

CONSIDERATION REGARDING THE ANALYSIS THROUGH SPECTRAL METHODS OF LEADUM IN STEEL

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Abstract: According to the CE95/2002 (RoHS - Restriction of use of certain Hazardous Substances) directive, the use of 6 materials in the manufacturing of electric and electronic equipments will be restricted. These are lead (Pb), cadmium (Cd), mercury (Hg), hexavalent, PBB&PBDE. The directive has been adopted on the 1st of July 2006. Its goal is directly related to the WEEE (Waste Electrical and Electronic Equipment) directive. RoHS has a fundamental impact over the electronic industry. Legally, it will only be applied in UE, but it will rapidly become a worldwide "standard" due to the global character of this industry. Moreover, similar environment related legislation is being suggested in several countries outside UE. In the present work, several results obtained through methods of spectral analysis are being presented. These can be used to determine Pb in steels, respectively AAS, ICP and OES.

Keywords: lead, steel, OES, AAS, ICP.

1. Introduction

The purpose of the directive is to prevent electric and electronic equipment waste and to promote the reuse, the recycling and other ways to employ these in order to reduce the quantity of waste. Another aim is to improve the environment performances of all operators involved in the life cycle of electric and electronic equipment (manufacturers, distributors, consumers), and specially those operators involved in their processing.

2. Experimental

A spectrometer with sequential emission in plasma BAIRD ICP 2070, owned by S.C. MECHEL Targoviste S.A, has been used at ICP analyses. The spectrometer is designed to measure any of the spectral lines produced by individual elements. Whereas the wavelength of the spectral line identifies the element, the intensity of brightness of the line is proportional to the element's concentration in the sample. The line intensity is measured by a light sensitive detector, a photomultiplier tube (PMT), that converts the light energy in to a proportional electric current.

ICP-AES method is based on the fact that the atoms and ions produced in the plasma are excited and emit light. The intensity of light emitted at wavelengths characteristic of the particular elements of interest is measured and related to the concentration of each element from samples.

The ICP-AES spectrometer used by us is a Baird ICP 2070 - Sequential Plasma Spectrometer.

The technical data of this device are presented in Table 1.

GBC Avanta Ver 2.02 spectrometer owned by the Scientific and Technologic Multidisciplinary Research Institute from Valahia University of Targoviste has been used. The AAS is the most widely utilized method today for quantitative element analysis. The detection limit in AAS is up to about one ppb under optimum experimental conditions. A material sample, in a liquid solution, is atomized, through rapid heat application and placed in the radiation path of several elements – specific light sources. The atoms of sample absorb the wavelength corresponding to their excitation energy, thus reducing the radiated energy. The concentration of element can be determinate with the aid of Lambert-Beer law [4] through wavelength dispersive measurement of this reduction. The Lambert –Beer law give the value of absorbance from each element of sample. The absorbance is proportional with the element concentration. The Atomic Absorption Spectrometer used by us is an AAS-AVANTA GBC with hollow cathode lamp (HCL). Measurements were made separately for each element of interest from sample using the calibration curve – absorbance versus concentration. This AAS has a motor turret with 8 lamps: a double beam system and spatial and temporal indexing, self-adjusting flame, wavelength and slit, self-correction of fond with a deuterium lamp (D₂). Technical data for this devise are presented in Table 2 as well.

Samples preparation

The weighed sample (2g) dissolved in HCl and HNO₃, until the removal of nitric oxides, has been filtered, and the obtained solution has been analysed in parallel with a control sample.

Table 1. Technical data for spectrometer with sequential emission plasma BAIRD ICP 2070

Monochromator	
Optic cells	Crezy-Turner, f/11
Focal length	1 meter
Wave length	160-800 nm (vacuum) 190-800 nm (air)
Diffraction net	1800 striae/mm marked at 400 nm
Detectors	Two photomultiplier selected tubes UV 160-290 nm VIS 290-900 nm
ICP	
Frequency	40,68 MHz (crystal controlled)
Power	2 Kw
Frequency stability	±0,05%

Table 2. Technical data regarding AAS GBC Avanta.

Wavelength (λ)	283,30 nm
Lamp current	5,00 mA
Introduction manner	Manual
Work field	7÷50 µg/ml
Measuring manner	Integration
Calibrating manner	The method of the smallest squares
Fuel flow rate	1,00 l/min
Oxidant flow	15 l/min

At the AAS, GBC Avanta Ver 2.02 the equation for the calibration curve is:

$$conc = \frac{Abs}{0,0029 \pm 0,0006 * Abs} \quad (1)$$

Technical data regarding the Optical Emission Spectrometer owned by S.C. MECHEL Targoviste S.A are centralized in Table 3.

Optical assembly:

- Paschen-Runge assembly with Rowland circle radius of 1 m;
- Cambered inwards diffraction net with 1667 tras/mm;
- Optical range;
- Primary slit: 20 μm
- Secondary slits: between 37,5 and 75 μm
- 28 mm photomultiplier tubes with multiplication levels

Table 3. Technical data for Optical Emission Spectrometer (OES) owned by S.C. MECHEL Targoviste S.A.

Diffraction order	Blase angle (nm)	Spectral range (nm)	The reverse of dispersion (nm/mm)
1	347	220÷528	0,60
2	173	160÷260	0,30
3	116	130÷176	0,20

Excitation source:

- Discharge source as electrical spark
- Digital source with control over the form of the discharge current (CCS)
- Highest values of CCS source parameters
- Current peak: 250A
- Discharge frequency: 80 Hz
- Current plate: 30A
- Source CCS advantages:
 - Reduction of analysis time by 40%
 - Reduction of intermediate effects by 40% compared to the standard sources

Data regarding the calibration curve of Pb are presented in Table 4.

Table 4. Data regarding the calibration curve of Pb with Spectrometer with Inductively Coupled Plasma (ICP)

Calibration curve type	Concavity range (%)	BEC (%)	SEE (%)	r ²
Grade 1polynome Coefficients: a ₀ = -0,01105 a ₁ = 0,00001	0÷0,010	0,00758	0,00206	0,991

Detection limit: 0,025 ppm

3. Results and conclusions

The CE95/2002 RoHS (Restriction of use of certain Hazardous Substances) directive restricts the lead amount to maximum 0.1%.

The results obtained using the Atomic Absorption Spectrometer and ICP-AES spectrometer is given in Figure 1.

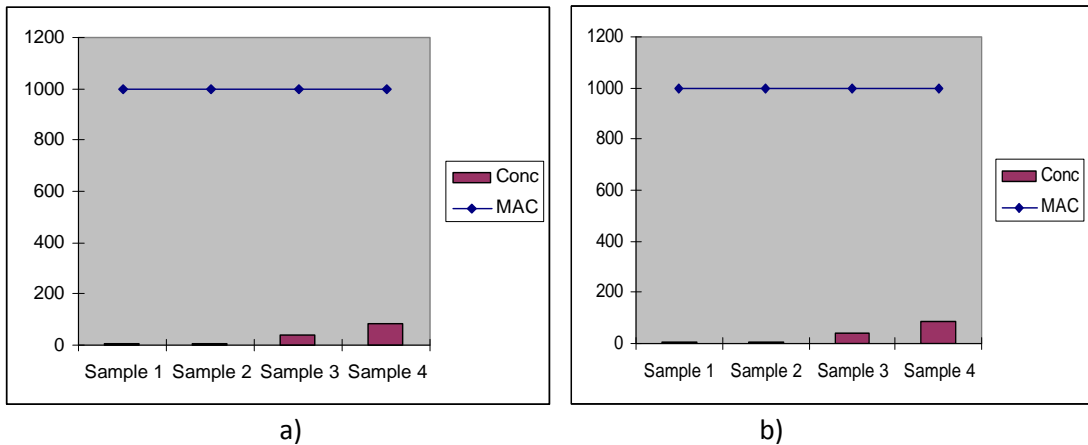


Figure 1. The results obtained by: a) AAS, b) ICP-AES spectrometer (where MAC is Maximum Admitted Concentration, and Conc. is concentration obtained in samples)

From this graph can be noted that the lead concentration in steel is well below 0.1%.

Lead can be easily analysed through the spectroscopic method of optic emission with excitation with electric spark in argon.

The spectral line used for lead analysis in Fe base is the 405.78 nm line, and the specific concentration level for this spectral line is 0.0000±0.500%.

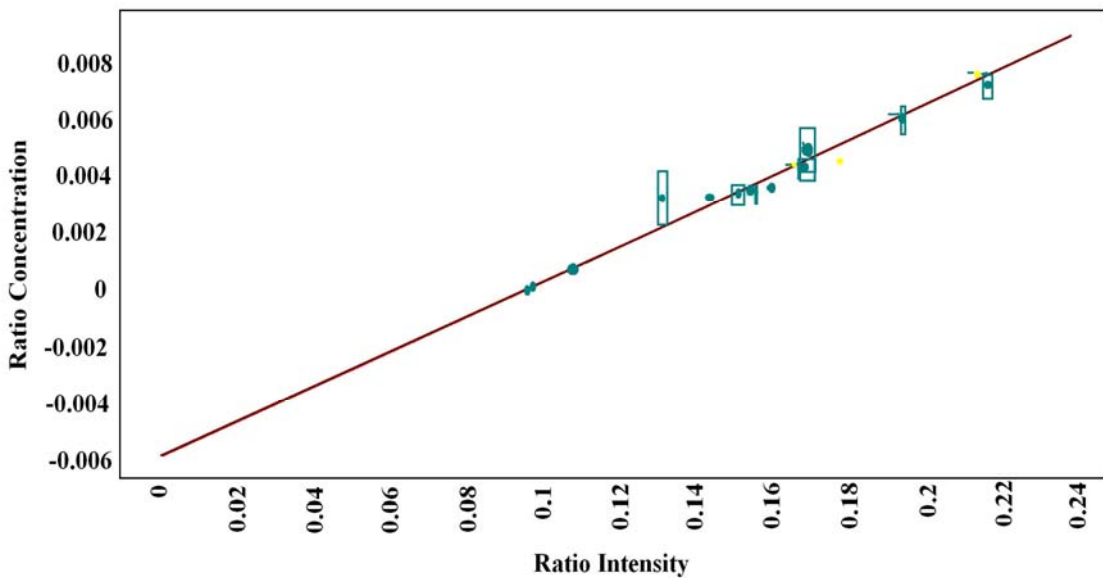


Figure 2. Calibration curve for lead

Using this spectral line in an Optic Emission Spectrometer ARL 4460, the following analytical performances can be:

- Typical detection limit: 1ppm
- Granulated detection limit: 2ppm
- Accuracy is shown in table 5.

Table 5. Concentration level and accuracy obtained with ARL 4460

Concentration level (ppm)	Accuracy expressed as absolute standard deviation at repeated measurements (ppm)
10	0.6
20	1
50	2
100	5
200	10
500	20
1000	40
2000	80
3000	120

- fond equivalent beaming(BBC)
- validity range of the calibration curve: 1÷14 ppm

According to this data, it can be concluded that using an Optic emission spectrometer ARL 4460, the lead in steels can be analysed according to the demands of the RoHS directive.

Another way to analyze the lead in steels is the spectroscopic method using X ray fluorescence.

In this method, a series of inconveniences appear:

- the PbK_{α} line, which is an intense one and would ensure a low detection limit, cannot be used because the X ray tubes usually used cannot withstand the high stress required to stimulate the PbK_{α} line
- using the PbL_{α} line, as technical alternative, is difficult due to the strong twinning with the intense line AsK_{α} . As in steels As is present in concentrations of the order 0,005-0,015%, determining the lead at concentrations below 0.1% becomes difficult.

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