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Slurry sampling electrothermal atomic absorption spectrometry as screening method for chromium in compost

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Abstract

Ultrasonic slurry sample introduction was applied to the determination of total chromium in composted materials by electrothermal atomic absorption spectrometry (ETAAS). The effect of grinding on the heterogeneity of the test samples and on the attainable precision was studied. The repeatability was influenced by the heterogeneity of the test samples at the μg-level, the R.S.D. of the measurements being 15%. The reproducibility depended on the heterogeneity of the test sample at the mg level, and it could be improved from 11 to 7% by increasing the grinding time. The characteristic mass was 2.6 pg and the detection limit for the optimised procedure at the 0.04% (w/v) slurry concentration, 370 ng g^{-1}. Good agreement with a certified reference material and with the conventional microwave assisted digestion method was found by using external calibration with aqueous standards. The performance of the method for screening purposes was evaluated.

Keywords: Electrothermal atomic absorption spectrometry; Slurry sampling; Screening; Compost

1. Introduction

The composting process is an efficient method of waste management for stabilizing the organic fraction of urban solid residues (USR). The stabilised end-product (compost) is widely used in agriculture, as soil amendment to improve the physical properties of soils [1] and provide plant nutrients [2], as well as for remediating soils contaminated with toxic organic and inorganic compounds [3].

USR compost is an heterogeneous mixture of organic and inorganic materials, which can contain high levels of heavy metals, restricting its agricultural uses [2]. The heavy metals content information is of limited value, because the actual environmental impact of an element depends on the mobility, bioavailability and toxicity of its different chemical forms present in the compost [4]. In spite of this, the maximum total concentrations for a range of heavy metals are used to establish the compost quality standards in a number of countries, through their different local regulations [5].

Chromium is an essential element, which is involved in the metabolism of carbohydrates. The toxicity of the element depends on its chemical form: Cr(VI) compounds are toxic, mutagenic and carcinogenic, whereas the Cr(III) toxicity is considered low, although potential genotoxic effects have been documented [6]. The maximum allowable concentration of total chromium for compost in the countries with the most strict regulations range from 50 mg kg^{-1} in the Netherlands to 100 mg kg^{-1} in Germany [5]. The European Communities have established a maximum total chromium content of 100 mg kg^{-1} for soil improvers awarded with the Eco-label [7].

A number of methods are available for the determination of total chromium and other heavy metals in compost. They are based on the wet digestion of samples and the element determination by ICP-AES [8,9] or AAS [10], as well as on the direct analysis by neutron activation [11,12]. Slurry sample introduction in combination with electrothermal atomic absorption spectrometry (slurry-ETAAS) is a well recognised method for direct analysis of solids, avoiding the digestion of samples, shortening the time of analysis and reducing the risk of contamination [13]. Slurry-ETAAS has been successfully applied for the determination of chromium in various environmental materials:

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soils [14–17,20–22], sediments [15,16,20,21] and sludges [15,17].

Slurry ETAAS has been considered a well suited method to be used as screening system [18]. The conventional wet digestion of the sample prior to the ETAAS determination can be replaced by the simple preparation of the slurry, obtaining a rapid binary response which will indicate if the analyte is present above or below a pre-set concentration threshold and if the sample meets the requirements of customers or regulations [19].

The aim of this work is to evaluate the performance of ETAAS slurry sampling introduction for the direct determination of chromium in compost as a rapid method for screening purposes. The method was validated against a compost reference material and the conventional wet digestion of the samples.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer model A-300 spectrometer, equipped with electrothermal atomiser HGA-800, autosampler AS-72 and ultrasonic probe USS-100 was used for atomic absorption measurements. Chromium absorption was measured at 357.9 nm. The spectral bandwidth was set at 0.7 nm and the hollow cathode lamp current at 25 mA. Pyrolytically coated graphite tubes with pyrolytic platforms were used for the experiments. Transient signals were evaluated by their peak areas (integrated absorbance). No background correction was used.

2.2. Reagents and samples

Standard stock solutions of chromium (1000 mg l^{-1}) were prepared from analytical reagent grade K_2CrO_4 (Merck).

Stock solutions of magnesium nitrate (1000 mg l^{-1}) were prepared from analytical reagent grade (Merck).

Ultrapure water was obtained from a Milli-Q system (Millipore).

Compost samples from urban solid residues (USRC-1 and USRC-2) were obtained from a composting plant of Tecmed, S.A. (Spain).

The CP-1 compost reference material was obtained from SCP Science (Canada).

2.3. Slurry preparation and introduction

Compost samples from urban solid residues were ground in a vibrating rotary cup mill Pulverisette 9 (Fritsch) made of agate for 30 or 60 min to reduce the particle size.

The slurries were prepared by weighing the test portions of the material (around 20 mg) into pre-cleaned polyethylene test tubes and mixed with 200 μl of 5% (v/v) Triton X-100 (Sigma) and 1% (v/v) HNO_3 (Merck Suprapure) to obtain a final volume of 50 ml. The masses were measured by a Mettler Toledo AG245 balance, with a precision of ± 0.01 mg. The tubes were placed in an ultrasonic bath (Selecta) for 15 min, aliquots of 2 ml were removed to be placed in the autosampler vials and then ultrasonicated for 10 s at 50 W, finally 20 μl of the homogenised slurry were injected into the furnace.

2.4. Determination of analyte partitioning

For the determination of the percentage of chromium extracted to the liquid phase of the slurry, the homogenised slurry was first analysed following the procedure described above, then the slurry was centrifuged for 30 min at 3000 rpm (Megafuge 1.0 Heraeus) and the supernatant was analysed.

2.5. Wet digestion

For comparison, determinations were also performed with wet digestion of compost samples. Test portions (0.1 g) were accurately weighed into PTFE decomposition vessels and 3 ml of concentrated HNO_3 (Merck), 1 ml of H_2O_2 30% (v/v) (Panreac) and 1 ml of concentrated HF (Merck) were added. The programme used in the microwave oven (Anton Paar, Perkin-Elmer) consisted of three steps: 700 W for 6 min, 1000 W for 15 min and 15 min for cooling. The solution obtained was transferred to a volumetric flask and diluted to 25 ml with ultrapure water. Solutions were analysed by ETAAS.

2.6. Screening simulation

Nine test samples (20 mg) were withdrawn from a laboratory sample and slurries were prepared following the procedure described above. Ten replicates were measured from each single slurry preparation, the replicates were combined in groups of five, obtaining 252 results per slurry, and a total population of 2268 results for the nine slurries. Averaged recalls were calculated from the 2268 results by using the mean or the median and different tolerance margins.

3. Results and discussion

3.1. Optimisation of the furnace programme

The temperature programme and the effect of using magnesium nitrate as chemical modifier on both standards and slurries were studied. Slurries prepared from the USRC-1 compost sample, following the procedure described in Section 2, were used for these optimisation experiments.

As can be seen in Fig. 1a, a similar behaviour with respect to the pyrolisis temperature was observed for chromium in the aqueous standard and the slurry, showing a maximum pyrolisis temperature of 1500 °C, as it has been reported for sediment and soil slurries by Mierzwa et al. [16]. The use of

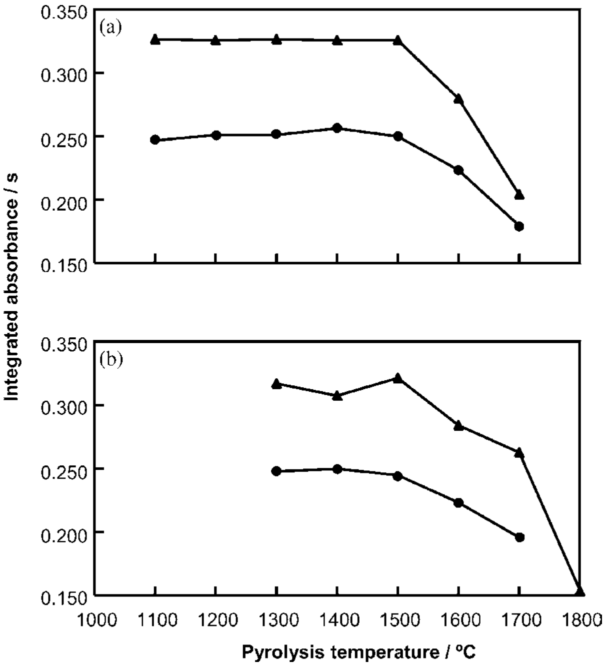

Fig. 1. Pyrolysis temperature curves of chromium from aqueous solution (●) and compost slurry (▲). (a) Without chemical modifier, (b) with 50 µg of $Mg(NO_3)_2$. Mass of chromium: 0.15 ng (aqueous solution) and 0.20 ng (slurry).

magnesium nitrate (50 µg per injection) did not result in any additional improvement in the thermal stability of chromium or the slurry, as it is shown in Fig. 1b. The atomisation temperatures were studied in the range of 1900–2600 °C and an optimum atomisation temperature of 2500 °C was selected. The temperature programme shown in Table 1 was used for standards and slurries without chemical modification. Under the measurement conditions selected, no significant background absorption was observed.

3.2. Optimisation of the slurry preparation

Slurries are usually prepared by weighing some milligrams of the powdered material and adding a volume of a diluent containing nitric acid and Triton X-100 [13]. The surfactant serves as wetting agent and avoids agglomeration of the particles, although a decrease of chromium sensitivity at high Triton X-100 concentrations has been reported [23].

Table 1
Optimised temperature programme for the determination of chromium in compost

Step	Temperature (°C)	Ramp (s)	Hold time (s)	Ar flow rate (ml min^{-1})
Drying	120	5	30	250
Pyrolisis	1500	10	40	250
Atomisation	2500	0	5	0
Cleaning	2600	2	3	250

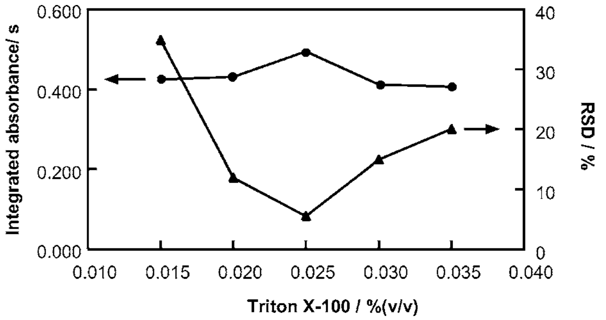

Fig. 2. Effect of Triton X-100 concentration in the slurry diluent on chromium signal (●) and its precision (▲). Mass of chromium: 0.25 ng.

Fig. 2 shows the effect of Triton X-100 concentration on the chromium signal and the precision of the measurements. Whereas the surfactant concentration was not critical on sensitivity, a concentration of 0.02% (v/v) was required to reduce the imprecision of the measurements.

Nitric or other acids added to the diluent facilitate the extraction of the analyte to the liquid phase, although a high degree of extraction is usually not a condition to obtain reliable results [24]. A concentration of 1% (v/v) nitric acid was used as default. For this acid concentration the chromium extracted to the liquid phase, was 31% for the USRC-1 and 22% for the USRC2, in the range of the values obtained for soils and sediments.

The slurry concentration is a compromise between the expected analyte concentration in the sample, the weighing of a representative amount of sample, the analytical range of the calibration and the volume of the slurry injected into the furnace. If the analyte concentration in the slurry is too high, smaller volumes can be injected, alternative less sensitive absorption lines can be selected, the gas flow can be maintained during the atomisation step or slurry preparations can be further diluted. In order to avoid contamination of the atomiser, this last option was selected and slurries were prepared by diluting 1–60 mg of samples in large volumes (50 ml). For the USRC-1 compost, a linear response was obtained for slurries prepared up to concentrations of 0.06% (w/v), when the most sensitive line of chromium was used.

Working at such low slurry concentrations, care must be taken to ensure that a representative number of particles is injected for analysis. Miller-Ihli [13] related particle size and density of the material with the minimum slurry concentration required to ensure a 2% imprecision due to the aliquot withdrawing from the slurry and injected into the furnace. A density of 1.2 g cm^{-3} was estimated experimentaly for the compost materials studied and a medium particle size of less than 100 µm (Table 2) was considered; from data of reference [13], a mass between 6.5 and 10 mg suspended in 50 ml would fulfil the condition of representativeness, assuming that the analyte is homogeneously distributed in the solid. A default mass of 20 mg of ground compost was used for analysis.

Table 2
Particle size distribution of USR compost for different grinding times

Grinding time (min)	Particle size			
	<125 μm (%)	125–250 μm (%)	250–500 μm (%)	>500 μm (%)
30	58.6	36.7	3.3	0.6
60	75.3	23.5	0.7	0.4

3.3. *Heterogeneity of samples and particle size*

Sample heterogeneity is often the limiting factor to obtain reliable results in slurry and solid sampling ETAAS. The USR composts used along this work were very heterogeneous materials with particles of different nature, and sizes up to 5–10 mm. The purpose of the particle size reduction was to obtain less heterogeneous test samples. To study the effect of the particle size reduction and the heterogeneity of the test samples on the determination of chromium, a laboratory sample (500 g) was divided in two subsamples which were ground for 30 and 60 min to obtain the corresponding test samples. The particle size distribution was established by sieving through 500, 250 and 125 μm sieves, and are shown in Table 2. From the results obtained it can be observed that size reduction to less than 250 μm was easily achieved for 95% of the material after grinding for 30 min. When grinding was extended for 60 min, almost 99% of the material was reduced to less than 250 μm, increasing the fraction smaller than 125 μm up to 75%.The heterogeneity of a test sample becomes manifest when determining the analyte content in a series of test portions taken from the test sample. The variance of the analytical result can be expressed as [25]

$$\sigma^2_{\text{anal}} = \sigma^2_{\text{det}} + m\sigma^2_{\text{het}} \qquad (1)$$

where σ^2_{anal} is the total variance associated with the analysis of the test portions, σ^2_{het} the variance associated with the heterogeneity of the test sample at the mg-level, σ^2_{det} the variance associated with the analyte determination, which depends on the heterogeneity of the test sample at the μg-level as it will be discussed below, and *m* the number of replicated measurements per test portion.

To study the effect of the grinding time on the test sample heterogeneity, the variance due to heterogeneity at the mg-level was estimated from a one-factor analysis of variance and Eq. (1). Thus, nine test portions (20 mg) were withdrawn from each test sample, and ten replicated measurements were performed from each of the nine slurries prepared. Outliers (around 2% of data) were discarded by applying the Dixon test before statistical calculations. Table 3 shows the results of the one-factor analysis of variance performed for each grinding time, expressed as relative standard deviations (R.S.D.). The results show that the main contribution to the total R.S.D. associated with the analysis of the test portions (around 18%) is related to the analyte determination (between 13 and 17% for the experiments performed). When the sample was ground for 30 min, the contributions of the sample heterogeneity and the analyte determination to the total R.S.D. were of the same order, whereas the R.S.D. from the test sample heterogeneity after grinding for 60 min was almost negligible with respect to the R.S.D. from the determination.

3.4. *Analytical performance*

The characteristic mass, defined as the mass of analyte corresponding to 0.0044 integrated absorbance units, was 2.6 pg. The limit of detection of the optimised procedure, following the three sigma criterion, was 370 ng g^{-1}.

The repeatability represents the random error associated with the analyte determination in the slurry and it was calculated using the relative standard deviation for 10 successive injections of the slurry, the averaged relative standard deviation for 18 slurries was 15.0%. If the repeatability from the ETAAS measurement of an aqueous standard of chromium ranges from 1 to 3%, the main contribution to the slurry repeatability should come from the measurement of chromium in the solid particles, including the withdrawing of them from the suspension. Assuming a contribution from the aliquot withdrawing of less than 2%, as it has been discussed in 3.2, the repeatability obtained can be explained by the heterogeneity at the μg-level, due to the different nature of the particles and the different chromium content of them, which work as another source of imprecision. The presence of “nuggets”, particles with very high contents of analyte [26], cannot be considered responsible

Table 3
Contribution of the test sample heterogeneity and the slurry determination to the total R.S.D. of the analysis for different grinding times

Grinding time (min)	R.S.D.$_{\text{anal}}$ (%)	R.S.D.$_{\text{det}}$ (%)	R.S.D.$_{\text{het}}$ (%)
30	17.7	13.0	12.6
60	17.9	16.8	6.5

Table 4
Results for the determination of chromium in compost samples

Sample	Concentration (μg g^{-1})		
	Slurry[a]	Microwave[b] digestion	Certified value
CP-1	38 ± 3	38 ± 1	41 ± 6
USRC-1	40 ± 3	40 ± 1	
USRC-2	22 ± 3	19 ± 1	

[a] $n = 3$; mean ± S.D.
[b] $n = 4$; mean ± S.D.

of such heterogeneity, because the level of outliers along the experiments was low (around 2%). When the number of particles was increased by grinding the samples for 60 min, no significant improvement on repeatability was observed.

The reproducibility, which reflects the heterogeneity of the analysed material at the mg level, was calculated from the relative standard deviation of the analysis of nine different slurries, by using the median a R.S.D. of 11.5% was obtained. This value could be reduced to 7.3% when the sample was ground for 60 min, although the improvement was not statistically significant due to the repeatability obtained.

3.5. Analysis of compost samples

Two samples of compost from urban solid residues (USRC-1 and USRC2) and a compost reference material (CP-1) were analysed following the optimised slurry procedure described in Section 2. Results were compared with those obtained from the samples dissolved by microwave assisted digestion. In all cases, recoveries in the range of 94–99% were obtained, therefore, aqueous standards were used for calibration.

As it is shown in Table 4, good agreement was observed for results obtained by the slurry and the wet digestion procedures. Results of the reference material analysed by the two tested procedures were well comparable with the certified values.

3.6. Evaluation of the method for screening purposes

The use of the slurry-ETAAS method developed for screening purposes implies to perform the minimum number of measurements on the minimum number of sample aliquots. A screening method is characterised by its recall [27], which can be calculated using the mean or the median

$$\text{recall} = \frac{\text{no. of correct identifications}}{\text{no. of attempted identifications}} \quad (2)$$

where correct identifications are considered those in which the mean or the median is within a pre-established tolerance margin. When the number of measurements is low, the use of the median is preferred because the occurrence of potential outliers is difficult to detect, and under such conditions the median can provide better results than the mean [28].

Belarra et al. stated that five measurements were sufficient to guarantee a recall higher than 0.95, when solid sampling ETAAS was used as screening method with a tolerance margin of ±20% and a sample heterogeneity lower than 20% [28]. The screening of one slurry preparation from each laboratory sample by performing five measurements on the slurry was considered. In order to study the validity of the proposed procedure, the simulation described in Section 2 was performed. Recalls were calculated by using the mean and the median, considering that the target value was the averaged content of chromium obtained from the analysis of ten test samples from the same laboratory sample ground for 30 min (22.6 $\mu g\, g^{-1}$). Tolerances for the maximum allowable concentrations of heavy metals in composted materials range from 25 to 50%, depending on the country regulations [5], thus recalls for ±20, ±25 and ±50% are presented in Table 5.

Table 5 shows that it is possible to obtain a recall of 1 when the tolerance margin of ±50% is applied. If potential outliers are absent, recalls equal or higher than 0.90 can be obtained for tolerance margins of ±20%, although it should be taken into account that going from 1.00 to 0.90 was due to the low recalls obtained with one of the nine sets of experimental results used. With regard to the use of the mean or the median, in the presence of outliers and for tolerance margins lower than ±50%, the median is clearly superior, making possible to obtain a recall of 0.99 (single values higher than 0.90) for tolerance margins equal or higher than ±25%.

The use of a test sample ground for 60 min (results not shown) allowed to improve the recalls calculated from the mean, although averaged recalls lower than 0.95 were obtained for tolerance margins of ±20 and ±25%.

Table 5
Recalls for a screening simulation experiment at three levels of outliers

Recall	Tolerance margin					
	±20%		±25%		±50%	
	Mean	Median	Mean	Median	Mean	Median
No outliers						
Averaged value[a]	0.90	0.92	0.92	0.99	1.00	1.00
Range	0.12–1.00	0.50–1.00	0.29–1.00	0.92–1.00	–	–
2% Outliers						
Averaged value[a]	0.83	0.92	0.86	0.99	1.00	1.00
Range	0.12–1.00	0.50–1.00	0.30–1.00	0.92–1.00	–	–
10% Outliers						
Averaged value[a]	0.47	0.92	0.56	0.99	1.00	1.00
Range	0.12–0.56	0.50–1.00	0.26–0.84	0.92–1.00	–	–

Screening procedure: one slurry per sample, five measurements per slurry.

[a] Nine sets of 252 results.

4. Conclusions

The direct injection of slurries into the graphite furnace permits the rapid and reliable determination of chromium in compost. The R.S.D. values obtained can be attributed to the small sample masses introduced into the atomiser and the non uniform distribution of the analyte in the particles, due to the heterogeneous nature of the compost obtained from urban solid residues.

The proposed method is simpler and faster than the wet digestion, and is suitable for the routine screening of total chromium in compost. It must bear in mind that the tolerances for maximum allowable concentrations of heavy metals in composted materials established in countries with the most strict quality levels range from 25 to 50% and sampling errors of 40% have been reported [5], which are higher than the uncertainty attainable by slurry introduction. If the median is used, five measurements performed on a single slurry preparation from a test sample ground for 30 min allows to obtain recalls close to 1 in less than 15 min, in spite of the presence of outliers. Thus, samples can be filtered and those with suspicious results can be analysed by a more precise method, like conventional ETAAS and wet digestion of the sample.

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