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COMPARATIVE STUDY OF MERCURY DETERMINATION IN SOIL AND VEGETABLE BY METHODS BASED ON THERMAL DECOMPOSITION-AAS AND WET DIGESTION CV-AFS

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ABSTRACT. The aim of this study was to evaluate and compare the analytical parameters of two methods used for mercury determination from solid samples (soils and vegetables): direct determination from solid samples by thermal decomposition - atomic absorption spectrometry (TD-AAS) with gold amalgamation and determination using wet digestion followed by measurements by cold vapor atomic fluorescence spectrometry (CV-AFS). Two commercially available mercury (Hg) analyzers were used for the study. Using direct measurement in solid sample by TD-AAS, a detection limit of 1.2 μg kg^{-1} and a RSD of 3.8% for 1441 μg kg^{-1} Hg were obtained, while by using wet digestion and CV-AFS measurement, a detection limit of 2.5 μg kg^{-1} and a RSD of 4.5% for 1438 μg kg^{-1} Hg were calculated. The accuracy of the methods was verified by the determination of mercury in certified reference materials and good agreement between found concentrations and certified values was obtained for the both methods. Five real soil samples and five vegetable samples from Baia Mare area were analyzed. The Hg concentrations in soils ranged between 653–2004 μg kg^{-1} using TD-AAS method and between 644-1998 μg kg^{-1} using CV-AFS method, while in vegetables the concentrations ranged between 4,60-53,4 μg kg^{-1} using TD-AAS method and between 4,32-55,8 μg kg^{-1} using CV-AFS method. According to the t-Test and regression analysis, no significant statistical difference between the datasets obtained by the two methods was found.

Keywords: *mercury determination, soil samples, vegetable samples, TD-AAS, CV-AFS*

INTRODUCTION

As a consequence of natural and anthropogenic processes high amounts of mercury is released into the hydrosphere, atmosphere and biosphere. This element occurs naturally as the metallic form and/or its sulfide ores such as cinnabar (HgS) [1]. The earth's crust contains 0.5 mg kg^{-3}, ambient air may contain 0.002-0.02 pg dm^{-3}, and sea water contains about 0.03 mg dm^{-3}

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mercury. It is also found in trace amounts in most animal and plant tissues. Due to his volatility, elemental mercury is efficiently transported as a gas around the globe, and even remote areas [2, 3].

Hg poisoning may lead to damage in the central nervous system [4]. Due to its high toxicity, mercury (Hg) is considered one of the most dangerous pollutants, being in the lists of priority dangerous substances established by the United States Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the European Water Framework Directive (2000/60/EC) [5]. From 2011 export of mercury from the EU will be prohibited in order to further reduce its release [5]. As a consequence of its toxicity, it is very important to make accurate determinations of mercury in environmental samples.

A variety of analytical techniques can be used for mercury determination. The most popular methods for determining mercury in almost any type of sample are based on cold vapor atomic absorption spectrometry (CV-AAS) and cold vapor atomic fluorescence spectrometry (CV-AFS) [6-8]. The way of liberating mercury from aqueous or digested samples is reduction, followed by volatilization and introduction of the mercury by aid of a gas stream. A gold amalgamation method to purify the mercury vapor can be used [9]. Inductively coupled plasma mass spectrometry (ICP-MS) can be also successfully applied for mercury analysis [10, 11], including for mercury speciation, but not always under routine operating conditions.

The majority of analytical methods for the determination of mercury in solid samples are based on wet digestion [12, 13]. Ultrasound-assisted leaching is an alternative and effective way of extracting the analytes from samples [14]. The techniques using wet digestion followed by cold vapor generation are generally time-consuming and in addition, high amounts of harmful and expensive reagents are necessary. Also, the risk of contamination by supplementary pretreatment steps is high [15, 16]. A good alternative to wet digestion is the use of *reagent-free* methods, based on thermal decomposition of solid samples or extraction and preconcentration from liquid samples. These alternatives are in accord with new approach of use non-chemical methods leading to green analytical chemistry [17- 20].

Thermal decomposition (pyrolise) - atomic absorption spectrometry is a *reagent-free* analytical method in that decomposition products are carried to a catalyst by an oxygen flow, then sample oxidation is completed and halogens and nitrogen/sulphur oxides are trapped. The final decomposition products pass through a mercury amalgamator which collects Hg^0. The Hg amalgamator is heated at high temperature and the Hg^0 is released and quantified using the spectral method [21-26].

The aim of this study was to evaluate and compare the analytical parameters of the method based on thermal decomposition atomic absorption spectrometry with those of wet digestion – cold vapor atomic fluorescence spectrometry, and to apply these methods for mercury determination in real solid samples (soils and vegetables) collected from Baia Mare (NW Romania) area.

RESULTS AND DISCUSSIONS

Performance parameters of analytical methods

Mercury determinations in soil and vegetable samples were carried out using two commercially available automated Hg analyzers. Direct measurements on solid samples were done using a TD-AAS analyzer, while the solutions obtained by wet digestion were analysed using a CV-AFS analyzer.

Limits of Detection (LOD) and Limit of Quantitation (LOQ) were calculated using the 3s criteria. For TD-AAS method, the SBR was determined for a concentration of 1400 μg kg^{-1} Hg, while the relative standard deviation of the background (RSDB) was calculated from 10 successive measurements for the background signal, at analytical wavelength of 253.65 nm. The calculated value for detection limit was 1.2 μg kg^{-1}, using high sensitivity cell for measurement. Limit of quantitation was calculated as being 3.6 μg kg^{-1} in solid samples (was considered to be three times the LOD). For CV-AFS method, the SBR was determined for a concentration in solution of 10 μg L^{-1}, while the RSDB was calculated from measurements of 10 independent black solutions at wavelength of 253.65 nm. The detection limit in liquid solution was 0.025 μg L^{-1}. For digestion of 1 g of sample, and dilution to 100 mL the detection limit in solid sample was calculated as being 2.5 μg kg^{-1}, while the limit of quantitation was 7.5 μg kg^{-1}.

Working ranges. In the Mercury Analyzer TD-AAS, the signal is measured in series by a high sensitivity cell followed by a low sensitivity cell. Using the two cells, a wider working range is obtained. For high sensitivity cell, the calibration curve was linear up to 50 ng Hg, and for low sensitivity cell, up to 600 ng Hg. If 10 mg sample is weighted and introduced in the system, the upper limit of working range is 600 mg kg^{-1}. Using the CV-AFS system the upper limit of working range is 250 μg L^{-1} in liquid sample and 25 mg kg^{-1}, if 1g of solid sampled is digested.

According to the Romanian legislation the normal value for Hg concentration in soil is 100 μg kg^{-1}, the alert threshold for sensitive areas is 1000 μg kg^{-1}, and the intervention threshold 2000 μg kg^{-1}. All this values can be easily measured by TD-AAS and also by CV-AFS methods.

The **trueness** was studied by analyzing a Certified Reference Material in soil matrix, SRM 2709, and two CRMs in vegetable matrices, NCS 85 006 (Tomato) and IAEA-359 (Cabbage). The obtained results compared to certified values of mercury are presented in Table 1.

Table 1. Results of Mercury Determination in Various CRMs by TD-AAS and CV-AFS (mg kg^{-1})

CRM	*Certif. value*	*Found*	
		TD-AAS	*CV-AFS*
SRM 2709 soil	1.40±0.08	1.441±0.055	1.438±0.067
NCS ZC 85 006 tomato	0.14±0.022	0.152±0.006	0.144±0.014
IAEA-359 cabbage	0.013±0.002*	0.014±0.001	0.014±0.002

Values are reported with 95% confidence limit (*n* = 10).
* Information Values

For all analyzed CRMs: SRM 2709, NCS ZC 85006 and IAEA-359, good agreements of the results obtained by TD-AAS and CV-AFS with the certified values were obtained. No significant statistical differences were found at the significance level $p<0.05$ in all the cases.

Table 2. Mercury content in soil and vegetable samples measured by TD-AAS and CV-AFS (μg kg^{-1}), presented as confidence interval

Sample	**TD-AAS directly from solid sample**	**CV-AFS using microwave digestion**
Soil 1	1253±50	1143±79
Soil 2	653±28	644±47
Soil 3	983±32	985±63
Soil 4	2004±76	1998±97
Soil 5	1050±44	1071±65
Vegetable 1	19.7±1.0	18.8±2.2
Vegetable 2	53.4±3.4	55.8±5.2
Vegetable 3	4.92±0.42	4.96±0.58
Vegetable 4	20.8±1.5	20.0±1.8
Vegetable 5	4.60±0.44	4.32±0.38

Values are reported with 95% confidence limit (*n* = 10).

Precision of the method was evaluated in terms of repeatability. The repeatability was checked by carrying out 10 replicates on separate soil and vegetable subsamples, using the two methods: TD-AAS and CV-AFS, after microwave digestion. The results are presented as confidence interval, in Table 2.

In to compare the two sets of data obtained by the two methods, regression analysis and T-test for dependent samples were used. Using the T-test for dependent samples, and adopting the null hypothesis, no significant differences were found, the value of t_{calc} being lower than t_{tab} ($p=0.05$, $\nu=8$).

In the regression analysis, satisfactory agreement between the two sets of results was obtained, the correlation coefficient (r) and the slope (b) of the regression equation do not differ significantly from the unity and the intercept does not differ significantly from zero for a 95 % probability level considered within this study. The parameters of linear regression are presented in the Table 3.

Table 3. Linear regression parameters for a 95% confidence level for mercury determination in soil and vegetables by TD-AAS and CV-AFS

Regression analysis	Values
Intercept	-5.667±15.497
Slope	0.984±0.017
Correlation coefficient	0.9987

CONCLUSIONS

A comparison study of performance parameters of two methods used for Hg determination in solid samples: TD-AAS and wet digestion followed by CV-AFS was conducted. Detection limits in solid samples are lower in TD-AAS method, but in the same order of magnitude for the two methods. Working range of the both methods make possible the easily determination with a good accuracy of normal value, the alert threshold and the intervention threshold for Hg concentration in soil established by Romanian environmental legislation. The accuracy of methods was verified by the determination of mercury in the certified reference materials of soil and vegetables an no significant differences were found at the significance level $p<0.05$ in all the cases.

Differences between values measured in soil and vegetables by CV-AFS and TD-AAS were statistically evaluated using multiple regression and T-test for dependent samples. No significant differences between the two methods were found.

EXPERIMENTAL PART

Instrumentation

The direct measurements of mercury from solid samples were carried out using an Automated Direct Hg Analyzer Hydra-C (Teledyne Instruments, Leeman Labs, USA), based on thermal desorption atomic absorption spectrometry.

A Cold-Vapor Atomic Fluorescence Spectrometer Hydra-AF (Teledyne Instruments, Leeman Labs, USA) was used for mercury determination from digested samples.

A mortar grinder PM 100 Retsch (Germany) and a sieve shaker Fritsch Analysette 3 Spartan (Germany) were used for samples grinding and sieving.

A closed-vessel microwave system Berghof MWS-3+ with temperature control mode, (Eningen, Germany) was used for wet digestion.

Reagents, Standard Solutions and CRMs

Stock standard solutions of mercury (1000 mg L^{-1}) Merck (Darmstadt, Germany) was used for instruments calibration. For all dilutions ultrapure water (18 MΩ cm^{-1}) was obtained from a Millipore Direct Q3 (Millipore, France).

$SnCl_2 \cdot 2H_2O$ and 30% (v/v) HCl ultrapure both from Merck (Darmstadt, Germany) were used as reductant reagent for CV-AFS system.

Concentrated HNO_3 and HCl suprapure from Merck (Darmstadt, Germany) were used for samples digestion.

Soil CRM SRM 2709 San Joaquin Soil (New York, USA) and vegetable CRMs NCS ZC 85006 Tomato (Beijing, China) and IAEA-359 (Vienna, Austria) were used in the internal quality control of Hg determination.

Oxygen (4.5 quality) for Hydra-C Analyzer and Argon (5.0 quality) for Hydra-AF Analyzer supplying, both from Linde Gas SRL Cluj-Napoca, Romania were used.

Direct Hg determination in solid samples

Soil and vegetable samples were collected in Jully 2009 from Ferneziu, Baia Mare, NW of Romania. Ferneziu is a district of Baia Mare, situated in the north-east of it. This is located near to plant ROMPLUMB, whose activity has caused extensive pollution of the area with heavy metals [27-29].

Soils were sieved through a 2 mm sieve in order to eliminate stones and other materials extraneous to soil, and then stored in polyethylene bags for transport to the laboratory. The sieved soils were spread over a polyethylene sheet and air-dried at room temperature for one week. Samples were ground to a fine powder in a tungsten-carbide swing mill for 3 min and sieved through 100 micron mesh sieve. The fraction below 100 microns was further homogenised by mixing in a PVC drum for 1 h, then stored in brown glass bottles at room temperature until analysis. The vegetable samples were dried in oven, grounded using a grinder and sieved through 100 micron mesh sieve.

The Hydra-C Hg Analyzer includes a furnace module in that the sample is dried and decomposed at high temperature that assures a homogenous decomposition of sample. Decomposition products are carried to a catalyst by an oxygen flow, where sample oxidation is completed and halogens and nitrogen/sulphur oxides are trapped. The final decomposition products pass through a mercury amalgamator which collects Hg^0. By heating of amalgamation tube, mercury is released and carried to the atomic absorption spectrometer.

The transient signal is measured in series by two cells: a high sensitivity cell and a low sensitivity cell. The samples were weighted in nickel boats. Table 4 shows the instrument parameters employed for soils and vegetables.

Calibration was completed using aqueous standards prepared in 10% HNO_3. Working standards were blank, 0.1, and 1.0 ppm at six different injection weights. The calibration curve plots microabsorbance vs total mercury injected.

Table 4. Instrumental parameters of TD-AAS system

Parameter	***Setting***
Dry	300°C for 45 sec.
Decomposition	800°C for 150 sec.
Catalyst	600°C
Catalyst Wait Period	60 sec.
Gold Trap	700°C for 30 sec.
Measurement	90 sec.
Oxygen Flow Rate	300 mL min^{-1}

Determination of Hg by wet digestion and CV-AFS

Amounts of 1.000 g soil were digested with 10 ml *aqua regia* in closed PTFE containers of the microwave system. For vegetable, amounts of 1.000 g sample were digested with 6 ml concentrated nitric acid and 2 ml hydrogen peroxide in closed PTFE containers of the microwave system. After cooling to room temperature, the slurry was diluted to 100 ml with ultrapure water and then filtered under vacuum through a 0.45 μm cellulose membrane using the Sartorius vacuum filter equipment. At the end of this process, clear solutions were obtained. Digested samples were analyzed by CV-AFS method. Hydra AF is a continuous flow system where sample and reductant, in this case 2% $SnCl_2 \cdot 2H_2O$ in 3.6% (v/v) HCl ultrapure, are pumped into a gas/liquid separator. There the mercury in the sample is reduced to elemental mercury, which enters in the gas phase and is carried to the spectrometer. Instrument parameters are provided in the Table 5.

Table 5. Instrumental parameters of CV-AFS system

Parameter	***Setting***
Argon Flow Rate	700 mL min^{-1}
Sample Flow Rate	5 mL min^{-1}
Reductant Flow Rate	1 mL min^{-1}
Uptake time	20 sec.
Rinse time	60 sec.
Integration time	15 sec.

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REFERENCES

1. M. Morita, J. Yoshinaga, J. Edmonds, *Pure & Appl. Chem.*, **1998**, *70*, 1585.
2. F.M.M. Morel, A.M.L. Kraepiel, M. Amyot, *Annu. Rev. Ecol. Syst.,* **1998**, *29*, 543.
3. L.D. Hylander, M.E. Goodsite, *Sci. Total Environ.*, **2006**, *638*, 352.
4. A.G. Bravo, J. Loizeau, L. Ancey, V. Ungureanu, J. Dominik, *Env. Sci. Pollut. Res.*, **2009**, *16-S1*, 66.
5. K. Leopold, M. Foulkes, P. Worsfold, *Anal. Chim. Acta*, **2010**, *663*, 127.
6. V.L. Dressler, E.M.M. Flores, D. Pozebon, L.E. Kaercher, *J. Anal. At. Spectrom.*, **2002**, *17*, 790.
7. P.R. Aranda, R.A. Gil, S. Moyano, I. De Vito, L.D. Martinez, *J. Hazard. Mater.*, **2009**, *161*, 1399.
8. H. Ashkenani, S. Dadfarnia, A.M.H. Shabani, A.A. Jaffari, A. Behjat, *J. Hazard. Mater.*, **2009**, *161*, 276.
9. M.J. Chang, R.L. McDaniel, J.D. Naworal, D.A. Self, *J. Anal. At. Spectrom.*, **2002**, *17*, 710.
10. I. López, S. Cuello, C. Camara, Y. Madrid, *Talanta*, **2010**, *82*, 594.
11. J.L. Rodrigues, S.S. de Souza, V.C. de Oliveira Souza, F. Barbosa, *Talanta*, **2010**, *80*, 1158.
12. A. Krata, E. Bulska, *Spectrochim. Acta Part B*, 2005, 60, 345
13. O.T. Butler, J.M. Cook, C.F. Harrington, S.J. Hill, J. Rieuwerts, D.L. Miles, *J. Anal. At. Spectrom.*, **2007**, *22*, 187.
14. C. Lomonte, D. Gregory, A.J.M. Baker, S.D. Kolev, *Chemosphere*, **2008**, *72*, 1420.
15. F.X. Han, W.D. Patterson, Y. Xial, S.B.B. Maruthi, Y. Su, *Water Air Soil Pollut.,* **2006**, *170*, 161.
16. A. Collasiol, D. Pozebon, S.M. Maia, *Anal. Chim. Acta*, **2004**, *518*, 157.
17. A. Zierhut, K. Leopold, L. Harwardt, M. Schuster, *Talanta*, **2010**, *81*, 1529.
18. C. Fernandez, A.C.L. Conceicao, R. Rial-Otero, C. Vaz, J.L. Capelo, *Anal. Chem.*, **2006**, *78*, 2494.
19. Y. Li, C. Zheng, Q. Ma, L. Wu, C. Hu, X. Hou, *J. Anal. At. Spectrom.*, **2006**, *21*, 82.
20. K. Leopold, M. Foulkes, P.J. Worsfold, *Anal. Chem.*, **2009**, *81*, 3421.
21. Xun Li, Z. Wang, *Anal. Chim. Acta*, **2007**, *588*, 179.
22. Garcia-Sanchez, A. Murciego, E. Alvarez-Ayuso, I. Santa Regina, M.A. Rodriguez-Gonzalez, *J. Hazard. Mater*, **2009**, *168*, 1319.
23. M.J. Sierra, R. Millan, E. Esteban, *Food Chem. Toxicol.*, **2009**, *47*, 2761.
24. J. Canario, C. Vale, L. Poissant, M. Nogueira, M. Pilote, V. Branco, *J. Environ. Sci.*, **2010**, *22*, 1151.
25. A. Sahuquillo, G. Rauret, M. Bianchi, A. Rehnert, H. Muntau, *Anal. Bioanal. Chem.*, **2003**, *375*, 578.
26. *Teledyne Instruments Leeman Labs*, Hydra-C automated direct Hg Analyzer, Operations Manual.
27. E. Levei, M. Senila, C. Roman, M. Ponta, T. Frentiu, E. Cordos, *Studia UBB Chemia,* **2008**, *3*, 51.
28. M. Miclean, E. Levei, M. Senila, B. Abraham, C. Roman, E. Cordos, *Studia UBB Chemia,* **2008**, *3*, 57.
29. T. Frentiu, M. Ponta, E. Levei, E. Gheorghiu, M. Benea, E. Cordos, *Chem. Spec. Bioavailab.*, **2008**, *20*, 99.