Abstract In line with recent European environmental guidelines on biomasses, one of the most important parameters to take into account is the As concentration, especially when present in biomasses and complex matrices. The goal of the present study is to give information about possible technical-analytical problems during the determinations of such elements by means of different instrumental spectroscopy techniques, in particular inductively coupled plasma atomic emission (ICP-AES) and atomic absorption (AAS), using two different wavelengths, 188.98 nm and 193.70 nm.

In the Laboratory of Hygiene of National Institute of Health in Italy, a specific study has been carried out concerning the determination of As contents in environmental solid matrices, using as reference material BCR 141 R, represented by a calcareous soil. In particular, whereas recovery tests did not show particular drawbacks, difficulties were met in the As detection in reference material. Spectral interference was seen during determination by ICP-AES and matrix interference during determination by AAS, in particular using ETAAS with deuterium background correction and HAAS. Using ETAAS with Zeeman background correction at 193.70 nm, the As line did not show particular matrix interference during the reading of samples.

A ring test involving two more laboratories and another certified reference material (IAEA-356 in marine sediment matrix) produced important information about problems of under/over estimation of data. Two different instrumental techniques, ICP-MS and HAAS, confirmed previous data, i.e., overestimation for inductively coupled plasma mass spectrometry and that As values achieved by HAAS were of the same order as the references, but affected by considerable standard deviation.

Introduction

Usually, in Italy and other European states, environmental regulations related to the presence of inorganic micropollutants (in particular As) present in different kinds of amendments are inclined to associate such elements with soil, which is considered as the final receptor and/or cleanup matrix. However, in Italy, requests addressed to several commissions and working groups in environmental matters concerning the marketing of new products such as fertilizers and amendments, have given an important impetus to scientific departments to produce data and assess more specific procedures, taking into account the specific behavior of As in terms of toxicity with relation to its chemical state [1, 2]. In fact, dose-response relationships are different in the case of inorganic and organic compounds.

For inorganic compounds of As, the acute and subacute effects of short/medium terms of exposure depend on the oxidation state (trivalent form is more toxic than pentavalent form) and solubility (sodium arsenate is ten times more toxic than trivalent As); however, human data on the differences in toxicity between As(III) and As(V) are still limited [3]. The non-carcinogenic effects of long-term exposure are mainly changes to the respiratory system and skin and are related to high levels of airborne inorganic As as a result of occupational exposure in specific industries (smelting, pesticide manufacturing) [4].

Organic As compounds exert different patterns of toxicity and only for certain organs, because such compounds do not constitute a homogenous group with relation to the effects in biological systems. Both organic and As bound...
compounds are highly affected by the interaction with other chemicals and elements. Investigations concerning combined exposures to As and other different agents (thiol compounds, selenium, copper and lead) are in progress in order to explain not well known mechanisms and controversial data [5].

In the light of what has been said, considering an assumed daily intake (ADI) for As equal to a concentration of 0.3 µg/kg body weight/day and assuming the weight of an average man to be about 70 kg, the ADI turns out to be equal to 21 µg/day.

In the environment, the normal concentration of As in plants is supposed to be between 0.07 and 2.83 mg/kg. Since in usual cultivation (corn, cereals, wheat, oats, barley, vegetables), As is present with an average concentration of 0.3 mg/kg, performing a precautionary estimate using the criteria of “worst case” (i.e. 300 µg of As in 1 kg of plant at 70–80% of moisture content would lead to an ADI value of 60 µg/day), it is reasonable to say that the amount of As in plants should not increase in any case [6, 7].

Considering that As concentration in soil ranges on average between 2 and 20 mg/kg d.m. (in Italy, an average value of 10 mg/kg d.m. has been detected), a value of 10–15 mg/kg d.m. in compost could be protective from a sanitary point of view, because it would not allow an increase in the amount of As in the soil–plant system, using compost at 100 quintals/ha [8].

The value of As in compost, presupposed to be 10–15 mg/kg d.m., turned out to be detectable with no particular problem using the most common analytical procedures and instrumental techniques. In fact, detection limits of every analytical method are about ten times lower, both than the threshold value of As in compost and the threshold value in soil (20 mg/kg d.m. for urban areas and 50 mg/kg d.m. for industrial areas, according to Italian Regulations [9]). A recent study concerning a wide monitoring of compost plants in Italy (about 60% of Italian production of quality compost) has shown As concentrations of 2–16 mg/kg d.m. [10].

In order to settle a specific limit value for As in complex matrices such as compost or soils, it is necessary to fix an analytical method for accurate detection of even small quantities of As. Literature data confirm relevant discrepancies between As concentrations detected in several matrices by comparative ring tests involving different techniques of digestion and instrumental determination [11, 12, 13, 14].

**Materials and methods**

**Treatment of sample**

In the present study, a reference material BCR 141R represented by a calcareous soil with an As concentration of 8.84 mg/kg and standard deviation 0.43 has been used.

Because it was not been possible to obtain a compost certified reference, a solid matrix as similar as possible to the sample considered was chosen. The concentrations of analyte elements present in the certified material were as near as possible to concentrations in unknown samples and similar to environmental threshold values settled by Italian law. Unknown samples of compost were composed of organic fractions of waste, yard trimmings, agroindustrial and wastewater sludge in variable ratios, with As concentrations ranging between 7.6 and 14.8 mg/kg d.m.

Before analysis, the sample was conditioned as written in the methods enclosed with certified materials; two aliquots of 200 and 500 mg were weighed and each one put into six Teflon vessels. Such vessels underwent two programs of mineralization using a high pressure microwave oven Milestone MLS 1200 Mega; the first with the addition of 8 mL of aqua regia (HNO₃+HCl, ratio 1:3) and the second with the addition of 5 mL of HNO₃, with previous cooling, as shown in Table 1.

<table>
<thead>
<tr>
<th>Program 1</th>
<th>Power (Watt)</th>
<th>Time (min)</th>
<th>Program 2</th>
<th>Power (Watt)</th>
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<tbody>
<tr>
<td>Step 1</td>
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<td>Step 1</td>
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<td>Step 2</td>
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<td>Step 4</td>
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<td>Step 7</td>
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HCl was not used for digestion as recommended for soil samples because HF addition would have needed following neutralization with boric acid and such further addition of acids to solution would have resulted in a strong depletion of the signal during readings.

Considering that the reference values of As quoted in the method enclosed with certified material had been achieved using instrumental neutron activation analysis (INAA), such a technique is slightly affected by the presence of HF in samples, unlike for example the ICP-AES technique, which must be equipped with specific devices in order not to run the risk of melting and breaking the nebulizer and torch kit. Besides, a recent study demonstrated that an extraction procedure using only HCl yielded 97% of total As present in a contaminated soil [15].

The use of H₂O₂ during the digestion step has not been considered because it was not contemplated amid the mineralization procedures enclosed with reference materials [16].

After cooling, the sample was put into class A calibrated glass (previously washed with an acid solution) and brought to final volume of 50 mL with deionized water. Any sediment present was let particulate before instrumental analysis. A blank was prepared with the same criteria of sample treatment.

**Recovery test**

Due to volatility of As, in order to assess the potential loss of analyte during the mineralization process and/or the potential influence of the amounts of acid used, recovery tests were carried out so as to have As concentrations of 100 and 50 µg/L in the final solutions. Aliquots of 500 and 250 µL were taken from a 10 mg/L standard solution of As and each put into six different Teflon vessels, for a total of 12 vessels. Each underwent the same mineralization programs mentioned above and taken to a final volume of 50 mL with deionized water.

Standard solutions and reference material, after mineralization, were analyzed by means of two different spectroscopic techniques, inductively coupled plasma atomic emission (ICP-AES) and atomic absorption (AAS).