Operational speciation of Cd, Cr, Cu, Mn, Ni, Pb, V and Zn in dust samples from schools in Caracas, Venezuela

H. HANDT, R. FERNÁNDEZ, Z. BENZO, C. GÓMEZ, E. MARCARNO, F. GALÁRRAGA and R. GONZÁLEZ

Keywords: Operational speciation, metals, dust, schools.

ABSTRACT

A sequential extraction approach has been applied to analyze Cd, Cr, Cu, Mn, Ni, Pb, V and Zn in dust samples from different schools chosen according with their location in areas with different concentrations of total suspended particles (TSP). The aim of this work is to provide information about the chemical fractionation of metal content. Hence, information about the origin, mode of occurrence, mobilization and transport of metals could be obtained. Total and partial metal concentrations were further determined by analyzing the samples after acid digestion procedure. The results compare very well for both methods. The metals are associated with various chemical forms as distinguished by sequential chemical extraction. The carbonate and Fe-Mn oxide phases dominate for Pb, Zn and Cu, whereas for Ni the organic phase is most important. V, Mn, Cr, Cd are mainly present in the oxide phases, however they are too in a residual phase but in minor proportion. The different sources for the elements studied are supported by the results from multivariate (PCA) analysis.
CONTENIDO


A. P. GARCÍA-MARÍN, F. J. JIMÉNEZ-HORNERO and J. L. AYUSO-MUÑOZ, Universal multifractal description of an hourly rainfall time series from a location in southern Spain.

A. TEJEDA-MARTÍNEZ, C. CONDE-ÁLVAREZ and L. E. VALENCIA-TREVISO, Climate change scenarios of extreme temperatures and atmospheric humidity for México.

C. ESCALANTE-SANDOVAL, Bivariate distribution with two-component extreme value marginals to model extreme wind speeds.

M. CONV, E. HERNÁNDEZ and T. DEL TESO, Influence of synoptic scale in the generation of extremely cold days in Europe.
Operational speciation of Cd, Cr, Cu, Mn, Ni, Pb, V and Zn in dust samples from schools in Caracas, Venezuela

H. HANDT, R. FERNÁNDEZ,
Instituto de Ciencias de la Tierra, Facultad de Ciencias, Universidad Central de Venezuela,
Apo. Postal 47325, Caracas 1041-Venezuela

Corresponding author: R. Fernández, e-mail: ruizdelvalle@yahoo.com, rfernanz@ciens.ucv.ve

Z. BENZO, C. GÓMEZ, E. MARCAÑO, F. GALÁRRAGA,
Laboratorio de Química Analítica, Centro de Química,
Instituto Venezolano de Investigaciones Científicas,
Apo. Postal 21827, Caracas 1020-A, Venezuela

R. GONZÁLEZ
Facultad de Ciencias, Centro de Microscopía Electrónica,
Universidad Central de Venezuela, Caracas 1041-A, Venezuela

Received November 16, 2007; accepted April 30, 2008

RESUMEN
Un método de extracción secuencial fue aplicado para analizar Cd, Cr, Cu, Mn, Ni, Pb, V y Zn en muestras de polvo urbano provenientes de colegios ubicados en zonas con diferentes concentraciones de partículas suspendidas totales. El objetivo de este trabajo fue estudiar el fraccionamiento químico de los elementos en este tipo de muestras. Esta información permite entender los procesos relacionados con el origen, la movilización y el transporte de los metales. Una vez realizada la digestión de las muestras fue determinadas las concentraciones totales y parciales de los metales. Los resultados obtenidos tanto para la digestión total como para la extracción secuencial son comparables. Los metales determinados están asociados a diversas formas químicas. Pb, Zn y Cu están asociados principalmente a las fases carbonato y óxido, Ni a la fase orgánica y V, Mn, Cr y Cd están presentes principalmente en la fase óxido, aunque también están presentes, en menor proporción, en la fase residual. El análisis multivariado (componentes principales) permitió establecer el fraccionamiento y posibles fuentes de estos elementos.

ABSTRACT
A sequential extraction approach has been applied to analyze Cd, Cr, Cu, Mn, Ni, Pb, V and Zn in dust samples from different schools chosen according with their location in areas with different concentrations of total suspended particles (TSP). The aim of this work is to provide information about the chemical fractionation of metal content. Hence, information about the origin, mode of occurrence, mobilization and transport of metals could be obtained. Total and partial metal concentrations were further determined by analyzing the samples.
after acid digestion procedure. The results compare very well for both methods. The metals are associated
with various chemical forms as distinguished by sequential chemical extraction. The carbonate and Fe-Mn oxide
phases dominate for Pb, Zn and Cu, whereas for Ni the organic phase is most important. V, Mn, Cr, Cd are
mainly present in the oxide phases, however they are too in a residual phase but in minor proportion. The
different sources for the elements studied are supported by the results from multivariate (PCA) analysis.

Keywords: Operational speciation, metals, dust, schools.

1. Introduction

Many heavy metals are very common in industrial and domestic usage. Consequently, dust containing
heavy metals have been dispersed into the environment and could cause human health problems
through the atmosphere. Heavy metals have an effect on biochemical mechanisms, especially
because they can be bioaccumulated. The extent of bioaccumulation and bioavailability depends
on the characteristic chemical composition of the particles (Fernández and Ternerod-Rodriguez,
2004). Thus, quantification of the chemical form of metals present in those particles is necessary.
Determination of total concentration is often insufficient and speciation is a mean of determining
the real activity of a metal in the environment. Most studies (Orlova et al., 1995; Tong, 1998; Tong
et al., 2000; Shorteen and Hooven, 2000) on metal atmospheric contamination have reported total
metal concentration. The need for speciation studies in environmental studies is a new trend in
analytical chemistry (Szpanar and Lobinski, 1999). Sequential extraction methods using a series
of chemicals of increasing strength are widely used for metal fractionation and evaluation of metal
leaching (Tongtavee et al., 2005). Metal speciation in airborne particles and dust has been reported
(Fernández et al., 2002). Sequential extraction approach can provide detailed information about
the origin, mode of occurrence, biological and physicochemical availability, mobilization and
transport of metals (Das et al., 1995). Thus, the information obtained by applying this approach is
of a great utility in environmental research.

The purpose of this study was to determine the chemical speciation pattern of dust in seven
schools at different locations according with the concentration of total suspended particles (TSP)
and hence to assess the degree of environmental hazard of children attending to these schools.

2. Methods

2.1. Sampling

Dust samples were collected (7 schools samples, one for each school) from the floor site by
careful sweeping of dust using a conventional clean brush and stored in polyethylene bags at room
temperature. The samples used in this study were selected from those collected in two campaign
samplings in 1998 and 2003, in Caracas, Venezuela. Sample A comes from a school, previously
classified as a contaminated area related to the TSP concentration; samples B, D, E and F from
schools located in moderately contaminated areas, and C and G from schools in low contaminated
areas (Morales et al., 2003).
2.2 Sample treatment
Indoor dust samples collected from classroom places in the schools were passed through a 35 meshes sieve to remove all large particles. This was followed by subsequent passing through a 230 mesh sieve (63 μm) and through a 325 mesh sieve (45 μm). Only the fractions of particle size between 45-63 μm and <45 μm were analyzed. This was followed by the sequential extraction procedure outlined in Table I. For the purpose of this publication just the results from the 325 mesh sieve (45 μm) are showed.

<table>
<thead>
<tr>
<th>Step</th>
<th>Fraction</th>
<th>Extractant</th>
<th>Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Soluble and exchangeable metals</td>
<td>15 mL H₂O (pH = 7)</td>
<td>3 h at room temperature. Shaker agitation.</td>
</tr>
<tr>
<td>2</td>
<td>Carbonates, oxides and reducible metals</td>
<td>10 mL NH₃·OH·Cl 0.25M (pH = 2)</td>
<td>5 h at room temperature. Shaker agitation.</td>
</tr>
<tr>
<td>3</td>
<td>Bound to organic matter, oxidable and sulphidic metals</td>
<td>Two portions of 7.5 mL H₂O₂ 30%</td>
<td>At 95 °C until near dryness. Shaker agitation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15 ml AcONH₄ 2.5M (pH = 3)</td>
<td>90 min at room temperature. Shaker agitation.</td>
</tr>
<tr>
<td>4</td>
<td>Residual metals*</td>
<td>10 mL HNO₃; HCl; HF; HClO₃ and H₂O₂ (6:2:2:2:4)</td>
<td>5 h at 60 °C. Shaker agitation.</td>
</tr>
</tbody>
</table>

*This step was different from the one of Fernández et al. (2002).

2.3 Standard reference material (SRM)
SRM 1648 Urban Particulate Matter from the National Institute of Standards and Technology (NIST) (Gaithersburg, MD) was used to validate the acid digestion procedure.

2.4 Preparation of standard solutions and glassware
All chemical reagents were of analytical grade. Deionized water from a Milli Q water purification unit (Millipore, Bedford, MA) was used throughout this work. All glass and plastic ware used was cleaned and soaked in HNO₃ (5% v/v) and rinse several times with deionized water before use. Multi-element (Cd, Cr, Cu, Mn, Ni, Pb, V and Zn) standard stock solution (1000 mg L⁻¹) Merck (Darmstadt, Germany) were used to prepare the working standard solutions for calibration purposes.

2.5 Analytical fractionation scheme
The fractionation scheme used was based on Fernández et al. (2002) because it simulates the pH condition found through the human respiratory tract.