

Electrochemical and Spectrophotometrical Methods for the Environmental Control

Maria POPA, "1 Decembrie 1918" University, Alba Iulia, Romania, mpopa@uab.ro

Abstract: *The electrochemical and spectrophotometrical methods are some of the most important methods for studying the chemical and biochemical processes and for finding traces of metals in various environments.*

We are interested in the field of the electroanalytical methods applied for the control of inorganic pollutants concentration (metal ions, nitrates) [1] and organic pollutants [2,3]. This paper presents the performance of different electrochemical and spectrophotometrical methods [4] applied for the control of environment.

Introduction

The environmental pollution entered the colloquial language not only as a result of the industrial emancipation but it broke into the scientists' preoccupation and conscience as a call and an imperative for implication.

As atmosphere pollutants, heavy metals through oxides and vapours (which are transformed in oxides in the atmosphere) contaminate especially the industrial areas surrounding Baia Mare, Zlatna, Copsa Mica etc., pollution thus becoming specific as in Baia Mare the pollution is caused especially by lead, in Zlatna by lead, cadmium, zinc, in Copsa Mica by zinc and cadmium [1].

The electrochemical and spectrophotometrical methods are some of the most important and interesting methods for studying the chemical and biochemical processes and for finding traces of metals in various environments.

The paper presents the principle of the electrochemical and spectrophotometrical methods and their application in the environmental protection, for the control of metallic pollutants.

Experimental Methods and results

1. Spectrophotometrical methods

Getting the analytical information in atomic spectrometry is based on the interaction between the electromagnetic radiation and the matter, this interaction covering a wide range of frequencies in the electromagnetic spectrum.

The UV range methods of atomic spectrometry, also visible in the infrared are generically called optic spectrometry. Toward the end of the past century the fact that the free atoms have an emission spectrum consisting of lines was already known, as well as the fact that the molecules have a spectrum consisting of very closed lines, apart from the solids and dense gases have a continuous spectrum. The atoms' feature of absorbing radiation with the same wavelength and to transmit them with emission and absorption frequencies, specific for each atomic species was also known [3].

1.1. Prepare the Basic Units of the Atomizer

Atomic absorption spectrometry is generally used for analysing liquid samples, which contain metal ions or heavy metal ions. During sample preparation, different mineral acids are used.

The burner-nebulizer system is moved to the park position with the help of the instrument-controlled software, and is then rotated to the right out of the sample chamber. The graphite tube atomizer, which was lowered into the rear of the sample chamber can now be cranked up into the sample chamber and locked. In the rotated and locked state, the respective atomizer is immediately, and without further adjustment aligned to the optical axis. The height of the flame atomizer can also be adjusted so that the measurement height within the flame can be adapted to suit the particular analysis conditions [4].

1.2. Measurement Principle

Instrumentation and software

The measurement principle entails the absorption of the element-specific primary radiation from a hollow cathode lamp (HCL) by atoms in their basic state, whereby the absorption signal shows a measure for the concentration of the respective element in the analysed sample. The HCL supplies a line spectrum, from which a suitable resonance line is uncoupled.

The desired HCL is rotated into the path of the beam by the PC-controlled 6-piece lamp turret. An optical beam splitter with squared reflection and transmission ranges in the checker pattern combines the radiation from the line radiator with the continuum radiation to form an identical emission path. In the area of the angle applicable for measurement, both sources of radiation have the same beam distribution and density, so that background compensation with the D2HCL to an absorbance of 2.0 is possible.

The continuum radiation of a D2HCL is used for compensation of the background absorption. The line radiator, with its extremely narrow resonance line encompasses the total absorption. The radiation from the D2HCL is mainly attenuated by the broadband element-non-specific absorption. The element-specific absorption is the difference between the two sizes. The intensities of both sources of radiation are checked automatically during routine operation and are adjusted if necessary [5].

Experimental parameters determination of Cd, Pb in plants

The investigation were performed using AAS vario[®] 6 equipped with autosampler MPE 5.

Tab. 1 Instrumental parameters

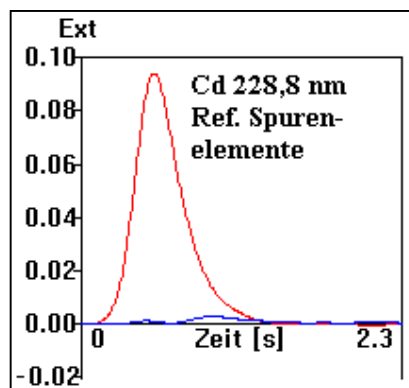
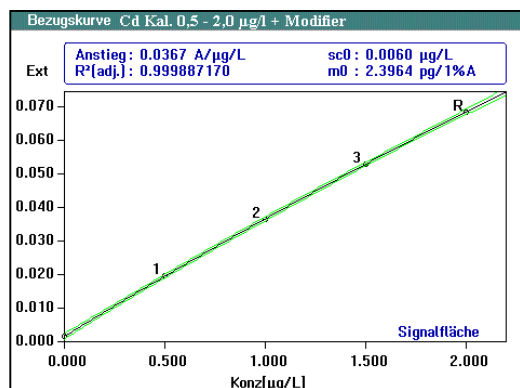
| Element | Wavelength [nm] | Slit [nm] | Lamp current [mA] | Graphite tube |
|---------|-----------------|-----------|-------------------|--------------------|
| Cd* | 228,8 | 0,8 | 8,0 | Pyrolytical coated |
| Pb* | 283,3 | 0,5 | 3,5 | Pyrolytical coated |

| Element | T _{pyrol} [°C] | T _{atom} [°C] | Ramp [°C/s] |
|---------|-------------------------|------------------------|-------------|
| Cd | 850 | 1500 | 1000 |
| Pb | 1000 | 1800 | 1300 |

* Deuterium background correction

Calibration

Cd: standard calibration; performed by diluting of autosampler MPE 5 in the furnace; stock solution 2.0 µg/l (0.5/ 1.0/ 1.5/ 2.0 µg/l Cd); standard were prepared in 0.6% HNO₃; 5 µl Pd/ MgNO₃ modifier; non-linear curve, peak area integration



Pb: standard calibration; performed by diluting of autosampler MPE 5 in the furnace; stock solution 20 µg/l (5,0/ 10,0/ 15,0/ 20,0 µg/l Pb); standard were prepared in 0.6% HNO₃; 5 µl Pd/ MgNO₃ modifier; linear curve; peak area integration

1.3. Automatic optimising routine – a prerequisite for efficient multielement analysis

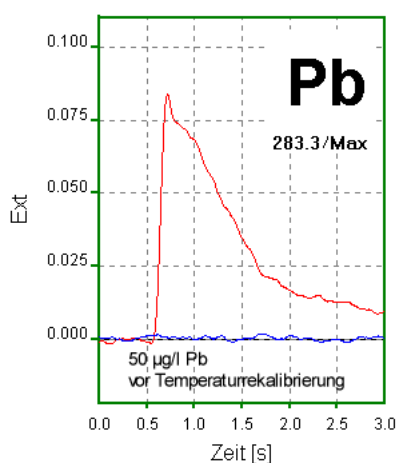
Advantage: Flame sensor control; High air volume for gently quenching; over pressure valve (protection of gas); Burner code to avoid false gas type; Siphon control.

Effect of uncorrected furnace temperature deviations

Optimisation of atomisation temperature for lead
(Peak-height analysis - left and peak-area analysis - right)

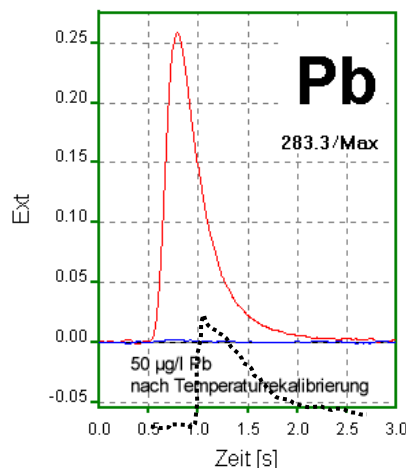
For testing the temperature effects through tube ageing, the optimised method for Pb was applied to a tube with approx. 800 runs without and with temperature recalibration

◆ Pb signal before temperature recalibration



ABS(H): 0,0897 RSD: 5,06 %
ABS(A): 0,0825 RSD: 4,57 %

◆ Pb signal after temperature recalibration

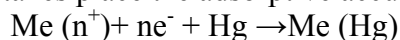


ABS(H): 0,2438 RSD: 2,74 %
ABS(A): 0,1178 RSD: 1,24 %

The comparison clearly shows the loss in sensitivity in the case of faulty atomisation temperature and the importance of the formation routine also during the analytical process.

2. Electrochemical Techniques

Preconcentration (plating) consists in the application of a constant reductive potential for a period of time, when takes place the adsorptive accumulation of metal on Hg surface:



In the case of stripping, the metal ions or metal-complex accumulated on Hg surface are oxidised and the oxidation current is proportional with the metal concentration.

2.1. Instrumentation and software

The computer aided instruments used for potential control was BAS 100W equipped with Controlled Growth Mercury Electrode (CGME) West Lafayette, USA and the Portable Trace Element Analyser, PTEA –WAGTECH equipped with glassy carbon electrode, GCE. The classical three electrodes cell has been used for the cyclic voltammetry determinations (WE- GCE; CE- Pt wire and RE - Ag/AgCl). Reference (Ag/AgCl) and Pt wire auxiliary electrodes used to this work, were from BAS Co. The UNICAN Helios β UV-VIS spectrometer has been used to control the results of the electrochemical methods.

Tab. 2 Experimental parameters

| Experimental parameters | Cr | Ni | Cu | Zn |
|-------------------------|-------|-----------|-------|-------|
| E1 | -1600 | -1400 | -1000 | -1400 |
| E2 | 600 | -650 | -350 | -1200 |
| E3 | 900 | -100 | 0 | -850 |
| E4 | 1500 | 500 | 50 | 100 |
| T2 | 10 | 10 | 10 | 10 |
| Potential (max) | 850 | -500 | 10 | -900 |
| Potential (min) | 500 | -150 | -150 | -1100 |
| Electrolyte | ACCH | Con. ACCH | ACCH | ACCH |

The samples were rendered soluble in HNO₃ 0.5 M, at a volume of 50 ml. The quantity of dried vegetable material used was of 0.5 g [6].

Results and discussions

Consequent to measurements, high concentration values were registered in the area under study (Zlatna-Romania)[6]. The precision of the results is higher in the case of the samples that had a high concentration in heavy metals (Pb or Cd).

Tab.3 Lead in vegetal material

| Analysed sample | Pb (($\mu\text{g/g}$)) | |
|-----------------|--------------------------|-------|
| | Stripping Potentiometry | GFAAS |
| Corn | 88,9 | 90 |
| Potatoes | 59,5 | 60 |
| Cabbage | 149,6 | 150 |
| Spinach | 188 | 200 |
| Wine (Riesling) | 27,8 | 28 |
| Wine (Cabernet) | 13,8 | 14 |
| Onion | 96 | 100 |
| Carrot | 57,9 | 60 |
| Pepper | 9,1 | 9 |

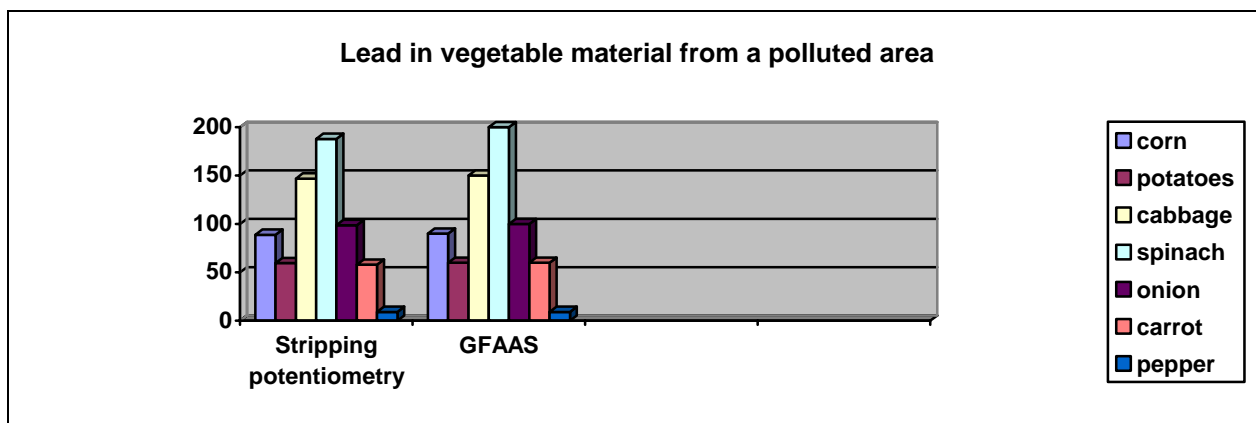


Fig.1 The value in the Table is the average of five determinations

For soils, the method of atomic absorption in flame (AAS) was used because the concentration of heavy metals in the soils is much higher than in the vegetable material samples. Through dilutions systematic errors may occur, this method of AAS in flame being thus preferred. Likewise, hydrochloric acid cannot be used for rendering soluble the samples that will be measured in the graphite furnace, as there is the possibility of losing the metals from the samples under analysis by (volatile) metallic halogens formation [6].

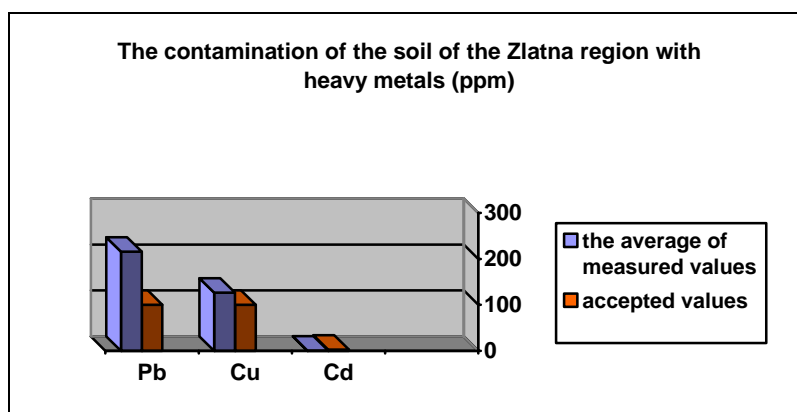


Fig.2 The contamination of the soil the Zlatna region with heavy metals (ppm)

Conclusions

We can notice that the difference between the two methods is not very significant, but the choice of the work method is important when the concentration of the researched element is of ppm or ppb values. In the case of the exposed methods especially samples that contain heavy metal in traces are used; AAS in flame is recommended for the environment samples that contain heavy metals in a higher concentration (soils, waste waters etc.)

The heavy metals retained by the organic and mineral part of the ground substantially limit the biological activity of the ground having as effect inhibition of the processes of nitrification, one of the essential conditions of the fertility of the ground

By holding account also of impacts on the human component of the studied area but not only, a rigorous control [7] of the exceeding concentration of the pollutants in the affected areas is necessary as well as the evaluation of the consequences and the application of measurements for the reduction in this disastrous phenomenon.

Acknowledgements

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