

Trace element availability in compost

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Introduction

Landfill disposal has been severely restricted in both Europe and elsewhere and new methods of dealing with solid wastes have become essential. Of these alternative methods, composting is considered as a vital method of solid waste disposal. Traditionally, compost was mainly made up of green waste; however, many organic substances including municipal solid waste (MSW), sewage sludge (SS) and other industrial waste are now being introduced to composting. As a consequence, the level of heavy metals in compost has increased substantially when compared with traditional green waste compost and therefore it has become important to study the effects of introducing heavy metals to compost. There have been environmental studies into the applications of compost in contaminated land reclamation, the bioavailability of heavy metals in soil, their interaction with organic matter in compost and their effects on soil microorganisms and enzyme activity. This article will, however, concentrate on the techniques used to measure the heavy metals rather than the environmental significances. In particular we will discuss the determination of heavy metals in compost using inductively coupled plasma mass spectrometry (ICP-MS), with the emphasis on the sample pretreatment procedures that are designed to obtain fractionation and speciation information about heavy metals in compost samples. It should be noted that one of the most difficult aspects of characterising compost is the sampling process. On municipal waste sites the composting occurs on a very large scale in the form of large heaps

called windrows, which are regularly turned. The initial material supplied to these windrows is not decomposed and is therefore very heterogeneous, meaning many samples are required, with sampling challenges such as heaps of decomposing onions!

Determination of heavy metal content in compost by using ICP-MS

Since its introduction in the early 1980s, ICP-MS has become one of the most important tools for trace element analysis. Several manufacturers have introduced compact, automated ICP-MS instruments that exhibit a superior overall performance in terms of detection limits, sensitivity, elemental coverage and calibration range. When compared with previously existing techniques for element analysis (such as atomic absorption spectrometry, AAS), ICP-MS possesses many advantages such as very low detection limits, capability for multi-element detection, wide calibration range and rapid analysis time. Also, the ICP source provides a high enough energy to efficiently ionise over 80 elements in the periodic table, so the technique has a wide analytical range. These attributes makes it very suitable for the determination of heavy metals in compost samples because, as with environmental studies, the analysis of several elements at very different concentrations is often required in one sample. With carefully prepared standards, ICP-MS can accomplish this task quickly and with very low limits of detection. Normally aqua regia is recommended for total digestion (i.e. ISO 11466 protocol) of soils and sediments; however, nitric acid is the preferred acid for diges-

tion of compost samples for analysis by ICP-MS. This is possible because of the compost matrix, which is mainly organic and therefore quite different to soil and sediment. In our work, therefore, the pseudo total of all the compost samples was achieved with nitric acid digestion, which is the United States Environment Protection Agency (USEPA) recommended method for microwave digestion of botanical matrices. The advantage of using nitric acid over aqua regia is that you are not introducing chloride into the digestion matrix, which may cause polyatomic ion interferences to the ICP-MS analysis of ^{56}Fe ($^{40}\text{Ar}^{16}\text{O}$), ^{52}Cr ($^{35}\text{Cl}^{16}\text{O}$) and ^{75}As ($^{40}\text{Ar}^{35}\text{Cl}$). Hseu compared four different digestion methods for the determination of heavy metals in composts and recommended nitric acid digestion based on the recovery studies.¹

Fractionation of heavy metal content in compost

The ICP-MS alone will only provide information about the total elemental composition. Many of the elements may, however, be strongly bound to the compost matrix and therefore would cause less environmental problems than weakly bound elements that easily leach from the compost. This means that it is vital to obtain information about this availability. There are many ways of studying this but the most common are fractionation and speciation. In fractionation, different extraction solutions are used sequentially to identify how easily the elements can be removed; in speciation, the different chemical species of the same compound are determined. These techniques require either sample

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pretreatment procedures or hyphenated techniques such as HPLC-ICP-MS.

Sequential extraction methods are frequently used to characterise and predict the mobility and bioavailability of heavy metals in compost or compost-amended soils. They do, however, lack uniformity in procedure, which can make it difficult to compare the results obtained in different studies. In fact the results obtained by different sequential extraction procedures may give very different answers about the geochemical phase within which an element exists. This problem has been solved to some extent by the introduction of the European Commission's Bureau Communautaire de Référence, BCR, three-step sequential extraction method, which has made it possible to harmonise the extraction schemes for the determination of extractable trace metals in compost and compost amended soil.² This development has been enhanced by the availability of reference materials which can be used to enhance the quality control of the whole analysis procedure, a key issue in interpreting this type of operationally defined speciation. In the BCR method, the sample is subsequently extracted with three extraction steps. The first step involves extracting with 0.11 mol L^{-1} HAc, which represents the water and acid soluble as well as exchangeable fraction. The second step is the extraction with 0.1 mol L^{-1} $\text{NH}_2\text{OH}\cdot\text{HCl}$, which represents the reducible fraction and the fraction combined with Fe/Mn oxides. The third step represents the fraction combined with organic materials, which is accomplished by extraction with 1.0 mol L^{-1} NH_4Ac after the sample has been digested with H_2O_2 .

Greenway and Song³ applied the BCR sequential extraction procedure to study of the fractionation of eight elements in four open-air windrow-composting processes. After the three-step extractions, the extracted solutions were analysed using ICP-MS. The high sensitivity of the ICP-MS instrument allowed the extraction solutions to be diluted up to 100 times and this was invaluable in reducing any interference effects from the matrix. A main drawback shared by all sequential extraction schemes, however,

is that the procedures themselves are complex and very time-consuming. This is because the extraction procedure takes several hours, whilst the sample is mechanically shaken to allow the heterogeneous system to approach equilibrium. A whole protocol, which typically contains three to five steps, often takes several days to complete, which makes the sequential extraction method inappropriate for frequent environment monitoring. One approach to overcome this is to use the ultrasound accelerated extraction method. For example, in the standard BCR method each extraction step takes 16h whereas with the ultrasonic extraction method each step took only 15min due to the much more rapid extraction process. This ultrasound extraction method was compared with the traditional method using the BCR reference material and this confirmed that the results were comparable.⁴ The speed of the new extraction method provided two advantages; first, it allowed the composting process to be monitored more frequently which helps to provide a more detailed understanding of the partitioning behaviours of heavy metals. Second, it allowed one extra step to be included into the BCR sequential extraction procedure. This extra step was designed to look at the portion of elements combined with humic substances, and this involved extraction

with 0.1 mol L^{-1} sodium pyrophosphate solution before the residue was digested with hydrogen peroxide. An example of elemental partitioning profiles for nickel in a mixed waste stream composting process is shown in Figure 1. It can be seen that the fraction of Ni extracted with acetic acid (step 1) decreased with increasing composting time whereas the fractions of Ni combined with humic acid increased with the increase of composting time.

As well as using the accelerated sequential extraction method, we have also investigated the elemental leachability in compost by using a kinetic approach.⁵ These leaching experiments provide useful and rapid information about how easily an element can be leached from its matrix. A non-selective leaching agent (such as ethylene diamine tetra acetic acid, EDTA) is usually chosen to carry out the leaching experiment and this allowed passage through dried samples packed into burette columns. In our work the eluents were collected at different times and subjected to ICP-MS analysis. By recording the amount of leached element versus time taken with a given reagent, a kinetic leaching curve was obtained. A non-linear regression model was then applied such that the leached species can be catalogued into two compartments, i.e. those which are easily extracted (labile species) and

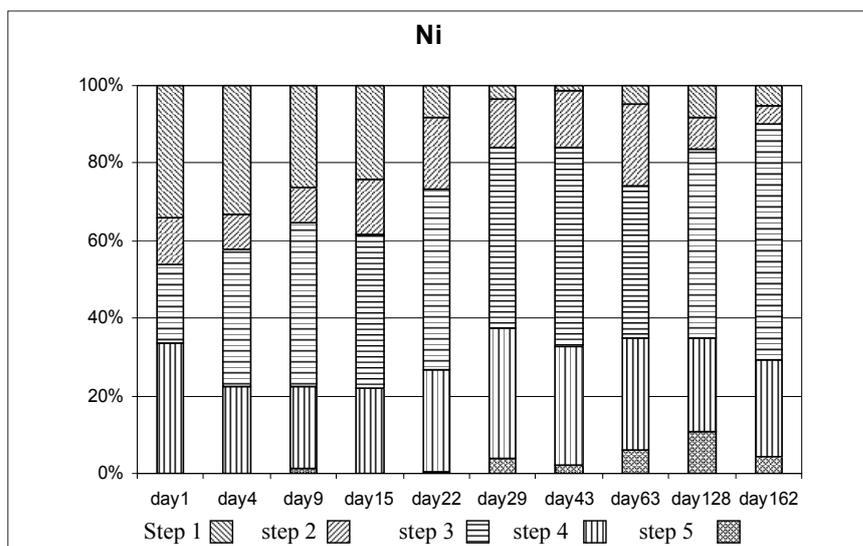


Figure 1. Changes in the elemental partitioning profile for Ni as the composting process proceeds. [Adapted from G.M. Greenway and Q. Song, *J. Environ. Monit.* 4, 950 (2002)].

those which are extracted more slowly (non-labile species). From the regression parameters obtained, the lability of an element in compost could be quantitatively defined. Figure 2 gives an example of the kinetic profiles of Zn in a mixed-waste stream compost. From the regression parameters, it was concluded that 25.6% of Zn could be catalogued as labile fractions and rest of Zn was non-labile, which meant the later fraction was not likely to be leached out from the compost by EDTA.

Interfacing microchip-based capillary electrophoresis with ICP-MS for elemental speciation

Operationally defined fractionation methods do not actually identify the chemical species in the sample.

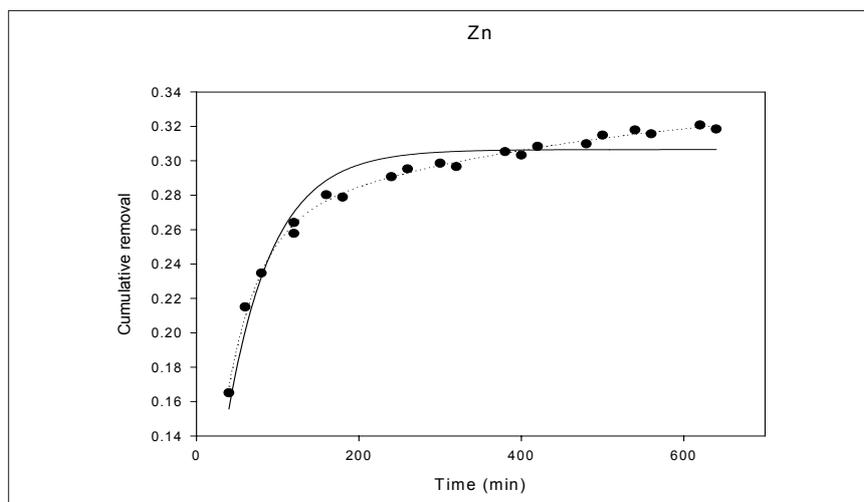
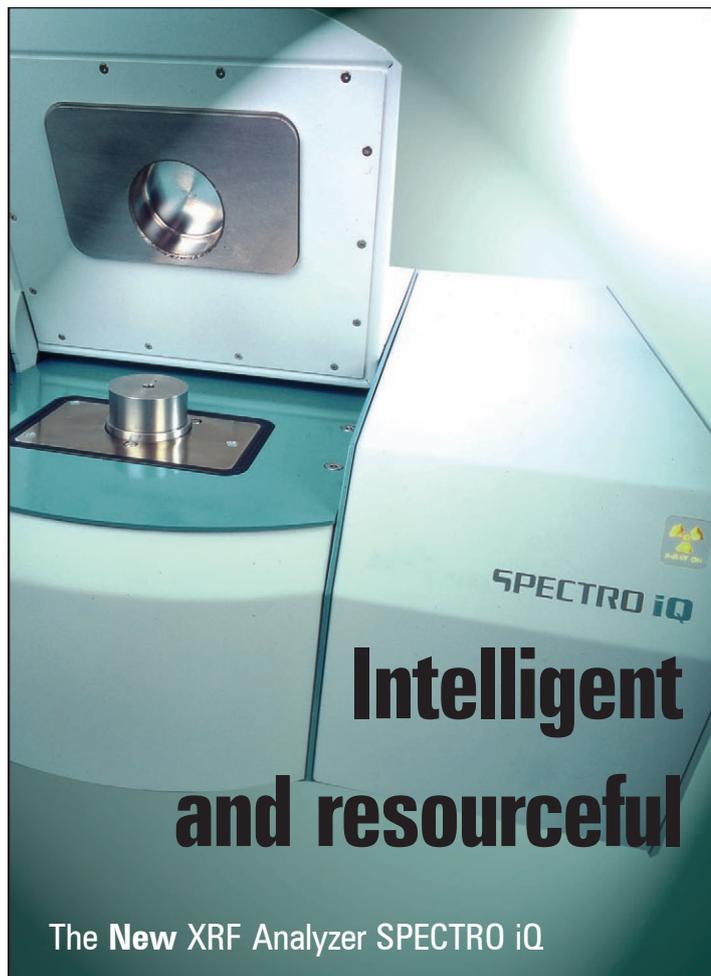


Figure 2. Non-linear regression curves of the EDTA column leaching data and regression curves. (•) experimental data; (—) one-component model; (---) two-component model. [from Q. Song and G.M. Greenway, *J. Environ. Monit.* **6**, 31 (2004)].

For trace element speciation, at least two analytical techniques are usually

required. One technique is used to separate the species, which can then



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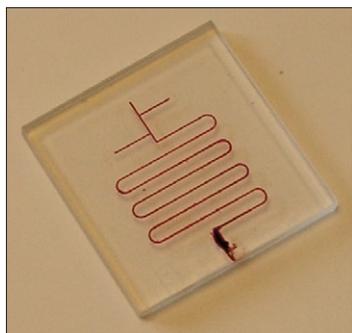


Figure 3. Picture of the microchip.

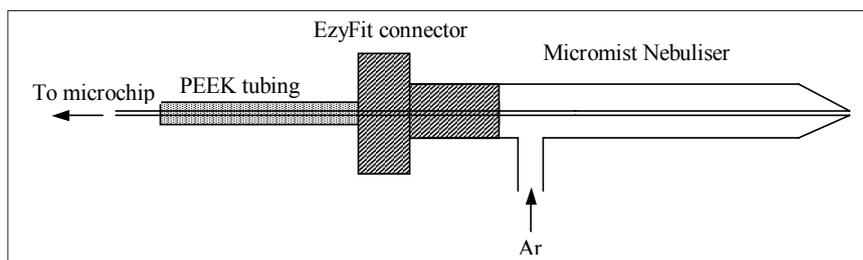


Figure 4. Schematic diagram of the interface [from Q. Song, G. M. Greenway and T. McCreedy, *J. Anal. Atomic Spectrom.* **19**, 883 (2004)].

be identified and quantified by the other analytical technique. Finding two analytical techniques that can efficiently perform the individual tasks and at same time be compatible can be challenging. Much of the speciation work carried out using ICP-MS detection has involved gas chromatography (GC)^{2,3} and liquid chromatography (LC).^{4,5}

More recently, the coupling of capillary electrophoresis (CE) with ICP-MS (as well as ICP-AES) has been investigated. In CE the separation is achieved by applying a high voltage across the capillary and this is of interest for speciation studies because it could be argued that it is less likely to change the speciation state of the sample than chromatographic processes. However, there are several intrinsic mismatches between these techniques. First, there is a large difference between the flow rates used in these two systems. The sample uptake by a conventional nebuliser in ICP-MS is around the one millilitre per minute level while the carrier electrolyte flow in a CE system is typically around the one microlitre per minute level. Second, the nebuliser gas flow creates a vacuum in the sampling tubing, which causes a suction effect. If not prevented, it could naturally suck the carrier electrolytes from the capillary, which will not only introduce laminar flow and deteriorate the separation but also cause a serious problem for control of the sample injection. Finally, the time scales for CE separations and ICP-MS determination are also very different. If these processes are not well matched, the overall efficiency of the hyphenated technique is compromised.

These first two problems associated with the interface have been overcome and CE-ICP-MS has already become a very useful tool in elemental speciation studies. The difference in time scale between CE separation and ICP-MS detection, however, is less frequently addressed. Conventional CE separations typically take several minutes or even longer during which time, the ICP-MS is idle. This reduces the overall efficiency of the hyphenated technology by decreasing the sample throughput and increasing the running cost per analysis. The obvious area where increases in efficiency can be made is to reduce the separation time considerably, either by using a higher separation voltage or a shorter capillary length and therefore faster separation system.

Microfabricated analytical systems using electrophoresis as the separation mechanism have been shown to drastically reduce separation times and to simplify instrumental design. Conventional CE systems use capillaries with small diameters to allow rapid dissipation of the Joule heating produced by electric current. Heat is generated uniformly across a tube section, but dissipation only takes place through the walls of the capillaries. A temperature gradient results, which affects a density gradient (leading to convection) and a viscosity change across the capillary. Since heat is much better dispersed in small diameter capillaries, analysis times can be shortened significantly, as high voltages can be applied to short capillaries.

In microfabricated CE system, the separation channels etched in a solid substrate replace the capillaries used in

conventional CE. The channels can be etched with very small diameters and more importantly the walls of the channels are much thicker than the capillaries, which would allow more efficient heat dispersion.⁶ Furthermore, even if temperature control were needed, practically it would be much easier to disperse the heat from a microchip than that from coiled capillaries. Another advantage of microchip technology is that pre-etched channel networks can be used to provide several flow streams, omitting tube connectors and thus reducing dead volumes.

Greenway and co-workers⁶ interfaced a microfluidic chip based electrophoresis system with ICP-MS to provide rapid elemental speciation capabilities. The microfluidic chip, size of 30 × 25 × 3 mm, had an 8 cm long, 100 μm wide and 20 μm deep separation channel etched in a serpentine way on the glass base plate (Figure 3).

The microchip was interfaced to the ICP-MS (Thermo Elemental PQ2+) via a commercially available, low flow rate concentric nebuliser. The interface was achieved by using a short length of encapsulated PEEK[®] tubing. The far end of this tubing was then directly connected to the nebuliser by using a Teflon[®] connector as shown in Figure 4.

Hydrodynamic sample injection was accomplished by a flow injection mode through an externally controlled gravity pump and a three-way valve. With application of an electric field up to 500 V cm⁻¹, base line separations were readily achievable in 30 s for oppositely charged species such as Cr³⁺ and Cr₂O₇²⁻; Cu²⁺ and Cu(EDTA)²⁻. For species like AsO₃³⁻

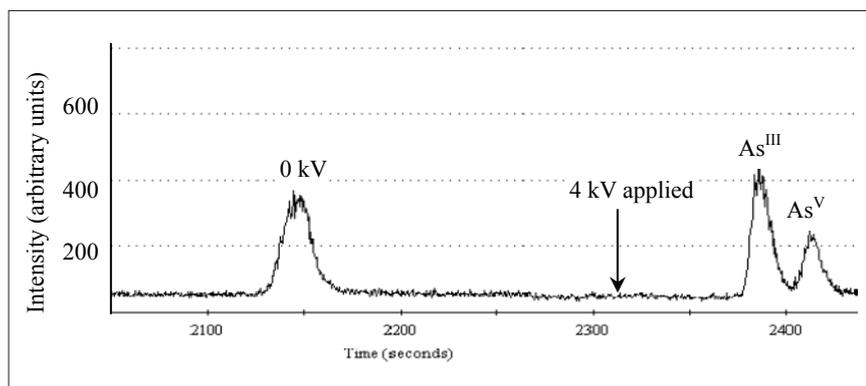


Figure 5. Separation of AsO_3^{3-} and AsO_4^{3-} . Carrier electrolyte consisted of 50 mmol L^{-1} borate buffer and $5 \times 10^{-4} \text{ mol L}^{-1}$ CTAB, pH 9.3. Sample solution consisted of $100 \mu\text{g L}^{-1}$ As(III) and $50 \mu\text{g L}^{-1}$ As(V) in 20 mmol L^{-1} borate buffer. Sample injection 5s [from Q. Song, G. M. Greenway and T. McCreedy, *J. Anal. Atomic Spectrom.* **19**, 883 (2004)].

and AsO_4^{3-} , the separation was achieved in an alkaline buffer system with the use of hydrodynamically modified electroosmotic flow (HMEOF) to control the fluid. With the addition of surfactant CTAB, the electro-osmotic flow in the channel was reversed. Under this condition the EOF flowed against the hydrodynamic flow such that the net flow rate of the bulk solution was reduced and the residence time was increased. As shown in Figure 5, clear separation of AsO_3^{3-} and AsO_4^{3-} was achieved in an 8 cm long separation channel with the application of an electric field 400 V cm^{-1} .

Conclusion

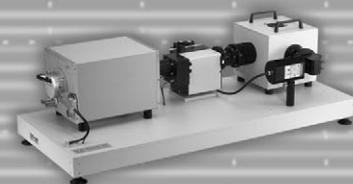
The excellent analytical performance of ICP-MS, including low detection limits, high precision, multi-element detection capabilities and isotopic selectivities makes ICP-MS an extremely powerful instrument for elemental analysis. Unfortunately total elemental analysis does not give the vital information required for samples such as compost, which is its bioavailability, related to how easily the element is extracted from the sample. Although this information can be obtained by various selective sample pretreatment procedures to give elemental fractionation information, this is time consuming and methods such as accelerated extraction with ultrasound or kinetic leaching experiments are needed if lots of samples are to be analysed. Chemical speciation by hyphenated techniques is also time-consuming and miniaturisation

of the separation process can reduce the time required for sample transport and increase the efficiency. The interfacing of a microchip-based CE system with an ICP-MS for the elemental speciation study is a step in the right direction but this can be further improved by fabricating a low flow rate nebuliser within the microchip by micromachining techniques.

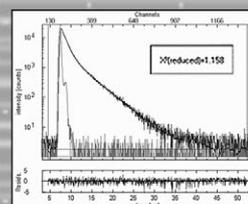
The urgent need for improvements in monitoring bioavailability is leading to many other rapid developments that increase the speed and quality of the information obtained. To speed up the procedure, on-line flow-through extraction procedures are now being investigated by some groups. Others are trying to improve the sampling procedures by monitoring soil pore waters using passive dosimeters or microdialysis.⁷

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