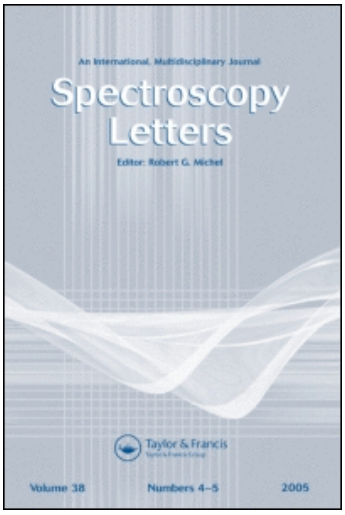


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# The Zeeman Splitting of Aluminium Monochloride Molecular Absorption Bands as the Possible Interference in Atomic Absorption Spectrometry

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# THE ZEEMAN SPLITTING OF ALUMINIUM MONOCHLORIDE MOLECULAR ABSORPTION BANDS AS THE POSSIBLE INTERFERENCE IN ATOMIC ABSORPTION SPECTROMETRY

Key words: Aluminium chloride molecular absorption, Zeeman background correction interference.



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## ABSTRACT

The molecular absorption was measured using a sharp line irradiation source together with the Zeeman background correction. The measured absorption was caused by aluminium chloride that was measured using lead hollow cathode lamp. Some kind of Zeeman splitting has been found in the case of studied molecular absorption bands having sharp lines. The absorptions measured were very unstable and noisy. However there was found some relationship between the measured absorption and the amounts of chlorine.

## INTRODUCTION

Graphite furnace atomic absorption spectrometry (GFAAS) is a highly sensitive technique for the determination of most metallic elements. The basic principle in the atomic absorption spectrometry (AAS) is very simple. However the atomisation in the graphite furnace is often incomplete, resulting both atomic and molecular species those are in vapour also during the measurement step. So the light at the resonance wavelength of an element can be absorbed in addition of atoms of studied element by suitable molecules. In addition of the molecular absorption the interference can be caused by scattering. Various techniques have been used for the correction of the continuous and fine- structured absorption caused by non atomic components. This include the measurement of the background by the continuum source systems, by systems using hollowcathode lamps emitting splitted lines or by splitting the lines in graphite furnace. The splitting in furnace is achieved by operating at high lamp currents (Smith- Hieftje correction) or by applying a magnetic field (Zeeman correction).

The Zeeman background correction system is based on the fact that in an intense magnetic field the energy levels in atom are altered slightly. The simplest case is when the line is split in tree components so that one component, polarised in the plane of the magnetic field is at the original wavelength ($\pi$ -component) and contains half of the original intensity. The two other components those are polarised in a plane perpendicular to magnetic field are displaced on equal distances from the original wavelength ($\delta$ -components), both of them being one quarter of the original intensity. This is called a normal Zeeman pattern. For elements having anomalous Zeeman pattern the splitting is more complex in which eighter or both $\pi$ and sigma components are themselves further split.

The same kind of Zeeman splitting may happen with the suitable bands of a molecule. However only a few examples of this kind of phenomena has been reported [1]. The interference's have been found to be caused by the Zeeman splitting of OH rotational band that is nearly coincident with Bi [2]. The serious

interference has been found to be caused by PO in the measurement of silver [1] and cadmium [3]. The other mechanism for the interference may occur if a sigma component from a molecular band is sifted to overlap the atomic absorption line during the magnet- on cycle [4].
In this work our aim was to measure possible absorption signal caused by the molecular absorption of aluminium chloride using Zeeman background correction.

## EXPERIMENTAL

In measurements was used a Perkin- Elmer Model 3030 and 5100 Zeeman atomic absorption spectrometers equipped with an HGA- 600 graphite furnaces and AS-60 autosamplers. The additional data was obtained using a PU- 9200 and SP- 9 graphite furnace atomic absorption spectrometers equipped with deuterium lamp background correction system. The measurements has been performed using Perkin- Elmer and Chatodeon Ltd. lead hollow cathode lamps. As the slitwidth has been used 0.2 nm. The analyses were performed using wall atomisation in uncoated and pyrolytically coated graphite tubes (Perkin- Elmer). Argon was used as the purge gas. The instrumental parameters in the measurements are shown in Table 1.



## REAGENTS

All reagents used for analysis were suprapur or analytical grade of Merck. The aluminium solution used as the matrixmodifyier contained 0,01 M Al, Sr and Ag. Metallic elements used were added in solutions as nitrates and chlorine as its sodium salt. The solutions were prepared using ultrapure water, obtained by purifying the deionized and distilled water with a Water- 1 apparatus (Barnstead).

## RESULTS AND DISCUSSION

The optimisation of temperature program was performed by PU 9200 and SP-9 atomic absorption spectrometers equipped with deuterium lamp background

TABLE 1.

The instrumental parameters for the measurement of aluminium monochloride molecular absorption ( Wall atomisation, wavelength 261.4 nm, slit 0.2 nm).

| Step | Temperature C | Ramp time, s | Hold time, s | Gas flow | Read | Rec |
|---|---|---|---|---|---|---|
| 1 | 110 | 10 | 10 | 300 | | |
| 2 | 700 | 20 | 20 | 300 | | |
| 3 | 1900 | 0 | 4 | 0 | + | + |
| 4 | 2700 | 1 | 3 | 300 | | |



correction system. By that system is easy to measure the molecular absorption and the system has been earlier used for determination of chlorine as AlCl molecule by molecular absorption spectrometry. The molecule studied is very stable in furnace so that it really exist and have long lifetime in vapour phase in high temperatures. The dissociation energy of aluminium monochloride is 5.1 eV. In this work the measurements was performed using uncoated or pyrolytically coated graphite tubes and the wall atomisation, because the lifetime of the molecule is increasing when it is evaporating from the hot wall to a colder gas atmosphere inside the tube. The models of temperature distributions in furnace predict that the time-dependent gas temperature distribution in the radial direction is affected by the tube wall heating rate, initial and final tube wall temperatures. It also predicts a maximum temperature difference of about 100 K between the tube wall and gas phase at the furnace centre (for a tube wall heating rate 2 K/ ms and an initial tube wall temperature of 470 K) occurring near beginning of the cycle. Thereafter, the gas temperature asymptically approaches the tube wall temperature. This difference of temperatures seem to be favourable for formation and life of molecules. In the aluminium solution was added silver in order to bind the chlorine during drying and ashing steps, also the strontium that has high pKa value was added to prevent the

evaporation of HCl during drying step. In the base of this study the ashing temperature has selected to be 500 $^{O}$C and the evaporation and measurement temperature 1900 $^{O}$C for AlCl. The highest possible ashing temperature was used in order to minimise the amount of other possible molecules in the furnace. Some additional measurements was done by replacing the silver in the matrixmodifier by cobalt but that had no affect on the obtained absorptionsingals.

Aluminium chloride molecular absorption

The diatomic aluminium chloride (AlCl) has a strong absorption spectrum between 261 and 263 nm. The strongest bands of this spectrum lies at 261,44 nm [5] (Table 2.). For the measurement of AlCl molecular absorption has been used the atomic line of lead at 261,418 nm [6] when using the deuterium lamp background correction system and now this same atomic line was used in the measurements with Zeeman background correction.

The measurements have been performed mainly using solutions containing 0.1 , 1.0 and 3.0 mg/l of chlorine and matrix modifier containing aluminium, strontium and silver 0.01 M. The measured signals caused by molecular absorption were however very noisy and unstable when using Zeeman background correction, so that absorbances obtained by measuring area of the absorption signal were unpredictable. The level of the absorption varied between the different measurement periods so that same solutions gave different heights of signals in different times. These differences in the height of signals may be caused by the small differences in the existence and formation of AlCl in the furnace, depending on the age of the furnace and general conditions of the spectrometer combined to slight difference of the wavelengths of emitted and absorbed signals. Solutions containing over 1mg/l of chlorine gave always strong absorption. In Fig. 1. are presented the absorption signals measured using these different solutions and in fig. 2 are compared the absorption signals obtained by these both background correction methods from the same sample solutions. In the table 3. are presented

TABLE 2.

The line heads of AlCl molecular lines[8].

| Line nm | 262.24 | 262.00 | 261.82 | 261.70 |
|---|---|---|---|---|
| Intensity | 4 | 4 | 3 | 4 |
| Line nm | 261.44 | 261.02 | 260.67 | 260.07 |
| Intensity | 8 | 6 | 2 | 2 |

absorbances obtained in the measurements when using the height of the absorption signal. The smallest chlorine concentrations observed were at 0.02 mg/l level. As the result of these measurements has been found that the Zeeman background correction is not able to correct the molecular absorption of aluminium chloride. In these measurements the measured background absorption was not very high and so the Zeeman background correction system should be able to correct it.



## CONCLUSIONS

The Zeeman background correction is not able to correct the background absorption caused by the sharp absorption lines in the molecular spectra of aluminium chloride. Generally the absorption intensities measured were not so high that Zeeman background correction system would have any difficulties in correcting them as the normal background. So in the measurement of this molecule seems to occur Zeeman effect. This behaviour is not perfect and the measured absorption signals were very unstable and noisy. The phenomena that the measured absorption lines are unstable can be caused partly by the slight difference between the emitted signal of the hollow-chatode lamp and the absorbing molecular peak. This difference is causing the unstability in function of Zeeman background correction. However the lines are so near each other that when using deuterium lamp background correction system the lines can not be separated. It was possible to find some relationship between the concentrations and the measured

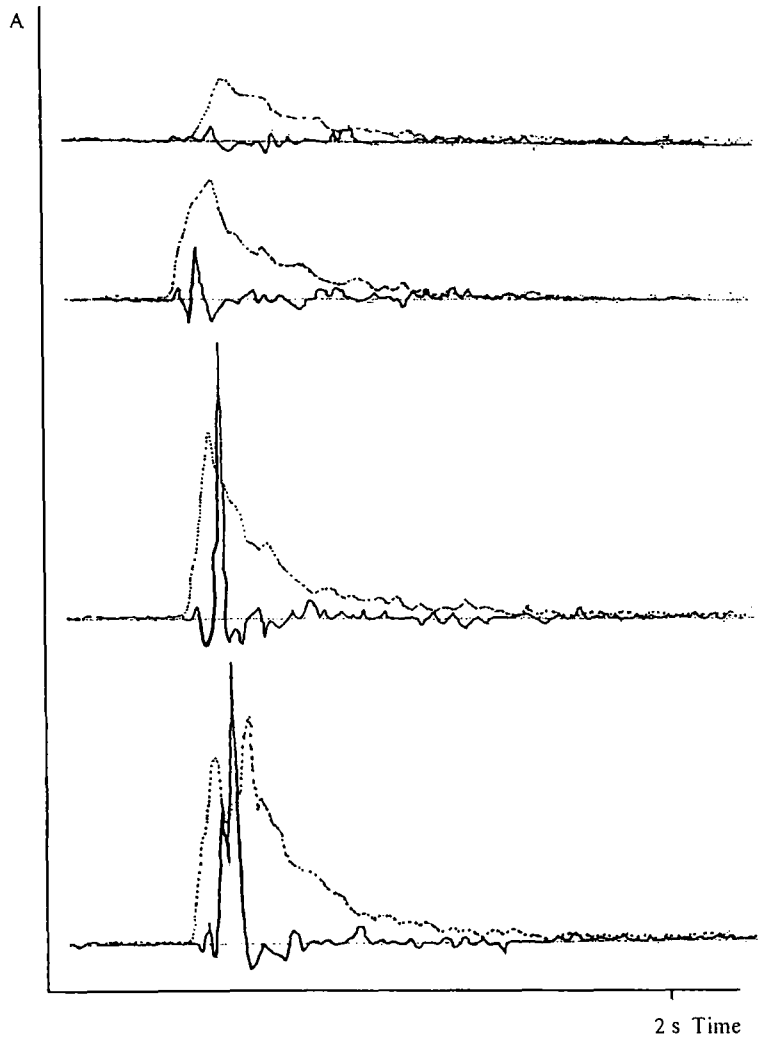


FIG. 1. The aluminium chloride absorption signals measured by solutions containing 0 mg/l, 0,1 mg/l, 1 mg/l and 3 mg/l of chloride using spectrometer equipped by Zeeman background correction.

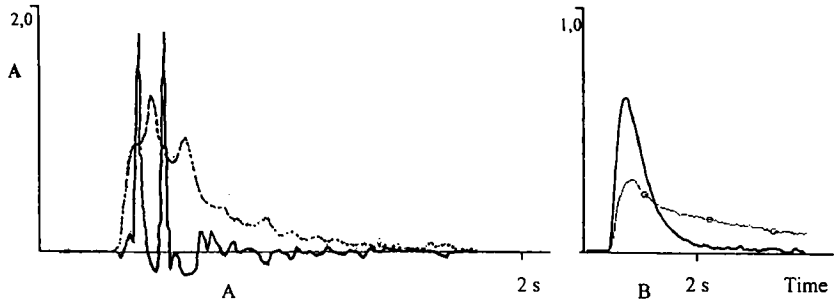


FIG. 2. The AlCl molecular absorption signals measured from the same solution ( 2 mg/l of chloride) using spectrometers equipped by Zeeman background correction (A) and deuterium lamp background correction system (B).



TABLE 3.

The molecular absorption of aluminium monochloride measured using the Zeeman background correction (A) and deuterium lamp background correction (B).

| Chlorine mg/l | A height of signal | B height of signal | B area of signal |
|---|---|---|---|
| 0.1 | 0.08 - 0.10 | 0.080 | 0.041 |
| 0.5 | 0.74 - 0.90 | 0.358 | 0.164 |
| 1.0 | 1.0 - 3.0 (0.36) | 0.589 | 0.279 |
| 2.0 | 1.6 - 3.0 | 0.979 | 0.454 |
| 3.0 | 2.7 - 3.0 | 1.563 | 0.852 |

absorbances also when using Zeeman background correction. In some cases it seem to be possible to evaluate the amount of the chlorine by this way. The dependence of the measured absorbances on the concentration of NaCl in the sample solutions proved that in the measurements has been really measured the molecular absorption of AlCl. That because the sodium has no alternative lines those could cause interference near this wavelength and the different molecules possibly formed by sodium in these conditions does not have strong absorption lines in this region. In the base of this study it can be thought that molecules those have strong and sharp molecular absorption bands overlapping with atomic lines of measured metallic elements may cause interference. The interference's caused by molecular absorptions of aluminium chloride may be serious when measuring lead using alternative line of this element. However when measuring real samples these errors can be minimised by matrix modifier and by optimising the temperature program of the furnace. This interference may occure as unstability of the measured absorption signal increasing the RSD values.



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