

Slurry-based procedures to determine chromium, nickel and vanadium in complex matrices by ETAAS

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Abstract

Two slurry-based ETAAS methodologies are compared to determine directly Cr, Ni and V in coal fly ash, soils and sediments: current slurry analysis (USS) and 'slurry extraction' (SE). Slurries for USS-ETAAS were prepared in 0.5% HNO₃. HF and HNO₃ were evaluated as chemical modifiers. HF was the extractant for the SE-ETAAS approach.

A unique slurry-based procedure to measure Cr, Ni and V could not be established. Cr concentrations up to 100 µg g⁻¹ were accurately determined by USS (0.5% HNO₃; λ=429.0 nm; LOD=0.35 µg g⁻¹) whereas higher contents required the SE procedure (sample grinding, 30% HF; LOD=0.02 µg g⁻¹). Both methods were appropriate to determine Ni (LOD=0.11 and 0.08 µg g⁻¹, for USS and SE, respectively). V was satisfactorily quantified only with the USS approach (LOD=0.80 µg g⁻¹).

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1. Introduction

Classical procedures to determine heavy metals in solid samples by atomic absorption methods often involve ashing or acid digestion steps, which are time-consuming and prone to contamination and analyte loss, especially when dealing with complex matrices such as coal combustion residues or geological samples.

Accordingly, the use of slurries to analyse directly solid samples by electrothermal atomic absorption spectrometry (ETAAS) is a highly appealing alternative to deal with complex solid matrices of environmental concern and to minimise the problems posed above. As automation can be easily accomplished, the use of the automated ultrasonic probes (USS-ETAAS) has steadily simplified analyst's work. Besides, ultrasound probes improved turnaround times in research and routine analysis thanks to their versatility, operational simplicity and good results. Never-

theless, slurry analysis is not free of pitfalls, such as high background absorption and chemical interferences, since a large amount of matrix is introduced into the atomiser. These can be overpassed by the use of powerful background correction systems or by adding chemical modifiers [1].

The direct analysis of solid samples containing high amounts of silicates requires addition of HF to the slurry diluent. Removal of silicon during the drying and calcination steps as SiF₄ diminishes the background absorption, as most of the matrix was removed before atomization. Another advantage of HF is that it slows down the otherwise rapid deterioration of the graphite tube (caused by the formation of silicon carbides). Hence, it has been used to quantify Cr [1,2], Ni [1,3,4] and V [2] successfully in refractory matrices. Other fluoride compounds, as polytetrafluoroethylene (PTFE), have been reported for in-situ removal of silicon from siliceous and refractory samples to also determine Cr [5], Ni [6] and V [7].

Unfortunately, HF is incompatible with Ti probes, widely employed to ultrasonically homogenise the slurries [1]. This calls for other agitation means as magnetic stirring, ultrasonic bath or Vortex mixing. Disappointingly, they are less

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automated and required (usually) addition of stabilising agents to the slurries, which, in turn, can cause loss of precision during pipetting or increase the blanks. Hence, an alternative when using the Ti-probe is to pipette HF separately into the atomiser, just as a chemical modifier [8]. However, satisfactory results have also been reported with HNO₃ as diluent for the determination of Cr [9–11], Ni [9,11,12] and V [4,10] in inorganic samples.

On the other hand a recent methodology, coined 'slurry extraction' (SE-ETAAS), based on the analysis of the liquid phase of the slurry was applied. It shows clear advantages over current slurry-sampling procedures when the quantitative extraction of the analyte is achieved: shorter turnaround times; simplified calibrations; less or none problems related to high background signals and/or build-up of residues inside the atomiser; no slurry homogenisation is needed during the analysis and, finally, the matrix effects are reduced because of the minimal matrix solubilisation [13]. To the best of our knowledge, SE-ETAAS was applied only to determine Cr in organic matrices (using a HNO₃ + HCl + H₂O₂ mixture) [14,15], and Ni in vegetables [16] (where an incomplete extraction using 0.75 mol L⁻¹ HNO₃ was attained). No applications were found for V.

The aim of the present work is to compare the two slurry-based procedures to determine Cr, Ni and V in complex matrices (coal fly ash, soils and sediments) by ETAAS. Besides, nitric and hydrofluoric acids are evaluated as chemical modifiers for the direct analysis using ultrasonic slurry-sampling. The slurry extraction procedure is tested using HF as liquid medium.

2. Experimental

2.1. Instrumentation

A 4100 Perkin-Elmer atomic absorption spectrometer (Überlingen, Germany), equipped with an HGA-700 graphite furnace, an AS-70 autosampler, and an USS-100 ultrasonic slurry mixer, using deuterium arc background correction, were employed to measure Cr, Ni and V. Argon was used as the inert gas. Measurements were made by using hollow-cathode lamps (Perkin-Elmer) of Ni, Cr and V at 230.0 nm (0.2 nm bandwidth); at 357.9 nm (0.7 nm) and at 318.4 nm (0.7 nm) wavelengths, respectively. Pyrolytically-coated tubes with preinserted L'vov platform for Cr and Ni were used (Z-tek, Amsterdam, The Netherlands), whereas tube wall atomization on pyrolytic atomisers (Z-tek) was applied for V.

An Ultrasons-H (Selecta, Barcelona, Spain) ultrasonic bath was used to homogenise the slurries, and a planetary agate balls micro mill (Pulverisette 7 Fritsch, Idar-Oberstein, Germany) was employed to reduce particle size (whose distribution was assessed by laser dispersion with a Coulter[®] LS Particle Size analyser, Malvern Instruments, Worcestershire, UK).

It is worth noting that the direct analysis of slurries (slurry-sampling) has a limited dilution capability since when low masses (so, few particles) are in the slurry representativeness is not guaranteed. Therefore, to analyse solid materials with high contents of Cr and V, other approaches were undertaken to reduce sensitivity: first, the use of non-resonance lines at 429.0 nm (0.2 nm bandwidth) [11] and 305.6 nm (0.2 nm) [10] for Cr and V, respectively, and second application of an Ar flow during atomization.

2.2. Reagents

All reagents were of analytical grade. Ni and Cr standards were prepared daily in HNO₃ (0.5% v/v) from stock standard solutions of 1000 µg mL⁻¹ (Panreac, Barcelona, Spain), as well as V standards (from a 1000 µg mL⁻¹, Fluka standard). HNO₃ and HF were Baker Instra-analyzed grade (J.T. Baker, Phillipsburg, USA). Ultrapure water (18 mΩ cm⁻¹ resistivity, Milli-Q Water System, Millipore, Madrid, Spain) was employed throughout.

All material, glassware and plasticware were soaked in 10% v/v HNO₃ for 24 h and rinsed with ultrapure water, at least three times before use.

2.3. Slurry preparation

Two different liquid media were studied: HNO₃ and HF. In both cases slurries were prepared directly in polyethylene autosampler cups using 2–50 mg of solid sample and 1 mL of diluent.

2.3.1. Slurry-sampling

Samples were suspended in 1 mL 0.5% (v/v) HNO₃ and homogenised automatically before analysis using the USS-100 probe (10 s and 40% power, maximum power 40 W). All variables regarding the slurry preparation itself had been optimised previously using multivariate chemometric methods [17].

2.3.2. Slurry-extraction

When HF was used as liquid phase, samples were suspended in 1 mL of the appropriate concentration of HF and homogenised by manual shaking or ultrasonic bath agitation. The autosampler cups were, then, placed in the autosampler tray and aliquots of the supernatant were injected directly into the atomiser without rehomogenisation. No centrifugation was needed.

2.4. Analytical procedure

2.4.1. Slurry-sampling

Slurry aliquots (2–10 µL) were automatically injected after ultrasonic homogenisation of the samples and analysed using the temperature furnace programs shown in Table 1. The autosampler was programmed to aspirate sequentially

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