

# Fractionation of metals and metalloids by chemical bonding from particles accumulated by electrostatic precipitation in an Argentine thermal power plant

Darío Gómez<sup>a</sup>, Marina Dos Santos<sup>a</sup>, Fabián Fujiwara<sup>a</sup>, Griselda Polla<sup>b</sup>, Julieta Marrero<sup>c</sup>,  
Laura Dawidowski<sup>a</sup>, Patricia Smichowski<sup>a,d,\*</sup>

<sup>a</sup> Comisión Nacional de Energía Atómica, Unidad de Actividad Química, Av. Gral. Paz 1499, B1650KNA-San Martín, Pcia. de Buenos Aires, Argentina

<sup>b</sup> Comisión Nacional de Energía Atómica, Unidad de Actividad Física, Av. Gral. Paz 1499, B1650KNA-San Martín, Pcia. de Buenos Aires, Argentina

<sup>c</sup> Comisión Nacional de Energía Atómica, Unidad de Actividad Combustibles Nucleares, Av. Gral. Paz 1499, B1650KNA-San Martín, Pcia. de Buenos Aires, Argentina

<sup>d</sup> Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) - Argentina

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## Abstract

A study was undertaken to evaluate the distribution of Al, As, Cr, Cu, Fe, Mn, Ni, Pb, Ti, V and Zn in fly ashes collected in the electrostatic precipitator of a thermal power plant in San Nicolás (Argentina). Five samples were collected during one week of operation. For the fractionation, the scheme applied consisted in extracting the elements in four fractions namely (i) soluble and exchangeable elements; (ii) carbonates, oxides and reducible elements; (iii) bound to sulfidic metals; and (iv) residual elements. Metals and metalloids at  $\mu\text{g g}^{-1}$  level were determined in each fraction by inductively coupled plasma optical emission spectrometry (ICP OES). For validation, a standard reference material (SRM 1633 coal fly ash) from NIST was subjected to the same chemical sequential extraction procedure that the samples. X-ray diffraction powder (XRD) analysis and scanning electron microscopy (SEM) were used to characterize the major minerals present in the matrix. Total analyte concentration (in  $\mu\text{g g}^{-1}$ ) varied from 10.6 for Pb to 17,622 for Al. Minimum and maximum concentrations (in  $\mu\text{g g}^{-1}$ ) found in individual samples in the four fractions were: Al, 92.7–9668; As, <0.3–143; Cr, 2.0–10.4; Cu, <0.2–35.6; Fe, <0.3–4992; Mn, <0.1–128; Ni, <0.3–139; Pb, <0.5–9.1; Ti, <0.3–2243; V, 17.0–112.9; and Zn, <0.1–68.2. The leachability of the 11 elements under study proved to be different. Low percentages of Al (1%), V (7%) and Cr (8%) were detected in the most bioavailable fraction. Arsenic was found to be most abundant in the non-silicate phase, represented by the second and third fractions, while Cr, Fe, Ni, Pb and Zn were mostly associated to the residual fraction.

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## 1. Introduction

The major use of coal today is the generation of power through combustion. The coal combustion by-products in thermal power plants are significant sources of potentially toxic elements into the environment. A 1000 MW power plant has a normal consumption of 12,000 t day<sup>-1</sup> of sub-bituminous coal

[1] and coal ashes are generated in a very aggressive combustion process. The amount and nature of metals and metalloids released are related to the composition of the coal burned and the technology employed in the power station. Coal contains many elements (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Sn, etc.) and most of them have been reported to be human carcinogens [2]. After combustion, these elements are typically found in the bottom ashes, the fly ashes and the gaseous phase. Electrostatic precipitators can remove more than 95% of the fly ashes but particles with aerodynamic diameters less than 10  $\mu\text{m}$  are likely to be emitted directly to the atmosphere. Studies on the mobility of metals and metalloids during coal combustion

\* Corresponding author. Comisión Nacional de Energía Atómica, Unidad de Actividad Química, Av. Gral. Paz 1499, B1650KNA-San Martín, Pcia. de Buenos Aires, Argentina.

E-mail address: [smichows@nea.gov.ar](mailto:smichows@nea.gov.ar) (P. Smichowski).

have demonstrated that their volatility depends on their affinities and concentrations, and on the physical changes and chemical reactions of these elements with sulfur or other volatile elements [1].

A percentage of coal fly ash (~ 10–20%) is used in the concrete and cement manufacturing industries [3,4] and in other construction areas. However, ashes are more often discarded in sites such as lagoons, settling ponds or landfills [5], requiring investments for the non-productive use of land resources and long-term maintenance. As a consequence, alternative uses for fly ash other than the cement and construction industry have been and still are sought. Iyer and Scott [6] have reviewed such possible uses that include synthesis and application in materials, adsorbents and waste management, materials recovery and agriculture. In this context, knowledge of the chemical composition, physical characteristics and fractionation by chemical bonding of the ashes are of prime importance to assess the environmental impact and health risks. The leaching and consequent mobilization of the elements present in the ashes into waters and soils constitutes a serious risk that has to be evaluated.

Studies based on chemical sequential extractions provide useful information about solubility, origin, mode of occurrence, biological and physicochemical availability, mobilization, fate and transport of trace metals into the environment. Recently, Smichowski et al. [7] have reviewed metal fractionation of atmospheric aerosols via sequential chemical extraction procedures. The same authors also reviewed the role of atomic spectrometric techniques in the determination of chemical elements in atmospheric aerosol, including fractionation studies [8]. It is important to remark that the information gained by employing chemical sequential extraction procedures is operationally defined. Thus, the term “operational” is meant to indicate that the data obtained are dependent on the experimental approach adopted. Their operationally defined nature may be considered a weakness. In spite of this, sequential extraction methods are important approaches and the knowledge gained using these schemes would considerably improve our understanding of the risks for human health and the environment.

Different schemes have been developed and applied to the chemical fractionation of fly ashes from different origins both for research and regulatory controls [9–11] developed a five-stage leaching procedure that was applied to fly ash samples collected at several emission sources in Austria, Hungary and Switzerland. The analysis of the extracts by atomic absorption spectrometry (AAS) and graphite furnace atomic absorption spectrometry (GFAAS) showed different leachability of Cd, Cr, Cu, Pb, V and Zn exhibiting different distribution patterns. Cadmium distribution in coal fly ash, soil and sediment was assessed by sequential extractions of three certified reference materials and subsequent determination of the metal in the extracts by GFAAS [12]. Smeda and Zyrnicki [13] applied a modified BCR extraction scheme [14] for studying the partitioning of metals in fly ashes.

In this study, fractionation of ashes by chemical bonding was performed using a four-step chemical sequential leaching pro-

cedure similar to that developed by Fernández Espinosa et al. [15] to establish the distribution of 11 elements between (i) soluble and exchangeable metals, (ii) bound to carbonates, oxides (reducible elements), (iii) bound to oxidizable and sulfidic elements and (iv) environmentally immobile fractions (included in the crystal lattice).

This study is part of a national project funded by the Agencia de Promoción Científica y Tecnológica (Agency for Scientific and Technological Development) of Argentina aimed to quantifying metals and metalloids in urban APM as well as identifying their sources.

## 2. Experimental

### 2.1. Instrumentation and reagents

A Perkin-Elmer (Norwalk, CT, USA) ICP Optima 3100 XL (axial view) simultaneous inductively coupled Ar plasma optical emission spectrometer provided with a Model AS 90 autosampler was used for trace elements determination. Instrumental details and operating conditions are summarized in Table 1.

Welding Ar from Indura (Buenos Aires, Argentina) was used for ICP OES determinations. Deionized distilled water (DDW) was produced by a commercial mixed-bed ion-exchange system Barnstead (Dubuque, IA, USA) fed with distilled water. All reagents were of analytical grade. Hydrochloric, perchloric and nitric acids and hydroxylamine chloride, ammonium acetate and hydrogen peroxide (Merck, Darmstadt, Germany) were used for sample treatment and preparation of the standards. Commercially available 1000 mg l<sup>-1</sup> standard solutions (Merck) of the elements

Table 1  
Instrumental details and operation conditions for the determination of metals and metalloids in fly ashes by ICP OES

Instrument	Perkin-Elmer Optima 3100 XL
Forward rf power	1300 W
Frequency of rf generator	40 MHz (axial view)
Coolant gas flow rate	15 l min <sup>-1</sup>
Auxiliary gas flow rate	0.5 l min <sup>-1</sup>
Sample gas flow rate	0.8 l min <sup>-1</sup>
Solution delivery	1.0 ml min <sup>-1</sup>
Automatic sampler	Perkin-Elmer AS90
Nebuliser	Cross-flow with Scott type expansion chamber
Polychromator	Echelle grating, cross-dispersed, wavelength range (nm): 165–403
Detector	Segmented-array charge coupled device
Measurement mode	Continuous nebulisation
Signal processing mode	3 pixels peak area
Background correction	2 points
Wavelengths (nm)	As, 188.979; Al, 308.215; Cr, 267.716; Cu, 324.742; Fe, 238.204; Mn, 257.610; Ni, 232.003; Pb, 217.000; Ti, 337.279; V, 290.880; Zn, 206.200

analysed were used. Diluted working solutions were prepared daily by serial dilutions of those stock solutions. All glassware and plastic bottles were treated in a solution 10% v/v nitric acid for 24 h and then washed with deionized water. All samples and standards were stored in polyethylene bottles (50 ml) or Falcon® tubes.

X-ray diffraction patterns were collected at ambient temperature on a Philips X'Pert System, using a PW-3710 controlled diffractometer, with Cu graphite monochromatized radiation ( $\lambda = 1.5418 \text{ \AA}$ ) with  $0.5^\circ$  scattering slit, a  $2\theta$  step of  $0.02^\circ$  and 2 s by step ( $2\theta$  between  $10^\circ$  and  $70^\circ$ ). For phase identification, the diffraction patterns obtained were analyzed using PC-Identify and ICDD database.

Compositional identification was performed by energy dispersive X-ray analysis on a Philips 515 scanning electron microscope. All spectra were obtained at 10–20 kV in a 50-s analysis time.

## 2.2. Sample collection

Five fly ash samples were collected manually from the hopper of electrostatic precipitators of the San Nicolás power plant located in Buenos Aires province, Argentina. This 650 MW power plant is the only one in Argentina that burns coal. This sub-bituminous coal is normally imported from Australia, Colombia or South Africa; however, no attempt was made to characterize the coal that was used during the ash collection period. The sampled ashes were placed in clean polyethylene bags during transport and were stored in a dark and dry place in the laboratory.

## 2.3. Sample preparation for elemental analysis

Aliquots of 0.5 g of each sample were introduced into a reaction vessel and subjected to acid digestion using 13 ml of a mixture of  $\text{HNO}_3$ ,  $\text{HCl}$  and  $\text{HClO}_4$  (6:2:5). The vessel was covered and placed in a hot plate with shaker agitation for 5 h at  $95^\circ\text{C}$ . After cooling, the resulting solution was dissolved in a few milliliters of deionized water and then was made up to 25 ml with deionized water. The digestion procedure was run on without sample and the blank values thus obtained (reagents + vessel) were subtracted from the ICP OES measurements of the elements evaluated.

Three portions were weighted for each sample. For checking accuracy, aliquots of the SRM NIST 1633b coal fly ash (USA) were subjected to the same treatment and included in the overall analytical process.

## 2.4. Chemical sequential extraction of elements from coal fly ashes

Once in the laboratory, the five samples were simultaneously subjected to a four-step leaching procedure and the following fractions were obtained:

Fraction 1: about 100 mg were carefully weighted and 15 ml of water at pH 7.4 were added in a 50 ml Falcon® tube. Agitation at room temperature in a mechanical shaker at a

speed of  $30 \pm 10$  rpm was maintained for 3 h. After this period, samples were centrifuged for 3 min at 5000 rpm. An aliquot of 10 ml of the supernatant was taken with a micropipette and placed in a clean Falcon® tube (fraction 1).

Fraction 2: a 10 ml aliquot of a  $0.25 \text{ mol l}^{-1} \text{ NH}_2\text{OH}\cdot\text{ClH}$  solution at pH 2 was added to the residue of step 1. Four hours of shaker agitation at room temperature was applied. The procedure described above was repeated and fraction 2 was obtained.

Fraction 3: 7.5 ml of  $\text{H}_2\text{O}_2$  (30%) were added to the residue of fraction 2 and the solution was heated at  $95^\circ\text{C}$  until near dryness. This step was repeated once and then an aliquot of 15 ml of a  $2.5 \text{ mol l}^{-1} \text{ NH}_4\text{AcO}$  solution at pH 3 was added and shaker agitation was maintained for 60 min at room temperature. The solid residue was separated by centrifugation (5000 rpm) and then an aliquot of 10 ml of this solution was taken with a micropipette and placed in a clean Falcon® tube (fraction 4).

Fraction 4: the final residue was dissolved in a mixture of 5 ml of  $\text{HNO}_3$ , 2 ml of  $\text{HCl}$  and 2 ml of  $\text{HClO}_4$ , which was then placed in hot plate with shaker agitation for 5 h at  $95^\circ\text{C}$ . These acids were chosen as each helps in the decomposition of a specific part of the matrix.

In all cases, no delay has occurred between the addition of the reagents and the beginning of the shaking. All fractions were stored in a refrigerator at about  $4^\circ\text{C}$  prior to analysis.

The same four-step chemical extraction procedure was run on without sample and the blank values thus obtained (reagents + tubes) were subtracted from the ICP OES measurements of the elements evaluated.

## 2.5. Analysis

Inductively coupled plasma optical emission spectrometry (ICP OES) was employed for the determination of metals and metalloids in fly ash samples. This technique can be applied to different matrices after a suitable dissolution procedure and is characterized by extended dynamic concentration ranges (4–6 orders of magnitude), is multi-elemental in nature, and possesses high sensitivity and appropriate detection power.

For ICP OES determinations, four sets of multi-elemental calibrants were prepared to analyze each fraction from  $1000 \mu\text{g l}^{-1}$  standard solutions of the individual elements in the same matrix as the fraction. Screening experiments showed that in spite of the complexity of the matrix analyzed no standard addition was necessary for calibration. All measurements were performed by triplicate and the reported results are averaged values.

## 3. Results and discussion

### 3.1. Characterization of fly ashes by X-ray diffraction

The mineralogical composition of fly ashes was determined by X-ray diffraction (XRD). All the samples revealed a similar diffraction pattern, consisting basically of aluminosilicates and large amounts of amorphous material. The predominant



crystalline phases found in all ash samples were mullite and quartz as the major phases. The other mineral phases present as minor or accessory are lime, anhydrite, hematite, magnetite, gypsum and rutile.

Different types of particles, agglomerates, spheres, organic constituent (char) and non-crystalline phases (amorphous) compose predominantly the fly ashes studied as it is shown in Fig. 1. The presence of char may be attributed to an incomplete combustion of coal. All the samples studied by EDAX show a relatively similar chemical composition: they are abundant in Si and Al, and in minor concentrations Ca, Mg, Ti, Fe and S.

### 3.2. Detection limits and precision

Using optimized conditions, analytical figures of merit including detection limit and precision of replicate measurements were established. Detection limits were calculated following the

IUPAC rules on the basis of  $3\sigma$ -criterion for 10 replicate measurements of the blank signal calculated from four individual calibration curves. Limits of detection are set forth in Table 2.

The RSDs for the 11 elements evaluated in the coal fly ash samples are in general in a more than satisfactory interval (3.3% to 9.0%) considering the complexity of the matrix analyzed and the considerable number of manipulations performed. This variability depends on the element and the extraction step. The contribution of sample heterogeneity is another factor to take into account in this kind of samples because the instrumental variability of the technique used is estimated to be not higher than 1% relative. On the contrary; the contribution from sample heterogeneity in the SRM may be considered, in principle, non-significant as reflected in the RSDs achievable (Table 3). Lower precision for fly ash samples was observed for those elements that in the water-soluble fraction exhibited very low concentrations or concentrations close to their detection limits.

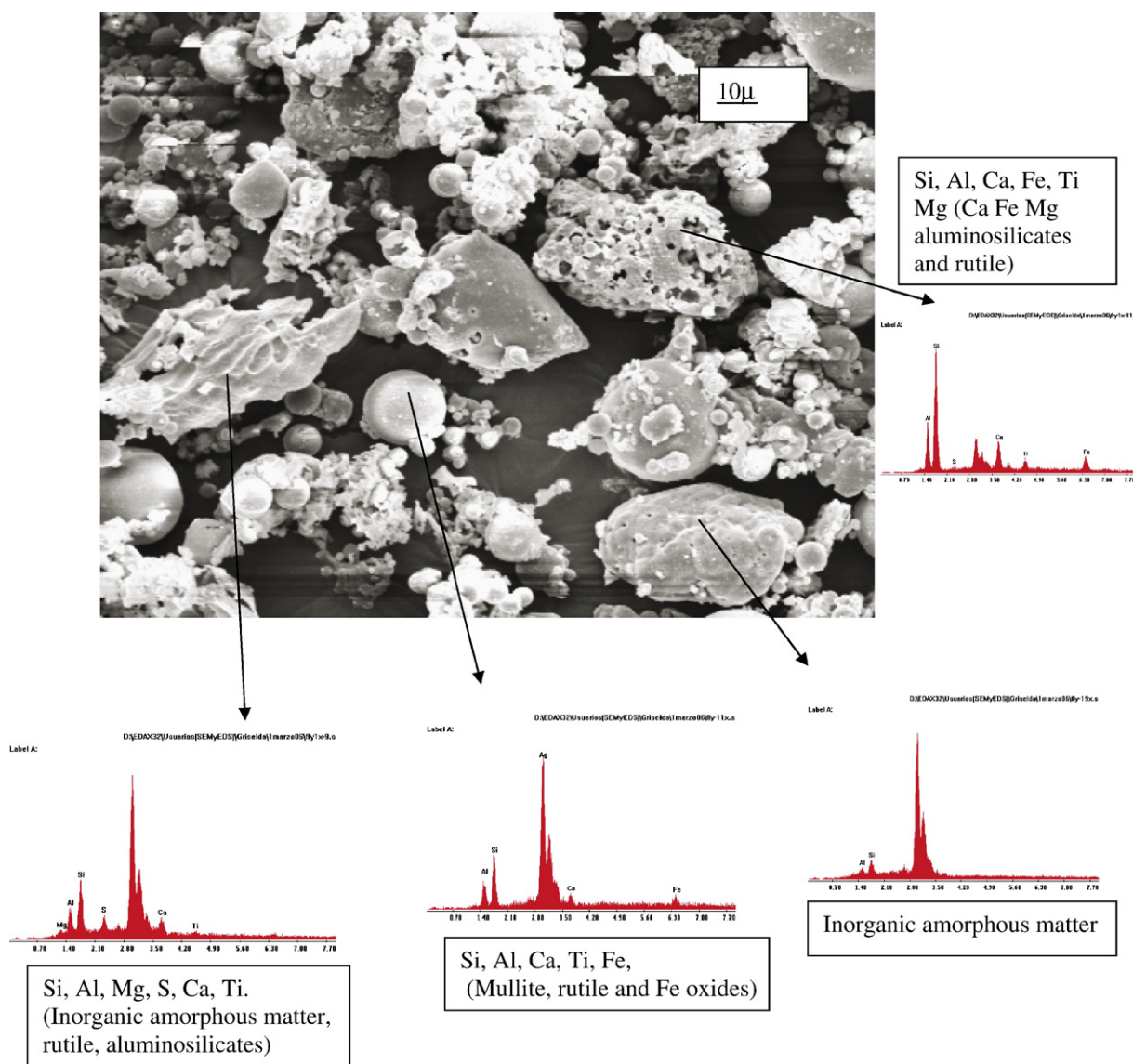


Fig. 1. SEM and EDX image of a general view of fly ashes particles. The image reveals the presence of porous aluminosilicates glass particles, irregular particles, solid and spherical components, inorganic amorphous matter and organic no burning material.

### 3.3. Validation of trace elements measurements

Since coal fly ash standard reference materials (SRM) regarding the phase dependent composition are not available, a rigorous validation of the complete chemical sequential extraction procedure was not possible. Comparison between total concentrations obtained applying the procedure adopted and the subsequent sum of the individual concentrations in the fractions is a possible alternative to check for possible systematic errors arising from element losses, contamination or other undetermined causes. In this context, the Standard Reference Material NIST 1633b (coal fly ash) was subject to the same sequential extraction scheme that the samples. For the determination of total metal concentration, the SRM was digested using the same acid mixture employed to dissolve the residual fraction. Table 3 summarizes the total concentration of the analytes in the digested SRM and the results of the sum of the individual fractions as determined by ICP OES as well as the certified values. The overall picture can be considered satisfactory except for Al and Zn with recoveries of 55% and 73%, respectively. On the light of the results achieved between our results and the certified value for Al (Zn is a non-certified element in the SRM used) when the SRM was digested ( $15.05 \pm 0.27\%$  vs.  $13.5 \pm 0.7\%$ ), it is plausible to conclude that the acid mixture used resulted adequate but a problem occurred in some steps of the extraction of these elements.

### 3.4. Sample treatment and total elemental concentration

Considering the low concentrations of some elements, the order of magnitude of matrix elements and the different composition of different coals, the choice of an adequate digestion method for fly ashes is of prime importance. The addition of nitric acid is necessary because it forms water-soluble salts with most of the elements present in fly ashes and consequently losses due to precipitation are not expected. Even though, screening experiments using only nitric acid for coal fly ashes digestion showed low recoveries for many elements due to an incomplete dissolution of the matrix. In other attempt, a mixture of HNO<sub>3</sub> and HCl was tested and in this case an incomplete dissolution of Mn, Ti, V and Zn was observed. A combination of HNO<sub>3</sub>, HCl and HClO<sub>4</sub> (6:2:5) resulted to be the most appropriate acid mixture for complete dissolution of the samples.

Table 2  
Limits of detection (LOD) achievable for fly ashes by ICP OES

Element	LODs ( $3\sigma$ ) in fly ashes ( $\mu\text{g g}^{-1}$ )
Al	0.5
As	0.3
Cr	0.5
Cu	0.2
Fe	0.3
Mn	0.1
Ni	0.3
Pb	0.5
Ti	0.3
V	0.2
Zn	0.1

Table 3

Results obtained in the analysis of the standard reference material NIST 1633b (coal fly ash)

Element	Certified	Found (digestion) <sup>a</sup>	Found ( $\Sigma$ of fractions) <sup>a</sup>
Al	$15.05 \pm 0.27\%$	$13.5 \pm 0.6\%$	$8.2 \pm 0.5\%$
As	$136.2 \pm 2.6 \mu\text{g g}^{-1}$	$139 \pm 8 \mu\text{g g}^{-1}$	$125 \pm 11 \mu\text{g g}^{-1}$
Cr	$188.2 \pm 4.7 \mu\text{g g}^{-1}$	$191 \pm 8 \mu\text{g g}^{-1}$	$177 \pm 11 \mu\text{g g}^{-1}$
Cu	$112.8 \pm 2.6 \mu\text{g g}^{-1}$	$117 \pm 4 \mu\text{g g}^{-1}$	$104 \pm 7 \mu\text{g g}^{-1}$
Fe	$7.78 \pm 0.23\%$	$7.2 \pm 0.3\%$	$6.8 \pm 0.4\%$
Mn	$131.8 \pm 1.7 \mu\text{g g}^{-1}$	$129 \pm 4 \mu\text{g g}^{-1}$	$136 \pm 9 \mu\text{g g}^{-1}$
Ni	$120.6 \pm 1.8 \mu\text{g g}^{-1}$	$106 \pm 5 \mu\text{g g}^{-1}$	$98 \pm 4 \mu\text{g g}^{-1}$
Pb	$68.2 \pm 1.1 \mu\text{g g}^{-1}$	$66.0 \pm 2.0 \mu\text{g g}^{-1}$	$63.0 \pm 2.6\%$
Ti	$0.791 \pm 0.014\%$	$0.82 \pm 0.05\%$	$0.74 \pm 0.04\%$
V	$295.7 \pm 3.6 \mu\text{g g}^{-1}$	$306 \pm 11 \mu\text{g g}^{-1}$	$289 \pm 18 \mu\text{g g}^{-1}$
Zn	$(210) \mu\text{g g}^{-1}$	$177 \pm 7 \mu\text{g g}^{-1}$	$154 \pm 9 \mu\text{g g}^{-1}$

Data enclosed in brackets are non-certified values.

<sup>a</sup> Two sets of replicates, each set consisting of ten measurements.

The 20 sub-samples obtained by sequentially extracting the four fractions from each of the five ash samples considered were analyzed simultaneously and the measured concentrations are summarized in Table 4. Although these concentrations showed a fairly similar pattern per fraction in the corresponding five ash sub-samples, a clustering analysis was attempted to assess the variability in chemical composition for the concentration matrix of all measured elements (20 sub-samples  $\times$  11 elements). Fig. 2 shows a hierarchical tree plot obtained using the STATISTICA software (Statsoft, Tulsa, USA) with a single linkage (nearest neighbor) rule and the geometrical (Euclidean) distance in the 11-dimensional concentration space. Each fraction is neatly separated from the rest in the tree plot of Fig. 2, emphasizing the distinct nature of the corresponding concentration profiles and the efficiency of the sequential chemical extraction. Since the Euclidean distances were computed from raw measured data, the linkage distances in the different fractions reflect the differences in magnitude of the multi-elemental concentration profiles, which are shown in Table 4. The relatively small linkage distances in fraction 1 are consistent with the fact that only Al, Cr and V were present, while the largest linkage distance of this group ( $\sim 180 \mu\text{g g}^{-1}$ ), joining sub-groups (1-S1, 1-S3 and 1-S2) with (1-S4 and 1-S5), is dominated by the differences in Al concentration ( $93\text{--}146 \mu\text{g g}^{-1}$  vs.  $327\text{--}534 \mu\text{g g}^{-1}$ ). In general terms and except for sub-sample 3-S5 (fraction 3, extracted from sample 5) that is clearly differentiated from the rest, the largest dissimilarity was observed in fraction 4 with a maximum linkage distance of  $\sim 950 \mu\text{g g}^{-1}$ . It is worth noticing that this value is one order of magnitude smaller than the mean values of the concentrations of Fe ( $4506 \mu\text{g g}^{-1}$ ) and Al ( $1987 \mu\text{g g}^{-1}$ ), indicating the similarity between the five samples under consideration. The concentrations in sub-sample 3-S5 were noticeably lower than those of the other sub-samples in fraction 3 with differences of about 76% (Ti) > 40% (Zn) > 30% (Al, Cu, Fe, Ni, V) and implying a linkage distance  $> 2600 \mu\text{g g}^{-1}$ .

On the basis of the similar concentration profiles of the five ash samples considered, the average of the summed up fractional concentrations were calculated. For each element, a comparison of these average sums of fractional concentrations with the mean total concentration in the five samples analyzed is shown in

Table 4

Arithmetic mean and range (in brackets) of each element in each fraction of the five ash samples analyzed

Element	Fraction 1 ( $\mu\text{g g}^{-1}$ )		Fraction 2 ( $\mu\text{g g}^{-1}$ )		Fraction 3 ( $\mu\text{g g}^{-1}$ )		Fraction 4 ( $\mu\text{g g}^{-1}$ )	
Al	206	(92.7–354)	3082	(2623–3709)	8603	(6552–9668)	4987	(4544–5566)
As	ND		4.4	(3.9–5.0)	132	(119–143)	16.7	(9.4–27.8)
Cr	2.2	(2.0–2.5)	3.1	(2.8–3.4)	9.4	(8.3–10.2)	9.4	(8.8–10.4)
Cu	ND		13.4	(11.7–16.5)	28.2	(21.2–34.2)	24.8	(20.2–35.6)
Fe	ND		1108	(953–1301)	2736	(2009–3104)	4506	(3837–4992)
Mn	ND		109	(104–117)	116	(92.0–128)	72.1	(60.6–83.3)
Ni	ND		31.0	(25.5–36.9)	103	(75.0–116)	103	(55.5–139)
Pb	ND		1.9	(1.5–2.7)	ND		9.0	(9.0–9.1)
Ti	ND		61.1	(54.5–67.3)	1562	(439–2243)	1375	(1043–1950)
V	17.5	(17.0–17.8)	48.8	(44.3–54.4)	99.4	(75.0–113)	41.7	(34.1–56.4)
Zn	ND		23.1	(7.5–66.0)	24.2	(15.6–32.7)	42.1	(19.6–68.2)

ND: non-detected.

**Table 5.** Recovery is defined as  $100 \times (\sum \text{fractional concentrations} / \text{average total concentration})$ . These mean total concentration in the five samples analyzed were in the order (in  $\mu\text{g g}^{-1}$ ): Al (22264) > Fe (8260) > Ti (2952) > Mn (296) > Ni (231) > V (199) > As (169) > Zn (158) > Cu (65.8) > Cr (28.5) > Pb (11.1). Recoveries ranged from 56% (Zn) to 105% (V). No convincing explanation could be found for the low recovery of Zn in real samples. Since its recovery resulted unsatisfactory, this metal was not included in the discussion.

### 3.5. Distribution of elements in the four fractions

The fractionation of the fly ashes by the four-step extraction procedure adopted was performed to evaluate the distribution of 11 elements in the five samples analyzed. The distribution, expressed as percentage of each metal and metalloid in the fractions considered, is set forth in Fig. 3. An overall picture shows that the elements present different distributions in the four fractions.

For the first step, water was used to simulate real environmental conditions. The driving forces influencing the partial dissolution of matrix components are the solubility, the diffusion rate of the element forming part of the matrix and the wash off of the compounds which are on the surface. In general terms, low percentages of the elements evaluated were found in the soluble fraction, which is the most biodisponible. The leachates of this fraction exhibited pHs ranging from 9 to 11 possible due to the presence of alkaline oxides such as mainly CaO and also MgO. To check Ca and Mg levels, the leachates of two out of five samples were analyzed and concentrations found were: Ca, 1030 and 1791  $\mu\text{g g}^{-1}$  and Mg, 0.7 and 4.7  $\mu\text{g g}^{-1}$ . Other alkaline elements less soluble or linked to matrix of the ash are expected to be present in the fly ashes. In the five samples under study only Al (1%), Cr (3%) and V (7%) were detected in the aqueous leachates. Water extractable concentrations expanded from 92.7 to 354  $\mu\text{g g}^{-1}$  for Al, 2.0 to 2.5  $\mu\text{g g}^{-1}$  for Cr and 17.0 to 17.8  $\mu\text{g g}^{-1}$  for V. At the pH of the leachate, it would be plausible to think that these elements might be present as

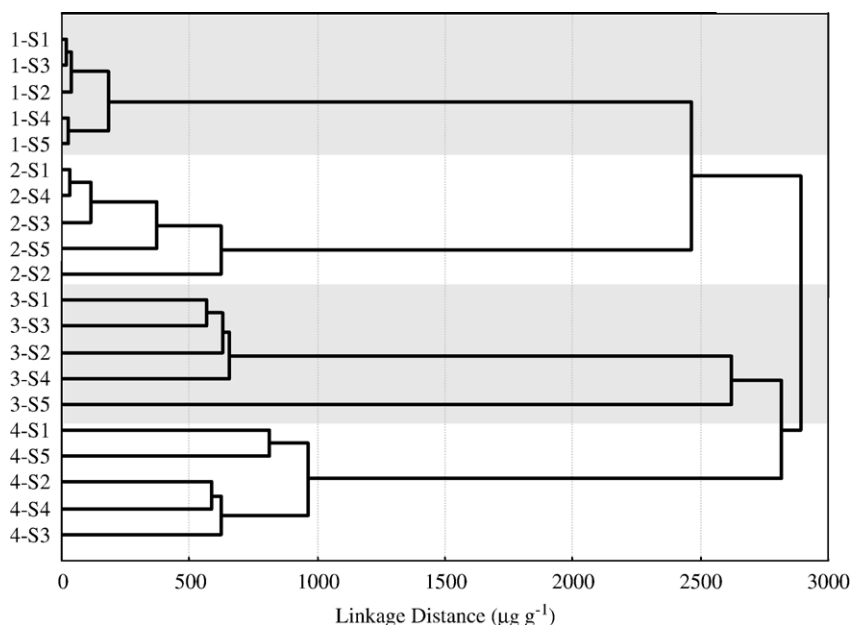


Fig. 2. Results of the clustering analysis performed on the concentration matrix (20 sub-samples  $\times$  11 elements) using Euclidean distance and the nearest neighbor amalgamation rule. Sub-sample  $i$ - $S_j$  indicates that fraction  $i$  ( $i=1$  to 4) was extracted from ash sample  $j$  ( $j=1$  to 5).

Table 5  
Comparison between total metal and metalloid concentrations and the sum of the fractions

Element	Total concentration <sup>a,b</sup>	Σ of fractional concentration	Recovery (%)
Al	22264±1896	16877±1073	75.8
As	169±6	154±13	91.1
Cr	28.5±1.5	24.1±1.3	84.6
Cu	65.8±3.7	66.3±3.4	101
Fe	8260±544	8350±396	101
Mn	296±14	297±17	100
Ni	232±11	237±38	102
Pb	11.1±0.6	10.9±0.4	98.2
Ti	2952±136	2998±351	102
V	198.6±2.2	207±10	105
Zn	158±6	89.4±16.1	56.2

Results are expressed in  $\mu\text{g g}^{-1}$ .

<sup>a</sup> Value±standard deviation.

<sup>b</sup> Two sets of replicates, each set consisting of ten measurements.

$\text{Al}_2\text{O}_6^-$ ,  $\text{CrO}_4^{2-}$  and  $\text{VO}_4^{3-}$ . For the other elements, their concentrations in aqueous extracts were below or close to their detection limit indicating that these metals and metalloids will not be released under typical environmental conditions.

Most of the elements under study have affinities with aluminosilicates and were found in different percentages in the residual fraction in the order  $\text{Al}>\text{Fe}>\text{Ti}>\text{Ni}>\text{Mn}>\text{Cu}>\text{Zn}>\text{V}>\text{As}>\text{Cr}>\text{Pb}$ . Aluminium also exhibits affinity with mullite and feldspar. Elements with iron oxide affinity (hematite and magnetite) (Fe, Cr, Cu, Mn and Ni) are partially associated with iron oxides.

Geological elements such as Al and Fe were distributed with different percentages in the other three fractions. In this study, average Al content in the three remaining fractions was found to be in the following ranges: 2623–3709  $\mu\text{g g}^{-1}$  (carbonates, oxides and reducible), 6552–9668  $\mu\text{g g}^{-1}$  (bound to sulfidic) and 4544–5566  $\mu\text{g g}^{-1}$  (residual). In the reducible fraction, Al is expected to be as  $\text{Al}_2\text{O}_3$ .

Arsenic is in general enriched in fly ashes and its levels depend on the characteristics of the coal and combustion con-

ditions during coal burning. Since fly ashes are currently disposed in landfills, the presence of high levels of As and other potentially toxic elements is of environmental concern. Mean total As content in the five ashes analyzed was  $169\pm6 \mu\text{g g}^{-1}$  which is consistent with average As levels in coal fly ashes, with concentrations varying typically from 20 to  $190 \mu\text{g g}^{-1}$  [16,17]. Typical concentrations in coal are in the range  $0.5\text{--}80 \mu\text{g g}^{-1}$  [18] which evidences the enrichment of As in the ashes. At combustion temperatures, As may be dissolved in silicate glasses or form calcium compounds, particularly calcium arsenate through the reaction of CaO with volatile  $\text{As}_2\text{O}_3$  [19]. In their study of metals distribution in coal fly ash, Kim and Kazonich [20] determined that As was predominantly associated with non-silicates. Consistent with these results, in our study, As was found to be most abundant in the non-silicate phase, represented by the second and third fractions with overall concentrations ranging from 123 to  $148 \mu\text{g g}^{-1}$ , while its concentrations were much lower in the residual fourth fraction ( $9.4\text{--}27.8 \mu\text{g g}^{-1}$ ).

Total Cr concentration in the world coals ranges from 0.5 to  $60 \mu\text{g g}^{-1}$  [18]. In this study, overall Cr concentrations were found to vary in a narrow range ( $22.4 \mu\text{g g}^{-1}$  to  $25.5 \mu\text{g g}^{-1}$ ). During the combustion of coal in the San Nicolás power plant, temperatures of  $1300 \text{ }^\circ\text{C}$  are reached. Consequently, a great portion of Cr(III) would be oxidized to Cr(VI) during combustion. In our study, we found that Cr was distributed in the four fractions and partially dissolved in the (alkaline) water-soluble fraction (9%). Cr(VI) is soluble in water, so leaching of Cr(VI) into groundwater and surface water may occur when ashes be deposited in a landfill. In this context, cost-effective environmental remediation studies for converting Cr(VI) (originated in coal power plant) to Cr(III) have been reported [21]. A 13% of Cr was detected in the reducible fraction, 39% in the oxidizable and 39% in the residual fraction.

According to Swaine and Goodarzi [18] typical Cu levels in coal varies from 0.5 to  $50 \mu\text{g g}^{-1}$ . In our study, total Cu exhibited a homogeneous pattern with minimum and maximum concentrations between 60 and  $69 \mu\text{g g}^{-1}$ , respectively. The

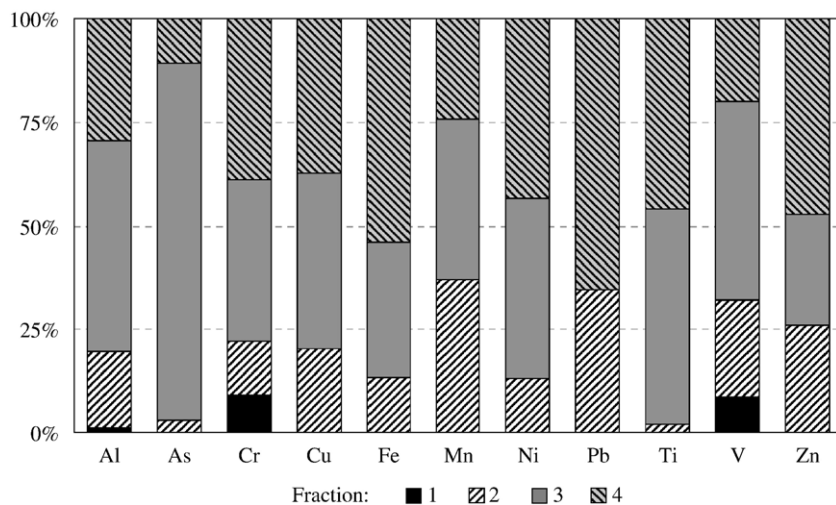


Fig. 3. Distribution of metals and metalloids as percentage of the elemental concentration in fly ashes.



formation of Cu (Se, Hg, Sn) volatile species from coal in a combustion plant burning low/medium volatile coal (high-grade ash) was reported by Pavageau and coworkers [22]. Thermodynamic calculations and experimental metal species spiking experiments suggested the formation of CuO–CuSO<sub>4</sub> or CuSO<sub>4</sub>·H<sub>2</sub>O. The volatility of an element depends on the combustion technology (temperature, time of exposure, type of ash generation) used. In this fractionation study, no soluble compounds of Cu were detected which would indicate that volatile Cu compounds were not generated and consequently not adsorbed onto the surface of the material. Copper was distributed in the other three fractions with a 20% detected in the reducible fraction (13.4 μg g<sup>-1</sup>), a 42% (28.2 μg g<sup>-1</sup>) in the fraction bound to organic matter (probably as Cu<sub>2</sub>S, CuS, CuFeS<sub>2</sub> and Cu<sub>5</sub>FeS<sub>4</sub>) and a 37% (24.8 μg g<sup>-1</sup>) in the environmental immobile fraction bound to silicates.

Overall Fe concentration in the ashes ranged from 7919 to 8817 μg g<sup>-1</sup>. This metal was mainly found in residue (54%) but it also occurred (17%) in the ashes forming oxides, probably hematite and magnetite. A 28% of total Fe was associated with the sulfidic phase (2736 μg g<sup>-1</sup>).

Manganese concentrations in coal are reported to be from 5 to 300 μg g<sup>-1</sup> [18]. Manganese of ashes collected in the San Nicolás thermal power plant was found in the interval 273–318 μg g<sup>-1</sup>. No water-soluble species of Mn were detected. About 39% of Mn was bound to organic matter and sulfides (e.g., MnS). This metal was also measured in the reducible phase (37%) probably as MnO or MnFe<sub>2</sub>O<sub>4</sub>. The residual fraction where Mn can be associated to aluminosilicates accounts for 24%.

Total Ni in the fly ashes under study ranged from 198 to 282 μg g<sup>-1</sup> showing a significant enrichment in comparison to the typical reported values for coals. Considering these values, it is of prime importance to have information on the distribution of Ni in coal fly ashes because of its known toxicity. All Ni compounds are classified as potential human carcinogens with different intrinsic cancer risk. Studies on animal showed that Ni<sup>0</sup>, Ni oxides and soluble Ni salts induce different risks and tumor incidents [23]. Nickel compounds of natural origin are likely to be silicate in nature and as a consequence they are not soluble in water. A 13% of Ni was detected in the reducible fraction, a 43% in the oxidizable fraction and 43% in the residue. The presence of Ni in the third fraction might be comprised of a variety of Ni compounds, the most common of which is the most carcinogenic compound, NiS. The Ni fraction soluble in NH<sub>2</sub>OH·HCl is probably composed by the poorly water-soluble Ni compounds NiCO<sub>3</sub> and hydrated basic Ni salts such as Ni<sub>x</sub>(OH)<sub>y</sub>·(CO<sub>3</sub>)<sub>z</sub>.

Lead in coal is reported to be in the interval 1.9–80 μg g<sup>-1</sup> [18]. In this study, total Pb levels in fly ashes were detected in the five samples analyzed with similar overall concentrations that spanned from 10.9 to 11.7 μg g<sup>-1</sup>. In the fractionation study, Pb was only found in the reducible (24%) and residual fractions (66%). It is worth noticing that this metal is typically associated with organic and sulfidic; however, in ash samples analyzed, it was not detected in the oxidizable fraction.

Titanium is the ninth most abundant element in the earth's crust and is primarily found in the minerals rutile (TiO<sub>2</sub>),

ilmenite (FeTiO<sub>3</sub>) and titanite (CaTiSiO<sub>5</sub>). It can also be present at low levels in biotite (K(Mg,Fe<sup>+</sup>)<sub>3</sub>AlSi<sub>3</sub>O<sub>10</sub>(OH,F)<sub>2</sub>). Total Ti in ash samples ranged from 2445 to 3352 μg g<sup>-1</sup>. In this fractionation study, Ti was present as compounds that are not water-soluble because in all cases Ti concentrations in the first fraction were below the detection limits of the technique used for quantification. The almost exclusive presence of Ti in fractions 3 and 4 (with percentages of 52% and 46%, respectively) suggests that this element is a component of low solubility minerals. In their study on leachability of major elements from minerals in strong acids (HCl, HNO<sub>3</sub> and aqua regia), Snäll and Liljefors [24] obtained the following ranking of solubility for fractions of equal size of Ti minerals: biotite > titanite > ilmenite > rutile, being TiO<sub>2</sub> barely leachable (~ 1%). On the basis of this ranking, it could be infer that it is likely that, in our study, part of the most soluble Ti minerals has been dissolved in fraction 3 leaving the insoluble minerals for the last extraction step.

Coal and especially oil fly ash are well-known V sources. This metal is characteristic of coals from different sources. Total V was found to be between 193 and 217 μg g<sup>-1</sup>. Vanadium was distributed in the four fractions but in much less extent in the first fraction (8%). At the pH measured in the leachate, it would be plausible to think V might be present as VO<sub>4</sub><sup>3-</sup> in the first fraction. The percentages of V in the other fractions were: 24% (reducible), 48% (oxidable) and 20% (residual).

#### 4. Conclusions

This study further supports the contention that the knowledge of the levels of toxic and potentially toxic elements, especially in the most mobile fractions, is an important tool for environmental risk assessment. Although only a limited number of samples were available, the experimental results obtained so far are indicative of the high levels of toxic elements such as As (154 μg g<sup>-1</sup>), Ni (237 μg g<sup>-1</sup>) and V (207 μg g<sup>-1</sup>) in the ash samples. The leachability of the elements was different and only Al, Cr and V were associated to the most bioavailable water-soluble fraction. This information may well raise some concern to select an appropriate final disposal of the ashes. However, it is worth noticing that the elements measured were mostly detected in the less soluble fractions.

The lack of uniformity of the different schemes proposed for fly ashes fractionation does not allow either a worldwide comparison of results or a validation of procedures. For this reason, it will be recommendable to launch programs by official organizations to harmonize and optimize the different sequential procedures proposed in order to facilitate comparability of data as well as to optimize the operating conditions.

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