



Simultaneous determination of V, Ni and Fe in fuel fly ash using solid sampling high resolution continuum source graphite furnace atomic absorption spectrometry



A. Cárdenas Valdivia^a, E. Vereda Alonso^{a,*}, M.M. López Guerrero^a, J. Gonzalez-Rodriguez^b, J.M. Cano Pavón^a, A. García de Torres^a

^a Department of Analytical Chemistry, Faculty of Sciences, University of Malaga, Campus of Teatinos, 29071 Málaga, Spain

^b School of Chemistry, University of Lincoln, Brayford Pool, Lincoln LN6 7TS, UK

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ABSTRACT

A green and simple method has been proposed in this work for the simultaneous determination of V, Ni and Fe in fuel ash samples by solid sampling high resolution continuum source graphite furnace atomic absorption spectrometry (SS HR CS GFAAS). The application of fast programs in combination with direct solid sampling allows eliminating pretreatment steps, involving minimal manipulation of sample. Iridium treated platforms were applied throughout the present study, enabling the use of aqueous standards for calibration. Correlation coefficients for the calibration curves were typically better than 0.9931. The concentrations found in the fuel ash samples analysed ranged from 0.66% to 4.2% for V, 0.23–0.7% for Ni and 0.10–0.60% for Fe. Precision (%RSD) were 5.2%, 10.0% and 9.8% for V, Ni and Fe, respectively, obtained as the average of the %RSD of six replicates of each fuel ash sample.

The optimum conditions established were applied to the determination of the target analytes in fuel ash samples. In order to test the accuracy and applicability of the proposed method in the analysis of samples, five ash samples from the combustion of fuel in power stations, were analysed. The method accuracy was evaluated by comparing the results obtained using the proposed method with the results obtained by ICP OES previous acid digestion. The results showed good agreement between them.

The goal of this work has been to develop a fast and simple methodology that permits the use of aqueous standards for straightforward calibration and the simultaneous determination of V, Ni and Fe in fuel ash samples by direct SS HR CS GFAAS.

1. Introduction

The on-going economic growth coupled with the increasing standards of living has made us rely heavily on energy in our lives, especially after the Industrial Revolution in the last few centuries [1]. Energy is typically generated from the combustion of fossil fuels in various sectors including agricultural, transportation and industrial sectors. Diesel is highly consumed to generate electricity in Power Stations. The complete combustion of heavy fuel or diesel is not possible and the incomplete combustion will come out with mixture of substances known as fly ash [2,3]. These ashes may contain heavy metals as part of the natural composition of the fuel and/or inorganic material that was added through the refining process [4]. For example, the content of Molybdenum in some diesel samples comes from the use of molybdenum oxide in the oxidative desulphuration of diesel fuels [5].

Other metals such as nickel, vanadium or manganese may have both a natural or artificial origin [6]. If these ashes are not properly disposed of, they become environmental problems, such as dusting, leakage of acid liquids, and pollution with heavy metals. The research on this topic indicated that fly ash produced in heavy fuel power stations is rich in Ni, V, Fe, Mo, Mg, Na and C and among these metals Ni and V are the most valuable. Accordingly, fly ash would be a source of pollution due to metal leaching and in the same time it is commercially attractive due to the presence of high levels of V and Ni [3].

Thus, it is important to characterize fuel and its ashes. Different analytical techniques could be employed for the monitoring of trace elements in fly ash: inductively coupled plasma optical emission spectrometry (ICP OES), inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) and wavelength-

* Corresponding author.

E-mail address: eivereda@uma.es (E. Vereda Alonso).

dispersive X-ray fluorescence (WDXRF).

GFAAS is frequently used to determine trace elements due to its simplicity, low limits of detection and its extremely high tolerance for complex matrices. This potential has been further enhanced with the arrival of high-resolution continuum source (HR CS) GFAAS, in particular when aiming at the direct analysis of complex samples. The main advantages of HR CS GFAAS can be summarized as follows [7]: this technique allows the introduction of solid samples directly into the atomizer, eliminating the sample preparation procedure, which is time consuming, requires the use of hazardous acids and results in a significant dilution of the samples, and hence a decrease in the analyte concentration [8], it often makes possible the use of aqueous standard solutions for calibration [9]; the array detector permits the simultaneous monitoring of two hundred “wavelength sectors” (pixels), enabling efficient correction for many unwanted spectroscopically events. This aspect, in combination with the higher radiation intensity of the Xe (only one lamp source is needed) makes it feasible to obtain better-defined signals at lower analyte levels, which means, better limits of detections, on the other hand, it is possible to decrease the sensitivity and therefore expand the working range to majority elements by measuring the absorbance at the wings of absorption lines [10,11], the technique still offers a considerably superior approach for the mathematical correction of complex, high and even rapidly changing backgrounds, since they are monitored simultaneously with the atomic absorption lines [12–16]; non-metals, such as Cl, F, P or S, can be determined at relatively low levels, since the most sensitive atomic lines for these elements are situated in the far UV region, which is not accessible for line source AAS instrumentation [17,18].

The employment of chemical modifiers has earned a place of privilege in GFAAS. Chemical modification has evolved from the classic matrix modifiers described by Ediger [19], towards the permanent modification introduced by Shuttler in 1992 [20]. Amongst the chemical modifiers, the noble metals of high melting point (Ir, Pd, Pt, Rh and Ru) and the carbide forming elements (Hf, Mo, Nb, Ta, Ti, V, W, Zr) are the most employed either as mono-compound modifiers or combined [21]. Particularly in the case of the platinum group modifiers, the study by Pedro et al. [21] found that Ir showed the most homogeneous distribution on the graphite furnace. The most important advantages of permanent modifiers over conventional modifiers application include extended tube lifetime, lower reagent blank and detection limit [22]. Iridium was the permanent modifier employed in this work to solve some problems found concerned with tailing of the atomization curves of V and carbide formation. In the pre-atomization stage, thermal decomposition of vanadium compounds leads to formation *inter alia* of vanadium carbide, which results in reduction of sensitivity and reproducibility [23], else of memory effects. Carbide forming modifiers are not recommended because produced poor sensitivity and also increased the memory effect [24].

Given the above considerations, the present work describes the simultaneous determination of V, Ni and Fe in fuel fly ashes by SS HR CS GFAAS, employing Ir as permanent modifier. The goal was to develop a fast and simple methodology that permits the use of aqueous standards for straightforward calibration and the simultaneous determination of these three elements.

To the best of the authors' knowledge, no report has made use of SS GFAAS to investigate the simultaneous determination of V, Ni, and Fe in solid samples. However, the use of SS GFAAS can be a very suitable analytical method for this purpose, due to the potential of this technique to the direct analysis of these samples with minimal previous preparation, showing sufficient sensitivity for small amounts of solid ash samples, in which the analytes may be found at high or low concentrations.

2. Experimental

2.1. Instruments

All the experiments in this work were carried out using a HR CS AAS, ContrAA 700, commercially available from Analytik Jena AG (Jena, Germany) and equipped with both graphite furnace and flame atomizers. The optical system comprises a xenon short-arc lamp (GLE, Berlin, Germany) operating in “hot-spot” mode as the radiation source, a high-resolution double echelle monochromator (DEMON) and a linear CCD array detector with 588 pixels, 200 of which are used for analytical purposes (monitoring of the analytical signal and BG correction), while the rest are used for internal functions, such as correcting for fluctuations in the lamp intensity. The selected wavelengths for the analysis were 294.2357 nm for V (one of the less sensitive V atomic lines), the spectral bandwidth per pixel is 1.3 pm, 294.3912 nm for Ni, the spectral bandwidth per pixel is 1.4 pm and 294.2357 nm for Fe, the spectral bandwidth per pixel is 0.36 pm. More details on this type of instrumentation can be found elsewhere [25].

The CS HR GFAAS instrument is also equipped with a transversely heated graphite tube atomizer, pyrolytic graphite tubes for solid sampling (without dosing hole) and an automated solid sampling accessory (SSA 600), which incorporates a microbalance with a readability of 1 mg [9]. The samples were introduced using solid sampling graphite platforms.

2.2. Samples and standards

All solutions were prepared using ultrapure water with resistivity of 18.2 MΩ cm, which was obtained from a Milli-Q purification system (Bedford, MA, USA). The vanadium and nickel solutions were prepared daily by diluting commercially available 1000 mg L⁻¹ standards and iron solution was prepared daily by diluting commercially available 10,000 mg L⁻¹ standard (Merck, Darmstadt, Germany). The solution of chemical modifier was prepared from the stock solutions 1000 mg L⁻¹ (Merck, Darmstadt, Germany).

A number of fuel ash samples provided from the University of Lincoln have been analysed in order to demonstrate the applicability of the developed method for real samples. These samples were also analysed by ICP OES previous acid digestion.

2.3. Procedure for solid sampling HR CS GFAAS analysis

All samples were directly analysed without any sample pretreatment, only a manual homogenization was performed for 2–3 min using a small agate mortar, immediately before analysis. The instrumental conditions and the temperature program used were carefully optimized and are summarized in Table 1. For the determination of V, Ni and Fe, external calibration was carried out simply against aqueous standard solutions; the calibration was performed by using the appropriate volumes of aqueous solutions of the specific concentrations, added with a micropipette onto the stamping platform. All the experiments were carried out in graphite platforms, preliminary treated with Ir as

Table 1
Temperature program adopted for the simultaneous determination of vanadium, nickel, gallium and iron in fuel ash samples by HR CS GF AAS.

| Stage | Temperature (°C) | Ramp (°C s ⁻¹) | Hold time (s) | Ar flow rate (L min ⁻¹) |
|-------------|------------------|----------------------------|---------------|-------------------------------------|
| Drying 1 | 110 | 15 | 30 | Max |
| Drying 2 | 130 | 1 | 30 | Max |
| Pyrolysis | 1350 | 50 | 5 | Max |
| Gas flow | 1350 | 0 | 5 | Min |
| Atomization | 2650 | 3000 | 11 | Min |
| Cleaning | 2650 | 0 | 5 | Max |

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