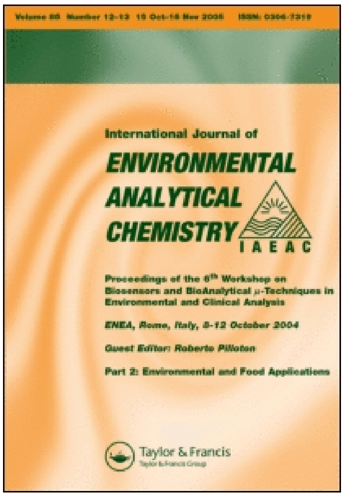

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SPECIATION OF HEAVY METALS IN MUNICIPAL COMPOSTS

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Polish composts obtained from municipal wastes by the DANO technology have been examined. The total contents of major components and heavy metals were determined and the speciation of the latter was carried out. This was performed using two sequential extraction techniques (Tessier's metod and a modified Tessier's method) as well as single extractions. The determination of individual elements was carried out by atomic absorption spectrometry with flame atomization. On the basis of a comparison of the obtained results a simple test for evaluation of composts is proposed.

Keywords: Composts; heavy metals; speciation

INTRODUCTION

Increasing amounts of municipal wastes constitute a serious hazard for the environment. Therefore, efficient methods of disposal are needed. Composting is one of such methods. It enables recycling of organic matter as well as of the nutrients present in wastes. The composting product should meet some requirements in order to be applied for agricultural purposes. It should contain sufficiently high amounts of nutrients (organic matter, N, P, K) and limited contents of toxic elements. The content of heavy metals is of prime importance. In many countries there exist standards, which specify permissible contents of heavy metals in composts. Some examples are shown in Table I. [1,2] It follows from Table I that permissible values for individual metals vary from country to country depending on the present "state of the art" of the composting technology.

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TABLE I Admissible contents of heavy metals in composts (mg/kg dry mass)

Country	*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Hg*	*Zn*	*Co*
Poland[1]								
Class I	5	300	300	100	350	5	1500	
Class II	15	500	600	200	500	10	2500	
Class III	25	800	800	200	800	10	2500	
Switzerland[2]	3	150	50	50	150	3	500	25
Italy[2]	10	500	600	200	500	10	2500	
Belgium[2]								
agriculture	5	150	100	50	600	2	900	10
beyond agriculture	5	200	500	100	1000	5	1500	20
Austria[2]	4	150	400	100	500	4	1000	
Germany[2]								
REL	2	100	100	50	150	1.5	400	
France[2]	8			200	800	8		
Spain[2]	40	750	1750	400	1200	25	4000	

Heavy metals in composts exist in various chemical forms, which determine their bioavailability, toxicity and transport in the environment. Hence, speciation of heavy metals should be an additional criterion for compost evaluation.

The literature lacks in data on speciation of heavy metals in composts. However, methods for speciation in soils and sediments have been described [3-8]. In these works the sequential extraction using Tessier's method or its modification is the most frequently used. Recently, the BCR of the Commission of the European Communities has recommended a three stage sequential extraction procedure and single extraction methods for spectiation of heavy metals in soils and sediments [9-13].

The aim of the present work was to carry out speciation analysis of heavy metals in compost using various methods in order to find out which one provides sufficient information for evaluation of a compost from the view point of its application as fertilizer.

The samples used in this study were prepared from municipal waste using the DANO type technology, mainly at the composting plant Warszawa-Radiowo (Poland). According to the DANO technology municipal wastes are fed to a biostabilizer, where they are subjected to crushing and homogenization and where biochemical processes are initiated. After sieving and electromagnetic separation the obtained biomass is subjected to composting in boxes for one week and in prisms in open air for six weeks.

EXPERIMENTAL

Apparatus

A Pye-Unicam Sp-9-800 spectrometer with a PU-9090 microprocessor (Philips) and a SWAN gamma-ray spectrometer (Institute for Nuclear Studies, Świerk, Poland) with a HPGe detector (ORTEC) were used.

Sample preparation

Samples were collected from a batch of ripe compost, ready for the distribution, in the way described in a Standard method[14], at the storage site. The average laboratory sample was divided by quartering and the obtained samples were used before and after drying.

Our preliminary studies[15] on the effect of drying of compost samples on the results of the analysis have shown that samples should be dried in air at room temperature. For drying the sample was uniformly spread on a porcelain cuvette as a layer of about 20 mm thick and placed in a special compartment. The sample was weighed every day until its weight differed by no more than 0.25% of the initial weight (the drying time was about seven days). The dry sample was ground in a porcelain ball grinder, followed by grinding in a vibrating mill with an agate ball. The grinding was continued until the particle size of the material was less than 0.5 mm.

Determination of the total content of heavy metals

The total contents of heavy metals mentioned in the Standard procedure (except mercury) were determined after complete decomposition of the compost sample (2 g) by wet digestion using a mixture of acids ($HClO_4$+ HNO_3) followed by removal of silicon compounds with a mixture of ($HClO_4$+HF). In the obtained solution the elements studied were determined by atomic absorption spectrometry (AAS) with flame atomization. The most sensitive spectral lines of individual elements were used in the measurements. The composition of the flame, width of the band passed by the monochromator, lamp current and height of the measuring zone were selected for each analyte. When determining cobalt (λ =240.7 nm), zinc (213.9 nm), lead (217.0 nm), cadmium (228.8 nm) and nickel (232.0 nm) a deuterium lamp system was used for correcting nonspecific absorption. In the determination of copper (324.8 nm), chromium (357.9 nm) and potassium (766.5 nm) no background correction was applied.

In order to determine mercury the samples (0.5 g) were decomposed with a mixture of ($HClO_4$+HNO_3) in a closed system (Bethge's apparatus). The mercury content in the solution was determined by cold vapour AAS.

Speciation analysis of heavy metals

In this work two sequential extraction methods, namely the Tessier's speciation, which is frequently used in the analysis of soils and sediments, and a modified one, as well as single extractions were used.

Tessier's speciation (TS) [16]

A sample of compost (2 g) was subsequently extracted with 20 ml of the leaching solution. After each extraction the solid was separated from the leachate by centrifugation at 3000 rpm for 30 min. The solid was washed with water. The washings were separated by centrifugation and combined with the leachate. The following fractions were obtained:

I. **exchangeable** [shaking with 1 mol l^{-1} $MgCl_2$ solution (pH 7) for 1 h];
II. **bound to carbonate** [shaking with 1 mol l^{-1} NaOAc (pH 5) for 5 h];
III. **bound to iron and manganese oxides** [shaking with 0.04 mol l^{-1} $NH_2OH.HCl$ solution in 25 % HOAc at 95 ^{0} C for 5 h];
IV. **bound to organic matter** [shaking with 30 % $H_2 O_2$ solution in 20 % HNO_3 at 85 °C for 5 h followed by shaking with 3.2 mol l^{-1} NH_4OAC for 30 min.];
V. **residual** [decomposition with $HClO_4$+HF].

Modified Tessier's speciation (MTS)

In the modified Tessier's speciation some other leaching agents were introduced. The optimal leaching parameters (e.g. leaching time) were established by activating a compost sample in a nuclear reactor (neutron flux -$3x10^{13}$ n cm^{-2} s^{-1}, irradiation time -16 h) and measuring the count rates of selected radioisotopes of the elements of interest in individual fractions. The following fractions were obtained:

I. **readily soluble** [shaking with H_2O (pH 7) for 1 h];
II. **exchangeable** [shaking with 1 mol l^{-1} $MgCl_2$ solution (pH 7) for 1 h];
III. **soluble in weak acids** [shaking with 0.44 mol l^{-1} HOAc (pH 2.5) for 1.5 h];
IV. **bound to iron and manganese oxides** [shaking with 0.04 mol l^{-1} $NH_2OH.HCl$ in 25% HOAc at 96 °C for 5 h];
V. **bound to organic matter** [shaking with 30 % $H_2 O_2$ in 0.02 mol l^{-1} HNO_3 at 85 °C for 5 h, followed by shaking with 3.2 mol l^{-1} NH_4OAc solution for 30 min];
VI. **residual** [decomposition with $HClO_4$+HF].

Single extractions

The extractants to be used in single extractions have been selected on the basis of recommendations of the BCR of the Commission of the European Communities[10] in which preliminary speciation schemes were proposed for soils and sediments. The Toxicity Characteristic Leaching Procedure (TCLP) used by the EPA (USA)[17], as well as the recommendations of the Canadian Ministry of Environmental Protection[18] have also beeen taken into account. Two extractants were used: 1 mol $l^{-1}NH_4OAc$, pH 5 (1 g of compost, 20 ml of the extractant, shaking time -5 h) and 0.05 mol l^{-1} EDTA in acetate buffer pH 4.8 (1 g of compost, 20 ml of the extractant, shaking time-5 h).

A leaching test recommended by the Polish National Inspectorate of Environmental Protection[19] was also used . The test was carried out as follows: 10 g of wet compost was shaken with 100 ml of water for 4h. After 24h the solution was separated from the solid.

In all the above mentioned extractions the phases were separated by centrifugation.

RESULTS AND DISCUSSION

The chemical composition of composts obtained from municipal wastes by the biothermal DANO method is shown in Table II The compost contains high amounts of nutrients, particularly of organic matter and potassium. The total amounts of heavy metals (Table III) do not exceed the permissible amounts foreseen in the Polish standard for composts of Class II. Some of the elements, particularly Cr, Cu, Ni and Hg, meet the requirements given in the regulations of other European countries..

TABLE II Contents of major components in compost

Component	*Content, % dry mass*
Organic matter	48.3 ± 1.0
Organic carbon	23.1 ± 0.5
Nitrogen (N)	0.90 ± 0.04
Phosphorus (P_2O_5)	0.60 ± 0.03
Potassium (K_2O)	1.10 ± 0.06

TABLE III Total contents of heavy metals in compost

Element	*Content, mg/kg dry mass*
Cd	10.5 ± 1.0
Pb	480 ± 30
Cu	256 ± 21
Ni	42.5 ± 3.2
Co	17.8 ± 1.5
Cr	123 ± 6.0
Zn	1870 ± 95
Hg	5.0 ± 0.3

The present investigation comprised the following heavy metals: Cd, Pb, Cu, Ni, Co, Cr and Zn. Speciation of mercury was not included in the procedure. The speciation analysis was carried out on samples from the composting plant Warszawa-Radiowo collected every month for a period of one year. The average contents of major components and the average total contents of heavy metals in those samples are presented in Tables II and III, respectively.

The two methods of sequential extraction used in this work differ with respect to the division into fractions of metals to be released to the environment. In the conventional Tessier's extraction method (TS) two fractions are obtained (exchangable and bound to carbonates) whereas in the modified procedure (MTS) three fractions are obtained (fairly soluble in water, exchangeable and soluble in weak acids). Therefore, the latter method provides more information on the transfer of the studied metals to the environment.

The results obtained by the sequential extraction techniques are presented in Figures 1 and 2. It follows from these figures that the content of the examined elements in individual fractions varies from element to element. The fractions containing metals easily released to soil (I TS fraction , I and II MTS fractions) contain significant amounts of only Cd (10%), Co and Ni (about 5%) and Zn (about 3%) . The contents of the other elements studied are lower than 1%. The amount of zinc in II TS as well as III MTS fractions is very high. This indicates that in acidic soils about 45% of zinc can be released from the compost. Taking into account the total zinc content in the composts studied this can limit the amounts of the compost applied as fertilizer and the frequency of its application.

In the fractions of metals bound to organic matter there occur mainly copper (up to 90%) and lead (about 50%). The risk of contamination of ground waters

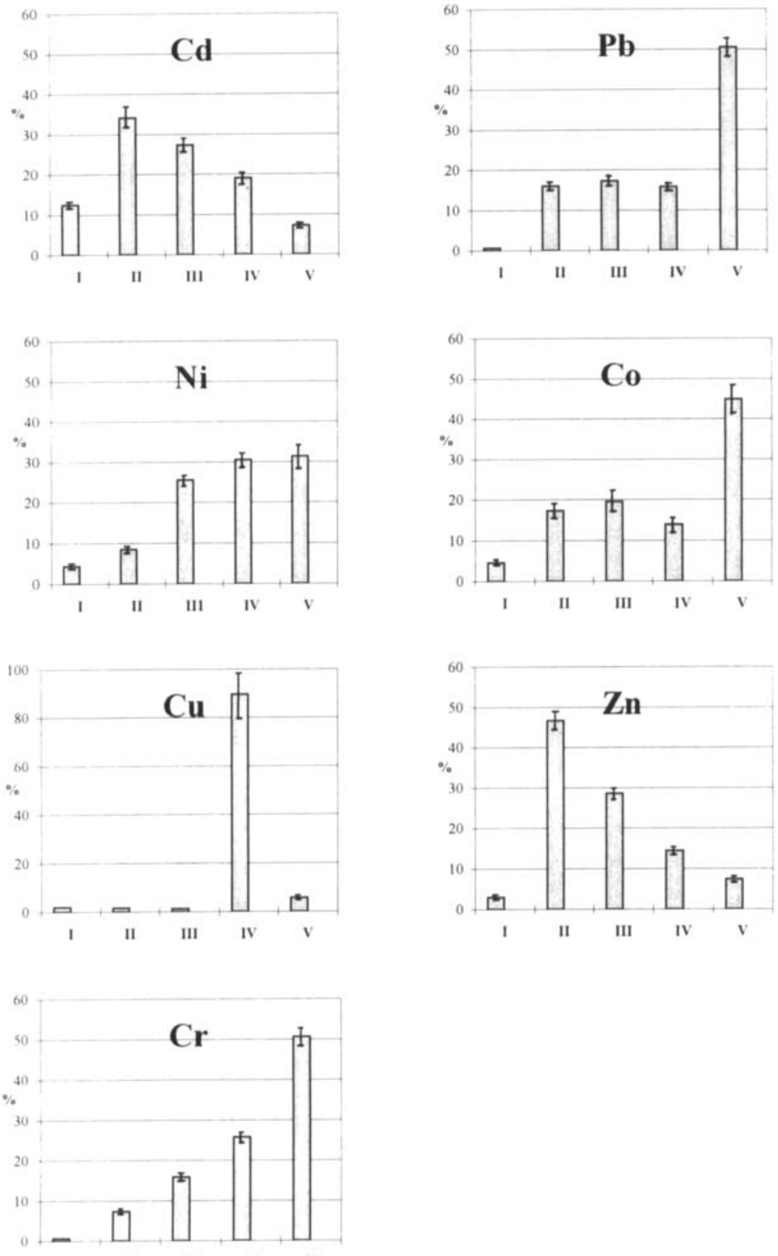

Fig. 1

FIGURE 1 Tessier's speciation of heavy metals in compost I-V fractions - The content of metals in individual fractions is expressed as percentage of the total content

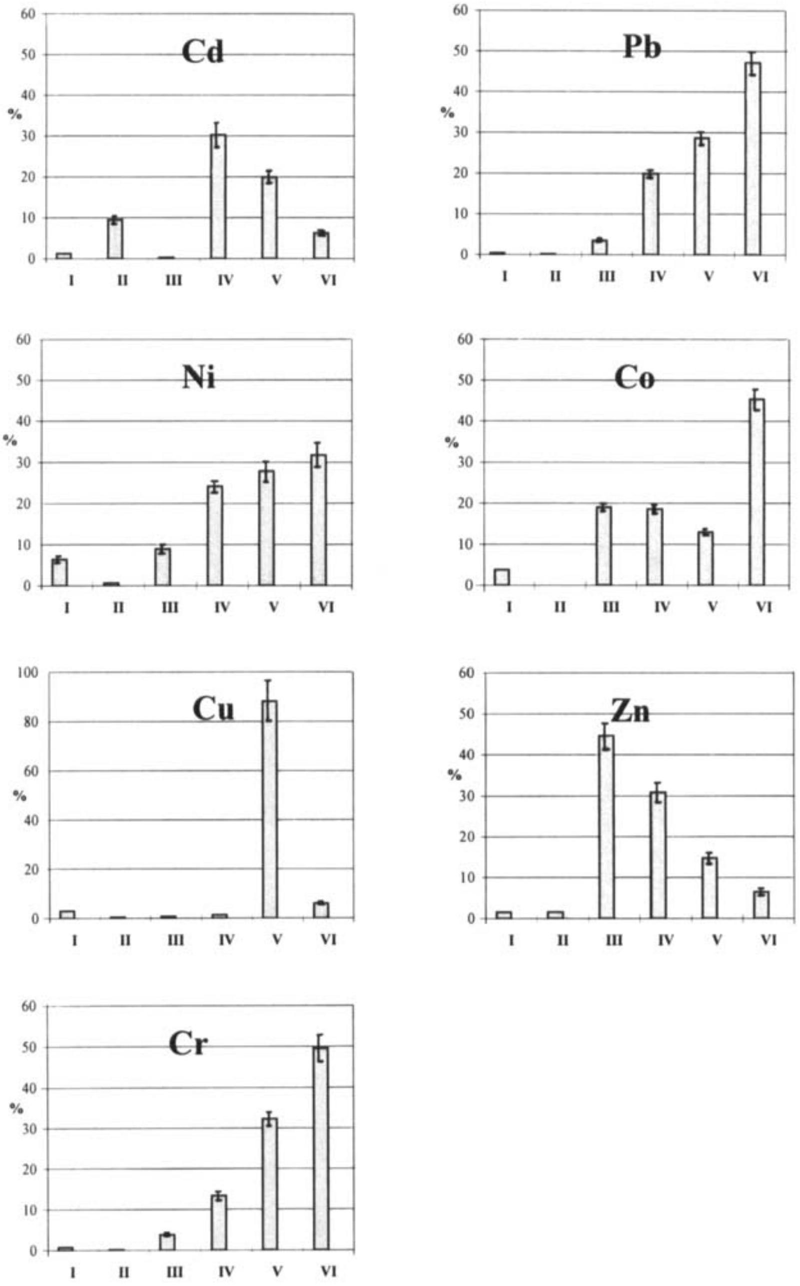

FIGURE 2 Modified Tessier's speciation of heavy metals in compost I-VI fractions - The content of metals in individual fractions is expressed as percentage of the total content

and plants with these elements is rather low because the mineralization of organic substances under natural conditions is a slow process dependent on the physico-chemical parameters of the soil.

The residual fraction contains metals bound to silicon minerals and to other stable compounds. The metals contained in that fraction, chronium (about 50%), lead (40-50%), cobalt (about 40%) and nickel (about 30%), are chemically stable and biologically inert.

The results obtained by single extractions are presented in Figure 3. The ammonium acetate fraction (pH 5) comprises elements considered to be mobile in the enviroment. It follows from the obtained results that this fraction contains significant amounts of Cd and Zn (about 45% of the total content). The contents of the remaining elements are significantly lower e.g. Pb-20%, Ni-15%, Cr-19%, Cu -5%.

The EDTA fraction comprises the elements of the ammonium acetate fraction as well as the elements that occur in the form of complexes less stable than those with EDTA. The contents of elements in the EDTA extract are significantly higher than in the acetate extract. This pertains particularly to the elements that form high stability complexes with EDTA at pH 4.8 such as Pb, Cu and Ni. Their contents in the EDTA fraction are: Pb -65 %, Cu and Ni -30 % each.

TABLE IV Contents of heavy metals in water extracts

Metal	*Content in water extract, % of total content*
Cd	3.2
Pb	2.6
Cu	6.0
Ni	8.0
Co	5.5
Cr	2.3
Zn	4.0

Analysis of the results obtained by the single extractions indicates that 1 mol l^{-1} ammonium acetate solution (pH 5) extracts those elements that occur in the exchangeable and bound to carbonate TS fractions as well as in the readily soluble, exchangeable and acid soluble MTS fractions. Hence, extraction of composts with 1 mol l^{-1} ammonium acetate solution can be a good test for indicating the maximum amount of heavy metals able to be released to the environment in natural conditions. On the other hand, the extraction with EDTA is not suitable for composts because EDTA complexes with elements such as Pb, Ni and Cu are

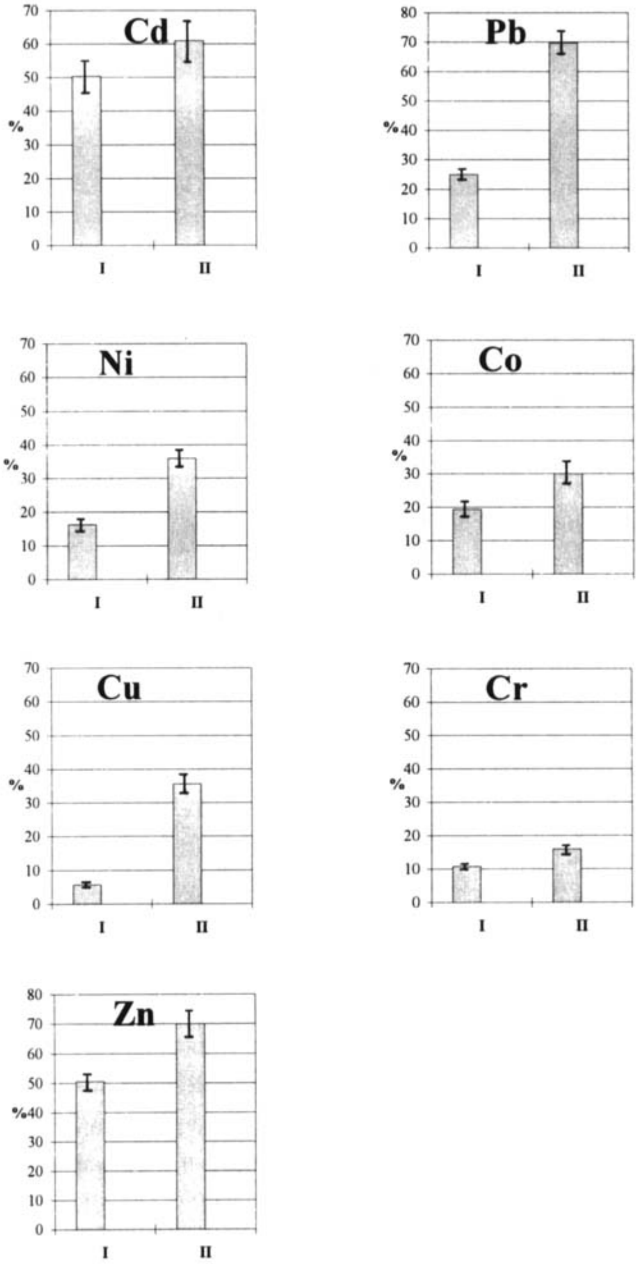

FIGURE 3 Single extractions of heavy metals in composts I-1 M ammonium acetate (pH 5) II-0.05 M EDTA (pH 4.8) The content of metals in individual fractions is expressed as percentage of the total content

so strong that these elements can pass from sparingly soluble compounds (minerals, sulphates) to the extract. Such systems are not typical for the natural environment.

The extract obtained by the leaching test, performed under established conditions, contains elements that pass to soil readily. From the obtained results (Table 4) it can be inferred that, under the conditions of the test, the following elements pass to the water extract: copper and cobalt (6 %) , nickel (8 %) and zinc (4 %). The contents of the remaining elements in the water extract amount to 2-3% of their total content.

CONCLUSIONS

The determination of the total amounts of elements in compost is insufficient for a correct evaluation of its quality. It is necessary to carry out speciation analysis. The sequential extraction makes it possible a more precise definition of the forms in which metals exist in compost and a knowledge of the mechanisms involved in the release of the elements to the environment under natural conditions. However, the procedure of this extraction is fairly complicated so it can not be carried out routinely. The technique of single extraction is simple and fast so it is more suitable for routine analysis.

On the basis of the obtained results we recommend the extraction with 1 mol l^{-1} NH_4OAc (pH 5) as a simple test for the assesment of maximum amounts of heavy metals that can pass to the environment under conditions of the compost application. In our opinion this test can be recommended for the evaluation of the compost quality. The proposed test differs with respect to pH from the acetate test recommended for soils and sediments by the BCR of the Commission of the European Communities[13]. The latter test is carried out at pH 7. However, in our opinion pH 5 is more typical for the natural environment .

Acknowledgements

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References

[1] Standard BN-89/9103-09. Compost from municipal wastes, Poland.

[2] A review of Compost Standards in Europe, ORCA Technical Publication No 2, December 1992.

[3] A.M. Ure, *Fresenius J. Anal. Chem.*, **337**, 577-581 (1990).

[4] V. Speračkova and J. Kučera, *Intern. J. Environ. Anal. Chem.*, **35**, 241-251 (1989).

[5] F.M.G. Tack and M.G. Werloo, *Intern. J. Environ. Anal. Chem.*, **59,** 225-238 (1995).
[6] R.P. Thomas, A. M. Ure, C.M. Davidson and D. Littlejohn, *Anal. Chim. Acta,* **286**, 423-429 (1994).
[7] T.E. Clevenger, Water, Air and Soil Pollution, **50**, 241-254 (1990).
[8] S.S. Krishhan, R.E. Jervis and L.D. Vela, *J. Radioanal. Nucl. Chem., Articles,* **161,** 181-187 (1992).
[9] B. Griepink, *Fresenius J. Anal. Chem.,* **338,** 486-488 (1990).
[10] Ph. Quevauiller, F.X. Donard and E.A. Maier, *Mikrochim. Acta,* **109,** 169-190 (1992).
[11] Ch.M. Davidson, R.P. Thomas, S.E. McVey, R. Perala, D. Littlejohn and A.M. Ure, *Anal. Chim. Acta,* **291,** 277-286 (1994).
[12] Ph. Quevauviller, G. Rauret and B. Griepink, *Intern. J. Environ. Anal. Chem.,* **51,** 231-235 (1993).
[13] A.M. Ure, Ph. Quevauviller, H. Muntau and B. Griepink, *Intern. J. Environ. Anal. Chem.,* **51,** 135-151 (1993).
[14] Standard BN-89/9103-01. Composts from municipal wastes. Sampling using a sampler of special construction. Poland.
[15] J. Chwastowska, K. Wolska and W. Golębiewska, *Chem. Anal. (Warsaw),* **41,** 71-76 (1996).
[16] A. Tessier, P.G.C. Campel and M. Bisson, *Anal. Chem.,* **51,** 844-855 (1979).
[17] US EPA Federal Register, **51,** No 9, 1750-1756 (1986).
[18] Ontario Ministry of the Environmental Regulation, **309,** 46 (1988).
[19] Leaching test for wastes. Instructions of the Principal Inspector of Environmental Protection, No **78,** 19 Nov. 1992, (in Polish).