



Simultaneous determination of Cd and Fe in sewage sludge by high-resolution continuum source electrothermal atomic absorption spectrometry with slurry sampling

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ABSTRACT

This work describes the method development for the simultaneous determination of Cd and Fe using the main resonance line of Cd at 228.802 nm and a secondary Fe line at 228.725 nm, and high-resolution continuum source electrothermal atomic absorption spectrometry (HR-CS ET AAS). Two certified reference materials and two 'real' samples of industrial and domestic sewage sludge have been analyzed as slurries prepared in a mixture of HF and HNO₃. The simultaneous determination has been performed using a short temperature program of only 30 s, without a pyrolysis stage and with two atomization stages, at 1300 °C and 2300 °C, taking into consideration the significantly different thermal characteristics of Cd and Fe. Structured background, which is likely due to the presence of one or more diatomic molecules, including SiO, has been detected. However, there has been no spectral overlap between molecular bands and the atomic lines of Cd and Fe, making possible the determination to be carried out using only automatic correction for continuous background. Calibration against aqueous standards lead to good agreement between certified or informed values and the determined values, at a statistical confidence level of 95%; recovery tests were performed for real samples, resulting in recoveries ranging from 90 to 105%. Detection limits of 0.03 and 90 µg g⁻¹ for Cd and Fe, respectively, have been obtained, which are adequate for the purpose.

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1. Introduction

Population growth is responsible for a massive increase in the amount of sewage produced daily, and the final destination of sewage is a considerable environmental issue [1]. Sewage sludge usually contains metallic elements deriving from the very nature of the waste and from plumbing. Sewage sludge originating from industrial activities also contains metals from the dumping of industrial waste, usually at higher concentrations than those found in domestic sewage [2].

One of the main concerns involving sewage sludge is related to its use as a fertilizer in agriculture as an alternative to commercial fertilizers, as some elements might be accumulated in the soil reaching toxic levels. This way, toxic elements might be introduced into the food chain through plants; water contamination is another issue, potentially leading to serious environmental problems [3,4]. Due to these effects, there is a growing need for assessment of

environmental risks associated to the concentration of metallic elements in the environment due to the implementation of sewage sludge for agricultural purposes [1].

Cadmium has essentially no physiological function and is considered highly toxic even at low concentrations [5]. Iron, however, is an essential element for fauna and flora in general, but an excessive amount of iron in the soil has been proved to induce harmful effects, such as a significant decrease in the absorption of some essential nutrients for plants [6]. Monitoring the concentration of elements such as Cd and Fe is, therefore, of high importance in order to evaluate the potential environmental impact and set guidelines for the recovery of affected areas, as well as to define the use of materials such as sewage sludge for agricultural purposes. However, the analysis of complex samples, such as sewage sludge, frequently requires intensive analytical procedures to bring the solid sample into solution. Such procedures are usually labor-intensive and time-consuming, also bringing disadvantages such as excessive sample dilution and the risk of contamination or analyte loss. Slurry sampling is an interesting alternative to the usual dissolution processes, offering advantages such as the use of autosamplers, reduced time required for sample preparation and lower risk of contamination and loss of analyte [7,8].

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The introduction of solid samples as slurries into the graphite furnace may lead to excessive background due to the presence of relatively large amounts of matrix inside the atomizer. In this sense, high-resolution continuum source atomic absorption spectrometry (HR-CS AAS) is ideally suited for such an application. Some of the characteristics of HR-CS AAS include its unsurpassed background correction capability and visualization of the entire spectral environment at about ± 0.2 nm in the vicinity of the analytical line, providing a new level of information. In addition, analytical lines of two or more elements that fall within the same spectral region may be monitored simultaneously, increasing the analytical frequency significantly [9–12]. This second line, almost inevitably, is a less sensitive analytical line, and, although there are ways to increase or reduce sensitivity in HR-CS AAS, the sensitivity ratio between the two lines has to be in accordance with the analytical task [12]. This approach has been successfully applied to the simultaneous determination of cadmium and iron in grain products [13] and beans and soil of different regions of Brazil [14], and also to the determination of Cr and Fe in crude oil samples [15].

The aim of this work has been to employ HR-CS AAS with electrothermal atomization (ET) for the simultaneous determination of Cd and Fe in sewage sludge prepared as slurries, using a fast temperature program to obtain maximum analytical frequency.

2. Experimental

2.1. Instrumentation

Method development has been carried out using a prototype high-resolution continuum source atomic absorption spectrometer, developed at ISAS (Berlin, Germany), based on a model AAS 6 Vario (Analytik Jena AG, Jena, Germany), which has been described in detail elsewhere [12]. The instrument is equipped with a xenon short arc lamp, a high-resolution double monochromator and a linear charge coupled device (CCD) array with 512 pixels, 200 of which are used for analytical purposes. The conventional transversely heated graphite tube atomizer supplied with the model AAS 6 Vario has been used for all determinations.

Argon (99.996%, White Martins, São Paulo, Brazil) has been used as purge and protective gas. Pyrolytically coated graphite tubes with PIN platform (Analytik Jena) have been used throughout. An AG 204 analytical balance (Mettler Toledo, Geifensee, Switzerland) has been used to weigh the samples, and a T-50 ultrasonic bath (Thornton, São Paulo, Brazil) has been used to prepare the slurries in 15-mL polypropylene (PP) tubes (Sarstedt, Newton, NC, USA). The simultaneous determination of Cd and Fe has been carried out at the Cd resonance line at 228.802 nm and a secondary Fe line at 228.725 nm. The optimized graphite furnace temperature program is shown in Table 1.

2.2. Reagents and materials

All reagents used were at least of analytical grade. Nitric acid (Carlo Erba, Milan, Italy) was doubly-distilled below the boiling point

in a quartz still (Kürner Analysentechnik, Rosenheim, Germany) and hydrofluoric acid (Merck, Darmstadt, Germany) was distilled in a PTFE apparatus (Kürner Analysentechnik). De-ionized water from a Milli-Q system (Millipore, Bedford, MA, USA) with a resistivity of 18 M Ω cm has been used throughout. A stock standard solution containing 1000 mg L⁻¹ Cd has been prepared by appropriate dissolution of high-purity CdO (Spex, Edison, NJ, USA). Stock solution of Fe (1000 mg L⁻¹) has been prepared from a Titrisol® ampoule (Merck). Two certified reference materials have been used, BCR 146R “industrial sewage sludge” and BCR 144R “domestic sewage sludge,” from the Community Bureau of Reference (BCR, Brussels, Belgium).

2.3. Analytical procedure

All CRM samples have been ground in a ball mill (Retsch, Düsseldorf, Germany) and passed through a polyester sieve for particle sizes ≤ 50 μ m. Aliquots containing between 5 and 15 mg of each sample have been weighed directly into P flasks, containing approximately 2–3 mL of deionized water. The addition of HNO₃ and HF to a final concentration of 0.7 mol L⁻¹ and 0.2 mol L⁻¹ followed this procedure, and the flasks have been immersed in an ultrasonic bath for 30 min. Afterwards, deionized water was added to make up the final volume to 10 mL. Real samples of domestic and industrial sewage have also been collected and analyzed. The domestic sewage sludge sample was dried in a stove at 85 °C for 48 h; the resulting material was then ground in an agate mortar and passed through a polyester sieve, similarly to the procedure described above for the CRM, prior to preparation of the slurries. Aliquots containing approximately 60 mg were used. Industrial sewage was collected at a paper recycling industry. The sewage consisted of paper fibers and particulate matter suspended in the aqueous medium. A filter paper was used to separate coarse cellulose fibers, and the resulting suspension has been analyzed without dilution, after addition of acids, as described above for the CRM.

An autosampler has been used to deliver 10- μ L aliquots of the slurries into the graphite furnace. Prior to each injection, the samples have been homogenized manually, stirring with a micropipette. The temperature program in Table 1 followed each injection. Calibration has been carried out against aqueous standards in 0.1 mol L⁻¹ HNO₃.

3. Results and discussion

3.1. Effect of the preparation medium of the slurry

The medium in which the sample is prepared has a direct effect on the homogeneity and on the extraction of the analyte to the aqueous phase. Several approaches have been evaluated in order to prepare sewage sludge slurries, involving combinations of deionized water, HNO₃ and HF. It became clear, from the analysis of the supernatant phase of the slurries following centrifugation, that according to expectation, the addition of acids increased the extraction of Cd and Fe to the aqueous phase significantly, resulting in improved precision. However, the addition of HF to the slurry also promoted a reduction in the intensity of the structured background observed during the atomization stage at 2300 °C, which is most likely due to the $\Delta\nu = +2$ band of the X ¹ $\Sigma^+ \rightarrow A$ ¹ Π electronic transition of the SiO molecule [12]. The addition of HF to the slurry should promote premature volatilization of a significant fraction of silica as SiF₄, therefore decreasing the background. The remaining structured background, however, was found to be significantly different from the one observed for slurries prepared in 0.7 mol L⁻¹ HNO₃ and in deionized water, without HF, which suggests that another diatomic molecule is contributing to the background as well. It should be emphasized, however, that the molecular spectrum showed no significant overlap with the Cd or Fe lines, i.e., it did not interfere in the measurement, if a proper integration time interval was selected. Due to the reduction in

Table 1
Temperature program adopted for the determination of cadmium and iron in sewage sludge by HR-CS ET AAS with slurry sampling.

Stage	Temperature °C	Ramp °C s ⁻¹	Hold time (s)	Ar flow rate (L min ⁻¹)
Drying	90	50	3	2.0
Drying	130	20	3	2.0
Atomization I	1300	2000	4	0
Atomization II	2300	1000	5	0
Cleaning	2550	1000	3	2.0

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