraviolet region.

Molecular absorption of aluminium monohalides formed at a high temperature has been used for the determination of fluorine, chlorine and bromine (Tsunoda et al, 1977, Dittrich et al, 1986 and Pearce et al, 1976). Aluminium monochloride which formed in the furnace shows a molecular absorption band at 261.4 nm. In previous papers a deuterium lamp of the thermal cathode or hollow cathode type has been used as a light source, but this was found to be inconvenient due to the slit width and background correction (Tsunoda et al, 1978). In the case of the slit width the sensitive measurement of aluminium chloride molecular absorption requires a narrow spectral bandpass. If the background correction is performed at the same wavelength as the aluminium monochloride band, a wide spectral bandpass is needed for background correction. That is why a wavelength different from 261.4 nm has been used for background correction. Therefore the absorption intensity at 260.1 nm, where aluminium chloride absorption is minimal, has been subtracted from that at 261.4 nm using a 2-channel spectrometer. These two problems may be solved by using a line-like irradiation source for the aluminium monochloride absorption measurements.

In this paper, the use of atomic lines from various elements for the determination of chlorine is examined for the convenient use of the molecular absorption technique with simultaneous background correction. As the result the atomic line of lead at 261.4 nm was found to be most suitable for requirements mentioned above.

EXPERIMENTAL

Apparatus

The molecular absorption of aluminium monochloride was measured with a Pye Unicam SP 9 spectrometer, fitted with a graphite furnace. The instrument offers the possibility of simultaneous background correction with a deuterium lamp. Nitrogen gas (4 l/min) was flowed to purge the carbon rod furnace from air. Lead, iron and manganese Cathodeon Ltd hollow cathode lamps were used

Table 1. Experimental Conditions for AlCl Molecular Absorption Measurement.

1	Aluminium solution	10 µL	
	Drying	120 °C	20 s
	Ashing	700 °C	20 s
	Cooling		
2	Addition of sample solution	5 µL	
	Drying	120 °C	20 s
	Ashing	700 °C	20 s
	Atomization and measurement	1900 °C	7 s

as the light sources for the molecular absorption. The spectral band width of the monochromator was usually set at 0.2 or 0.5 nm.

Procedure

The experimental conditions for the measurement of the AlCl molecular absorption are given in Table 1. In practical measurements, so as to obtain the absorption spectrum of AlCl in an aluminium nitrate solution (0.01 M), cobalt nitrate (0.01 M) and strontium nitrate (0.01 M) were added in order to enhance the sensitivity and improve the precision of analysis as reported by Tsunoda et al. (Tsunoda et al, 1978).

Chemicals

All the reagents used were a pro analysis grade of Merck. To prevent the escape of chlorine during ashing, the measurements were done from base solutions.

The atomic line of lead (261.4 nm) gave the strongest AlCl molecular absorption. In the case of iron and, manganese the observed absorbances were weak. The practical measurements proved

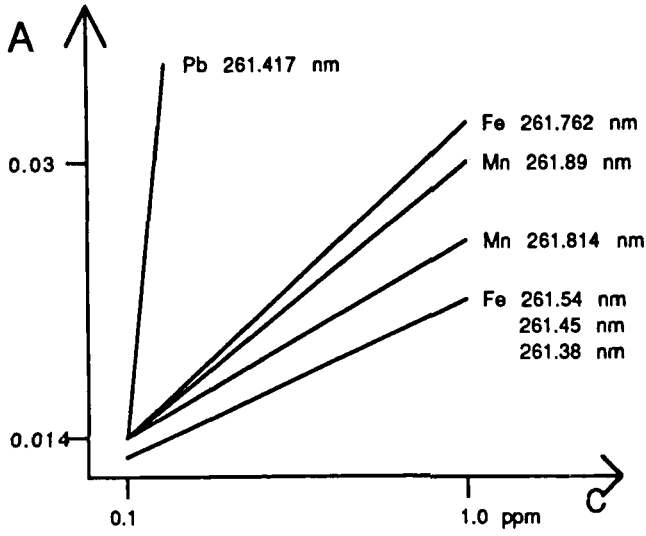

Fig. 1. Calibration curves obtained by different atomic lines using hollow-cathode lamps of metallic elements.

that the sensitivity did not depend significantly on the slit width when using the lead atomic line. Thus, it can be concluded that a lead hollow cathode lamp is the most suitable light source for AlCl molecular absorption spectrometry.

In atomic absorption spectrometry, background correction using a deuterium lamp is the conventional procedure. The same procedure for the background correction in AlCl molecular absorption spectrometry was tested by measuring the absorbances with and without background correction using solutions containing 1 mg L^{-} chlorine and solution containing no chlorine at all. It can be seen from Table 2 that the background absorption can be corrected quite well by the D_2-lamp system. Simultaneously, the dynamic range of the whole method became very wide.

In practical analysis the interferences caused by other halogenides are smaller in this method than in methods reported

Table 2. The Effect of Background Correction on the Absorption Intensities Obtained from a Solution Containing a 1 mg/L Chlorine and Pure Aliminium Solution Without Chlorine.

Solution	Absorption intensity	
	background corrected	no correction
Al - solution	0.125	0.875
Al - solution + 1 mg/L chlorine	0.685	1.105

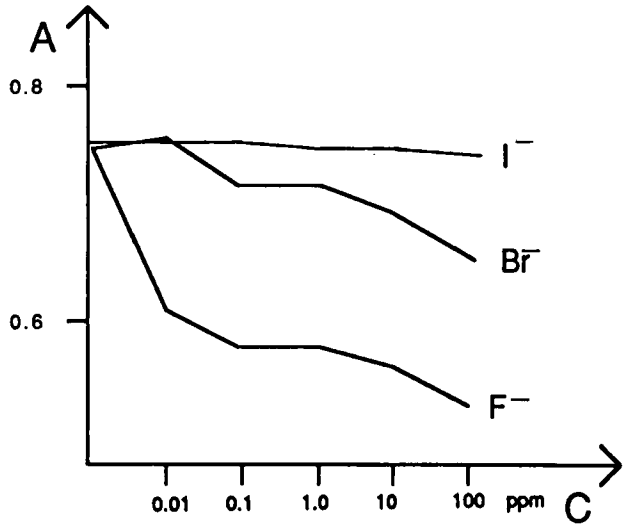

Fig. 2. The interferences of the other halogenides on the determination of chlorine.

Table 3. Content of the Standard Sample.

SiO_2	46.92 %	CaO	Spuren	
Al_2O_3	38.16 %	$K_2O + Na_2O$	0.36 %	
Fe_2O_3	1.10 %	Gluhverlust	12.95 %	
MgO	0.51 %	Cl	0.503 %	Added.

Cl measured 0,501 %, standard deviation 0,023, highest value 0,521 %, lowest value 0,463 %

Table 4. Analytical Data on AlCl Molecular Absorption Spectrometry.

	Pb - lamp	Continuum light source (Tsunoda et al, 1978)
Characteristic concentration (1 % -absorption)	0.03 mg/L	0.02 mg/L
Dynamic range mg/L	up to ca. 3	up to ca. 1
Precision (RSD)	3 %	2 - 4 %

Table 5. Interference caused by other halogenides on the AlCl absorption. The concentration of the interferring halogenide was always 100 mg/L. (Cl 1 mg/L).

Element	Absorption intensity	
	present method	earlier methods (Dittrich et al, 1986)
I^-	100 %	~77 %
Br^-	77 %	~71 %
F^-	46 %	~20 %

earlier. In figure 2 these interferences are described for measurements done on a 1 mgL^{-} chlorine solution. As can be seen the most serious interference is caused by fluorine which is obvious because it has the most stable molecule with aluminium in these circumstances. The effect of bromine is not serious up to a bromine concentration of 10 mgL^{-} and iodine has no effect at all under these circumstances.

As an calibration sample we have used a standard sample where the chlorine was added as sodiumchloride (Table 3). Four samples have been taken from this mixture, dissolved in hydrofluoric acid, precipitated chlorine as AgCl and this is dissolved in an ammonium solution where the measurements have been done.

CONCLUSIONS

The sensitivity and precision of the present system and by using a continuum light source (Tsunoda et al, 1978), are practically the same. However, the dynamic range is about three times larger with this method than that reported earlier (Table 4). Also the interferences caused by the other halogenides are smaller in this method (Table 5).

These experimental results suggest that the method proposed here can be useful for practical analysis of chlorine.

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