

MEASUREMENT OF MOBILE TRACE METALS FROM POLLUTED SOILS IN INDUSTRIAL SITES

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Abstract. Mobile trace elements in soils can adversely affect the quality of food, the growth of plants, the activity of soil microorganisms and the quality of the groundwater. To establish the level of pollution induced in the environment (transfer through solubilisation in groundwater, accessibility for plants) it is very important to know the content of mobile forms of heavy metals. The standard method ISO 14970/99, with the modified ratio between soil and solution of extraction (1:10 for acid soils), was used as a basis of assessment, as a sensitive instrument to detect soils with high amounts of potentially leachable elements (Cd and Pb). It was necessary to apply traceability concept on environmental soil measurements ('in house' validation of method), to ensure reproducibility, accuracy (trueness and precision) of measurements of mobile trace metals. The experiments conducted to conclusive and valuable data regarding the pollution of industrial activities (e.g. mining, metallurgic activities) on the environment.

Keywords: mobile trace element, measurement, polluted soil, traceability, Cd, Pb.

AIMS AND BACKGROUND

As a result of the accelerated industrial activities during the last decades, in several areas of the world, exposure of the population to the high levels of metals caused some effects like critical diseases among sensitive groups. The major critical organs exposed to the influence of the environmental pollution with heavy metals are the kidney (Cd) and the central nervous system of the developing fetus and the child (Pb and Hg)¹.

The increased concentration of Cd and Pb in polluted soils from the vicinity of the industrial areas (mining and metallurgic plants) is the effect of the migration of the pollutant from mining waste disposal storage and the result of atmospheric depositions, mainly from smelting and reforming of the nonferrous metals, fossil fuel combustion and municipal waste incineration. The atmospheric conditions of the last years (e.g. acidification, global warm, floods) allow cadmium and lead migration inside soil structure in groundwater.

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For these reasons, estimation of mobile Cd and Pb from polluted soils became very important analyses in monitoring studies of the environmental protection.

Because the most researches developed in our country are related to microelements availability from agricultural land, the method used for extraction of mobile Cd and Pb from soil² is adapted for these types of soils.

This method uses a ratio between soil and extraction solution of 1:2 (w/v), ineffective for the extraction of mobile species of metals from polluted soils. In principal, the mobility percentage depends on different factors, e.g. pH values, geo-morphological structure and the total content of the metals. The extraction percentage from soils with neutral or alkaline pH is higher than from soils with acid pH, because the mobility is lower.

In the first stage of the research activity it was necessary to select an optimal extraction method³. During the experiments were used both European and international standards^{2,4-6} and non-standard method (extraction with 1M MgCl₂ at a buffer solution of pH= 7 ± 0.2 and a ratio soil/solution of 1:10)⁷.

The solution used for extraction of the mobile forms of metals (mixture of weak acids, salts, organic ligands) is not specific for one element and for this reason during the extraction procedure are extracted different elements (e.g. Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn). It is very important to find the optimal working condition to ensure the extraction of all mobile species.

In the research³, the tests were performed on polluted soils with clay structure, acid and easy alkaline pHs, drawn in the vicinity of a mining waste disposal storage.

The conclusion of the research is that the method² is not able to extract all mobile species of metals in one single step of the chemical extraction. The method⁶, which uses a ratio between soil and solution of 1:10, provides a good report for extraction of high quantity of mobile forms of metals from polluted soils.

When method SR ISO 14870/01 (Ref. 2) (mixture of DTPA, TEA and CaCl₂ in a buffer solution of pH 7.3) was used with the purpose to extract mobile species of metals from anthropic soils it was necessary to improve the ratio between soil and solution or to use successive steps of the extracture procedure with fresh buffer solution at a ratio 1:2 (w/v)⁸. The next analytical experiments⁹ established an optimal ratio of extraction, which allows the use of the method² also for the analyses of polluted soils.

The total results of successive steps of extraction were compared with the results obtained with one single chemical extraction at different ratios (1:5, 1:7, 1:10, 1:12) (Ref. 9). The total values from 5 successive steps of extraction were similar with the results obtained with one extraction at a ratio soil/solution of 1:10 (for soil with acid pH). A higher ratio is not necessary because the differences are not significant, the ratio 1:10 being enough to extract the mobile species of metals from polluted soils with acid pH. In conclusion, using one single step of extraction

is a major advantage, because the procedure with successive steps is difficult to be performed and is time consuming (at least 2 h for each step of extraction)⁹.

The actual researches were continued with the 'in-house' validation of the method developed in the laboratory for the extraction and determination of mobile Cd and mobile Pb.

Method validation means the process of verifying that a method fits for the purpose, i.e. for solving a particular analytical problem. Validation studies for quantitative analytical method typically determine some or all of the following parameters: detection limit, quantification limit, working range, specificity, selectivity, ruggedness or robustness, recovery, accuracy, precision, repeatability and reproducibility.

This paper proposes to validate a method of Cd and Pb extraction mobile forms using the standard method² with a single chemical extraction procedure and modifying the extraction ratio, which allows extraction of high quantity of metals from anthropic soils with acid pH.

A flame atomic absorption spectrometry method¹⁰, adapted to the extraction solution (mixture of DTPA, TEA and CaCl₂), was used for the quantitative determination.

EXPERIMENTAL

Apparatus. Atomic absorption spectrometer ATI UNICAM type 929, shaker.

Reagents. Merck solution for calibration (1 g Cd/l), hydrochloric acid 37%, DTPA (Merck), TEA (Merck), calcium chloride (Merck), extraction solution ($c_{\text{TEA}} = 0.1$ mol, $c_{\text{CaCl}_2} = 0.01$ mol/l, $c_{\text{DTPA}} = 0.005$ mol/l, pH = 7.3 ± 0.2).

Procedure. 5 g of pretreated sample¹¹ were mixed with 50 ml of extraction solution by shaking at 40 rot./min for 2 h. The dried mater content was determined on a separate fraction of the sample¹². The filtrated solution was analysed maximum for 48 h. For each set of samples was prepared a blank sample, using the same procedure.

The experiments consisted of analyses of blank samples fortified at lowest acceptable concentration and of sample with known concentration prepared from a standard solution. The calibration curve was made in the range from 0.25 to 2.5 mg/l for Cd and 1.0-21 mg/l for Pb. The results were used for evaluation of the working range.

For the determination of the detection limit, the quantification limit and the lowest value of the working range it was necessary to prepare 5 blank solutions fortified at the lowest acceptable concentration (0.08 mg Cd/l; 0.1 mg Pb/l).

The intermediary precision was established by analysing 11 samples of known concentration (2 mg Cd/l; 8 mg Pb/l) by two different analysts, using the same equipment, same method, within appropriate time interval (one day).

The standard deviation, variation coefficient and repeatability of the method were checked using 11 solutions of known concentration (2 mg Cd/l; 8 mg Pb/l), prepared from a reference material. Also, it was necessary to prepare other 11 solutions for each concentration: 0.5 mg/l, 2.5 mg/l for Cd and 1 mg/l, 16 mg/l for Pb. Recovery was calculated using data produced by 3 different analysts.

RESULTS AND DISCUSSION

The values of performance parameters are presented in Table 1 for Cd and in Table 2 for Pb.

Table 1. Performance parameters for extraction and determination of Cd mobile form from polluted soils

Parameter	Value	Parameter	Value
Standard deviation	100.54%	bias	0.54%
Coefficient of variation (RSD)	1.54%	working range	0.1-2.5 mg Cd /l
Repeatability	1.56%	intermediary precision	1.59%
Equation of the curve	$y = 0.00547 + 0.10865 x$	sensitivity	$b = 0.10865$ absorbance/mg l ⁻¹
Coefficient of correlation R ²	0.9992	intersection with y axes	0.00547
Limit of detection	0.0078 mg/l	limit of quantification	0.106 mg/l
Recovery	analyst I: % recovery = 100.9-105 % analyst II: % recovery = 99.6-104.3 % analyst III: % recovery = 103-104.4 %		

Table 2. Performance parameters for extraction and determination of the mobile form of Pb from polluted soils

Parameter	Value	Parameter	Value
Standard deviation	100.87%	bias	0.87%
Coefficient of variation (RSD)	1.85%	working range	1.0-16 mg Pb /l
Repeatability	1.64%	intermediary precision	1.89%
Equation of the curve	$y = 0.0043 + 0.0243 x$	sensitivity	$b = 0.0243$ absorbance/mg l ⁻¹
Coefficient of correlation R ²	0.9996	intersection with y axes	0.0043
Limit of detection	0.0095 mg/l	limit of quantification	0.130 mg/l
Recovery	analyst I: % recovery = 98.6-101.7 % analyst II: % recovery = 100.8-101.4 % analyst III: % recovery = 99.5-100.8 %		

Standard deviation is optimal, respectively 100.54% for Cd and 100.87% for Pb and also the bias is optimal, both values being less than 1%. The correlation coefficient of the calibration curves has a very good value (0.9992 for Cd and 0.9996 for Pb).

The working range is linear in the concentration range of 0.1-2.5 mg/l for Cd and 1.0-16 mg/l for Pb, which allows analysing a lot of samples with a large spectrum of concentration.

The values of coefficient of variation (1.54% for Cd and 1.85% for Pb), less than 2% according to the Horwitz function¹³, situate the test method as a good spectrometric method. The repeatability studies performed by the same analyst, on the same equipment in a short period of time, show the competence of the analyst and the good working conditions of the equipment. Also for the experiments of the intermediary precision, when was used the same equipment, but different analyst performed the analyses were obtained good results, even if it was observed a difference induced by the working abilities of each analyst.

For a concentration of 1-10 mg/l, recovery must be in the range between 80 and 110% (Ref. 13, Table 5, accepted recovery percentage as a function of the analyte concentration). In Tables 1 and 2, all the values of recovery obtained by three different analysts for the mobile Cd and Pb are situated in this range.

In Fig. 1 is presented the calibration curve for extraction and determination of mobile forms of Cd from polluted soils and in Fig. 2 – the curve for mobile Pb.

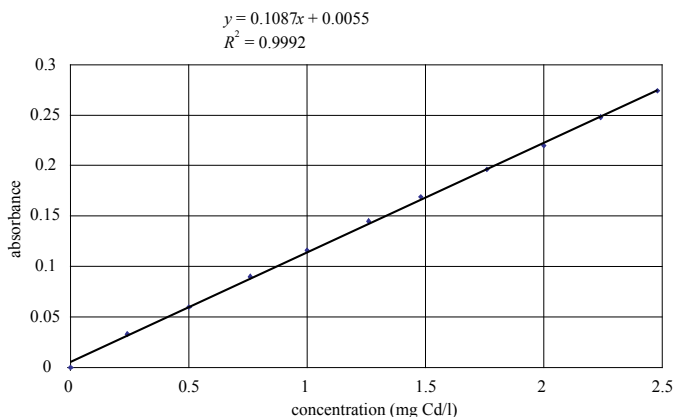


Fig. 1. Calibration curve for determination of mobile Cd with a mixture of DTPA, TEA and CaCl₂

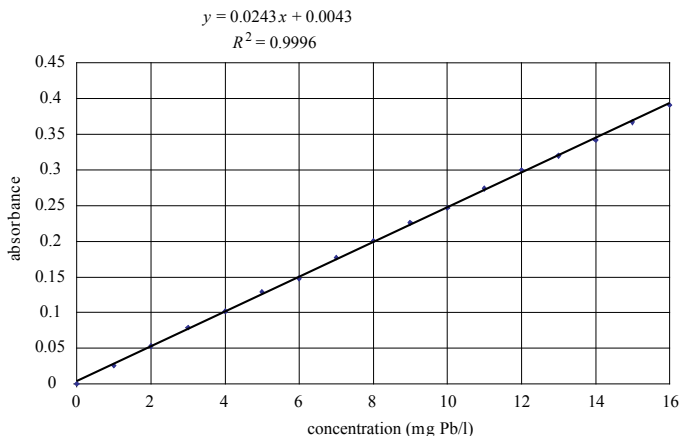


Fig. 2. Calibration curve for determination of mobile Pb with a mixture of DTPA, TEA and CaCl₂

CONCLUSIONS

The statistical interpretation of the experimental results proved that the proposed method can be successfully used for the analytical control of the mobile forms of Cd and Pb. The method of extraction and determination was validated.

REFERENCES

1. A. M. BERNARD: Contaminated Soils. Ed. INRA, Paris, 1997, 21-34.
2. SR ISO 14870/01: Soil Quality–Extraction of the Microelements in Solution of DTPA.
3. G. VASILE, L. CRUCERU, J. PETRE, V. IANCU, R. MITRAN: Analytical Investigation Concerning the Methodology for Extraction of Exchangeable Forms of Heavy Metals from Different Types of Soils. *J. of Environ. Protection and Ecology*, **7**(3), 562 (2006).
4. ONORM L 1094-2/1994. Chemical Analyses of Soil: Extraction of Mobile Elements Using Ammonium Acetate.
5. DIN 19730/1997. Extraction of Mobile Form of Microelements Using Ammonium Nitrate.
6. NF X 31-120/1992. Determination of Cd, Cu, Mg and Zn from Soils Using a Buffer Solution, Mixture of EDTA and Ammonium Acetate.
7. A. TESSIER, P. G. C. CAMPBELL, M. BISSON: Sequential Extraction Procedure for the Speciation of Particulate Trace Metals. *Anal. Chem.*, **51**, 844 (1979).
8. W. P. COFINO: *Mikrochim. Acta*, **123**, 151 (1996).
9. G. VASILE, L. CRUCERU: Optimized Method Used for the Extraction of Mobile Species of Heavy Metals from Polluted Soils. *J. of Environ. Protection and Ecology*, **8**(4), 801 (2007).
10. SR ISO 8288/01. Water Quality – Determination of Cd, Co, Cu, Pb, Ni and Zn. Flame atomic Absorption Spectrometry Method.
11. SR ISO 11464. Soil Quality – Pretreatment of the Samples for Physicochemical Analyses.
12. SR ISO 11465. Soil Quality: Determination of Dry Matter Content – Gravimetric Method.
13. I. TAVERNIES, M. De LOOSE, E. VAN BOCKSTAELE: Trends in Quality in the Analytical Laboratory. II. Analytical Method Validation and Quality Assurance. *Trends in Analytical Chemistry*, **23** (8), 535 (2004).

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